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Influence of Order-Disorder Transformations on the Electrical Resistivity of Vanadium Carbide*†

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The electrical resistivity of single crystals of vanadium carbide has been studied as a function of composition and temperature. Particular attention has been devoted to the resistivity of the two ordered phases of vanadium carbide, V_6C_5 and V_8C_7. Both solids have been shown to undergo first-order transformations to the disordered state at elevated temperature. The results of this investigation have been used to assess the role of carbon vacancies in determining the resistivity of the disordered solids. Vacancy scattering accounts for over 90% of the residual resistivity (resistivity at liquid-He temperatures) of the disordered solids but reduces in importance as temperature increases. The change in the resistivity of V_6C_5 at its critical point was found to be 5.4 ± 0.3 $\mu\Omega$ cm or $(3.6 \pm 0.2)\%$ of the total resistivity of the disordered solid. The corresponding change found for V_8C_7 was 20.1 ± 1.4 $\mu\Omega$ cm or $(14.7 \pm 1.0)\%$. The critical temperatures for disordering in the two ordered phases were determined to be (1275 ± 8) °C for V_6C_5 and (1124 ± 15) °C for V_8C_7. The vanadium-carbon system was also shown to have a strong preference for one or the other of the ordered phases for nearly all compositions in the range $0.83 \leq x \leq 0.90$, where x is the carbon-to-metal ratio.

I. INTRODUCTION

In an earlier work[1] we measured the change in resistivity at the order-disorder transformation from the hexagonal ordered phase of vanadium carbide, V_6C_5, to the corresponding disordered NaCl phase, $VC_{0.83}$. We related this change in resistivity to the influence of carbon vacancies on electron transport in the disordered solid. Our results indicated that vacancy scattering is dominant in the disordered carbide at low temperatures but of lessening importance as temperature increases.

The finding that carbon vacancies are important scattering centers in the transition-metal carbides was in agreement with the results of earlier studies by Williams[2] and others.[3–7] Our experiment, however, was free of a serious qualification common to all of the other measurements. In the previous measurements the influence of changes in vacancy content on resistivity was investigated by adding or subtracting carbon. However, measurements of the magnetic susceptibility and electronic heat capacity[8] in transition-metal carbides clearly show that the density of states at the Fermi level is a function of carbon-to-metal ratio. It is thus difficult to determine whether in resistivity studies the major effect of varying the carbon-to-metal ratio is to vary the number of scattering centers (carbon vacancies) or to alter the scattering cross section via the band structure. The present study represents a different approach, in that the carbon-to-metal ratio is kept constant.

Venables, Kahn, and Lye[9] have shown that vanadium carbide having the composition $VC_{0.833}$ (V_6C_5) possesses long-range order characterized by an hexagonal superlattice. The superlattice is formed chiefly through a rearrangement of carbon atoms and vacancies on the fcc carbon sublattice. The vanadium metal atoms remain in the nominally cubic positions of the rocksalt structure common to all fourth- and fifth-group transition-metal carbides. Therefore, the ordering process essentially involves only the rearrangement of a single species, carbon vacancies (or carbon atoms).

Since Venables and Lye[10] also demonstrated that V_6C_5 undergoes an order-disorder transformation, an avenue was provided for a determination of the scattering power of vacancies which was independent of earlier limitations. Because "vacancies" do not scatter electrons in the perfectly ordered solid but do scatter in the disordered solid, a measure of the scattering power of vacancies can be obtained from the change in electrical resistivity at the critical point.

When the disordered solid $VC_{0.83}$ becomes the ordered compound V_6C_5, the carbon-atom vacancies in the former, arranged randomly on the fcc carbon sublattice, take on a periodic arrangement. These atomic voids are no longer vacancies, strictly speaking, but part of the new structure.

