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Solid State Studies in Ceramic Alloys

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Research Institute for Advanced Studies
(RIAS)

Martin Marietta Corporation
1450 South Rolling Road
Baltimore, Maryland 21227



Principal Investigators

Robert G. Lye
Robert G. Lye

John D. Venables
John D. Venables

Program Director

A.R.C. Westwood
A.R.C. Westwood

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Phase A. Band structure and bonding studies of the refractory carbides, nitrides and their alloys. Dr. R. G. Lye (Principal Investigator.)

1. Interatomic charge transfer and ionic bonding in TiC.

The magnitude and direction of the charge transfer between atoms in TiC has remained in question for several years largely because of the difficulty in obtaining appropriate experimental data. Recently, however, two rather unusual studies⁽¹⁻⁴⁾ have provided evidence in support of our views regarding the electronic structure of the transition metal carbides^(5,6).

a) In an investigation of the energy distribution of photoelectrons produced by X-irradiation (called the ESCA technique by Kai Siegbahn and coworkers⁽⁷⁾, who have developed it to a high level of sophistication), Ramqvist et al.⁽¹⁻³⁾ have observed that the 1s states of the carbon atom lie at higher energies in the transition metal carbides than they do in carbon. For example, they find that the carbon 1s levels are raised by 3.3 eV in TiC, by 2.6 eV in VC, and by 2.9 eV in NbC and TaC. The result for TiC is in rather satisfying agreement with the displacements of the carbon 2s and 2p levels that were employed in Lye's calculations⁽⁵⁾ of the TiC band structure. In these calculations, it was found necessary to raise the 2p levels by 2.77 eV and the 2s levels by 4.15 eV in order to obtain agreement between the experimental reflectivity and photoemission spectra and the optical properties derived from the band structure. The average of these two displacements, 3.46 eV, is unexpectedly close to the value observed by Ramqvist. Moreover, the direction of the displacement is the same as that observed experimentally, even though Ramqvist has concluded that his results disagree with our proposed band structure.

This misunderstanding results primarily from Ramqvist's failure to distinguish between two different parameters that may be required to characterize diatomic or polyatomic solids:

- a) the charge associated with the constituent atoms, and
- b) the occupation of energy bands derived from the electronic states of the different atoms.

The need to distinguish between these parameters is not obvious if only prominently ionic solids such as NaCl are considered, for the electrons that are transferred from the outer shell of the metal atom occupy a single vacancy in the outer shell of the halogen atom to form positive and negative ions having reasonably well-defined radii. The electrons transfer almost their whole charge with them and they occupy energy bands derived almost exclusively from the outer electronic state of the halogen atom.

On closer analysis, however, even some of the alkali halides prove to be more complex than this simple description suggests, and the problems become more apparent in divalent and other polyvalent compounds. In transition metal compounds the incompletely filled d-bands contribute to the difficulty, but the properties of TiC and related carbides can be understood on the basis of a simple model that considers the balance between two opposing effects:

i) The outer electrons of the six metal atoms surrounding a carbon atom overlap onto the carbon atom sites and deposit a negative charge there. Although the outer electrons of the carbon atoms do likewise, there are only two, the 2p-electrons, that contribute appreciably to the reverse overlap charge transfer. Thus, a net negative charge is left within the atomic volume assigned to the carbon atoms.

ii) The negative overlap charge on the carbon atom sites raises the potential energy of the electrons on the carbon atoms, thereby lifting electrons in the upper portions of the bands derived from the 2p-states of the carbon atom to energies above vacant states in the 3d- and 4s-bands of the metal atom. Consequently, these electrons are redistributed into the lower-lying bands, mostly 3d-bands, and transfer negative charge back to the metal atoms. Although the newly occupied 3d-states overlap again onto the carbon atom sites and deposit negative charge there, the net effect of this exchange between 2p- and 3d-states is to transfer negative charge to the metal atom sites.

