INVESTIGATION OF SUPERCONDUCTING INTERACTIONS AND AMORPHOUS SEMICONDUCTORS

Contract No. NASW-1760

Final Report

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PART I. SUPERCONDUCTING INTERACTIONS

I. Introduction

The contract support of the National Aeronautics and Space Administration for studies of superconductors by Westinghouse had its inception in June 1965 with the beginning of an investigation of superconductor properties by means of ultrasonic attenuation. The original contract (NASW-1214) was subsequently renewed in 1966 (NASW-1406) and in 1967 (NASW-1647). The present contract (NASW-1760) was a renewal initiated in June 1968. Work under this last contract has continued through October 1972.

The scope of the investigation of superconductor properties was broadened during the course of these contracts to include work on superconducting interaction mechanisms, thin-film superconductor studies, effects of high pressure on superconductors, and other areas, with the overall goal of gathering knowledge and testing hypotheses about those aspects of superconductivity which could bring about improvements in superconducting properties, such as enhancing transition temperatures and improving critical current and critical field levels.

This final report covers the work done on superconductors under the present contract (NASW-1760), but to preserve continuity a short summary of the work done under the previous contracts is presented in the next section.
This final report is only a summary of the significant achievements reached. The detailed results are to be found, of course, in the scientific papers published as a result of these contracts. The bibliography lists all of the papers containing results of work done under all four of the contracts. The papers published under the present contract are presented in their entirety in the appendices.

II. Ultrasonic Investigation of Superconductors

All of the studies of superconductors by means of ultrasonic techniques were carried out under the three predecessor contracts, with the exception of the work on molybdenum-rhenium alloys (B20, A5)*. These studies were concerned with measurement of magnitude, temperature dependence, and degree of anisotropy of superconducting energy gaps in such materials as rhenium (B3) and molybdenum (B7). The intermediate state of lead was investigated ultrasonically, and information on flux penetration and trapping (B2) and on structure effects (B5) was obtained. The element niobium was studied extensively by ultrasonic attenuation, with information being obtained on flux penetration (B1), effects at low magnetic fields (B4), order parameter dependence (B6), anisotropy and temperature dependence (B9), and hysteresis near \( H_{c1} \) (B12). Some data was obtained on ultrasonic attenuation in superconducting reduced strontium titanate (B8). The effects of magnetically induced structures in superconductors on ultrasonic attenuation were reviewed (B14).

* The references in parentheses with prefixes A or B refer to an appendix or bibliography entry, respectively.
Review articles were prepared on superconductivity in semiconductors and semimetals (B15), and on the effects of magnetic fields (B16) and the Fermi surface (B18) on ultrasonic attenuation.

III. Thin Film Studies

The portion of the contract dealing with the search for new superconductors with improved properties was largely concentrated on the study of the properties of thin films. As the program developed the thin film experimental work became divided into two distinct lines of research. The first comprised efforts to experimentally evaluate various theoretical proposals which suggested the possibility of new and superior superconducting interaction mechanisms. The authors of these proposals suggested that these new mechanisms might be able to sustain the superconducting state up to very high temperatures. In the second line of research, investigations were carried out on thin films of superconducting materials which were known to possess good superconducting properties in the bulk form, but which had never been studied in thin film form.

Wide interest in the possible existence of new superconducting interaction mechanisms which might be capable of producing superconductors with very high transition temperatures \( T_c \)'s had been generated by the publication of several papers, particularly one by Little\(^{(1)}\) and another by Cohen and Douglass.\(^{(2)}\) In Little's paper the possibility of fabricating an "organic superconductor" was discussed. As described by the author this proposed superconductor would be a
polymer consisting of a spine made up of conjugated double bonds to which would be attached a series of highly polarizable side chains. He suggested that in such a polymer the itinerant pi electrons from the double bonds might sufficiently polarize the side chains to attract a second electron, thereby establishing the attractive electron-electron interaction mechanism necessary for superconductivity. It was calculated that this non-phonon or "excitonic" mechanism might persist, in a properly constructed molecule, to very high temperatures. Although this idea of an organic superconductor generated much theoretical interest, no experimental attempts to synthesize such a superconductor had ever been made. The reason for this was stated by a well-known organic chemist who commented that he was left with enough questions after trying to translate Little's theory into a real organic structure that he wouldn't know where to begin. This conclusion, typical of the thinking of organic chemists on this subject, indicates why no serious attempt to synthesize an "organic superconductor" will probably ever be undertaken. Though the actual synthesis of an "organic superconductor" could not be seriously attempted, it has been possible to investigate Little's excitonic mechanism in inorganic thin film structures. It was originally suggested by Ginzburg that in a thin film, dielectric-metal-dielectric sandwich structure, electrons from the metal portion of the sandwich could polarize the dielectric and thus set up an attractive electron-electron interaction, analogous to the one visualized by Little for his organic polymer. In order to investigate the possible existence of the excitonic mechanism, we chose to perform thin film
experiments along the lines suggested by Ginzburg. Although the performance of this type of thin film experiment and the obtaining of unequivocal results presented various difficulties, these problems were finally overcome and useful although negative results were eventually obtained. These experimental difficulties and the results are described below.

In addition to the study of the excitonic mechanism, we also investigated the proposed "pairing across the barrier mechanism" of Cohen and Douglass, again using thin film techniques. In this case it was proposed that in another type of sandwich structure, consisting of a dielectric layer between two superconducting films, superconducting electron pairing might occur across the dielectric barrier. It was suggested that the barrier would exert a greater influence on the coulombic repulsion between electrons than on the phonon-mediated attraction, and would thus produce a net strengthening of the interaction and an improvement in certain superconducting properties, namely an enhanced transition temperature. Some experimental evidence had been published dealing with enhanced $T_c$'s in aluminum films which, it was suggested, indicated that this mechanism might actually be operative.

In addition to these proposals, other theories on strengthening the superconducting interaction mechanism were considered and experimentally investigated. The results from these thin film experiments are summarized in the following section.
IV. Experimental Investigation of Proposed New Interaction Mechanisms

Our initial $T_c$ enhancement thin film experiments were carried out using the transition metal element rhenium. Rhenium was chosen because it is a transition metal analog of aluminum. Aluminum had been reported to have an enhanced $T_c$ of $\sim 5^\circ K$ when incorporated into the Cohen-Douglass type sandwich configuration described above. Our purpose in doing these experiments was to try to duplicate this result with a rhenium based structure, and then to try to obtain a similar enhancement starting from a high $T_c$ material. Our first attempt to deposit rhenium resulted in films with $T_c$'s as high as $7^\circ K$, about a factor of four greater than the bulk value of $1.7^\circ K$. These films were prepared by standard evaporation techniques in $\sim 10^{-6}$ Torr vacuum. Thus about a fourfold increase in $T_c$ was obtained before any of the supposedly required sandwich type configurations were even fabricated. Our conclusion concerning these enhanced $T_c$'s in the Re films was that they resulted from residual gas contamination of the films during the growth process. To verify this and also to determine the amount of contamination required to significantly affect the $T_c$'s of deposited films, the following experiments were performed. First, rhenium films were deposited in a specially developed ultra-high-purity sputtering system. The background impurity level (i.e. the sum of contaminant gas partial pressures) in this system prior to sputtering was of the order of $10^{-10}$ Torr. The rhenium films sputtered in this system were found to have $T_c$'s of $1.7-1.9^\circ K$, similar to the $T_c$ of bulk material. Following the preparation of these films, rhenium was sputtered in an environment having controlled amounts of gaseous contamination present. This was done by
evacuating the system to its typical base pressure of \( \sim 5 \times 10^{-10} \) Torr and then bleeding in oxygen until a preselected pressure was obtained. Using this technique it was determined that an oxygen pressure as low as \( 10^{-8} \) Torr produced a significant increase (up to \( \sim 3^\circ K \)) in the \( T_c \) of the sputtered films. After thus establishing to our satisfaction that impurities had indeed caused the enhanced \( T_c \)'s, the question remained whether this increase was due to the presence of some new interaction mechanism. As discussed above, this possibility had been suggested by workers who had performed analogous thin film experiments.\(^{(5,6)}\) Our conclusion, which is now part of the general consensus, was that the introduction of a foreign material (in this case oxygen and in other cases organic molecules or various dielectric materials) produced films with an amorphous structure. The enhanced \( T_c \)'s in these films were the result of changes in the electron-phonon mechanism due to a change in structure, rather than resulting from the presence of any new mechanism. A possible way that an amorphous structure could produce a rise in \( T_c \) has been discussed by Schrieffer.\(^{(7)}\)

This situation, in which it is easy to produce \( T_c \) enhancements in thin films of the low \( T_c \) elements (such as Al and Re), made the search for unambiguous evidence for the existence of a new interaction mechanism in structures made from these elements extremely difficult. This caused us to decide to perform all further \( T_c \) enhancement experiments starting from thin films of high \( T_c \) (\( \sim 15 \) K) materials. There was much less chance of obtaining ambiguous results using these materials, since it was an established experimental fact that contamination in thin
films of high $T_c$ materials resulted in degraded transition temperatures.

Although there had been experimental work performed on films of high $T_c$ materials (notably on Nb$_3$Sn), no process had been reported which was capable of depositing high $T_c$ films of the order of $<\sim 100$ Å thick. Since films of this thickness were required for our experiments, it was necessary to develop such a process. This was accomplished by further development of the previously mentioned ultra-high-purity sputtering process, a full description of which is given in Appendices A2 and A10.

The first high $T_c$ material prepared by sputtering was NbN which in thin film form was found to have a transition temperature of $\sim 16^\circ$K, the same as the bulk value. Using thin films of NbN as the conducting layer (or layers) of the sandwich structure, experiments investigating the excitonic and the "pairing across the barrier" mechanisms were carried out. In these experiments the dielectric layer of the sandwich was a thin film of Si$_3$N$_4$ which was made by reactively sputtering Si in an argon-nitrogen atmosphere of appropriate composition. We found in all of these experiments that no increase in transition temperature was obtained above that of the NbN starting material. Subsequent to the completion of this set of experiments, the theories which they tested were somewhat modified by their authors. In both cases it was now suggested that the center portion of the sandwich (the dielectric in Cohen-Douglass and the metal in the Ginzburg scheme) would have to be $\sim 8$ Å thick for the proposed mechanisms to be operative. Based on our experiments and our experience with the deposition of thin
film superconductors, we believe that the deposition of continuous and
colorable films of this thickness would be extremely difficult,
and we conclude that an experimental affirmation or an unequivocal
egation of these two modified theories may be impossible using thin
film techniques.

In addition to the study of the multi-layer thin film con-
figurations, the hypothesis that ultra-thin films of high $T_C$ compounds
might possess very high $T_C$'s due to a predominant influence of surface
states was investigated by depositing NbN thin films in thicknesses
down to $\sim 20 \, \text{Å}$. These experiments are described in detail in Appendix
A6. In essence, however, no enhancement in transition temperature was
observed in these ultra-thin films.

Thus, to briefly summarize this phase of the work, we can
state that we have found no experimental evidence for the existence of
any new superconductivity mechanism. In all cases, when the pertinent
experiments were performed using NbN films, $T_C$ either stayed the same
or decreased. Despite the lack of positive $T_C$ enhancement results,
these studies produced a valuable spin-off. As was described, the
performance of these experiments made it necessary to develop a process
for the deposition of high $T_C$ superconductors in thin film form. The
development of this process made it possible for us to study, for the
first time, the properties of many high $T_C$ Type II materials, and we
found that the properties of the thin films of these materials were
in some cases dramatically different from the values observed in bulk
samples. These results are discussed in the next section.
V. Improved Superconducting Properties of Sputtered Type II Thin Films

As described above, the original motivation for the development of a high-purity thin film deposition process was to prepare high $T_C$ films which were to be used in our investigation of possible new superconductivity mechanisms. However, it was soon discovered that the thin films deposited by this process had unique properties, different from and in some cases greatly superior to those exhibited in bulk samples. Because of this fact the work in the thin film portion of the program gradually became concentrated on research on the properties of known high $T_C$ Type II materials prepared in thin film form. The results of these studies have formed the basis for the series of scientific papers which are included as Appendices to this report (A1-A4, A6-A11, A13-A23). Because the results of this phase of the work are covered in detail in these papers, only the highlights are summarized here.

We have observed improved superconducting properties (i.e. enhanced transition temperature, higher critical current ($J_C$) and/or higher critical field ($H_{c2}$)) in thin films of several Type II materials including NbN, Nb-C-N, Nb-Ti-N, Nb-Al-Ge, and Mo-Re. In general, the critical current and critical field values were found to be much higher in the thin films than in corresponding bulk samples. The most dramatic example of this is in NbN films, for which $J_C-$H data at 4.2°K in fields up to 210 kOe indicate that the thin films of this material possess the highest critical current densities presently known for any superconductor. We have attributed the very superior $J_C-$H properties of NbN films to their unique microstructure. Electron microscopy results indicated that
films of NbN sputtered onto \(\sim 500^\circ C\) substrates exhibit a columnar structure, resulting from the absence of lateral grain growth during the deposition process, this being due to the relatively low substrate temperature. In addition, electron microscopy indicated the presence of voids between the NbN grains. These "voids" may contain nonconducting gaseous atoms relatively invisible to electron microscopy. These nonconducting intergranular spaces are undoubtedly the cause of the extremely high resistivities, of the order of \(~1000\) micro-ohm-cm, measured in the sputtered films. These high resistivities are in turn the source of the enhanced upper critical fields, as follows from well known Type II theory. Presumably this column-void type structure is also the source of the very high critical current densities found in these films, because the structure provides the required large number of flux pinning sites.

Enhancement of critical current and/or critical magnetic field was also observed in other sputtered films besides NbN. In these instances the absolute values obtained were not as high as those found in the NbN films. In these other films a columnar and/or small-grained microstructure has also been observed, but no indication of non-conducting voids between grains was found. We believe this fact explains why the critical currents and fields of these films, while much greater than those of corresponding bulk samples, do not reach the very high values found for NbN films, despite similarities in \(T_c\)'s.

The superconducting transition temperatures of the sputtered films typically were found to be the same as or slightly lower than the
$T_c$'s observed in corresponding bulk samples. An exception was found in the molybdenum-rhenium alloy system. In this case sputtered films with the approximate composition $\text{Mo}_{70}\text{Re}_{30}$ were found to have enhanced $T_c$'s of $\sim 15^\circ\text{K}$ compared to values of $\sim 12.5^\circ\text{K}$ for bulk samples of similar composition. X-ray analysis of the films showed the presence of an A-15 structure. Bulk Mo-Re of this composition crystallizes in the $\alpha\text{Mo}$ (bcc) structure and no bulk A-15 phase has ever been reported in this alloy system.

Since it is a well established experimental fact that the A-15 crystal structure is favorable for high $T_c$'s, we assume that the increase in $T_c$ of the films over the $T_c$ of the bulk alloy is associated with the presence of the metastable A-15 phase in the film sample. This ability to induce the formation of a high $T_c$ metastable structure in the Mo-Re system has very important implications, since it suggests that the sputtering of films of other metallurgical systems may be a fruitful means for preparing new, higher $T_c$ superconductors.

To conclude, we have found that the high purity deposition process developed for this program provided us with an important tool for studying, for the first time, many high $T_c$ Type II superconductors in thin film form. These films were found to possess enhanced critical currents and critical fields compared to the bulk samples, due to the presence of a unique microstructure. A significant $T_c$ enhancement was also observed in one system as a result of the formation of a metastable high $T_c$ A-15 phase in the sputtered films.
VI. High Field Pulsed Magnet $H_{c2}$ Measurements

With the development of high field thin film superconductors such as NbN, it became necessary to attempt to extend the range of available magnetic field strength above that of the 210 kOe static field available at the Francis Bitter National Magnet Laboratory. It was therefore undertaken to design a pulsed field solenoid capable of providing fields in excess of 300 kOe and preferably in excess of 400 kOe. Because the main area of interest of this program was superconductor properties and not pulsed solenoid design, a great deal of effort could not be diverted toward this part of the project. Nevertheless, over the past few years several pulsed field solenoids producing a maximum field of 160 kOe were constructed and tested for stability and longevity. The typical solenoid was 3.15" long, had an internal coil diameter of 0.825", and was wound with 400 turns of round, solid copper wire 0.039" in diameter (19 gauge), in five layers with mylar interlayer insulation. It was calculated that such a coil was capable of attaining a maximum field of 330 kOe with a time constant of 12 msec, using the pulsed power supply which we had available for this project. However, two problems were encountered which precluded attainment of this field. These were collapse of the winding and shorting in the mylar interlayer insulation. The latter problem was solved by substituting a total epoxy impregnation of the coil. Mechanical stresses in the coil then became the limiting factor and kept the maximum attainable field below 200 kOe. By changing from round copper wire to rectangular cross section wire, the coil collapse problem was ameliorated to the extent that 314 kOe
could be attained. Efforts to achieve 400 kOe were unsuccessful due to coil collapse caused by flowing of the copper. Another attempt was to be made to reach 400 kOe by employing a multifilimentary superconductor wire with a copper to superconductor ratio of 2:1. This wire has about four times the tensile strength of copper alone. Use of this wire and a special all-metal dewar designed specifically for pulsed field work could finally allow attainment of 400 kOe, but the coil has not been tested at this writing.

VII. Pressure Effects in $V_3Si$

X-ray measurements were recently performed on $V_3Si$ to determine the behavior of cell constant deformation versus pressure up to 98 kilobars. Preliminary results indicate that $V_3Si$ does not follow normal cubic behavior. In fact, it would seem that lattice softening sets in at about 10 kilobars, after which the structure stiffens up to 70-80 kilobars, where softening again appears to set in. This indicates the possibility that there are at least two structural transformations in $V_3Si$ under hydrostatic pressure, and that the lower one of these may be connected with the observed increase in $T_c$. 
PART I. REFERENCES

PART II. AMORPHOUS MATERIALS

I. Introduction

The electrical switching behavior of certain amorphous semiconducting materials\(^1\) indicated that it may be possible to develop radiation hard, inexpensive switches and memory elements. In order to investigate the possible applications of these devices it was determined that more information was needed about the materials and device properties. Our investigations were aimed at these two problems, and numerous materials and bulk and thin film devices were studied. The literature available in this area is quite voluminous but several recent publications summarize this field quite well.\(^2\)-\(^5\)

Near the end of this program the techniques developed were used to investigate the properties of some selected amorphous magnetic materials.

II. Amorphous Semiconductors

Four component semiconducting glasses were used for the initial materials work and for the majority of the device work. The two most commonly used compositions were: 1) Te 65.5\%, As 24.3\%, Ge 7.3\%, Si 2.9\%, and 2) Te 64.7\%, As 23.9\%, Ge 7.6\%, Si 3.8\%. These compositions are weight percent. The glasses were prepared by sealing the correct proportions of the components in quartz tubes and slowly heating the material to 1100°C where it was held for one week. During this time the tube was
continuously agitated mechanically. After the heating period the material was water quenched and x-ray and microstructure examinations made. Both of the above compositions could be formed as single phase glasses, down to a resolution of \( \sim 1 \) micron. The results obtained using these two compositions were virtually identical.

Sputtering cathodes for thin film deposition were prepared by heating the bulk material up to its softening point, \( \sim 300^\circ C \), and then casting it in Mo molds. Cathodes up to 2" in diameter and 1/4" thick could be prepared in this manner.

Samples for measurement of bulk properties were prepared by cutting and polishing of as-cast material. Bulk switching devices were prepared by dipping two tungsten wires with a separation of 0.5-1 mm into molten glass, thus forming a bead of glass around the wires.

Conductivity measurements on bulk samples in the vicinity of room temperature yielded an energy gap of 1.14 eV for both of the previously quoted compositions. The dielectric constant of these materials is 10.

Switching measurements on bulk devices were made at DC and 60 Hz. In this discussion the low voltage, high resistance state is referred to as the off-state while the low resistance state is referred to as the on-state. The voltage where the device switches from the off to on-state is the threshold voltage \( V_T \). In general for \( V \ll V_T \) in the off-state the I-V curve is linear, becoming nonlinear as \( V \) approaches \( V_T \). When the device switches to the on state the resistance drops by one or more orders of magnitude and the dynamic resistance \( = dV/dI \) is negative for all \( I \) and \( V \).
Resistance measurements showed that the resistance in the on-state was analogous to that of the glass in the vicinity of its melting point. This result is consistent with a high temperature (liquid) filament being formed between the electrodes when the device switches. In addition, measurements of the temperature dependence of $V_T$ showed that $V_T$ approaches 0 as $T$ approaches the melting point. These results indicated that the switching action was associated with a thermal phenomenon.

The results discussed above refer to devices which were operated as "threshold devices" meaning that if the power is removed while the device is in the on-state it returns to the off-state. The other possible mode of operation is as a "memory device" where once the device has been put into the on-state it can only be returned to the off-state by a pulse of current with a sharp trailing edge (fall time < 50 nsec). While studying the DC properties of threshold switching it was found that the on-state could be stabilized (memory type behavior) if the current applied in the on-state exceeded a certain maximum value.

This effect was investigated in more detail using a 60 Hz sine wave applied voltage, allowing the I-V characteristics to be continuously monitored on an oscilloscope. A device would operate in the threshold mode continuously for a fixed maximum on state current but a gradual transition to memory behavior was observed as this current was increased. Once the device had achieved a permanent on state it could only be returned to threshold operation using a reset pulse. These experiments verified the conclusion that the difference between threshold and memory devices is one of degree rather than kind.
Due to the low intrinsic conductivity of semiconducting glasses it is not possible to sputter thin films using the dc technique developed by Westinghouse for the deposition of high $T_c$ superconductors. Thermal techniques are not suitable because of the large composition changes which occur when a multi-component system is evaporated in this manner. The only technique which will allow the deposition of a thin film whose composition is close to that of the starting material is rf sputtering. We developed an rf sputtering system which was used to deposit the thin film devices. A 500 watt, 13.56 MHz transmitter was used as the power source, and high purity argon was used for the rf discharge gas. The substrate holder-cathode separation is adjustable and the cathodes are easily demountable from the rf feed through. This allowed for easy and rapid changes in the sputtering conditions and materials being deposited.

The thin film devices were usually fabricated in a sandwich configuration with the amorphous material between either Al or Cr-Au electrodes. The device area was typically 2 mm$^2$. Electron diffraction results were used to verify that the amorphous material was truly amorphous.

A series of approximately 200 thin film devices with thicknesses varying from 1 to 5 microns was prepared. For devices operating in the threshold mode both the threshold voltage and the delay time would vary in a random fashion from one switching event to the next. The variations were usually on the order of 30 to 40%. In some instances oscillations would be observed either before during or after the device had switched. The occurrence of these oscillations could be suppressed by reducing the amount of resistance in series with the device but this would increase the
likelihood of the device exhibiting memory rather than threshold switching.

These devices could be operated in the memory mode by increasing the power dissipation in the on state above that allowed during threshold switching just as in the case of the bulk devices. Most any type of reset pulse would return the device to the high impedance state as long as it had a sharp trailing edge (falling \( \approx 50 \) nsec). Some memory devices were operated for several thousand cycles without failure.

The failure (destruction) of these devices can be attributed to two causes. The first has to do with the capacitive stored energy of the device itself. When switching occurs this energy dissipates within the device as a current pulse which in some instances can physically destroy the device. The high off/on ratio of these devices also contributes to their failure by making the switching transients very high.

Our conclusion based upon all our device measurements was that the switching phenomena was definitely thermal in nature, thereby seriously limiting their stability reproducibility and lifetime.

In addition to the work described above, one other aspect of the film devices was investigated; the formation of a blocking contact on the amorphous semiconductor surface during device fabrication.

Shaw, et al.\(^6\) have described a blocking contact on a thin film amorphous semiconductor, made by exposing the semiconductor surface to a humid atmosphere before depositing the metal electrode. Quite asymmetric behavior was found in the current-voltage, capacitance, and photovoltage characteristics of this electrode.
Our specimens were deposited on glass substrates and consisted of (1) a base electrode, composed a 500 Å vapor-deposited layer of either aluminum or gold-chromium, (2) the amorphous semiconductor film, composed of a 2 to 4 micron layer of R.F. sputtered Te$_{64.7}$As$_{23.9}$Ge$_{7.6}$Si$_{3.8}$, and (3) the top electrode, composed of a 500 Å layer of aluminum or gold-chromium. Prior to deposition of the top electrode, the amorphous semiconductor film was exposed to a humid atmosphere to form the blocking layer. This procedure is the same as that used by Shaw, et al., although distinctly different DC and AC electrical characteristics were observed.

DC current-voltage characteristics were taken with a Keithley electrometer. Typical results are shown in Fig. 1. Up to approximately 50 millivolts the behavior was ohmic, with resistances ranging from 50 megohms to 10,000 megohms for different depositions but nearly constant for a given deposition. Above 50 millivolts the resistance decreased with increasing voltage, eventually being limited by the amorphous semiconductor film resistance of approximately 1 megohm. It can be seen that the characteristics were not sensitive to the polarity of the applied voltage, nor were they changed qualitatively when the electrode metal was changed from aluminum to gold-chromium.

AC admittances were measured by a bridge technique over a frequency range of 1 Hz to 10 kHz and a DC bias range of -4 volts to +4 volts. Examples of the data are shown in Figs. 2 and 3. These are plotted in the complex admittance plane, a procedure which facilitates the choosing of an appropriate equivalent circuit for the specimen. The circuit shown in Fig. 4 was found to be consistent both with the experimental data.

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and the physical structure of the specimen. Section $R_1$, $C_1$ corresponds to the amorphous semiconductor film, and section $R_2$, $C_2$ corresponds to the blocking layer. Rough estimates of the four circuit parameters are refined by a trial-and-error procedure until optimum agreement is obtained between the calculated points and the experimental points on the admittance plot. (See Figs. 2 and 3). An example of the parameters obtained for one specimen are given in Table I.

Our AC data can be summarized as follows: Values obtained for the amorphous semiconductor film resistance $R_1$ and capacitance $C_1$ corresponded to the bulk resistivity and dielectric constant of the amorphous semiconductor. Furthermore, $R_1$ and $C_1$ showed no dependence on bias voltage. The blocking layer resistance $R_2$ decreased toward zero for increasing bias voltage of either sign. The blocking layer capacitance $C_2$ remained constant ($\approx 0.2 \mu F/cm^2$) for zero or negative bias but increased by almost a factor of 2 for positive bias.

Most of our results are consistent with the hypothesis that exposure of the amorphous semiconductor to moisture produced a semi-insulating film approximately 200-500 Å thick and with a resistivity of $10^{11}-10^{13}$ ohm-cm, which was subsequently covered by the metal electrode. This hypothesis would account for (1) the non-linear but symmetric behavior of the i-V curves (Poole-Frenkel conduction) (2) the qualitative similarity of the data for aluminum electrodes and gold-chromium electrodes, and (3) the constant value of the blocking layer capacitance (for zero and negative bias) and the bias sensitive resistance in parallel with this capacitance. It cannot account for the increase in blocking layer capacitance with positive bias.
A simple p-n junction capacitance effect at the semiconductor surface can be ruled out because the polarity of the effect is wrong for our p-type amorphous semiconductor. A field effect can be ruled out for the same reason and because the capacitance change would be too small. Our only conjecture at this time is that electrochemical changes at the interface between the amorphous semiconductor and the semi-insulating layer may be involved.

A final comment should be made concerning the pronounced difference between our results and those of Shaw, et al. Although our basic specimen preparation procedures were the same, our amorphous semiconductor contained a much higher percentage of tellurium than Shaw's (65% vs. 28%). This could conceivably affect the surface reaction with moisture and hence the type of blocking layer which would result. Further work would be necessary using more accurately controlled conditions in the formation of the blocking layer as well as investigating the effects of the amorphous semiconductor composition to resolve this discrepancy.

In parallel with the above device work, several semiconducting glass systems were investigated, principally the chalcogenide-halide glasses. These glasses were among the first amorphous materials in which switching was observed, and include systems which are insulating such as As-S-I and As-S-Br and some which have conductivities in the semiconducting range such as As-Te-I and Sb-S-I. The semiconducting glasses, although they have low conductivities exhibit the logarithmic dependence of conductivity on temperature. In addition, the semiconducting glasses exhibit switching, usually of the memory type, although in some cases threshold switching has
been observed and again in some cases both in the same device.

Since it is possible to form binary mixtures of some of the insulating and semiconducting glasses it is possible to obtain material with most any value of electrical conductivity. This allows one to study the occurrence of switching as a function of the off-state conductivity of the material.

The glasses were prepared by first sealing the appropriate amounts of each element in an evacuated quartz ampoule. The ampoule was then heated slowly in order to allow the reaction to take place as the temperature is raised. After reaction, the samples were held at approximately 600°C for several hours and then water quenched. This technique has been used by most workers in preparing these type of glasses.

The Sb-S-I system was the first system investigated. Two small glass forming regions centered at Sb$_{36}$S$_{50}$I$_{14}$ (atomic %) and Sb$_{36}$S$_{40}$I$_{24}$ were found. Sb$_{40}$S$_{50}$I$_{10}$ material exhibited switching at room temperature while the other glasses would only switch if the temperature was raised to ~250°C. In addition we found it was possible to form a glass from Sb$_2$S$_3$, which previously was reported as existing only in the crystalline state. This material requires a rapid quench and usually only the outer layer of material is glassy.

Powder patterns showed no crystallinity in any of the glasses except possibly the Sb$_{40}$S$_{50}$I$_{10}$ sample which showed switching at room temperature. Since this composition is well within the middle of the glass forming region this could possibly be a spurious result. If not, the presence of crystallites could explain why this material switched at a
lower temperature than the other compositions.

Three mixtures of semiconducting Sb-S-I and insulating As-S-I glasses and the composition AsSbS$_3$ were prepared. Three of these glasses, AsSbS$_3$, As$_{15}$Sb$_{15}$S$_{45}$I$_{25}$ and As$_{20}$Sb$_{20}$S$_{50}$I$_{10}$ exhibited switching at elevated temperatures while As$_{20}$Sb$_{20}$S$_{40}$I$_{20}$ would switch at any temperature up to the vaporization temperature. Several compositions in the Sb-Te-I and (As,Sb)-Te-I systems were investigated but all were crystalline. Three samples in the (As,Sb)-(S,Te)-I system--As$_{20}$Sb$_{20}$S$_{30}$Te$_{30}$, As$_{20}$Sb$_{20}$S$_{20}$Te$_{20}$I$_{20}$ and As$_{16}$Sb$_{16}$S$_{22}$Te$_{22}$I$_{24}$--all exhibited switching at room temperature.

III. Amorphous Magnetic Materials

It has been proposed theoretically for sometime that crystallinity is not a requirement for ferromagnetism.\textsuperscript{(13)} The present study was initiated to understand the problem of how the magnetic properties of random lattices are different from what the general band theory predicts.

Recently, there have been several reports indicating the existence of amorphous ferromagnets.\textsuperscript{(14-16)} It is now known that amorphous alloys may be produced when two metals which are normally insoluble in each other and which show a large atomic size difference are co-deposited onto a substrate.

Duwez and co-workers\textsuperscript{(14-16)} have used the so-called splat cooling or piston and anvil technique to prepare amorphous magnetic films. The properties of such films were likely to vary from specimen to specimen because of the difficulty associated with evaporation of phosphorus and oxidation of carbon in preparing the alloys. In addition the quenching
conditions used cannot be controlled accurately enough to give reproducible compositions.

In our study a multicomponent (Fe_{75}P_{15}C_{10}) cathode was first prepared. Required amounts of Fe_{2}P, Fe and C were first melted in an r.f. furnace. The material was then ground and pressed into a disc of about 2" diameter and 1/4" thickness. The disc was then sealed in a quartz tube and sintered at 500°C for about 72 hours. The same r.f. sputtering technique, used with the amorphous semiconductors was used to sputter the film onto a 10 mil mylar substrate. The substrate was kept at room temperature in one case and at liquid nitrogen temperature in the other. The failure to resolve discrete grains by electron microscopy with a resolution down to 15-20 Å was used as a criterion to establish amorphous character. Both the films were found to be amorphous.

In the present study, we measured the temperature and field dependence of the magnetization using a vibrating sample magnetometer. The temperature range used was between 100°K to 773°K and a superconducting magnet that gives a maximum field of about 60 kOe was used to provide the field variation. One bulk (sintered) sample and two amorphous films deposited at room and liquid nitrogen were analyzed. The results show that all the three samples were ferromagnetic with saturation field less than 10 kOe. Two ferromagnetic phases appearing at 498°K and 673°K were observed in the bulk sample. However, the two films showed one ferromagnetic phase appearing near 558°C. The magnetization results seem to be in accord with the measurements made on amorphous films prepared using splat cooling techniques. The ferromagnetic phase in the later appears around
590°K compared to ours at 558°K.

