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THE SUPERCONDUCTIVITY OF CERTAIN
TERNARY MOLYBDENUM COMPOUNDS

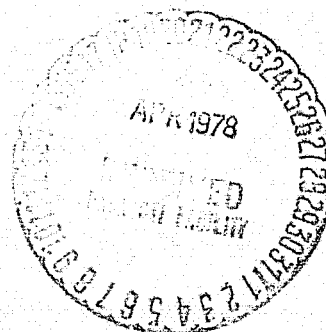
R. Odermatt

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16. Abstract This document is a thesis research project which studied three compounds: $(\text{Cu}_{1.5}\text{Mo}_{4.5}) (\text{SmMo}_5\text{S}_6) (\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6)$. The objectives of the work was to measure the superconductivity and critical fields of these compounds in order to reproduce the published results and by introduction of magnetic impurities into these superconductors observe the compensation effect proposed by Jaccarino and Peter. Six chapters, 18 figures, 3 tables, 87 pages.		
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TABLE OF CONTENTS

1. INTRODUCTION	1
2. $M_x Mo_{6-x} S_6$ SAMPLES	2
a) Structure	2
b) Obtaining the phases	5
c) Preparation for measurements	7
d) Critical-temperature measurement	9
3. STUDY OF THREE $M_x Mo_{6-x} S_6$ COMPOUNDS (M = Cu, Sn, Pb)	13
a) Critical temperatures	13
b) Critical-field measurement	23
c) Experimental critical fields	25
d) Critical fields: some theoretical aspects	32
e) Comparison of experimental results with theory	35
4. INVESTIGATION OF OTHER SUPERCONDUCTING SUBSTANCES	39
a) $Mo_3 S_4$ and its derivatives	39
b) Substances furnished by the Rennes laboratory	42
c) Critical temperatures and transitions in superconductive compounds	44
d) Summary	50
e) Critical fields of four of the superconducting compounds	50
5. THE $A_x Sn_{1-x} Mo_5 S_6$ COMPOUNDS (A = Cr, Mn, Fe, Co, Ni, Gd)	54
a) Compensation effect	54
b) Choice and preparation of compounds	55
c) Critical temperatures	56
d) Experimental critical fields	59
e) Theory and experimental critical fields: "non'magnetic" impurities	61
f) Critical fields of compounds containing magnetic impurities: theoretical survey	65

g) Theory and experimental critical fields: magnetic impurities	68
6. STRUCTURE AND SUPERCONDUCTING PROPERTIES	74
a) Critical temperature and structure	74
b) Role of interstitial elements	77
c) Pressure and structure	83
d) Critical field and structure	83
7. CONCLUSIONS	85
REFERENCES	86

LIST OF FIGURES AND TABLES

Figure	
1.a. Structure of Mo_3Se_4 , after [6]	4
1 b. Structure of $\text{Ni}_{0.33}\text{Mo}_3\text{Se}_4$, after [6]	4
2. Structure of PbMo_6S_8 , after [7]	5
3. Shape of the transition for various treatments	8
4.a. Schematic of induction bridge	10
4 b. Calibration of bridge	10
5. Shape of transition depending on bridge calibration	11
6. T_c as a function of x for $\text{M}_x\text{Mo}_{6-x}\text{S}_6$ ($M = \text{Cu}, \text{Sn}, \text{Pb}$)	16
7. T_c as a function of the number of operations in forming the phase	18
8. T_c as a function of annealing time for small pellets	20
9. H_{c2} as a function of T for 5 sulfides	27
10. Initial slopes of $H_{c2}(T)$ for 6 sulfides	28
11. Superconducting transitions in 5 selenides	46
12. T_c as a function of x for $\text{S}_x\text{Mo}_3\text{Se}_{4-x}$ and $\text{Cu}_x\text{Mo}_3\text{Se}_4$	48
13. H_{c2} as a function of T for 4 of the superconducting selenides	50
14. T_c as a function of x for $\text{A}_x\text{Sn}_{1-x}\text{Mo}_5\text{S}_6$ ($A = \text{Cr}, \text{Mn}, \text{Fe}, \text{Ni}, \text{Gd}$)	57

Figure

15.	H_{c2} as a function of T for "non-magnetic" impurities	60
16.	H_{c2} as a function of T for magnetic impurities	62
17.	H_{c2} as a function of T for $Mn_{0.06}Sn_{0.94}Mo_5S_6$	69
18.	H_{c2} as a function of T for $Fe_{0.03}Sn_{0.97}Mo_5S_6$	71

Tables

1.	FORMULAS AND CRITICAL TEMPERATURES OF THE 3 SULFIDES STUDIED, AFTER VARIOUS AUTHORS	14
2.	T_c AS A FUNCTION OF ANNEALING FOR SMALL PELLETS	22
3.	HEAT TREATMENT, CRITICAL TEMPERATURE T_c , AND CRITICAL FIELD AT $T = 0$ FOR 5 SULFIDES	26

1. INTRODUCTION

Publication of the paper of Matthias et al. [1] showing the existence of superconductors among the Chevrel phases [2] suggested to Professor Fischer the idea of giving me a research problem on these materials as the subject of my thesis.

/1*

At the outset there were two principal objects:

- preparation of the substances in order to reproduce the published results and to measure their critical fields,
- introduction of magnetic impurities into these superconductors to observe the compensation effect proposed by Jaccarine and Peter [3].

We chose to study three compounds: $\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$, SnMo_5S_6 , $\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$ because of their high critical temperatures. This will make up Chapter 3.

In Chapter 2, we shall discuss the preparation of the samples, which involved many difficulties and provided some information about the behavior of these substances.

* Numbers in the margin indicate pagination in the original foreign text.

The presence of Messieurs Chevrel and Sergent, from Rennes, at Geneva for the "IV International Conference on Solid Compounds of Transition Elements" allowed an exchange of ideas and results which upset the intended research plan somewhat. Mo_3S_4 , which was unknown until Sergent's communication [4], can be made! In addition, the Rennes group furnished us a number of the compounds which had been tested for their superconducting properties. We shall look at this in Chapter 4.

In chapter 5 we shall discuss the question of adding magnetic impurities to these materials.

Finally, the relationships between structure and superconducting properties will be considered in Chapter 6.

2. $M_x Mo_{6-x} S_6$ SAMPLES

a) Structure

/2

The majority of the ternary sulfides and selenides of molybdenum crystallize in the hexagonal-rhombohedral system with an occasional triclinic deformation [2, 4, 8]. The exceptions to this rule, which have triclinic lattices, are outside the scope of this work. The structure of these compounds can be described by the same general scheme (references 4 to 8). Selenium plays the same role as sulfur.

Sulfur atoms are placed at the corners of a deformed cube whose faces are occupied by molybdenum atoms, which thus form a deformed octahedral Mo_6 "cluster". This forms the Mo_6S_8 sub-units. These sub-units are then stacked together, leaving voids between them which form channels centered on $(x,y) = (0,0), (0,1/2), (1/2,0)$ (Figure 1a). This is the structure of Mo_3S_4 .

The M element lies in the channels (Figures 1b and 2). In the sulfides, indirect S-S bonds between the sub-units are created through the M atoms in addition to the direct S-S bonds [8, 9], while the Mo-Mo bonds between the sub-units are weak. In the selenides, however, it is the indirect Mo-Mo bonds which are created. They are added to the already-existing direct Mo-Mo bonds, which are quite strong.

If the M element has a large radius (lead, tin), there is one per Mo_6S_8 sub-unit for the so-called ideal stoichiometry (MMo_6S_8). The substance has a well-defined composition. M occupies a definite site in the channel centered on $(x, y) = (0, 0)$ (Figures 1a and 2). If the M element has a small radius, a solid solution results

(copper). This can be explained [7] either by the fact that there is more than one M atom per sub-unit, as for $\text{Ni}_{0.33}\text{Mo}_3\text{Se}_4$ [6] (Figure 1b), or by saying that M occupies molybdenum sites. M will also have the possibility of lying in the channels centered on $(x, y) = (0, 1/2)$ or $(1/2, 0)$ [9].

The deviations from ideal stoichiometry which can be observed for large-radius M atoms have two possible explanations:

- according to Marezio et al. [7], the sites reserved for M and sulfur would be only partially occupied. The Rennes group does not seem to agree with this explanation [9];

- it can also be thought [9], as do Bars et al. [5] for the non-stoichiometry of Mo_3Se_4 , that if they are in excess the molybdenum atoms themselves also go into the channels.

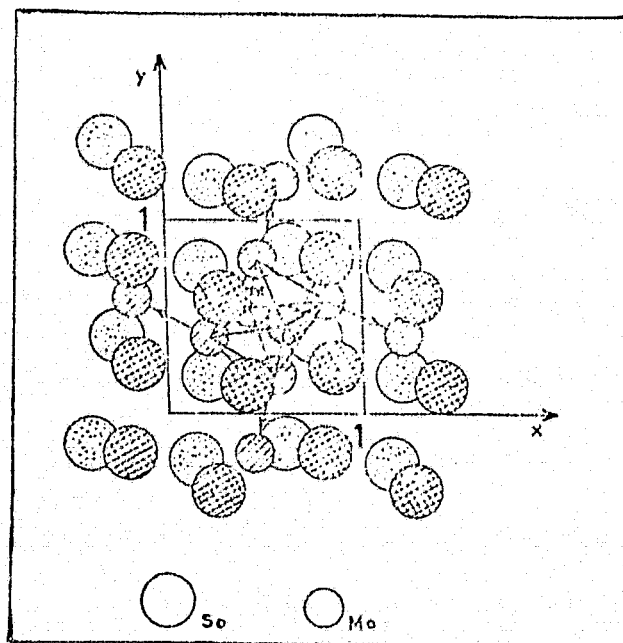


Figure 1a

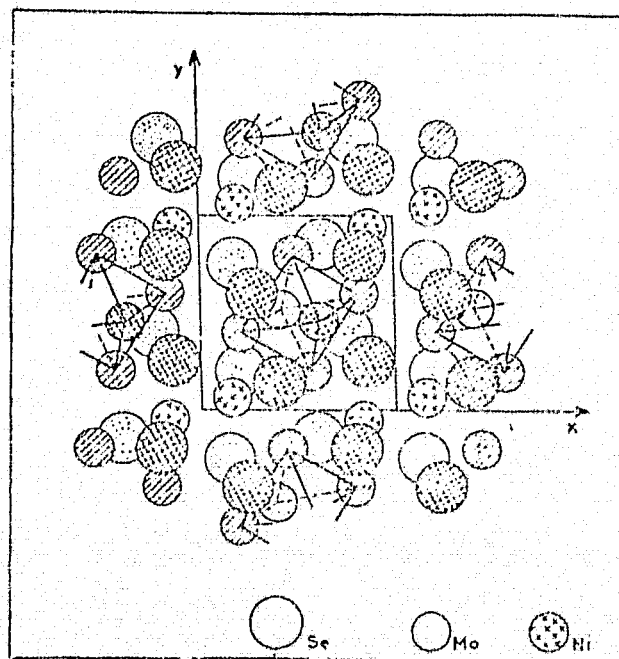


Figure 1b

Figure 1. Structure of Mo_3Se_4 after Bars et al. [6]

It was impossible to use thicker quartz (4-mm wall) because the heat needed to seal the tubes was large enough to initiate the reaction. However, experience has shown that normal tubes do not explode, even if one does not take the precaution of going to the final temperature by stages. The sulfur reacts quite quickly, so that the internal pressure does not become too high.

Where possible, the component elements were powders; otherwise, they were in small lumps. Their purities were better than 3 N (99.9%). The pellets weighed 2 to 3 grams and were pressed at 4 to 5 metric tons/cm² into cylinders 10 mm in diameter by 5 to 10 mm long (large pellets).

Although the samples did not look very homogeneous after the first passage through the furnace, x-ray analysis gave essentially the values reported by Chevrel et al. [2]. Some very low intensity lines did indicate the presence of a small amount of one or more other phases. These samples were milled, pressed (at 1 to 2 tons/cm²) and /7 again heated at the same temperature for one day. After milling again, a gray-black powder was obtained, which looked homogeneous and was sprinkled with tiny crystals. X-ray analysis gave essentially the same results as after the first passage through the furnace.

Previously-formed lead and tin compounds were heated in a resistance furnace to 1300° C under one and one-half atmospheres of argon. No sign of melting was observed. At about 1000° C, the powder seemed to settle in the crucible. On rapid heating, a gas was seen to escape from the sample at about 1200° C. This gas formed a deposit on the cold parts of the furnace. If the temperature was increased less rapidly and held at about 1100° C, the same phenomenon took place after a few hours.

During cooling, no anomaly indicating a phase transition was observed in the time-temperature curve.

The measuring apparatus was designed for cylindrical samples 3.6 mm in diameter by 5 to 8 mm long (small pellets). When we tried to press the powders into such pellets, we were surprised to learn that for a pressure above 2 or 3 tons/cm² it was impossible to form a cylinder. The sample separated into layers of widely varying thickness, which ranged from less than 1 to several millimeters.

Measurements of critical temperature were made with the aid of the induction bridge described in the following paragraph. The samples treated as we have just seen showed an abnormally wide transition (more than 6° K). We thought at first that it was due to inhomogeneity of the substance, that is, to the presence of several superconducting phases with different critical temperatures. The materials were milled, pressed, and annealed to homogenize them. The transitions remained just as wide, however.

To facilitate manipulations, we also tried different ways to agglomerate the powders to give them the proper form: mixing with Araldite, compacting the powder with a thin coating of Araldite.

Comparison of the transitions in the pressed samples (transition width greater than 6° K) with those in the annealed powders bonded with Araldite (transition width of the order of 2° K) shows that the greater width is not an effect of inhomogeneity, but is rather an effect of the pressure applied to the powders in pelletizing them.

For lower pressures, of the order of 1 ton/cm², the cylinders remained relatively compact. The preceding results gave us the idea of annealing such samples, in the hope of eliminating pressure effects. In that way, we obtained correct transitions whose widths were not greater than a tenth of a degree. The shapes of these various transitions are given in Figure 3.

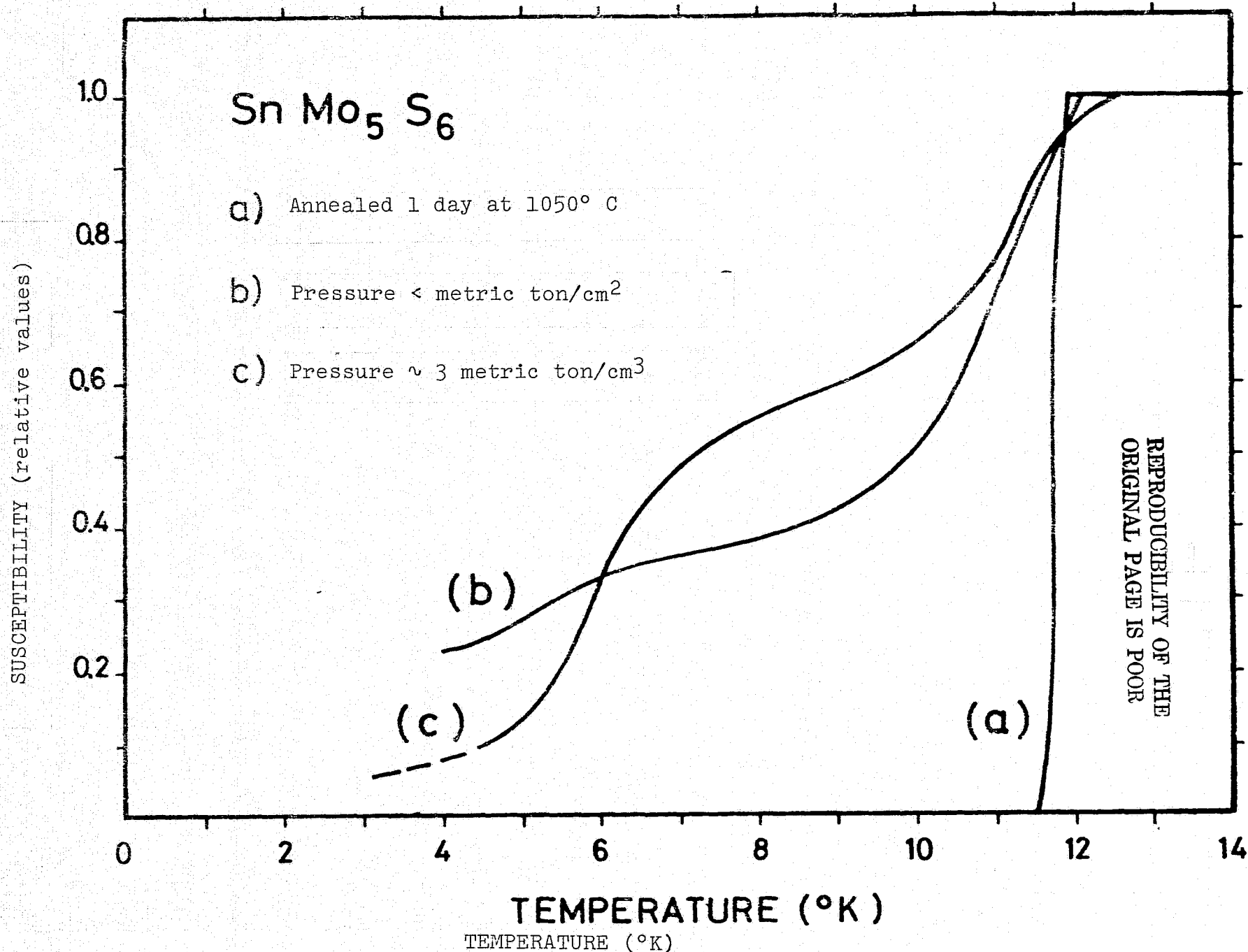


Figure 3. Shape of the transition for various treatments

It will be seen that the beginning of the transition in the pressed (unannealed) samples and in the bonded powders lies at a higher temperature than in the annealed samples.

The exact action of the pressure on these compounds is not very clear. It is probable that it is the structural properties of the substances which are modified. We shall return to this point in Chapter 6.

d) Critical-temperature measurement

/12

Here we are going to define what we mean by "induction bridge" and the way in which we used it. The bridge is built of two oscillator circuits, each containing a variable capacitor, a variable resistor, and a coil (Figure 4a) [13]. The sample to be measured is inserted into one of the coils. The principle of the measurement is based on the difference in the susceptibilities of the material in the normal and superconducting states. This is the inductive transition. This difference affects the self-inductance of the coil containing the sample. All that is needed is to balance the bridge ($e = 0$) both when the sample is in the normal state and when it is in the superconducting state. Passage from one state to the other unbalances the bridge and causes a voltage $e \neq 0$ to appear. The sensitivity depends on the way in which the bridge is balanced. The highest sensitivity is obtained when the bridge is adjusted to give a position of the resonance curves as shown in Figure 4b.