An equilibrium is established between these two opposing processes when a sufficient number of electrons has been transferred from 2p- to 3d-states that the two sets of energy bands are occupied up to a common Fermi level. This equilibrium is attained in TiC when approximately $1\frac{1}{4}$ electrons have been transferred from the 2p-states of the carbon atom into the 3d-bands of the metal atom. To achieve this balance, however, requires that the 2p-states be elevated by approximately 2.77 eV. The 1s- and 2s-states of the carbon atom are displaced upward also, but possibly by somewhat different amounts because they may be influenced by the surroundings to different degrees.

The equilibrium value of this displacement can be used to estimate the magnitude of the charges associated with the Ti and C atoms, following a method suggested by Professor J. W. McClure (personal communication). The result can then be used to estimate the contribution of ionic forces to the total cohesive energy.

If a negative charge of z electrons is deposited within the carbon atomic sphere and an equal positive charge resides in the metal atomic sphere, the electrostatic potential on the carbon atom is decreased by the excess negative charge within its atomic sphere and is increased by the Madelung potential contributed by the charges on the atoms distributed throughout the remainder of the lattice. If the excess negative charge is distributed uniformly over a carbon atomic sphere of radius r_c , the potential due to this charge is

$$\phi_{cz} = - \frac{ze}{2r_c} \left[3 - \left(\frac{r}{r_c} \right)^2 \right].$$

The average value of this potential over the sphere is

$$\bar{\phi}_{cz} = - \frac{6ze}{5r_c}.$$

The Madelung potential at the carbon atom site is

$$\phi_{cM} = \frac{\alpha ze}{R},$$

where R is the nearest-neighbor atomic separation, i.e. one-half the TiC lattice parameter, and α is the Madelung constant for the rocksalt lattice. These two effects together provide a net change in potential

$$\varphi_c = \bar{\varphi}_{cz} + \varphi_{cM} = -\frac{6}{5} \frac{ze}{r_c} + \frac{\alpha ze}{R}.$$

If the excess positive charge on the metal atoms is distributed uniformly over a sphere of radius r_t , the same two effects change the electrostatic potential at the titanium atom sites by

$$\varphi_t = \bar{\varphi}_{tz} + \varphi_{tM} = +\frac{6}{5} \frac{ze}{r_t} - \frac{\alpha ze}{R}.$$

The difference in potential between the carbon and metal atom spheres is, therefore,

$$\Delta\varphi = \varphi_c - \varphi_t = ze \left[\frac{2\alpha}{R} - \frac{6}{5} \left(\frac{1}{r_c} + \frac{1}{r_t} \right) \right],$$

and the difference in potential energy for an electron, $-e\Delta\varphi$, is

$$\Delta V = ze^2 \left[\frac{6}{5} \left(\frac{1}{r_c} + \frac{1}{r_t} \right) - \frac{2\alpha}{R} \right].$$

If it is assumed that TiC can be represented as a close-packed array of metal atoms with carbon atoms in the octahedral interstitial positions, then $r_t \approx R/\sqrt{2}$ and $r_c = R(\sqrt{2} - 1)/\sqrt{2}$. Thus

$$\begin{aligned} \Delta V &= \frac{ze^2}{R} \left[\frac{6}{5} \left(\frac{\sqrt{2}}{\sqrt{2}-1} \right) - 2\alpha \right] \\ &\approx 2.302 \, ze^2/R, \\ &\approx 15.32 \, z \, \text{eV}, \text{ if } R = 2.165 \, \text{\AA}. \end{aligned}$$

If the average, 3.41 eV, of the experimentally observed displacement of the 1s- level and the empirical displacements of the 2s- and 2p- levels is used for ΔV , there results the value

$$z = \Delta V / 15.32 = 3.41 / 15.32 = 0.2225e.$$

The electrostatic interactions between these separated charges contribute an amount $\alpha(ze)^2/R$ per ion pair to the total cohesive energy. For the value of z estimated here, the ionic contribution is 0.575 eV, or 13.2 kcal/mol. Thus, these ionic forces are a small fraction ($\approx 4\%$) of the total cohesive energy of TiC (327.6 kcal/mol).