However, as was noted in our previous paper,[1] there are special difficulties inherent in this technique as well. Chief among these is the concern that ordering brings on changes in the electronic structure of the solid which may affect the resistivity. Our contention has been that at least a part of this effect must be anisotropic because of the hexagonal nature of the superlattice in V_6C_5, and in any event the band-structure changes will be different from those in the earlier experiments.

In the present work we report the results of a further detailed investigation of electrical conduction in vanadium carbide. Our earlier conclusions are supported by the observations which we have since made on the behavior of the resistivity of V_8C_7, a cubic-ordered phase of vanadium carbide, near its critical point. We also include the results of a search for anisotropy in the resistivity of V_6C_5, and an examination of the kinetics of ordering in V_6C_5 and V_8C_7.

II. VANADIUM CARBIDE: ORDERED COMPOUNDS

The ordered phases of vanadium carbide have been characterized by Venables *et al.*[9] (V_6C_5) and by de Novion *et al.*[11] and Froidevaux and Rossier[12] (V_8C_7). The structure of the superlattices of the two materials are shown in Figs. 1 and 2. Although the vanadium sublattice in the two solids is essentially fcc, the actual superlattice structures of V_6C_5 and V_8C_7 are markedly different. Most important, the symmetry of the former is hexagonal while the symmetry of the latter remains cubic.

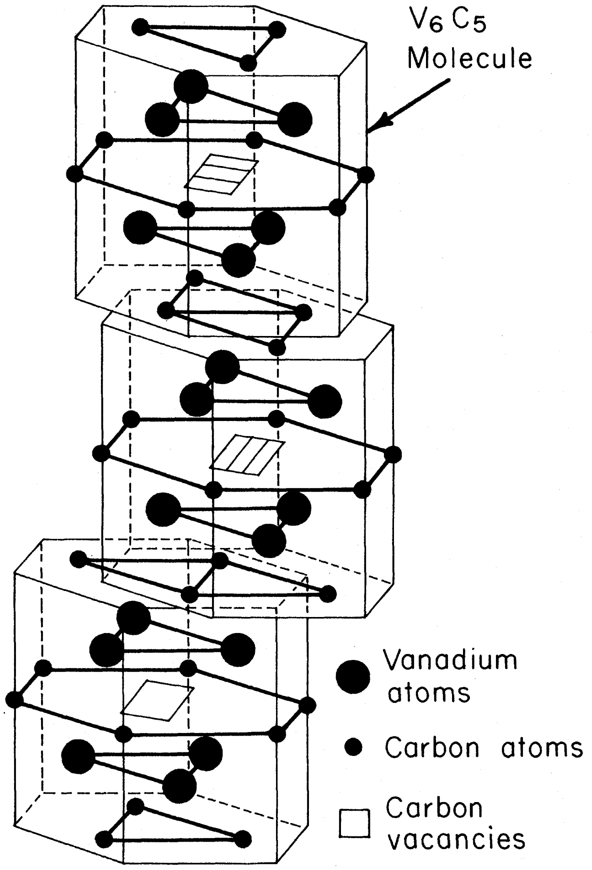

FIG. 1. Superlattice structure of V_6C_5 viewed as spiraling chains of V_6C_5 "molecules." The complete unit cell composed of three such chains contains 54 vanadium atoms and 45 carbon atoms and has the dimensions $a = 5.09$ Å and $c = 14.40$ Å [after Venables *et al.* (Ref. 9)].

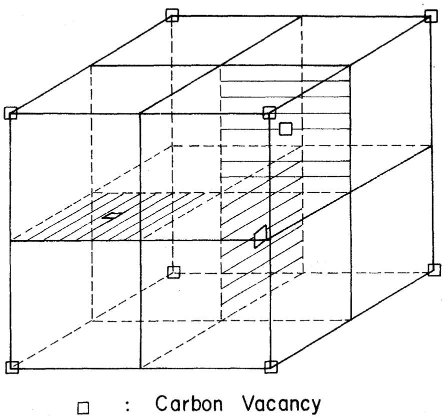

FIG. 2. Distribution of carbon vacancies in the carbon superlattice of the ordered V_8C_7 compound. The dimensions of the cubic unit cell of the superlattice ($a = 8.334$ Å) shown here is twice that of the normal rocksalt unit cell [after de Novion *et al.* (Ref. 11) and Froidevaux and Rossler (Ref. 12)].