In practice, the bridge is balanced at 4.2° K with a test sample (Mo_3Re) for which the critical temperature is above 4.2° K (9.95° K). If the sample to be measured is entirely superconducting at 4.2° K , the same results are obtained whether the bridge is balanced with the test sample or with the sample to be measured. On the other hand, if it is not entirely superconducting, the behavior of the transitions and the value of the critical temperature depend on the way in which the bridge has been balanced. The difference is shown qualitatively in Figure 5. We call this type of transition a partial

$$e_i = E_i \cos(\omega t + \psi_i)$$

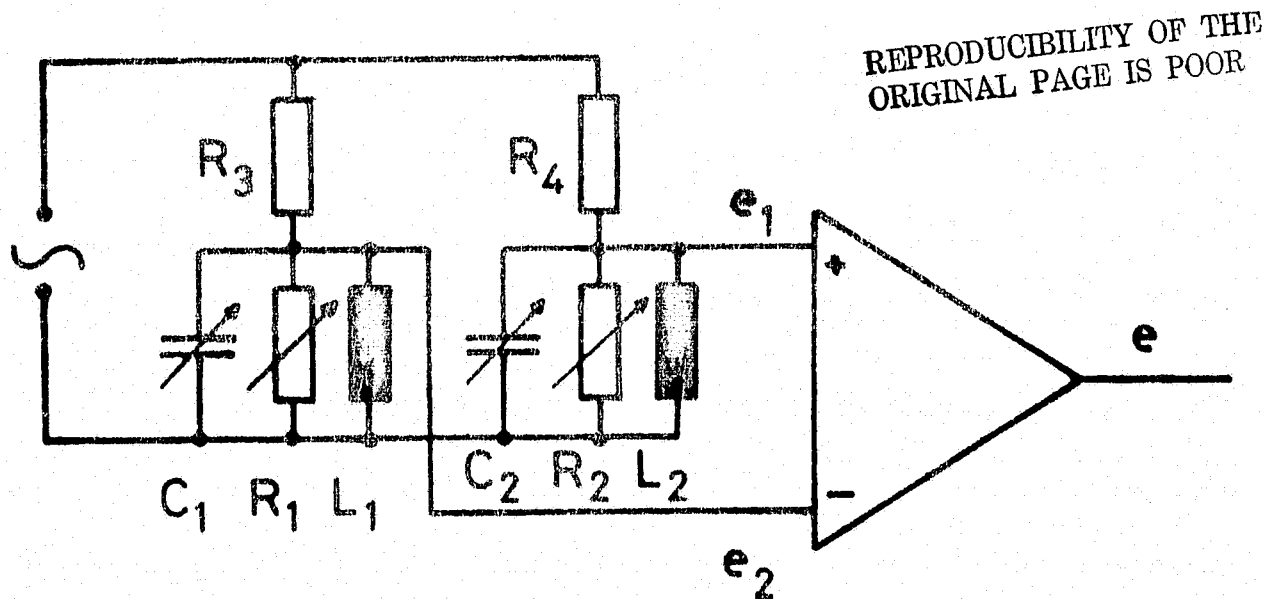


Figure 4a

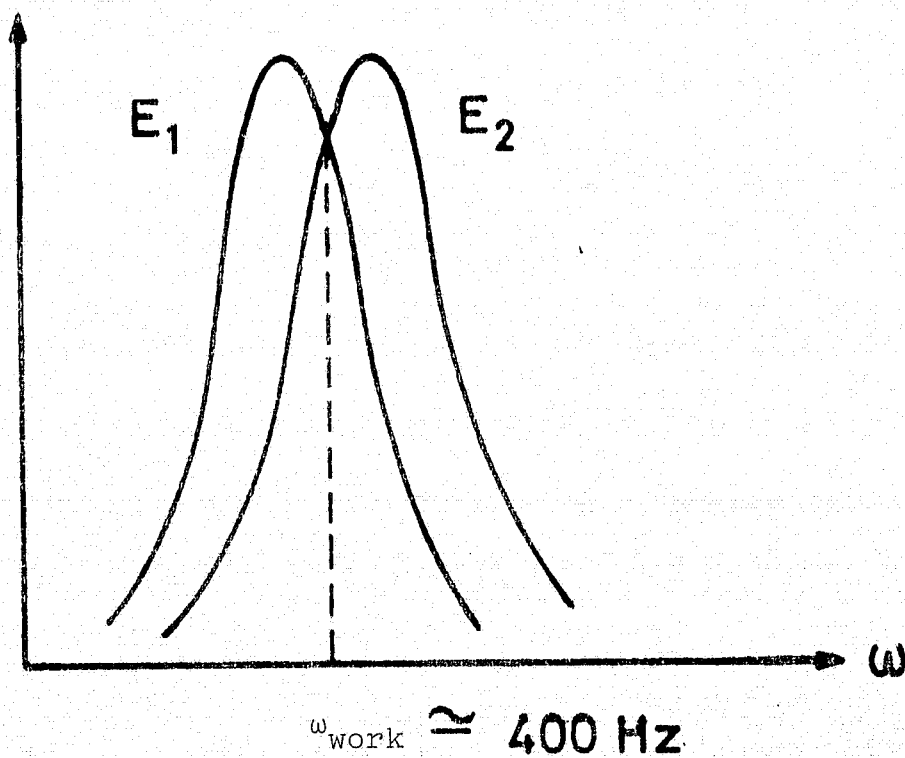


Figure 4b

Figure 4. a. Schematic of induction bridge;
b. calibration of bridge

Bridge balanced with:
 1) Mo_3Re
 2) the sample itself

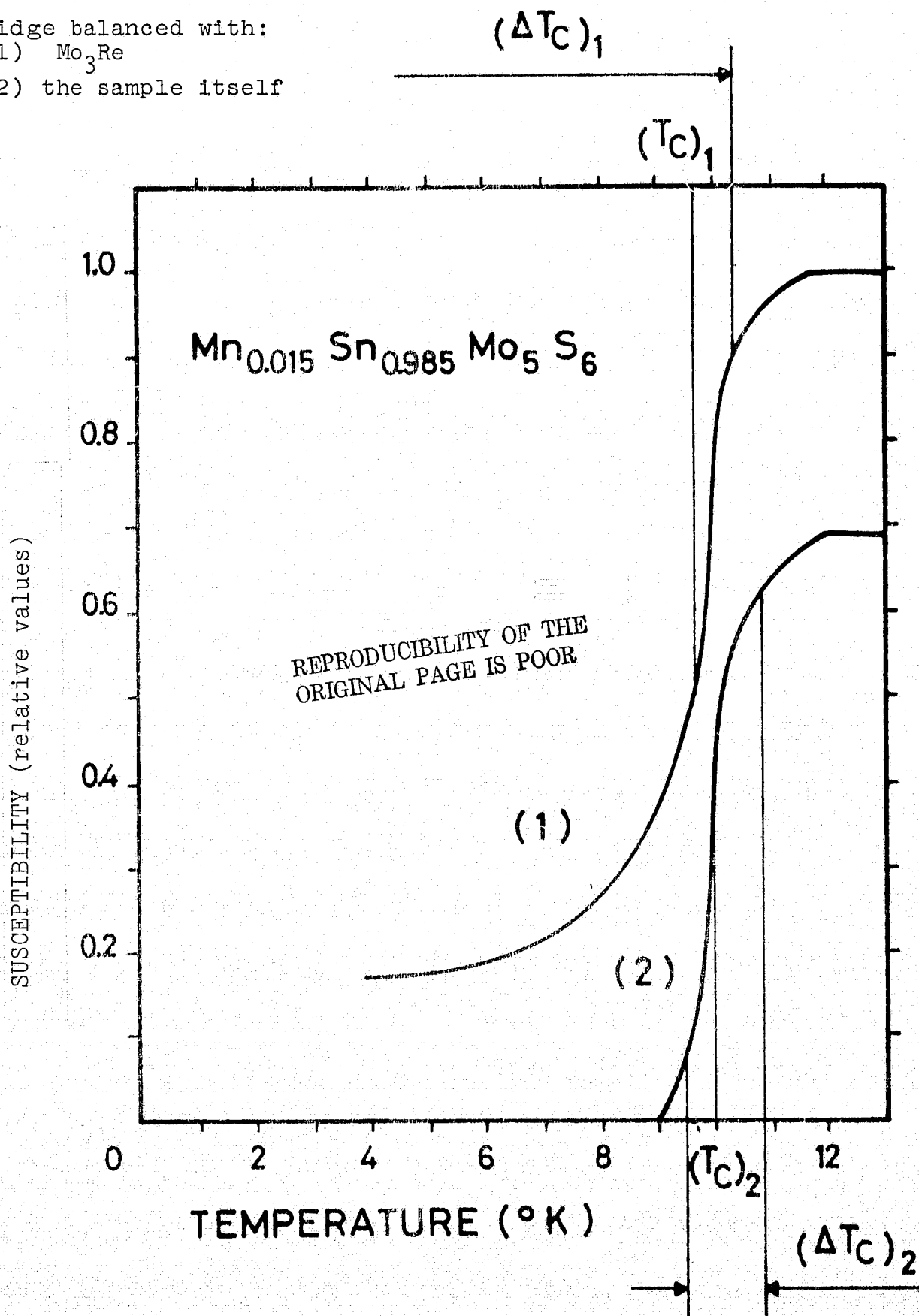


Figure 5. Shape of transition depending on bridge calibration

one. The transitions were always measured with a bridge balanced at 4.2° K with a completely superconducting sample.

The critical temperature T_c was determined from the half-height of the transition. The transition width ΔT_c was taken between 10% and 90% points of the total height (Figure 5).

/14

The precision of the temperature measurement was always better than $\pm 0.05^{\circ}$ K.

The chemical formulas which we have used are based on the general expression $M_x\text{Mo}_{6-x}\text{S}_6$ [1]. For lead and tin, the exact formulas are $\text{Pb}_{0.92}\text{Mo}_6\text{S}_{7.5}$ [7] and $\text{Sn}_{0.6}\text{Mo}_{3.17}\text{S}_4$ [9], respectively. For copper there is a double existence range given by $\text{Cu}_y\text{Mo}_n\text{S}_{n+1}$, with $1 < y < 2$ and $n = 3$ and 4 [2].

Table 1 lists the formulas used in various papers, together with the corresponding critical temperatures. The formulas assumed to be exact are underlined. The disagreement between the Rennes group and Marezio et al. is reflected in the formulas they use. An important point, however, is that for both groups the existence range of the lead and tin compounds is narrow.

a) Critical temperatures

Figure 6 gives the results of measurements made to determine the effect of the concentration x of element M .

For $M = \text{Pb}$, the critical temperature does not depend on x , which agrees with the extreme narrowness of the existence range of the phase [7].

For tin, a slight dependence is observed, about 1.5°K . This indicates a wider existence range than for lead.

For $M = \text{Cu}$, we are outside the existence ranges for the two extreme concentrations ($x = 1$ and $x = 2$). By changing our formula $\text{Cu}_x\text{Mo}_{6-x}\text{S}_6$ ($x = 1$ and 2) into $\text{Cu}_y\text{Mo}_n\text{S}_{n+1}$ with $n = 3$ and $n = 4$ in succession, we see that in each case there is the possibility for two extreme phases to form:

TABLE 1. FORMULAS AND CRITICAL TEMPERATURES OF THE THREE SULFIDES STUDIED, AFTER VARIOUS AUTHORS

R. Chevrel et al.(2)(9)	B.T. Matthias et al.(1)	R.Viswanathan A.C.Lawson(11)
$M Mo_n S_{n+1}$	$M_x Mo_{6-x} S_6$	
$Cu_y Mo_n S_{n+1}$ $1 \leq y \leq 2; n = 3, 4$ $Cu Mo_3 S_4$	$Cu_{1.5} Mo_{4.5} S_6$ $T_C = 10.9 - 10.8$	
$Sn Mo_5 S_6$ $Sn_{0.6} Mo_{3.17} S_4$ (9)	$Sn Mo_5 S_6$ $T_C = 11.3 - 10.9$	$Sn Mo_5 S_6$ $T_C = 10.9$
$Pb Mo_6 S_7$	$Pb_{0.9} Mo_{5.1} S_6$ $T_C = 13.2 - 12.5$	$Pb Mo_6 S_7$ $T_C = 11.1$

(Table continued on following page)

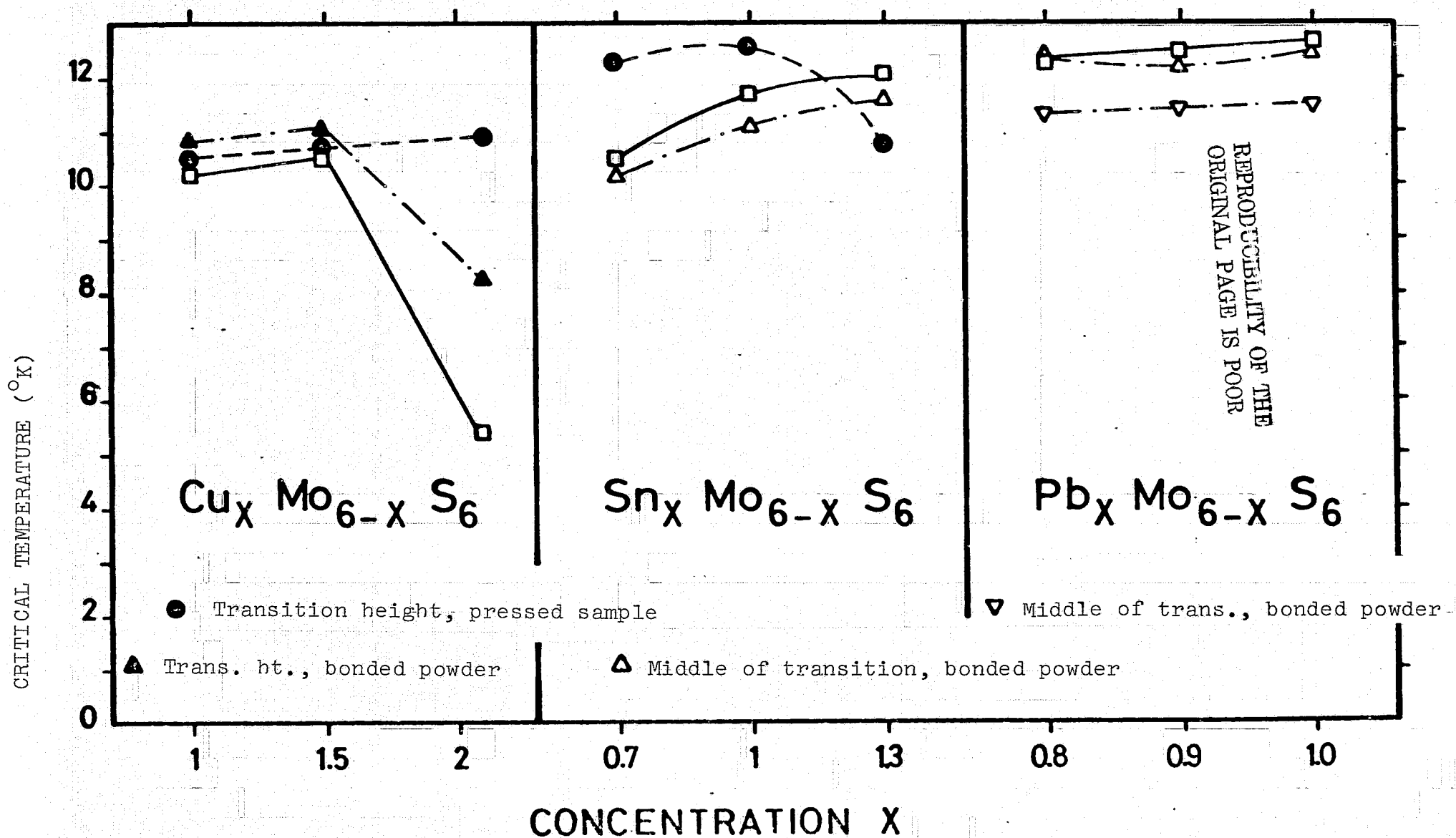
TABLE 1. (continued)

A.C. Lawson (12)	M. Marezio et al. (7)
	$M_X Mo_3 S_4$
$Cu Mo_4 S_5$ $T_C = 10.5$	$T_C = 10.9$
$Sn Mo_5 S_6$ $T_C = 11.1$	$T_C = 14.2$
	$Pb_{0.92} Mo_6 S_{7.5}$ $T_C = 15.2$ $Pb_{0.5} Mo_3 S_4$ $T_C = 14.1 - 14.5$

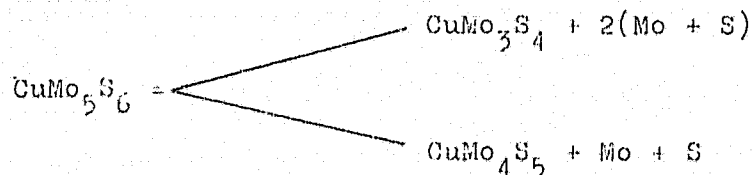
Figure 6. T_c as a function of x for $M_x Mo_{6-x} S_6$ ($M = Cu, Sn, Pb$)

□ Middle of transition. Annealed small pellets: 1 day at $1050^\circ C$ + 1/2 day at $800^\circ C$ for Cu

1 day at $1050^\circ C$ + 2 days at $800^\circ C$ for Sn and Pb

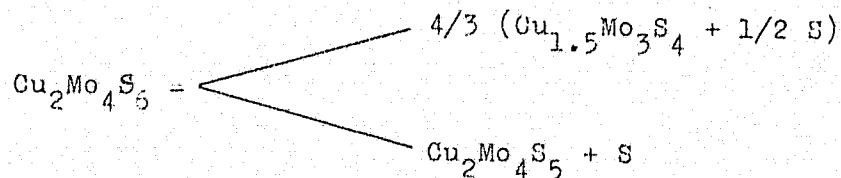


For $x = 1$:



... temperature is slightly lower than that of $\text{Cu}_{1.5}\text{Mo}_4\text{S}_5 \xrightarrow{3/2} (\text{CuMo}_3\text{S}_4)$. This can be due to the real formation of CuMo_4S_5 , which would have a critical temperature slightly lower than that of CuMo_3S_4 , or to appearance of a small amount of non-superconducting phase due to the surplus of Mo and S.

For $x = 2$:



the critical temperature is lower than that of CuMo_3S_4 by a few degrees. But we see that the copper concentration is higher than we had for $x = 1$. This result is similar to that of Fischer et al. [10], which showed that adding too much Nb, Cu, or V in SnMo_5S_6 lowers the critical temperature.

The beginning of the transition in high-concentration pressed copper and tin compounds behaves contrary to that of the T_c (Figure 6). It is possible that this result is due to the fact that it is difficult to estimate the beginning of the transition in these samples (Figure 3), when the middle of the transition does not have any very accurate meaning in this case.

To obtain pure phases, it was sometimes necessary to repeat the preparative operations (milling, pressing, heating 1 day at 1050°C) [2]. Figure 7 gives the change in critical temperature with the number of these operations. /20

Figure 7. T_c as a function of the number of operations in forming the phase

81

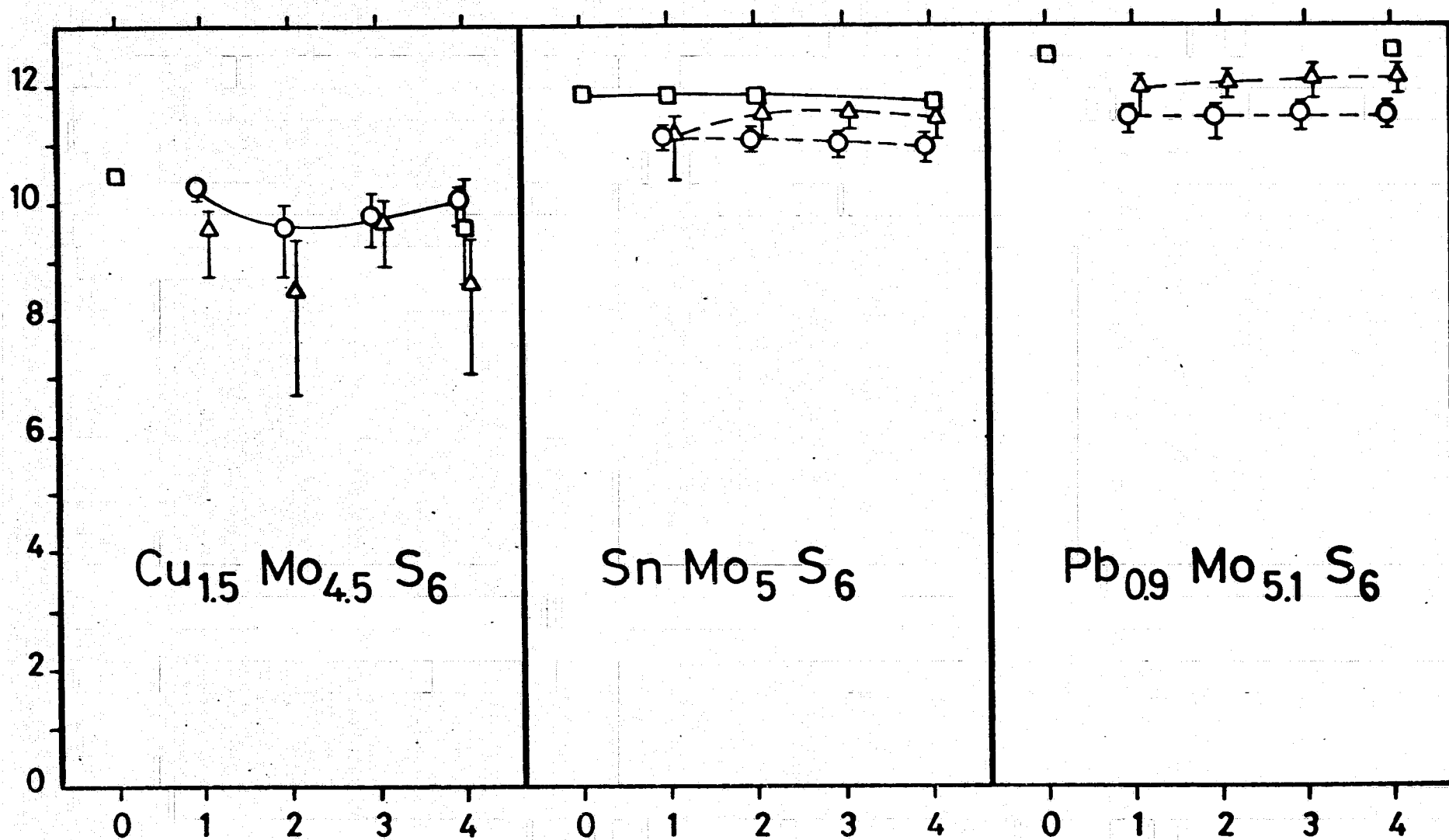
Annealed small pellets: 1 day at 1050° C + 1/2 day at 800° C for Cu

+ 2 days at 800° C for Sn and Pb

○ 1 day at 1050° C

△ 6 days at 800° C

CRITICAL TEMPERATURE (°K)



Number of operations (grinding + pressing + annealing for 1 day at 1050° C)

In this figure and the following one, the sign $\text{---}\bigcirc\text{---}$ means:

|: 10% and 90% of the transition;

O: middle of transition;

————: width of transition.

With $M = \text{Pb}$ and Sn , it is clear that there is no change in the critical temperature or transition width. Reacting the constituents once for one day at 1050°C is enough. For Cu , neither the critical temperature nor the transition width is improved. The observed fluctuations must certainly come from the fact that the copper concentration is poorly controlled during the operation, and this concentration can vary over a wide range, unlike that for lead or tin.

The effect of heat treatment after pressing can also be seen (annealing of small pellets). This effect is given in Figure 8 and Table 2.