Although these estimates of z and of the ionic contribution to the cohesion are admittedly imprecise, they are in qualitative agreement with the behavior anticipated from the small difference in electronegativities of the two atoms of TiC.

It should be noted that Ramqvist also has estimated a value for z by rather different methods and obtained $z \approx 0.4 e$, which would imply that the ionic contribution to the cohesion is approximately 42.8 kcal/mol, or 13% of the total. Although Ramqvist's estimate is more than three times as large as the value obtained here, both are subject to uncertainties that make a quantitative comparison meaningless at present. In any event, both estimates indicate that the ionic bonding provides a small fraction of the total cohesive energy. The remainder of the cohesion arises from band formation in the manner described in detail previously.

Ramqvist has also examined the low-lying electronic states of the metal atom in TiC and finds that they are depressed relative to the corresponding states of the pure metal. Moreover, the magnitude of the displacement increases with increasing carbon content. Although a detailed analysis has yet to be made, this behavior can be understood if the position of the Fermi level is determined primarily by the distribution in energy of the 3d-bands of the metal atom and by the number of electrons available to occupy these bands. Thus, as the carbon content is increased, the 2p-electrons contributed by the carbon atoms fill the 3d-bands to increasingly higher energies. The distance below the Fermi level at which the 1s- and 2p-states lie consequently increases with increasing carbon content, in agreement with Ramqvist's observations. Indeed, the change in the displacement of the

$2p_{3/2}$ -state of the metal atom observed by Ramqvist for compositions in the range $TiC_{0.59}$ to $TiC_{0.97}$ agrees within experimental error with the elevation of the Fermi level predicted by the band structure we have proposed for TiC .

These observations by Ramqvist thus provide unexpected support for our model of the electronic structure and bonding in the carbide, despite his conclusions to the contrary. Additional support has been provided also by Merisalo and coworkers⁽⁴⁾ at the University of Helsinki, who have examined the charge distribution in NbC using X-ray diffraction techniques. Completed copies of this paper are not yet available, so analysis of their results must be delayed until a later report.

2. Optical Reflectivity. (Dr. J. P. Martin, Co-Investigator, not funded under this Contract.)

a) Broad-band reflectivity.

In the previous quarterly report on this Contract, the electronic specific heat of VC_x was discussed. The results indicated that as the carbon content was increased the Fermi level swept through a peak in the density-of-states curve. This behavior suggested that a critical point may exist near the Fermi level of VC , and that electronic states in the bands connected to this critical point would be occupied for carbon contents near the high-carbon side of the VC phase and vacant near the low-carbon side. Consequently, it was expected that the near-normal-incidence reflectivity spectrum of VC_x should depend on the carbon content.

Prior to our recent studies of the specific heat of VC_x , it had been observed that the near-normal-incidence reflectivities of V_8C_7 and V_6C_5 differed by only small amounts, which were approximately the same size as the experimental uncertainties. This behavior can now be understood in terms of the variation of the specific heat with composition, for in both of these compounds the electronic states connected with the critical point are expected to be largely occupied. On the other hand, these states should be at least partially vacant when the carbon concentration is decreased below

V_6C_5 toward the lower side of the VC phase. Thus, optical excitations from these states to higher-lying vacant states should be less prominent in low-carbon VC than they are in V_8C_7 , whereas transitions to these states from low-lying occupied states should be somewhat stronger in low-carbon materials than in V_8C_7 .