Because there is a slight noncubic distortion[9] in the positions of the vanadium metal atoms when the V_6C_5 ordered structure is formed, it is natural to suspect that any alteration of the electronic structure of the solid which occurs upon ordering will have some anisotropic effect on the resistivity. Furthermore, one might also expect an additional anisotropic effect from the formation of Brillouin superzones in the ordered state.[1] Since the $\hat{c}$-axis dimension (14.40 Å) of the V_6C_5 superlattice unit cell is over three times the dimension of the rocksalt unit cell (4.16 Å) characteristic of the disordered solid, the superzone boundary along the $\hat{c}$ direction will lie well within the normal boundary. If the new superzone boundaries contact or cut the Fermi surface, energy gaps will be formed at the zone edge. If these gaps lie near the Fermi level they can have a marked effect on the resistivity. Although V_8C_7 also possess superzones in the ordered state, the symmetry is cubic and no anisotropic effect on the resistivity is expected.

The presence or absence of anisotropy in the resistivity of V_6C_5 implies the presence or absence of important changes in the electronic band structure at the order-disorder transformation. Furthermore, the existence of two ordered phases of vanadium carbide having dissimilar ordered structures provides yet another check on the earlier conclusions.[1] Since possible electronic changes induced by ordering in the two materials must also be different, a similar behavior in the resistivity of the two phases would suggest that the electronic effects of ordering are not significant in either.

Unfortunately, a complication enters in the form of a domain structure in both materials. The $\hat{c}$ axis of the V_6C_5 ordered structure may be oriented along any one of the four $\langle 111 \rangle$ directions in the nominally fcc vanadium sublattice.[9] This circumstance results in the formation of a domain structure (type I).[9,11] The hexagonal nature of the order within these domains gives rise to birefringence causing individual domains to be optically visible when viewed in reflection through crossed polarizers. Because the superlattice is oriented differently in the separate domains, there will be an averaging out of the actual anisotropic effects when a measurement is made over a great number of domains (an unavoidable circumstance). This averaging process complicates the situation but does not preclude the possibility of observing anisotropic effects if they exist. If one assumes that the resistivity measured along the $\hat{c}$ axis of the superlattice is ρ_c and the resistivity measured in the basal plane is ρ_b, then the diagonalized resistivity tensor has the form

$$\rho = \begin{pmatrix} \rho_b & 0 & 0 \\ 0 & \rho_b & 0 \\ 0 & 0 & \rho_c \end{pmatrix} \tag{1}$$

when the c axis lies along the z direction. Within each domain the resistivity tensor will be diagonalized along one of the four directions: $\langle 111 \rangle$, $\langle \bar{1}11 \rangle$, $\langle 1\bar{1}1 \rangle$, and $\langle \bar{1}\bar{1}1 \rangle$, where the indices refer to the cubic vanadium sublattice. For a current direction parallel to $\langle 111 \rangle$ the resistivity within an individual domain may have one of two values: for $\hat{c} \parallel \langle 111 \rangle$, $\rho = \rho_c$; for $\hat{c} \parallel \langle 1\bar{1}1 \rangle$, $\langle \bar{1}11 \rangle$, or $\langle 11\bar{1} \rangle$, $\rho' = \frac{8}{9}\rho_b + \frac{1}{9}\rho_c$. An actual crystal which contains a great number of domains presents a resistance to the flow of current which is the result of a series-parallel arrangement of individual domains. The average resistivity measured for such a crystal must lie between the limit for a purely series arrangement, $\rho_{\langle 111 \rangle} = \frac{1}{4}(\rho + 3\rho') = \frac{2}{3}\rho_b + \frac{1}{3}\rho_c$, and the limit for a purely parallel arrangement,