Again, the lead and tin compounds have similar behaviors, different from that of the copper compound. For the first two, annealing at 450° raises the beginning of the transition, at 800°C increases the critical temperature, at 1050°C reduces the transition width. The highest critical temperatures accompanied by the narrowest transitions were obtained by annealing 1 to 2 days at 1050°C , followed by 1 to 2 days at 800°C . The copper compound shows a lowering of T_c and a widening of the transition on annealing at 800°C and at 450°C . What seemed best for it was either a rather long (4-day) anneal at 1050°C or a 1-day anneal at 1050°C followed by a short time (1/2 day) at 800°C .

/22

One of the parameters whose effect was not studied systematically is the cooling rate of a small pellet after annealing. It cannot be said that this parameter has a negligible effect on the superconducting properties.

The highest observed values of the beginning of the transition for $\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$, SnMo_5S_6 , $\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$ are, respectively:

Figure 8. T_c as a function of annealing time for small pellets

▲ 2 days at 1040° C + 2 days at 800° C

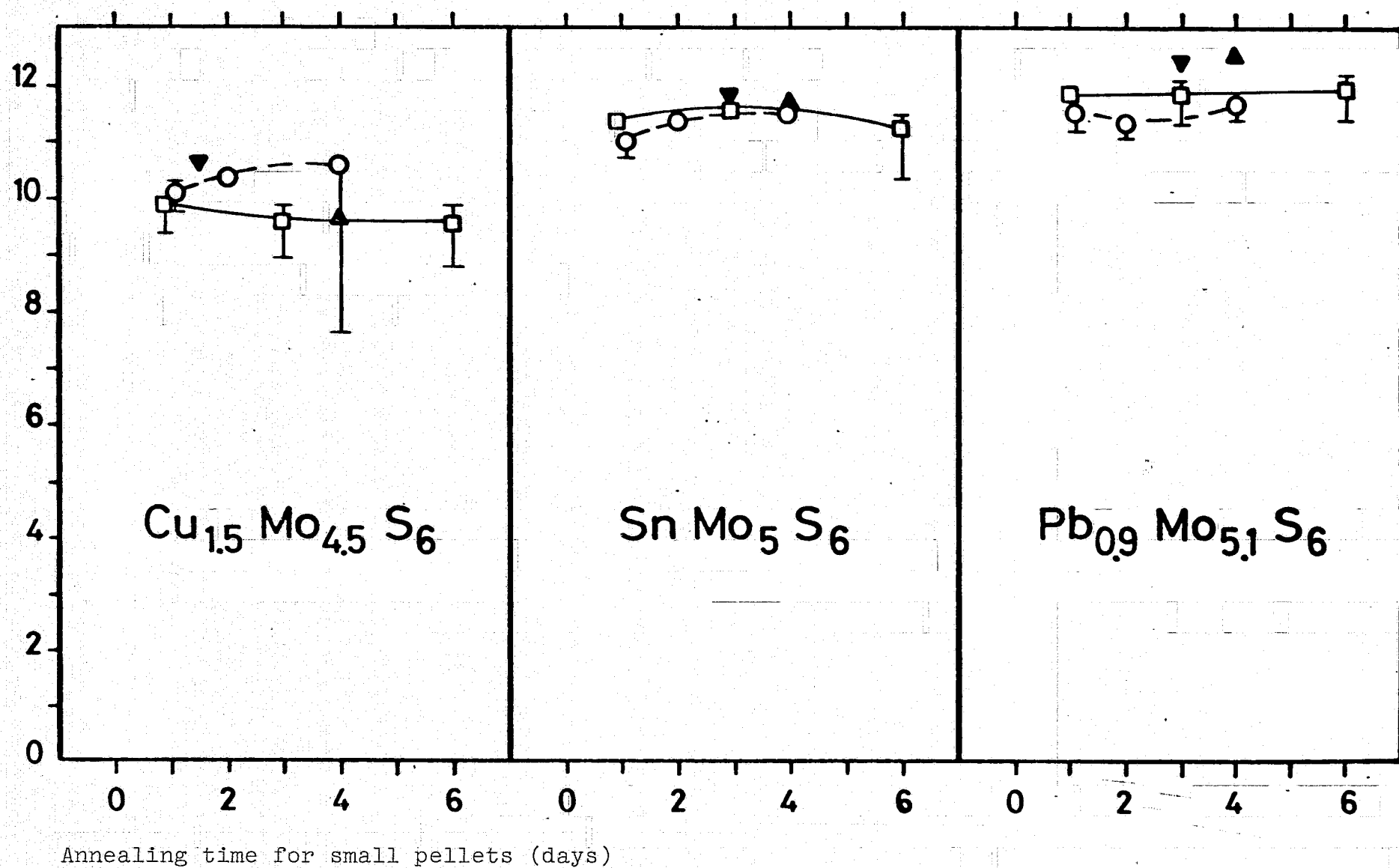
▼ 1 day at 1050° C +

○ Temperature 1050° C

2 days at 800° C for Sn and Pb

□ Temperature 800° C

1/2 day at 800° C for Cu



- for pressed samples:

10.8 , 12.7 , 13.4 °K

- for bonded samples:

10.9 , 13.6 , 14.0 °K

The best transitions measured (high T_c , low width) are:

	<u>T_c (°K)</u>	<u>ΔT_c (°K)</u>
$Cu_{1.5}Mo_{4.5}S_6$	10.5	0.1
$SnMo_5S_6$	11.8	0.1
$Pb_{0.9}Mo_{5.1}S_6$	12.6	0.2

The publications cited in Table 1 give no definition of the critical temperature, no description of the method of measuring this temperature, and no discussion of the exact thermal treatment of the samples which were measured. Under these conditions, comparison with the results we have obtained is difficult. Aside from this, it can be said that the agreement is good except for the highest published values [7] for the lead and tin compounds. Even considering the beginning of the transitions, these values were never reached in our samples.

/24

An appropriate heat treatment might perhaps lead to an increase in the critical temperature, or at least in the beginning of the transition. In view of the results of this section, it seems difficult to do that without widening the transition, however.

It is possible that the method of synthesizing the compounds has an influence. Instead of starting with the elements M, Mo, and S, one can start with the MS sulfide and the elements Mo and S [2]. It is the compounds prepared this way which seem to show the highest T_c values [7]. It may be that this method of synthesis leads to phases slightly different from those we have obtained.

TABLE 2. T_C AS A FUNCTION OF ANNEALING FOR SMALL PELLETS

Annealing of
small pellets
in chrono-
logical
order

	$\text{Cu}_{1.5} \text{Mo}_{4.5} \text{S}_6$			$\text{Sn Mo}_5 \text{S}_6$			$\text{Pb}_{0.9} \text{Mo}_{5.1} \text{S}_6$		
	(°K)			(°K)			(°K)		
	T_d	T_C	ΔT_C	T_d	T_C	ΔT_C	T_d	T_C	ΔT_C
1 day at 1050°C	10.6	10.3	0.4	11.6	11.2	0.4	11.9	11.5	0.5
1 day at 1050°C 2 days at 800°C	10.6	9.6	2.8	12.0	11.7	0.1	12.7	12.5	0.2
1 day at 1050°C 2 days at 800°C 4 days at 450°C	10.6	9.0	4.1	12.0	11.8	0.1	12.8	12.7	0.2
2 days at 800°C 4 days at 450°C	10.6	~ 4.2	> 6	12.6	11.9	0.2	12.8	12.1	> 8
4 days at 450°C	10.6	~ 4.2	> 6	12.5	11.1	4.6	13.0	7.2	> 8

T_d = temperature of beginning of transition

We note again that adding a fourth element into SnMo_5S_6 pushes the critical temperature toward values similar to or higher than [10] the highest published value for this compound [7].

b) Critical-field measurement

/25

At a given temperature, the upper critical field H_{c2} is generally determined [14] from a curve of magnetization as a function of field. The magnetization of the substances being studied is so low that it does not allow this determination. For the copper compound, however, a good estimate is possible — at least at low temperatures.

Below 50 kGauss the static field was furnished by a superconducting coil. The critical field was determined at a fixed field strength by measuring either the susceptibility or the resistivity as a function of temperature, or at a fixed temperature by measuring the resistivity as a function of field.

At temperatures below 4.2°K , the field was given by a pulsed-field technique [14]. We determined the critical field at a fixed temperature by measuring the resistivity as a function of field.

During resistivity measurements, the current in the sample was along the field axis.

Below 4.2°K (pulsed field), one of the methods generally used to obtain these contacts is that of clamping the sample between four plates in a semicircle. Unfortunately, this method was not applicable to the materials being studied here. The pellets are so fragile that the pressure of the plates necessary for obtaining good contact and the pressure produced by the thermal stresses was sufficient to reduce them to powder. The problem was finally solved by holding the leads against the sample mechanically, then providing electrical conductivity by silver point. In this way, we could make four-point resistivity measurements. The current leads were placed on the two end faces of the cylinders; those for voltage measurement — opposite each other, on the side.

/26

Above 4.2° K (static field), the existing sample holder required contacts to be soldered to the samples because the current leads are at the same time sample supports. An ultrasonic welder allowed us to make a zinc-tin alloy stick on the (planar) end faces of the cylinders. This was not possible by simply heating with a soldering iron. Since soldering could not be done on the (rounded) side of the cylinders, two-point measurements were made. The solder held on the sample, but the sample broke just beyond it.

Another difficulty was that of successfully obtaining samples long enough (more than 5 mm) that resistivity measurements were possible. A number of samples broke into two or three shorter cylinders during heat treatment or during manipulation. In general, the samples are very brittle, and it was rare that all measurements (critical temperature, static and pulsed critical field, resistivity, and susceptibility) could be made on the same specimen. Thermal cycling from room temperature to 4.2° K and back to room temperature was sometimes enough to fracture the sample.

At zero field, the devices described allowed the critical temperature to be measured by resistivity. When T_c was higher than 4.2° K, the second device had to be used (two-point measurements) because it had a double wall which allowed heating. Both devices (for four-point and for two-point measurements) could be used to measure T_c values below 4.2° K.

The high critical fields of SnMo_5S_6 and $\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$ required fabrication of fast coils giving maximum fields of 300 kGauss, then of 350 kGauss. These coils had rise times, defined as the time needed to establish the maximum field starting from zero field, of 36 msec and 21 msec, respectively.

With a static field, the precision of the temperature measurement was better than $\pm 0.05^{\circ}$ K. With a pulsed field, it was better than $\pm 0.01^{\circ}$ K. Precision of the magnetic field measurement was ± 0.2 kGauss for the static field; for the pulsed field it was ± 1 kGauss below 100 kGauss, and ± 2.5 kGauss above that value.

Results

Figure 9 gives values of $H_{c2}(T)$ for the samples whose properties are given in Table 3.

Figure 10 shows the initial slope of the $H_{c2}(T)$ curves for the same samples and for SnMo_5S_6 (b) (number 6). The latter sample had the same thermal treatment as sample 1; its inductive critical temperature was 10.9° K .

In Table 3 are listed the critical temperature and the transition width for the inductive measurements. For samples 1, 4, and 5 $H_{c2}(T=0)$ is an extrapolation of the measurements, while for samples 2 and 3 it is the value of $H_{c2}^*(T=0)$ (see below).

In the figures, the solid points indicate the middle of the resistive transitions, while the empty points indicate magnetization measurements below 4.2° K (pulsed field) or the middle of inductive transitions below 50 kGauss (static field).

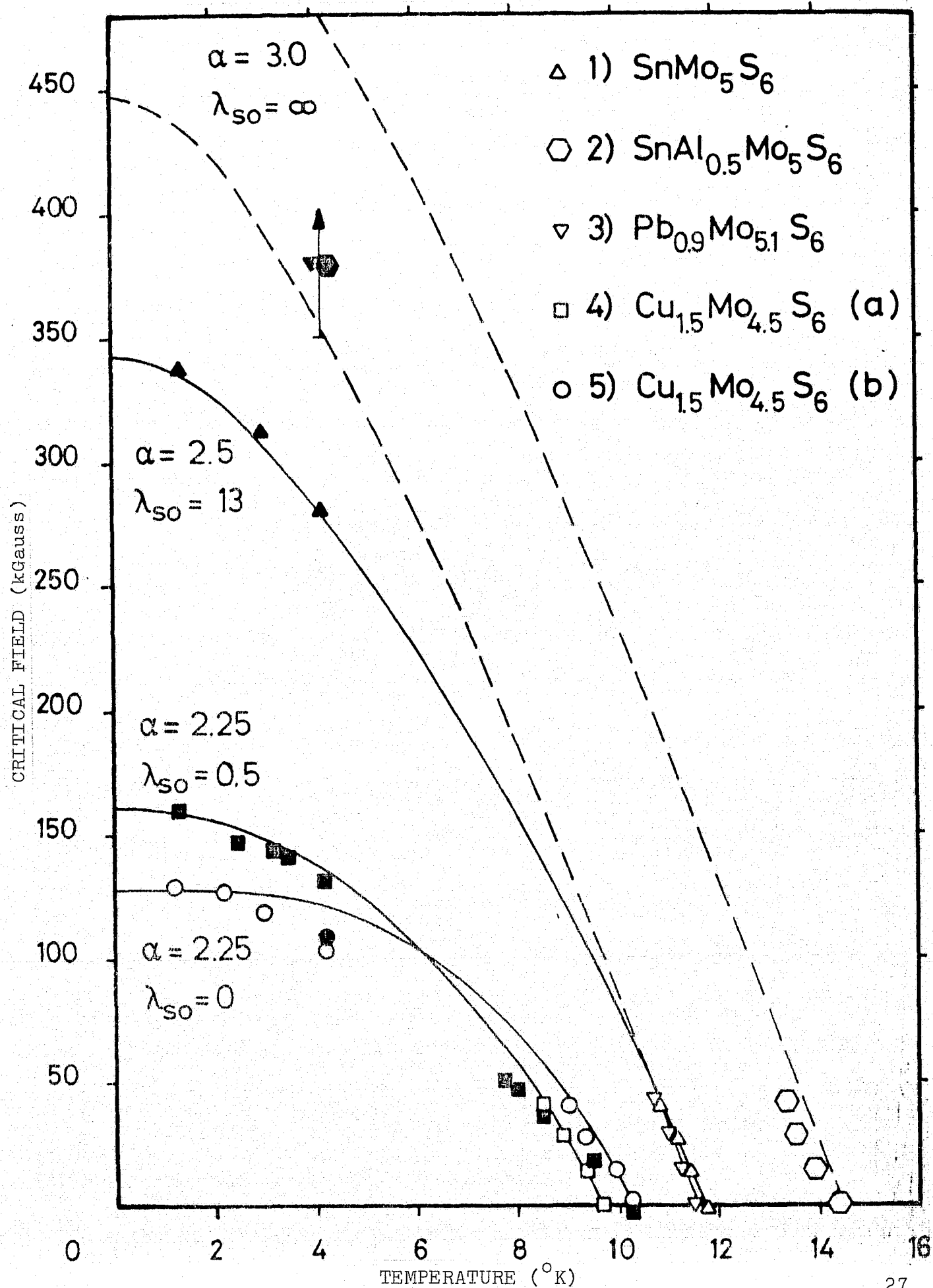
The transition widths taken between 10% and 90% of the total height are the following: for pulsed field, of the order to 50 kGauss; for static field, of the order of 1.5° K at fixed field or 35 kGauss at fixed temperature for copper compound (a), and 0.2 to 0.7° K at fixed field or of the order to 20 kGauss at fixed temperature for the other compounds.

The critical fields at 4.2° K could not be measured for samples 2 and 3 because no sign of transition to the normal state could be observed up to 350 kGauss. Assuming that these compounds had the transition width of sample 1, it can be said that the center of the transition lies above 380 kGauss.

TABLE 3. HEAT TREATMENT, CRITICAL TEMPERATURE T_c , AND CRITICAL FIELD AT $T = 0$ FOR % SULFIDES

Sample no.	Composition	Heat treatment	T_c ($^{\circ}\text{K}$)	ΔT_c ($^{\circ}\text{K}$)	H_{c2} ($T = 0$) (kGauss)
1	SnMo_5S_6	1 day at 1050°C 2 days at 800°C	11.7	0.2	344
2	$\text{SnAl}_{0.5}\text{Mo}_5\text{S}_6$	1 day at 1050°C	14.4	0.15	(560)
3	$\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$	1 day at 1050°C	11.5	0.4	(450)
4	$\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$ (a)	3 days at 800°C	9.6	0.7	160
5	$\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$ (b)	1 day at 1050°C	10.30	0.3	130

Figure 9. H_{c2} as a function of T for 5 sulfides



Δ 1) SnMo_5S_6 (a)

$\circ$ 2) $\text{SnAl}_{0.5}\text{Mo}_5\text{S}_6$

∇ 3) $\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$

$\square$ 4) $\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$ (a)

$\circ$ 5) $\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$ (b)

$\emptyset$ 6) SnMo_5S_6 (b)

	<u>Slope (kG/°K)</u>	<u>α</u>
I	- 57	3.0
II	- 47	2.5
III	- 42	2.25
IV	- 22	1.15

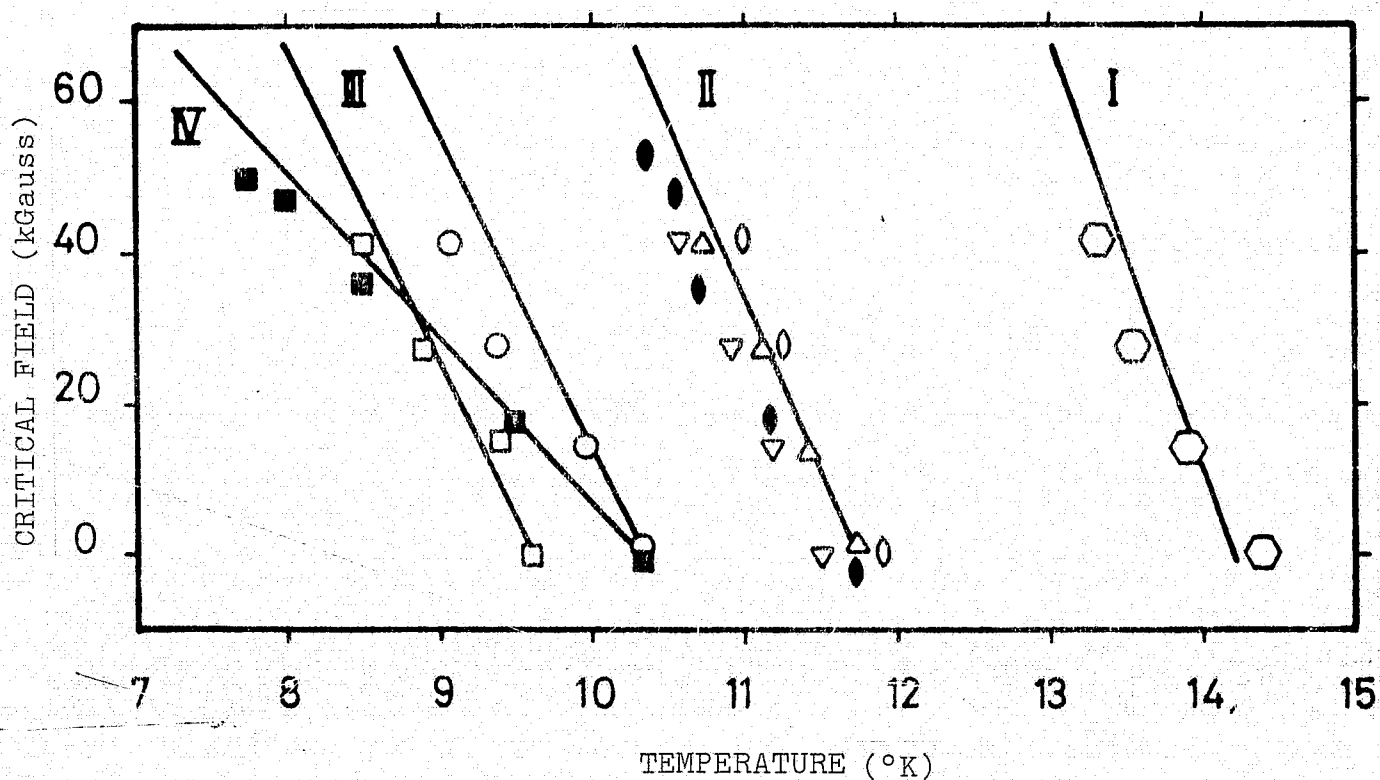


Figure 10. Initial slopes of $H_{c2}(T)$ for six sulfides

The initial slopes, given in Figure 10, lie between -40 and -60 kGauss/°K, except for the value obtained from resistivity measurements on sample 4 [copper compound (a)] which was about -22 kGauss/°K.

Another lead compound with a T_c of 12.5° K and $\text{SnNb}_{0.5}\text{Mo}_5\text{S}_6$ ($T_c=13.6^\circ\text{K}$) [10] were also tested at 4.2° K, and no sign of transition to the normal state was observed up to 350 kGauss.

Magnetization of copper compounds which underwent various thermal treatments was also measured. All these samples had 4.2° K critical fields lying between 85 and 105 kGauss.

The initial slopes for a tin compound ($T_c=11.2^\circ\text{K}$) and for a lead compound ($T_c=12.5^\circ\text{K}$) had values very close to those which have been given here.

