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MAGNETIC SUSCEPTIBILITY OF VANADIUM CARBIDE

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ABSTRACT

The magnetic susceptibility of single-crystal VC_x ($x=0.76$, 0.81, 0.84, 0.87) has been found to decrease sharply as x increases from 0.76, in qualitative agreement with the results of previous measurements made by Bittner and Goretzki on powder specimens. The present results, however, show a minimum near $x=0.84$ followed by a slight increase at $x=0.87$, and in this respect are similar to the observations of Borukhovich et al. in their studies of the other Group V carbides NbC_x and TaC_x. This variation of the susceptibility is attributed primarily to the (Van Vleck) orbital paramagnetism, supporting the suggestion made previously by Froidevaux and Rossier. A simple model for the orbital paramagnetism in VC_x is shown to account qualitatively for the observed variation with carbon content.

§ 1. INTRODUCTION

The transition metal carbides have been studied extensively in recent years because of their technological interest and because the origins of their physical properties remain obscure. There have emerged recently two independent model calculations of the electronic band-structure of TiC. The LCAO calculations of Bilz (1958) and the APW calculations of Ern and Switendick (1965) and Conklin and Silversmith (1968) indicate that a major portion of the bonding arises from interactions between the 2p orbitals of the carbon atoms, and from hybridization interactions between these orbitals and the 3d orbitals of the metal atoms. Moreover the energy bands derived from the 2p states of the carbon atoms lie lower in energy than those derived from the 3d states of the metal atoms. This model thus suggests that the bonding is contributed predominantly by strong covalent interactions between the metal and nonmetal atoms and that electrons are transferred from energy bands derived from the 3d states of the metal atoms to 2p states of the carbon atoms.

In contrast to this model, that of Lye and Logothetis (1966) indicates that the electronic structure of TiC exhibits a close resemblance to that of the fcc transition metals (Lye 1967). They conclude that the bonding is predominantly due to metal-metal interactions and that the carbon 2p bands lie higher in energy than those derived from the metal atom 3d bands, i.e., that electrons are transferred from the carbon 2p states to the metal atom 3d states. Recent low temperature specific heat measurements (Lowndes, Finegold and Lye 1970;

Lowndes, Finegold, Bloom, Lye 1970) lend support to this interpretation in that a peak in the density-of-states curve was found near the composition $VC_{0.85}$. The width and position of this peak were similar to those predicted by Lye et al. (1968). A search (Bloom, Finegold, Lye, Radebaugh and Siegwarth 1970) for superconductivity in these samples indicated that none of them became a superconductor above 30 mK. This then implies, through the use of McMillan's (1968) equation, that the densities of states determined from the specific heat measurements are probably not greatly enhanced over the "bare" values. Comparison of the specific heat results with the other calculations is prohibited by their lack of sufficient resolution.

The present investigation was undertaken for the purpose of determining whether the magnetic susceptibility, χ, also reflects the peak in the curve of density of states versus energy, which it should if the spin susceptibility were the dominant contribution to χ, because

$$\chi_{spin} = 2\mu_\beta^2 N(E_f)/(1-\mu), \qquad (1)$$

where μ_β is the Bohr magneton, $N(E_f)$ is the density of states for a single spin at the Fermi energy and $1/(1-\mu)$ is the Stoner enhancement factor (Stoner 1936). Previous measurements of the magnetic susceptibility of vanadium carbide and other transition metal carbides (Bittner and Goretzki 1962, Costa and Conte 1964, Caudron, Ducastelle and Costa 1970, Borukhovich, Dubrovskaya, Matveenko and Gel'd 1969) usually indicate that the susceptibility decreases with increasing carbon content. The exceptions are the monocarbides of niobium and tantalum for which χ exhibits sharp minima at the compositions $NbC_{0.80}$ and $TaC_{0.78}$ (Borukhovich, Dubrovich, Dubrovskaya, Matveenko and Gel'd 1969). Other workers used samples produced by various sintering processes, whereas the samples used in the present work are very pure well-characterized single crystals grown by zone-melting.