$$\rho_{\langle 111 \rangle} = \frac{4\rho\rho'}{\rho' + 3\rho} \ . \tag{2}$$

The choice of the best model depends on the resistance encountered by an electron in crossing from one domain to another in a direction perpendicular to $\langle 111 \rangle$. The series limit holds only if this transverse resistivity is nearly infinite. Clearly this transverse resistivity is not infinite, but more the order of ρ or ρ'; thus, the actual resistivity measured along the $\langle 111 \rangle$ direction should lie nearer to the resistivity of the parallel limit.

For a current direction along $\langle 001 \rangle$ the resistivity within each of the four types of domains is the same ($\rho = \frac{2}{3}\rho_b + \frac{1}{3}\rho_c$). In this case the average resistivity for the series or parallel case is also the same:

$$\rho_{\langle 001 \rangle} = \frac{2}{3}\rho_b + \frac{1}{3}\rho_c \ . \tag{3}$$

Evidently the anisotropy can be averaged completely away only if the series limit is used. But it has already been shown that the series limit is inappropriate. Therefore, any strong anisotropy in the resistivity of V_6C_5 should be observable even in a polydomain sample.

We should also note that there is the possibility of a domain structure in V_8C_7. A metastable state in which domains are present is possible if there are at least four crystallographically distinct ways of forming a domain.[13] In general, crystals possessing an fcc lattice contain four distinct sublattices which are related through displacements of the type $\frac{1}{2}a\langle 110 \rangle$. In addition, an examination of Fig. 2 reveals that the superlattice structure of V_8C_7 is brought into itself only after four successive 90° rotations about the $\langle 001 \rangle$ axis. This combination of circumstances makes possible the formation of out-of-step (antiphase) boundaries of at least four distinct types. Such antiphase domains have in fact been found for $VC_{0.87-0.90}$ in an electron-microscope study of vanadium carbide performed by Billingham and Lewis.[14] Their study of the vanadium-carbon system further demonstrated the existence of a second type of domain boundary within the optically observable domains (type I) in V_6C_5. They found that antiphase boundaries (type II) are formed inside domains to type I through a displacement of the superlattice by a partial lattice vector. Antiphase boundaries such as these can be expected to have a less significant effect on the resistivity because they do not involve the difference in orientation that characterizes type-I boundaries.

III. ELECTRICAL CONDUCTION IN ORDERED PHASES

The ideal ordered sample is defect free, consists of a single domain, and has the exact composition $VC_{0.833}$ (V_6C_5) or $VC_{0.875}$ (V_8C_7). Since one can never produce the ideal sample, it is necessary to formulate a theoretical basis for dealing with the problems of defects, composition deviations, and domain boundaries.

This problem was considered in our earlier paper,[1] and the following expression was used:

$$[\rho_{\text{total}}(T_0)]_{T_0 < T_c} = \rho_i + \rho_d + \rho_D + \rho(T_0) \ , \tag{4}$$

where ρ_i is the resistivity due to impurities, ρ_d is the resistivity due to superlattice defects resulting from composition deviations, ρ_D is the resistivity due to domain boundaries, and $\rho(T_0)$ is the resistivity due to phonons at temperature T_0. Since the Hall coefficient R and the effective mass m^* of the charge carriers are typically temperature dependent in the carbides,[15] it is desirable to represent R and m^* explicitly. Then

$$(\rho_{\text{total}})_{T<T_c}=\frac{m^*R(T)}{e}\left(\frac{1}{\tau_i}+\frac{1}{\tau_d}+\frac{1}{\tau_D}+\frac{1}{\tau(T)}\right) , \tag{5}$$