Comments

/33

The 4.2°K critical field for the lead compounds for $\text{SnAl}_{0.5}\text{Mo}_5\text{S}_6$ and for $\text{SnNb}_{0.5}\text{Mo}_5\text{S}_6$ is higher than 380 kGauss. This result is not very surprising for the latter two compounds, which have high critical temperatures (14.4° and 13.6° K, respectively [10]). On the contrary, for the lead compounds, and especially for sample 3, this value is higher than would be expected from its T_c and the initial slope.

The initial slopes are large for all the compounds. In the copper compounds, however, $H_{c2}(T)$ has completely different behavior from that of the other compounds.

While the ratio $H_{c2}(T=0)/T_c$ is of the order of 15 kGauss/°K for the copper compounds, it is about 30 kGauss/°K for the tin compound and probably more than 39 kGauss/°K for the lead one. This latter value is almost double those found up to now for substances with critical fields of the same order of magnitude [20].

Experimental Conditions

With the static field, the current for measuring the resistivity was 50 mA (0.5 A/cm^2). With the pulsed field, it was 500 mA (5 A/cm^2) for the copper compounds and 2 A (20 A/cm^2) for the tin compound. The latter current was used to test the compounds in which the beginning of the transition to the normal state was not observed at 4.2° K .

All measurements of magnetization were made by means of a coil with a 36 msec rise time. The 4.2° K resistivity transition in sample 5 [copper compound (b)] was also done with this coil. For the other measurements, the coil with the 21 msec rise time was used. For the copper samples, the 21 msec coil gave the same resistivity at 4.2° K as the 36 msec coil. Under the same conditions, but now for magnetization measurements, the coils with 36 msec and 120 msec rise times gave the same critical fields.

/34

Remarks on the Resistivity Measurements

Figure 10 shows that for sample 4 [copper compound (a)] there is a large difference between the inductive initial slope (around $-42 \text{ kGauss/}^\circ\text{K}$) and the resistive initial slope ($-22 \text{ kGauss/}^\circ\text{K}$). For sample 6, the resistivity measurements also gave a slightly smaller initial slope than the inductive measurements.

This disagreement can be understood if it is assumed that there was a slight heating of the sample due to the passage of current during the resistivity measurement. The real temperature of the sample was therefore higher than indicated by the thermometric device. The samples were formed of pressed and annealed powders. There is certainly resistance to the passage of current between grains agglomerated this way. Contact resistance between the solder and the sample itself, which is rather large, can also induce such heating.

During pulsed field measurements, the same phenomenon was much smaller, if it occurred at all, for several reasons. The time during which the current was applied was much shorter (about 1 sec to maximum field). The sample was held by a screw between two copper plates which acted as current leads. The two faces of the cylinder forming the sample were covered with a thin coating of silver paint before they were pressed against these plates. This ensured very good passage of the current when the paint had dried. Finally, the sample was immersed directly in the helium bath. Heat transfer was thus much better than above 4.2° K (static field), where it took place by exchange through the gas phase.

/35

For the tin compound, heating by less than 0.5° K, which is of the order of what can be expected, would be enough to explain the disagreement.

For the copper compound, the difference is larger and the situation is different: the two slopes intersect.

The fact that the resistivity measurements give transitions at higher temperatures than are given by the inductive measurements can be explained by another phenomenon. Resistivity measures the transition to the superconducting state of the first filament of material which can carry the measuring current. Susceptibility and magnetization measure the transition of the sample in its entirety.

We can thus understand why resistivity measurements at 4.2° K give higher critical fields for the copper compounds than do magnetization measurements, while for sample 4 the beginning of the resistive initial slope is higher than the beginning of the inductive initial slope. Note that sample 4 has been annealed at only 800° C and could thus be more inhomogeneous than the others. The large transition widths observed in this sample confirm this impression.

Limitations on the Value of the Critical Field

Above a certain maximum field, called the upper critical field in Type II superconductors, a superconductor becomes normal. Since the transition between the superconducting and the normal states takes place at the moment when the energies of the two states are equal, the value of the critical field is fundamentally limited by two phenomena:

- the paramagnetism of the electron spins in the normal state, which lowers the energy of the normal material when it is plunged into a magnetic field;

- the orbital diamagnetism of the electrons of the superconductor, which increases the energy of the superconducting state.

If we consider only the paramagnetic effect in the normal state — that is, assuming that the susceptibility $\chi_s(T=0)$ in the superconducting state is zero — at °K the transition takes place when the lowering of the energy of the normal state $1/2 \chi_n H^2$ (χ_n is the susceptibility of the normal state) is equal to the condensation energy of the superconducting state. This transition is a first-order one. For a simple BCS superconductor (weak coupling), the condensation energy is:

$$\Delta^2 N(0)/2$$

where Δ is the forbidden band, and

$N(0)$ is the density of states at the Fermi level.

Taking the Pauli susceptibility $2 \mu_B^2 N(0)$ for χ_n , the transition thus takes place when:

$$\frac{\Delta^2 N(0)}{2} = \mu_B^2 N(0) H^2 \quad (1)$$

which gives Clogston's limit H_p [15]:

$$H_p = \frac{\Delta}{2^{1/2} \mu_B} = 18.4 T_c \quad (\text{kGauss}) \quad (2)$$

when the BSC relation (weak coupling) is used:

$$\Delta = 1.76 T_c \quad (3)$$

By considering only the orbital diamagnetism, it is assumed that $\chi_n = 0$, and in χ_s the contribution from the paramagnetism of spins in the superconducting state is neglected. The transition thus takes place when the increase in the energy of the superconducting state $\int M dH$ is equal to the condensation energy. The corresponding critical field H_{c2}^* is called the orbital critical field. This is a particular solution of the equation which we are going to see in the second part of this section.

WHH Theory

Werthamer, Helfand, and Hohenberg (WHH) [16, 14] have developed a theory in which the diamagnetic and paramagnetic effects are taken into consideration for both the normal state and the superconducting state.

The principal hypotheses employed by WHH are the following. The superconductor - normal transition is second order. The Fermi surface is spherical. The electrons are coupled by a weak BCS-type interaction. Spin-orbit scattering (scattering with spin reversal) is rare in comparison to nonmagnetic scattering (without spin reversal). Finally, the dirty limit is taken.

/38

Under these conditions, the upper critical field $H_{c2}(T)$ is given by the expression:

$$H_{c2}(T) = 2 \gamma_E H_{c2}^*(T=0) h(t) \approx \frac{1}{0.281} H_{c2}^*(T=0) h(t) \quad (4)$$

where:

$C = \ln \gamma_E$ — Euler's constant, and

$h(t)$ — solution of the following equation:

$$\ln\left(\frac{1}{t}\right) = \left(\frac{1}{2} + \frac{1}{4}\frac{\lambda_{so}}{\gamma}\right) \psi\left(\frac{1}{2} + \frac{h + \frac{1}{2}\lambda_{so} + i\gamma}{2t}\right) + \\ + \left(\frac{1}{2} - \frac{1}{4}\frac{\lambda_{so}}{\gamma}\right) \psi\left(\frac{1}{2} + \frac{h + \frac{1}{2}\lambda_{so} - i\gamma}{2t}\right) - \psi\left(\frac{1}{2}\right) \quad (5)$$

where:

ψ is the digamma function defined by: $\psi(z) = \frac{d}{dz} \log \Gamma(z)$,
 Γ being the gamma function;

$t = T/T_c$ is the reduced temperature;

$$\gamma = (\alpha^2 h^2 - 1/4 \lambda_{so}^2)^{1/2}$$

λ_{so} is the spin-orbit scattering parameter;

α is the Maki parameter.

For BCS superconductors, the Maki parameter can be defined by:

$$\alpha = 2^{1/2} \frac{H_{c2}^*(T=0)}{H_p} \quad (6)$$

It is thus an expression for the relative value of the two limitations /39 discussed at the start of this section.

In the dirty limit we can write:

$$\alpha = -5.28 \cdot 10^{-2} \left(\frac{dH_{c2}}{dT} \right)_{T=T_c} \quad (7)$$

where dH_{c2}/dT is expressed in kGauss/°K.

The spin orbit scattering parameter expresses the magnitude of the spin-orbit interaction, that is, the frequency of scattering with spin reversal.

A large λ_{so} indicates a strong spin-orbit interaction. Spin is thus no longer a good quantum number, and the paramagnetism of the superconducting state tends toward that of the normal state. On the other hand, if λ_{so} is very small, there is very little spin-orbit scattering, spin is conserved during collisions, and the paramagnetism of the superconducting state is zero.

The situation is as follows:

- α small (≈ 0) means that $H_{c2}^*(T=0) \ll H_p$, the critical field is limited mainly by diamagnetic effects.

- λ_{SO} large ($\approx \infty$) means that the paramagnetism is practically the same in the two states, and the critical field is also limited mainly by diamagnetic effects.

- λ_{SO} small (≈ 0) and $\alpha \gtrsim 1$ means that the normal state is responsible for the critical field limitation. This limitation induces a first-order transition for λ_{SO} smaller than a certain value depending on α .

The two limits $\alpha = 0$ and $\lambda_{SO} = \infty$ are seen to be equivalent.

The preceding discussion leads us to expect what is actually the case — that the orbital critical field $H_c^*(T)$ is given by Equation (4) provided that one sets $\lambda_{SO} = \infty$, or what is equivalent, $\alpha = 0$, in Equation (5). /40

If the paramagnetic effects are much larger than the diamagnetic effects, the transition can become first-order. The WHH expression for $H_{c2}(T)$ no longer holds under those conditions.

e) Comparison of experimental results with theory

/41

The Clogston Limit

The difference in the behavior of $H_{c2}(T)$ in the copper compounds and in the other compounds is also shown by comparison of the Clogston's limits H_p [Equation (2)] and of the estimated or extrapolated critical fields $H_{c2}(T=0)$.

For samples 1 through 5, the respective values are:

$$H_p = 215, 265, 212, 176 \text{ and } 190 \text{ kGauss}$$

$$H_{c2}(T=0) = 344, (560), (450), 160 \text{ and } 139 \text{ kGauss}$$

for samples 2 and 3, the value of $H_{c2}(T=0)$ is an estimate (see the second part of this section). But it is still possible to say that the real value is higher than 380 kGauss, since $H_{c2}(T=0) > H_{c2}(T=4.2^\circ\text{K}) > 380 \text{ kGauss}$.

We thus see that for the copper compounds $H_{c2}(T=0)$ is smaller than H_p , while for the other compounds it is distinctly larger than this limit.

Application of the WHH Theory

Knowledge of the initial slope allows the Maki parameter [Equation (7)] to be calculated, assuming a dirty BCS superconductor. Knowing T_c , one can then calculate $H_{c2}^*(T=0)$ via Equation (6).

A computer program solved Equation [5] and gave us $h(t)$ for known values of α and λ_{so} . α was calculated from the initial slope [Equation (7)], and then all that needed to be done was to adjust λ_{so} to obtain the theoretical curve which best fit the measurements.

Maki parameters corresponding to various initial slopes are given in Figure 10. The curves drawn in Figure 9 are the results of the calculations just described.

/42

The initial slope for sample 1 [tin compound (a)] corresponds to $\alpha = 2.5$; for this value, the measurements below 4.2 K fall on the theoretical $\lambda_{so} = 13$ curve.

The inductive initial slopes of the copper compounds suggest $\alpha = 2.25$. For this value, the other experimental points of compound (a) (sample 4) correspond to $\lambda_{so} = 0.5$, and the ones for compound (b) (sample 5) are below the curve $\lambda_{so} = 0$.

For this latter case, ($\alpha = 2.25$, $\lambda_{so} = 0$) $H_{c2}(t)$ is a maximum for $t_m = 0.26$ and decreases for smaller values of t . In fact, for $t < t_m$ the transition is first-order and the theoretical WHH curve no longer represents the critical field — we have replaced it with a horizontal line.

A trial was made with the resistive initial slope for sample 4 [copper compound (a)], which gave a Maki parameter of 1.15. The experimental points below 4.2°K are above the $\lambda_{so} = \infty$ curve and, in particular, the shape of the theoretical $H_{c2}(T)$ curve is very different from that of the experimental $H_{c2}(T)$ curve.

For the lead compound, the initial slope indicates that $\alpha = 3$. The 4.2° K critical field for this compound is above the $\alpha = 3$, $\lambda_{so} = \infty$ curve. The estimate of $H_{c2}(T=0)$ was given by the value of $H_{c2}^*(T=0)$ corresponding to these parameters.

We have assumed the same values ($\alpha = 3$, $\lambda_{so} = \infty$) to estimate the critical field at $T = 0$ for sample 2.

Comments

/43

To the extent that the WHH theory applies to these substances, the theoretical results indicate a strong limitation on the critical field by the effects of spin paramagnetism in the copper compounds ($\lambda_{so} = 0$), while this limitation is very small for the other compounds (λ_{so} large).

It is necessary, however, to mistrust the large values of λ_{so} obtained by trying to fit the theoretical curves to the experimental results: they may be false [14]. Several examples (MoGa₄, La₃In) are known [14, 21] for which the experimental points are above the theoretical $\lambda_{so} = \infty$ curve which is compatible with the initial slope. The experimental curve is linear out to very low temperatures (T/T_c very small), which cannot be reproduced by the WHH theory. In MoGa₄ [14], spin paramagnetic effects were seen, which shows that it would be wrong to take $\lambda_{so} = \infty$ in this case.

Let us examine the hypotheses made in the WHH theory which might be able to explain these deviations.

It has been shown [22] that if a strong coupling is taken instead of the weak coupling used, the theoretical curve straightens out. This correction is a small one, however, and is not enough to explain the experimental values [22].

Another hypothesis is that of the dirty limit. Relaxing that — i.e., considering a pure semiconductor — the value of $H_{c2}^*(T)$ is increased [23]. If the assumption of a spherical Fermi surface is retained, this correction is also small.

If one now considers the effects of anisotropy of the Fermi surface, one comes to the conclusion [24] that they are negligible in the dirty limit. On the other hand, for the pure material, they do affect the theoretical curve in the desired direction [24]. The magnitude of this correction is appreciable, although an estimate has not been made [24].

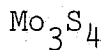
In short, to raise the theoretical curve enough to explain some of the experimental results, it is necessary to assume that the superconductor in question is pure and that it has a non-spherical Fermi surface.

It seems reasonable to believe that the ternary molybdenum sulfides studied here do not have a spherical Fermi surface. One possibility of theoretically understanding the experimental critical fields for $Pb_{0.9}Mo_{5.1}S_6$, and perhaps other compounds, would be to assume that these substances are at the pure limit.

All of the substances which we shall be talking about in this chapter are in the form of powders. The problems encountered with sulfides in the preparation of samples from powders (section 2-c) for making the measurements were also present here. However, all the substances did not react the same when they were pressed. Some formed layers the way the three sulfides discussed above did; others remained powders despite high pressure; still others, such as Mo_3S_4 , Mo_3Se_4 and $\text{Cu}_x\text{Mo}_3\text{Se}_4$, held together relatively well.

The bridge used for measuring the inductive transitions and the calibration method are the ones described in section 2-d. Resistivity transitions were measured with the equipment discussed in 3-b: four-point below 4.2°K and two-point above.

a) Mo_3S_4 and its derivatives



Shortly after the appearance of the paper by Matthias which said that if Mo_3S_4 were stable it would be a superconductor and would have a critical temperature higher than 20°K [17], we learned how to manufacture this product [4, 9]. Mo_3S_4 cannot be obtained by direct synthesis from the components.

To prepare Mo_3S_4 , it is sufficient to take a phase of composition MMo_3S_4 with $\text{M} = \text{Cr, Mn, Fe, Co, Ni, Cu}$ and react it with HCl [4]. In practice, the procedure is the following. The substance is conscientiously ground and put into a solution of concentrated HCl diluted 1 to 1 with distilled water. The whole is stirred mechanically for about 24 hours, then filtered. The powder obtained is rinsed in distilled water. The process is repeated a second time.

Mo_3S_4 is isotypic with Mo_3Se_4 [4, 5]; there is a slight triclinic deformation of the lattice [9], which is rhombohedral for the ternary sulfides with the highest T_c values. Its structure was described in section 2-a. Mo_3S_4 is a powder like the ternaries, but is easier to form into pellets than they are (cf. 2-c). The side of the pressed cylinder had a bright, metallic appearance, which was not the case for the ternaries studied. Mo_3S_4 decomposes above 470°C .

Mo_3S_4 produced from CuMo_3S_4 was tested in several ways to observe the superconducting transition. Down to 2°K , the susceptibility showed no transition for three sorts of sample: pressed powder, bonded powder, powder pressed and annealed 2 days at 450°C . Above 1.2°K , magnetization was not detectable in the pressed powder and the bonded powder. The resistivity of the annealed sample did not show any transition down to 1.2°K . Finally, the resistivity of the sample pressed without annealing decreased from 1.7°K ; the middle of the transition was 1.6°K , and its width was about 0.5°K .

In short, it can be said that Mo_3S_4 is not a superconductor down to 1.2°K unless it has previously been subjected to a certain amount of pressure.

It is not very surprising that we did not detect any magnetization in a sample which was nevertheless superconductive according to its resistivity. We have already pointed out that the magnetization of these substances is very weak. It was even weaker here since we were working near T_c .

Although it is not at all very probable, it is possible that the furnace temperature went above 470°C during annealing, which would result in destruction of the structure. This would explain why the annealed sample was not a superconductor according to its resistivity. A more plausible explanation of this phenomenon is that the pressure had an influence which made it possible for superconductivity to appear.

/47

High critical temperatures are often linked to instability of the crystal structure [12, 17]. It appears that Matthias [17] made use of this experimental fact to suppose that Mo_3S_4 would have a critical temperature above 20° K. Since Mo_3S_4 had been reported to be unstable, it appeared that the essential role of the interstitial M element was that of stabilizing the structure by reinforcing the bonds between the sub-units. If Mo_3S_4 could exist without the M element, it would be normal to suppose that it would have a critical temperature higher than the highest known T_c for these compounds. In this context, our result must indicate that the principal role of M is not to stabilize the structure, and that it plays another role in the appearance of superconductivity. Another possibility, which itself does not seem very probable, is that instability of structure is not important for the appearance of superconductivity.

Derivatives of Mo_3S_4

/48

Some MMo_3S_4 phases do not form if one attempts direct synthesis from the elements.

We have attempted to make Mo_3S_4 react with $M = \text{Al, Ga, In; Cu, Pb}_{0.6}; \text{AlPb}_{0.6}, \text{MgPb}_{0.6}$. These mixtures were held 2 days at 450° C, then ground and returned to 450° C for another 12 days.

According to information from the Rennes group [9], the phases with $M = \text{Al or In}$ do exist, while the one with $M = \text{Ga}$ does not. Aside from Al, which was a powder, all the elements we tried to introduce here were in small lumps. When the samples were broken open after the treatment just described, it could be seen that these lumps still remained. The phases were thus not completely formed, even those which do exist. It might be that after several cycles of grinding and annealing one could obtain formation of these compounds. However, one must not discard the possibility that the structure of Mo_3S_4 once formed is no longer capable of easily accepting interstitial elements.

None of these substances was entirely superconductive above 4.2° K. Three of them, M = Cu, Ga, and AlPb_{0.6}, showed an inductive partial transition which corresponded to 5%, 5%, and 15%, respectively, of the total height and took place at 5.0°, 5.5°, and 9.7° K, respectively.

This confirms that the phases with M = Cu and Pb_{0.6} are not formed — or are perhaps formed in only a small amount.

Discussion of M = Al, Ba, and In will be in the following section since the Rennes laboratory furnished us with the compounds into which they inserted those elements.

b) Substances furnished by the Rennes laboratory

Mo₃Te₄ and Mo₃Se₄ can be obtained either by direct synthesis /49
from the elements (noted as "direct") or by action of HCl on
M_xMo₃Te₄ or M_xMo₃Se₄ (noted as M_xMo₃Te₄ or M_xMo₃Se₄) [4, 9].

Mo₃Te₄ is isotypic with Mo₃Se₄ and Mo₃S₄ [9]. The ternary molybdenum tellurides have structures derived from those of the sulfides and selenides [9] which have been described together in section 2-a.

The susceptibility shows no sign of superconductivity:

- above 1.5° K in unannealed pressed powders of:

Mo₃Te₄ (direct)

Mo₃Te₄ (from CuMo₃Te₄)

SMo₃Te₃

S_{1.5}Mo₃Te_{2.5}

Al_{1.5}Mo₃S₄

BaMo_{6.5}S₈

CuMo₃Te₄

REPRODUCIBILITY OF THE
ORIGINAL PAGE IS PO

Pb_{0.6}Mo₃Se₂Te₂

- above 2.2° K in unannealed pressed powders of:

Mo₃Te_{4.38}

BaMo₇S₈

K₂Mo₅S₆

Ga_{0.66}Mo₂S₄

InMo₃S₄

Ag_{0.6}Mo₃SeTe₃

Pb_{0.45}Mo₃Se₃Te

in Mo₃Te₄ (direct) annealed 3 days at 800° C,

in BaMo₇S₈ annealed 1 day at 1050° C.