§ 2. EXPERIMENTAL TECHNIQUES AND RESULTS

2.1. Specimen Characterization

Large single crystal samples of VC_x were grown by a floating zone technique (Precht and Hollox 1968). Chemical analyses performed on boules representative of these samples indicate that they contain approximately 0.01 w/o each of oxygen and nitrogen, as well as traces of metallic, non-magnetic impurities. From four of these boules, three of which were used previously for measurements of the specific heat ($x = 0.76$, 0.81 and 0.87) (Lowndes et al. 1970), small, cylindrically shaped samples approximately 10 mm in length and 4 mm in diameter were cut for use in studies of their superconducting transition temperatures (Bloom et al. 1970) and for the present investigation of their magnetic susceptibility. The $VC_{0.84}$ sample was machined from a larger cylinder, similar to the one used in the specific heat measurements. The compositions of the four VC_x samples were determined (as in Lowndes et al. 1970) from measurements of their x-ray lattice parameters to be $x \approx 0.755$, 0.807, 0.836, and 0.866.

2.2. Magnetic Susceptibility Measurements and Results.

The magnetic susceptibility measurements were performed in the temperature range 77 to 300 K with a vibrating-sample magnetometer (Model FM-1, Princeton Applied Research Corp., Princeton, New Jersey; Foner 1959) at 8 kG. The susceptibility-field relation was linear to 8 kG. The precision of the measurement is within ± 1%. The samples were measured on consecutive days and the room temperature values were all rechecked within one hour. The contribution to the total susceptibility arising from the Teflon holder in which the samples were individually mounted was determined after each measurement. Each sample was cooled by allowing cold nitrogen gas to flow by it, and the resulting temperature was measured to within ± 3 K using a copper-constantan thermocouple. This large uncertainty in the measurement of temperature, caused by temperature gradients in the sample chamber, has little significance for our results, because the susceptibility was found to change only slowly with temperature, as shown in fig. 1.

A plot of the room temperature susceptibilities versus composition shows a sharp decrease from the value at $x = 0.76$ to a minimum near $x = 0.84$, followed by a slight increase at $x = 0.87$. Extrapolation of the data in fig. 1 to 0 K yields a closely similar variation of the susceptibility with carbon content. For clarity and convenience, the latter curve only is shown in fig. 2. The rapid decrease of the susceptibility from $x = 0.76$ to $x = 0.81$ is in qualitative agreement with the results of measurements made by Bittner and Goretzki (1962) on polycrystalline (powder) specimens of VC_x.