Two important inferences can be deduced, 1) there is no difference in the magnetic properties of the two films and substrate temperature does not influence the Curie temperature, 2) this method of film deposition is more attractive in that the conditions of deposition can be controlled accurately enough to give reproducible compositions.
TABLE I
EQUIVALENT CIRCUIT PARAMETERS FOR SPECIMEN 1-7

<table>
<thead>
<tr>
<th>$V_{bias}$ (volts)</th>
<th>$R_1$ (M)</th>
<th>$C_1$ (pf)</th>
<th>$R_2$ (M)</th>
<th>$C_2$ (pf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4</td>
<td>1.4</td>
<td>60</td>
<td>0.14</td>
<td>8000</td>
</tr>
<tr>
<td>-0.8</td>
<td>1.46</td>
<td>60</td>
<td>1.19</td>
<td>8000</td>
</tr>
<tr>
<td>0</td>
<td>1.46</td>
<td>60</td>
<td>15.5</td>
<td>8300</td>
</tr>
<tr>
<td>+0.8</td>
<td>1.36</td>
<td>64</td>
<td>0.71</td>
<td>11500</td>
</tr>
<tr>
<td>+4</td>
<td>~ 1.4</td>
<td>63</td>
<td>0.084</td>
<td>15000</td>
</tr>
</tbody>
</table>
PART II. REFERENCES

FIGURE CAPTIONS

Fig. 1  Current-voltage characteristics for thin film amorphous semiconductor with blocking electrode.

Fig. 2  Complex plane plot of admittance data for Spec. 1-2. Numbers adjacent to points indicate frequency in Hz.

Fig. 3  Complex plane plot of admittance data for Spec. 1-7, showing effect of various DC bias potentials. For sake of clarity, positive bias data is not shown.

Fig. 4  Equivalent circuit for thin film amorphous semiconductor with blocking electrode.
Fig. 1
Fig. 2
Fig. 3

Spec. 1-7

- Measured
- Calculated

Curve 649418-A

B (10^{-6} \text{ ohm}^{-1})

G (10^{-6} \text{ ohm}^{-1})

0 Volts Bias

-0.8 Volt Bias

-4.0 Volt Bias

Volts Bias

1K

500
Fig. 4
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APPENDICES*


A8. The Very High Critical Current and Field Characteristics of

* Publication references are given in the bibliography. Bibliography numbers (B prefix) follow the appendix numbers (A prefix). The appendices include all papers containing results of work performed under NASA contract NASW-1760.


The rock salt structure (B1) carbon and nitrogen compounds of the transition metals comprise one of the classes of materials exhibiting the highest known superconducting critical temperatures and are, therefore, potentially of considerable technological as well as academic interest. Many of these compounds are extremely stable chemically and can be prepared relatively easily in thin film form by reactively sputtering the metallic component in an appropriate atmosphere. Niobium nitride, NbN, for example, is prepared by sputtering niobium in an argon-nitrogen atmosphere having a total pressure of approximately $10^{-3}$ Torr. Films of different compositions are produced by varying the nitrogen partial pressure over the range from $10^{-7}$ to $10^{-4}$ Torr. Earlier work on this and other similar compounds resulted in films with transition temperatures, $T_c$, significantly below the bulk values. Since these values appeared to correlate with the background pressures employed, considerable efforts were made in the present work to make this as low as possible. By utilizing ultrahigh vacuum techniques, giving a background pressure $\lesssim 5 \times 10^{-11}$ Torr, and an electrode configuration which results in a gettering of the volume surrounding the sample substrate area, films have been consistently produced which, for thicknesses in excess of 500 A, have critical temperatures of 15.5 K, the bulk value for nearly stoichiometric NbN. Films having essentially identical properties have been produced on both
hastalloy and fused silica substrates.

The properties of these films in high magnetic fields are of interest since preliminary results indicate that the upper critical field $H_{c2}$ is significantly higher than that of the bulk material.

Resistive measurements at relatively low current densities were employed for the determination of $H_{c2}$ as a function of temperature. Experiments were carried out with the applied magnetic field $H$ always perpendicular to the plane of the film and the direction of current flow. Following previous practice, the field at which the film resistance was equal to half its normal value was defined as the resistive transition field $H_r$. For measurements near $T_c$, this field was found to be essentially independent of current density over several orders of magnitude (from 1 to $10^3 \, \text{a/cm}^2$) and has accordingly been identified with $H_{c2}$.

The results obtained in this way for a typical NbN film of thickness 1500 A are summarized in the figure, with the values for a sample of bulk material having a very similar $T_c$ included for comparison. It is evident that a considerable difference in properties exists between these samples.

Since data on the electronic specific heat coefficient of the normal state is available, and the nor-
mal state resistivity $\rho_n$ and $T_c$ could be determined experimentally, comparison with present theory was possible.

In the limit of short electronic mean free path (the dirty limit), the zero degree upper critical field $H^*_c(0)$ is given by

$$H^*_c(0) = -0.69 (\frac{dH_c}{dt})_{t=0} = 0.69 H_o$$

where $t = T/T_c$. Experimentally it is found that $H_o = 760$ koe for the film sample and $H_o = 210$ koe for the bulk. (If the onset of detectable resistance is employed for the film case a value for $H_o$ of 600 koe results.)

In terms of the material parameters according to theory,

$$H^*_c(0) = 3.1 \times 10^4 \rho_n \gamma T_c$$

where the usual units are employed. For $\gamma = 3.2 \times 10^3$ ergs cm$^{-3}$ K$^{-2}$, $\rho_n = 6.49 \times 10^{-4}$ $\Omega$ cm; $T_c = 15.3^\circ$K a value for $H^*_c(0)$ of 1020 koe, or $H_o = 1.480$ koe results from Eq. (2), considerably larger than the value for $H_o$ obtained experimentally.

The influence of Pauli spin paramagnetism (PSP) in determining the high field properties of a superconductor has been discussed by a number of authors. In Maki's notation (9) the parameter $\alpha$, defined as

$$\alpha = \frac{\sqrt{2} H^*_c(0)}{H_p}$$

where

$$H_p = 18400 T_c$$

is employed to denote the relative importance of this effect. From Eqs. (2), (3) and (4) we get

$$\alpha = 2.4 \rho_n \gamma$$

which for the NbN film discussed above gives $\alpha = 4.97$. Alternate-
It is possible to estimate $\alpha$ from the experimental results using the relationship\(^{(7)}\)

$$\alpha = 5.28 \times 10^{-5} \left( \frac{dH_c}{dT} \right) T = T_c$$

which gives

$$\alpha = 2.48$$

In the absence of spin orbit scattering, the reduced field $h(t) = H_c(t)/H_0$ decreases with increasing $\alpha$, giving

$$h(0) = 0.69 (1 + \alpha^2)^{-1/2}.$$  \hspace{1cm} (6)

For $\alpha = 4.97$, this expression gives $h(0) = 0.135$, so that $H_c(0) = H_0 h(0) = 103$ koe employing the measured value of $H_0$. Using the experimental value of $\alpha$, $h(0) = 0.260$, so that $H_c(0) = 200$ koe. Preliminary measurements on this sample in a pulsed field show that $H_c$ is in excess of 150 koe from 1.3° to 4.2°K. There are, however, indications of the onset of resistance near 180 koe in other samples, suggesting that $H_c$ lies in the general vicinity of 200 koe.

Provisionally, it seems therefore that in these films the PSP may not produce the full effect predicted by theory, but the influence of spin-orbit scattering in reducing its effectiveness is considerably less than for the solid solution alloys of the transition metals.\(^{(4)}\) A detailed study of the low temperature variation of $H_c$ appears to be very desirable to establish this point unambiguously, and is currently in progress.

The technical assistance of D. W. Deis and A. Patterson in performing these experiments is gratefully acknowledged.

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\(^{4}\) A detailed study of the low temperature variation of $H_c$ appears to be very desirable to establish this point unambiguously, and is currently in progress.
References

THE PREPARATION AND SUPERCONDUCTING PROPERTIES
OF THIN FILMS OF TRANSITION METAL INTERSTITIAL COMPOUNDS*

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Abstract

The importance of geometrical parameters in determining the superconducting properties of a material has recently been a topic of considerable theoretical interest. Experimental investigation in this area so far has been restricted principally to thin film structures of the non-transition elements, composed of materials possessing relatively small superconducting order parameters ($K$). In this paper we shall discuss some recent studies on thin film structures of transition metal compounds having both high critical temperatures ($T_c \gtrsim 14^0K$) and large upper critical fields ($H_{c2} \gtrsim 100$ Koe). The materials in this work have the rocksalt structure (B1) and are based upon the compound niobium nitride, NbN. The films were prepared by reactive sputtering in argon-nitrogen atmospheres in an ultra-high vacuum system with a background pressure $\lesssim 5 \times 10^{-11}$ Torr. Variation of the nitrogen partial pressure over the range $10^{-3}$ to $10^{-6}$ Torr was used to obtain different film compositions.

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The preparation and superconducting properties
of thin films of transition metal interstitial compounds

Introduction

The importance of geometrical parameters in determining the superconducting properties of a material has recently been the subject of considerable theoretical interest. Experimentally, this problem can best be investigated by the study of superconducting thin film structures where any fluctuations in these parameters can be expected to exert a maximum, and thus most readily observable, influence. There have been, over the past several years, various publications reporting changes in superconducting transition temperatures \( T_c \) from the bulk values, when these superconductors were prepared in thin film form. For example, in 1954 Bücket and Hilsch\(^{(1)}\) observed rises in transition temperatures in a number of metal films deposited on substrates held at liquid helium temperatures. More recently, other results have been published reporting enhanced \( T_c \)'s in some transition metal films and also in more complex structures consisting of both superconducting and normal components.\(^{(2-6)}\)

The conclusions drawn from these results usually have been tentative in nature. However, the tendency has generally been to ascribe these variations in properties to physical fluctuations such as changes in grain size, disorder, structural modifications, or in some cases to new or modified superconducting interaction mechanisms. While any one or all of these explanations cannot, with complete certitude, be eliminated as
the cause for the changes in $T_c$ in these thin film structures, the
typical methods of preparation of these films suggests other and perhaps
more likely explanations. In general, these film structures have been
either evaporated or sputtered under high vacuum conditions ($\lesssim 10^{-7}$ Torr)
and, in many cases, they have been deposited on substrates held at low
temperatures ($\sim 4^\circ$K). Since the concentration of residual gases at
these pressures is appreciable (approximately $10^{13}$ molecules/cm$^3$) and
since the sticking coefficient of gaseous impurities at liquid helium
temperatures is essentially unity, one must have severe reservations
concerning the purity of films deposited under these conditions.
Therefore, another interpretation, regarding the variation of transition
temperatures in many of these experiments, might well be the formation
of meta-stable superconducting impurity compounds.

In an attempt to obtain some unambiguous conclusions concerning
the relative importance of physical parameters or the formation of
impurity compounds regarding changes of superconducting properties in
thin films, we have been investigating a number of transition metal
elements and compounds. Thin films of these superconductors have the
distinct advantage of being stable at elevated temperatures, thus they
can be deposited at these temperatures as very thin films ($\lesssim 75-100 \AA$)
without agglomerating. This eliminates the necessity of using low
temperature substrates to obtain continuous thin films of uniform thick-
ness. Among the transition metals, much effort has already been
expended in preparing thin niobium films. All of these experiments have
amply demonstrated that contamination introduced in films deposited by
ordinary high vacuum techniques severely depressed the transition
temperature of niobium compared to its bulk value. To minimize this
contamination, during the growth process several techniques have been
developed, including deposition under ultra-high vacuum conditions, (7)
getter sputtering, (8) bias sputtering, (9) or the use of high temperature
(\sim 500^\circ C) substrates. (10) All of these methods have been successful in
producing Nb films with transition temperatures similar to that of the
bulk. The evidence for contamination causing rises in transition
temperatures in superconducting films is not as strong; however, Bond (3)
and co-workers suggested the formation of impurity compounds as the
cause for the higher T_c 's in a number of transition metal thin films.
Our earlier work on rhenium films supports these authors' conclusion. (11)
By the use of ultra-high purity growth techniques we have prepared
rhenium films with the bulk value transition temperature of 1.7^0K.
Subsequently, by reactively sputtering rhenium in a proper argon-oxygen
mixture, we have succeeded in raising the T_c of these films to nearly
4^0K. Based on these results, it was concluded that to perform completely
unequivocal experiments on transition temperature variations, the thin
films must be prepared under conditions of highest purity to try to
eliminate contamination as the cause for any fluctuation in supercon-
ducting properties. Since there are a very large number of supercon-
ductors which could profitably be studied in this program, the choice
of materials was made on practical considerations. The transition metal
\beta-W and rocksalt structure compounds (including Nb_3Sn and NbN respectively)
possess the highest known superconducting properties. These classes of
materials were therefore chosen, since the preparation of films of these superconductors with properties similar to that of the bulk would have some immediately practical implications. In this paper we report on the preparation and superconducting properties of NbN and some related compound thin films.

Experimental Technique

The interstitial compound NbN has been prepared in bulk form by many workers by high temperature diffusion of nitrogen into niobium. The most recent publication on the preparation of these compounds reports that the optimum $T_c$ of $>16^\circ\text{K}$ is obtained in a compound with slightly less than the stoichiometric concentration of nitrogen. Stoichiometric NbN is reported to have a transition temperature of between 15 and $16^\circ\text{K}$. The first reported effort to make thin films of NbN was by Gerstenberg and Hall who reactively sputtered niobium in an argon-nitrogen atmosphere and obtained films superconducting at approximately 6-9$^\circ\text{K}$. These experiments were performed in a system with a background pressure of $\sim 10^{-6}$ Torr. Very recently, Bell et al. also reported attempts to reactively sputter niobium nitride and other related compounds. Their sputtering was done in an ultra-high vacuum chamber where the background pressure was reduced into the $10^{-9}$ Torr range. These workers also deposited their films on heated substrates up to $450^\circ\text{C}$. The reactively sputtered NbN films deposited under these conditions showed transition temperatures of approximately $12^\circ\text{K}$. Similar deposition experiments on some related compounds produced a maximum $T_c$
of ~ 13.5°K. These figures, while above those reported previously, are still well below values obtained in bulk samples. Assuming these lower values were still the result of contamination, an all glass and metal sputtering system was constructed capable of being evacuated down to the low 10^{-10} Torr range. The actual deposition chamber consists of two glass halves attached to stainless steel flanges which can be joined together using copper gaskets to make the necessary ultra-high vacuum seal. Multiple electrodes are introduced into the chamber through glass presses to permit (in addition to the actual sputtering operation) the use of a quartz crystal μ-balance, temperature monitor thermocouples, bias sputtering, or substrate heating as desired. The system is evacuated with a liquid nitrogen trapped oil diffusion pump. After a twenty-hour bake-out at approximately 400°C, the system routinely achieves a pressure of \( \lesssim 5 \times 10^{-10} \) Torr. The sputtering technique used in these experiments has been simple cold cathode dc sputtering. However, a unique cathode configuration has been employed. Instead of the usual flat configuration, the cathodes are shaped in the form of a square box open on one end. The substrate holder is then positioned inside the box. In addition to removing the substrate from the line of sight of the residual gas impurities in the system, this technique provides a gettering action from the material sputtered from the back and sides of the cathode. The niobium cathode targets were made from 0.015" thick sheet purchased from Kawecki Chemical Co., who specified the major impurity as Ta (500 ppm). The total gaseous impurities (predominantly oxygen) is about 100 ppm. Other cathode targets were
fabricated from alloys processed at this Laboratory. The sputtering gases used are Matheson Research Grade argon and nitrogen. The manufacturer claims no detectable impurities in these gases at a threshold of less than 1 ppm. The films were deposited on both stainless steel and fused quartz substrates. The transition temperature measurements were done in liquid hydrogen by observing the onset of resistance in the samples.

Results and Discussion

Using the apparatus just described, we have reproducibly grown thin films of NbN with transition temperatures equal to that obtained for the stoichiometric compound reported by Hechler et al.,(12) i.e. between 15 and 16°K. The procedure and conditions developed in these experiments which produced films with the highest $T_c$'s are as follows: The system is first evacuated and baked out to a pressure of $< 5 \times 10^{-10}$ Torr. With the pumps still operating, nitrogen is leaked into the system until the pressure reaches $6 \times 10^{-5}$ Torr. Argon is then introduced into the apparatus until the desired current-voltage conditions are established, namely $1700$ V and $80$ ma. At this current the cathode is being bombarded at $\sim 1$ ma/cm$^2$. The argon pressure required for this power is $\sim 50 \times 10^{-3}$ Torr. The sputtering rate under these conditions is approximately $5 \text{ L/sec}$ at a substrate-target distance of $3/8''$. No external heating of the substrates was used in these experiments, since under the conditions described the substrates achieve a temperature of $\sim 500^\circ$C, in about thirty seconds, and remain there during the course of
the experiment. The duration of these experiments was usually such to produce films of the order of 1000 Å to 3000 Å thick. The significance of these variables may be judged from the results of other experiments. For example, films prepared under otherwise identical conditions but with a background pressure as low as $3 \times 10^{-8}$ Torr were found to be non-superconducting down to $4.2^\circ$K. In another experiment the usual background impurity level of $< 5 \times 10^{-10}$ Torr was maintained; however, the voltage and current were set at 1000 V and 40 ma. These settings produced a deposition rate of 1 Å/sec and a substrate temperature of 250°C. Films from this experiment exhibited transition temperatures of less than $8^\circ$K. On the other hand, raising the voltage to 1800 V and the current to 100 ma produced NbN deposits similar to those obtained at the lower settings. Finally, changes in the partial pressure of nitrogen also produced significant variations in the $T_c$ of the sputtered films. Reducing the partial pressure of nitrogen below $5 \times 10^{-5}$ Torr results in a continuous decrease of transition temperature to less than $4.2^\circ$K. Raising the nitrogen produced a similar but much smaller effect. Niobium films sputtered in pure nitrogen had a transition temperature of about $12^\circ$K. The lower values for the films sputtered in pure nitrogen are most probably associated with lower sputtering rates in this gas compared to those achieved in argon.

Some selected films prepared with various nitrogen partial pressures but under otherwise optimum growth conditions were studied by electron and X-ray diffraction techniques. A NbN film with a $T_c$ of $15.2^\circ$K sputtered at a nitrogen partial pressure of $6 \times 10^{-5}$ Torr exhibited
the f.c.c. rocksalt structure with an expected lattice parameter of 4.39 Å. In addition, this film showed a very weak hexagonal structure which was correlated with the compound NbN₂. A second film, T_c = 8.6°K, sputtered at a nitrogen pressure of 10⁻⁶ Torr had the hexagonal NbN₂ structure plus an extra line which could not be indexed. Finally, a third film with a T_c of 12.1°, prepared at an intermediate nitrogen pressure, exhibited both the cubic NbN and the hexagonal NbN₂ structure. The high T_c films, when observed by electron diffraction, also showed preferred orientation in the <111> perpendicular to the substrate surface. This result strongly suggests that NbN can probably be prepared as a single crystal film by a proper choice of substrate material.

After establishing conditions for the preparation of niobium nitride, other related compounds can easily be sputtered by varying the composition of the cathode target. For example, the effect of replacing niobium with titanium in these films can be studied by sputtering from alloys containing various niobium-titanium compositions. Titanium was initially chosen for these experiments since the addition or substitution of titanium in NbN in bulk samples produces a rise in T_c to over 17°K. Thus far, in all of our experiments however, the highest T_c's have been obtained in the NbN samples. In the experiments using niobium-titanium targets the highest T_c's observed have been approximately 13.5°K. These relatively low transition temperatures have tentatively been attributed to the greater chemical affinity of titanium toward the oxygen and water, compared to niobium. It is thus presently felt that further refinements in growth techniques may be necessary to produce uncontaminated films of these compounds.
In addition to the results discussed, some additional measurements have been made on our highest $T_c$ samples, i.e. the ~15$^\circ$K NbN films. Attempts to determine the upper critical fields of these samples were made in an apparatus capable of generating pulse fields of up to 180 kgauss. It was found that the NbN films at 4.2$^\circ$K were still superconducting at the maximum field. Theoretical calculations based on critical field measurements at temperatures near $T_c$ indicate an upper critical field for the NbN films at 4.2$^\circ$K of over 200 kgauss. This is about 70 kgauss greater than the highest fields reported for bulk NbN. The results and discussions of our critical field measurements will be considered in greater detail in subsequent publications.

Summary

We have successfully produced, for the first time, thin films of NbN with transition temperatures similar to that of the bulk material. These films have been prepared by a reactive sputtering process. Ultra-high vacuum techniques were used to reduce the background residual gas contamination in the films. Additionally, impurities were further reduced by the gettering afforded by a unique cathode configuration and by deposition on substrates heated to ~500$^\circ$C. Magnetic field measurements indicate that these samples possess upper critical fields at least 50 kgauss higher than bulk samples.

Acknowledgment

The considerable technical assistance provided by D. W. Deis and A. L. Foley is gratefully acknowledged.
References


THE HIGH FIELD PROPERTIES OF PURE NIOBIUM NITRIDE THIN FILMS

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Abstract

Thin films of the rocksalt structure (B1) compounds of the transition metals can be prepared by the method of reactive sputtering. By a refinement of this technique we have produced, for the first time, thin films of niobium nitride (NbN) with transition temperatures similar to those of the bulk materials (> 150K). Films have been prepared on both hastelloy and fused silica substrates. Measurements of the normal state resistivity $\rho_n$ yield values in excess of 200 $\mu$-ohm-cm. Preliminary studies of the resistive transitions in these materials near $T_C$ indicate that $H_r(J)$, the field at which $\rho/\rho_n = 1/2$, is independent of current density below 200 A/cm$^2$ for films 1000 to 4000 Â thick. Identifying $H_r(J)$ ($J < 50$ A/cm$^2$) with the upper critical field $H_{c2}(t)$, the measurements indicate that $H_{c2}(0)$ is significantly in excess of 200 Koe, and

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Abstract (cont'd)

thus is substantially higher than the values obtained for the bulk material. These results will be discussed in terms of the current theories of high field superconductivity with particular reference to the importance of Pauli spin paramagnetism and spin-orbit scattering in these materials.
THE HIGH FIELD PROPERTIES OF
PURE NIOBIUM NITRIDE THIN FILMS

I. INTRODUCTION

In view of recent theoretical and experimental developments in high field superconductivity, the rocksalt structure nitrides and carbides of the transition elements have proven very interesting.\(^{(1,2)}\)

Many of these compounds are very stable at high temperatures and can be prepared in thin film form using the technique of reactive sputtering. In the past, however, attempts at preparing thin films of these materials, specifically NbN, yielded \(T_c\) values significantly below the values obtained in the bulk systems. This discrepancy in transition temperatures has recently been shown to be attributable to impurities, coming mostly from high background pressure in the vacuum system.

Gavaler et al.\(^{(3)}\) have recently developed a method by which NbN films with bulk \(T_c\)'s can be prepared. This was accomplished by constructing an all metal and glass vacuum system, capable of achieving a background pressure in the \(10^{-11}\) torr range. Using this system with gettering and substrate temperatures near 500\(^\circ\)C, we have been able to make NbN films 1000 to 5000 \(\AA\) thick with \(T_c\) values between 15 and 16\(^\circ\)K -- that of stoichiometric bulk NbN.
II. EXPERIMENTAL PROCEDURE

The experimental techniques used to prepare these films are discussed in detail in the preceding publication; however, the results can be summarized as follows: The films were sputtered in an argon-nitrogen gas mixture and the transition temperature of the films, as a function of the nitrogen gas partial pressure, is shown in Fig. 1 (the nitrogen partial pressure is measured with a Bayard-Alpert high vacuum gauge prior to the admission of argon gas). With a background pressure of $10^{-10}$ torr or less and using only argon gas to sputter, niobium films have been produced with $T_c$'s $\approx 9.2^\circ$K, the $T_c$ of bulk niobium. As small amounts of nitrogen gas are added, the $T_c$ drops rapidly to below $4^\circ$K. This is the characteristic behavior of impure niobium films. At nitrogen pressures in the $10^{-6}$ to $10^{-7}$ torr range, the $T_c$ rises above $4^\circ$K and around $10^{-6}$ torr the compound $\text{Nb}_2\text{N}$ is formed with a $T_c$ of $\approx 8.6^\circ$K, which agrees favorably with measurements of bulk $\text{Nb}_2\text{N}$. As the nitrogen pressure is increased further, the $T_c$ continues to rise due to the formation of films containing both $\text{NbN}$ and $\text{Nb}_2\text{N}$ until at a pressure of $\approx 6 \times 10^{-6}$ torr relatively pure $\text{NbN}$ films are formed. If the nitrogen pressure is increased further, the $T_c$ begins to fall again since the deposition rate drops and impurities begin to have an effect. If films are sputtered with pure nitrogen gas, $T_c$'s around $12^\circ$K are obtained.

Besides varying the nitrogen partial pressure, the current and voltage during sputtering can be controlled by varying the total gas pressure in the system. A current density at the cathode of 1 ma/cm$^2$, corresponding to 1700 volts and 80 ma, was found to be sufficient to
produce good films. Using these conditions on current and voltage and working with a nitrogen pressure corresponding to the highest $T_c$ films, a deposition rate of $5 \text{Å/sec}$ is obtained.

X-ray and electron diffraction measurements were made to identify the two compounds appearing in the films and to measure the lattice parameters. The lattice parameter for the pure NbN films was determined to be $4.39 \text{Å}$ in agreement with the data of Pessall, Hulm and Walker. The high $T_c$ films on hastelloy substrates showed a preferred orientation in the (111) direction perpendicular to the substrate surface. This indicates that if proper substrate materials are employed, it may be possible to grow single crystal films. So far only fused silica and hastelloy substrates have been used, with essentially identical electrical properties.

III. EXPERIMENTAL RESULTS

Preliminary measurements indicated that the upper critical field of these films was significantly higher than that of the bulk material. To date, two sets of measurements have been made to try to determine the high field properties.

At temperatures near $T_c$, low current density, resistive measurements have been made in a 50 Koe superconducting magnet to determine $H_{c2}$ as a function of temperature. The experiments were carried out with the external magnetic field perpendicular to the substrate surface and the direction of current flow. Following the usual practice, the field at which the resistance of the film was equal to half its normal value was taken as the resistive transition field $H_r$. For the measurements
near $T_c$ this field was found to be independent of current density for $J < 1000 \, A/cm^2$. The results for a NbN film 1780 Å thick are shown in Fig. 2. For comparison, the data of Hechler, Saur and Wizgall\textsuperscript{(2)} for bulk NbN has been included.

The other set of measurements were made in the National Magnet Laboratory 220 Koe dc field magnet. These measurements were carried out at 4.2 K with the sample surface and direction of current flow perpendicular to the magnetic field. The results of these measurements are shown in Fig. 3. Since the sample was on a hastelloy substrate which would begin to conduct current as soon as the film entered the normal region, we have used the onset of resistance to define the critical field in these measurements. At current densities over $1.5 \times 10^5 \, A/cm^2$, some problems were encountered with heating effects in the samples. From this figure it can be seen that the sample has not shown any signs of resistance at 210 Koe at a current density of $3.5 \times 10^3 \, A/cm^2$. From this data we infer that $H_{c2}(0)$ is probably in the region of 250 Koe, or higher.

\section*{IV. DISCUSSION}

By making use of the magnetic measurements described above, the normal state resistivity, $\rho_n$, and the electronic specific heat coefficient $\gamma$, comparison with present theory is possible. Table 1 summarizes the experimentally determined parameters which are used in the analysis. For comparison, the experimental parameters of bulk NbN are also shown. The data on the bulk material is taken from the work of Hechler, Saur and Wizgall.\textsuperscript{(2)} The normal state resistivity was
determined from the films deposited on fused silica substrates, and is approximately 15 times larger than that measured in the bulk. This difference is difficult to account for since the films appear to be polycrystalline rather than amorphous, with crystallite sizes ranging up to 1000 Å or more. The value of γ is taken from the data on bulk NbN of Pessall, Hulm and Walker.\(^{(1)}\)

According to the theories of Maki,\(^{(4,5)}\) and Werthamer, Helfand and Hohenberg,\(^{(6)}\) the upper critical field at \(T = 0\) in the dirty limit and in the absence of Pauli Spin Paramagnetic (PSP) effects is related to the slope \(H_o = -(\frac{dH_c^2}{dt})_{t=1}\), where \(t = T/T_c\), by the expression

\[
H_{c2}^*(0) = 0.69 H_o.
\]

(1)

\(H_{c2}^*(0)\) may also be expressed in terms of the normal state parameters of the material as

\[
H_{c2}^*(0) = 3.1 \times 10^4 \rho_n \gamma T_c.
\]

(2)

Using the data in Table 1 to obtain estimates of \(H_{c2}^*\) from Eqs. (1) and (2), we obtain 379 Koe and 1164 Koe respectively. These two calculations yield widely different estimates of the upper critical field but they do indicate that the effects of PSP must be quite large in this material, since these values both appear to be larger than the experimental upper critical field.

The importance of paramagnetic effects is characterized by the parameter \(\alpha\) in Maki's theory, and in terms of the normal state parameters is given by
\[ H_{c2}(0) = 0.69 H_0 (1 + \alpha^2)^{-1/2} \] 

\[ H_{c2}(0) = 3.1 \times 10^4 \gamma \rho_n T_c (1 + \alpha^2)^{-1/2} \] 

Using the value of \( \alpha \) calculated above, estimates of \( H_{c2}(0) \) of 63 Koe and 194 Koe are obtained from Eqs. (4) and (5) respectively.

The parameter \( \alpha \) may also be expressed in terms of the experimental \( H_{c2} \) vs. \( T \) slope at \( T = T_c \) as

\[ \sigma = 5.28 \times 10^{-5} \left( -\frac{dH_{c2}}{dT} \right)_{T=T_c} \]

Evaluation of this equation yields a value of 1.90 for \( \sigma \). Using this value for \( \sigma \), we may again calculate \( H_{c2}(0) \) from Eqs. (4) and (5) obtaining 176 Koe and 540 Koe respectively.

Of all these calculations there are probably three sets of numbers which are most important, as shown in Table 2. First, if we ignore paramagnetic effects (\( \alpha = 0 \)) and calculate the predicted upper critical field, the value obtained using the experimentally determined slope at \( T = T_c \) is higher than can be justified on the basis of the measurements, and the value obtained using the normal parameters is about 3 times higher yet. This tells us that paramagnetic effects must be limiting the upper critical field. We now have two ways of incorporating these effects. The value of \( \alpha \) and subsequently the upper critical field can be calculated using the normal state parameters, as shown under II, or they can be calculated using the slope of \( H \) vs. \( T \) at \( T = T_c \) as shown in III.
The value of $H_{c2}$ in II is closer to what we would expect experimentally than that in III but it depends very strongly upon the value of the bulk resistivity, which as mentioned previously appears to be unusually high in these materials.

The important factor which has been left out of these calculations is an estimate of the magnitude of the spin-orbit scattering. This effect is important since it would tend to counteract the reduction in the upper critical field due to PSP.

Based upon the experimental facts that the Knight shift and susceptibility in NbN are quite small, Geballe and his colleagues have proposed a band structure for NbN which is primarily s-p like in character. In this model the Fermi level lies in a band made up of Nb 5s,5p and $N_2$ 3s,3p wave functions. Above the Fermi level is an anti-bonding band made up of Nb 4d and $N_2$ 2p wave functions, but this band will be almost totally empty. On the basis of this model, we would expect a relatively small spin-orbit scattering effect in NbN. This is consistent with our estimated $H_{c2}(0)$ near 250 Koe. It is of interest to compare this result with the work of Foner et al. on NbAl-Nb$_3$Ge$_2$ alloys, where the effects of PSP on the upper critical field appear to be totally suppressed by spin-orbit scattering. A very small paramagnetic effect was also observed by Neuringer and Shapira in their work on Nb-25% Zr.

Hake has calculated the maximum $H_{c2}$ value to be expected in NbN as 250 Koe which is not inconsistent with our data. This calculation was based on an estimated maximum resistivity of 250 micro-ohm-cm
which is a factor of 3 lower than that measured in our films. Also, Hake predicted that PSP effects in NbN would be suppressed and that the upper critical field would be given by Eq. (1).

In the near future we hope to be able to obtain a more complete set of data on $H_{c2}$ vs. $T$ for NbN so that the relative importance of PSP and spin-orbit scattering can be calculated with greater precision.