Some pressed powders showed inductive partial transitions. These are:

<u>Compound</u>	<u>A (%)</u>	<u>T (°K)</u>
$S_{1.8}Mo_3Se_2$	0.5	< 4.2
$Pb_{0.6}Mo_3Se_4$	10	7.2
$Br_{1.5}Mo_3Se_{2.5}$	0.5	~ 3.9
$Ag_{0.6}Mo_3Se_2Te_2$	1	< 4.2

A is the height of the transition in percent of the total height;
T is the temperature at which this partial transition took place.

The sample $Br_{1.5}Mo_3Se_{2.5}$ annealed 4 days at 450° C showed no sign of superconductivity down to 2.2° K by the inductive method.

Comments

The partial transition observed for the $Pb_{0.6}Mo_3Se_4$ sample has a strong change of being that of free lead, which has a critical temperature of 7.2° K.

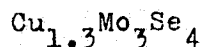
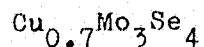
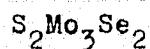
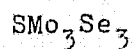
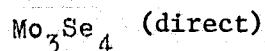
In the preceding section, we were not certain that the $AlMo_3S_4$ and $InMo_3S_4$ phases were formed. Here, with information from the Rennes group [9], we can say that $Al_{1.5}Mo_3S_4$ and $InMo_3S_4$ are formed, and that they are not superconductors.

The compound $GaMo_3S_4$ does not exist [9, 18]. On the other hand, $Ga_xMo_2S_4$ does exist, with x around 0.5 [18]; it is ferromagnetic and has a Curie temperature of about 16° K [18]. This phase does not have the usual rhombohedral structure of the Chevrel phases, but rather the spinel structure [18]. The susceptibility measurement customarily used to detect the superconductive transition allows the Curie point to be seen. We were able to convince ourselves of that by measuring $Ga_{0.66}Mo_2S_4$ furnished by Rennes. This sample also showed magnetic saturation at a low field.

/51

We note again that according to a figure published in [7], molybdenum sulfide with Ba as the third element is not a superconductor down to 1.2° K. This agrees with our result.

Other compounds are superconductors. These are:



Their properties will be discussed in the following sections.

Two known samples $\text{Pb}_{1.5}\text{Mo}_{6.2}\text{S}_8$ and $\text{Cu}_2\text{Mo}_3\text{S}_4$, produced at Rennes, have also been tested by susceptibility. Their critical temperatures correspond to those of the compounds we synthesized. This control test allows us to say that the compounds used at Rennes do not seem at first glance to contain impurities harmful to superconductivity.

c) Critical temperatures and transitions in superconductive compounds

/52

Results

Before annealing, pressed SMo_3Se_3 , $\text{S}_2\text{Mo}_3\text{Se}_2$ and $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$ showed very weak partial transitions with heights of 2%, 0.5%, and 7% of the total height, respectively. They took place at 4.3°, below 4.2°, and 3.7° K, respectively. Measurements were made down to 1.5° K.

The inductive and resistivity transitions of these compounds after annealing small pellets for 1 day at 1050° C are given in Figure 11.

$\text{Cu}_{0.7}\text{Mo}_3\text{Se}_4$ has almost the same inductive transitions before and after annealing for 1 day at 1050° C. The beginning of the transition in the unannealed sample was 0.4° K higher than that of the transition in the annealed sample. The transition in the latter sample is presented in Figure 11. The centers of the transitions are

at the same temperature. The amount of this compound available was too small for resistivity measurement, so only the inductive transition is given.

The resistivity transitions for Mo_3Se_4 (direct) (Figure 11) refer to an unannealed pressed sample. The sample annealed 1 day at 1050°C was completely cracked and greatly swollen, so that resistivity measurement was impossible.

Inductive transitions in the Araldite-bonded powder and in the pressed and annealed sample are identical within one-tenth degree. As Figure 11 shows, the transition in the unannealed pressed sample takes place at a higher temperature, and its behavior is not the same. /54

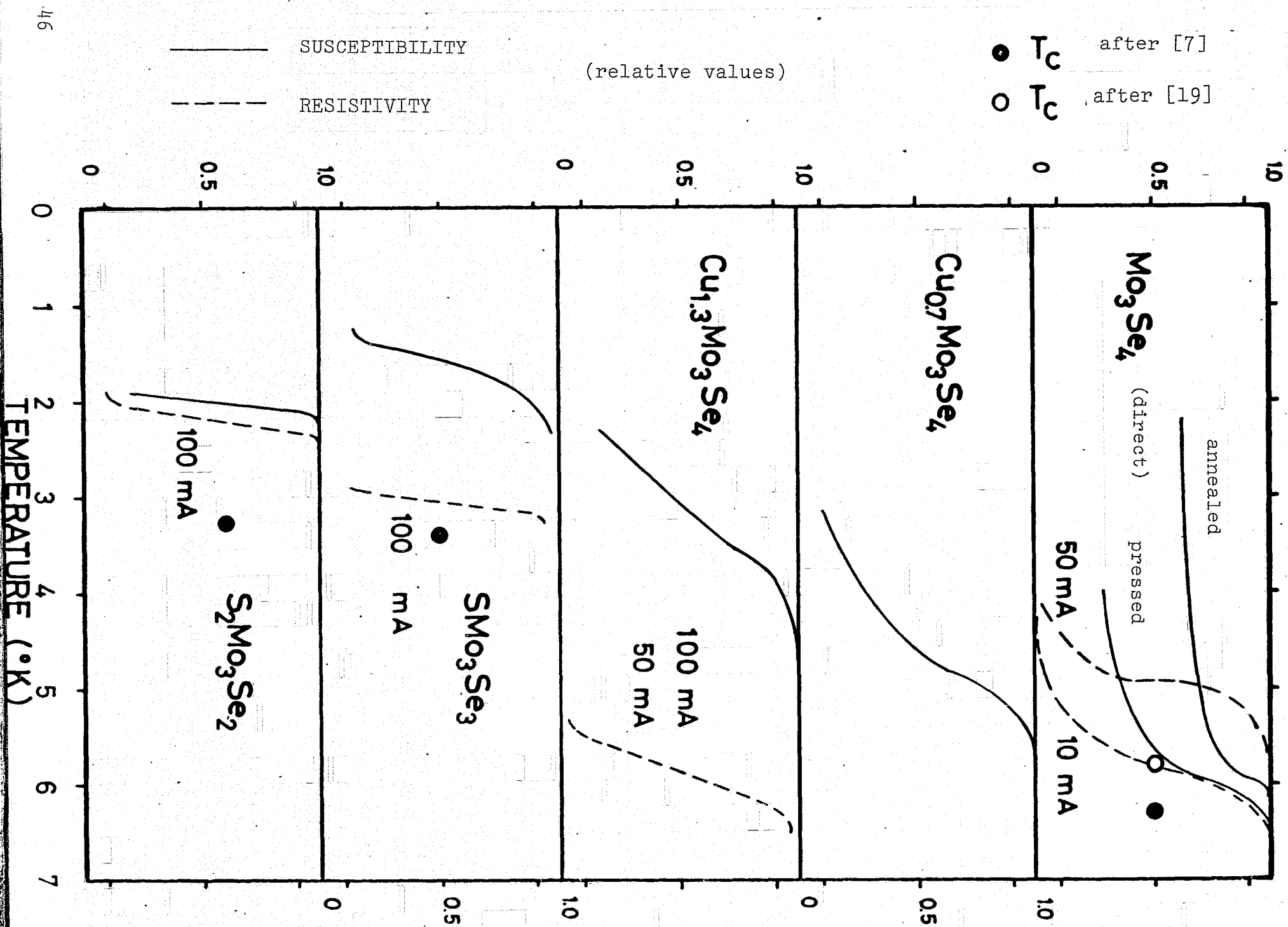
A sample of Mo_3Se_4 produced from $\text{Fe}_{0.6}\text{Mo}_3\text{Se}_4$ has also been tested by susceptibility: no sign of superconductivity could be discerned either in the bonded powder or in the pressed powder before or after annealing 1 day at 1050°K .

Comments

Too much importance should not be attached to the shift between the inductive transitions in annealed and unannealed Mo_3Se_4 (direct). The shape of a partial transition depends strongly on the adjustment of the bridge; since the two measurements were not made on the same day, it is not certain that the adjustment was exactly the same. One can, however, compare this result with the one obtained for Mo_3S_4 . We have seen that for this compound (section 4-a) the pressed sample was a superconductor (resistivity T_c of 1.6°K), while the annealed sample was not. Pressure thus increased the T_c in these two cases.

The fact that Mo_3Se_4 (from $\text{Fe}_{0.6}\text{Mo}_3\text{Se}_4$) is not a superconductor is surprising. From the x-ray data [9], all the iron has been taken out of the material; it is possible, however, that a small quantity remained, not detectable by x-rays but enough to destroy superconductivity. Another possibility is that the structure of Mo_3Se_4

Figure 11. Superconducting transitions in 5 selenides



not exactly the same after iron removal, in spite of annealing, as that of the compound obtained by direct synthesis. We shall go into detail about this point in Chapter 6. It would be necessary that the difference there be small enough to be indiscernible by x-rays, but large enough to destroy the superconductivity.

The change in inductive critical temperature as a function of x for both the $S_x Mo_3 Se_{4-x}$ and $Cu_x Mo_3 Se_4$ systems is outline in Figure 12 for annealed samples. In both systems, the height and the 10% point of the inductive transition, as well as the mid-height of the resistivity transition in $S_x Mo_3 Se_{4-x}$, decrease with x . The middle of the inductive transition has a maximum.

Marezio et al. [7] report critical temperatures of 3.3° , 3.4° , and 6.3° K for $S_2 Mo_3 Se_2$, $SMo_3 Se_4$ and $Mo_3 Se_4$, respectively. They do not define the measurement method nor the heat treatment. Under these conditions it can be assumed that our results agree with theirs (Figure 11).

Hulliger [19] gives 5.8° K for the critical temperature of $Mo_3 Se_4$. This value corresponds exactly to the mid-height of our resistivity transition for a current of 10 mA (Figure 11).

Partial transitions: Remarks

There is a large difference between the behaviors of the annealed and the unannealed $SMo_3 Se_3$, $S_2 Mo_3 Se_2$ and $Cu_{1.3} Mo_3 Se_4$ samples. It is curious that samples in which such a small part was superconducting before annealing became entirely superconductive after annealing. Such a large difference in behavior has never been observed in the $M_x Mo_{6-x} S_6$ phases studied. This indicates a very strong pressure effect on the three compounds mentioned.

This phenomenon can make us believe that some of the compounds in which we observed no signs of superconductivity do in fact have this property. The $S_2 Mo_3 Se_2$ sample could have been transformed during annealing: when the quartz ampoule which contained it was opened, a whitish vapor escaped.

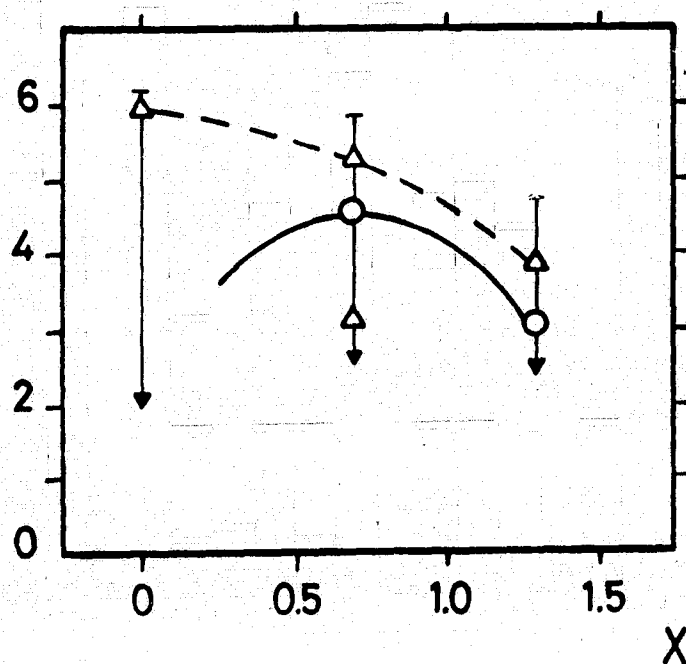
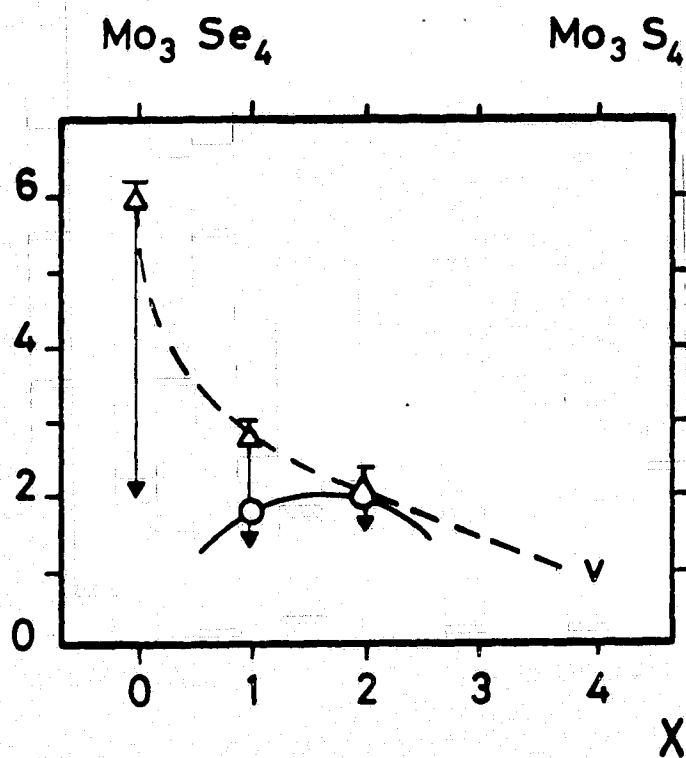
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/57

- top and bottom
 Δ 10% and 90%
 ○ middle
- of the inductive transition

Figure 12. T_c as a function of x for $S_x Mo_3 Se_{4-x}$ and $Cu_x Mo_3 Se_4$

CRITICAL TEMPERATURE ($^{\circ}K$)



The inductive partial transition in annealed Mo_3Se_4 and the observed shift between the resistivity and inductive transitions in at least two other compounds are odd.

The resistivity transition measures the critical temperature of the first filament of superconducting material. An inductive partial transition is generally explained by saying that only part of the sample is superconductive. Thus, a sample can show an inductive partial transition while it has a complete resistivity transition.

The fact that the resistivity transition for unannealed Mo_3Se_4 depend strongly on the measuring current (Figure 11) would confirm this explanation for this compound. Note, however, that this strong dependence can be explained in another way. In an unannealed sample the resistance between grains is certainly high. This resistance can produce local heating which makes the material normal, and hence leads to a lowering of the resistivity critical temperature.

Explanation by a filament of superconducting material is not very satisfactory for $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$. So that the resistivity transition can be complete before the inductive transition begins, it is necessary for the superconducting filament to make up only a very small part of the volume of the sample. This does not seem possible when it is seen that a current of 100 mA can be passed — an overall current density of 1 A/cm^2 — in this sample without affecting the resistivity transition.

Another possibility of explaining this phenomenon is to think that these substances have a very weak complete Meissner effect. This can be expressed in other words by saying that the lower critical field H_{c1} is very small. The inductive transition will be total only for a temperature T_0 such that $H_{c1}(T_0)$ is larger than the value of the peak field created by the measuring coil. In our apparatus, this peak value is of the order of ten Gauss. In the same way, one would explain the partial transition in annealed

/58

Mo_3Se_4 and the shift between the resistivity and inductive transitions, as well as the smallness of the magnetization.

d) Summary

/59

It is not impossible that some of the compounds called non-superconducting in the preceding paragraphs do in fact have this property, provided that an appropriate heat treatment is given them after pelletizing. The critical temperatures of the superconductors could perhaps be improved in the same way. It is not very likely that large improvements would be obtained, however.

Aside from these reservations, the results obtained can be summarized as follows:

- Mo_3Se_4 is not a superconductor under normal conditions.
- None of the new $\text{M}_x\text{Mo}_3\text{S}_4$ compounds is a superconductor.
- None of the tellurium-containing phases tested is superconducting.
- Adding an M element (Cu, Pb, or Br) to Mo_3Se_4 does not increase the critical temperature of the compound.
- Replacement of selenium by sulfur in Mo_3Se_4 lowers the critical temperature.

e) Critical fields of four of the superconducting compounds

/60

Experimental Results

The critical fields are given as function of temperature in Figure 13.

The solid points indicate the middle of the resistivity transitions. The empty points on the temperature axis show the height of the inductive transitions.

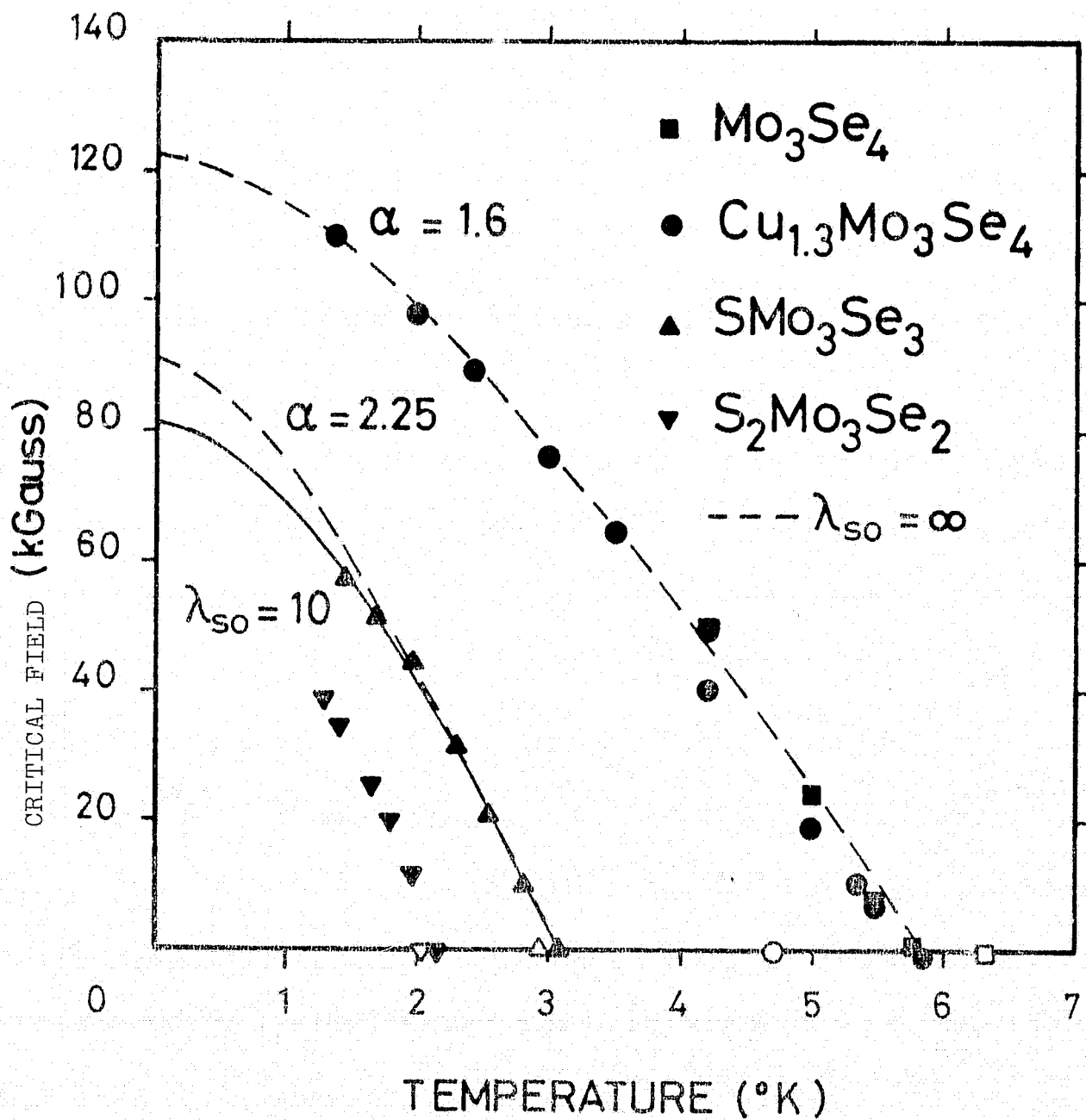


Figure 13. H_{c2} as a function of T for 4 of the superconducting selenides

The measurements were made on pressed samples annealed 1 day at 1050° C, except for Mo_3Se_4 (cf. section 4.c).

The current was 10 mA (0.01 A/cm²) for Mo_3Se_4 , and 100 mA (0.1 A/cm²) for the other substances.

The coils employed for pulsed-field measurements had rise times of 21 msec (fast coil) and 120 msec (slow coil); they gave the same results.

Magnetization of these compounds was even weaker than that of the three ternary sulfides studied, not more; it did not allow determination of H_{c2} .

The transition widths taken between the 10% and 90% points of the total height are as follows: Pulsed field — for SMo_3Se_3 and $\text{S}_2\text{Mo}_3\text{Se}_2$, 25 kGauss; for $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, 55 kGauss. Static field — for $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, 25 kGauss; of the order of 60 kGauss for Mo_3Se_4 at fixed temperature. Around 1.5° K for $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$ at fixed field.