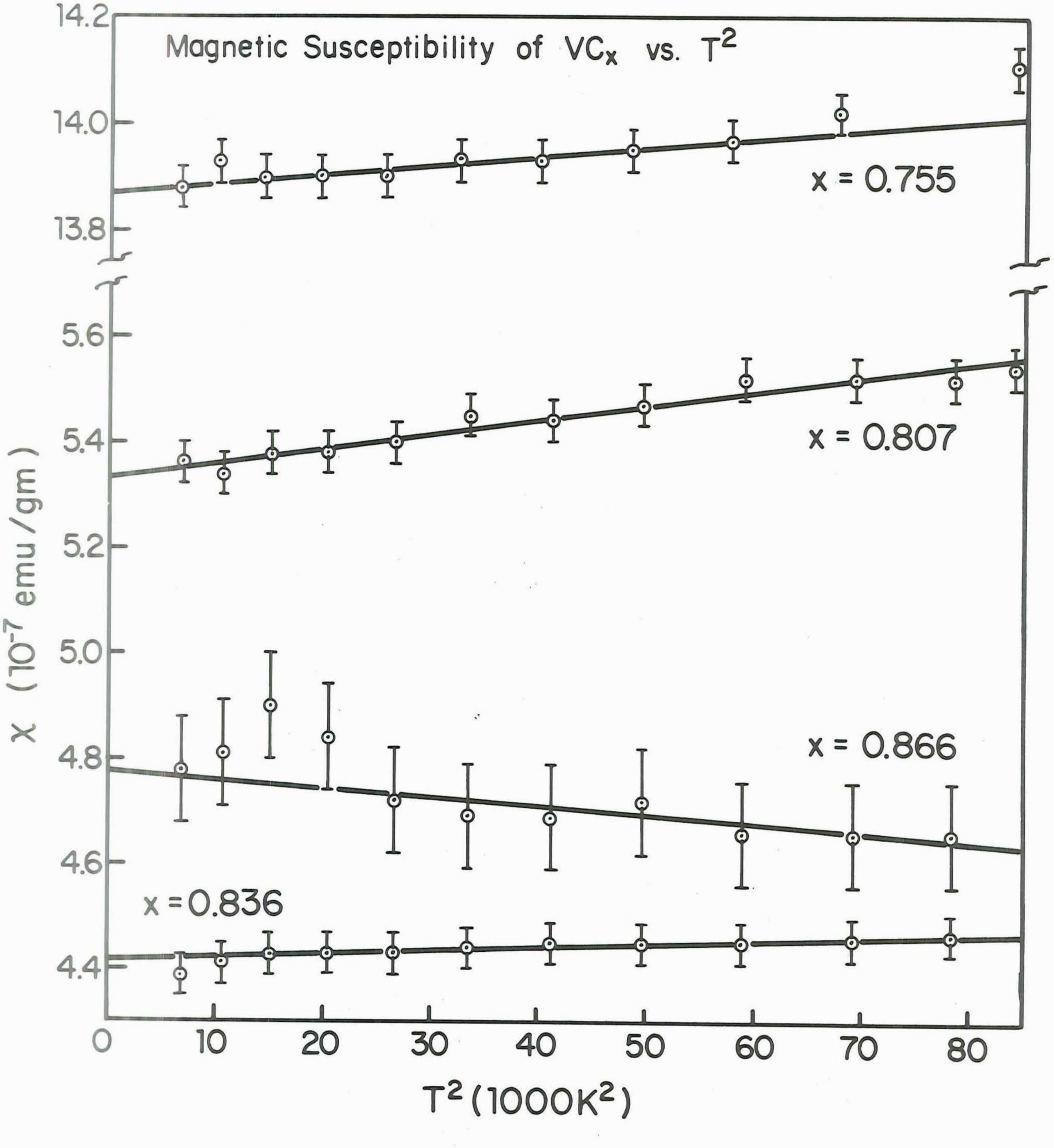


Figure 1. The magnetic susceptibility/gm of VC_x crystals plotted as a function of $T.^2$ The extrapolated values at 0 K are shown as χ_{meas} in fig. 2.

§3. DISCUSSION

The susceptibility, χ, is the sum of several contributions (see, e.g., Gladstone, Jensen and Schrieffer 1969):