where m^* is the effective mass, R is the Hall coefficient $\cong 1/ne$, and τ is the relaxation time. To a first approximation $1/\tau_d$ and $1/\tau_D$ are independent of temperature and proportional to the volume density of superlattice defects (n_d) and the linear density of optically observable domain boundaries (q), respectively. This assumption can be used to obtain an expression for the difference in resistivity between two ordered samples having only a slight difference in composition and domain size[1]:

$$\delta\rho(T)\propto m^*R(T) . \tag{6}$$

Equation (6), and Eq. (1) from which (6) was obtained, assume the applicability of Matthiessen's rule—i.e., that all the scattering events are mutually independent, such that their probabilities are additive. This point is discussed in Refs. 1 and 2. Caution should be taken in the application of Eq. (6) since the approximation that τ_d and τ_D are independent of temperature requires that there be no serious band-structure changes with temperature.

It remains to express the form of the resistivity at temperatures greater than the critical point. The resistivity of the disordered solid may be represented by

$$(\rho_{\text{total}})_{T_0>T_c}=\rho_i+\rho_v+\rho(T_0) , \tag{7}$$

where ρ_v is the resistivity due to vacancies in $VC_{0.833}$ ($VC_{0.875}$), and ρ_i and $\rho(T_0)$ are defined as in Eq. (4).

Equations (4) and (7) can be used to express the change in resistivity at the order-disorder transformation as

$$\begin{aligned}\Delta\rho(T_c)&\equiv[\rho_{\text{total}}^{T>T_c}-\rho_{\text{total}}^{T<T_c}]_{T_c}\\&=\rho_v-\rho_d-\rho_D+[\rho_i^{T>T_c}+\rho(T_c)^{T>T_c}\\&\qquad-\rho_i^{T<T_c}-\rho(T_c)^{T<T_c}] .\end{aligned}\tag{8}$$

Because of the change in crystal symmetry above the transformation temperature, there will be changes in the electronic band structure leading to possible changes in R, m^*, and the mobility μ. However, we will temporarily ignore these changes and see where the analysis leads. Later we will argue that whatever changes occur do not affect the present conclusions in an important way.

If it is assumed that there is no change in the electronic band structure in going through the transition, then $R(T_c)^{T<T_c}=R(T_c)^{T>T_c}$, $e\tau_i/m^*=\mu_i^{T<T_c}=\mu_i^{T>T_c}$, and $\mu(T_c)^{T>T_c}=\mu(T_c)^{T<T_c}$. In this case the bracketed expression in Eq. (8) disappears, and the change in resistivity of an ideal sample ($n_d=0$, $q=0$) at the critical point is simply equal to the resistivity due to vacancies in the disordered solid.

IV. SAMPLE PREPARATION

Single-crystal boules of "V_6C_5" were kindly provided for this work by Murray of Cambridge University and Lye of the RIAS Laboratory of the Martin Marietta Corporation. A third single crystal having composition $VC_{>0.89}$ was purchased from the Alfa Crystals Division of the Ventron Electronics Corporation.

The level of impurities in each of these samples was determined by a semiquantitative mass-spectrographic analysis performed by Evans of the Materials Research Laboratory of the University of Illinois. Table I summarizes the results of this analysis. The error in the measurements is given by $\frac{1}{3}x<x<3x$. That is, a reported value of 10 means the true value lies between 3 and 30.

Samples were cut from the boules using a high-speed diamond saw and then polished with diamond paste of successively finer grit until a grit of $\frac{1}{4}\mu$ was reached. Finally, the samples were etched briefly in a mixture of hydrofluoric and nitric acids. Rectangular samples were prepared in this manner to have the dimensions 0.040×0.040×0.250 in.