For $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, there are two field values at 4.2° K. The upper point (50 kGauss) corresponds to the pulsed-field measurement; the lower point (40 kGauss) — to the static field.

/62

This difference is probably not due to dynamic effects in the pulsed field, because the fast-coil and slow-coil measurements agree. As was discussed in section 3.c, one possible explanation is that the current heats the sample slightly during the static-field measurement. It can be seen that heating the sample of 0.25° K would be enough for the two measurements to be consistent.

The initial slopes of the $H_{c2}(T)$ curves are as follows. For Mo_3Se_4 and $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, of the order of -27 kGauss/°K, based on static-field measurements. Using the point at 4.2° K with the pulsed field, for $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$ an initial slope of -30 kGauss/°K is obtained. For

SMo_3Se_3 and $\text{S}_2\text{Mo}_3\text{Se}_2$, it is -40 kGauss/ $^\circ\text{K}$ and -55 kGauss/ $^\circ\text{K}$, respectively.

Comments

It appears that replacing some of the selenium in Mo_3Se_4 by sulfur increases the initial slope until it reaches values comparable to those which have been measured in the $\text{M}_x\text{Mo}_{6-x}\text{S}_6$ phases.

Adding copper to Mo_3Se_4 does not change the behavior of $H_{c2}(T)$ above 4.2°K .

For the three compounds, $\text{S}_2\text{Mo}_3\text{Se}_2$, SMo_3Se_3 and $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, the Clogston limit [15] (cf. section 3-d) is, respectively:

$$H_p = 39.5, 58 \text{ and } 108 \text{ kGauss}$$

/63

The critical field measured at the lowest temperature reached in each case is approximately equal to this value. It can thus be taken that $H_{c2}(T=0)$ is larger than H_p for these three compounds.

For these three compounds, the ratio $H_{c2}(T=0)/T_c$ must thus be larger than 18.4 kGauss/ $^\circ\text{K}$. For $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, it can be estimated that:

$$H_{c2}(T=0) = 120 \text{ kGauss and so } H_{c2}(T=0)/T_c = 20.5 \text{ kGauss}/^\circ\text{K}$$

In the other cases, it is difficult to make an estimate.

Comparison with WHH Theory

As in section 3.e, we have tried to account for these results by the WHH theory [16, 14] (cf. section 3.d).

For $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, the Maki parameter can be calculated in two ways: based on the measurements above 4.2°K , which gives an

initial slope of $-27 \text{ kGauss}/^\circ\text{K}$ and $\alpha = 1.4$, or by taking the initial slope given by the 4.2° K pulsed-field point ($-30 \text{ kgauss}/^\circ\text{K}$), which gives $\alpha = 1.6$. In the first case, the experimental points fall above the theoretical curve given by $\lambda_{\text{SO}} = \infty$; in the second, they fit this curve well, at least for temperatures below 4.2° K . This latter curve is shown in Figure 13.

For SMo_3Se_3 , the initial slope of $-40 \text{ kGauss}/^\circ\text{K}$ corresponds to $\alpha = 2.25$; for this value $\lambda_{\text{SO}} = 10$ gives a theoretical curve which agrees well with the experimental points. It can be seen from Figure 13 that it is difficult to decide the value of λ_{SO} for this compound. The theoretical curve for $\lambda_{\text{SO}} = \infty$ also fits these measurements quite well. /64

This difficulty comes from the fact that it is the critical fields for small values of $t = T/T_c$ which are used in determining λ_{SO} .

For $\text{S}_2\text{Mo}_3\text{Se}_2$, the initial slope of $-55 \text{ kGauss}/^\circ\text{K}$ leads to an α of 2.9. The situation for determining λ_{SO} is even more unfavorable than for SMo_3Se_3 and so we did not try to make an estimate.

These results indicate a weak limit to the critical field by paramagnetic effects. Reservations about this conclusion are the same as those made in section 3.e.

Note the difference in behavior of $H_{c2}(T)$ between the copper sulfide and selenide.

5. THE $A_x\text{Sn}_{1-x}\text{Mo}_5\text{S}_6$ COMPOUNDS

(A = Cr, Mn Fe, Co, Ni, Gd)

In this chapter, the subscript "o" (as H_{po} , T_{co}) will indicate /65 values for the compound with no impurities.

a) Compensation effect

In dense ferromagnets, the exchange field H_j is generally large enough to prevent the appearance of superconductivity, even in zero exterior field H . The compensation effect was proposed for such ferromagnets [3]. The idea is that if the exterior field is opposed to the exchange field, it will cancel the effect of the exterior field over a certain interval. If the ferromagnet in question has a tendency to superconductivity, it will actually become a superconductor in this interval.

Observation by the compensation effect under these conditions was difficult, however, for two reasons [14]:

- the orbital effects of the exterior field must be negligible with respect to paramagnetic effects (cf. section 3.d). This condition is not generally met in high critical field superconductors [14], except perhaps in some of the phases studied ($\text{Cu}_{1.5}\text{Mo}_{4.5}\text{S}_6$) or in other phases of the same type;

- it was not known whether the ferromagnets we started with would really become superconductors if the exchange field were compensated.

The same effect can, however, be observed in a superconductor containing magnetic impurities [25]. Let us assume that at a temperature T below T_c the exterior field $H = H_{c2}(T)$ can align the

spins of the impurities, and that the resulting exchange field is opposed to the exterior field. Then the influence of these two fields on the spins is zero, and the only limitation on the critical field is the orbital limitation [14]. If $H_{c2}^*(T=0)$ is much larger than H_{po} and the exchange field is larger than the paramagnetic limitation, the effect will be spectacular. Thus, at a temperature below the critical temperature, the following should be observed: first, a superconducting region, then a normal region, then a superconducting region again. The compensation effect can be seen even if $H_{c2}^*(T=0)$ is smaller than H_{po} , however [14].

b) Choice and preparation of compounds

To observe compensation, it was necessary to introduce magnetic impurities into one of the three sulfides studied: $M_xMo_{6-x}S_6$ ($M = Cu, Sn, \text{ and } Pb$). The choice of $SnMo_5S_6$ was made because of the following considerations.

$H_{c2}(T)$ has to be known for the pure sample. Since it was impossible to measure the critical field for $Pb_{0.9}Mo_{5.1}S_6$, that compound had to be eliminated. As we have just mentioned, we did not have very good control of the copper concentration in the compound containing it. It was thus surer to work with the tin compound. In addition, the compensation effect becomes larger as the ratios $H_{c2}^*(T=0)/H_{po}$ or $H_{c2}^*(0)/T_{co}$ become larger. Assuming identical spin-orbit coupling (cf. section 3.d), this means that it is necessary to take the compound with the largest possible value of $H_{c2}^*(T=0)/H_{po}$. It is clear that the latter ratio is larger for the tin compound than for the copper one. However, if the sulfides studied all have Maki parameters ($H_{c2}^*(T=0)/H_{po}$) of about the same size as we assumed in section 3.e, but the spin-orbit coupling constant is smaller for the copper compound and large for the tin, it is in the copper compound that the compensation effect would be the larger.

Since in $M_xMo_{6-x}S_6$ it is the M element which seems to play a determining role for superconductivity, it seemed natural for us to

introduce impurities by replacing some of the M atoms (here, tin) by these impurities. The choice is even more natural because the $\text{MMo}_n\text{S}_{n+1}$ phases ($M = \text{Cr, Mn, Fe, Co, Ni}$) do exist [2]. We could thus expect that the $\text{A}_x\text{Sn}_{1-x}\text{Mo}_5\text{S}_6$ phases would form and that the impurities would fit well on the sites of the missing tin atoms.

The compounds were synthesized by direct reaction of the components pressed into pellets (as in section 2.b). After being held in the furnace at 1050°C for one day, the samples were milled, pressed, and returned to the furnace at the same temperature for one more day. The second operation was intended to increase the chances of forming the phase and of homogenizing the impurity distribution.

After pressing into small pellets for measurement, the samples were annealed 1 day at 1050°C + 2 or 3 days at 800°C .

c) Critical temperatures

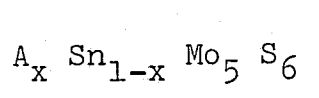
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Critical temperatures as a function of impurity concentration are shown in Figure 14.

They were measured by the induction-bridge method (cf. section 2.d).

All the samples were tested after pressing (before annealing). Except for the iron-containing compounds, the beginning of the transition before annealing was at a temperature as high as or higher than it was after annealing. The same phenomenon occurred in the pure compound. For the iron compound with lowest concentration ($x = 0.03$), the beginning of the transition was at 3.1°K before annealing, and at 6.9°K after annealing.

As a general rule, the transition width before annealing increased with the impurity concentration.



A = ○ Cr ● Mn
 □ Fe ■ Co
 △ Ni ▲ Gd
 ▽ Cr, Ni, Co, Gd

/70

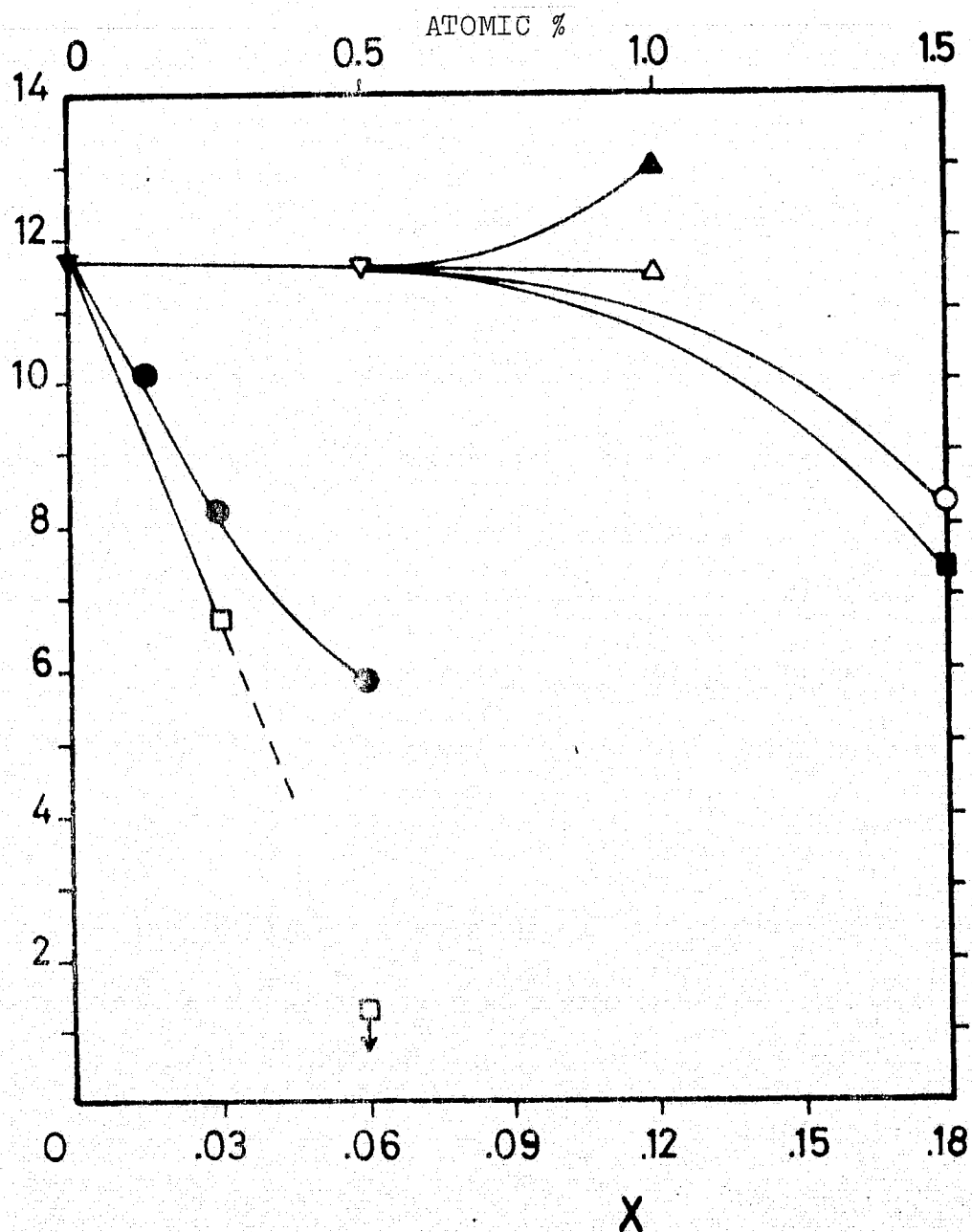


Figure 14. T_c as a function of x for $A_x \text{ Sn}_{1-x} \text{ Mo}_5 \text{ S}_6$ ($A = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Gd}$)

After annealing, the transition widths were of the order of 0.1° K for the pure compound, and for those containing Gd and Ni, as well as for those containing the least Cr and Co ($x = 0.06$). For the other compounds and/or the other concentrations, the transition widths were between 0.3 and 0.5° K.

The compound containing 0.5 a/o iron ($x = 0.06$) was tested down to 2.3° K by susceptibility and to 1.2° K by resistivity: it was not a superconductor.

Fe and Mn were the only impurities which produced the decrease in critical temperature with concentration which would be expected for magnetic elements. /71

For $A = \text{Cr, Ni, Co, and Gd}$, the critical temperature remained virtually the same at low concentration. In fact, for $x = 0.06$ (0.5 a/o), it dropped by 0.1 to 0.2° K for $A = \text{Cr, Co, Ni}$, and remained the same for $A = \text{Gd}$. Note that the critical temperature of different pure samples (SnMo_5S_6) which had all undergone the same thermal treatment after pressing (1 day at 1050° C + 2 days at 800° C) varied over a range of 0.15° K. The decrease observed for $A = \text{Cr, Ni, Co}$ is thus not really significant.

At higher concentrations, the critical temperature decreased slightly for Ni (0.4° K from the pure value for 1 a/o Ni), fell several degrees for Cr and Co, and increased for Gd.

The slight decrease in critical temperature for samples containing Cr and Co at low concentrations (0.5 a/o) — if it is real — and for samples containing Ni can be attributed to an increase in the non-magnetic scattering on the impurities.

The fall in the critical temperature for the highest concentrations of Cr and Co (1.5 a/o) cannot be attributed entirely to this effect. The cause of this decrease is probably to be found in the fact that replacement of tin by chromium or cobalt modifies other

properties of the compound, especially structure, in a sense unfavorable to superconductivity.

Since gadolinium is certainly magnetic (rare earth), the increase in critical temperature which it produces when it replaces part of the tin is surprising. The explanation is probably in the fact that gadolinium also modifies certain properties of the compound (structure, for example), but this time in a sense favorable to superconductivity. This modification increases the critical temperature more than the magnetic scattering decreases it.

/72

d) Experimental critical fields

Figures 15 and 16 give the measurements performed. Figures 17 and 18 give more detailed results for the compounds measured which contained Mn and Fe, respectively.

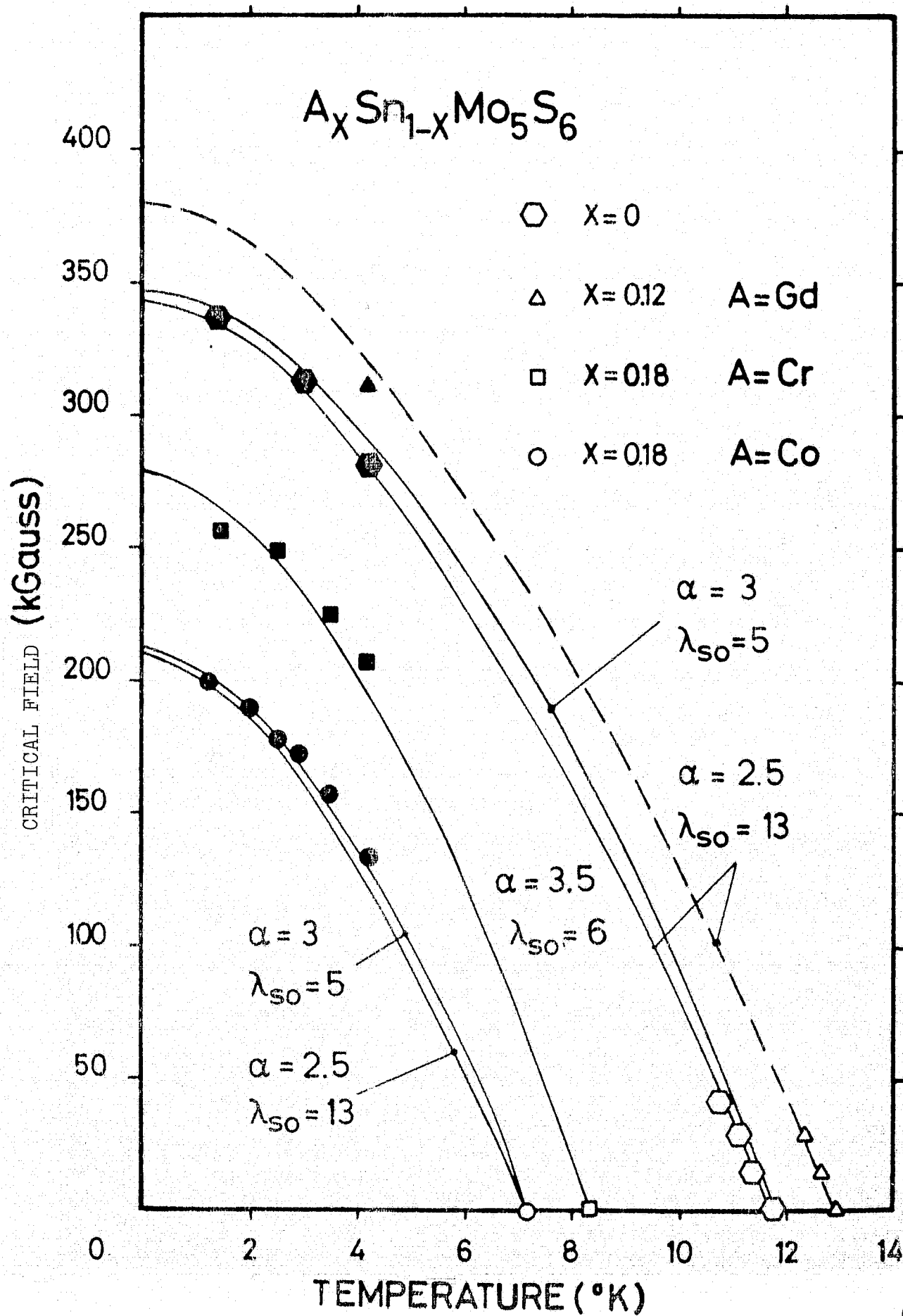
The solid points indicate the middle of the resistivity transitions, and the empty points — those of the inductive transitions.

The curves drawn in Figures 15, 17, and 18 are theoretical curves (see below); in Figure 16 they show the qualitative behavior of $H_{c2}(T)$.

The SnMo_5S_6 and $\text{Mn}_{0.06}\text{Sn}_{0.94}\text{Mo}_5\text{S}_6$ (b) samples were annealed as small pellets for 1 day at 1050°C + 2 days at 800°C . For the other samples measured, this annealing was for 1 day at 1050°C + 3 days at 800°C .

For pulsed-field measurements, the current was 1 A (10 A/cm^2) for the samples containing Mn, 0.5 A (5 A/cm^2) for those containing Co and Fe, and 0.2 A (2 A/cm^2) for the one which contained Cr. For static-field measurements, it was 50 mA (0.5 A/cm^2) for the two samples measured [Mn(a) and Fe].

Figure 15. H_{c2} as a function of T for "non-magnetic" impurities



The coil used had a rise time of 21 msec. Mn-containing sample (a) had also been measured at 4.2° K with the 120-msec coil. The two coils gave the same results.

No anomaly was observed in the 4.2° K field-magnetization curve for the samples containing Mn and Fe. The magnetization seems to show saturation due to spin alignment. The sensitivity of the apparatus and the weakness of the effect do not allow us to be definite on this point, however. The magnetization was very weak and did not allow H_{c2} to be determined. /75

Transition widths taken between 10% and 90% of the total height are the following. For static field: of the order of 0.75° K at fixed field and 20 kGauss at fixed temperature for Fe; of the order of 1° K at fixed field and 35 kGauss at fixed temperature for Mn. For pulsed field: 100 kGauss for Mn, 75 kGauss for Co and Cr, and 60 kGauss for Fe. For the pure compound, they were of the order of 60 kGauss with the pulsed field.

The dissimilarity between the $H_{c2}(T)$ curves of Mn (a) and Mn (b) should be pointed out. The only difference between these two compounds is the time of annealing at 800° C. For sample (a) the time was 2 days, and for (b) it was 3 days.