$$\chi = \chi_{ion}+\chi_P+\chi_L+\chi_{VV} ,$$

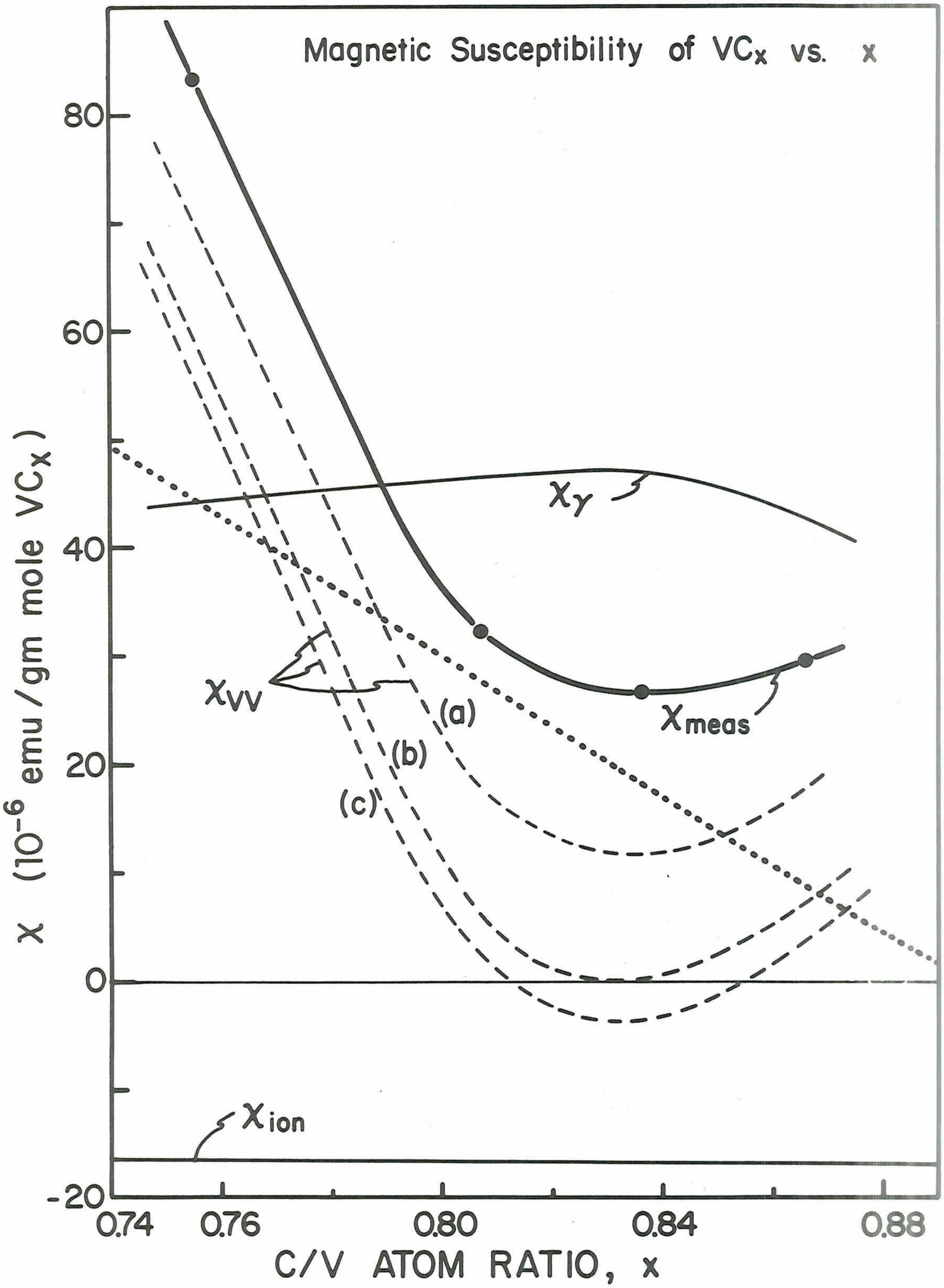
where χ_{ion} is the diamagnetism of the ion cores, χ_P is the Pauli paramagnetism of the conduction electrons, $\chi_L = -\frac{1}{3}(m/m^*)^2\chi_P$ is the associated Landau diamagnetism (m is the free electron mass and m^* is the band structure effective mass), and χ_{VV} is the Van Vleck orbital paramagnetism (Kubo and Obata 1956).

χ_{ion} can be estimated by using -15×10^{-6} emu/mole for the diamagnetic contribution of the vanadium ion cores (Huguenin and Baldock 1966) and $x(-1.9 \times 10^{-6}$ emu/mole) for the carbon ion cores, where x is the carbon atom fraction in VC_x. The contribution of the ion cores obtained in this manner is plotted as χ_{ion} in fig. 2. It varies much too slowly with composition to account for the behavior observed experimentally.

χ_P can be estimated from the values of the electronic specific heat measured previously (Lowndes et al. 1970). If the effects of electron-electron and electron-phonon interactions are neglected, the curve shown as χ_γ in Fig. 2 is obtained.