This proposition has been examined by measuring the near-normal-incidence reflectivity of a crystal with a composition near $VC_{0.76}$ and comparing the spectrum with that from a crystal of $VC_{0.87}$. Because the total reflectivities are almost equal, the change with composition is small and subject to relatively large uncertainties. Nevertheless, there appears to be a band between 2.7 eV and 4.0 eV with a maximum near 3.3 eV in the reflectivity spectrum of $VC_{0.76}$, which is not present in the spectrum of $VC_{0.87}$.

This structure cannot be identified conclusively in the absence of additional information, but it is consistent with the proposal discussed in the previous quarterly report that the peak in the specific heat curve arises from the W_1 critical point. In particular, if the electronic states near W_1 are vacant in $VC_{0.76}$, transitions to these states will be possible by optical excitation from states connected to the W_2 critical point. (Similar transitions contribute significantly to the optical properties of aluminum⁽⁸⁾.) In $VC_{0.76}$, the W_2 - W_1 band gap is expected to be approximately 3.6 eV, in satisfactory agreement with the position of the observed peak in the excess reflectivity of $VC_{0.76}$. The corresponding band gap is expected to be greater than 4.1 eV in $VC_{0.87}$, but optical excitations across this gap are prohibited because both the upper and lower states are occupied when the carbon content is high.

More positive identification of this and other features in the optical reflectivity of $VC_{0.76}$ must rely on other experimental techniques and on the acquisition of more precise information regarding the electronic structure of VC_x as a function of carbon content.

b) Modulated reflectance.

A crystal of V_8C_7 has been prepared for examination by the modulated piezoreflectance technique. Although the crystal was damaged while polishing the first face, it is being studied in preliminary tests of the apparatus and technique. At present, the signal-to-noise ratio is inadequate to permit extracting useful information. Current work is being directed toward improving the electronic, optical and acoustical components of the equipment to remedy this deficiency.

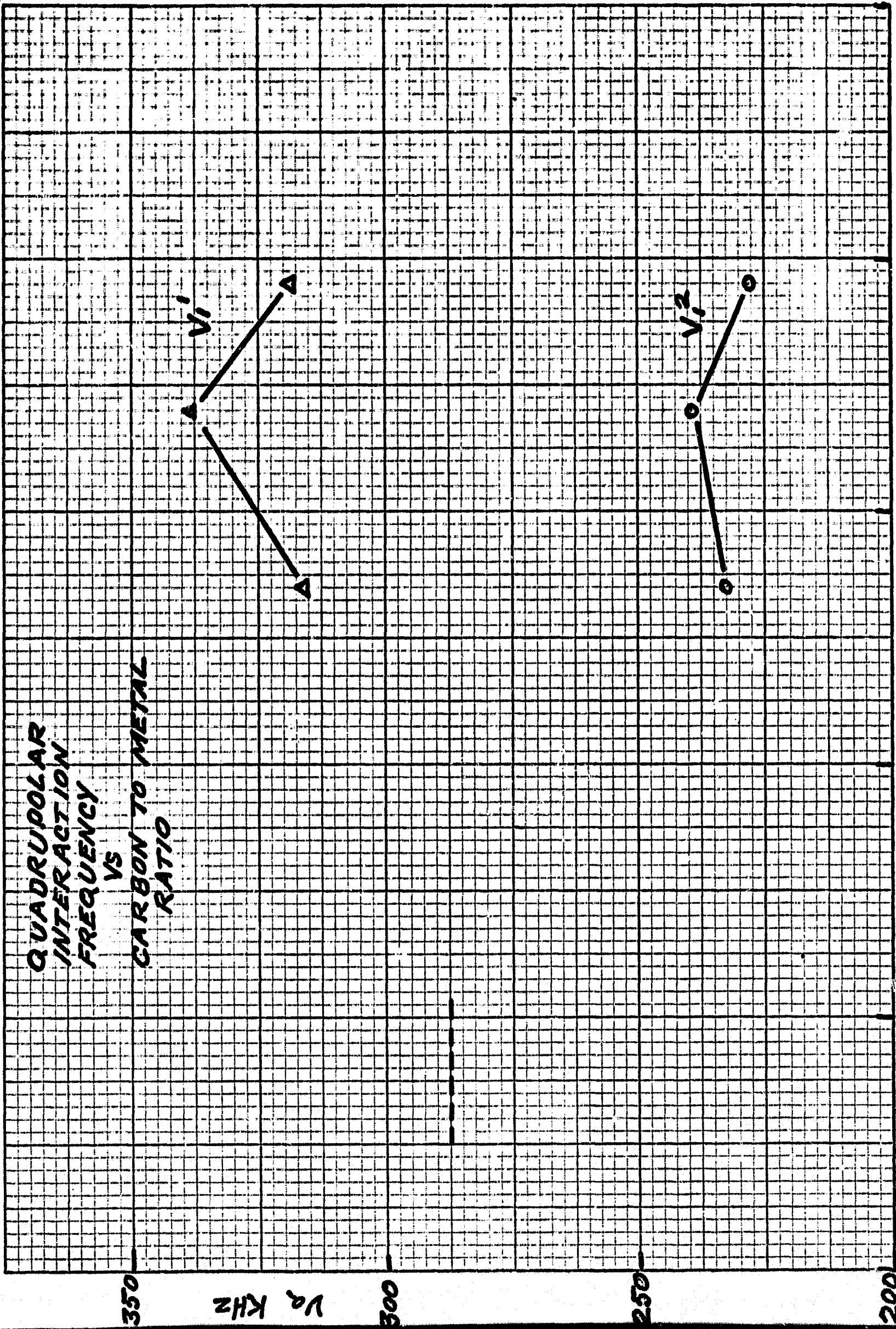
3. Nuclear magnetic resonance. (Dr. D. Kahn, Co-Investigator, not funded under this Contract.)