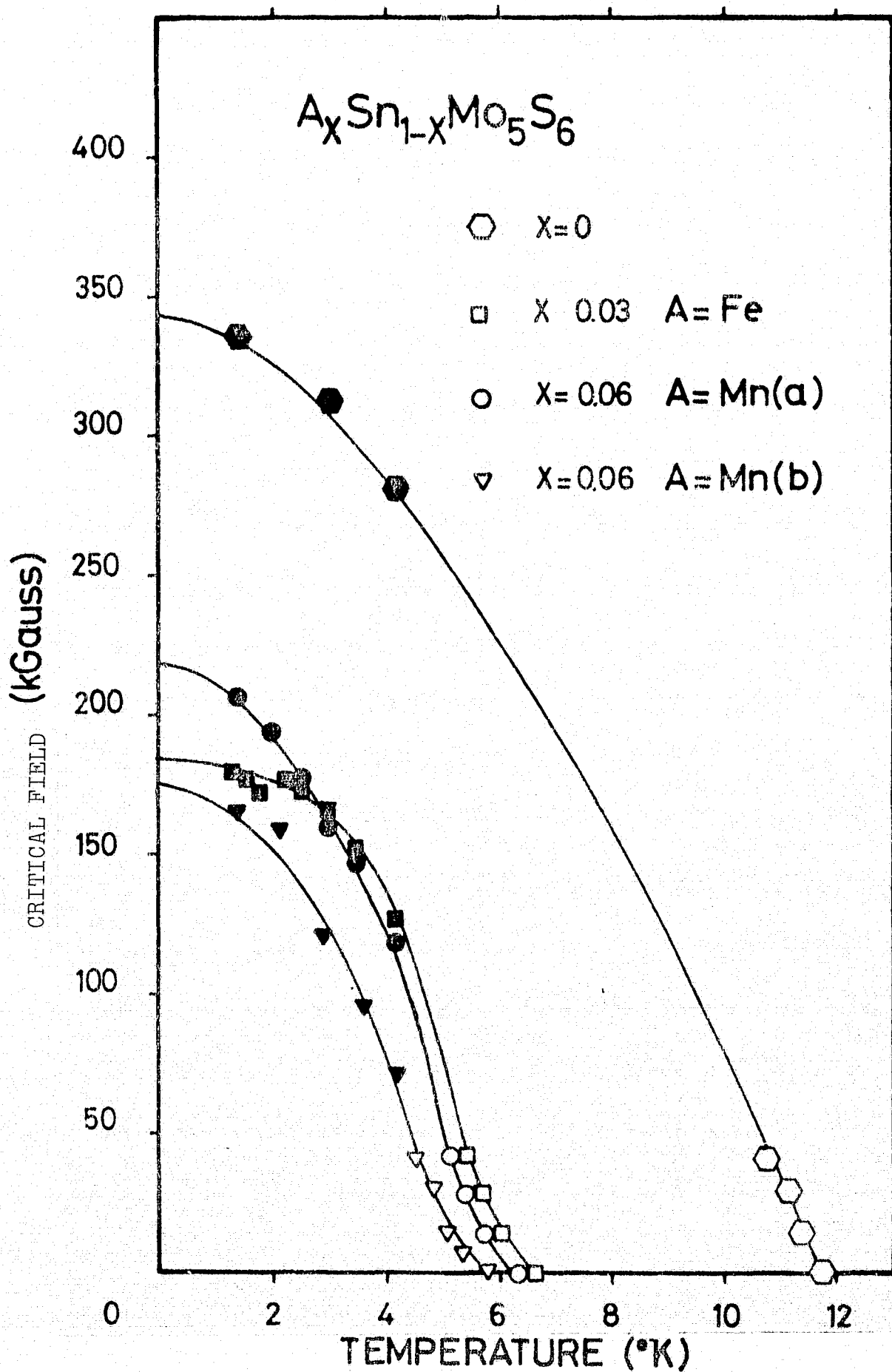
The initial behaviors of the $H_{c2}(T)$ curves for the compounds containing Fe and Mn (Figures 16, 17, 18), together with the strong decrease in the critical temperature as a function of concentration, make us believe that these impurities have a magnetic influence on the electrons.

e) Theory and experimental critical fields:
"non-magnetic" impurities

/77

In this section we are going to treat the case of impurities (A = Cr, Co, and Gd) for which the behavior of the critical temperature with concentration is not what is expected for magnetic ions.

Figure 16. H_{c2} as a function of T for magnetic impurities



Let us assume that these impurities do not have any magnetic effect on the electrons. The experimental results can then be compared with the WHH theory (section 3.d) by the same reasoning which was employed previously (sections 3.e and 4.e).

For the Gd-containing compound, the initial slope is of the order of $-47 \text{ kGauss}/^\circ\text{K}$. The corresponding Maki parameter is 2.5. It can be seen that the point measured at $4.2 \text{ }^\circ\text{K}$ lies a little below the theoretical curve for $\alpha = 2.5$, $\lambda_{\text{SO}} = 13$, drawn in broken line in Figure 14. These values of α and λ_{SO} are those we assumed for the pure compound (section 3.e) (Figure 15).

For the other two compounds, we could deal with the experimental results only by assuming that the initial slope is larger in absolute value than that of the pure compound ($47 \text{ kGauss}/^\circ\text{K}$). The measurements are compatible with theoretical curves with $\alpha = 3.5$, $\lambda_{\text{SO}} = 6$ for the Cr-containing compound, and with $\alpha = 3$, $\lambda_{\text{SO}} = 5$ for the one containing Co (Figure 15).

Thus, to deal with the experimental results for Cr and Co, it is necessary to assume Maki parameters and spin-orbit coupling constants which are respectively larger and smaller than those considered for the pure compound.

/78

Let us assume that the values of these two parameters are correct for the three compounds (pure, Cr, Co). The increase in the value of the Maki parameter, linked to the increase in the initial slope (section 3.d) can be explained by the following facts.

The additional scattering produced by impurities, which produces the slight decrease in critical temperature, increases the resistivity of the pure compound in the normal state. Now, in the dirty limit, which we are using to apply the WHH theory (section 3.d), the Maki parameter can also be written:

$$\alpha = 2.35 \rho \gamma \quad (8)$$

where ρ is the resistivity in the normal state (ohm-cm);
 γ is the specific heat ($\text{erg}\cdot\text{cm}^{-3}(\text{°K})^{-2}$).

Assuming that γ remains constant, it can be seen that an increase in ρ increases α , thus increasing the absolute value of the initial slope.

Experimental verification of this variation in ρ is possible in principle, but is difficult in practice for two reasons:

- the distance between the contacts for measuring the voltage is known only to about 2 mm out of an average distance of 5 mm;
- in the normal state, the resistance between the grains certainly varies widely from one sample to another.

These two effects can mask a real variation in the resistivity. Taking the average value of the distance between the contacts, the resistivity ratio does not always correspond to the ratio of the Maki parameters. In view of the imprecision in sample length, one could just as well have equal resistivities or resistivities in the same ratio as the α . /79

It cannot be believed that the resistivities could vary that much for 18% of the tin being replaced by another element. Another possibility of understanding the results is thus to question the value of the Maki parameter for the pure sample determined from the initial slope (section 3.e).

The low-temperature experimental points for SnMo_5S_6 do allow several values for α and λ_{SO} (for example, $\alpha=3$, $\lambda_{\text{SO}}=5$ instead of $\alpha=2.5$, $\lambda_{\text{SO}}=13$); only the initial slope pushed us to take $\alpha \approx 2.5$. The $\Delta T/T_c$ interval in which measurements are possible below 4.2° K is larger for the compounds containing impurities than for the pure compound, and so determination of α and λ_{SO} from these measurements is easier. From this point of view, it would be the values determined

for the pure compound which ought to be in doubt, instead of those determined on the compounds containing impurities.

We have mentioned that the drop in critical temperatures observed in these samples cannot be attributed entirely to additional scattering on impurities (section 5.c). The phenomenon which produces this drop can also be the cause of the variation in the initial slope (Maki parameter).

We also recall the reservations given on the subject of the large value of λ_{SO} (section 3.e) for the compound SnMo_5S_6 . We suggested that this compound might be at the pure limit (section 3.e). If it is assumed that the decrease in critical temperature for the compounds containing Cr and Co is due at least in part to additional scattering on the atoms introduced, the pure-limit assumption is no longer applicable to these compounds. This could explain why agreement with the WHH theory, which involves reasonable spin-orbit coupling parameters (of the order of unity), is better for the samples which contain Cr and Co than for SnMo_5S_6 .

/80

As we shall see in section 5.g, it is not necessary to consider that the agreement of the experimental points with the WHH theory (non-magnetic impurities) is a proof that the electrons are not affected by any magnetic influence of the ions. The only thing which can be said is that the measurements are compatible with such an explanation.

f) Critical fields of compounds containing magnetic impurities: theoretical survey

/81

The WHH theory [16] introduced in section 3.d can be generalized to superconductors containing magnetic impurities [14]. The theory generalized in this way takes into account effects of orbital diamagnetism and spin paramagnetism, of scattering, magnetic or not, and of the presence of magnetic impurities. It does not include spin dynamics due to possible spin-spin interactions.

With the same assumptions used by WHH,

$$H_{c2}(c,T) = \frac{1}{0.281} H_{c2}^*(c=0,T=0) h(t) \quad (9)$$

where $t = T/T_{c0}$;

and $h(t)$ is the solution of an equation similar to Equation (5) [14]. However, this equation involves two additional parameters: the reduced exchange field h_j and the exchange scattering constant λ_m .

The equation obtained shows that if H_J is opposed to the exterior field, $H_J = H_{c2}(c,T)$ and $\alpha = 0$ are equivalent [14]. In other words, if the exchange field is equal to the critical field at a given temperature, the critical field is then equal to the orbital limit $H_{c2}^*(c,T)$.

The orbital limit is given as a function of concentration and temperature by:

$$H_{c2}^*(c,T) = H_{c2}^*(c=0,T) - H_{c2}^*(c=0,T=0) \frac{\lambda_m}{\lambda_{m\text{crit}}} \quad (10)$$

where $\lambda_{m\text{crit}} \approx 0.281$ is the critical value of the exchange scattering constant above which all superconductivity is destroyed [14, 27]. /82

Comments:

1) $\lambda_m/\lambda_{m\text{crit}} = c/c_{\text{crit}}$, where c_{crit} is the critical value of the concentration above which all superconductivity is destroyed.

2) The second term of the right-hand member of Equation (10) is a constant independent of temperature.

A reduced critical field is defined as [14]:

$$H_{\text{red}}(c,T) = \frac{H_{c2}(c,T)}{H_{c2}^*(c,T)} H_{c2}^*(c=0,T) \quad (11)$$

At a fixed temperature low enough for the magnetic ions to be aligned at $H = H_{c2}(T)$, study of this field as a function of concentration

allows us to say whether or not there is compensation [14]. If there is compensation, the H_{red} curve as a function of concentration has a maximum [14]. This process is the surest way of showing compensation. In addition, it allows determination of various important parameters of the theory, especially H_J , α , and λ_{SO} [14]

For a given concentration effect, the compensation effect can, however, also be revealed by analysis of the experimental $H_{\text{c}2}(T)$ curve.

At low fields (near the critical temperature) the magnetic ions are not completely aligned, and the field behaves approximately as:

$$H_{\text{c}2}^0(c, T) = H_{\text{c}2}^e(T) - \text{constant} \quad (12) \quad /83$$

where $H_{\text{c}2}^e(T)$ is the experimental critical field for the pure compound. This is for the following reasons. Since the exchange field is weak, its effect on electron spins is weak. At low fields, the paramagnetic effects of the exterior field are also weak. The critical field must thus follow a curve approximately like that for $H_{\text{c}2}^*(c, T)$, which is given by Equation (10), as if there were no effects on the spins.

On lowering the temperature, the experimental values must leave this curve to the extent that the ions are aligned and that the exchange field increases. Let us assume that the exterior field is opposed to the exchange field. As soon as $H_{\text{c}2}(c, T) = H_J$, there is compensation, and $H_{\text{c}2}(c, T) = H_{\text{c}2}^*(c, T)$, which is the maximum value $H_{\text{c}2}(c, T)$ can assume. Continuing to lower the temperature, $H_{\text{c}2}(c, T)$ increases and exceeds H_J ; there is no longer compensation, and $H_{\text{c}2}(c, T)$ again becomes smaller than $H_{\text{c}2}^*(c, T)$.

To obtain this result it is, of course, necessary that the equality $H_{\text{c}2}(c, T) = H_J$ can be achieved in the available temperature interval.

In summary, when the temperature decreases, the experimental field must approach the theoretical $H_{\text{c}2}^*(c, T)$ curve given by Equation (10), then move away from it.

g) Theory and experimental critical fields:
magnetic impurities

Interpretation of the experimental critical fields for the compounds containing Mn and Fe is even more difficult than it was in section 5.e [for non-magnetic impurities]. A sure interpretation would be possible only if other results were known. In particular, the susceptibilities and the critical fields of compounds with other impurity concentrations would give valuable information. The experimental difficulties, especially those related to measurement of high critical fields, and the level of effort, necessarily limited to a dissertation, did not allow these measurements.

Effects on Electron Spins

In Figures 17 and 18, the dotted curves (.....) show the critical field $H_{c2}^0(c,T)$ [Equation (12)] which would be expected if there were no effect on the electron spins. The experimental values below 4.2° K are much higher than these curves.

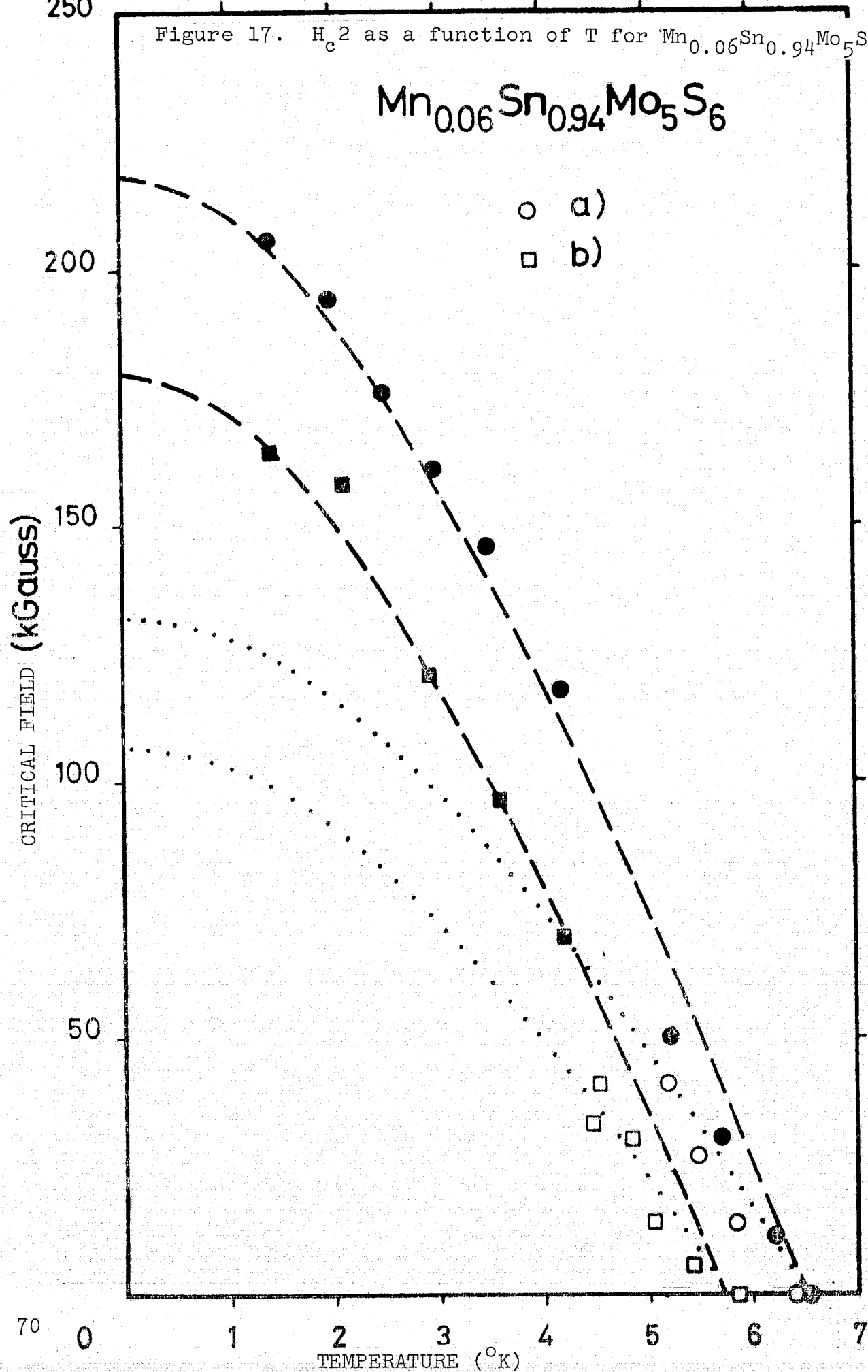
Insofar as these compounds behave like known superconductors, this shows the importance of spin effects.

The curve used for $H_{c2}^e(T)$ is in fact the interpolation of the experimental points for the pure sample by the theoretical WHH curve (section 3.d) with $\alpha = 2.4$, $\lambda_{so} = 13$ (3.e). The H_{c2}^0 curve depends quite strongly on the interpolation used. For the pure sample, it seems that α has a value larger than 2.5 instead of smaller (5.e, 3.e). For an interpolation of H^e by means of a theoretical curve for which α is larger than 2.5, the H_{c2}^0 curve lies below the one drawn. Thus the spin effect shown in Figure 17 and 18 is underestimated rather than overestimated.

/85

Samples containing Mn

The experimental points, both resistive and inductive, below 50 kGauss have roughly the expected behavior. For the two samples,

Figure 17. H_c2 as a function of T for $Mn_{0.06}Sn_{0.94}Mo_5S_6$ 

the experimental critical fields below 4.2° K fall on the theoretical $H_{c2}^*(c,T)$ curves given by Equation (10), in which $H_{c2}^*(c=0,T)$ was calculated with an α of 3.5. These $H_{c2}^*(c=0,T)$ curves are drawn in broken lines (-----) in Figure 17. To apply Equation (10), one simply proceeds in the following manner. The curve is translated along the field axis until the curve cuts the temperature axis at $T = T_c$. Thus, below 4.2° K, the experimental behavior of the critical field thus no longer corresponds to what was described in the preceding section.

There would be compensation whatever the value of the field below 4.2° K.

Faced with this fact, three attitudes can be adopted:

- doubt that the WHH theory and its generalization apply to these substances;

- doubt that the impurities have a magnetic interaction with the electrons;

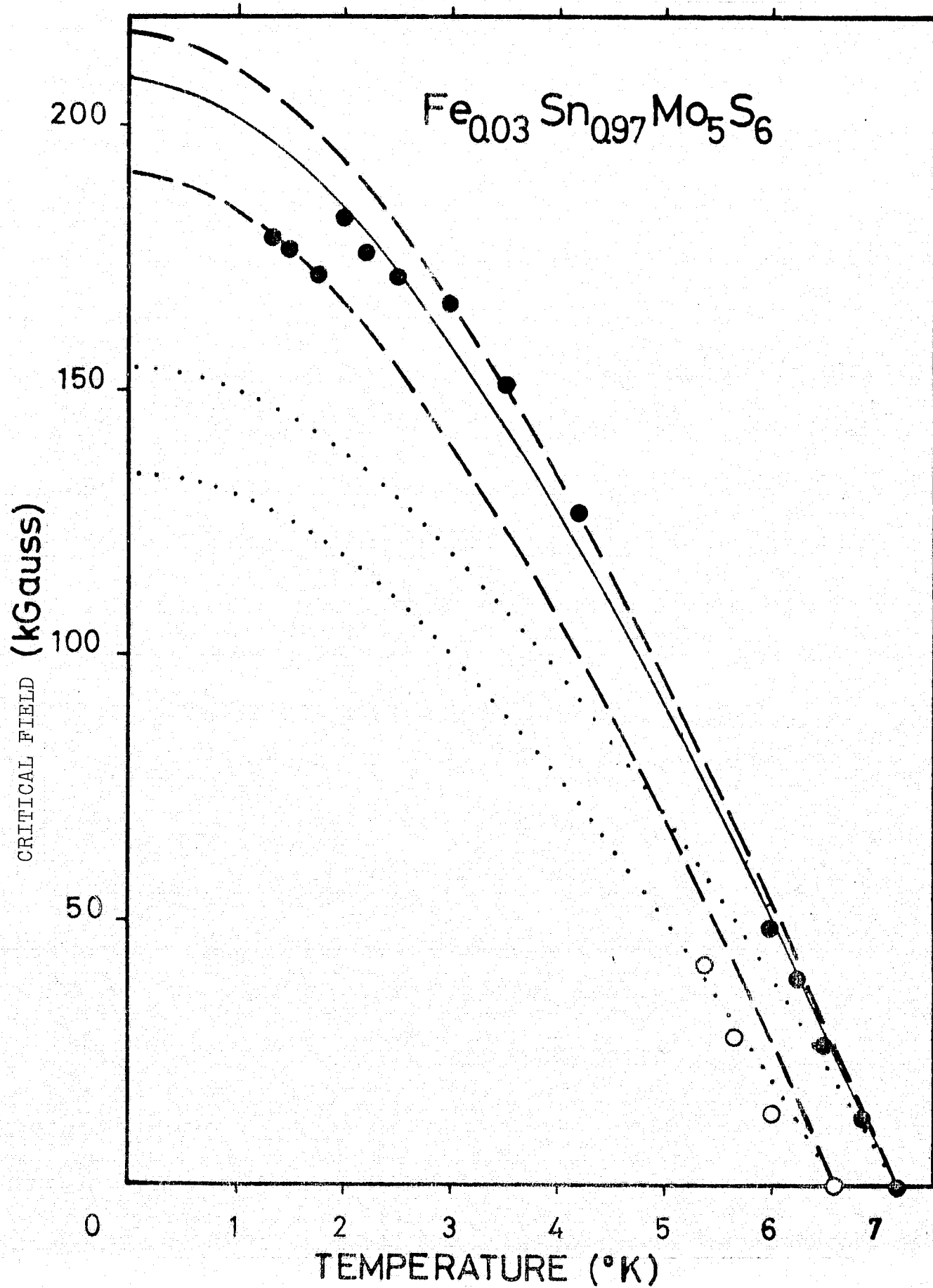
- assume that the theory applies, and that the impurities do have a magnetic interaction with the electrons.