The Landau diamagnetism is proportional to χ_P, but probably is substantially smaller in magnitude. It is evident, therefore, that their sum, $(\chi_P + \chi_L)$, also varies too slowly with composition to account for the observations, and in addition exhibits a curvature opposite to that determined experimentally.

Figure 2. The magnetic susceptibility/gm mole of VC_x, extrapolated to 0 K, plotted as a function of the carbon concentration, x. χ_{ion} is the ion core diamagnetism. χ_{γ} is the Pauli paramagnetism as estimated from the electronic specific heat. χ_{VV} is the Van Vleck orbital paramagnetism as calculated by subtracting from χ_{meas} the sum of χ_{ion}, χ_{γ} and χ_L, where $\chi_L = -1/3(m/m^*)^2\ \chi_{\gamma}$ and $m^*/m=1,\ 2,$ and ∞ for curves a, b, and c, respectively. The dotted curve represents χ_{VV} as calculated from the tight-binding model discussed in the text, using the electronic density of states inferred from the low-temperature specific heat (Lowndes et al. 1970).


Magnetic Susceptibility of VC$_x$ vs. x
χ (10^{-6} emu/gm mole VC$_x$)
80
60
40
20
0
-20
0.74
0.76
0.80
0.84
0.88
C/V ATOM RATIO, x
χ$_γ$
χ$_{meas}$
χ$_{vv}$
(a)
(b)
(c)
χ$_{ion}$

The orbital paramagnetism, χ_{VV}, remains to be examined as a possible explanation for the observations, but too little information is available regarding the electronic band structure of VC_x to permit calculating in detail the magnitude of this contribution to the susceptibility. The possible existence of orbital paramagnetism in VC_x was recognized by Froidevaux and Rossier (1967) and by Caudron, Ducastelle and Costa (1970), but Caudron, Castaing and Costa (1970) concluded that its magnitude is abnormally small. Studies of the V^{51} Knight shift and spin-lattice relaxation time at lattice sites of cubic symmetry in V_8C_7 (Lye and Kahn 1969) provided support for the latter conclusion by demonstrating that the orbital contribution to the Knight shift is small, probably less than 10% of that due to core polarization. The question may be resolved in part by using the present results to estimate $\chi_{VV} \simeq \chi_{meas}-(\chi_{ion}+\chi_P+\chi_L)$. A range of values will be obtained for χ_{VV}, depending on the effective mass ratio m^*/m, chosen to calculate χ_L. Curves of χ_{VV} versus x derived in this manner are shown in fig. 2 for $m^*/m = 1$ (curve a) and 2 (curve b), and for $\chi_L=0$ ($m^*/m = \infty$)(curve c). This approach suggests that χ_{VV} indeed is small for $x \gtrsim 0.8$ if, as expected, $m^*/m > 1$. For x near 0.76, however, $\chi_{VV} \simeq 60 \times 10^{-6}$ emu/mole, or approximately one-third as large as the quite considerable orbital paramagnetism in vanadium metal (Clogston, Gossard, Jaccarino and Yafet 1962, Butterworth 1964), and, as in vanadium metal, accounts for more than half of the measured susceptibility.

This behavior cannot be explained readily on the basis of the simple model often used in discussions of χ_{VV}. This model suggests that $\chi_{VV} \propto N_oN_u$, where N_o and N_u are the numbers of occupied and unoccupied states, respectively, in the energy bands that produce the orbital paramagnetism, and $N_o + N_u = 10/\mathrm{atom}$ for d-bands. Although χ_{VV} is only 50% larger at $x = 0.76$ than would be expected by extrapolating from the orbital paramagnetism of vanadium metal, its magnitude changes with carbon content much too quickly to be accounted for on this basis.