Because of the problems created by selective evaporation of one constituent over another during the growth of a single crystal, a method had to be devised to restore "V_6C_5" samples to their ideal composition. As described earlier[1] the technique which was adopted consists of heating samples of the single crystals to 2100 °C while they are surrounded with powdered V_6C_5. The powder is prepared by reacting vanadium and carbon powders in the ratio 6 : 5 by molecular weight. Observation of the final domain structure revealed that the most important factor in determining the ultimate domain size is the concentration of superlattice defects. Long periods of annealing below the critical temperature are markedly less important than

TABLE I. Mass-spectrographic analysis (values in ppm).

Impurity	Cambridge Crystal	RIAS Crystal	Alfa Crystal
W	200	100	2
Mo	40	40	10
Nb	30	30	3
Zr	20	60	2
Cu	60	20	≤2
Ni	5	≤5	200
Co	100	10	≤3
Fe	500	50	200
Cr	2000	200	50

ensuring that the sample has a nearly ideal composition ($VC_{0.833}$).

Although no single-crystal samples of V_8C_7 were available, the powder-annealing procedure outlined above provided a method for preparing such samples. Instead of surrounding V_6C_5 crystals with powdered $VC_{0.833}$, samples were surrounded with powders of composition $VC_{0.843}$, $VC_{0.853}$, or $VC_{0.875}$ (V_8C_7). In this manner samples were prepared with compositions approximated by the composition of the powder used. The V_6C_5 crystals were used as the starting point for approaching the composition $VC_{0.875}$ (V_8C_7) from below (carbon-deficient side). The Alfa crystal (composition, $VC_{0.89}$, determined from the lattice parameter[16]) was used to approach V_8C_7 from above (carbon-rich side).

V. RESISTIVITY RESULTS: V_6C_5

All resistivity measurements were performed using a four-probe dc technique. Data were taken point-by-point with four-digit precision. A continuous chart record was also made to aid in determining the shape of the curve between points.

The behavior of the resistivity around the critical point in V_6C_5 is presented in Fig. 3. The curves represent the resistivity of a typical well-annealed sample having a residual resistivity (resistivity at liquid-He temperature) near 10 $\mu\Omega$ cm. A similar curve from our earlier paper[1] shows much more rounding at the transition point. This behavior is typical of partially annealed samples. The residual resistivity of the earlier sample was ~ 45 $\mu\Omega$ cm. Still more rounding is evident in unannealed samples having residual resistivities in the range 70–115 $\mu\Omega$ cm. The discontinuous change in the resistivity of all samples at the critical point is typical of solids undergoing a first-order transformation.

A calculation of the temperature dependence of the order parameter in the Bragg–Williams (B-W) approximation by Emmons[17] implies a nonlinear variation in resistivity over the range $0.7 < T/T_c < 1.0$.[1] Although experimentally derived curves typically show less rounding than curves generated by such theoretical calculations,[18] the degree of sharpness evidenced in Fig. 3 is rather surprising. Differential-thermal-analysis (DTA) results obtained by Emmons[17] for powdered vanadium carbide also show less rounding at the transition than the theoretical calculations imply. His data for powdered samples, however, do show more rounding than do the resistivity results for single crystals.

VI. ANALYSIS OF $V_6C_5 \rightleftarrows VC_{0.833}$ RESULTS

We must now try to eliminate ρ_d and ρ_D from Eq. (8) in order to find the contribution of vacancies to the resistivity of the disordered solid, ρ_v.

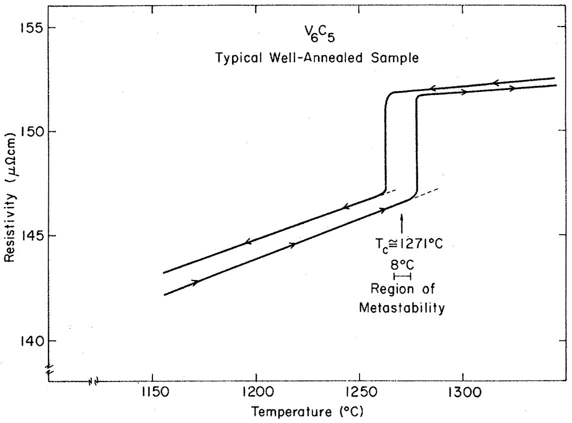

FIG. 3. Electrical resistivity of a well-annealed sample of V_6C_5 (Cambridge crystal). The two curves represent the heating and cooling of a single sample ($\rho_0 \sim 10$ $\mu\Omega$ cm). Heating and cooling rates of ~ 0.5 °C/min were employed.