V. ACKNOWLEDGMENTS

We would like to acknowledge the considerable assistance of A. Patterson in making the measurements presented here and the invaluable cooperation of the personnel of the National Magnet Laboratory.
<table>
<thead>
<tr>
<th>NbN Film No. 16</th>
<th>NbN Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \rho_n = 770 , \mu\Omega\cdot\text{cm} )</td>
<td>( \rho_n = 50 , \mu\Omega\cdot\text{cm} )</td>
</tr>
<tr>
<td>( \gamma = 3.2 \times 10^3 , \text{ergs/cc} \cdot K^2 )</td>
<td>( \gamma = 3.2 \times 10^3 , \text{ergs/cc} \cdot K^2 )</td>
</tr>
<tr>
<td>(- \left( \frac{dH_c^2}{dT} \right)_{T=1} = 550 , \text{Koe})</td>
<td>(- \left( \frac{dH_c^2}{dT} \right)_{T=T_c} = 220 , \text{Koe})</td>
</tr>
<tr>
<td>(- \left( \frac{dH_c^2}{dT} \right)_{T=T_c} = 36 , \text{Koe}/\text{K} )</td>
<td>(- \left( \frac{dH_c^2}{dT} \right)_{T=T_c} = 13.7 , \text{Koe}/\text{K} )</td>
</tr>
<tr>
<td>( T_c = 15.23^\circ K )</td>
<td>( T_c = 16.10^\circ K )</td>
</tr>
<tr>
<td>Thickness = 1780 ( \AA )</td>
<td>/</td>
</tr>
<tr>
<td>Table 2</td>
<td>Results of the Theoretical Calculation of the Upper Critical Field</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------------------------</td>
</tr>
</tbody>
</table>

I. \[ \alpha = 0 \]

\[ H_{c2}^*(0) = 379 \text{ Koe (Experimental)} \]

\[ H_{c2}(0) = 1164 \text{ Koe (Normal State Parameters)} \]

II. \[ \alpha = 5.92 \text{ (Normal State Parameters)} \]

\[ H_{c2}(0) = 194 \text{ Koe} \]

III. \[ \alpha = 1.90 \text{ (Experimental)} \]

\[ H_{c2}(0) = 176 \text{ Koe} \]
REFERENCES


FIGURE CAPTIONS

Fig. 1  Transition temperatures of niobium-nitrogen films sputtered in an argon-nitrogen atmosphere as a function of the nitrogen partial pressure.

Fig. 2  $H_{c2}$-$t$ curve for a 1780 Å NbN film near $T_c$.

Fig. 3  Transverse $J_c$-$H$ curve at 4.2°K for the same NbN film shown in Fig. 2.
Fig. 1

Transition Temperature, $T_c$ (K)

$N_bN$

$N_b$

$N_2$ Pressure, torr

Curve 587264-A
Fig. 2
Fig. 3
SUPERCONDUCTING PROPERTIES OF
NIOBIUM TITANIUM NITRIDE THIN FILMS*+

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ABSTRACT

A series of Nb-Ti-N films have been prepared, with various Nb/Ti ratios, by a high purity, reactive sputtering process. A maximum in transition temperature (at ~ 15.5°K) has been obtained at a composition of Nb_{0.5}Ti_{0.5}N. Critical field and critical current measurements indicate a degradation in these properties with increasing titanium content, contrary to results reported previously.

*This work supported in part by the National Aeronautics and Space Administration.

+Part of this work was performed at the Francis Bitter National Magnet Laboratory which is supported at M.I.T. by the Air Force Office of Scientific Research.
Superconducting critical temperatures up to about 18°K have been reported for a number of the Bi structure (rocksalt) compounds based upon the group IV and group V transition metals.\(^{(1,2)}\) In bulk form, these compounds exhibit lower critical current densities, \(J_c\), and smaller values of upper critical field, \(H_c^2\), than high \(T_c\) compounds of the well-known A15 structure (B-W). We recently found, by careful attention to purity, that thin films of NbN can be made with \(T_c\) around 15°K, which is equal to the bulk material \(T_c\). Moreover, we have found that the high field properties of NbN are greatly improved when prepared in thin film form.\(^{(3,4)}\) In this paper we report on the superconducting properties of thin films in the Nb-Ti-N system.

The films in this investigation were prepared by a high purity sputtering technique similar to that previously used for the deposition of NbN films.\(^{(3)}\) This technique involves deposition under ultra-low background pressures of \(< 5 \times 10^{-10}\) Torr and the use of high substrate temperatures (500°C). To obtain films of various compositions, flat sputtering cathodes were used, made either from a Nb-Ti alloy or from pure niobium and titanium welded together into a single cathode. The compositions of the films were estimated either from the composition of the Nb-Ti alloy, or from the location of the substrates, when the two section niobium and titanium cathode was used.
In our experiments the addition of titanium to the NbN structure produced a maximum $T_c$ of $\sim 25.5^\circ$K, in the general compositional range of Nb$_{.6}$Ti$_{.4}$N-Nb$_{.4}$Ti$_{.6}$N. Although considerably lower than the bulk value ($T_c \sim 18^\circ$K), this is the highest $T_c$ reported thus far for a film of uniform composition and a thickness of the order of 1000Å. All of these higher $T_c$ films were deposited from the two section niobium-titanium cathode.

Figure 1 shows critical current versus field data on four of our films with various concentrations of titanium. As can be noted the addition of titanium resulted in lower $J_c$ and $H_{c2}$ values compared to the pure NbN film. Table I lists some additional experimental data on two typical film samples of NbN and Nb-Ti-N which were deposited in a single experiment using a two sectional cathode. The $H_{c2}(0)$ values of $\sim 250$ K0e, listed in Table I, are estimated from the data shown on Fig. 1. Both the critical current and the critical field values of the Nb-Ti-N film are much higher than that reported for bulk samples in the Nb-Ti-N system, by Pessall and co-workers.\(^{(2)}\) Bell, et al\(^{(5)}\) previously reported higher $J_c$ and $H_c$ values in Nb-Ti-N films than found in bulk samples. However, they also reported that the addition of titanium to the NbN structure caused an enhancement in $J_c$ and $H_{c2}$ properties as well as raising the maximum $T_c$'s of their films from $\sim 12^\circ$K to $\sim 13.5^\circ$K. Although higher $J_c$ and $H_{c2}$ values have been observed in some of our Nb-Ti-N films, our results differ most significantly from those of Bell, et al, in that the addition of titanium to NbN caused a depression in critical current and field properties rather than an enhancement.
The theory of type II superconductors suggests certain simple relationships involving $H_{c2}(0)$ and the other experimental properties of Table I. These are:

**Paramagnetic upper limit** $(6,7)$

$$H_{c2}(0) < 18,400 \ T_c$$

**Paramagnetically modified zero temperature critical field in terms of the critical field slope at $T_c$** $(8-10)$

$$H_{c2}(0) = 0.69 \ H_o / [1 + (5.28 \times 10^{-5} \ H_o / T_c)^2]^{1/2}$$

**Paramagnetically modified zero temperature critical field in terms of normal state parameters** $(8,9,11-13)$

$$H_{c2}(0) = 3.1 \times 10^4 \ \gamma \ \rho_n \ T_c / (1 + [2.4 \ \gamma \ \rho_n]^2)^{1/2}$$

These derived values of $H_{c2}(0)$ which are listed on Table I are not appreciably different from the experimental values. While this is satisfactory as far as it goes, it obscures the fact that equations (2) and (3) involve completely different values of the paramagnetic correction factor, $\alpha$. Thus for NbN, equation (2) yields $\alpha = 5.28 \times 10^{-5} \ H_o / T_c = 1.9$, whereas equation (3) gives $\alpha = 2.4 \ \gamma \ \rho_n = 5.4$. We are unable to derive a reliable value of $\alpha$ from the present data, primarily because $H_{c2}(0)$ is insensitive to the exact value of $\alpha$ when this quantity is large.

Regarding the observed degradation of $H_c$ and $T_c$ properties with increased titanium content in our Nb-Ti-N films, we suggest the
following tentative explanation. Due to the greater affinity of titanium to gaseous impurities in the deposition apparatus, it is possible that the titanium is contaminated during the deposition process by these gases. Simultaneously, however, due to the somewhat lesser affinity of Nb to these same impurities, comparatively pure NbN is also formed. The resulting film is thus a mixture of NbN and slightly contaminated Nb-Ti-N and the properties observed in these films are primarily associated with the NbN. This explanation appears to be consistent with all of the experimental data on these film samples.

If this suggestion is correct, it would appear likely that even more superior superconducting properties than those presently observed may be achieved in very pure Nb-Ti-N films. Preparation of these films may be possible by a further sophistication of our present film growth techniques to further reduce residual gas contamination of the films. In any case, it has been shown that the superconducting properties of NaCl structure compounds are entirely comparable to those in the well known β-W compounds and thus further research in this relatively unexplored area should prove extremely fruitful in terms of useful high field superconductors.
<table>
<thead>
<tr>
<th><strong>Measured</strong></th>
<th>( T_c )</th>
<th>( H_o )</th>
<th>( \rho_n )</th>
<th>( H_{c2}(0) )</th>
<th>( T_c )</th>
<th>( H_o )</th>
<th>( \rho_n )</th>
<th>( H_{c2}(0) )</th>
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<tbody>
<tr>
<td>( 15^\circ K )</td>
<td>( 15.5^\circ K )</td>
<td>( 550 \text{ kOe} )</td>
<td>( 570 \text{ kOe} )</td>
<td>( 700 \mu \text{ ohm cm} )</td>
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<td>( \lesssim 250 \text{ kOe} )</td>
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<tr>
<td><strong>Derived</strong></td>
<td>( H_{c2}(0) ) [Eq. 1]</td>
<td>( 276 \text{ kOe} )</td>
<td>( 285 \text{ kOe} )</td>
<td>( H_{c2}(0) ) [Eq. 2]</td>
<td>( 174 \text{ kOe} )</td>
<td>( 173 \text{ kOe} )</td>
<td>( H_{c2}(0) ) [Eq. 3]*</td>
<td>( 190 \text{ kOe} )</td>
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</table>

*Using \( \gamma = 3.2 \times 10^3 \text{ ergs cc}^{-1} \text{ deg}^{-2} \)
References


Figure Caption

Fig. 1  $J_c$-$H$ characteristics of Nb-Ti-N films with various concentrations of titanium: No. 1 - NbN, No. 2 - Nb$_{6}$Ti$_{4}$N, No. 3 - Nb$_{5.5}$Ti$_{5.5}$N, No. 4 - Nb$_{4}$Ti$_{6}$N.
Curve 589246-A

$J_c \perp H$

$T = 4.2^\circ K$

$\text{NbN} \; 1$

$[T_c \sim 15^\circ K]$

$\text{NbTiN} \; 2$

$[T_c \sim 15^\circ K]$

$\text{NbTiN} \; 4$

$[T_c \sim 15^\circ K]$

$\text{NbTiN} \; 3$

$[T_c \sim 15.5^\circ K]$

$J_c$, amperes/cm$^2$

$H$, kOe
ULTRASONIC ATTENUATION IN
SUPERCONDUCTING MOLYBDENUM-RHENIUM ALLOYS*

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ABSTRACT

The attenuation of longitudinal sound in superconducting molybdenum-rhenium has been investigated as a function of temperature, T, magnetic field, H, and frequency, v. Measurements up to 3 GHz were possible in a [100] sample of Mo-25Re (T_c = 10.25°K) using evaporated thin film CdS transducers. The normal state attenuation coefficient (0.43 db/cm at 1 GHz) was found to be proportional to v^2 over this range, consistent with the condition q\ell \ll 1, as would be expected from the measured residual resistivity ratio of 2.8.

Measurements in zero magnetic field yielded a value of the energy gap parameter close to the theoretical value of 3.56 kT_c appropriate to a weakly coupled (T_c/\Theta_D \ll 1) dirty limit (\ell \ll \xi_o) superconductor. It is found that \alpha varies linearly with H over most of the region of the mixed state H_{cl} < H < H_{c2}, in general qualitative agreement with the theory of Houghton and McLean for the extreme dirty limit of a type II superconductor.

*This work supported in part by the National Aeronautics and Space Administration.
Ultrasonic attenuation measurements in superconductors have proven very useful in probing the structure of the intermediate and the mixed states.\(^{(1)}\) For the most part, these measurements have been performed on materials of intermediate to high purity; i.e., \(\xi_0/\ell < 1\), in which \(\xi_0\) is the superconducting coherence length and \(\ell\) is the electron mean free path. Niobium has been the principal experimental system because of its availability in controlled, relatively high purities. By working at acoustic frequencies as high as several hundred megahertz, it has been possible to achieve \(q\ell\) values as high as 10, where \(q\) is the sound wave vector. There has been generally good agreement with theory in the pure limit,\(^{(1)}\) although many important details remain to be cleared up. In the dirty limit, \(\xi_0/\ell \gg 1\), only a very small amount of experimental work has been done because of the difficulties associated with such measurements at praetersonic frequencies.

We chose the Mo-Re alloy system, for which magnetic and calorimetric measurements have already been carried out.\(^{(2,3)}\) In order to reach into the frequency range of interest, where the electronic contribution to the attenuation is dominant, we used thin film, vapor deposited cadmium sulphide transducers.\(^{(4)}\) The samples were mounted in a 1-3/4" bore, 60 kilogauss, superconducting solenoid, allowing data to be taken both as a function of temperature and magnetic field. Attenuation measurements were made in transmission using standard pulse
echo techniques. The sample was 2.5 cm long and 0.5 cm in diameter.
The [100] direction was parallel to the rod axis. The attenuation measurements used to determine the energy gap were taken at 1430 megahertz on the fourth echo. Data was taken between 1.5°K and \( T_C \) (10.25°K). The results obtained in the temperature range \( 0.35 < t < 0.65 \) (\( t = T/T_C \)) were fitted by a least squares technique to the usual equation (5)

\[
\frac{\alpha_s}{\alpha_n} = \frac{2}{[1 + \exp \Delta(t)/kT]}
\]  

This relationship is valid for all values of \( q^2 \). \( \alpha_s \) and \( \alpha_n \) are the superconducting and normal state attenuation respectively and \( \Delta(t) \) is the temperature dependent energy gap parameter. The temperature dependence of \( \Delta(t) \) is assumed to obey the BCS relationship and the quantity \( A \), where \( 2\Delta(0) = 2A kT_C \) is taken as an adjustable parameter. A typical set of data is shown in Fig. 1. The best fit was obtained with a value of 1.70 ± 0.1 for \( A \). Thus, Mo-25 At. % Re may be classed as a high \( T_C \) weak-coupling alloy in contrast to other compounds such as NbN and the element lead, which are strong coupling (\( A \) values of 2 or higher) . (7,8)

Measurements of the normal state attenuation at 700, 1430 and 2800 MHz showed that \( \alpha_n \) varies quadratically with frequency. This is characteristic of the \( q^2 << 1 \) regime.

The normal state attenuation, normalized to 1 GHz, was 0.43 db/cm. Using a free electron model \( \alpha_n \) may be expressed as (9)
\[ \alpha_n = \frac{2}{15} \frac{N_m V_F \omega}{\rho_o V_s^2} q^2 \]  

where \( N_m, V_F, \omega, \rho_o \) and \( V_s \) are respectively the carrier density, electron mass, Fermi velocity, sound frequency, sample density and the sound velocity. The Fermi velocity \( (5 \times 10^7 \text{ cm/sec}) \) was estimated from heat capacity data \(^3\) and the sound velocity was measured as \( 4.5 \times 10^5 \text{ cm/sec} \). The carrier density \( N \), can only be calculated if the details of the band structure are known. None of this information is available for the Mo-Re alloy system but the band structure of Mo is well known, and Sparlin and Marcus \(^{10}\) have concluded that there are 0.44 carriers per atom. This yields a value of 0.26 db/cm-GHz for \( \alpha_n \) from equation 2. In assuming the band structure of Mo, a lower estimate of \( N \) is obtained. An upper estimate can be obtained by taking 0.44 carriers per Mo atom and a full 7 for each Re atom as if an impurity doping mechanism were operative. This approximation yields \( \alpha_n = 0.41 \) db/cm-GHz. The very close agreement here between experiment and the free electron model is probably fortuitous, but can be contrasted with the case of the pure transition metals, such as tungsten and molybdenum, where divergences of up to two orders of magnitude occur. \(^{11}\)

The theory of ultrasonic attenuation in the mixed state of superconductors in the dirty limit has been developed by McLean and Houghton, \(^{12}\) and Maki and Fulde. \(^{13}\) The principal result relates the attenuation
relative to the normal state, $\alpha_s/\alpha_n$ to the magnetic field, $H$. For $H$ near $H_{c2}$ this is

$$\frac{\alpha_s}{\alpha_n} = 1 - \frac{1}{2} \left( \frac{\Delta}{2kT} \right)^2 F(p)$$  \hspace{1cm} (3)

$$1 - \frac{\alpha_s}{\alpha_n} = \frac{3}{4\pi} \frac{me^2}{N\tau^2 \nu_F^2} \frac{H_{c2} - H}{H_{c2} (2\kappa^2 - 1) \beta}$$

In distinction to the pure limit in which the attenuation has a linear dependence on the order parameter $\Delta$, the attenuation for the dirty limit is quadratically dependent upon $\Delta$. In equation 3, $e$ and $\tau$ represent, respectively, electronic charge and collision time; $p = \tau \nu_F^2 e H_{c2}/6\pi kT$, and $L(p)$ is a function which varies between 0 and 1, as defined in reference 12, and $\beta = 1.116$.

Measurements of the magnetic field dependence of the attenuation were made at $T = 4.2^\circ$K and $2.2^\circ$K for $H \parallel \mathbf{q}$. These curves are shown in Fig. 2. This data was obtained at a frequency of 700 MHz, on the tenth echo. While the theory predicts a linear dependence of $\alpha$ on $H$ only at $H_{c2}$, the curves indicate a linear region extending over a large portion of the mixed state. These two curves are identical when plotted as reduced attenuation vs reduced field. The normalized slope, $\frac{H_{c2}}{\alpha_n} \frac{\partial \alpha}{\partial H}$, that is determined from these curves is 2.7. Calculating the normalized slope from equation 3 involves two problems. One is determining the value of the carrier density to be used as discussed.
previously, the other is calculating the mean free path necessary to find the scattering time. The electronic mean free path may be estimated from the relationship

\[ \ell = \sigma \frac{12 \pi^3 \hbar}{e^2 S} \]

(4)

where \( \sigma \) and \( S \) are the low temperature conductivity and effective fermi surface area respectively. The problems associated with calculating \( S \) are the same as those with finding \( N \). We may get high and low estimates of \( \ell \) by again assuming the band structure of Mo and then either neglecting the Re or assuming a full 7 electrons per atom. This yields estimates of the mean free path of 240 \( \AA \) and 85 \( \AA \) respectively. Using these values in equation 3 the normalized slopes obtained are .29 and .49 respectively. These values are relatively low but not surprising since it is extremely difficult to obtain reliable values of \( N \) and \( \ell \) for an alloy system. Even though the experiment-theory values are not very close, the linearity of \( \alpha/\alpha_n \) versus \( H \) clearly shows that we are in the dirty limit, and not the intermediate region such as is characterized by the data of Tittman and Bömmel on V-5% Ta.\(^{(16)}\) In the latter work which corresponded to \( t_0/\ell \sim 5 \) the attenuation showed neither the linear dependence of the dirty limit nor the \( \alpha/\alpha_n \propto H^{1/2} \) dependence of the clean limit.

In conclusion we can say that the energy gap and normal state attenuation measurements show rather conclusively that Mo-25 At. % Re
is a weak coupling, dirty limit superconductor. The agreement between
the calculated normal state attenuation in the $q^2 << 1$ region and that
measured experimentally is very good. A lack of normal state data precludes
an accurate theoretical calculation of the normalized attenuation versus
magnetic field slope near $H_{c2}$. Even so, the large discrepancy between
experiment and theory is difficult to explain since such good agreement
was obtained in the calculation of $A$ and $\alpha_n$. This may indicate that
further modification of the theoretical expression is necessary.
References


Figure Captions

Figure 1  Normalized ultrasonic attenuation versus reduced temperature. A is defined by the expression $2\Delta(0) = 2A\kappa T_C$.

Figure 2  Ultrasonic attenuation in the mixed state of Mo-25 % Re, as a function of magnetic field.
$M_0 - 25\% \text{ Re}$

Length = 2.5 cm

$q \parallel [100]$

$\nu = 1430 \text{ MHz, 4th Echo}$

$\alpha_N = 15.3 \text{ db}$

$A = 1.70 \pm 0.1$

$\frac{a_S}{a_N}$

$t = \frac{T}{T_c}$
ABSTRACT

Niobium nitride, NbN, films with thicknesses ranging from 5000 Å down to approximately 10 Å have been prepared by a high purity reactive sputtering process and their superconducting properties measured. A depression in transition temperature, $T_c$, with decreasing thickness has been observed, starting from a maximum $T_c$ of $\sim 15.2^\circ$K in the thicker films down to $\sim 6.5^\circ$K in a 25 Å film. The critical current vs. applied magnetic field curves were found to be independent of thickness or even to increase slightly down to a thickness of 100 Å. Below this point the critical current at high fields decreased sharply, the films apparently becoming discontinuous. The average resistivity of the NbN films was $\sim 1000 \mu$ ohm cm.

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SUPERCONDUCTING PROPERTIES AS A FUNCTION OF THICKNESS IN NbN FILMS*†

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In the study of superconductivity, the effect on superconducting properties produced by changes in specimen dimensions or geometry, has long been a subject of considerable interest. Recently, for example, a significant part of the effort to produce higher transition temperature materials has been centred on the study of superconductors prepared in thin film form. In general, the work in this area has been concentrated on the study of superconducting elements -- all of which have transition temperatures in bulk form of 9°K or lower. In a few cases, substantial increases in transition temperature have been reported. However, all of these enhancements were observed with elements having low transition temperatures, and in no case have materials been prepared with transition temperatures in excess of 10°K. Very limited data is presently available on thin films of the high Tc compounds such as occur in the rocksalt or β-tungsten structures, even though enhancement of any of the superconducting properties of these materials would be of immediate practical importance.

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This lack of data is undoubtedly associated with the considerable difficulties involved in the preparation of these compounds in thin film form. The effect on $T_c$ of preparing very thin films of some of these compounds has been considered by a number of theorists. The conclusions which have been drawn, however, have been dissimilar, or even contradictory.\textsuperscript{(5,6)}

Recently, we have successfully prepared films of the rocksalt compound NbN, with $T_c$'s of approximately $15^\circ K$ and with enhanced high field properties relative to those of the bulk material.\textsuperscript{(7)} The thicknesses of these films were approximately 2000 Å. Films of NbN have now been prepared with thicknesses ranging from 5000 Å down to about 10 Å. In this paper, we report on the superconducting properties of these films.

**Experimental Procedure**

The NbN films used in this study were deposited by a high purity reactive sputtering process which has previously been described in detail.\textsuperscript{(7)} Briefly, this process involves sputtering niobium in an argon-nitrogen atmosphere with a total background impurity pressure of $5 \times 10^{-10}$ Torr or less. The NbN which is thus formed is deposited on substrates which are maintained at approximately $500^\circ C$. The thicknesses of the films were measured with an interferometer which has an accuracy of ±10 Å. The thicknesses of the very thin films (≈ 50 Å and less) were estimated from the duration of the growth experiments. Transition temperatures were measured with a silicon resistance thermometer in a system using helium exchange gas to cool the samples. Films with $T_c$'s above $13.7^\circ K$ were also measured in pumped liquid hydrogen by observing the vapor pressure of the hydrogen at the transition. The agreement between the two measurements was
0.1°K or better. High field data were obtained in the 220 kilogauss Bitter solenoid located at the National Magnet Laboratory. In all of these measurements the samples were mounted so that the magnetic field was applied perpendicular to the plane of the film and to current flow.

Results and Discussion

Figure 1 shows transition temperature data on NbN films deposited on both metallic and insulating substrates. This figure illustrates the depression in $T_c$ which occurs with decreasing film thickness. The last point shown on the curve is for a ~25 Å thick film on sapphire with a $T_c$ of ~6.5°K. NbN films approximately 10 Å thick have been prepared; these films, however, remained normal down to a temperature of 1.2°K. Following the usual convention, the value for $T_c$ used to plot this data is that temperature at which the specimen has lost one-half of its normal state resistivity. To illustrate the entire transitions, some representative curves are reproduced in Fig. 2. As typified by curves 1, 2 and 3 in this figure, all of the NbN layers down to a thickness of 100 Å became resistance-less. Starting at approximately 50 Å, however, the films began to retain some of their normal state resistance. These results indicate that between 50 and 100 Å, the deposited films start to become discontinuous and as the thickness is further decreased the discontinuity becomes increasingly greater.

An interesting feature of the $T_c$ curves in this figure is that with the exception of the 25 Å film, the onset of superconductivity in every case is at approximately 15°K. Therefore, is the highest temperature at which superconductivity is observed were plotted against film thickness, no depression in $T_c$ would occur until some thickness below 50 Å. Regardless
of what criterion for $T_c$ is used, however, our results demonstrate that no enhancement in $T_c$ occurs with decreasing thickness in NbN for films on the substrates employed so far. The reason for the observed depression in transition temperature is not known with certainty at present. The deleterious effect on $T_c$ of residual gas impurities in the growth system has been shown for NbN thin films prepared in the earlier work. Our present growth techniques greatly minimize the level of residual gases; however, these gases have not been completely eliminated. The portion of these remaining impurities, which originate from outgassing in the substrate region could be expected to exert a maximum effect on the initially deposited NbN. Thus the degradation in $T_c$ in the thinnest films could be interpreted as resulting from this type of contamination. Alternatively, the changes in $T_c$ could be attributable to a greater lattice disorder, which may be present to a greater degree in the thinner films. The character of this disorder would be sensitive to the conditions of nucleation. A mechanism by which lattice disorder influences transition temperature has been proposed by Garland and co-authors.\(^{(5)}\) Since no evidence exists to confirm either of these possibilities, the explanation for the depression in $T_c$ is still an open question. We are currently preparing a deposition system in which we hope to lower the background impurity level by at least another two orders of magnitude. The influence of various substrate materials will also be investigated.

Figure 3 shows $J_c$ vs. $H$ data for three NbN films. Both the 5000 Å film on stainless steel and the 100 Å film on sapphire have higher current density values than the 5000 Å film on sapphire. These results suggest that the current carrying capacities of these samples were limited
by heating effects at the current contacts. Using this assumption the higher \( J_c \) values for the 100 Å sample on sapphire probably result from the lower currents required to drive this film normal, compared to the 5000 Å film. In the case of the NbN film on stainless steel, the contact problem is apparently minimized by the stabilizing effect of the conducting substrate. This would account for the higher values in this sample. From these results, it is probable that our \( J_c \) values are somewhat conservative, especially in the thicker films measured at lower fields. Our most accurate current densities should be those measured in the thinnest continuous films and at the highest field. Using this criterion, our most reliable value is the \( \sim 3 \times 10^5 \) Amps/cm\(^2\) observed in the 100 Å film in a 210 kgauss field. It is worth noting that this is the highest current density, at this field, yet reported for any material.

In Fig. 4 current density versus thickness data on seven NbN films deposited on sapphire substrates are shown. Films on insulating substrates were used for these measurements since the detection of changes in resistance in very thin NbN films deposited on metallic substrates is greatly complicated by electrical noise problems. The figure shows an upward trend in \( J_c \) values in films between 5000 Å and 100 Å thick. This apparent enhancement may be due to the heating effects at the current contacts. At a minimum, however, these results demonstrate that there is no decrease in current densities down to a thickness of about 100 Å. This, in turn, suggests that the NbN films down to 100 Å are continuous with uniform thickness and composition. At thicknesses below 100 Å, there is a sharp drop in the \( J_c - H \) curves. In addition, the character of the transition from the superconducting to the normal state is found to change radically.
from that observed in the thicker films. This difference is shown in Fig. 5. Curve A typifies the transitions for films 100 Å thick and greater, while Curve B is a transition for a 50 Å film. As previously observed in the Tc measurements, only a part of the 50 Å thick NbN film enters the superconducting state, suggesting physical discontinuity in this film. It would seem probable that the sharp drop in current density, as well as the broad transition, are related to this apparent discontinuity. An alternative possibility is that at 50 Å, the film thickness is less than the optimum size for the pinning centers required to maintain superconductivity at the high fields. The drop in Jc-H properties in the 50 Å film could also simply be related to the low Tc of this film (~ 10°K). However, a drop in Tc from 15°K to 12.5°K in the 100 Å film did not produce a similar depression in its Jc-H properties.

In addition to the measurement of the superconducting properties of NbN, we have also determined the normal state resistivity of these films as a function of thickness. These measurements were made at room temperature, 77°K, and 20°K.

It was found that in every film measured the resistivity either stayed constant or rose slightly with decreasing temperature. The resistivity of these films showed no apparent dependence on film thickness down to and including films approximately 20 Å thick. The average resistivity (ρn), of all the samples measured was approximately 1000 µ ohm cm. The upper critical field, Hc2(0), of these films is estimated to be about 250 kGauss. This is considerably below the value suggested by the GLAG theory for a material with this very high resistivity. Using the GLAG formulation,
\[ H_{c2}(0) = 3.1 \times 10^4 \rho_n \gamma T_c \]  \hspace{1cm} (1)

where \( \gamma \) is the electronic specific heat coefficient; a value of 1400 kilogauss is calculated for the upper critical field. (The value for \( \gamma \) used in this calculation is \( 3.2 \times 10^3 \text{ erg/cc} \cdot \text{°K} \) - the bulk value.)

Taking into account paramagnetic effects, according to the equation of Maki, \( H_{c2}(0) = 3.1 \times 10^4 \rho_n \gamma T_c (1 + \alpha' \gamma)^{-1/2} \) \hspace{1cm} (2)

where \( \alpha \), the term used to characterize the paramagnetic effects, equals 7.7; the calculated upper critical field at zero temperature equals approximately 180 kilogauss. This result indicates that \( H_{c2}(0) \) is probably limited by the electron spin paramagnetism. This effect would be consistent with the proposed band structure for this compound.
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FIGURE CAPTIONS

Fig. 1 Transition temperature as a function of thickness in NbN films approximately 5000 Å down to 25 Å thick.

Fig. 2 Transition temperature curves for NbN films of five different thicknesses.

Fig. 3 J–H curves of: 1) 100 Å NbN film on sapphire, 2) 5000 Å NbN film on stainless steel and 3) 5000 Å NbN film on sapphire.

Fig. 4 Current density as a function of thickness in seven NbN films deposited on sapphire substrates.

Fig. 5 Typical transitions with field for: A) continuous NbN films between 100 Å and 5000 Å thick and B) for NbN films ~ 50 Å thick or less.
Fig. 1 - $T_c$ as a function of NbN film thickness

Curve 550443-A

- S. S. Substrate
- Sapphire Substrate

Transition Temperature, $K$

Thickness, $\AA$
Fig. 2—Typical $T_c$ curves for NbN films of various thickness
1) 100 Å ($T_C - 12.5^\circ K$)

2) 5000 Å ($T_C - 15.2^\circ K$)

3) 5000 Å ($T_C - 15.2^\circ K$)

$J_C \perp H$

$T = 4.2^\circ K$

1 NbN on Sapphire substrate
2 NbN on stainless steel substrate
3 NbN on Sapphire substrate

Fig. 3
Fig. 4—Current density as a function of thickness in NbN films

- $T = 4.2^\circ K$
- $H = 150$ kOe
- $J_C \perp H$
A) Typical transition curve for continuous NbN films
   (~100 to ≥ 5000 Å thick)

B) Typical transition curve for discontinuous NbN films
   (~50 Å thick and less)

Fig. 5
ABSTRACT

Superconducting compounds having the \( \beta \)-tungsten (Al5) structure are important materials for use at extremely high magnetic fields. One of these, \( \text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2}) \), has a superconducting transition temperature of 21°K, the highest known. High purity sputtering techniques developed to prepare Nb-Al-Ge compounds for the first time in the technologically advantageous thin film form will be described. These techniques include processing of the vacuum enclosure to reach pressures of \( \sim 10^{-10} \) Torr, sputtering with very high purity argon, and monitoring the impurity level in the system while sputtering by sampling the effluent gas and analyzing it with a quadrupole mass filter. Use of these techniques has resulted in the successful deposition of superconducting Nb-Al-Ge films with the \( \beta \)-tungsten structure, as verified by x-ray diffraction. The properties of these films in magnetic fields up to 220 kOe will be discussed in terms of current theory.

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PREPARATION AND PROPERTIES OF SUPERCONDUCTING THIN FILMS OF β-TUNGSTEN STRUCTURE COMPOUNDS

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As a class the β-tungsten structure superconducting compounds are very interesting because of their high transition temperatures, \( T_C \), and large upper critical magnetic fields, \( H_{c2} \). Preparation of these compounds in thin film form would lead to development of superconducting devices operable in liquid hydrogen and would thus have important technological implications. Also, as our previous work with NbN films suggests, thin films of these compounds could have critical current densities, \( J_C \), and critical magnetic fields considerably higher than those found in the bulk material.