As Clogston, Jaccarino and Yafet (1964) have emphasized, however, this model neglects the effects of differences in the matrix elements of orbital angular momentum connecting electronic states within the various bands responsible for the orbital paramagnetism. Inclusion of this factor allows a qualitative explanation to be given for the variation of χ with x. In particular, when χ_{VV} is written in the tight-binding approximation (Kubo and Obata 1956; Clogston, Jaccarino and Yafet 1964);

$$\chi_{VV} \equiv \int \frac{dk}{(2\pi)^3} \sum_{nn'} \frac{f(E_{nk}) - f(E_{n'k})}{E_{n'k} - E_{nk}} \mu_\beta^2 (nk|L|n'k)(n'k|L|nk),$$

it is evident that a strong component of orbital paramagnetism will arise only if the members of at least one pair of energy bands, n and n' lie on opposite sides of the Fermi level ($f(E_{nk}) \neq f(E_{n'k})$), at small energy separations ($E_{n'k} - E_{nk}$), and have large matrix elements of angular momentum connecting the states in these bands at the same point k in the Brillouin zone. Only a limited number of such pairs of energy bands can be expected to satisfy these criteria simultaneously. For the most simple case, in which the orbital paramagnetism arises from a single pair of bands having matrix elements of L that do not change rapidly over the relevant portion of the Brillouin zone, χ_{VV} is approximately proportional to the integrated density of vacant states in the upper band.

The rapid decrease of χ_{VV} as the carbon concentration of VC_x is increased beyond x = 0.76 can be understood on this basis to result from the elevation of the Fermi level through a narrow peak in the density-of-states curve. In accord with a previous proposal regarding the electronic specific heat of VC_x (Lowndes et al. 1970), it is suggested that the peak responsible for this variation of the magnetic susceptibility arises from an accumulation of states near the W_1 point in the Brillouin zone. The more pronounced variation of the susceptibility relative to that of the specific heat is a consequence of the fact that the electronic specific heat is determined by the density of states at the Fermi level, whereas the orbital paramagnetism is proportional to the integral of these states from the Fermi level to the top of the relevant band.

An approximate band structure for VC (Lye and Logothetis 1966; Lye, Hollox and Venables 1968) suggests that two sets of occupied bands may interact with those connected with W_1 to provide a major portion of the orbital paramagnetism. One of these, a single band connected with W_2, lies approximately 0.75 eV below W_1, the other, a doubly degenerate band at W_3 lies approximately 1.77 eV below W_1. An order of magnitude estimate can be made for the orbital paramagnetism contributed by these bands if it is assumed that the matrix elements of orbital angular momentum (abbreviated M), are approximately the same for each pair of bands. Under these circumstances,

$$\chi_{VV} \simeq 2\mu_\beta^2 \, N_u(W_1)\,|M|^2 \left\{ [E(W_1)-E(W_2')]^{-1} + 2[E(W_1)-E(W_3)]^{-1} \right\} ,$$

where $N_u(W_1)$ is the integrated density of unoccupied states within the W_1 peak. If these pairs of bands provided the only contributions to the orbital paramagnetism, it would be expected to decline monotonically from its value at low carbon concentrations, and vanish when the upper bands were filled. Using as a guide the density-of-states curve inferred from measurements of the electronic specific heat (Lowndes et al. 1970), the composition at which the W_1 bands are filled is estimated at approximately $VC_{0.9}$. The variation of χ_{VV} at lower carbon concentrations can then be determined if it is assumed that most of the states at the Fermi level of VC_x contribute to the orbital paramagnetism. The result, calculated for $|M|^2=2$ (Clogston et al. 1962), is shown as the dotted curve in fig. 2. It should be noted that a closely similar curve is obtained if it is assumed that approximately one electron is added to the d-band for each carbon atom incorporated into the VC_x lattice (in which case, $d\chi_{VV}/dx \simeq -320 \times 10^{-6}$).