The variation of the electronic specific heat in VC_x indicates that the density of states at the Fermi level passes through a maximum as the carbon content is varied. Measurements of the magnetic susceptibility of VC_x crystals grown at RIAS have not yet been made, but previous measurements by Bittner and Goretzki⁽⁹⁾ showed only a monotonic decrease as the carbon content increased. Consequently, it has seemed desirable to obtain independent information regarding the variation of the density of states at the Fermi level using NMR techniques.

According to the analysis of Watson et al.⁽¹⁰⁾ the principal contribution to the electric field gradient (EFG) in metallic conductors arises from the redistribution of electrons at the Fermi level that have an appreciable density at the resonating nucleus. This contribution to the EFG is proportional to the non-cubic component of the charge distribution outside of the resonating atom, q_{latt} , and to the density of states at the Fermi level provided by electrons near the resonating nucleus. Thus the quadrupolar interaction frequency, ν_Q , also must be proportional to this density of states.

The quadrupolar interaction frequencies of V_1^1 and V_1^2 sites in VC_x are plotted in Fig. 1 as a function of the carbon concentration. Both curves exhibit a maximum at a carbon-to-metal atom ratio near $x = 0.85$.

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7 X 10 INCHES MADE IN U.S.A.
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0.6 0.7 0.8 0.9 1.0
FIG. 1 CARBON TO METAL RATIO, X

These results are in agreement with the behavior expected from measurements of the low temperature specific heat if the principal variation in the electronic density of states is due to changes in the density of 3d-states at the Fermi level.

This analysis neglects the changes in q_{latt} that may result from changes in the lattice parameter with composition. Such changes could not account for the maxima observed, however, because the lattice parameter varies monotonically with carbon content in VC_x .

These results provide additional support for the behavior observed in measurements of the electronic specific heat, and for the assignment of the peak to structure that is derived primarily from the d-bands. Thus, the W_1 critical point, which has predominantly 3d-character, becomes an increasingly logical choice for this peak in the density-of-states curve.