In this paper we report efforts to sputter films of \( \text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2}) \), the β-tungsten structure compound which has the highest known transition temperature, over 20°K. It has been found that a prerequisite for sputtering high \( T_C \) transition metal superconducting compounds is a sputtering enclosure capable of reaching very low background pressures, in order to reduce contamination of the sputtering

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gas by impurities from the enclosure walls and interior hardware. The sputtering enclosure used in this work is a commercial all-metal Varian ultra-high vacuum system equipped with VacIon and titanium sublimation pumps. This system is routinely processed to reach the low $10^{-10}$ Torr range before the sputtering gas is admitted. Conventional dc diode sputtering has been used. The sputtering cathode was approximately four by six by one cm in size, of nominal composition $\text{Nb}_3\text{Al}_{0.8}\text{Ge}_{0.2}$, prepared by arc melting the constituents in an argon atmosphere. Starting materials of 99.97% or better purity were employed. The $T_c$ of the unannealed bulk cathode material was measured in liquid hydrogen as 18.5°K. This cathode target was suspended by niobium straps from a stainless steel backing plate faced with niobium sheet. Ground potential dark-space shielding was used around the feedthrough, the cathode support rod, and the back of the cathode backing plate. Additional dark-space shielding was fabricated from niobium sheet and was arranged to suppress sputtering from the niobium support straps and from the niobium cathode facing. Thus, all sputtering was confined to the bottom surface of the target. The argon used was 99.995% pure, the major impurity being neon. The gas was introduced through an ultra-high purity regulator and leak valve via a small diameter stainless steel tube directly into the vicinity of the cathode.

A dynamic sputtering environment was maintained, high purity argon gas being introduced continuously and pumped out by an auxiliary vacuum system via an isolation valve located at a point remote from the cathode. The inlet flow rate was adjusted to maintain a constant
pressure in the enclosure. Part of the effluent gas stream was diverted by a sampling valve into another auxiliary vacuum system where it was analyzed continuously by a Varian quadrupole residual gas analyzer (QRGA). The mass spectrum was displayed continuously on an oscilloscope to permit real-time monitoring of the impurity levels in the enclosure. The QRGA sensitivity in this continuous mode of operation was $10^{-9}$ Torr for a total pressure of $5 \times 10^{-6}$ Torr in the QRGA auxiliary vacuum system. Thus, for sputtering gas pressures in the 100 millitorr range the detectable impurity level was $2 \times 10^{-5}$ Torr or 0.02%. No impurities such as hydrogen, water vapor, oxygen, nitrogen or CO$_2$ were detected during any sputtering run except as noted below. The auxiliary vacuum systems were liquid nitrogen trapped and employed oil diffusion pumps in order to pump the argon sputtering gas.

An electrically heated stainless steel substrate platen was located 1.5 cm from the bottom face of the cathode. The heating element was Pt-Rh wire threaded through high purity alumina insulators. Temperatures were monitored by a Pt-Pt$_{90}$Rh$_{10}$ thermocouple located on the top surface of the platen about one cm from the center of the substrate ribbon. Temperatures could be controlled within twenty degrees over the range from room temperature to above 1000°C. A lower temperature limit was set by the sputtering power used, since the platen was not cooled. Substrates were Hastelloy ribbon, in a continuous length, which was unrolled from a reel, drawn across the substrate platen, and wound onto a take-up reel. To prevent galling, all moving shafts were run in stainless steel ball bearings lubricated by molybdenum disulfide powder.
Using this tape transport device, twenty to thirty samples could be sputtered under various conditions before opening the vacuum system. Argon sputtering gas pressures were typically 100 to 200 millitorr and sputtering voltages and currents of 2 kilovolts and 40 to 120 milliamps were used.

Results

Films deposited using this arrangement were found by X-ray diffraction analysis to have the desired 8-tungsten (Al5) structure. The highest $T_c$ obtained, however, was 11.4°K. $T_c$'s were found to be independent of sputtering characteristics over a range of sputtering power from six to ten watts/cm$^2$. Substrate temperatures between 500° and 650°C produced $T_c$'s above 10°K. $T_c$'s fell off very sharply to below 4.2°K as substrate temperatures were raised above 700°C. Hydrogen and CO$_2$ impurity levels detectable by the QRG$A$ appeared only when the substrate platen temperature was raised above 850°C. Evidently impurities are not the cause of the low $T_c$'s observed for substrate temperatures below 650°C. With optimum sputtering characteristics and substrate temperature, there was a random scatter of $T_c$ between 9° and 11.4°K even for successive samples sputtered under nominally identical conditions, which suggests that the surface characteristics of the cathode were changing. Subsequent slicing, polishing and etching of the cathode target showed some inhomogeneities probably due to incomplete reaction of the starting materials. Thus, the cathode composition at the sputtering surface may not have corresponded to the nominal composition. This cathode target could therefore have produced non-stoichiometric
films which would account for the low $T_c$'s. The cathode composition at the surface may also have been changing due to diffusion processes, which could account for the scatter of $T_c$'s of otherwise identically prepared samples. This diffusion could have been occurring in the cathode, since cathode temperatures above 1100°C were reached for the higher sputtering powers. Heat treatment of several samples in evacuated quartz tubes at 750°C for various lengths of time was performed, but these treatments always lowered the $T_c$. This method of heat treatment, while satisfactory for bulk materials, probably exposes thin film samples to excessive contamination.

Steady state critical current versus transverse magnetic field data were taken for several samples at 4.2°K with the 220 kG solenoid at the Francis Bitter National Magnet Laboratory. Figure 1 shows a $J_{cs}$ vs. $H$ curve for a 2000 Å thick sample with a $T_c$ of 10.7°K, along with the bulk data of Hartsough, Zackay, and Parker$^{(4)}$ which shows a peak effect. No peak effect was observed in any of our thin film samples. $J_{cs}$ is the value of current which causes onset of resistance in the film, as opposed to $J_{cn}$, the value for which the sample becomes completely normal. We chose as $J_{cs}$ the current at which the sample reached 10% of its normal state resistance. Extrapolating $J_{cs}$ and/or $J_{cn}$ to very small currents gives $H_{c2}$, the magnetic field which alone is sufficient to drive the sample normal. The highest upper critical field $H_{c2}$ observed for any sample was 180 kG for a 4000 Å thick sample with a $T_c$ of 11.4°K. This is somewhat below the 210 kG limit imposed by Pauli spin paramagnetism for this $T_c$.$^{(5)}$ In the absence of reliable specific
heat and resistivity data for the thin films, comparison with the predictions of the GLAG theory\(^{(6)}\) is not possible at this time. A significant feature of the high field measurements was that for all of our films the critical current at fields lower than 120 kG is much higher than that of the bulk, even though the \(T_c\)'s are much lower.

By sputtering from a suitably homogeneous cathode of the proper composition, it should be possible to produce stoichiometric films with \(T_c\)'s the same as the bulk value. Efforts to prepare such films are continuing since our present results suggest that they will have superior magnetic properties and will thus be most useful for device applications at high magnetic fields.
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Fig. 1 Critical current density $J_c$ vs. magnetic field $H$ for a $\text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2})$ film, $T = 10.7^\circ\text{K}$. Bulk curve for an annealed sample, $T_c = 19.0^\circ\text{K}$, from Hartsough, Zackay and Parker.\(^{(4)}\)
Fig. 1

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APPENDIX A8
THE VERY HIGH CRITICAL CURRENT AND FIELD CHARACTERISTICS
OF NIOBIUM NITRIDE THIN FILMS*

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ABSTRACT

Previous results indicated that NbN thin films possess critical
current and field characteristics significantly superior to that of
bulk NbN having a similar Tc. Further measurements made on NbN films,
with thicknesses between 50 Å and 8μ, now show that, at 4.2°K, certain
of these films exhibit the highest current densities of any presently
known superconductor in all fields from zero up to the limit of our
measurement capability, (210 kOe). In addition, anomalously high current
and field values have been measured in very thin (< 300 Å) films. These
thinner films show no depressions in Jc (measured at 4.2°K) or in
Hc2(0) values despite decreases in Tc from almost 16°K (in the thicker
films) down to 11°K.

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THE VERY HIGH CRITICAL CURRENT AND FIELD CHARACTERISTICS OF NIOBIUM NITRIDE THIN FILMS

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INTRODUCTION

In a preceding publication we described a sputtering process for depositing niobium nitride (NbN) thin films with superconducting transition temperatures similar to that of the bulk material, i.e. 15-16°K. Critical current and field measurements on some of these original films prepared by this process indicated that the high field properties of NbN films were significantly superior to those found in bulk NbN. Since that time we have improved the deposition process somewhat and have prepared a large number of films ranging in thickness from 20Å to 8μ. In this paper we report on the critical current and field characteristics of these films.
EXPERIMENTAL PROCEDURE

The procedure used to deposit all of the NbN films for this study is similar to that described previously\(^1,2\) with one major exception. In the current process, a flat 0.020" thick niobium sheet has been employed as the sputtering target rather than the box-like configuration used for the preparation of our original films. It was found that by using a substrate heater to bring the substrate to the desired temperature of \(>500^\circ C\), the additional heating and gettering action provided by the "box cathode" was not required to produce the high \(T_c\) films. The successful use of a flat sputtering cathode made it a simple task to incorporate a shutter mechanism into the deposition apparatus. This in turn permitted for the first time, the deposition of NbN films of controlled composition and thicknesses, since the optimum sputtering conditions could now be established while the substrates were masked from the target. After deposition, the actual thickness of the films in most cases were measured directly with a Tolansky type interferometer which has an accuracy of \(\pm 30\)\(A\). The thickness of very thin films (<50\(A\)) and very thick films (>10,000\(A\)) were estimated from growth time and, in the latter case from the gain in weight. Critical current versus field measurements at 4.2\(^\circ K\) were done in a 210 kOe dc magnet located at the Francis Bitter National Magnet Laboratory. Upper critical field versus temperature data was obtained in a 150 kOe larger
bore magnet located at the same facility. The larger bore magnet was required because of the greater space requirements of the gas bulb thermometer used to measure temperature in these latter experiments. This type of thermometry was employed to avoid the problems usually associated with ordinary resistance type thermometers, when used in a high field environment. Most of the high field data was taken on 1/8" wide NbN films on sapphire substrates. For reasons that will be discussed, some of the critical current versus field data was also obtained using specially prepared NbN "weak link" samples. The widths of the NbN in these samples at the weak link are of the order of 1-2μ and less. The techniques developed to etch films into this configuration are described elsewhere. (3) Finally, in all of the high field measurements the samples were oriented so that the direction of the field was perpendicular to the plane of the film.
RESULTS

We have previously reported that an approximately 2000Å thick NbN film, in a 210 kOe field, was found to exhibit a current density, $J_c$, of well over $10^4$ Amps/cm$^2$. Since that time we have made critical current and field measurements on a series of NbN films, ranging in thickness from 8μ down to 20Å. (The widths of all of these films are 1/8".) From these data we have calculated current densities, at a fixed field (150 kOe), for all of these films. From these results, the $J_c$ values, for films which were found to be physically continuous, have been plotted as a function of films thickness and are shown in Fig. 1. (The criterion used to decide that a film was not continuous was when it did not lose 100% of its normal state resistance after nominally becoming superconducting. This occurred in films which were ~50Å thick and less.) As can be noted, this curve indicates an inverse relationship between current density and film thickness. In addition to providing evidence for this relationship in NbN films, there are some other interesting aspects to the critical field and current data. Specifically, it has been found, as illustrated in Fig. 1, that no depression in current density with decreasing film thickness, occurs in films less than 300Å. Actually a sharp decrease in $J_c$ was noted only when the films became discontinuous, i.e., as noted above, at 50Å and less. In a previous study on the effect of film thickness on transition tempera-
ture, we had found that a sharp drop in $T_c$, occurred in NbN films at thicknesses below about $300\ang$. For example the $100\ang$ film plotted on Fig. 1 had a $T_c$ of only $10.8^\circ K$. The fact that no corresponding depression in current densities at these thicknesses occur made the high field properties of those ultra-thin film worthy of some additional study. To do this we have measured the upper critical field of a number of these films as a function of temperature in fields up to 150 kOe. As a basis of comparison this same measurement was also done on a comparatively thick (2000Å) film. The results of the measurements, where $H_{c2}$ is plotted against reduced temperature, are shown in Fig. 2. This figure illustrates that a 200Å film, despite a $T_c$ of only $11.4^\circ K$, shows, within experimental error, the same $H_{c2}$ values as the $15.2^\circ K$ film when plotted against reduced temperature. The curve for the 90Å film is somewhat confusing. However the irregularity of this curve is believed to result from this sample being non-homogeneous. Thus the first data point near $T_c$ is probably due to the presence of a small amount of high $T_c$ material in the film while the remaining values are associated with a slightly lower $T_c$ material. Finally, it is only in the discontinuous 50Å film where there is a sharp drop in $H_{c2}$ values. The data from these $H_{c2}$ vs. temperature experiments have been used to determine extrapolated upper critical fields at zero temperature and also the change in critical field per degree in these NbN films. These are shown in Table I. Here again, we see that these values drop off sharply only in the 50Å film, despite wide differences in $T_c$. 

A8-6
These $H_c^2$ vs. temperature results on the very thin NbN films reinforced the results discussed above which indicated an inverse dependence of high field properties on thickness, in NbN films. However, although our evidence indicated that the $J_c$ values shown in Fig. 1 were correct at least on a relative basis, there were features of the $H_c$ data used to calculate these values which suggested that the actual current densities were probably somewhat higher. In Fig. 3, a series of $H_c$ curves are shown for a 2500Å film, which are typical of all of the critical field data from which the results shown in Fig. 1 were derived. To obtain these curves the current was first set and then the field was swept up and back. In Fig. 3, only the recorder traces for the upward sweep are reproduced since the return sweeps, although invariably occurring at a lower field, were not reproducible. As can be seen from these curves $\Delta H_c$ from these measurements are extremely small. This combination of factors, i.e., the very sudden transitions from the superconducting to normal state, and also the large and unpredictable hysteretic behavior in these films strongly suggested that the NbN was going normal prematurely, due to heating effects at the current contacts. Therefore to try to obtain more accurate $J_c - H$ values for NbN thin films, additional data was taken on a number NbN weak link samples whose cross-sectional areas, at the weak link, are approximately four orders of magnitude, smaller than the 1/8" wide films that had been measured previously. It was assumed that the corresponding decrease in the critical current, required to drive these weak link samples normal, would sufficiently minimize heating effects.
at the current contacts to obtain more reliable data. Figure 4 illustrates
a series of $H_c$ curves for a NbN weak link sample which indicate that
this has indeed occurred. As can be seen the $\Delta H_c$ of these transition
curves are greater than 40 kOe and, in addition, the curves exhibit
essentially no hysteresis. Taking the conservative value for $H_c$ where
the transition curves make their first sharp upward turn, current density
values for a 1.5μ x 800A weak link sample have been determined in fields
from zero to 210 kOe. These $J_c - H$ values are plotted in Fig. 5. To
our knowledge, the current densities shown in this figure are the
highest for any presently known superconductor, measured at 4.2°K, in
all fields from zero to 210 kOe.
DISCUSSION

At this time we do not have a complete explanation for the critical current and field characteristics of NbN thin films, which have just been described. Undoubtedly part of the explanation is related to the method of preparation, wherein the niobium nitride is essentially quenched immediately upon formation. This could be expected to produce a material of very small grain size and a correspondingly high resistivity. Very high resistivities have in fact been measured in NbN films. The minimum value which has been observed in any NbN film, regardless of thickness, is 250μ ohm cm, which is five times greater than the ~50μ ohm cm resistivity measured in bulk NbN. Despite the method of preparation and despite the high resistivity values, nearly single crystal X-ray diffraction patterns which were obtained from these films, indicated a fairly large grain size of 500Å or more. This apparent anomaly is currently being studied by observing some NbN films by transmission electron microscopy. This work is still in progress and will be discussed in detail later, however, from present results, the NbN films appear to consist of multi-sized grains ranging in size from over 500Å down to a few angstroms. This type of crystal structure would be consistent with both our resistivity and X-ray diffraction results.

To explain the inverse dependence of current density on thickness which was observed in the NbN films, it would be reasonable to assume that some grain growth had occurred in the thicker films.
resulting in a decrease in the number of pinning centers. Resistivity measurements were made on films of various thicknesses to try to obtain experimental support for this explanation. However the results from these measurements were inconclusive since an inexplicably large spread in resistivity values was obtained and no trend relating thickness with resistivity could be observed. An additional explanation for the very high critical current properties in the ultra-thin (<300 Å) NbN films is, that at these thicknesses the contribution from surface pinning would constitute a significant part of all the flux pinning occurring in the superconductor. Assuming that the number of pinning centers at the surface is proportionally larger than in the bulk of the film (as, in fact, might be expected,) this would cause a rise in Jc values.

In a previous paper\(^{2}\), the theoretical upper critical field at zero temperature was calculated for a \(<2000\) Å film, both from "GLAG" theory\(^{6}\) and also from the \(H_{c2}\) versus temperature data taken near \(T_c\)\(^{7}\). Experimentally, \(H_{c2}\) near zero is not known. However because of the improbably high \(H_{c2}(0)\) values obtained from these calculations, it was concluded that the upper critical field in NbN films was, at least partially, limited by paramagnetic effects. Similar calculations have been repeated on a number of films of various thicknesses and in general this conclusion still appears to be valid. However, the results from a 200Å thick film offers evidence that this conclusion may not apply in the case of very thin films. For this film, using the GLAG equation

\[
H_{c2}^*(0) = 3.1 \times 10^4 \rho_n \gamma T_c
\]  

\(1\)
where $H_{c2}^* (0)$ represents the non-magnetically limited, upper critical field, a value of 282 kOe is calculated. The experimental values of the parameters used in this calculation are $\rho_n = 250\mu$ ohm cm, $\gamma = 3.2 \times 10^3$ ergs/cc - °K$^2$ (bulk value), and $T_c = 11.4$°K. From the equations derived by Werthamer, Helfand and Hohenberg (WhH), $H_{c2}^* (0)$ was also calculated from the slope of the $(H_{c2} - t)$ curve shown in Fig. 2 as follows:\(^{(7)}\)

$$H_{c2}^* (0) = 0.69 H_0$$

(2)

$H_0$ in this equation represents $- (dH_{c2}/dt)_{t=1}$ and from Table I this value for the 200Å film is 568 kOe. Thus $H_{c2}^* (0)$ from Eq. 2 equals 392 kOe. The magnetically limited $H_{c2}^2 (0)$ values for this film have also been calculated according to equations by Maki:\(^{(8)}\)

$$H_{c2}^2 (0) = H_{c2}^* (0) [1 + \alpha^2]^{-1/2}$$

(3)

where,

$$\alpha = \frac{\sqrt{2} [H_{c2}^* (0)]}{18,400 T_c}$$

(4)

From Eq. 3, an $H_{c2} (0)$ value of 130 kOe is calculated starting from the GLAG upper critical field value of 282 kOe. Starting with the WHH value of 392 kOe, a value of 135 kOe is obtained. Since from our experimental results, an actual $H_{c2} (0)$ value in the vicinity of 300 kOe seems likely, for this film, the conclusion can be drawn that, at least in some instances, the upper critical fields of NbN films are not
paramagnetically limited to any significant degree. Presumably, in this case the paramagnetic effects are counteracted by spin orbit scattering, according to theories proposed by Maki and WHH (7,8).
<table>
<thead>
<tr>
<th>Thickness</th>
<th>$T_c$</th>
<th>$\frac{dH_{c2}}{dt}$ at $t=1$</th>
<th>$\frac{dH_{c2}}{dT}$ at $T=T_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000Å</td>
<td>15.2°K</td>
<td>550 kOe</td>
<td>36.2 kOe</td>
</tr>
<tr>
<td>200</td>
<td>11.4</td>
<td>568</td>
<td>49.9</td>
</tr>
<tr>
<td>90</td>
<td>10.8</td>
<td>504</td>
<td>46.7</td>
</tr>
<tr>
<td>50</td>
<td>9.6</td>
<td>240</td>
<td>25.0</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1 Current Density as a function of thickness in NbN films

Fig. 2 $(H_{c2} - t)$ curves for NbN films of various thicknesses

Fig. 3 $H_{c}$ curves for various currents for a NbN film with a cross sectional area of $\sim 8 \times 10^{-5}$ cm$^2$

Fig. 4 $H_{c}$ curves for various currents for a NbN weak link sample with a cross sectional area of $\sim 6 \times 10^{-11}$ cm$^2$

Fig. 5 $T_{c}$ vs. $H$ values for an NbN weak link sample with a cross sectional area of $1.2 \times 10^{-9}$ cm$^2$
REFERENCES


Fig. 1—Current density as a function of thickness in NbN films.
Fig. 2 - \((H_{c2} - t)\) curves for NbN films of various thicknesses.
Fig. 3 - Hc curves for various currents for a NbN film with a cross-sectional area of \( \sim 8 \times 10^{-5} \) cm\(^2\).
Fig. 4 - Hc curves for various currents for a NbN weak link sample with a cross sectional area of \( \sim 6 \times 10^{-11} \text{ cm}^2 \).
Fig. 5 - $T_c$ vs. $H$ values for an NbN weak link sample with a cross sectional area of $1.2 \times 10^{-9}$ cm$^2$. 

$T = 4.2\text{°K}$

$J_c \perp H$
APPENDIX A9
CHARACTERISTICS OF NbN DAYEM BRIDGES*

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ABSTRACT

Dayem bridge weak links have been fabricated by sputter etching niobium nitride thin films having Tc's of \( \approx 15 \)K. These junctions exhibit a negative resistance region extending to 45 mV at 3.2K, in which are seen self induced subharmonic current steps and structure near the energy gap voltage. Temperature dependence of these features and effects of applied microwave radiation are discussed, and possible explanations of the negative resistance region and of the self induced step structure are given.

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Introduction

The Dayem bridge form of Josephson junction has inherent advantages over point contacts or sandwich structures in terms of reproducibility, stability, and resistance to thermal cycling, especially if the bridges are made of a hard and chemically resistant material such as niobium nitride. We have developed a sputtering method for depositing thin niobium nitride films which have the bulk transition temperature of 15-1/2K and very high critical magnetic fields and critical current densities. We are investigating Dayem bridges made from these films as possible sub-millimeter wave detectors which might also be operable at liquid hydrogen temperatures.

Junction Preparation

We have developed a simple sputter etching process for making Dayem bridges, which we have used to produce widths as small as 600Å in some long bridges. Because this method is applicable generally to the transition metals and their compounds and because it also may be useful in fabricating long, thin and very narrow structures for the study of fluctuation phenomena, the process will be briefly described.

First a 1000Å thick niobium nitride film is deposited on a sapphire substrate. Over this is deposited a 1000Å thick layer of aluminum. The desired configuration is photoresist masked and the aluminum is etched chemically to leave aluminum in the desired weak link pattern, which
serves as the mask for the subsequent r.f. sputtering process. (3) Aluminum is used as the mask rather than the photoresist because it sputters away much more slowly from a hot substrate. The niobium nitride is inert to the usual chemical etchants but sputter etches at about the same rate as aluminum. If the sputter etching is stopped when the substrate is exposed and with some of the aluminum mask remaining, the minimum weak link width which can be produced is limited to one or two microns by the resolution of the photoresist exposure process, if light exposure is used. This is how the weak links which are the subject of this paper were produced. If, however, one continues sputtering after the aluminum mask is gone, the width of the bridge decreases, apparently without much decrease in film thickness, because the sputtering takes place preferentially at the edges for niobium nitride. We first saw this effect in a long form of bridge, which was initially 20 microns long and 8 microns wide. The etched film width varied between 600 Å and 1000Å, but with very sharp edges, though the strip meandered somewhat over its 20 micron length. This bridge had a critical current density of over $10^7$ Amps/cm$^2$ at 4.2°K in zero magnetic field and over $10^6$ Amps/cm$^2$ at 200 kOe. Though the I-V characteristic of this bridge exhibited a negative differential resistance region, it did not extend to as high a bias voltage as that for bridges made in the short link configuration first investigated by Anderson and Dayem. (4)

**DC Characteristics**

Data are presented here for a weak link of the form shown in Fig. 1, four microns wide at the isthmus and 1000Å thick, on a sapphire substrate, with a critical temperature of 14.9K. The normal state
junction resistance was about 800 ohms, not unexpected given the high resistivity of our sputtered niobium nitride films, which is never less than 200 micro ohm cm. Weak links of soft superconductor films usually have resistances much less than one ohm.

D.C. measurements were made using four-point current and voltage leads ultrasonically soldered with indium directly to the niobium nitride film. The measuring circuit was patterned after one described by Adler and Jackson. The junction was mounted in the center of an X-band wave guide, with the current flow perpendicular to the broad faces, above a tunable short. The sample end of the waveguide was either immersed in liquid helium or isolated in an evacuated can to control temperature. Curves were traced at very low speeds on an X-Y recorder.

With a high impedance measuring circuit we initially obtained a current-voltage characteristic similar to that of the 3.6 micron wide tin bridges investigated by Dayem, et al. but on a much higher voltage scale—millivolts instead of microvolts of bias voltage. Dayem observed a load line switching typically to about five microvolts after exceeding the critical zero voltage current of one milliamp. We observed load line switching to about 150 millivolts, with a measuring circuit impedance of 100 ohms. Lowering the impedance of the measuring circuit results in the I-V characteristic at 4.2K shown in Fig. 2. There is a voltage controlled negative differential resistance (NDR) region extending to 35 millivolts and ending in an abrupt decrease in current which is a transition to a positive differential resistance (PDR) region. The NDR region is a resistive superconducting state of the film in the vicinity of the isthmus.
The abrupt transition at 35 millivolts is due to a heating effect which induces a transition to the fully normal state at the isthmus. The current is unstable at this transition point when the junction is immersed in liquid helium, and switches back and forth between the NDR and PDR curves. This instability is due to bubbling of the liquid helium and does not occur when the sample is isolated with only a heat exchange gas. In this isolated case, the transition is hysteretic, occurring up to ten millivolts lower on the return voltage sweep, as would be expected for a heating effect.

Above the transition from NDR to PDR the normal region extends outward from the isthmus until the whole of the sample between the voltage leads becomes normal, that is, ohmic, at 2.5 volts and 4 milliamps.

Figure 3 shows the NDR region on an expanded scale, for various temperatures. There are current jumps at 2.2 and 4.4 millivolts at 3.25K which would seem to be related to the energy gap. Above this there is a temperature dependent, apparently self-induced step structure between 7 and 40 millivolts. These steps correspond to subharmonics of some fundamental voltage X, as can be seen for the data at 4.2K for example. Here X=80.4 millivolts is assumed and calculated values of X/n for n from 2 to 12 are shown. The linear dependence of the voltage X on temperature between 3 and 9K is shown in Fig. 4. Above 9K the steps have washed out, along with almost all of the NDR region.

The temperature dependence of the zero voltage current, shown in Fig. 5, is also linear between 6 and 11.6K, with a tailing off to zero at 14.9K, which is the resistive transition temperature for a measuring current of 10 microamps.
Effects of Applied Radiation

We were unable to induce step structure with applied microwave radiation at 9 and 70 GHz, though the radiation does affect the zero voltage current and the I-V curve as a whole.

Figure 6 shows the dependence of zero voltage current on 9 GHz applied power at 4.2K. The effect is similar to that observed for soft superconductor weak links, except that we have not observed any magnetic field effect.

The points between 10 and 15 dbm had to be obtained by raising the r.f. power level from zero with zero sample current and voltage and then increasing the current until switching to the resistive state occurred; once the junction had switched to the resistive state it could not be switched back to the zero voltage state without first reducing the r.f. applied power.

Figure 7 shows the I-V characteristics of the junction driven into the resistive region at power levels up to one milliwatt. There is much noise for power levels between 10 and 16 dbm, those being the levels where the junction can also have a zero-voltage current mode. These curves are similar to those reported by Dayem, et al., for soft superconductor weak links. Results for 70 GHz were similar, though exact applied power levels were not determined. The junction exhibited no current steps at the expected voltages given by the Josephson voltage-frequency relation for any power level, to a limit of sample current detection sensitivity of 10 nanoamps.
Though no step structure was seen, the junction was sensitive to very small power levels. Using lock-in detection on the sample voltage and choosing almost any operating point in the NDR region, we could detect $10^{-9}$ watts at 9 GHz at any temperature between 4.2K and 14K.

The characteristics of these junctions are very reproducible. Junctions fabricated with the same geometries show the same I-V curves. The junctions are also very stable. No deterioration or change occurred over a period of a year though the junction was thermally cycled many times and stored at room temperature in the open air.

**Interpretation of Results**

A fluxon motion treatment is appropriate for interpreting the characteristics of Dayem bridges, since tunneling would not ordinarily be expected in such a junction. However, we do observe current jumps at voltages in the vicinity of the expected energy gap for niobium nitride. If the relation $\frac{2A}{e} = 3.5 k_B T_C$ holds, then the energy gap $\frac{A}{e}$ at absolute zero would be 2.25 millivolts for a $T_C$ of 14.9K. There are substantial current peaks at 2.2 and 4.4 millivolts in the curve at 3.25K. We have some evidence (electron microscope transmission photographs of niobium nitride films detached from their substrates) that the sputtered films grow in the form of columns perpendicular to the substrate with voids between. This would account for the films high resistivity and upper critical field. Single particle tunneling between adjacent superconducting columns may be taking place, which would account for the current at 4.4 millivolts, but the current at 2.2 millivolts would have to be explained either by tunneling between a normal portion and a superconducting portion.
of the film or by multiparticle tunneling. If these current jumps are related to the energy gap, then the temperature dependence of the gap energy is not BCS-like, being linear between 4 and 10K and extrapolating to zero at 11.4K. In any case, these current jumps are small compared to the zero voltage current, indicating that tunneling is not the dominant process.

The NDR region can be explained in terms of fluxon motion and of the spreading of the resistive superconducting state out from the isthmus. Above the critical current, the current self-field penetrates the edges of the film in the form of vortices of opposite circulation, which are driven inward by Lorentz forces to annihilation in the interior. With the passage of each vortex is associated a phase slippage between the superconductors which gives rise to a corresponding voltage. Thus the time average rate of vortex flow is given by

$$\frac{dn}{dt} = \frac{2\, eV}{h}$$

the Josephson relation. If from a given bias point in the resistive superconducting region the voltage is increased, then the average frequency of passage of vortices across the isthmus must be increased. We hypothesize that the resistive (vortex flow) region of the junction is propagating outward from the isthmus to permit more vortices to flow, at the same speed, in the film, and this increased number of moving vortices increases the dissipation and the electrical resistance, thus accounting for the negative differential resistance region.
This explanation is supported by other findings, as we have seen changes in the I-V curve and NDR region when the angle of the open part between the superconducting films is reduced. If this multiple vortex picture is correct, then one would not expect to see induced step structure, for reasons as explained by Thiene and Zimmerman.\(^{(8)}\) It is possible that the large change in the overall slope of the I-V curve, which occurs for example at 5 millivolts at 4.2K, is indicative of the start of the expansion of the resistive region outward from the isthmus. There are probably still multiple vortices present in the isthmus before the region expands, but if the bridge can be made narrow enough, a single-vortex regime would be attained and synchronism of the single vortex motion with the applied radiation would permit observation of induced step structure.

The subharmonic step structure in the NDR region was initially thought to be produced by coupling of the Josephson radiation produced at each step voltage with a geometrically resonant mode of the junction, an effect seen by Coon and Fiske\(^{(9)}\) among others. At 4.2K the resonant voltage \(X\) of 80.4 millivolts would correspond to 38,900 GHz by the Josephson relation, a wavelength of 7.7 microns in free space. This wavelength is of the same order as the obvious feature to be associated with a geometrical resonance, the isthmus width of 4 microns. Response of a Josephson junction to frequencies this high would be of great practical importance. The temperature dependence of the resonant frequency was thought to be due to the slowing of the propagation velocity of electromagnetic waves in the vicinity of the superconducting film, caused by penetration of the r.f. magnetic field. The variation of penetration
depth with temperature would thus change the resonant frequency.

This explanation of the step structure was considered to be unlikely when repeated efforts failed to induce current steps with applied radiation. A recent and more likely explanation is that low frequency relaxation oscillations are associated with the steps. Vernon and Pederson have seen low frequency oscillations in the NDR region of sandwich structure Josephson junctions and have seen similar subharmonic steps, also in the NDR region, caused by pickup of a local radio station and beating with the low frequency self-induced oscillations. In general a NDR region and a low circuit impedance produce these oscillations, though different mechanisms would operate for the two types of junction—the junction capacitance would be the important factor for a sandwich structure, and the inductance for a Dayem bridge. We have recently found very low amplitude (\( \sim 10 \mu\text{V} \)) oscillations at frequencies of \( \sim 10^5 \) Hz associated with these steps. We have not yet determined whether radio pickup is involved, nor devised a switching oscillation model analogous to Vernon and Pederson's.