The agreement between this calculated curve and those inferred from the experimental data probably is as good as could be expected in view of the numerous approximations employed. On the other hand, the evident discrepancies suggest that i) the energy denominator employed here is too large, and ii) the matrix elements $|M|$ are not precisely the same for all states within the upper band. Moreover, the increase of χ_{VV} shown in fig. 2 at $x = 0.87$ suggests that some of the newly occupied states immediately below the Fermi level of $VC_{0.87}$ also contribute to the orbital paramagnetism through interactions with still higher vacant states.

Consideration of this question must be deferred for the present, however, because the Knight shifts of the V^{51} nuclear magnetic resonances in VC_x have been found to <u>decrease</u> with increasing carbon content (Froidevaux and Rossier 1967), opposite to the variation expected from the combined effects of χ_γ and χ_{VV} for $x \gtrsim 0.84$.

According to this analysis, the orbital paramagnetism depends primarily on the integrated density of states lying below the Fermi level within the W_1 peak. The variation of χ_{VV} with temperature is sensitive, therefore, to the manner in which thermal excitation influences the occupation of states in this peak. Because the W_1 peak is narrow ($\simeq 0.1$ eV) (Lowndes et al. 1970), the degree of occupation is expected to be influenced significantly by the presence of other overlapping bands that do not otherwise contribute importantly to the orbital paramagnetism. The measured temperature variations of the susceptibility could be accounted for in each case if the W_1 peak were superimposed on a background density of states that increased toward higher energies, but insufficient information is available at present to permit evaluating this proposal.

It may be noted that variations of both χ and $d\chi/dT$ with x similar to those reported here for VC_x have been observed also for NbC_x and TaC_x (Borukhovich, Dubrovich, Dubrovskava, Matveenko, and Gel'd 1969), except that the minimum susceptibilities for these compounds occur at lower values of x, and the increase is more pronounced at large x than is observed for VC_x. It appears desirable, therefore, to determine for these compounds also the magnitude of the orbital paramagnetic contribution to their susceptibilities.

§ 4. SUMMARY AND CONCLUSIONS

Measurements made between 77°K and 300 K on four crystals of VC_x (x=0.76, 0.81, 0.84, and 0.87) show that the magnetic susceptibility decreases rapidly with increasing carbon content to a minimum near x=0.84, followed by a small increase at x=0.87. An approximate analysis of the results indicates that this variation of the susceptibility is determined primarily by the (Van Vleck) orbital paramagnetism, χ_{VV}. This behavior has been interpreted in terms of a simple model relating the magnitude of χ_{VV} to the number of vacant states in a band that produces a narrow peak in the density-of-states curve near the Fermi level of $VC_{0.84}$. As the carbon concentration increases, the Fermi level rises through this peak and thereby causes the orbital paramagnetism to decrease. It is suggested that this peak arises from the energy bands connected with the W_1 point in the Brillouin zone, and that the orbital paramagnetism arises primarily from interactions between these bands and the fully occupied bands connected with the lower-lying W_2' and W_3 points. The orbital paramagnetism estimated in this manner for $VC_{0.76}$ agrees in order of magnitude with that inferred from experimental data, and the decrease of χ_{VV} with increasing x follows qualitatively the trend expected. The increase of χ_{VV} at x=0.87 suggests, however, that additional contributions to the orbital paramagnetism arise for $x \gtrsim 0.84$.

An apparent inconsistency arises from the fact that the variations of both χ_P and χ_{VV} seem to imply an increase of the V^{51} Knight shift with increasing carbon content for $x \gtrsim 0.84$, in opposition to the behavior observed by Froidevaux and Rossier (1967). As these authors indicate, however, the Knight shift is determined by relatively localized effects, whereas the magnetic susceptibility is a macroscopic average. The distinction is particularly evident in the substantial differences they observed between the Knight shifts of V^{51} atoms at the various inequivalent crystallographic sites present in VC_x. The problem deserves more detailed consideration than can be given in the present paper.

The variations of the susceptibilities with temperature suggest that the W_1 peak is superimposed on a background density of states that increases toward higher energies. A quantitative analysis of the results must await more detailed information regarding the electronic structure and density of states in VC_x.

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