We assume that the contribution of domain-boundary scattering to the resistivity can be estimated by considering only the optically observable (type-I) domains. Recalling that the resistivity due to these domain boundaries, ρ_D, is proportional to the linear density of type-I domains, q, we may write that at a temperature T_0

$$\rho_D = \left(\frac{m^* R(T_0) C}{e} \right) q \, , \tag{9}$$

where C is a constant. Equation (9) suggests that the contribution of scattering at domain boundaries can be found by measuring the total resistivity at a given temperature as a function of q. The results of performing this measurement at room temperature are presented in Fig. 4. The contribution ρ_D(298 K) can be found for any density of domains from the relation

$$\rho_D(298\text{ K}, q) = \rho_{\text{total}}(298\text{ K}, q) - \rho_{\text{total}}(298\text{ K}, 0) = C' q \, ,$$

where $C' \equiv C m^* R(298\text{ K})/e$. The average value of C' determined from Fig. 4 is $C' \simeq 5 \times 10^{-4}$ $\mu\Omega\,\text{cm}^2$. Since the average density of optically observable domains in a well-annealed sample is roughly 400 boundaries per cm, ρ_D at room temperature is only ~ 0.2 $\mu\Omega$ cm. Since this quantity decreases at high temperature because of the temperature dependence of $m^*R(T)$, the contribution of domain boundary scattering to the resistivity at the critical point can be considered negligible.

With some continued effort the superlattice-defect resistivity can also be eliminated, although a rather circuitous path is required. Consider the residual resistivity

$$\rho_0 = \rho_i + \rho_d + \rho_D = \frac{m^* R(0)}{e} \left(\frac{1}{\tau_i} + \frac{1}{\tau_d} + \frac{1}{\tau_D} \right) \, . \tag{10}$$

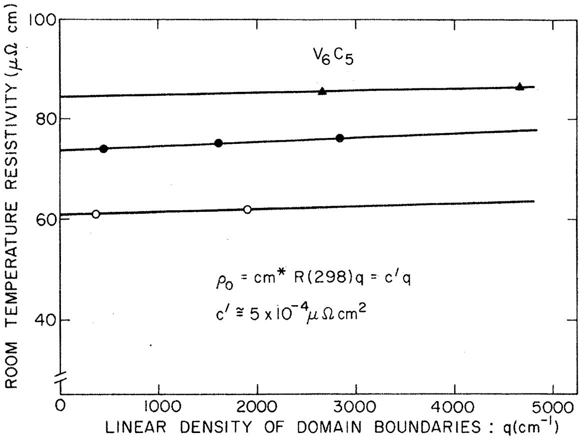

FIG. 4. Room-temperature resistivity as a function of the density of domains is presented for three samples with different concentrations of superlattice defects. The contribution to the resistivity from domain-boundary scattering is slight, but can be represented by $\rho_D = (5 \times 10^{-4}\ \mu\Omega\ \mathrm{cm}^2)\ [q(\mathrm{cm}^{-1})]$.