The effects of applied microwave radiation are the same as have been observed for Dayem bridges of soft superconductors, except for the absence of induced steps.

Conclusions

Niobium nitride Dayem bridges exhibit unusual characteristics which are results of material properties such as a very high flux pinning strength. Though induced Josephson steps have not been observed, this will probably be effected by decreasing junction widths. These junctions are very sturdy and stable and are indifferent to very high applied voltages.
which would burn out soft superconductor junctions. They are reproducible—
junctions fabricated with the same geometry have characteristics identical
to those presented here. The existence of a resistive superconducting region extending to 45 millivolts at 3.24K holds out the possibility that junctions of this type may be useful as non-linear elements at the very high corresponding frequencies.

We are indebted to C.J. Taylor for photoresist processing and for advice on the development of the sputter etching technique.
References

Figure Captions

Fig. 1  A four micron wide niobium nitride Dayem bridge.

Fig. 2  D.C. current-voltage characteristic at 4.2°K.

Fig. 3  Variation of current-voltage characteristic with temperature. Current zeros are displaced for each temperature.

Fig. 4  Resonance voltage X vs. temperature.

Fig. 5  Zero voltage critical current vs. temperature.

Fig. 6  Zero voltage critical current vs. 9 GHz applied microwave power at 4.2K. Odb = 1 mW.

Fig. 7  Current voltage characteristics at 4.2K, with 9 GHz applied radiation.
D.C. current-voltage characteristic at 4.2°K
Variation of I-V characteristic with temperature
Zero voltage current vs 9 GHz applied microwave power, at 4.2°K. 0 dB = 1 mW
Current-voltage characteristics at 4.2°K, with 9 GHz applied
Presently known, high transition temperature (> 15°C) superconducting materials have either the β-W (A-15) or rocksalt (B-1) crystal structure. Although these compounds retain the desired crystal structure over a wide phase field, optimum Tc's are obtained only when the compounds are nearly stoichiometric. Films of some of these materials, including compounds in the Nb-Al, Nb-Sn and Nb-Al-Ge systems have been prepared by sputtering. To control composition, various targets have been employed, including ingots made by arc melting, hot pressed powder mixtures, and multiple targets. Compound formation was achieved in most cases (as verified by x-ray diffraction analysis) regardless of target material used, however, the Tc's of the films varied from < 10°C to over 16°C. The influence of target material on stoichiometry and on Tc is discussed, and some of the high field superconducting properties of the deposited films are reported.

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INTRODUCTION

At present, all known high critical temperature superconductors (Tc ≥ 15°K) are transition metal compounds, having either the 6-3-W or the NaCl crystal structure. These compounds, including Nb₃Sn, Nb₃Al, and NbN, among others, were all prepared originally in bulk form. Since the time their superior high Tc and magnetic field properties were discovered in the bulk samples, many attempts have been made to fabricate these compounds into the technologically important thin film or wire forms. Because of the brittleness of these superconductors, the standard metallurgical techniques for fabricating wires or thin films are not usable and other methods have had to be developed. Recently, we have been investigating the possibility of preparing films of these materials by a high purity sputtering technique. With this technique we have successfully deposited thin films of the NaCl structure compound NbN which have superconducting properties equal or superior to those of the bulk material. (1) We have also attempted to sputter 6-W structure superconductors, including Nb₃Al₀.₈Ge₀.₂, the highest Tc material presently known. However, in this case, the Tc's of the films were found to be significantly lower than those of the bulk material. (2) From these latter experiments it was concluded that the depressed Tc's in our 6-W films were due to these films being slightly off stoichiometry. Unlike the sputtered NbN films where the composition is controlled by the
amount of nitrogen in the sputtering gas, the composition of the sputtered β-W films is almost entirely determined by the quality of the sputtering target. Therefore, to improve the stoichiometry of our sputtered β-W films, we have been investigating the use of various types of sputtering targets. In this paper we report on our results to date from these experiments.
EXPERIMENTAL PROCEDURE

The deposition technique used to prepare the thin films for this study is the same as that used in our previous work on NbN and Nb-Al-Ge films. Essentially this technique involves sputtering in a system with a total background pressure, prior to sputtering, of $5 \times 10^{-10}$ Torr or less, and the use of high substrate temperatures ($\geq 500^\circ C$). It has been amply demonstrated that contamination during the growth of thin films of the high Tc compounds will severely degrade the superconducting properties of these films. From our work with the deposition of NbN, we have shown that by minimizing contamination, we can sputter films with Tc's similar to that of the bulk material. In the present experiments with the 3-W films we have assumed that by using the same high purity sputtering methods the influence of impurities on the transition temperature of the deposited films is minimal and the main reason for any depressions in Tc is associated with the problems of achieving proper composition.

For this study we have attempted to deposit high Tc 3-W structure films from four different types of sputtering targets as follows: Nb-Sn films were deposited from an Nb$_3$Sn target prepared by a high temperature diffusion process. This process involved the submersion of a 0.010" thick niobium sheet into molten tin held at 950°C, for four hours. At this temperature the only stable phase among the three compounds
in the Nb-Sn system is \( \text{Nb}_3\text{Sn} \).\(^3\) From cross-sectioning studies this treatment produced a reacted layer on the surface of the niobium approximately 8μ deep. After cooling, the unreacted tin, remaining on the surface, was etched away in hydrochloric acid. The \( T_c \) of the \( \text{Nb}_3\text{Sn} \) surface layer produced by this technique was found to be 17.5°K. Nb-Al films were deposited from a target made by joining together two pieces of niobium and aluminum sheet into a single target. In these experiments, a large number of 1/8" wide substrates were used to cover the entire area beneath the target. The substrates were positioned so that their lengths were parallel to the dividing line between the niobium and the aluminum portions of the target. In this way deposited films ranging in composition from essentially pure niobium to pure aluminum were prepared and afterwards easily measured. Nb-Al-Ge films were sputtered from a hot pressed (at about 500°C) powder target made from a mixture of the elements in the atomic ratio of 3Nb, 0.8 Al, and 0.2 Ge. And finally, both Nb-Al and Nb-Al-Ge films were also sputtered from approximately 3" diameter ingots with nominal compositions of \( \text{Nb}_3\text{Al} \) and \( \text{Nb}_3\text{Al}_{0.8}\text{Ge}_{0.2} \) prepared by arc melting the constituent elements at over 2000°C in an argon atmosphere. The transition temperatures of small pieces taken from these ingots were between 18° and 18.5°K.

The transition temperatures of a representative sampling of all of the films sputtered from these various targets were measured by a standard resistive technique, with the temperatures at which the samples began to lose their normal state resistance being taken as \( T_c \). In addition to transition temperature, the high magnetic field properties of
the higher Tc films are in the process of being measured. These latter measurements are performed at the Francis Bitter National Magnet Laboratory. Presently, we have high field data only on Nb-Al-Ge films, deposited from a melted ingot target, which were the first films prepared during the course of this study. Critical current versus magnetic field data at 4.2°K for these samples were reported previously. In this paper results of upper critical field versus temperature experiments are presented. Finally to establish the structures of the sputtered films, the various films were analyzed by x-ray diffraction techniques.
RESULTS AND DISCUSSION

Measurement of the transition temperatures of films deposited from the Nb$_3$Sn sputtering target which was prepared by a high temperature diffusion process, resulted in Tc-values of approximately 2°K. Examination of one of these films by x-ray analysis indicated that no β-W phase was present - the strong lines that were seen could be related only to the compounds, Nb$_6$Sn$_5$ and NbSn$_2$. The Tc's of Nb$_6$Sn$_5$ and NbSn$_2$ have been reported to be 2.05 and 2.65°K respectively. From these results, therefore, it seems probable that the sputtered films consist of a mixture of these two tin rich compounds. Thus even though the high temperature diffusion process used to prepare this sputtering target produces a reacted layer which is predominantly Nb$_3$Sn, apparently there is sufficient excess tin incorporated within this reacted layer to cause the deposition of the undesired tin rich phases.

In the deposition experiments in which the two part niobium and aluminum cathode was employed, films with a wide variety of transition temperature were obtained. Figure 1 illustrates the effect of substrate location on the Tc's of these deposited films. As anticipated, the films under the niobium portion of the target had transition temperatures of about 9°K. In the general area beneath the dividing lines between the Nb and Al, the Tc peaked sharply, after which the transition temperatures fell off to less than 4.2°K. Although the peak Tc achieved
in these experiments was only 13°K, which is about 5° less than the bulk value, these experiments were interesting in that they proved that the Nb-Al β-W phase can be sputtered starting from the elements, at nominal substrate temperatures of approximately 600°C. A reaction temperature of ~2,000°C is required to form the same compound in bulk form. It is believed that the comparatively low maximum Tc of 13° in these experiments is associated with the fact that only on a very small area of the substrate was the exact ratio of three Nb to one Al atom deposited. This is indicated by the results shown in Fig. 1, where one can see that the transition temperatures of the films, positioned immediately adjacent to the 1/8" wide substrate which had the highest Tc, dropped off very sharply from the peak Tc of 13°K. There are undoubtedly many better target configurations that could produce the deposition of the proper ratio of Nb and Al atoms over a wider area of the substrate than that obtained with the two piece niobium and aluminum target. We felt, however, that perhaps the optimum configuration would be a well homogenized mixture of powders of the constituent elements. To investigate this type of target we chose to try to sputter films of Nb-Al-Ge. Although the first films sputtered from the Nb, Al, and Ge target were superconducting, they had transition temperatures of only about 7°K. Successive runs, however, sputtering from the same target under the same experimental conditions, produced a gradual rise in Tc. In our most recent experiments, films have been deposited with transition temperatures as high as 16°K. While this is still about 5° lower than the maximum that is obtained in bulk samples, it is, to our knowledge, the highest
value yet reported for any as-deposited (non-annealed) Nb-Al-Ge films. After the deposition of the first 16°K films, we found that subsequent experiments produced no additional rise in transition temperature. There are two possible explanations for this result. One of these is that due to the greater level of impurities in the pressed powder targets compared to previous targets which we have used, the maximum Tc's of the films may be limited by contamination. The fact that the early runs in this series of experiments produced films with low Tc's suggests that these films were in fact being contaminated. Apparently, over a period of time the amount of contamination from the target decreased, as indicated by the rise in Tc in subsequent runs. However, the possibility exists that some minimum level of impurities still remains in the target. The other possible explanation for the maximum Tc of 16° is that for some reason, such as inadequate mixing of the Nb-Al-Ge powders, there is still a problem of non-stoichiometry in the deposited films. At present we do not know which is the more probable explanation.

Finally, we have sputtered films from an Nb-Al-Ge arc-melted ingot similar to those reported previously. In these experiments we primarily attempted to determine whether higher Tc's than the maximum of 11.4°K obtained earlier, could be achieved by varying the substrate temperature. Films were grown in these experiments at nominal substrate temperatures ranging from 500°C to 1000°C. However, no increase in transition temperature was observed.

In addition to the transition temperature measurements, we plan to determine the magnetic field properties of the deposited films.
Thus far, we have collected high field data only on the first β-W structure films that were prepared, in which an arc melted Nb-Al-Ge target was used. As mentioned, the maximum Tc of these films was 11.4°K. Current density values as a function of magnetic field have already been reported for these films. In Fig. 2 upper critical field (He_2) vs. temperature data for a film with a Tc of 11.3°K are shown. Although the high field properties of the 16° Nb-Al-Ge films can reasonably be expected to be greater than those shown here, the present data are useful in that they establish the minimum values that can be obtained with the sputtered β-W structure Nb-Al-Ge films. Also, it is of interest to compare our experimental results with calculated results based on current high field theory. From work by Werthamer, Helfand, and Hohenberg (WHH), the non-paramagnetically limited zero temperature upper critical field, Hc_2*(0), can be calculated from the slope of the (He_2 vs. t) curves shown in Fig. 2 according to the following equation:

\[
Hc_2^*(0) = 0.69 \left[ - \frac{dHc_2}{dt} \right]_{t=1}
\] (1)

This calculated value, for the film shown in Fig. 2, of Hc_2^*(0) from this equation is 167 k Oe. According to theories by Maki (6) the paramagnetically limited upper critical field, Hc_2(0), can be calculated from the following equation:

\[
Hc_2(0) = Hc_2^*(0) \left[ 1 + \alpha^2 \right]^{-1/2}
\] (2)

where

\[
\alpha = \frac{\sqrt{2} \left[ Hc_2^*(0) \right]}{18,400 \, Tc}
\] (3)
From Eq. 2 an $H_{c2}(0)$ value of 114 kOe is calculated. Since at 4.2°K, $H_{c2}$ for this film is already >150 kOe the non-paramagnetically limited upper critical field value of 167 kOe appears to be the more correct. Thus the upper critical fields of the Nb-Al-Ge films are not paramagnetically limited. This is in agreement with the work of Foner et al. on bulk Nb-Al-Ge.
SUMMARY

Our sputtering experiments have demonstrated that the high Tc $\beta$-W phases in the Nb-Al and the Nb-Al-Ge systems can be sputtered from the elements at a relatively low (nominal) substrate temperature of approximately 600°C. A maximum Tc of 16°K has been obtained with films sputtered from a hot-pressed powder target made from Nb, Al, and Ge powders. Whether the Tc's of these sputtered films are being limited to a value of 16°K by contamination or by problems of composition is not known with certainty at this time.
FIGURE CAPTIONS

Figure 1 - Tc's of Nb-Al films as a function of their location beneath a two piece niobium and aluminum cathode. The width of each substrate is 1/8". The dividing line between the Nb and Al is at the 1 1/2" mark.

Figure 2 - Upper critical field of an Nb-Al-Ge film as a function of reduced temperature (t = T/Tc). Tc = 11.3°K.
REFERENCES


Fig. 1—Tc's of Nb-Al films as a function of their location beneath a two piece niobium and aluminum cathode. The width of each substrate is 1/8".
The dividing line between the Nb and Al is at the 1 1/2" mark.
Fig. 2 - Upper critical field of a Nb-Al-Ge film as a function of reduced temperature ($t = T/T_c$). $T_c = 11.3^\circ$K
APPENDIX A11
SUPERCONDUCTIVITY IN THIN FILMS OF HIGH $T_c$ COMPOUNDS

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ABSTRACT

Data is presented on the superconducting behavior of sputtered thin films of NbN and Nb$_3$(Al$_{0.8}$Ge$_{0.2}$). High values of $T_c$, and $H_{c2}$, and $J_c$ were obtained for these films. The high critical current density is attributed to the small grain size coupled with the pinning of fluxoids at intergranular impurities or voids.
SUPERCONDUCTIVITY IN THIN FILMS OF HIGH $T_c$ COMPOUNDS

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Although the bulk properties of high $T_c$ superconductors of the A-15 and B-1 structures have been studied quite extensively, the thin film properties of these materials have received less attention. Early efforts to prepare such films generally produced $T_c$ values much lower than the corresponding bulk values. We have shown that this problem can be surmounted in the case of NbN by reactively sputtering Nb onto a heated substrate in an argon-nitrogen atmosphere. More recently we have obtained promising films of Nb$_3$(Al$_{0.8}$Ge$_{0.2}$) by high purity sputtering. This paper discusses the superconducting behavior of these sputtered films relative to what is known about their structures.

NIOBium NITRIDE FILMS

Sputtered NbN films differ quite markedly from bulk NbN, as shown by the following properties:

<table>
<thead>
<tr>
<th></th>
<th>$T_c$ ($^\circ$K)</th>
<th>$\rho_n$ (micro-ohm cm)</th>
<th>$H_{c2}(4.2^\circ$K) (kOe)</th>
<th>$J_c(50$ kOe) (amps cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>15.2</td>
<td>50</td>
<td>90</td>
<td>$2 \times 10^3$</td>
</tr>
<tr>
<td>Film (2,400Å)</td>
<td>14.7</td>
<td>520</td>
<td>$&gt;250$</td>
<td>$3.5 \times 10^5$</td>
</tr>
</tbody>
</table>
The film data shown here are typical of extensive results published elsewhere\(^1\),\(^2\). Although \(\rho_n\), \(H_{c2}\), and \(J_c\) were found to be partly dependent upon film thickness and deposition temperature, the general level of these quantities was consistently higher for sputtered films than for bulk material. To try to understand this behavior we examined the structure of the film.

X-ray studies indicated that the films are definitely crystalline, with lattice parameter close to that of bulk NbN. Recently we made some electron microscope studies in which a 2000 \(\AA\) film was removed from its stainless steel substrate by dissolving the latter in bromine, and viewed by electron transmission at magnifications up to 66,000X. This revealed a grain pattern in the plane of the film with average diameter 400 \(\AA\). It was also apparent that large numbers of voids, of perhaps 10 or 20 \(\AA\) thickness, existed between the grains. We suspect that these voids extend right through the film and are filled with gaseous impurities. The formation of such voids can be understood if it is assumed that NbN crystallites are nucleated on the substrate and grow outwards in a columnar fashion. Presumably owing to the relatively low temperature of deposition (500°C), the voids cannot be eliminated by normal, lateral grain growth.

If this is a true picture of the film structure, the high \(\rho_n\) of this material obviously arises from poor electronic conduction through the voids between grains. The high \(H_{c2}\) values follow automatically from the high resistivity, according to type II superconductor theory. Finally the high \(J_c\) values can be attributed to strong pinning of fluxoids at the voids between NbN grains.
The proposed columnar structure also seems to be in accord with some \( J_c \) anisotropy data which we recently obtained. Fig. 1 shows \( J_c \) versus \( H \) for two films of different thickness, with \( H \) oriented both perpendicular to the plane and parallel to the plane, but normal to \( J \).

Note that in the case of the thin, 200 \( \AA \), film there is essentially no anisotropy of \( J_c \) with respect to the orientation of \( H \), which we attribute to the fact that the film thickness and lateral grain diameter are essentially the same. However, the thick, 5100 \( \AA \), film exhibits \( J_c \) anisotropy of about a factor 3 between the two \( H \) directions. For \( H \) perpendicular to the plane, \( J_c \) for the thick film is almost identical to that of the thin film, presumably because the void (or pinning center) spacing remains essentially unchanged as the film grows. However, for \( H \) parallel to the plane, \( J_c \) is much lower for the thick film than for the thin film, which may be attributed to a low population of extended defects aligned parallel to the plane of the film.

NIOBIUM-ALUMINUM-GERMANIUM FILMS

These films were made by two different methods, referred to as A and B. For type A the sputtering target was a large arc melted ingot of nominal composition \( \text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2}) \). The highest \( T_c \) obtained in this case was about 11\(^\circ\)K, but subsequent analysis of the target indicated severe inhomogeneities in composition.

Type B films were obtained by sputtering from a target consisting of hot-pressed (500\(^\circ\)C) metal powders in the \( \text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2}) \) composition. In this case it was possible to obtain film \( T_c \) values as high as 16\(^\circ\)K by varying the substrate temperature. It may be remarked that al-
though we have not yet attained the bulk $T_c$ of 21°C, the results are sufficiently encouraging to warrant further experimentation along these lines. Our $T_c$ values appear to be the highest so far obtained for Nb-Al-Ge thin films.

The 16°C film was obtained using a substrate temperature of about 650°C. Variations of the latter above or below this temperature caused $T_c$ to drop off. We suspect that for lower substrate temperatures the compound Nb$_3$Al$_{0.8}$Ge$_{0.2}$ is improperly reacted, while for higher substrate temperatures there is contamination due to degassing from neighboring parts of the vacuum system, which lowers $T_c$. It is of considerable interest that such a low reaction temperature (650°C) permits us to form a compound which must normally be reacted in bulk at about 2000°C.

$J_c$ versus $H$ data are shown in Fig. 2 for various types of Nb$_3$(Al$_{0.8}$Ge$_{0.2}$) sample at 4.2°C. Our type B film, despite its lower $T_c$, exhibits $J_c$ values superior to those of the bulk material studied by Hartsough, Zackay, and Parker. Neither film gives indication of the 'peak effect' which seems to occur in the bulk sample.

Our type B Nb$_3$(Al$_{0.8}$Ge$_{0.2}$) films gave $\rho_n$ values in the neighborhood of 20 micro-ohm cm, which is of the same order of magnitude as the bulk residual resistivities reported for other A-15 compounds. The transmission electron microscope indicated an average lateral grain diameter of about 2,000 Å, with no evidence for intergranular voids of the type observed for NbN. Possibly columnar grain growth also occurs for the A-15 film, since our preliminary $J_c$ data indicates fairly strong pinning. However, there is a good chance that at the substrate tempera-
ture of 650°C, the space between grains becomes filled with low melting constituents, such as Al and Ge, helping to maintain a low electrical resistivity in the normal state.

We conclude from this work that sputtered films of both B-1 and A-15 compounds exhibit exceptionally high critical supercurrent densities. The exceptional pinning strength is probable due to intergranular defects arising from the columnar grain growth which appears to be typical of this deposition technique. Such films show promise for technological applications.

We wish to thank NASA for supporting part of this work, the National Magnet Laboratory for use of their facilities, and R. Stickler for help in electron microscopy.

REFERENCES

FIGURE CAPTIONS

Fig. 1 - $J_c$ versus $H$ for NbN films of thickness 200 Å and 5,100 Å for $J$ both perpendicular and parallel to the film plane. ($T_c = 4.2^\circ K$)

Fig. 2 - $J_c$ versus $H$ for two types of Nb$_3$(Al$_{0.8}$Ge$_{0.2}$) film compared to bulk sample behavior. ($T_c = 4.2^\circ K$)
Sputtered Film Type A, 2000 Å
$T_c = 10.7^\circ K$

Sputtered Film Type B, 5000 Å
$T_c = 15.5^\circ K$

Bulk Material
$T_c = 19.0^\circ K$
Hartsough, Zackay & Parker (ref 3)
AN ULTRAHIGH VACUUM ELECTRICAL FEEDTHROUGH FOR CATHODIC SPUTTERING*

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ABSTRACT

A high voltage sputtering feedthrough has been developed which makes use of the "dark space" phenomenon and which can easily be incorporated into any vacuum apparatus including ultra-high vacuum systems.

*Supported in part by the National Aeronautics & Space Administration.
Cathodic sputtering has become an increasingly useful tool for the deposition of thin films for many and varied applications. In this deposition process an electrical discharge is maintained between electrodes in a low gas pressure environment. The cathode at a high negative potential is bombarded by the positively charged gas ions and is slowly disintegrated causing the deposition of the disintegrated material on the surface surrounding the cathode. However, in addition to the desired disintegration of the front cathode surface undesired sputtering also occurs from the back of the cathode and from the metals in the lead-in electrodes. This can cause various problems such as contamination of the deposited films, overheating, and the eventual failure of the electrical feedthrough. In practice this undesired sputtering can be suppressed by placing an anode electrode within the cathode dark space region adjacent to the high negative potential surfaces. This causes the discharge to cease in these areas and no material is sputtered. Although this technique for suppressing undesired sputtering is well known and is used in various commercial sputtering modules, there is at present no electrical feedthrough available which makes use of this "dark space" phenomenon and which can easily be incorporated into any vacuum apparatus by means of a standard copper gasketed flange. We have developed such a feedthrough. It is of exclusively metal and glass construction, helium leak tight, bakeable and has been used in ultra-high vacuum systems at pressures down to $2 \times 10^{-11}$ torr or better. Over a period of about two years, feedthroughs of this type have been cycled.
daily through 400°C bakeouts and have performed flawlessly in all of our sputtering experiments.

Figure 1 shows the specifications for this feedthrough which is constructed using a standard Kovar-glass sealing procedure. Kovar-glass seals of this type are the most mechanically sound of all the metal to glass combinations and can safely withstand a minimum of 50 baking cycles at a temperature of 400°C. Used exclusively at or near room temperature this feedthrough should last indefinitely. Regarding the remaining construction details of the feedthrough shown in Fig. 1, the stainless piece (2) was copper brazed to Kovar tube (3), and Kovar piece (7) was welded to flange (8). The glass to Kovar seals were then made, and while the metal parts were held in proper orientation the glass envelope was formed. The critical feature is the annular separation between the outside diameter of Kovar tube (3) and the inside diameter of Kovar tube (4). The optimum separation depends on the sputtering parameters to be used. In this feedthrough the separation is 1/16". In operation, the outer Kovar tube (4) is grounded to the flange (8) by a spot welded lead. When used so that the sputtering target hangs below, the feedthrough can be cooled by filling with water the reservoir formed by the glass envelope, thus keeping the temperature below 100°C. The high voltage leads to the sputtering cathode and to the power supply are connected to the tapped holes (1) and (6). Finally, an auxiliary metal piece, designed to suppress sputtering down to and back of the sputtering target, is attached to the outer Kovar tube (4) by means of set screws.
Summary

We have developed a high voltage sputtering feedthrough which makes use of the "dark space" phenomenon and which can be easily incorporated into any vacuum apparatus including ultra-high vacuum systems.
References

Figure Caption

Fig. 1 Cross-sectional view of feedthrough showing details of construction: 1-tapped hole for high voltage lead to sputtering cathode, 2-stainless steel connection for high voltage leads, 3-inner Kovar tube, 4-outer Kovar tube, 5-Kovar to glass seals, 6-tapped hole for external high voltage lead, 7-Kovar tube, 8- 2-3/4" diameter ultrahigh vacuum flange, 9-glass envelope.
ALTERNATING CURRENT LOSSES OF STABILIZED NbN*

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ABSTRACT

The alternating current losses of thin films of NbN have been measured on uncoated samples and samples coated with copper and aluminum. The reversibility of the superconducting to normal transition was studied under conditions of swept current at fixed field and swept field at fixed current. It is observed that stabilized NbN has ac losses significantly lower than those in the equivalent unstabilized material.

*This work supported in part by the National Aeronautics and Space Administration.
INTRODUCTION

The current interest in the large scale applications of superconductivity for electrical power generation and drive motors has renewed interest in the high field properties of superconductors relevant to their use in the above types of systems. Multi-filament Nb-Ti conductors are presently being used and their critical current, critical field and ac properties have been extensively investigated and are well understood.\(^{(1)}\)

It is envisaged that the use of superconductors in electrical machinery would be even more advantageous if new materials capable of carrying larger currents at higher fields could be used. Previous work\(^{(2,3)}\) has shown that thin films of NbN in some configurations are capable of carrying currents in excess of \(10^6\) A/cm\(^2\) at 100 kG, and, in addition, that the ac losses in this material are not prohibitively large. The one disadvantage of this material is that it has very irreversible normalization characteristics due to its very high normal state resistivity (e.g., usually > 500 \(\mu\Omega\)-cm). The purpose of this study was to prepare a stabilized NbN sample through the use of normal shunting material and to determine the effect of the shunting material on the ac losses.

EXPERIMENTAL PROCEDURE

The films used in this work were sputtered onto 1/8 in. x 1/2 in. x 0.020 in. sapphire substrates in an ultrahigh vacuum system.
The sputtering procedure has been described elsewhere.\textsuperscript{(4)} After the NbN deposition an equivalent thickness of copper was deposited, again using a sputtering technique in an ultrahigh vacuum system. Following these two depositions a layer of aluminum \( \sim 1 \) micron thick was thermally evaporated over the entire surface. The sample was then photographically masked, the aluminum covering the undesired portion of NbN removed, and then sputter etched to yield the sample configuration shown in the lower portion of Fig. 1. The excess aluminum covering the portion of the film which remained after the sputter etching procedure was left on the sample to protect the thin copper film from oxidizing. Two films were prepared in this manner, one having a NbN layer \( \sim 700 \) Å thick and one \( \sim 1400 \) Å thick. The results obtained on the two samples were virtually identical. The results presented here are for the 1400 Å film. The properties of this sample are listed in Table I.

The ac losses and the critical current - critical field curves were measured at 4.2°K using a 4-point probe shown in the upper portion of Fig. 1. The details of the loss measurement technique have been described elsewhere.\textsuperscript{(3)} Briefly, the method consists of measuring the ac voltage across the sample which is in phase with an applied ac current. These current and voltage values are then used to compute the sample power dissipation. The accuracy of the measurements is limited to \( \pm 10\% \) by the size of the out of phase voltage which arises from pickup in the leads and the sample inductance.
RESULTS AND DISCUSSION

All the data presented here was obtained by first performing the measurements on the sample coated with Cu and A& and then etching this material off and repeating the measurements on the bare NbN film. Figure 2 shows the dc critical current curves versus magnetic field for this sample. The data was obtained from current-voltage curves run at fixed applied magnetic field. The critical current was defined as the current at which the resistance of the sample was equal to 10% of its resistance at 20°K where the NbN is normal. The critical current, as defined above, for the stabilized sample (NbN + Cu-A&) is much lower than that for the unstabilized sample because of the high resistance of the NbN compared to that of the Cu and A& films. The critical current of the unstabilized sample corresponds to a sample resistance of 500 Ω (1 Rn), while in the case of the stabilized sample 10% of the current will have transferred to the normal material, yielding a resistance of .009 Ω (0.1 Rn), when the NbN resistance is only .01 Ω. In all cases the critical current has been calculated on the basis of the area of the NbN alone.

The reversibility of the superconducting to normal transition was studied under conditions of swept field at fixed current. For material with a very flat critical current-critical field curve, this is a more sensitive technique than sweeping the current at fixed field. The results are shown in Fig. 3. These hysteresis curves were obtained starting from a point where the sample was partially normal. This was necessary since the maximum field available was 50 kG, while the transitions at constant current are around 100 kG or more wide. As
can be seen in this figure, the Cu-Al coated sample has no hysteresis and thus may be considered as fully stabilized.

A good treatment of the ac losses in a type II superconductor has been given by Buchold.\(^{(5)}\). Two loss mechanisms are considered, the first due to magnetic hysteresis and the second due to eddy currents. The hysteresis losses will vary linearly with frequency, \(f\), for a fixed area \(B-H\) loop, and it is assumed that the hysteresis loop area will be proportional to \(J^2\) where \(J\) is the applied ac current density. The eddy current loss arises from the fact that the normal cores of the fluxoids penetrating the material are exposed to an ac magnetic field. These losses will be proportional to \(f^2J^2\). Depending upon the relative contributions of these two loss mechanisms, the observed power loss \(P\), should vary as \(f^nJ^2\) where \(1 < n < 2\).

The observed losses as a function of current density at zero applied field and at 10,000 Hz are shown in Fig. 4 for both the stabilized and unstabilized samples. The power dissipation/unit volume was determined using the volume of the NbN alone. In both cases \(P \sim J^2\) as predicted by Buchold's treatment. This is also in agreement with previous measurements on unstabilized NbN films.\(^{(3)}\) The stabilized material exhibits losses which are significantly lower than those in the unstabilized material. This result is in general agreement with the work of Slaughter et al\(^{(6)}\) who studied the effect of copper stabilizing material on the ac losses of thin niobium sheets. Their interpretation of the effect of the normal metal was that it would form a shunt around surface defects where magnetic flux would preferentially penetrate the surface causing "hot spots"
when an ac current was passed through the specimen. The effects of surface preparation on the losses in uncoated niobium were observed to be quite substantial by Rocher and Septfonds.\(^7\)

In addition to reducing the magnitude of the losses at 10,000 Hz, the stabilizing material also affects the zero field frequency dependence of the losses as shown in Fig. 5. For the unstabilized sample \(P \sim f^2\) over the full frequency range. The stabilized sample has \(P \sim f^2\) at high frequencies, but the data indicates that at lower frequencies near 1000 Hz \(P \sim f^{1.2}\).

Measurements similar to those presented in Figs. 4 and 5 were made in an applied magnetic field of 50 kG, but no change was observed in the losses. The magnetic field was applied perpendicular to the substrate surface.

Although it may be impossible to determine accurately the reason for the reduction in the losses, and the change in the frequency dependence upon coating the NbN with a normal metal, it seems reasonable that it is the effect of the normal metal upon the surface properties of the NbN which is of significance. These results do show that thin films of NbN can be stabilized by the use of normal metal overlays and that the losses in the stabilized material are substantially less than in the unstabilized material.
<table>
<thead>
<tr>
<th>Sample Properties</th>
<th>NbN Film</th>
<th>NbN Film + Cu-Al Films</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_c$ (°K)</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Thickness (Å)</td>
<td>1400</td>
<td>--</td>
</tr>
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<td>$\rho_n^*$ (μ-Ω-cm)</td>
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*Measured at 20°K
REFERENCES


7. Y.A. Rocher and J. Septfonds, Cryogenics 7, 96 (1967).
FIGURE CAPTIONS

Fig. 1  Schematic of four-point probe and stabilized sample for ac loss measurements.

Fig. 2  Critical current - critical field data at 4.2°K for ac loss sample.

Fig. 3  Superconducting - normal transition hysteresis curves for stabilized and unstabilized samples at 4.2°K.