4. Specific heat of VC_x . (In collaboration with Dr. L. X. Finegold and Mr. D. Bloom, University of Colorado.)

Measurements of the specific heat of VC_x reported in the previous quarterly report have been analyzed according to the procedure suggested by Hoare et al.⁽¹¹⁾ to obtain an estimate of the variation of the density of states with energy. Thus, if n electrons are transferred from each carbon atom to the energy bands derived from atomic states of the metal atom, the displacement, ΔE , of the Fermi level caused by a change in composition from x_1 to x_2 is given by

$$\Delta E = \frac{n}{2} \int_{x_2}^{x_1} dx/N(\epsilon).$$

The results of this calculation are plotted in fig. 2, using an energy scale normalized with respect to the number of electrons transferred.

This approach may be expected to yield a useful approximation to the density-of-states curve so long as the Fermi level is not displaced by large amounts, and the electronic structure is not altered drastically

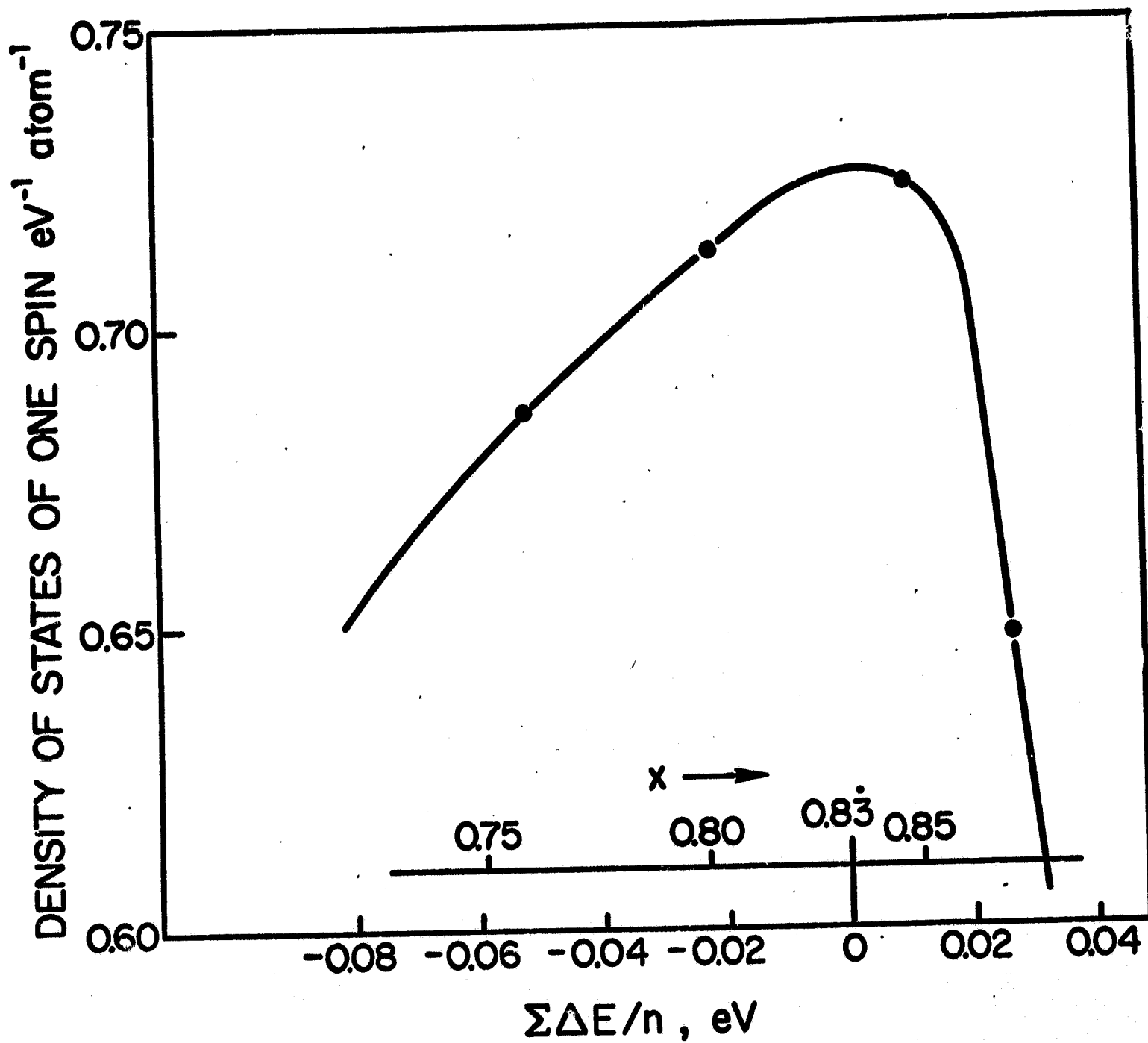


Figure 2. The electron density-of-states curve near the Fermi level of VC_x as derived from the low temperature specific heat by the method of Hoare et al. The zero of energy is chosen arbitrarily at the Fermi level of V_6C_5 ($\text{VC}_{0.833}$).

as the composition is changed. It appears likely that both restrictions are satisfied in VC_x (and TiC_x). For example, if the number of electrons transferred is assumed to be near unity (Lye^(6,12), Lye and Logothetis⁽⁵⁾), the Fermi level moves by only 0.1 eV as x varies from 0.76 to 0.87. Moreover, severe distortions of the energy bands are not expected, because elementary considerations of the electronic structures of TiC and VC (Lye and Logothetis⁽⁵⁾, Lye et al.⁽¹³⁾) suggest that the prominent features near the Fermi level in their density-of-states curves are determined primarily by energy bands derived from the 3d-states of the metal atoms. Although these energy bands can be expected to move slightly in energy as the composition is changed, the dominant characteristics of the peaks will remain, and the Fermi level will be established relative to these peaks according to the total number of electrons available.