/87

The first attitude needs no comment and would terminate the discussion.

Supporting the second attitude is the fact that the experimental results below 4.2° K are also in good agreement with the theoretical WHH curves (non-magnetic impurities, as in section 5.3). The parameters of these curves are: $\alpha = 3$, $\lambda_{so} = 10$ for sample (a) and $\alpha = 2.5$, $\lambda_{so} = 13$ for sample (b). These parameters are of the same order of magnitude as those assumed in sections 5.e and 3.e. The curves are practically the same as those for $H_{c2}^*(c,T)$, so they have not been drawn. On the negative side — and this seems decisive — it is true that the behavior of the experimental critical field below 50 kGauss, and in any event the inductive measurements and

Figure 18. H_{c2} as a function of T for $\text{Fe}_{0.03}\text{Sn}_{0.97}\text{Mo}_5\text{S}_6$



especially the rapid fall-off of T_c with concentration make one believe in the existence of a magnetic interaction.

Finally, let us discuss the consequences of the third attitude. It might be assumed that the value of α is in fact much larger than it is for the pure sample. This hypothesis does not seem very solid: for one thing, the value of α used here is already larger than that for the pure sample (3.5 instead of 2.5); for another, all the other measurements (sections 3.e, 4.e, and especially 5.e) give values of α less than or equal to 3.5.

Another solution is to assume that compensation is effective for all values of the field below 4.2° K. It is then necessary that the exchange field be able to assume values lying between about 70 and 210 kGauss, so that there would always be regions in the sample which are compensated. This is made possible by the following facts. The exchange field in a superconductor is averaged over distances of the order of the coherence length. In these compounds the average distance between the magnetic ions is of the same order of magnitude as the coherence length (a few tens of Å). For randomly distributed impurities, this allows values of the exchange field to lie within a large range. /89

Sample Containing Fe

First of all, we note the disagreement between the resistivity and inductive values of the critical temperature. This disagreement even extends to the initial values of $H_{c2}(T)$. It is probably due to the fact mentioned in sections 3.c and 4.c that resistivity measures the transition of the first superconducting filament, while susceptibility measures that of the sample as a whole. However, we see that the resistivity value of T_c is almost unvarying for measuring currents of 50, 100, and 500 mA.

The curves drawn in broken line (-----) in Figure 18 are those for $H_{c2}^*(c,T)$ [Equation (10)] for $\alpha = 3$ (cf. the preceding sub-section). The solid curve shows the theoretical WHH curve (non-magnetic

impurities, as in section 5.e) for parameters $\alpha = 2.5$, $\lambda_{so} = 13$ (which are those for the pure sample). It should be stated for clarity that these three curves have been drawn as examples: the fact that each corresponds to a series of three experimental points was /90 not considered to be significant.

Faced with these experimental results, the three reactions mentioned in the preceding sub-section are also possible. The arguments are the same, except for what follows. The resistivity initial slope does not indicate any magnetic interaction. The values below 3° K behave differently from the way the critical field would for a compound which does not contain magnetic impurities. This behavior corresponds roughly to what is expected in compensation, with a maximum exchange field of the order of 165 kGauss.

Conclusions

If these substances behave like other superconductors — that is, if temperature, magnetic field, and the presence of magnetic impurities are equivalent in pair breaking — it can be said that:

- the drop in critical temperature comes from a magnetic interaction;
- the effects on electron spins are important.

The principal question is then to know whether the WHH theory (weak coupling, spherical Fermi surface) and its generalization [14] apply, at least approximately. This question is still in large measure an open one.

6. STRUCTURE AND SUPERCONDUCTING PROPERTIES

In this chapter we are going to look at the principal factors connected with the structure of the Chevrel phases which seem to have a relation to the superconducting properties of some of these phases. Tellurides will not be discussed — up to now they have not given any superconductor — because their detailed structure is not known.

/91

The information gathered on these compounds is voluminous enough to allow much speculation. It is insufficient or too scattered, however, to allow a coherent overall explanation of their properties. What follows will thus of necessity be partial and speculative.

a) Critical temperature and structure

Situation before Knowledge of Mo_3S_4

Before the existence and preparation [4, 9] of Mo_3S_4 were known, the relationship between the critical temperature and the structure of the ternary molybdenum sulfides could be summarized as follows [7, 17, 12].

Structural instability prevents Mo_3S_4 from existing, but creates a situation favorable for the appearance of superconductivity. The interstitial M element (section 2.a), introduced between the Mo_6S_8 sub-units, stabilizes the structure and thus in some cases makes it possible for superconductivity to appear. The diversity of critical temperatures was then related to the ionic character of the M-S bonds [7]: the more ionic the M-S bond, the lower the critical temperature. The critical temperature of the compounds for which the M-S bond is practically covalent is thus essentially dependent on the lattice volume [7].

/92

The ionic character of the M-S bonds, calculated from the differences in the Pauling electronegativities of S and M, divides the superconducting sulfides into two quite distinct groups: in the first, M = Mg, Sc, and Y; in the second, M = Zn, Cd, Ag, Cu, Sn, and Pb. According to the scheme above, the critical temperatures of the second group ought to depend on the lattice volume: the greater the volume, the higher the critical temperature. However, Zn gives a critical temperature of 2.4° K [1] and has a lattice, calculated from the values of [2], larger than Ag and Cu, which have temperatures of 8.9° K [1] and 10.9° K, respectively; it is thus seen that this scheme is not really complete.

The four compounds with the highest critical temperatures (M = Ag, Cu, Sn, Pb) have two characteristics in common:

- M has an even natural valence, although for the compounds which have a low or zero critical temperature this valence is odd.
- The Pauling electronegativity of M is equal to (Sn and Pb) or slightly larger than (Ag, Cu) that of Mo. For the other compounds it is less than that of Mo.

The fact that Mo_3S_4 does exist and is not a superconductor changes some of the fundamentals of the problem. Fundamentally, this can be attributed to two causes:

/93

- deformation of the Mo_3S_4 structure;
- role played by the M element (see following section).

Influence of Lattice Symmetry

Mo_3S_4 has a slight triclinic deformation of the lattice [9], which is rhombohedral for the ternary molybdenum sulfides with the highest values of T_c [2]. It may be that this departure from the "ideal symmetry" is enough to destroy superconductivity. Besides, it can be accepted that a structural deformation is one of the

possible explanations of Mo_3Se_4 produced from $\text{Fe}_{0.6}\text{Mo}_3\text{Se}_4$ not being a superconductor (section 4.c).

However, it is surprising that a slight deformation would be sufficient to destroy superconductivity when it is known that CuMo_4S_5 undergoes a structural transformation at 260°K [12]. Below this temperature the lattice is orthorhombic, while it is rhombohedral — as it is for the other ternary sulfides — at 300°K [12]. CuMo_4S_5 is still a superconductor, however.

Neither InMo_5S_6 and AgMo_4S_5 [12] nor, it seems, $\text{Pb}_{0.9}\text{Mo}_{5.1}\text{S}_6$ [7] undergo such a transformation.

Variation of T_c with Thermal Treatment

From the structural point of view, there are three large differences between the copper-containing sulfide, on the one hand, and those with lead and tin, on the other:

- the compound with copper is a solid solution, whereas the other two are phases with fixed compositions.

/94

The Cu atoms can lie in the interstitial channels centered on $(x,y) = (0,1/2)$ or $(1/2, 0)$ (section 2.a), which is not the case for Sn or Pb.

- the compound with copper can, in principle, be written $\text{Cu}_2\text{Mo}_6\text{S}_8$, while the others are $\text{M}_x\text{Mo}_{6-x}\text{S}_6$ or $(\text{M}_y\text{Mo}_{2-y})\text{Mo}_6\text{S}_8$. In the latter case there are thus $(2-y)\text{Mo}$ interstitials per sub-unit (section 2.a) according to the interpretation of the Rennes group.

Study of the variation of the critical temperature with annealing conditions of both large and small pellets has shown that the compounds with copper have a different behavior from those with lead and tin (section 3.a). This difference in behavior is attributable to two primary structural dissimilarities. Annealing at low temperatures, harmful to superconductivity for compounds with copper

(partial transitions) may force some of the copper atoms to occupy unfavorable positions [for example, $(x,y) = (0,1/2)$ or $(1/2,0)$].

b) Role of interstitial elements

/95

The role played by interstitial elements, both for structure and for superconducting properties, is multifold. In the structure, these elements can:

- 1) stabilize the structure;
- 2) influence several structural characteristics, especially the volume and symmetry of the lattice, the shape of the sub-units and of the inter-unit "cubes";
- 3) supply electrons;
- 4) separate the Mo_6 "clusters" both spatially and in terms of bonding.

It is evident that all these aspects are not independent — sometimes they are even contradictory.

The importance of points 1) and 2) for superconductivity is difficult to estimate. We have already pointed out in the preceding section and in section 4.a the roles which may be played by structural stability, lattice volume, and crystal symmetry, and we shall not discuss them again. The shapes of the sub-units and the inter-unit "cubes", together with the "intercluster" distance, are more or less directly related to these two characteristics.

Introduction of Al and In into Mo_3S_4

We have introduced Al and In into Mo_3S_4 to try to determine the importance of point 3) for superconductivity. Although the phases do form, the compounds obtained are not superconductors (sections 4.a and 4.b).

/96

Thus, it appears that adding electrons between the sub-units is not enough to make Mo_3S_4 a superconductor.

The electronegativities and covalent radii of Al and In are nevertheless of the same order of magnitude as those of Zn and Cd, which do lead to superconducting phases [1]. Two differences appear between these two groups of elements:

- the phases have generic formulas $M_x Mo_6 S_8$ for $M = Al, In$ [9], and $MMo_5 S_6 = M_{1.3} Mo_{6.7} S_8$ for $M = Zn, Cd$ [1]. If one accepts the interpretation of the Rennes group [9] (section 2.a), there are thus 0.7 Mo interstitials on the average per sub-unit in the second group, while there are none in the first. It would be interesting to know whether the $M_2 Mo_6 S_8$ phases with $M = Zn$ or Cd , which do exist [2], are also superconductors. If not, it could be thought that the superconductivity of $M_{1.3} Mo_{6.7} S_8$ ($M=Cd, Zn$) is due to the presence of interstitial Mo.

- Al and In are naturally trivalent, while Zn and Cd are divalent.

Introduction of a Fourth Element into $SnMo_5 S_6$

The $A_{0.5} SnMo_5 S_6 = A_{0.7} Sn_{1.3} Mo_{6.8} S_8$ ($A = Al, Ga, Nb$) phases have critical temperatures higher than that of $SnMo_5 S_6$ [10]. However, if more Nb or $V_{0.5}$ of Cu is added, the critical temperature decreases [10]. For a larger amount of Al, the phase does not form, and the critical temperature therefore does not change.

Likewise, replacing 12% of the tin in $SnMo_5 S_6$ by gadolinium increases the critical temperature (section 5.c). Examination of the x-ray diffraction patterns shows that the phase contains at least some Gd [9]. Since gadolinium is magnetic, the explanation of this phenomenon is that the decrease in critical temperature due to the presence of magnetic ions is over-compensated by an increase in this temperature related to the introduction of Gd. One would thus expect quite a large increase in critical temperature if, instead of replacing part of the tin by gadolinium, it were replaced by an element which is chemically similar to Gd, but non-magnetic.

/97

The fourth elements which increase T_c are all trivalent. In addition, the effect becomes larger as the electronegativity of the element is smaller — in particular, smaller than that of Mo. This seems to indicate that addition of electrons is not negligible in increasing the critical temperature.

The characteristics of the fourth elements are not like those we deduced for the third element in the ternaries, however (preceding section). This finding does not necessarily have to cast doubt on either of the two criteria. A third element with certain characteristics is needed to obtain superconductivity; then a fourth element which increases T_c has different properties.

In some phases which do not have the $M_x Mo_6 S_8$ formula, but rather $M_x Mo_{6-y} S_8$, there is reason to suspect that interstitial Mo has a role similar to that of the fourth element.

Ideal Number of Interstitial Atoms per Sub-Unit

/98

The exact formula for the tin compound is $Sn_{1.2} Mo_{6.34} S_8$; with addition of aluminum it becomes $Al_{0.6} Sn_{1.2} Mo_{6.34} S_8 = Z_{1.94} Mo_6 S_8$ [9]. There are thus almost two interstitial atoms per sub-unit.

In $Cu_x Mo_6 S_8$ (second 3.d) the critical temperature becomes lower when x is greater than 2.

In $A_y Sn_{1.2} Mo_{6.34} S_8$ ($A = V, Nb, Cu$), we do not know the exact value of y beyond which the critical temperature [decreases]; this value is approximately 0.6, which also leads to about 2 interstitial atoms per sub-unit.

These three effects are certainly more than coincidence. Let us assume [9] that the small-radius elements can occupy sites in the channels centered on $(x,y) = (0,1/2)$ and $(1/2,0)$ (section 2.a), and also that the Z atoms are favorable to superconductivity. It then seems reasonable to say that:

- the "ideal" number (for superconductivity) of interstitial Z atoms per sub-unit is approximately 2;

- when this number is greater than 2 and the phase continues to form, the critical temperature falls. This occurs only for small-radius M atoms which can lie in the channels centered on $(x,y) = (0,1/2)$ and $(1/2,0)$;

- if Z has too large a radius, there cannot be two per sub-unit — for example, because of reasons involving stability of the phase. It is, however, possible to complete the number of interstitial atoms per sub-unit by introducing other elements with smaller radii. This leads to the two possibilities discussed above.

It may be that the Z elements in the channels centered on $(x,y) = (1/2,0)$ and $(0,1/2)$ create inter-unit Mo-Mo bonds.

/99

Comparison of Structures

Comparing the description given for the structure of $\text{Pb}_{0.98}\text{Mo}_{6.4}\text{S}_8$ [7] with the ones for the structure of Mo_3Se_4 [5] and $\text{Ni}_{0.66}\text{Mo}_6\text{S}_8$ [6], one is struck by the difference in the lengths of the inter-unit Mo-Mo bonds.

In Mo_3Se_4 and $\text{Ni}_{0.66}\text{Mo}_6\text{S}_8$, the inter-unit Mo-Mo bonds are strong because the inter-unit and intra-unit Mo-Mo distances are nearly the same. In addition, the interstitial M element (Ni) creates supplementary indirect inter-unit Mo-Mo bonds. The Mo-M and Se-M distances are nearly the same.

In contrast, the inter-unit Mo-Mo bonds in the sulfides are weak. The inter-unit Mo-Mo distances are much larger than the intra-unit Mo-Mo distances. Thus, the Mo_6 "clusters" are collected inside the cages of sulfur atoms, which is not the case for the selenides mentioned. In addition, the Mo-M distances are much longer than the M-S distances, which makes one think that the Mo-M bonds are weak.

The details of the structure of Mo_3S_4 are not known, so it is not possible to talk about the Mo-Mo distances in this compound.

Let us connect what we have just seen with the following facts:

- the critical temperature of Mo_3Se_4 is not as high as it is for some of the ternary sulfides;

- addition of interstitial elements to Mo_3Se_4 either does not increase, or decreases, the critical temperature, or removes it altogether (section 4.b).

The main point resulting from the preceding two subsections is /100 that the best values of T_c are obtained for Mo_6 "clusters" which are well separated from each other. By "separation" we mean both spatial distance and the absence of direct "intercluster" Mo-Mo bonds.

This separation can have several objects:

- to prevent the electrons from having direct passage from one "cluster" to another, thus requiring them to travel via the atoms situated at the corners of the "cubes" (S or Se);

- to keep the "clusters" independent of each other in terms of vibrations;

- to create optimum "intercluster" distances.

Remarks on Interstitial Molybdenum

Several times in this section and the preceding one we have seen the effect which the presence of interstitial molybdenum could have. Such presence may give another possibility for explaining the fact that Mo_3Se_4 obtained by direct synthesis is a superconductor, while Mo_3Se_4 obtained by "washing" $\text{Fe}_{0.6}\text{Mo}_3\text{Se}_4$ with HCl (section 4.a) is not (section 4.c).

The existing range of Mo_3Se_4 in fact extends from $\text{Mo}_3\text{Se}_{4.2}$ to $\text{Mo}_{3.15}\text{Se}_4$ [5]. Extra selenium and molybdenum atoms are introduced into the channels as interstitial elements [5]. The " Mo_3Se_4 " obtained by direct synthesis has every chance of not being stoichiometric. The fact that it is a superconductor would thus be due to the interstitial Mo or Se atoms. Mo_3Se_4 obtained by "washing" the iron compound with HCl, on the other hand, has a good probability of being stoichiometric. Thus, the presence of iron decreases the chance that Mo and Se would be sitting in the channels and, if HCl removes the Fe, there is apparently no reason why it should not also remove any interstitial Mo and Se atoms. The lack of superconductivity in the compound produced this way would thus be due to a lack of atoms in the channels.

/101

This explanation also holds for Mo_3S_4 which is obtained by "washing" (of CuMo_3S_4) with HCl.

Conclusions

In brief, in this section we have brought out two aspects of the role played by the interstitial element:

- it introduces electrons into the structure;
- in a general sense of the term, it separates the Mo_6 "clusters" from each other.

Of course, the other aspects of this role, mentioned or not, also have their importance.

For deviation from ideal $\text{M}_x\text{Mo}_3\text{S}_4$ (or $\text{M}_x\text{Mo}_3\text{Se}_4$) stoichiometry (section 2.a), it is the interpretation of the Rennes group [9, 5] which has been used in this discussion, rather than that of Marezio et al. [7]. This choice is an a priori one which is not based on any experimental fact. It has seemed to us that the interpretation of the Rennes group was clearer, easier to apply, and intuitively more plausible. The discussion made here in terms of additional molybdenum atoms could also be made in terms of missing sulfur

(or selenium) atoms. It does not seem that this would produce any more information, however.

c) Pressure and structure

/102

Several times we have pointed out some of the effects of pressing the powders. With the pressed powders, we observed:

- abnormally wide transitions (section 2.c);
- transitions beginning at higher temperatures (2.c);
- the appearance of superconductivity in Mo_3S_4 (4.a);
- the almost complete disappearance of superconductivity in SMo_3Se_3 , $\text{S}_2\text{Mo}_3\text{Se}_2$, $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$ (4.c);
- the increase in the transition temperature of Mo_3Se_4 (4.c)

All this allows us to say that pressure makes the substances inhomogeneous from the standpoint of superconductivity.

Until now, x-rays have not given any information about the effect pressure could have on structure. In terms of deformation, it is probable that pressure produces a deformation of the inter-unit cubes or a relative displacement of the cubes. It would be surprising if the sub-units, which are made rigid by the presence of the Mo_6 "clusters", could be deformed. In terms of bonds, this amounts to saying that pressure acts on the inter-unit bonds rather than on intra-unit bonds. It is also probable that some atoms are forced to occupy unfavorable interstitial positions, or that they are moved from favorable positions when the powders are pressed.

This high sensitivity to pressing is probably related to the instability of the structure.

d) Critical field and structure

/103

The large values of $H_{c2}^*(T=0)/T_{c0}$ and of the initial slope for the sulfides (sections 3.c, 3.e) indicate a very localized behavior of the superconducting electrons. This localization can be

considered the result of difficulty for the electrons to pass from one Mo_6S_8 sub-unit to another. According to section 6.b, this passage is easier in Mo_3Se_4 and $\text{Cu}_{1.3}\text{Mo}_3\text{Se}_4$, since for these substances the $H_{c2}^*(T=0)/T_{c0}$ ratios are smaller.

The difference between the behavior of the $H_{c2}(T)$ curves for the tin and lead compounds and their behavior for the copper compounds is important (section 3.c). In section 6.a (variation of T_c with thermal treatment), we have seen the structural differences between these two groups of compounds. The latter two differences have the most influence on the behavior of the $H_{c2}(T)$ curve.

The first steps of a metallurgical study of three $M_x Mo_{6-x} S_6$ $M = Cu, Sn, Pb$ sulfides have been made. They have allowed correct superconductor transitions to be obtained. The high values of $H_{c2}(T=0)/T_{c0}$ for some of the sulfides are one of the most interesting aspects of the results obtained. Another interesting aspect is the difference between the behavior of $H_{c2}(T)$ for the copper sulfides and its behavior for the other sulfides.

Aside from the fact that Mo_3S_4 is not a superconductor under normal conditions, the study of new compounds has not led to any very spectacular results. The measurements made have, however, improved our understanding of the ternary compounds of molybdenum.

Although the compensation effect was not definitely seen, study of compounds containing impurities has opened a possible path in that direction.

It can be said that this work is a first experimental approach to the superconducting properties of some of the ternary molybdenum compounds.

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/105

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