Fig. 4  Power dissipation as a function of current density at 10,000 Hz, 4.2°K and zero applied magnetic field for stabilized and unstabilized samples.

Fig. 5  Power dissipation as a function of frequency at fixed current density at 4.2°K and zero applied magnetic field for stabilized and unstabilized samples.
Width ~ .0025"
NbN Film + Cu-Al Films

Fig. 1
Fig. 2

$J_c \times 10^4$ amperes/cm²

$H$, kG

$T_c = 15^\circ$ K

t = 1400 Å

$\bullet$ NbN Film

$\circ$ NbN Film

+Cu - Al Films
Fig. 3

$R/R_n$ vs. $H$, kG

- NbN Film
- NbN Film + Cu-Al Films

$T_c = 15^\circ K$
$t = 1400 \text{ Å}$

$< 300 \text{ G}$

$3500 \text{ G}$
Fig. 4

- NbN Film
- Cu-Al Films

Tc = 15°K

J, amperes/cm²

RMS Power, watts

RMS Power/Unit Volume, watts/cm³
Fig. 5

- NbN
  \( T_c = 15^\circ K \)
  \( t = 1400 \, \text{Å} \)

- NbN Film
- Cu-Al Films
SUPERCONDUCTING PROPERTIES OF NIOBIUM CARBONITRIDE THIN FILMS**

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ABSTRACT

A method for preparing thin films of nominal composition NbC_0.3N_0.7 is reported. Maximum transition temperatures of 17.3°K are obtained for films deposited at ~ 700°C. However, higher critical currents and critical fields are obtained for films prepared at lower temperatures, even though Tc's are lower. This effect is attributed to structural differences in the two types of films.

*Work supported in part by the National Aeronautics and Space Administration.

+Part of this work was performed at the Francis Bitter National Magnet Laboratory, which is supported at MIT by the Air Force Office of Scientific Research.
Superconducting transition temperatures of almost 18°K have been reported for certain compositions in the B-1 (rocksalt) structure Nb-C-N ternary system. These values are close to the highest Tc's found in any superconductor and therefore have made the niobium carbonitrides the subject of considerable interest. In this paper we report on a method of preparing Nb-C-N thin films with a composition similar to the optimum reported for the bulk system viz., NbC$_{0.3}$N$_{0.7}$. We also report on some of the superconducting properties of these films.

The films for this study were prepared by d.c. diode sputtering in an apparatus in which the background impurity level prior to sputtering is typically $\sim 5 \times 10^{-10}$ Torr. The details of this apparatus and the entire sputtering process have been described previously. The sputtering target for the present experiments was prepared by hot pressing (at $\sim 1000^\circ$C) a niobium and carbon powder mixture into the desired form. The final dimensions of the target were 3.5" x 2.5" x 0.125", and the atomic ratio of niobium to carbon in this target was 3.33/1. The sputtering gases used in these experiments were either pure nitrogen or mixtures of nitrogen and argon. Films were deposited.
on substrates held at temperatures ranging from 500°C to 800°C. To permit an unambiguous observation of the effect of including carbon into the NbN structure, a number of deposition experiments were performed in which a niobium sputtering target was employed instead of the niobium-carbon target. Transition temperature measurements were made in liquid hydrogen under reduced pressure, using a standard resistive technique. The transition temperature here, is defined as the temperature at which the film begins to lose its normal state resistance. Finally, high field measurements were made in liquid helium in fields up to 210 kOe. In all cases the direction of the field was normal to the plane of the film.

The first Nb-C-N films that were prepared were sputtered in an argon-nitrogen atmosphere onto substrates held at ~ 500°C-conditions similar to that used to prepare NbN films. These films were found to have very low Tc's of about 6°K. Subsequent experiments in which no changes in experimental conditions were made produced a rise in Tc until values similar to those reported for our NbN films were obtained, i.e., ~ 15°K. After this point no further improvement occurred. This rise in Tc up to ~ 15°K we attribute to a gradual cleaning up of the pressed powder sputtering target. Following these experiments, we were able to achieve further increases in transition temperatures by raising the substrate temperature. Tc's of over 17°K have now been obtained with films deposited on substrates heated to 700°C. (The ΔTc's of these films are approximately 0.3°K.) Higher temperatures than 700°C produced no additional rise in transition temperature. It is felt that continually greater out-gassing from the hardware in the sputtering chamber, due to
these high substrate temperatures, may currently be limiting the maximum Tc's obtainable in these experiments. Changing other experimental parameters, such as the argon/nitrogen sputtering gas composition, produced no increase in Tc's.

In all of our Nb-C-N experiments the maximum transition temperature that we have obtained is 17.3°K. This Tc is the highest thus far reported for a niobium carbonitride thin film. However, Tc's up to 17.3°K have previously been reported for niobium nitride films. These films were also prepared by a sputtering process in which high (> 700°C) substrate temperatures were employed. To assess the importance of carbon in our films, a number of experiments were performed in which a pure niobium cathode was used instead of a niobium-carbon target. The maximum Tc obtained from these experiments was 16.5°K, the same as the maximum value reported for bulk NbN. Our results thus indicate that transition temperatures higher than the maximum reported bulk value are obtained only when a third component (in this case, carbon) is incorporated into the NbN structure.

While the use of high substrate temperatures (i.e., > 500°C) produces a beneficial effect on the Tc's of both Nb-C-N and NbN sputtered films, a deleterious effect has been noted with respect to the high field properties of these films. Figure 1 illustrates current density versus field values for two Nb-C-N films sputtered at different substrate temperatures. As can be noted the higher Tc film prepared at higher temperature possesses both lower current densities and a lower upper critical field. Similar results have also been obtained with our NbN
films. This inverse relationship between $T_c$ and high field properties is believed to be due to different physical structures of these films resulting from the different growth temperatures. This stronger dependence of critical current and field properties on metallurgical variables than on transition temperature is consistent with previous measurements on ultra-thin (< 200 Å) NbN films.\(^{(3)}\) As was reported, these films which had transition temperatures as low as 10°K, maintained critical current and field values as high as thicker NbN films which had $T_c$'s over 15°K.

In conclusion, we have found that by raising substrate temperature, Nb-C-N and NbN films have been prepared with maximum $T_c$ values of 17.3°K and 16.5°K respectively. However, this rise in $T_c$ has been accompanied, in both cases, by a degradation in high field properties. This degradation is believed to be the result of a different physical structure in the films grown at higher temperatures. We have previously reported that based on electron microscope studies, NbN films deposited on ~ 500°C substrates possess a columnar type structure.\(^{(6)}\) The NbN grains or "columns" grow normal to the film surface and average ~ 400 Å in diameter. Most significantly the individual grains appear to be separated from each other by distances of about 10 Å. These voids between grains which apparently contain only gaseous atoms (argon and/or nitrogen) are thought to be the source of the very high resistivities and relatedly the very high upper critical fields values found in NbN films. We believe that the deposition of films (both NbN and Nb-C-N) at higher temperatures reduces the size of these voids thus accounting for the lower
resistivities and lower upper critical field values found in these films. With respect to the lower current densities observed in the higher Tc films, it is felt that these result from the higher growth temperatures producing fewer dislocations and grain boundaries thus reducing the total number of pinning centers in these films. To substantiate these hypotheses we are continuing our investigation of thin films of various compositions in the Nb-C-N system to obtain more complete data on both the structural and superconducting properties of these films.
REFERENCES

FIGURE CAPTION

Fig. 1 $J_c-H$ curves illustrating the effect of substrate temperature on high field properties in Nb-C-N films. Nb-C-N (A) was sputtered at \( \sim 500^\circ C \) and Nb-C-N (B) at \( \sim 700^\circ C \).
Fig. 1—$J_C$-$H$ curves illustrating the effect of substrate temperature on high field properties in Nb-C-N films. Nb-C-N (A) was sputtered at ~500°C and Nb-C-N (B) at ~700°C.
TEMPERATURE DEPENDENCE OF UPPER CRITICAL FIELD IN Nb-Al-Ge FILMS**

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ABSTRACT

$H_{c2}(T)$ for sputtered B-W structure Nb-Al-Ge films is the same as that of the bulk, allowing for differences in $T_c$, while film $J_c-H$ curves are much higher. Comparison is made with results for films of another type-II superconductor, NbN.

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*Work supported in part by the National Aeronautics and Space Administration.

+Part of this work was performed at the Francis Bitter National Magnet Laboratory, which is supported at M.I.T. by the National Science Foundation.
Measurements by Foner, et al., have shown that bulk Nb-Al-Ge possesses the highest upper critical field values ($H_{c2}$) presently known.\(^{(1)}\) We have shown that a type II superconductor, NbN, when prepared in thin film form, can have much higher critical current versus magnetic field ($J_{c}$-$H$) curves and much higher $H_{c2}(T)$ values than those of bulk samples, and that Nb-Al-Ge films also have much higher $J_{c}$-$H$ curves than the bulk.\(^{(2)}\) We report here our measurements of $H_{c2}(T)$ for Nb-Al-Ge films and compare the results with the reported bulk values.

The techniques used to prepare the Nb-Al-Ge films for this study have been previously described.\(^{(3)}\) Briefly, the films were sputtered from a $\text{Nb}_{3}\text{Al}_{0.8}\text{Ge}_{0.2}$ cathode in an ultra-high purity environment. These films have the A-15 (bW) structure and they remain superconducting to over 16°K. Thickness of the films was $\sim 5000$ Å.

The $H_{c2}$ versus temperature data on the Nb-Al-Ge films were taken in a large bore 150 kG solenoid. To avoid magnetoresistance problems associated with conventional resistance thermometry, a temperature sensing gas bulb probe with the samples mounted directly on the gas bulb was employed in these experiments. The temperature was controlled manually by varying the flow of cooled helium gas into the chamber containing the probe. After establishing a constant temperature at zero field, the field was swept up slowly and the temperature and the voltage drop across the film were simultaneously recorded as a function of field strength. The temperature variations during the field sweep and during
the superconducting to normal transition were kept small, about 0.1°K and 0.01°K respectively. In these experiments we define \( Hc_2 \) as that field at which the sample has regained half of its normal state resistance. \( Tc \) is defined similarly, i.e., as the midpoint of the transition.

Figure 1 shows the dependence of the upper critical field on temperature in a Nb-Al-Ge film. An extrapolated \( Hc_2 \) value for 4.2°K taken from previously reported critical current vs field measurements, is also shown. The slope at \( Tc \) is 29.3 kG/°K, giving a dirty-limit GLAG \( Hc_2^* (0) \) of 304 kG where \( Hc_2^* \) is the non-PSP (Pauli Spin Paramagnetic) limited upper critical field. The magnitude of the parameter \( \alpha \), characteristic of PSP limiting, is given by

\[
\alpha = \sqrt{2 \over \frac{Hc_2^* (0)}{Hp}}.
\]

\( Hp \) is the Clogston-Chandrasekhar spin paramagnetic limited upper critical field and is equal to \( Tc \times 18.4 \) kG/°K. For this film the Clogston limit is 276 kG and \( \alpha \) is therefore 1.56. Paramagnetic limiting, with this \( \alpha \), would result in a curve much lower than the \( \alpha = 0 \) theoretical curve (shown in Fig. 1) taken from Werthamer, Helfand and Hohenberg. The \( \alpha = 0 \) curve, however, is obtained for any finite \( \alpha \) when \( \lambda_{so} \rightarrow \infty \), \( \lambda_{so} \) being the parameter characteristic of the amount of spin orbit scattering. Thus we conclude that the Pauli spin paramagnetic effect corresponding to an \( \alpha \) of 1.5 is totally suppressed by a large spin-orbit scattering. This is the same result obtained by Foner, et al., for the bulk material.

Figure 2 compares bulk Nb\(_3\)Al and Nb-Al-Ge alloy temperature dependence data of Foner, et al., with our thin film \( Hc_2 (T) \) data. The slopes at \( Tc \) for this film (29.3 kG/°K) and for the bulk Nb-Al-Ge alloy (30.6 kG/°K) are about the same, while the bulk Nb\(_3\)Al slope (25.6 kG/°K)
is substantially lower. We regard this as tending to confirm that the film
is of the Nb-Al-Ge type and not simply low Tc Nb₃Al.

We believe that the enhancement of Hc₂ seen in NbN films is not
seen in Nb-Al-Ge because of differences in structure as evidenced by
electron microscopy and resistivity measurements. The NbN sputtered
films have a columnar structure, revealed by transmission electron
microscope studies, in which the grains (or "columns") grow normal to the
substrate surface and are separated from each other by voids approximately
10 Å wide. These voids are assumed to be filled with non-conducting
gaseous atoms not detected by the electron microscope. Similar studies
of Nb-Al-Ge films, though indicating a columnar grain growth, do not show
any intergranular void structure.

The factor of 10 higher resistivity (≈ 500 micro-ohm-cm) of
NbN films over that of the bulk, caused by the void structure, is not seen
in the Nb-Al-Ge films, whose resistivity, ≈ 20 micro-ohm-cm is of the
same order of magnitude as those of other bulk A-15 type compounds. The
non-enhanced resistivity of the films directly implies the observed non-
enhanced Hc₂(T). The exceptional pinning strength observed in both NbN
and Nb-Al-Ge films (from the high Jc-H curves of both) is probably due to
intergranular defects arising from the columnar grain growth which seems
to be characteristic of these sputtered films. The Hc₂ enhancing void-
structure, however, does not occur for Nb-Al-Ge films as presently
prepared.
REFERENCES


FIGURE CAPTIONS

Fig. 1  \( H_{c2}(T) \) for an Nb-Al-Ge film. The curve is the theoretical one of Werthamer, et al., for \( \alpha = 0 \).\(^{(5)}\)

Fig. 2  \( H_{c2} \) vs. temperature for an Nb-Al-Ge film, and for the bulk samples of Foner, et al.\(^{(1)}\)
Fig. 1

A15-6
Fig. 2

- A - Nb-Al-Ge Film
- B - Nb$_3$Al Bulk
- C - Nb$_{79}$ (Al$_{73}$Ge$_{27}$)$_{21}$ Bulk
SUPERCONDUCTING PROPERTIES OF ANNEALED Nb-Al-Ge THIN FILMS*

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ABSTRACT

Annealed bulk Nb-Al-Ge possesses the highest presently known superconducting transition temperature ($T_c \sim 20^\circ$K). In this paper we report on $T_c$ and on other superconducting properties of annealed Nb-Al-Ge thin films, which were prepared by sputtering from a 3Nb·0.8Al·0.2Ge cathode. Annealing was performed in a high vacuum environment maintained at $10^{-9}$ Torr or less, for times and temperatures near the optimum conditions previously reported for bulk Nb-Al-Ge. Films with $T_c$'s from 12° to 16°K were annealed and in all cases a rise in $T_c$ was observed, with the maximum value obtained thus far being 17.5°K. The current carrying capacity ($J_c$) values, already substantially higher for unannealed thin films than for the bulk, were raised even further in the annealed samples, indicating that annealing has no detrimental effects on the flux pinning in these films.

*Work supported in part by the National Aeronautics and Space Administration.

Certain Nb-Al-Ge alloys, when suitably annealed, have the highest $T_c$ ($20.7^\circ\text{K}$) and upper critical field, $H_{c2}$ (415 kG at 4.2°K) of any known superconductor.\cite{1-4} We have previously reported efforts to produce these alloys in the technologically useful thin film form by diode sputtering in an ultra-clean environment.\cite{5-7} By sputtering from a hot pressed powder target of nominal composition $\text{Nb}_3(\text{Al}_{0.8}\text{Ge}_{0.2})$ we have now achieved as-deposited film $T_c$'s of up to 16.6°K. $T_c$'s higher than 18°K are obtained in the bulk by means of low temperature annealing which is generally considered to bring about an atomic ordering.\cite{2,8,9} We have performed low temperature annealing on our sputtered films and present the results in this paper.

Initial attempts to anneal sputtered films in evacuated fused silica tubes, as is done for bulk samples, were unsuccessful. Contamination of the films by residual or desorbed gases in the tubes caused degraded superconducting properties. To eliminate this problem annealing was carried out in one of the same ultra-high vacuum systems used for the film depositions. Up to twelve film samples on sapphire or polished alumina substrates were placed in the heater tube of a tantalum chimney-type evaporation source, which had been previously degassed at very high temperatures. The sputter-ion pumped vacuum system was then given the usual moderate temperature bakeout, at 250°C for about 30 hours. After cooling, pressures in the $10^{-10}$ torr range were attained before annealing was commenced. The samples were heated slowly, so as to maintain the vacuum below $10^{-9}$
torr. Sample temperatures were measured directly, through the open end of the heater tube, by optical pyrometer and were controlled manually by varying the heater current. At a given setting, temperatures did not drift more than 10°C over any annealing run and so automatic temperature control was not used. Ultimate pressures in the $10^{-11}$ torr range were usually obtained toward the end of annealing runs. After annealing, high field $J_C$-$H$ curves were taken at 4.2°K in a 200 kG solenoid at the Francis Bitter National Magnet Laboratory. $T_C$'s were measured resistivity in liquid hydrogen to obtain the most reliable temperature determinations.

Before discussing our sputtered film annealing results, it is necessary to summarize the previously reported $J_C$-$H$ and $Hc_2$ data for Nb-Al-Ge alloys, which are shown in Fig. 1 and Table I. Hartsough, et al.\textsuperscript{(10)} observed a peak effect (curve A) which they attribute to structural defects of an undetermined nature, possibly a multiphase microstructure, composition gradients, or local internal stresses. They obtained essentially the same $J_C$-$H$ curve for both the as-cast and annealed samples. Their annealing, which was carried out 200°C higher than the optimum 750°C, slightly raised $T_C$ and lowered $\rho_n$.

The only other bulk $J_C$-$H$ data, that of Yasukochi, et al.\textsuperscript{(11)} (curve B), is difficult to interpret. The sample was both of optimum composition and annealed at the optimum temperature, but $T_C$ was only 18.5°K, thus raising some questions about the sample preparation. Moreover, it is not clear whether $J$ was perpendicular to $H$ for their measurements—the curvature of $J_C$ vs $H$ is that obtained when $J$ is parallel to $H$. If this was the case then, with a resistive measurement, they were observing
Hc₃-limited surface sheath superconductivity, and not Hc₂. For Hc₃ ≥ 1.7 Hc₂, where Hc₃ is the field at which the sample is completely normal in the limit of zero current (∼ 470 kG from their data), Hc₂ would be ∼ 280 kG instead of their reported 420 kG. Also J||H gives Jc values a factor of ten higher than for J⊥H.(12) Thus curve B cannot be compared with the other curves for which J is perpendicular to H. Foner, et al.(4) give a magnetically determined Hc₂ of 415 kG (curve C) for material with a 20.7 °K Tc. Resistivities were not given for the materials of curves B and C.

Curves D and E1 are for our as-deposited films sputtered from a pressed powder target, D being previously reported.(6) The comparatively low resistivity for the film of curve D is only approximate, as its Hastelloy stainless steel substrate is conducting and precludes accurate resistivity measurement. Curve E1 is for a film subsequently annealed, which was deposited at a higher rate (∼ 500 Å/min vs. ∼ 100 Å/min) and lower substrate temperature than the film of curve D; this may account for its much greater resistivity and consequently higher Hc₂. The 1.1°K higher Tc of the E1 sample is probably due to the long term cleaning up and equilibration in the target,(6) and not to the particular sputtering conditions. Finally, point F is the only Jc-H datum given for the co-deposited Nb-Al-Ge films of Isao, et al(13) who obtained high Tc's after various heat treatments subsequent to deposition. Tc and ρn for the film of F were not given, and the point itself is approximate.

The available data, though sparse, exhibits a wide range of behavior. In view of our annealing results, summarized in Fig. 2 and Table II,
this is not surprising, since we obtained very different curves for the same sample. Again, the as-deposited film gives curve E1. The first anneal changed the $J_C$-$H$ curve to E2, which is close to D, the curve for the unannealed sample deposited more slowly at a higher temperature. The decrease in $\rho_n$ is associated with the decrease in $H_{c2}$. A second anneal at 775° for 90 hours raised $T_C$ to 17.4°K. A third anneal at 735°C for 40 hours had no effect on $T_C$. Curve E3 was taken after the third anneal. Resistivity and $H_{c2}$ have decreased still further. It is not unexpected that annealing resulting in ordering would decrease resistivity and $H_{c2}$. It is surprising, however, that the $J_C$ curve should change from a moderate slope to almost vertical—that is, that pinning should become much stronger. With this particular sample, the current necessary to obtain $J$ of $2 \times 10^4$ A/cm$^2$ is ~3 amperes which was the limit our experimental probe could carry. Thus high enough current densities could not be reached to observe the bending over of the $J_C$-$H$ curve, but it appears that the film after the third anneal could carry in the vicinity of $10^5$ A/cm$^2$ at 150 kG, and the current carrying capacity may be substantially higher at lower fields.

Many other samples were annealed, with results similar to those of Fig. 2, namely, a progression with annealing toward verticality of the $J_C$-$H$ curve. Samples with lower as-deposited $T_C$'s were also annealed. These were obtained from early sputtering runs with incompletely equilibrated pressed powder targets or from runs using an arc melted ingot target. These samples in general showed much larger rises in $T_C$, e.g., from 12°K to 15.5°K, a rise of 3-1/2°K, but ultimate $T_C$'s obtained were not as high as those for films which had high as-deposited $T_C$'s. Films deposited on
polished alumina substrates gave the same results as those deposited on optically smooth sapphire.

In Table II are given the experimental values for $H_{c2}^2 (4.2\degree \text{K})$ which were estimated for curves E1 and E2, and values of $H_{c2}^\ast (0)$ and the Ginzburg-Landau order parameter $\xi_{GL} (4.2\degree)$ calculated from the normal state parameters $\rho_n$, $\gamma$, and $T_C$. For these calculations the electronic specific heat $\gamma$ was assumed to be that of the bulk, which was extrapolated from the specific heat curve of Matthias, et al to be $62 \times 10^{-4}$ cal deg$^{-2}$ mole$^{-1}$ or $6.2 \times 10^3$ erg deg$^{-2}$ cm$^{-3}$. For $\rho_n$ in ohm-cm and $\gamma$ in erg deg$^{-2}$ cm$^{-3}$ we use

$$H_{c2}^\ast (0) = 31 \rho_n \gamma T_C \text{(kilogauss)} \quad \text{and}$$

$$\xi_{GL}(t) = 10^{-6}/(\rho_n \gamma T_C)^{1/2} (1-t)^{1/2} \text{(centimeters)}.$$

As can be seen, the calculated GLAG limit $H_{c2}^\ast (0)$ is much higher in each case than $H_{c2} (4.2\degree)$. This indicates that Pauli spin paramagnetic (PSP) limiting must be occurring. However, our $H_{c2} (T)$ studies for the film of curve D$^\prime$ (15) show that, to the contrary, PSP limiting is nullified by spin orbit scattering, in agreement with the results of Foner, et al for bulk material (4). For a possibly multi-phase alloy film of this type, it may not be appropriate to assume that the resistivity of the material as a whole is that which is associated with the GLAG $H_{c2}^\ast (0)$ limit. Clarification of the role of PSP limiting and spin orbit scattering in annealed Nb-Al-Ge films must await precise $H_{c2} (T)$ measurements on the annealed films.

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Extremely small values of $\xi_{GL}$ result from the normal state parameters. Given that defects larger than $\xi_{GL}$ will cause pinning, the low $J_c$'s and the high resistivity of the unannealed film imply disorder on a scale less than 17 Å, or just above an atomic scale. Ordering brought about by annealing will lower the resistivity but along with the ordering there may also be impurity segregation or phase precipitation such that non-superconducting areas larger than $\xi_{GL}$ may appear, which would increase pinning. Though some such mechanism is necessary to explain the appearance of this pinning, elucidation of the details will require extensive metallurgical and x-ray studies.

Concluding, we have shown that annealing of sputtered Nb-Al-Ge films in ultra-high vacuum results not only in raising $T_C$, but in changing the $J_c$-H curves in an extensive and unexpected way.
<table>
<thead>
<tr>
<th>Curve</th>
<th>Composition</th>
<th>Ref.</th>
<th>Heat Treatment</th>
<th>$T_c{^\circ K}$</th>
<th>$\sigma_n;\mu\text{ohmcm}$</th>
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<tr>
<td>A</td>
<td>bulk Nb$<em>3$(Al$</em>{1.8}$Ge$_{0.2}$)</td>
<td>10</td>
<td>as cast</td>
<td>18.5</td>
<td>55.4</td>
</tr>
<tr>
<td>A</td>
<td>bulk Nb$<em>3$(Al$</em>{1.8}$Ge$_{0.2}$)</td>
<td>10</td>
<td>950°C, 72 hr(1)</td>
<td>19.0</td>
<td>49.3</td>
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<tr>
<td>B</td>
<td>bulk Nb$<em>3$(Al$</em>{0.75}$Ge$_{0.25}$)</td>
<td>11</td>
<td>750°C, 8 days</td>
<td>18.5</td>
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<tr>
<td>C(2)</td>
<td>bulk Nb$<em>{79}$(Al$</em>{17}$Ge$_{27}$)</td>
<td>2-4</td>
<td>750°C, 1-20 days</td>
<td>18.5</td>
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<tr>
<td>D</td>
<td>sputtered film, Nb$<em>3$(Al$</em>{1.8}$Ge$_{0.2}$)</td>
<td>6</td>
<td>deposited at 650°C</td>
<td>15.5</td>
<td>~ 20</td>
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<tr>
<td>E1</td>
<td>sputtered film, Nb$<em>3$(Al$</em>{1.8}$Ge$_{0.2}$)</td>
<td>this study</td>
<td>deposited at 500°C</td>
<td>16.6</td>
<td>340</td>
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<tr>
<td>F(3)</td>
<td>co-deposited Nb$_3$(Al-Ge)</td>
<td>13</td>
<td>1000°C, &gt; 10 min</td>
<td>16.5</td>
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</table>

(1) Essentially the same curve, A, was obtained for both as-cast and annealed samples.
(2) $Hc_2(4.2)$ value only.
(3) Specific sample characteristics not given for this point.
<table>
<thead>
<tr>
<th>Curve</th>
<th>Heat Treatment</th>
<th>$T_c$ °K</th>
<th>$\rho_n$</th>
<th>$\rho_n$</th>
<th>$\gamma T_c$</th>
<th>$H_{c2}(4.2^\circ\text{K})$</th>
<th>$H_{c2}^*(0)$</th>
<th>$\xi_{GL}(4.2^\circ\text{K})$</th>
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<td>16.6</td>
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<td>1080 kg</td>
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<td>E2</td>
<td>790°C, 14 hr</td>
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<td>~ 250</td>
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<tr>
<td>E3</td>
<td>775°C, 90 hr; 735°C, 40 hr.</td>
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<td>9</td>
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REFERENCES


FIGURE CAPTIONS

Fig. 1 Curve identifications given in Table I.

Fig. 2 Curve identifications given in Table II.
Curve 643209-A

Fig. 1
Fig. 2

$J_c$, A/cm$^2$

$H$, kG
THIN FILM STUDIES OF HIGH $T_c$ COMPOUNDS

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ABSTRACT

Thin films of NbN and Nb-Al-Ge have been shown to exhibit interesting and sometimes dramatic effects in their critical parameters, $J_c - H_c^2 - T_c$, when compared with their corresponding properties in bulk. Many of these results can be explained in terms of the structure of these films. A monotonic relationship between $T_c$ and reciprocal Hall constant has been observed for short mean free path materials having the rocksalt structure, suggesting that their properties are rather insensitive to minor details of the Fermi surface topology. The above results are presented in some detail and compared with the theories of type II superconductors wherever possible.

*This work supported in part by the National Aeronautics and Space Administration under Contract NASW-1760.
Introduction

The properties of bulk high $T_c$ compounds, primarily those having the $\beta$-W or rocksalt structure, have been studied extensively for a number of years, whereas until recently, the thin film properties received much less attention. This has been primarily due to the fact that these materials are very sensitive to impurities and thus require special and carefully controlled deposition procedures. Currently, it is possible to produce structurally and chemically stable films of such compounds as NbN and Nb-Al-Ge which have $T_c$'s equivalent or close to those of the bulk material, in a consistent and reproducible fashion. We have studied the structure of these films and made extensive measurements of their high field properties as well as investigating possible $T_c$ enhancement effects in very thin film structures.
Film Preparation and Properties

The detailed preparation procedures of both the NbN and Nb-Al-Ge films have given elsewhere\textsuperscript{1,2} and only a brief review will be presented here.

NbN films are deposited by a dc reactive sputtering process using a Nb cathode and an argon-nitrogen gas mixture. The nitrogen partial pressure is adjusted to obtain the maximum $T_C$ in the films. An ultra-high vacuum system is used and is evacuated to < 10\textsuperscript{-9} torr prior to sputtering. The films produced are homogeneous, single phase and can be grown with large crystallite sizes on a variety of substrate materials. X-ray studies yielded a lattice parameter for the film material close to that of bulk NbN. Electron microscopy has shown that the NbN films grow with a preferred orientation, the (111) direction being perpendicular to the substrate, even when an amorphous substrate is used. In addition the films have a columnar texture with the column axis parallel to the (111) direction. The columns are NbN with a diameter depending upon the deposition conditions but usually $\sim$ 400 \AA. The columns are separated by Nb deficient material usually about 10 \AA thick. Resistivity measurements have yielded values of $250 < \rho_n < 1500 \mu\Omega\cdot\text{cm}$. The intercolumnar regions probably account for the large resistivity values as well as the variations in resistivity between various samples. Since any measured resistivity is some combination of the columnar and intercolumnar material it is
difficult to know what value to use to characterize the superconducting material itself. The effect of the columnar structure and high resistivity on the superconducting properties will be discussed in the following sections.

The Nb-Al-Ge films were produced by sputtering from a compound cathode in a pure argon atmosphere using the same type of system as was used for the NbN films. Two different types of cathodes, an arc melted ingot and a pressed and sintered (1000°C) powder mixture, both having the nominal composition Nb₃(Al₀.₈Ge₀.₂) were used. The highest as deposited \( T_c \)'s were obtained with the pressed target and a substrate temperature of \( \approx 650°C \). It is interesting that such a low substrate temperature can be used to form a compound which in bulk form reacts at about 2000°C. As deposited films have residual resistivity values of about 340 \( \mu\Omega\text{-cm} \) which decreases to 200 \( \mu\Omega\text{-cm} \) after annealing at 790°C for 14 hours and ultimately to 90 \( \mu\Omega\text{-cm} \) after an additional 90 hours at this temperature followed by a 40 hour anneal at 735°C. Transmission electron microscopy results indicated that lateral grain dimensions are \( \approx 2000\ \AA \). No indication of a void structure analogous to that in NbN was observed.
Transition Temperature Results

One of the approaches advocated for developing higher transition temperature superconductors is to modify the interaction parameters of known superconductors using specialized thin film structures. Amorphous films whereby modifications of the phonon spectrum can occur, or metal-dielectric sandwiches whereby the dielectric properties of the metal may be affected have been the two most popular approaches. Some encouraging results have been obtained with thin films of low $T_c$ materials. To obtain increases in $T_c$ of technological significance it appears to be necessary to start with a material having an intrinsically high $T_c$. In addition, from an experimental viewpoint, it is usually desirable to work with a system that is chemically and structurally stable as well as chemically and physically characterizable. The NbN system with a bulk $T_c$ of 16°K appeared to be promising in this regard.

The question of $T_c$ enhancement effects in these films was investigated by two means. First, the transition temperature was monitored as the film thickness was decreased to the point where the films became discontinuous ($\sim 50$ Å). The only effect observed, as is shown in Fig. 1, is that at $\sim 300$ Å the $T_c$ begins to drop rapidly. This decrease in $T_c$ may be due to impurities or the details of the nucleation process. Since at small thicknesses the films become discontinuous it may be impossible to make continuous films of NbN which are thin compared to the range of
the effective electron-phonon interaction. The second approach used was to try and modify the properties of the NbN via a highly polarizable material. SrTiO$_3$ substrates, TCNQ overlays and NbN-Si$_3$N$_4$-NbN sandwiches were used. In no instance was an increase in $T_C$ observed. In retrospect this result is not too surprising since the maximum enhanced $T_C$ from the Cohen-Douglass mechanism is only about 18°K, which is close to the bulk $T_C$ of these materials.