Indeed a peak similar to the one observed was expected to be present near the Fermi level of VC from the previous considerations of its electronic structure (Lye et al.⁽¹³⁾). Like the peak shown in fig. 2 the calculated peak is asymmetrical, with the edge at high energies slightly steeper than that on the low energy side, and both peaks are approximately 0.1 eV wide at 90% of the maximum. The calculated peak arises primarily from relatively flat energy bands extending from the corners of the fcc Brillouin zone (W_1) towards the centers of the hexagonal faces (L_3). Although these energy bands are derived largely from 3d _{γ} -states of the metal atom, they are hybridized with 2p-states of the carbon atom to various degrees at different points in the Brillouin zone. It must be acknowledged, therefore, that the density-of-states curve estimated in this manner is a somewhat distorted version of the true curve, because the energy bands will be altered slightly in shape as well as position as the composition is changed.

This correlation between the two peaks is reasonable if the band structure proposed by Lye and Logothetis is approximately correct, because no other prominent features are expected in this region of the energy spectrum. Nevertheless, the agreement is not quantitative; the maximum

density of states observed here is only 0.53 of that expected from the calculation. This discrepancy may not be serious, however, because the W_1-L_3 peak is superimposed on a diffuse, relatively structureless background that contributes almost half the total density of states near this energy. Small changes in the LCAO band parameters may permit a redistribution of these states without introducing new peaks, but more sophisticated calculations of the electronic structure would be required to resolve the question unambiguously. Unfortunately, recent calculations using the augmented plane wave (APW) method (Ern and Switendick⁽¹⁴⁾, Conklin and Silversmith⁽¹⁵⁾) have not yet provided a resolution in the density-of-states curve sufficiently detailed to permit comparison with these experimental data.