In addition to our work on high $T_C$ rocksalt structure materials such as NbN we have also made extensive studies of the SnTe system$^5$ which has the same structure as NbN. The transition temperature of SnTe (bulk material) can be varied by over two orders of magnitude by using self and impurity doping. When the results in this system are compared to the NbN system a very interesting result is obtained as illustrated in Fig. 2. This graph shows a plot of the log $T_C$ versus log $R_H^{-1}$ where $R_H$ is the 77°K Hall constant. $R_H$ for NbN was measured on a thin film sample. The SnTe-NbN systems exhibit a monotonic relationship between log $T_C$ and log $R_H^{-1}$ over 3 orders of magnitude in $T_C$ (.015-15°K) and more than 2 orders of magnitude in $R_H^{-1}$. In addition, the data on the rocksalt compound InTe$^6$ which has $T_C$'s intermediate between SnTe and NbN falls almost exactly in line with the SnTe-NbN data. For comparison the La$_3$Se$_4$ data$^7$ is also illustrated. This system is cubic but has the Th$_3$P$_4$ structure rather than the NaCl and would not be expected to fall in line with the SnTe-InTe-NbN data, but one does notice that the slope of this data is virtually the same as that obtained for the rocksalt structure materials. The data presented in this figure suggest that, for a given structure, the carrier density,
$n \sim R_H^{-1}$, is fundamentally related to the $T_C$, probably because the short electronic mean free path washes out local details of the Fermi surface topology. The nearly free electron Morel and Anderson theory, which employs a parameterized representation of the electronic structure and lattice excitation spectrum, has been used by a number of workers to analyze these and similar results with surprising success. An extension of this basically experimental approach to other systems should provide information of importance in relating $T_C$ to real metal parameters, particularly where the traditional, detailed investigations of the electronic structure are impractical, such as in the case of the short mean free path materials discussed above. This condition probably obtains for all high $T_C$, strong coupling superconductors of potential technological importance.

As mentioned previously arc melted and pressed and sintered targets were used in the deposition of Nb-Al-Ge films. Films sputtered from the arc melted material had a maximum as deposited $T_C$ of 15°K and typically were 11-12°K. The arc melted bulk material $T_C$ was 18.5°K. Using the pressed and sintered material as deposited $T_C$'s as high as 16.8°K were obtained and annealing raised this $T_C$ to 17.5°K. As discussed below, the annealing processes also had pronounced effects on $J_C$ and $H_{C2}$. 

A17-6-
Upper Critical Field Results

Although the $T_c$ results obtained for thin films of NbN are the same as those for the bulk material, the high field properties are significantly different. This is illustrated by the curves A and B in Fig. 3 which give the upper critical field as a function of the temperature for bulk and thin film NbN. A comparison of their experimental parameters is given in Table I. The solid portions of the curves represent the regions where experimental data has been obtained. The extrapolation of this data (dashed portion) to $T=0$ is performed according to the theoretical calculations of Werthamer, Helfand and Hohenberg\textsuperscript{12} for the case $\alpha = 0$, where $\alpha$ is the Maki paramagnetic parameter. We will not discuss the derivations of the equations used in calculating $H_{c2}$, but have included the relevant papers in reference 12. In the case of bulk NbN experimental data has been obtained\textsuperscript{13} at low enough temperatures to verify the accuracy of the above extrapolation procedure. The $H_{c2}$ values for the films, being significantly higher than those in the bulk, have only been determined in the linear region near $T_c$. It has also been demonstrated by pulse field measurements that $H_{c2} > 250$ kOe at 4.2$^\circ$K as indicated by the single point on this graph. Lacking $H_{c2}$ data at lower temperatures we can't justify the above extrapolation to $T=0$ in the case of the films since the shape of the theoretical curve in the region near $T_c$ is independent of $\alpha$. 
If we consider the equations at our disposal to estimate $H_{c2}(0)$ for the NbN films we have two basically different approaches which can be followed. The first is that illustrated in Fig. 3 where $H_{c2}(0)$ is calculated from the slope of the $H_{c2}(T)$ versus $T$ curve at $T=T_c$. The second approach involves the use of the film normal state parameters $\gamma, \rho_n$ and $T_c$. Either of these methods can theoretically be extended to include the effects of Pauli Spin Paramagnetism (PSP) and spin orbit scattering. Although it is a reasonable assumption that the enhanced $H_{c2}$ of the films is due to an increased resistivity, it is not possible at present to determine what value of resistivity should be used to characterize the films. This is due to their particular growth characteristics discussed previously. We have calculated $H_{c2}(0)$ using the range of resistivity values given in Table I and the results show:

1. In the absence of PSP corrections the larger values of $\rho_n$ yield excessively large values of $H_{c2}(0)$.

2. For large values of $\alpha$ the resultant $H_{c2}(0)$ values are insensitive to the exact value of $\alpha$.

3. When PSP corrections are included the resulting $H_{c2}(0)$ values are below the experimentally determined lower limit of 250 kOe.

The question of whether PSP effects are important in determining the upper critical field of the films is a difficult question which at this time cannot be answered with any precision. The difficulty is simply that there are two competing effects, one, the Pauli paramagnetism tries to lower the upper critical field while the second, spin-orbit scattering counteracts the first. The defects contributing most to the spin-orbit
scattering are probably vacancies in view of the previous characterization of the films. Changing the vacancy concentration in a controlled way may be a way to vary the spin-orbit scattering component and obtain information on the PSP component. Investigations into the temperature dependence of $H_{c2}$ at higher fields may also help resolve this question.

The $H_{c2}(T)$ versus $T$ curve of a thin film of Nb-Al-Ge is shown in Fig. 3 along with the data for bulk material.\(^{14}\) The Nb-Al-Ge film is as deposited material prepared from the pressed and sintered target. The results are identical to those of the bulk if they are scaled according to the $T_c$ difference. The 4.2\(^\circ\)K point for the film was determined by extrapolation of $J_c$-$H$ data. The analogous point for the bulk material was determined by pulse field measurements.\(^{14}\) Calculating $\alpha$ from the slope of $H_{c2}$ at $T_c$ yields a value of $\alpha = 1.5$ for the film data, yet the theoretical curve for $\alpha = 0$, shown in this figure gives the best fit to the low temperature data. This would indicate that the PSP effect is counteracted by a large spin-orbit scattering effect. Analogous results are obtained when this analysis is applied to the bulk data. When an as deposited film such as shown in this figure is given a low temperature anneal to increase $T_c$, $H_{c2}$ at 4.2\(^\circ\)K decreases from 300 to 188 kOe and $\rho_n$ decreases from 340 to 86 $\mu$-$\Omega$-cm.
Critical Current Results

The columnar structure of the NbN films yields a high density of pinning centers and also a large anisotropy in $J_c$ as illustrated in Fig. 4. The $J_c$ versus $H$ curves for two films are shown for $H$ parallel and perpendicular to the film face but normal to $J$. In the case of the 200 Å film the anisotropy is very small. This can be attributed to the fact that in this case the film thickness and lateral grain size are approximately equal. The 5100 Å film exhibits an anisotropy of ~a factor of three between the two $H$ directions. For $H$ perpendicular to the film face $J_c$ is very close to the same for the two film thicknesses indicating that the void (pinning center) spacing does not vary as the film grows. The lower value of $J_c$ for $H$ parallel for the thick film can be attributed to the lack of pinning centers (defects) aligned parallel to the plane of the film.

Due to the high normal state resistivities and high $J_c$ values of the films difficulties were sometimes encountered in measuring $J_c$ due to heating at the current contacts and also within the film itself when it began to enter the resistive region. To solve these problems an NbN film was sputter-etched so that a narrow bridge of NbN was formed between two large contact areas. A current density of $10^6$ A/cm$^2$ at 100 kOe was observed in this specimen. This value is believed to be the largest ever reported for a superconducting material.
All of the Nb-Al-Ge films exhibited current densities significantly in excess of those observed in bulk specimens. The most interesting effect observed in these films, though, was an increase in $J_c$ below 150 kOe when they were annealed. This may possibly be due to the growth of some form of second phase precipitate during the heat treatment.
Conclusions

The monotonic relationship observed between $T_c$ and $R_H^{-1}$ for short mean free path materials in a particular crystal structure suggests that their superconducting properties are rather insensitive to local details of the Fermi surface topology.

Thin films of NbN and Nb-Al-Ge exhibit interesting and sometimes dramatic effects in their critical parameters, $T_c$, $J_c$, $H_{c2}$, when compared with corresponding bulk materials. The temperatures at which these compounds can be formed in a sputtering process are significantly lower than in bulk form and thus sputtering may prove to be a valuable tool in studying compounds which we may not be able to prepare by any other means.
References

10. J.K. Hulm, M.S. Walker and N. Pessall, Presented at Int. Conf. on Sci. of Superconductivity, Stanford, California, August 1969.
11. The value of \(\gamma\) for the films is taken to be the same as the bulk. Measurements performed by R. Greene and T. Geballe (private communication) on a thick NbN film verify the validity of this assumption.
L.P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 36, 1918 (1959); 37, 1407 (1959) [English transl.: Soviet Phys.-JETP 9, 1364 (1959); 10, 998 (1960)].
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K. Maki, Physics 1, 127 (1964).
# TABLE I

Experimental Parameters of NbN Films and Bulk Material

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<th>NbN Bulk (a)</th>
<th>NbN Films</th>
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<td>$T_c \ (^oK)$</td>
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<td>15.5</td>
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<td>$\rho_n \ (\mu\Omega\cdot cm)$</td>
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<td>250-1500</td>
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<td>$\gamma \ (ergs\cdot cm^{-3}\cdot ^oK^{-2})$</td>
<td>$3.2 \times 10^3$ (b)</td>
<td>$3.2 \times 10^3$ (c)</td>
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<td>$-\left.\frac{dH_{c2}}{dt}\right</td>
<td>_{t=1} \ (G)$</td>
<td>$2.08 \times 10^5$</td>
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<td>$H_{c2}(0) \ (G)$</td>
<td>$1.58 \times 10^5$</td>
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</table>

(a) See ref. 9.
(b) See ref. 10.
(c) See ref. 11.
Figure Captions

2. Transition temperature as a function of reciprocal Hall constant for some B1 and C7\textsubscript{3} structure materials.
3. Upper critical field as a function of temperature for bulk and thin film NbN and Nb-Al-Ge.
4. $J_c$ versus H for 200 Å and 5100 Å NbN films for H both parallel and perpendicular to the plane of the film.
Fig. 1 $T_C$ as a function of NbN film thickness
Fig. 2
Fig. 4
APPENDIX A18
LOWER CRITICAL FIELD MEASUREMENTS IN NbN BULK AND THIN FILMS*

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ABSTRACT

Low field magnetization measurements have been made at 4.2°K on thin film and bulk NbN samples using a vibrating sample Foner magnetometer. These data can be used to calculate the upper critical field, $H_{c2}$, without having the resort to resistivity data, which particularly in the case of NbN, yields very anomalous results. In the present work the experimental value of $H_{c1}$ is obtained from the magnetization curves and $H_{c2}$ is then calculated using the GLAG equations. These calculations and the significance of the Pauli spin paramagnetism and spin orbit scattering in these materials is discussed.

*This work supported in part by National Aeronautics and Space Administration under Contract NASW-1760.
I. Introduction

Previous work has shown that thin films of the rocksalt structure (B1) compound NbN have very interesting properties and in particular that they have upper critical fields significantly in excess of that observed for bulk samples. Bulk NbN has a transition temperature of \( \sim 16^\circ\text{K} \) and is usually prepared by the diffusion of \( \text{N}_2 \) in Nb wires. A description of this process has been given by Horn and Saur. The resulting samples are very brittle, porous, and usually contain a central core of unreacted Nb. The bulk NbN sample used in this work was kindly provided by E. Saur. NbN thin films are prepared by a reactive sputtering process in an ultra high vacuum system. The details of this procedure have been described by Gavaler, et al. Samples of both bulk and thin film NbN, prepared as described above have been used in conjunction with a vibrating sample magnetometer to obtain \( \text{Hc}_1 \) values for these materials. Using this data we have tried to obtain a more accurate estimate of \( \text{Hc}_2 \) of thin film NbN. These results are discussed in Section III.

II. Experimental Procedure and Results

Magnetization measurements were made using a vibrating sample Foner Magnetometer in conjunction with a 50 kG superconducting solenoid. All measurements were made at 4.2\(^{\circ}\text{K}\) and at the same constant field sweep rate.
In Fig. 1 we show the magnetization measurements on a bulk sample of NbN. The lower critical field $H_{c1}$ is obtained from the M-H curve by noting the departure from linearity at low fields. In Fig. 2 and Fig. 3 we show the magnetization curves of NbN thin films on two types of substrates. In Fig. 2 the anomalous behavior at high fields seems to emanate from the magnetic contribution of the sapphire substrate. As shown in Fig. 3 the magnetization becomes positive for fields above a certain field. It has been recently reported by Hake\textsuperscript{5} that for specimens in which paramagnetism is important, the magnetization curve is different from the usual curve. It has been noted that at some point between $H_{c1}$ and $H_{c2}$ the magnetization of the vortex phase becomes positive, but the vortex phase continues to exist until its magnetization equals that of the normal phase at $H_{c2}$. Thus the mixed phase may be paramagnetic over an interval of the applied field. In such a case the magnetization of the electronic paramagnetism of the vortex phase exceeds the diamagnetism of the super electrons. This anomalous behavior in our thin films can also come about from the magnetic properties of the stainless steel. It might be difficult to separate these two contributions.

The $H_{c1}$ value for NbN bulk from the measurements is about 95 G but for the thin films it is between 40-50 G.

In order to check the accuracy of our experimental technique several samples of Nb$_3$Sn were measured. The results depend upon the sample preparation procedure but agree well with the data of Hecht.\textsuperscript{6} Fig. 4 shows the magnetization curve for a tape sample.
III. Discussion

The experimental properties of bulk and thin film NbN as determined in this and previous work are given in Table I. We have assumed that the electronic heat capacity coefficient, $\gamma$, for the films is the same as that of the bulk. Measurements by Greene and Geballe on a thick film show this to be a good approximation. The carrier density $n$ is determined by counting the number of electrons outside closed shells assuming that the $N_2$ atoms do not contribute. The ratio of the Fermi surface area, $S$, to that of a free electron gas of equivalent density, $S_F$, is assumed to be $0.6$. It is known that for V, Ta and Nb the apparent $S/S_F$ lines between 0.4 and 0.9. We would now like to use this information to calculate the parameters which characterize the superconducting properties of these materials. The results of these calculations show that both the films and bulk material are dirty type II materials and we have used the equations appropriate for this limit. The parameters of interest are:

1. Electronic Mean Free Path

$$\lambda = \frac{1.27}{\rho_n n^{2/3} (S/S_F)} \text{ cm}. \quad (1)$$
2. Ginzburg-Landau Coherence Length

\[ \xi_{GL}(0) = \frac{1 \times 10^{-6}}{(\rho_n \gamma T_c)^{1/2}} \text{ cm} \]  

(2)

3. Ginzburg-Landau Penetration Depth

\[ \lambda_{GL}(0) = \frac{1.05 \times 10^{-2} \rho_n^{1/2}}{T_c^{1/2}} \text{ cm} \]  

(3)

4. Kappa (\(\kappa >> \kappa_0\))

\[ \kappa = 7.5 \times 10^3 \rho_n \gamma^{1/2} \]  

(4)

5. Thermodynamic Critical Field

\[ H_T = 2.42 \gamma^{1/2} T_c \text{ G} \]  

(5)

6. Lower Critical Field

\[ H_{c1} = \frac{H_T \ln \kappa}{\sqrt{2\kappa}} \text{ G} \]  

(6)

7. Upper Critical Field (in the absence of Pauli Spin Paramagnetism (PSP))

\[ H_{c2}(0) = \sqrt{2\kappa} H_T \text{ G} \]  

(7)
\[ H_{c2}^*(0) = 0.69 H_0 \quad \text{G} \quad (8) \]

\[ H_0 = \frac{-dH_{c2}}{dt} \bigg|_{t=1, \ t = T/T_c} \]

\[ H_{c2}^*(0) = 3.1 \times 10^4 \rho_n \gamma T_c \quad \text{G} \quad (9) \]

8. Paramagnetic Critical Field

\[ H_p(0) = 1.84 \times 10^4 T_c \quad \text{G} \quad (10) \]

9. Maki Parameter

\[ \alpha = \frac{\sqrt{2} H_{c2}^*(0)}{H_p} \quad (11) \]

10. Upper Critical Field (including PSP effects)

\[ H_{c2}(0) = \frac{H_{c2}^*(0)}{(1+\alpha^2)^{1/2}} \quad \text{G} \quad (12) \]

The results of these calculations (excluding the upper critical field \( H_{c2} \)) are given in Table II. Since \( \rho_n \) for the film samples varies over a fairly wide range we assumed an average value of 500 \( \mu \text{-cm} \) for these calculations.
Hake\textsuperscript{9} has calculated the maximum resistivity for NbN assuming the minimum \( \lambda \) and obtained a value of 250 \( \mu\Omega \cdot \text{cm} \). This means that our value of 500 \( \mu\Omega \cdot \text{cm} \) yields a non-physical value less than one lattice spacing for \( \lambda \) as indicated in Table II. Since both \( n \) and \( S/S_F \) had to be approximated it is questionable whether 500 \( \mu\Omega \cdot \text{cm} \) is non-physical or not even though it yields a value of \( \lambda \) which is too small. The question of the resistivity of the films is complicated by their structure. Electron microscopy has shown that the NbN films grow with a preferred orientation, the 111 direction being perpendicular to the substrate, even when an amorphous substrate is used. In addition the films have a columnar texture with the column axis parallel to the 111 direction. The columns are NbN with diameters depending upon the deposition conditions but usually \( > 100 \) Å. The columns are separated by Nb deficient material about 10 Å thick. These inter-columnar regions probably account for the large resistivities observed. Since any measured resistivity value will be some combination of the columnar and inter-columnar material it is difficult to know what value of resistivity to use in these calculations.

The results for \( \kappa \) in the films are in good agreement with each other and show that this material has one of the largest \( \kappa \)'s ever observed.

The results of our calculations of \( H_{c2} \) are given in Table III. If we consider NbN bulk material where we have an experimental value of \( H_{c2} \) available\textsuperscript{11} we see that the best agreement is obtained using the slope of \( H_{c2} \) at \( T_c \) and ignoring PSP effects (H-2). This is not unreasonable since the experimental \( H_{c2} \) value is only about half of the paramagnetic limit \( H_p \).
The interpretation of the calculations for the thin film material are complicated by the high resistivities as mentioned previously. This is illustrated by the very large $H_{c2}$ value $H-3$, which is determined using normal state parameters $(\gamma, \rho_n, T_C)$ and ignoring PSP effects. When PSP effects are included ($H-5$) a value below the experimentally determined lower limit is obtained. When $\alpha$ becomes large as in this case, $H_{c2}$ becomes insensitive to $\alpha$. The most reasonable value obtained is $H-2$ which does not involve the use of the resistivity. Value $H-4$ which does not involve the resistivity but does include PSP effects is again below the experimental lower limit. The $H_{c2}$ value calculated using the $\kappa$ value determined from the $H_{c1}$ data ($H-1$) is above the experimental lower limit, but is larger than what we would expect for this material.

One explanation for the low $H_{c2}$ values obtained when PSP effects are included is that we have ignored the competing effect of spin orbit scattering. In order to obtain a better estimate of the relative contributions of PSP and spin orbit scattering it will be necessary to obtain more complete data on the temperature dependence of $H_{c2}$ at lower temperatures.
REFERENCES

8. Private communication.
<table>
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<tr>
<th>Property</th>
<th>NbN Film</th>
<th>NbN Bulk</th>
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<tr>
<td>$T_c$ ($^\circ$K)</td>
<td>15.23</td>
<td>16</td>
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<tr>
<td>$\gamma$ (ergs/cm$^3$°K$^{-1}$)</td>
<td>$3.2 \times 10^3$</td>
<td>$3.2 \times 10^3$</td>
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<td>$\rho_n$ ($\mu$-Ω-cm)</td>
<td>250-1500</td>
<td>114</td>
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<tr>
<td>$n$ (cm$^{-3}$)</td>
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<td>$2.39 \times 10^{23}$</td>
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<td>$S/S_F$</td>
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<td>$H_c_2$ (kG)</td>
<td>&gt;250</td>
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<td>$H_c_1$ (G)</td>
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<td>93</td>
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<td>$H_0 = -\frac{dH_c_2}{dt}</td>
<td>_{t=1}$ (kG)</td>
<td>540</td>
</tr>
<tr>
<td>Parameter</td>
<td>NbN Film</td>
<td>NbN Bulk</td>
</tr>
<tr>
<td>-----------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>$\xi (\AA)$</td>
<td>1.10</td>
<td>4.8</td>
</tr>
<tr>
<td>$\xi_{GL}(0)(\AA)$</td>
<td>20.3</td>
<td>41.4</td>
</tr>
<tr>
<td>$\lambda_{GL}(0)(\AA)$</td>
<td>6020</td>
<td>2810</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>2.2</td>
<td>48.4</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>195</td>
<td>&gt; 1</td>
</tr>
<tr>
<td>$H_T (G)$</td>
<td>2086</td>
<td>2189</td>
</tr>
<tr>
<td>$H_D (G)$</td>
<td>$2.8 \times 10^5$</td>
<td>$2.94 \times 10^5$</td>
</tr>
</tbody>
</table>
TABLE III

Calculated $H_{c2}$ Values of Bulk and Thin Film NbN

<table>
<thead>
<tr>
<th></th>
<th>NbN Film</th>
<th>NbN Bulk</th>
<th>Eqn.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-1</td>
<td>574</td>
<td>220</td>
<td>6,7</td>
</tr>
<tr>
<td>H-2</td>
<td>373</td>
<td>144</td>
<td>8</td>
</tr>
<tr>
<td>H-3</td>
<td>756</td>
<td>181</td>
<td>9</td>
</tr>
<tr>
<td>H-4</td>
<td>173</td>
<td>173</td>
<td>8,10,11,12</td>
</tr>
<tr>
<td></td>
<td>=1.9</td>
<td>=0.67</td>
<td></td>
</tr>
<tr>
<td>H-5</td>
<td>190</td>
<td>136</td>
<td>9,10,11,12</td>
</tr>
<tr>
<td></td>
<td>$\alpha$=3.84</td>
<td>$\alpha$=0.88</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

Fig. 1  Magnetization as a function of applied field for bulk NbN.

Fig. 2  Magnetization as a function of applied field for an NbN thin film deposited on sapphire.

Fig. 3  Magnetization as a function of applied field for an NbN thin film deposited on stainless steel (hastelloy).

Fig. 4  Magnetization as a function of applied field for Nb$_3$Sn tape.
Curve 642138-A

$T = 4.2^\circ \text{K}$

NbN Bulk

934 Gauss Per Inch

$\mathcal{H}_C = 93$ Gauss

Fig. 1
Fig. 2

Magnetic Field - Gauss

Magnetisation (Arbitrary)

-3

-2

-1

0

1

2

NbN C-13 E3
Sapphire Substrate

HC₁ = 40 Gauss

Curve 642142-A
Fig. 3

Magnetisation (Arbitrary)

Magnetic Field kG

 NbN-B12
 Stainless Steel Substrate
 $H_C = 50$ Gauss
Fig. 4

Curve 642137-A

$\text{Nb}_3\text{Sn (Tape)}$

$T = 4.2^\circ\text{K}$

$934 \text{Gauss Per ln}$

$H_{C1} = 250 \text{Gauss}$

Magnetic Field

Magnetisation (Arbitrary)
HIGH FIELD PROPERTIES OF SPUTTERED TYPE II SUPERCONDUCTING FILMS

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ABSTRACT

Thin films of Mo-Re and Nb-Ga have been prepared by sputtering from the elements in a high purity environment. Transition temperatures up to \( \sim 16.5^\circ K \) for the Nb-Ga films and \( \sim 14^\circ K \) for the Mo-Re films have been measured. The high field properties of these films are reported.

*Work supported in part by National Aeronautics and Space Administration under Contract No. NASW-1760.
Previously reported results of measurements on sputtered NbN thin films showed that these films had much higher critical current and field characteristics than corresponding bulk material. This enhancement phenomenon has been investigated further by preparing other type II superconducting films and measuring their high field properties. Our most recent measurements in these series of experiments have been made on films of Nb-Ga and Mo-Re. These results are described in this report.

The films for this study were made by a high purity sputtering process which has been described in detail elsewhere. Briefly, the process involves sputtering onto high temperature (>500°C) substrates in an environment which, prior to sputtering, has a background impurity pressure of ~5 x 10^{-10} Torr. In the case of the Mo-Re films the sputtering target was made by welding together pieces of molybdenum and rhenium sheet into a single unit. By proper positioning of the substrates beneath this target a series of films were prepared with compositions ranging from pure molybdenum to pure rhenium. The Nb-Ga films which were prepared were made in a similar manner with the following exception: the gallium portion of the target was prepared by reacting a niobium sheet in molten gallium at 800°C for 1/2 hour. This Nb sheet, which now had an extremely gallium rich surface layer, was joined to a piece of pure niobium and this combination was used as the sputtering target for the deposition of Nb-Ga films.
Transition temperature ($T_c$) measurements on these two types of films produced the following results. Certain Mo-Re films were found to have $T_c$'s as high as $\sim 14^\circ$K. These $T_c$'s were associated with the cubic phase Mo-Re alloy which has a composition of approximately $\text{Mo}_{0.6}\text{Re}_{0.4}$. The measurements on the Nb-Ga films produced a maximum $T_c$ of about $16.5^\circ$K. This transition temperature was associated with the $\beta$-W phase in the Nb-Ga system.

The highest $T_c$ films in these two sets of experiments were taken to the Francis Bitter National Magnet Laboratory and their critical currents ($J_c$) and critical field ($H_{c2}$) characteristics measured. These measurements were done at $4.2^\circ$K. The films, which are on $0.5'' \times 0.125'' \times 0.020''$ sapphire substrates were mounted so that the direction of the field was normal to the plane of the films.

Not unexpectedly, the highest $T_c$ films were found to possess the highest critical current and field values among the samples measured. In the remainder of this discussion, therefore, we will concentrate on these samples. Considering the molybdenum-rhenium system first, the Mo-Re film with a $T_c$ of $\sim 14^\circ$K was found to have an upper critical field of $\sim 110$ kOe. This is more than four times greater than the highest $H_{c2}$ value reported for any bulk Mo-Re alloy. The current density at 80 kOe was over $10^4$ amp/cm$^2$ and rising. Since more than 3 amps could not be put through the current leads of the measuring probe, the current density at lower fields was not determined. However, values well over $10^5$ amp/cm$^2$ areprobable as extrapolated from the data presently available. The highest $T_c$ ($\sim 16.5$K) Nb-Ga films were found to have upper critical field values near 200 kOe.
at 4.2°K. This is about 40 kOe less than the value reported for bulk Nb$_3$Ga which had a $T_c$ of $\sim 20°K$. The current carrying capacity however was comparatively low, i.e., $\sim 10^2$ amp/cm$^2$ at 150 kOe and $\sim 10^3$ at 100 kOe. These low $J_c$ values in the Nb-Ga films are believed to be due to the method of preparation. By sputtering from the two piece cathode described above, films with a wide range of compositions were produced. Thus, only over a very narrow region was the high $T_c$, Nb$_{75}$Ga$_{25}$, $\beta$-W phase deposited. It is believed that sputtering from a homogeneous Nb$_3$Ga target would produce at least the same $Hc_2$ values but much higher current densities. As mentioned above the Mo-Re films had comparatively higher $J_c$ values than the Nb-Ga films despite the fact that Mo-Re films were also sputtered from a two element cathode. The difference between the two types of films which could explain these results is the fact that the high $T_c$ phase in the Nb-Ga system is a compound while in the Mo-Re system it is an alloy. In the Mo-Re system therefore the high $T_c$ would persist over a substantially wider compositional range.

Enhanced high field properties as reported here have previously been observed in sputtered films of other type II superconductors such as NbN and Nb-Al-Ge among others. This phenomenon has been attributed to a unique structure of the sputtered films in which the deposited material grows in a columnar fashion. This type of structure produces a film with high resistivity than the bulk and a corresponding higher upper critical fields. Also the intercolumnar grain boundaries are believed to be strong pinning centers accounting for the high current carrying capacities of these films.
REFERENCES

6. S. Foner, Conf. on D and F Band Superconductors, University of Rochester (October 1971).
AN A-15 STRUCTURE Mo-Re SUPERCONDUCTOR*

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ABSTRACT

An investigation of the properties of Mo-Re thin films has been undertaken. Superconducting transition temperatures of up to ~ 15°K have been observed in films which have an approximate composition of Mo$_{0.7}$Re$_{0.3}$. This increase in Tc of 2-3°K over the corresponding bulk values is attributed to the formation of a metastable A-15 phase in the sputtered films of this composition.

*Work supported in part by the National Aeronautics & Space Administration.
We have recently begun an investigation of the properties of thin films of the molybdenum-rhenium system, and we report here on some initial results, including evidence for the existence of a previously unreported superconducting A-15 phase in this system.

The Mo-Re films under study were prepared by a d.c. sputtering process similar to that described previously. For the present experiments, a sputtering target was used which was made by welding two pieces of Mo and Re together into a single unit. By proper positioning of the (polished sapphire) substrates under this target, films ranging in composition from essentially pure Mo to pure Re were prepared. These Mo-Re alloy films were deposited onto ~ 500°C substrates at a rate of approximately 500 Å/min, for a period of two hours.

Superconducting transition temperatures ($T_c$) of the deposited films were measured, and correlated with their location under the cathode. Two peaks in $T_c$ occur as one progresses from the Re rich to the Mo rich alloys, a broad peak at ~ 9°K and then a narrower one at ~ 13°K. From their position under the sputtering target, the alloy films with $T_c$'s of ~ 9°K have compositions in the vicinity of $\text{Mo}_{0.3}\text{Re}_{0.7}$, and the films with $T_c$'s of ~ 13°K, a composition of $\text{Mo}_{0.7}\text{Re}_{0.3}$. X-ray diffraction analysis of the Re rich Mo-Re alloys ($T_c$ ~ 9°K) indicated that they have a tetragonal structure similar to that found in bulk alloys of this composition. The $T_c$'s of the bulk Mo-Re alloys however are only ~ 6°K. Testardi, et al., have previously reported a ~ 9°K transition for a tetragonal structure $\text{Mo}_{32}\text{Re}_{68}$ film sputtered under conditions similar to those used in our experiments. In the same paper a significantly enhanced $T_c$ of almost 15°K was reported for films of this same composition which were sputtered
at much higher substrate temperatures. The enhanced Tc was attributed to the formation of a strain induced A-15 like structure in the high temperature films.

One of the high (~13°K) Tc films from our experiments, which had a composition of Mo.7Re.3, was also examined by x-ray diffraction, and unlike bulk Mo.7Re.3 which crystallizes into a bcc structure, the film was found to have the A-15 crystal structure. The details of the x-ray analysis leading to this conclusion are as follows: a powder x-ray diffraction pattern of a Mo.7Re.3 film flaked from a sapphire substrate, was obtained using a 114 mm Debye-Scherrer camera and Ni-filtered copper radiation. All lines of the x-ray pattern were indexed. The material was almost completely A-15 structure, with only a trace of the body centered cubic molybdenum terminal solid solution. No lines were obtained which were incompatible with the requirements of the Pm3n space group, and no line splitting at high angles was seen, though the high angle lines were somewhat diffuse. The lattice parameter of the A-15 phase, obtained by extrapolation of values from high angle lines, was 4.980 Å ± 0.001.

The degree of long range order (LRO) in the A-15 structure has important effects on Tc (3,4) and we therefore looked for evidence of LRO in these films. The determination of LRO in the Mo-Re system is possible by x-ray diffraction, since the difference in x-ray scattering power between molybdenum and rhenium is large enough to cause the appearance of diffraction lines due solely to ordering. Several of these lines (specifically 110, 220 and 310) were obtained, but due to the uncertainties of line intensity and of material composition, a quantitative estimate of the long range order parameter could not be made. The mere appearance of these lines
does denote a considerable degree of ordering, however. As mentioned, the estimate of Mo$_7$Re$_3$ for the composition of the high Tc films was made from the substrate location under the composite cathode. This estimate is corroborated by the lattice parameter of the bcc second phase present, which was found to be 3.130 Å $\pm$ .005, and which corresponds to a composition of Mo$_{70}$Re$_{30}$ $\pm$ 10 at. %.(5)

Our discovery of an A-15 phase in Mo-Re alloy films is analogous to results in other metallurgical systems wherein metastable structures have been produced by thin film growth techniques. The indicated ability to form metastable A-15 phases by thin film techniques has special significance in superconductivity since, as is well recognized, this structure, for reasons not completely understood, is particularly favorable for obtaining high transition temperatures. We are currently trying to optimize experimental conditions to determine the maximum Tc of A-15 structure Mo-Re. To date we have succeeded in raising Tc to approximately 15°K. We are also interested in determining the compositional range over which this phase can be stabilized into Mo-Re alloys. Given the apparent departure from A$_3$B stoichiometry in our present A-15 Mo-Re films, one can conjecture as to the possibility of a very wide A-15 phase field, perhaps extending over into the Re rich side of the Mo-Re system. The results of these studies will be presented in subsequent publications.

We wish to thank R.D. Blaugher and A. Taylor for helpful discussions regarding the interpretation of the x-ray data.
REFERENCES


SUPERCONDUCTIVITY IN THIN FILMS OF THE Mo-Re SYSTEM**

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ABSTRACT

A series of Mo-Re alloy films has been prepared by sputtering from a composite molybdenum and rhenium cathode. These films were deposited in an ultra-high purity environment onto sapphire substrates which were held at temperatures ranging from 400°C to 1300°C. Maximum transition temperatures observed were \( \approx \) 15°K which is significantly greater than the highest reported bulk values. Critical current and field characteristics also were found to be considerably greater in the films compared to corresponding bulk samples. Upper critical fields of over 100 kOe were measured in the highest \( T_c \) films -- more than a factor of four higher than the maximum values reported for the bulk. These enhanced properties are discussed in relation to the structural characteristics of the sputtered films.

*Supported in part by the National Aeronautics & Space Administration.

+Part of this work was done at the Francis Bitter National Magnet Laboratory, which is supported at M.I.T. by the National Science Foundation.
INTRODUCTION

In recent years we have been investigating the properties of type II superconducting thin films prepared by a high purity sputtering process. In general, these films have been found to possess high transition temperatures ($T_C > 15^\circ K$) and also very high critical current and field ($J_C - H$) characteristics. In addition to their potential usefulness in high magnetic field applications, as suggested by their enhanced high field properties, we have been investigating the possibility of using these films in Josephson type devices. Such devices fabricated in the Dayem bridge configuration would have the important advantage of being extremely stable and also of being operable at relatively high temperatures. As reported, our original efforts in this area, using NbN thin films were unsuccessful. Recently, therefore, for this specific application and also as a continuation of our general investigation of type II materials, we have been attempting to prepare other high $T_C$ superconducting films. Included among the materials investigated are thin film alloys of the Mo-Re system. In this paper we report data on the superconducting properties of these alloy films.

EXPERIMENTAL PROCEDURE

The sputtering process used to deposit the Mo-Re films for this study has been described previously. For use in the present experiments a flat sputtering target was made by joining two pieces of 0.010 in. thick
molybdenum and rhenium sheet together into a single unit. By proper positioning of the substrates (0.5" x 0.125" x 0.020" polished sapphire) under the target, films ranging in composition from essentially pure Mo to pure Re have been prepared. The deposition rate used in these experiments was \( \sim 500 \text{ Å/min.} \) and the growth times ranged from five minutes to one hour. Under the sputtering conditions used, the substrate temperature reached \( \sim 400^\circ \text{C} \) from heating by the sputtering target. Substrate temperatures above \( 400^\circ \text{C} \) were obtained with the aid of a niobium strip heater which was heated directly by the passage of up to 250 amps through it. The substrate temperature was monitored during sputtering with a Pt-Pt Rd thermocouple which was placed on the top surface of the heater immediately adjacent to the substrates. The temperatures were also checked with an optical pyrometer; however, these measurements could only be made while the sputtering target was out of the system. Upper critical field values for the sputtered films were obtained from \( J_c-H \) measurements at \( 4.2^\circ \text{K} \). In these measurements, except where noted, the films were mounted so that the field was perpendicular to the current and also to the plane of the film. In addition to these measurements which were made on the standard size films, some \( J_c-H \) data have also been obtained on a few "weak link" samples. The cross-sectional areas of these films at the weak link are of the order of \( 10^{-8} \text{ cm}^2 \). The technique used to fabricate films into this configuration are described elsewhere.\(^{(2)}\)
RESULTS

Superconducting transition temperature measurements on all of our deposited films have been made and correlated with their locations under the sputtering target. Figure 1 illustrates results from a typical experiment in which $T_c$ is plotted as a function of substrate location. As can be noted, two peaks in $T_c$ occur as one progresses from the Mo rich to the Re rich alloys, a narrow peak at $\sim 14^\circ$K and a very broad one at $\sim 9^\circ$K. It was found that for the Re rich alloys, the shape of this curve was essentially independent of variations in substrate temperature between 400°C and 1300°C and also of variations in film thicknesses between 2500 Å and 3 microns. The $T_c$'s of the films located under the Mo portion of the cathode, however, showed a dependence on both substrate temperature and also, to a lesser degree, on film thickness. For example, the films reported in Fig. 1, which were sputtered for 10 minutes, had a maximum $T_c$ of $\sim 14^\circ$K. By increasing the sputtering time to 30 min. this maximum $T_c$ was increased to $\sim 15^\circ$K. Sputtering longer than 30 minutes, however, produced no further rise in transition temperature. In Fig. 2, the top curve shows the effect of substrate temperature on the maximum $T_c$'s obtained in a series of deposition runs in which other conditions were held constant. Here we can see that there is a several degree variation in $T_c$ with substrate temperature, with a broad peak up to about $15^\circ$K. The lower two curves in Fig. 2 illustrate the upper critical fields ($H_{c2}$) and the resistivities of some of these same films, as a function of substrate temperature. As illustrated, the maximum $T_c$ films have $H_{c2}$ values of up to 120 kOe and an approximate resistivity of $\sim 150 \mu\Omega \text{cm}$.
We do not as yet have complete \( J_c-H \) curves for any of our highest \( T_c \) films. These measurements are done on "weak link" samples, to avoid heating problems associated with the high critical currents at low fields of the standard size films. Figure 3, however, illustrates \( J_c-H \) data for an 11°K film, which has been etched into the Dayem bridge "weak link" configuration. From this curve we can see that sputtered Mo-Re films can support current densities of up to \( 10^6 \) amps/cm\(^2\) at 4.2°K.

**DISCUSSION**

**Critical Current and Field Measurements**

Similar to previous results reported on other type II superconductor films, we have found a large enhancement in the critical current and field characteristics of sputtered Mo-Re alloys. As an example, the upper critical fields of \( \sim 120 \) kOe, observed in some films, is approximately five times greater than the maximum reported bulk values. Similarly, \( J_c-H \) values of the films are much higher than those measured in bulk samples. These enhanced high field properties can be only partially explained by the increased \( T_c \)'s of the films, since we have measured upper critical fields of over 80 kOe, in films with \( T_c \)'s as low as 9°K. We therefore attribute most of the increase in these properties to another factor, namely, the fine grained structure that we have observed in the sputtered films. Scanning electron microscope measurements show that the average grain size of the films vary from a few hundred angstroms in the thinnest films grown at 400°C, to about...
3μ in the thicker films which were deposited at 1000°C. This grain structure can explain the observed high resistivities in the Mo-Re films which in the case of the highest Tc films, are about an order of magnitude greater than that observed in comparable bulk material. From type II theory, these high resistivities are the cause of the enhanced upper critical fields in the sputtered films. The high current carrying capacity of sputtered Mo-Re, it can be assumed, is the result of the presence of a large number of intergranular defects which provide the required pinning centers necessary to maintain a high superconducting current.

Although, as we have seen, the Mo-Re films exhibit enhanced high field characteristics compared to the bulk alloys, they do not approach the very high values observed in sputtered NbN films having similar Tc's. We have attributed the very high Jc-H and Hc2 properties of the NbN films to the presence of a columnar-like grain structure in these films. This structure resulted from an apparent absence of lateral grain growth during the deposition process. Electron microscope studies indicated that, apparently due to this type of grain growth, a several angstrom separation exists among the NbN grains. These voids are believed to contain only non-conducting gaseous atoms. Because of this type of structure NbN films, which are thicker than the diameter of the columns, exhibit a large anisotropy in Jc-H values when measured with the plane of the film perpendicular and then parallel to the direction of the field. Figure 4 shows similar measurements on a 1.5μ thick Mo-Re film. In this case, there appears to be only a very slight
anisotropy. Other Jc-H data of this type on Mo-Re films with various thickness produced similar results. These data thus indicate that the columnar type structure observed in sputtered NbN is not present in the Mo-Re films.

**Tc Measurements**

Our data show that sputtered Mo-Re films have an enhanced Tc of 2-3°C compared to bulk material. The maximum Tc of ~12°C, in the bulk system, occurs at the composition Mo0.6Re0.4. From their location under the sputtering target, Mo-Re films which have Tc's up to 15°C also have approximately the same composition. However, x-ray data show that, unlike the bulk material, which has a bcc structure, the sputtered alloys crystallize in the A-15 structure. As is well known, this crystal structure is particularly favorable for obtaining high transition temperatures and thus it seems probable that the enhanced Tc values of the Mo-Re films are associated with the formation of a metastable A-15 phase in the film samples. In the case of the Re rich films, we have not observed any enhancement such as was reported for a Mo32Re68 film by Testardi, et al. However, efforts to reproduce this enhancement effect are being continued. These results together with a more complete report on our study of the relationship of Tc with structure in Mo-Re films will be presented at a later time.
REFERENCES

Fig. 1 — $T_C$'s of Mo–Re films as a function their location beneath a two-piece molybdenum and rhenium cathode. The dividing line between the Mo and Re is at the 1" mark.
Fig. 2 - Resistivity, $T_C$, and $H_{C2}$ (4.2°) values of Mo–Re films as a function of substrate temperature.
Fig. 3 – $J_c$ vs $H$ curve for a Mo – Re weak link sample with a cross-sectional area of $1.5 \times 10^{-8}$ cm$^2$. 

$T_c = 11^\circ$K 

$J_c = 1$ H 

$T = 4.2^\circ$K
Fig. 4 - $J_c$ vs $H$ curves for a Mo-Re film measured with the field parallel and perpendicular to the plane of the film. Cross-sectional dimensions of the film are 0.125"x5μ.
THE PREPARATION OF THIN FILMS OF B-1 STRUCTURE SUPERCONDUCTING TERNARY COMPOUNDS**

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ABSTRACT

NbN, a binary B-1 structure superconducting compound, has been successfully prepared in thin film form by a high purity sputtering process. In this paper, we report on the deposition of ternary compounds, based on NbN, using a similar technique. The inclusion of a third element, such as carbon, titanium, or zirconium into the NbN structure was accomplished by sputtering in an argon-nitrogen atmosphere from a two-element target. These targets were made either by hot pressing a powder mixture of the elements into a proper form or by welding together two metal sheets into a single unit. Superconducting transition temperatures of \( \lesssim 17^\circ K \) have been obtained in both Nb-C-N and Nb-TiN thin films by depositing these films at very high temperatures. However, critical current and field data measured at 4.2\( ^\circ K \) showed that the use of very high substrate temperatures also caused a deleterious effect on these properties.

*Supported in part by National Aeronautics & Space Administration under Contract NASW-1760.
+Part of this work was done at the Francis Bitter National Magnet Laboratory which is supported at M.I.T. by the National Science Foundation.
INTRODUCTION

We have previously reported on the preparation of superconducting niobium nitride (NbN) thin films, by a high purity sputtering process.\(^1\) The NbN films deposited by this process were found to have maximum transition temperatures \((T_C)\) of over 15 K and critical current \((J_C)\) and field \((H_{c2})\) properties greatly superior to the maximum reported bulk values.\(^2\) From experiments with bulk samples, it is known that the addition of a third element, such as carbon or titanium, into the NbN structure results in compounds which have transition temperatures of between 17 and 18 K, placing these materials among the highest \(T_C\) superconductors presently known.\(^3\) Our early efforts to prepare this type of ternary compound in thin film form resulted in films which had maximum \(T_C\)'s of only \(\sim 15.5\) K.\(^4\) More recently, however, through modifications in our sputtering process we have succeeded in obtaining Nb-C-N films which remain superconducting to over 17 K.\(^5\) In addition to these Nb-C-N experiments, we have recently deposited films of Nb-Ti-N and Nb-Zr-N. In this paper we report all of our present data on the deposition and the superconducting properties of these three NbN based ternary compounds.

EXPERIMENTAL PROCEDURE

The films discussed in this paper were deposited using the same basic sputtering process which was developed for the preparation of NbN films.\(^1\) Briefly, in this process the background impurity level,
prior to sputtering is reduced to \( < 5 \times 10^{-10} \) Torr, and the films are then reactively sputtered onto heated substrates. In our original experiments the maximum obtainable substrate temperature was approximately 500°C. For the present study, the deposition apparatus was modified by incorporating into the system a new substrate heater capable of producing substrate temperatures up to 1200°C and higher. The substrate temperatures were monitored during the sputtering process with a Pt-Pt Rd thermocouple which was located on the top of the holder immediately adjacent to the substrates. To permit the use of very high substrate temperatures, our original glass and metal sputtering chamber was changed to one of all metal construction.

Two different types of sputtering targets were employed in these experiments. Those used for the deposition of Nb-C-N were prepared by hot pressing (at \( \approx 1000°C \)) three different niobium and carbon powder mixtures into the desired form. The atomic ratios of niobium to carbon in these targets were 5/1, 3.33/1, and 3.5/1. The targets used to sputter Nb-Zr-N and the Nb-Ti-N films were made by welding together sheets of Nb and Zr and sheets of Nb and Ti into single units. By properly positioning the substrates beneath these targets, films with progressively changing Nb/Zr and Nb/Ti ratios were deposited. In all cases the target-substrate separation was kept small, in the range between 0.25" and 1". The thickness of the deposited films were approximately 5-6 \( \mu \) m, after typical deposition times of 1 hour, giving a deposition rate of the order of 500 Å/min. The substrates used for all of the deposition experiments were 0.5" x 0.125" x 0.025" polished sapphire.
Superconducting transition temperatures were measured using silicon thermometry or, when possible, the vapor pressure of hydrogen. \( T_c \) is defined here as the temperature at which the films begin to lose their normal state resistance. Critical current and field measurements were made at 4.2°K in magnetic fields up to 210 kOe. In these measurements, the samples were mounted so that the current, direction of the field, and film plane were mutually orthogonal. Finally, the structural properties of the sputtered films were determined using electron microscope and x-ray techniques.

RESULTS AND DISCUSSION

In publishing our initial results on the sputtering of Nb-C-N films, we reported that films with a nominal composition of Nb C.3N.7 were deposited which had transition temperatures up to 17.3°K. A significant parameter in these experiments was found to be the substrate temperature, which had to be raised to \( \sim 700°C \) and above to produce the maximum \( T_c \)'s. The target-substrate separation in these experiments was 1/4". Our latest Nb-C-N experiments in which the target-substrate separation was changed to 1" have also produced films with \( T_c \)'s in the vicinity of 17°K. However, in this case the optimum \( T_c \)'s were obtained only after the substrates were heated to over 1000°C. We believe that these two sets of results can be explained by the fact that in our initial Nb-C-N experiments, the substrates were heated primarily by the sputtering target, due to their close (1/4") proximity to the target. Thus, although the nominal temperature as indicated by the thermocouple located on the substrate holder was only \( \sim 700°C \), we now believe that the temperature at the substrate surface was
actually much higher. In our most recent experiments wherein a larger (1") target-substrate spacing was employed, the very high substrate temperatures were obtained primarily with the aid of an auxiliary heater. In this case, it is believed that the thermocouple temperature more closely approximated the actual substrate surface temperature. Therefore, it is our present conclusion that with our present sputtering process, temperatures higher than 700°C are in fact necessary to obtain optimum $T_c$'s in the Nb-C-N films.

Although the use of very high substrate temperatures raised the $T_c$'s of Nb-C-N films, a deleterious effect was found with respect to their high field properties. For example, Nb-C-N films deposited at $\sim 500°C$, possess extrapolated upper critical field values, at 4.2°K, of well over 300 kOe, while films deposited at $\sim 1000°C$ have measured values of slightly less than 200 kOe. Correspondingly lower critical currents are also observed in the latter films. We attribute this large difference in high field properties between these two types of films to differences in their structures. Figure 1 shows electron microscope photographs of the surfaces of two films deposited at $\sim 1000°C$ and at $\sim 500°C$. As can be seen the grain size of the higher temperature film is significantly larger. We have previously attributed the very high critical current and field properties of NbN films sputtered onto 500°C substrates, to the presence of a very small grain size and also to the presence of a columnar-like structure in these films. The widths of the grains or "columns" were found to be of the order of 100 Å. This type of structure resulted from an absence of lateral grain growth in the films during the deposition process. Electron microscope studies on some of these films indicated that, apparently due to this type
of grain growth, a several angstrom separation exists between grains. These voids which are about 5-10 Å wide are believed to contain only nonconducting, gaseous atoms and thus are the apparent source of the very high resistivities and correspondingly the very high critical current and field values which have been measured in these films. The high resistivities and the high critical current and field properties of Nb-C-N films deposited at ~ 500°C indicate this same type of void structure is present in these films. In the case of the higher substrate temperature Nb-C-N films, however, the lower critical current and field values are consistent with our most recent electron microscope results which show a grain size approximately two orders of magnitude larger than that found in the ~ 500°C films and which also show no indication of the presence of any type of void structure.

As mentioned above, a composite niobium and titanium sputtering target was used for the deposition of Nb-Ti-N films. Prior to depositing films of Nb-Ti-N, a number of experiments were performed in which Nb-Ti alloys were sputtered, by using pure argon as the sputtering gas. Because of the type of target employed, these experiments produced a series of Nb-Ti alloy films with a wide variety of compositions, ranging from essentially pure Nb to pure Ti, depending upon the location of the substrates beneath the sputtering target. Following the completion of this set of experiments, Nb-Ti-N films were deposited by the addition of nitrogen to the sputtering gas. Transition temperature measurements were made on all of the films from both sets of experiments, and these $T_C$ values have been plotted as a function of substrate location. The results are shown in Fig. 2. In the case of both the Nb-Ti and the Nb-Ti-N films there is a maximum in $T_C$ which occurs over a very broad
compositional range. Similar to the niobium carbonitride results, the Nb-Ti-N films had $T_C$'s of up to $\sim 17^\circ K$. This is the highest reported $T_C$ for thin films of this ternary compound. Also as in the case of the Nb-C-N films the optimum $T_C$'s in these experiments were obtained through the use of very high ($\geq 1000^\circ C$) substrate temperatures. Employing otherwise optimum sputtering conditions, the maximum $T_C$'s of films deposited on $\sim 500^\circ C$ substrates were found to be no higher than $15.5^\circ K$. Raising the substrate temperature produced a very gradual rise in $T_C$ until at $1100^\circ C$ transition temperatures of $\sim 17^\circ K$ were obtained. Substrate temperatures above $1100^\circ C$ produced no further increase in transition temperature. Because of the very slow variation in transition temperature with Nb/Ti ratio in the Nb-Ti-N films (as seen in Fig. 2), the transition widths ($\Delta T_C$) were found to be very narrow. For example, in a typical film, the onset of superconductivity occurs at $17.0^\circ K$, and at $16.8^\circ K$ the film resistance is zero.

We have obtained critical current versus field ($J_{c}-H$) data at $4.2^\circ K$ on several Nb-Ti-N films sputtered at various temperatures, including three films which were deposited at temperatures of $\sim 500^\circ C$, $\sim 750^\circ C$ and $1150^\circ C$. Based on their identical locations beneath the sputtering target, these films all have approximately the same composition. Measurements of the Nb-Ti-N film deposited at $\sim 500^\circ C$ ($T_C \sim 15^\circ K$) produced results the same as obtained previously for films grown at this temperature. Namely, we have reported extrapolated $H_{c2}$ values at $4.2^\circ K$ of well over 210 kOe for this type of sample. However, measurements on a Nb-Ti-N film sputtered on a $\sim 750^\circ C$ substrate ($T_C \sim 16^\circ K$) indicated a maximum $H_{c2}$ value of less than 200 kOe, and data on a film deposited at $\sim 1150^\circ C$ ($T_C \sim 17^\circ K$) showed an upper critical field value of $A22 - 6 -$.
only ~ 130 kOe. These high field results thus parallel similar data on Nb-C-N films which showed that increasing substrate temperatures produces a rise in $T_C$ while at the same time reducing the upper critical field. We believe the explanation for these data are the same in each case, i.e., the higher growth temperatures which are necessary to achieve the maximum $T_C$'s, cause a change in microstructure in the films as was discussed earlier in this section.

Finally we have also prepared films of Nb-Zr-N by reactive sputtering. Other than the use of a Nb-Zr component sputtering target, these deposition experiments were performed using the same procedures as those used to sputter the Nb-Ti and Nb-Ti-N films. The pertinent data from these Nb-Zr experiments are shown in Fig. 3. The Nb-Zr films show a broad maximum in $T_C$ peaking at about 11.5°K, when plotted versus substrate location. However, in the case of the Nb-Zr-N films, no maximum occurs; instead $T_C$'s are seen to decrease linearly from ~ 15.5°K to ~ 9°K. These results are very similar to bulk Nb-Zr-N data, in that in both cases, the inclusion of zirconium into the NbN structure produces no enhancement in transition temperature.

$J_C$-$H$ data have also been obtained from some Nb-Zr-N films. Not unexpectedly, $H_{C2}$ values for the Nb-Zr-N films become smaller as the amount of zirconium in the films is increased. Maximum values of about 200 kOe were measured in Nb-Zr-N compounds which had only small amount of Zr. These films had $T_C$'s between 14 and 15.5°K. As the Nb-Zr ratio decreased, however, the upper critical field values went down sharply until in the samples which were essentially Zr-N ($T_C$ ~ 9°K) $H_{C2}$ was measured to be only about 20 kOe.
SUMMARY

We have for the first time sputtered NbN based Nb-C-N and Nb-Ti-N ternary compound films with $T_c$'s similar to the maximum values reported for the corresponding bulk samples, i.e., $\gtrsim 17^\circ$K. To obtain these optimum $T_c$'s it has been found necessary to use very high substrate temperatures (of the order of 1000°C or higher). The use of these high substrate temperatures, however, has also been shown to produce films which have critical currents and fields much lower than the values obtained in films sputtered at lower temperatures. This effect on high field properties is attributed to differences in microstructure between the two types of films.
REFERENCES

FIGURE CAPTIONS

Fig. 1  Electron microscope photographs illustrating the surfaces of Nb-C-N films grown at ~ 1000°C (a) and ~ 500°C (b). The T_c's of the two films are 17.3 K and 14.8 K respectively.

Fig. 2  Transition temperatures of Nb-Ti and Nb-Ti-N films as a function of their location beneath a composite Nb and Ti sputtering target. The dividing line between the Nb and Ti is at the 1" mark.

Fig. 3  Transition temperatures of Nb-Zr and Nb-Zr-N as a function of their location beneath a composite Nb and Zr sputtering target. The dividing line between the Nb and Zr is at the 1" mark.
Fig. 1 - Electron microscope photographs illustrating the surfaces of Nb-C-N films grown at ~1000°C (a) and ~500°C (b). The $T_c's$ of the two films are 17.3°K and 14.8°K respectively.
Fig. 2—Transition temperatures of Nb-Ti and Nb-Ti-N films as a function of their location beneath a composite Nb and Ti sputtering target. The dividing line between the Nb and Ti is at the 1" mark.
Fig. 3—Transition temperatures of Nb-Zr and Nb-Zr-N films as a function of their location beneath a composite Nb and Zr sputtering target. The dividing line between Nb and Zr is at the 1" mark.
SUPERCONDUCTIVITY AND METASTABILITY IN
ALLOYS OF THE Mo-Re SYSTEM*

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ABSTRACT

Using a high purity sputtering process, alloys of the Mo-Re system, ranging in composition from essentially pure Mo to pure Re, have been prepared. Superconducting transition temperature (Tc) and x-ray measurements are reported for these alloys. Included among these data is evidence for the existence of metastable A-15 phases which are not observed in Mo-Re alloys prepared by standard bulk techniques. The maximum Tc found thus far for Mo-Re films is \( \sim 15^\circ K \).

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Introduction

A thesis which is presently gaining wide currency is the belief that all high temperature superconductors are inherently structurally unstable.\(^1\) If one accepts this theory, it is apparent that the achievement of higher transition temperatures must be dependent upon the preparation of new metastable superconductors. Recently, we have been investigating the properties of thin film alloys of the Mo-Re system and have found that metastable Mo-Re phases, not observed in bulk samples, can be obtained in these alloys. In this paper, we report on these new structures and also on their effect on the maximum superconducting transition temperatures obtainable in the Mo-Re system.

Experimental Procedure

The sputtering process used to deposit the Mo-Re films for this study has been described previously.\(^2,3\) Briefly, in this process, the

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films are deposited onto heated substrates in a high purity environment. Prior to sputtering, the total pressure is typically $5 \times 10^{-10}$ Torr or less. The sputtering target for these experiments was made by welding sheets of molybdenum and rhenium together into a single unit. The substrates used were either single crystal sapphire or pressed and sintered alumina. In each case, the dimensions of the substrates are $0.5" \times 0.125" \times 0.025"$. By properly positioning these substrates beneath the sputtering target films ranging in composition from essentially pure Mo to Re have been prepared. The Mo-Re alloy films reported in this paper were deposited at two different sputtering rates of approximately 500 Å/min and 1000 Å/min. The deposition temperatures, which were measured by placing a thermocouple immediately adjacent to the substrates, ranged from 400°C to 1300°C. Film thicknesses are of the order of 5 microns. The structures of the films were identified by x-ray diffraction analysis. Transition temperatures were obtained by a standard resistive technique using silicon thermometry or, when possible, the vapor pressure of liquid hydrogen.

Results and Discussion

For our investigation of the Mo-Re alloy system we have sputtered a large number of thin film samples which have a wide range of compositions and also a wide range of structural and superconducting properties. This was accomplished through the use of the composite molybdenum-rhenium sputtering target and by varying some of the more important parameters of the sputtering process. To illustrate the diverse properties obtainable in the sputtered films prepared under different experimental conditions we will discuss here results from two separate series of deposition
experiments. These results will then be compared to similar data reported for the bulk alloys. In the first of these two series of deposition experiments the sputtering rate was held constant at approximately 500 Å/min and films were deposited at various substrate temperatures. Maximum $T_C$ values among films produced under these conditions were found in films sputtered onto substrates held at $\sim$ 1000°K. In the second series of experiments, which were sputtered over a similar range of substrate temperatures but at a deposition rate of $\sim$ 1000 Å/min, the Mo-Re films which exhibited the maximum transition temperatures were among those sputtered onto $\sim$ 1200°C substrates. In curves A and B of Fig. 1 we have summarized the transition temperature data from these two deposition experiments by plotting the $T_C$'s of the films versus their locations beneath the sputtering target. In curve C on this same figure, we also show the transition temperature of bulk samples as a function of their compositions. This latter curve was drawn from data reported by Blaugher, et al. (4) As can be noted the shape and locations of these three curves have distinct similarities particularly in the extreme Mo and Re rich regions of the curves. Because of this fact, we feel that estimates of film composition based on substrate location are, at the least, approximately accurate. Although there are similarities among these curves, there are also obviously areas of wide divergence, particularly at the compositions $\text{Mo}_{65}\text{Re}_{35}$ and $\text{Mo}_{40}\text{Re}_{60}$. In Fig. 2, $T_C$ curves are shown of three Mo rich alloys which all have the approximate composition $\text{Mo}_{65}\text{Re}_{35}$ but which have significantly different transition temperatures. The bulk sample, which has $T_C$ of $\sim$ 12.3 K (Curve A) was reported to have the
αMo (bcc) crystal structure. (4) We have analyzed the two film samples shown here (Curves B and C) and have found that these Mo-Re alloy have the (B-W) A-15 structure with only trace amounts of the bcc αMo structure present. (5) The lattice parameter of this A-15 phase is 4.980 Å ± 0.001. It is of course well known that the A-15 structure is particularly favorable for obtaining high transition temperatures, therefore, we can assume that the higher $T_c$'s of the thin films, compared to the bulk samples are associated with the presence of this metastable A-15 structure in the thin film alloys. With respect to the difference in $T_c$'s between the two thin film alloys, there is an indication of a correlation between transition temperatures and the degree of long range ordering which we have observed in these two samples. At present, however, we do not have sufficient x-ray data on these and similar alloy films to reach a definitive conclusion on the effects of ordering.

Although there are, as we have just shown, significant variations in structural and superconducting properties among Mo rich alloys, we have found an even greater diversity among compositionally similar Re rich alloys. Figure 3 shows $T_c$ curves for five Re rich alloys which all have the approximate composition Mo$_{40}$Re$_{60}$ but which have transition temperatures ranging from ~ 6 K to ~ 14.5 K. X-ray analysis of the bulk sample (Curve A) indicated a tetragonal $\sigma$ phase structure. (4) We have also observed a tetragonal structure in some of the thin film samples, however, in each case where the $\sigma$ phase appears we have also observed the presence of a second phase. Specifically, the ~ 9 K film (Curve B) also shows the (αMn) A-12 structure and the ~ 14.5 K film (Curve E), also exhibits the
A-15 structure. The presence of these second phases are most probably the source of the enhanced $T_c$'s in these films compared to the bulk sample. These data indicating a second A-15 phase in the Mo-Re system are somewhat similar to data reported by Testardi, et al. These authors, however, suggested that their "A-15 like" structure resulted from a high temperature deformation of the tetragonal $\sigma$ phase to a point where the lattice parameter ratio $c/a$ became equal to 0.5. With this degree of deformation the tetragonal structure would essentially become an A-15 structure. Our results do not support this interpretation. We have found two distinct phases in our thin film sample, namely an A-15 structure which has a lattice parameter of $4.967 \pm 0.002$, and a tetragonal structure, with lattice parameters, $a = 9.598 \pm 0.010$ and $c = 4.980 \pm 0.005$. The $c/a$ ratio in this case is 0.5189 which is only slightly different from the values 0.5192 and 0.5193 reported for bulk samples with the compositions $Re_{55}Mo_{45}$ and $Re_{68}Mo_{32}$.

As also previously reported by Testardi, et al., we have found that the formation of the high $T_c$ ($> 14$ K) Re rich phase apparently occurs over an extremely narrow temperature range. We have in fact experienced much difficulty in preparing the particular sample which has the transition temperature shown in Curve E in Fig. 3. Most of our films even though deposited under nominally the same conditions had transition temperatures similar to that of Curve D. X-ray analysis of a film which has this type of double slope transition curve indicated the presence of two phases. In this case, however, the predominant phase was found to have the $(\alpha\text{Mn}) A-12$ structure. The second phase has not been identified because of the faintness of the diffraction lines on the x-ray pattern. Based
on the high $T_c$ of this film, however, we suspect that it will in fact have an A-15 structure.

**Summary and Conclusions**

We have demonstrated that metastable Mo-Re alloys can be prepared, by high purity sputtering, which are not found in materials produced by bulk techniques. Two of these alloys, namely a Mo-rich A-15 phase and a Re-rich A-15 phase have been found to remain superconducting to $\sim 15$ K. This ability to induce the formation of high $T_c$ metastable structures in the Mo-Re system suggests that the sputtering of films of other metallurgical systems may be a fruitful means for preparing new higher $T_c$ superconductors.
REFERENCES


FIGURE CAPTIONS

Fig. 1 Curve $A - T_C$ versus substrate location for Mo-Re films sputtered at $\sim 500$ Å/min onto 1000°C substrates. Curve $B - T_C$ versus location for films sputtered at $\sim 1000$ Å/min onto 1200°C substrates. Curve $C - T_C$ versus composition for bulk Mo-Re samples (curve drawn from data of Blaugher, et al.\(^{(4)}\)).

Fig. 2 $T_C$'s of Mo-Re alloy samples all of the approximate composition $\text{Mo}_{55}\text{Re}_{35}$. A-bulk sample;\(^{(4)}\) B-thin film sputtered at $\sim 1000$ Å/min on a 1200°C substrate; C-thin film sputtered at $\sim 500$ Å/min on a 1000°C substrate.

Fig. 3 $T_C$'s of Mo-Re alloy samples all of the approximate composition $\text{Mo}_{40}\text{Re}_{60}$. A-bulk sample;\(^{(4)}\) B,C,D,E-thin films sputtered at $\sim 1000$ Å/min onto 600°C, 750°C, 1150°C and 1200°C substrates respectively.
Fig. 1—Curve A - $T_C$ vs substrate location for Mo-Re films sputtered at ~500 A/min onto 1000°C substrates. Curve B - $T_C$ vs location for films sputtered at ~1000 A/min onto 1200°C substrates. Curve C - $T_C$ vs composition for bulk Mo-Re samples (curve drawn from data of Blaugher et al).
Fig. 2—$T_c$'s of Mo-Re alloy samples all of the approximate composition, Mo$_{65}$Re$_{35}$. A - bulk sample (from data of Blaugher et al); B - thin film sputtered at ~1000Å/min on a 1200°C substrate; C - thin film sputtered at ~500Å/min on a 1000°C substrate.
Fig. 3—$T_c$'s of Mo-Re alloy samples, all of the approximate composition, Mo$_{40}$Re$_{60}$. A—bulk sample (from Blaugher et al); B, C, D, E—thin films sputtered at $\sim$1000A/min onto 600°C, 750°C, 1100°C and 1200°C substrates respectively.