The influence of ordering in the carbon sublattice (De Novion, Lorenzelli and Costa⁽¹⁶⁾; Froidevaux and Rossier⁽¹⁷⁾, Venables et al.⁽¹⁸⁾) has been neglected in this discussion, because the metal sublattice, which appears to dominate the electronic structure, is only slightly distorted from the fcc configuration. Thus, the extended zones of the ordered compounds will deviate from the fcc Brillouin zone primarily by the presence of small band gaps on certain interior planes. Only those band gaps that occur very close to the Fermi level will influence the electronic specific heat, but even these usually will introduce only small changes because the perturbation in the energy bands extends over only a very limited volume of the Brillouin zone. Although these interior band gaps may not be observable in the electronic specific heat or in other physical parameters that are obtained from sums over the complete Brillouin zone, it is anticipated that certain of them will be detectable in the modulated reflectance spectra of the ordered compounds.

The compositional variation in the density of states at the Fermi level of VC_x inferred from the present study of the specific heat differs from that expected from prior measurement of the magnetic susceptibility (Bittner and Goretzki⁽⁹⁾). Part of the discrepancy may arise from many-body enhancement effects that modify the two parameters by different amounts,

but it appears possible that differences in specimen preparation may also be a contributing factor. In an effort to resolve this question, portions of the crystalline boules employed in this study of the specific heat are now being used also for measurements of the magnetic susceptibility and superconducting transition temperature.

Like the specific heat density of states, the Debye characteristic temperature, θ_0 , also assumes its maximum value at the nominal composition $x \approx 0.85$. If the Lindemann melting formula is applicable to these materials, this variation in θ_0 is consistent with the phase diagram of the V-C system published by Storms^(19,20), and with qualitative observations of the melting behavior during growth of these crystals (Precht⁽²¹⁾). On the same basis, the variation of θ_0 observed here disagrees with the phase diagram proposed by Rudy⁽²²⁾, in which the maximum melting temperature occurs at a much lower carbon content, near the composition $VC_{0.75}$. More detailed investigations will be required to resolve this question, but the present results suggest that the maximum in the melting curve for the nominally cubic VC phase occurs at a composition corresponding to that of the ordered compound V_6C_5 .

Phase B. Electron microscope studies of ceramic alloys. J. D. Venables
(Principal Investigator).

The high temperature mechanical properties of TiC-VC alloys differ markedly from those of the parent monocarbides. For example, Hollox⁽²³⁾ has shown that the compressive yield strength of VC-25% TiC at 1800°C is approximately 20 times greater than that of either TiC or VC. The reason for this behavior is not as yet understood, however from electron microscope studies it appears that the material consists of two phases, an ordered precipitate and a relatively disordered matrix⁽²⁴⁾. It is tempting to attribute these unusual mechanical properties to the observed phase separation, but recalling that the order-disorder temperature of V_6C_5 is 1250°C, it must first be shown that ordering in the alloys is retained at temperatures up to 1800°C.

Since the previous methods used to determine the order-disorder temperature of V_6C_5 are not suitable for the alloys, an attempt is now being made to measure the degree of ordering at elevated temperatures in the

electron microscope. This requires that the sample be heated directly with the electron beam since the temperature range of interest here is beyond the capabilities of the present microscope hot stage. Using this method of heating, it is relatively easy to determine the degree of order by monitoring the intensity of a superlattice spot, but difficulties arise in measuring the temperature since the hot zone is only 20 μ in diameter. The magnification of an ordinary optical pyrometer is too low to resolve such a small area, however a special, long-working-distance optical microscope attachment has now been designed and constructed that will suitably magnify the hot zone.

With this pyrometer-microscope arrangement the sample can be viewed in its normal position within the specimen chamber through a prism that is mounted inside the electron microscope. Initial results indicate that useful temperature measurements can be made in this manner, and that the simultaneous observation of the electron diffraction pattern will allow a determination of the order-disorder transformation temperature of the alloys. The system is now being calibrated and the results will be described in the next report.

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