Since a variation of more than 100 $\mu\Omega$ cm has been observed between the residual resistivities of samples with different annealing histories, the dominant term in Eq. (10) must be ρ_d. Hence, the residual resistivity is indicative of how close a given sample is to the ideal composition ($n_d = 0$, $\rho_d = 0$). Moreover, from experimental results one expects a maximum in critical temperature T_c at the ideal composition. [Although theoretically a maximum in T_c occurs only for the AB (50%) alloy,[19] experimental evidence for maxima in alloys of other compositions abounds.[20,21]] Thus, an extrapolation of ρ_0 to low values (3 ± 2 $\mu\Omega$ cm) in a plot of ρ_0 versus T_c should give $T_{c\,\max}$, the transition temperature of the ideal material, $VC_{0.833}$ (V_6C_5). We find $T_{c\,\max} = (1275 \pm 2)$°C. This temperature represents the average of the values for cooling, T_{cL}, and for heating, T_{cH}. The range $T_{cH} - T_{cL}$ represents a region of metastability which is common to first-order transformations. The average size of this region for well-annealed samples is reported in Fig. 3, $T_{cH} - T_{cL} \cong 8$ °C. Since the actual critical temperature need not be at the midpoint of T_{cH} and T_{cL}, there is an additional uncertainty in T_c of ± 4 °C. Taking this value in conjunction with the uncertainty of thermocouple calibration gives the temperature of the critical point as (1275 ± 8) °C. (Thermocouples were standardized to the transition points in iron, taken to be 769 and 910 °C). This value of critical temperature is in general agreement with the approximate value of 1250 °C inferred from the disappearance of superlattice spots in electron-microscope studies of V_6C_5 by Venables and Lye[10] and by Billingham and Lewis.[14]

The relative size of the resistivity change in V_6C_5 samples at the critical point can be plotted as a function of critical temperature. The limiting value of this change will then correspond to the temperature $T_c = 1275$ °C. This has been done in Fig. 5 where one obtains

$$\frac{\Delta\rho(T_c)}{\rho_{\mathrm{total}}(T_c)} \times 100 = (3.6 \pm 0.2)\%$$

or

$$\Delta\rho(T_c) \cong \rho_v = 5.4 \pm 0.3\ \mu\Omega\,\mathrm{cm}.$$

Here, $\rho_{\mathrm{total}}(T_c)$ is defined as the total resistivity of the disordered solid at T_c and

$$\Delta\rho(T_c) \equiv [\rho_{\mathrm{total}}^{T > T_c} - \rho_{\mathrm{total}}^{T < T_c}]_{T_c}\ .$$

Hence, the contribution of vacancies to the total resistivity in the disordered phase ($VC_{0.833}$) at 1275 °C is $(3.6 \pm 2)\%$ or 5.4 ± 0.3 $\mu\Omega$ cm.

An interpretation of these numbers must await an examination of the full resistivity curve from low to high temperature. To this end a set of curves obtained for V_6C_5 samples is presented in Fig. 6. Each of the lower three curves represents a sample possessing optically observable domains. Since each sample was cut from the same boule (Cambridge crystal), they all must represent ordered V_6C_5 differing only in the density of superlattice defects and domain boundaries. The difference in resistivity between any pair of curves can, therefore, be represented by Eq. (6). Evidently $m^*R(T)$ decreases with increasing temperature.[1] Thus the difference in resistivity between an ideal ordered sample and a disordered one [$\rho_v = m^*R(T)/e\tau_v$] must also decline with increasing temperature.

A numerical estimate of this difference can be obtained from the upper and lower curves in Fig. 6, which approximate the behavior of disordered and ordered samples of V_6C_5. The upper curve was obtained from a sample cut from a part of the Cambridge boule which exhibited no observable domains. Domains just at the threshold of visibility appeared after the high-temperature run was completed. The room-temperature resistivity, however, remained essentially equal to its initial value (< 5% change). Since the sample suffers no discontinuity in the resistivity over the temperature range of interest it may be assumed to be essentially disordered. Thus, the difference between upper and lower curves provides an approximation to the resistivity due to vacancies in a disordered sample ($VC_{0.833}$) at any given temperature less than the critical temperature. This analysis implies that the vacancy contribution accounts for over 90% of the resistivity of $VC_{0.833}$ at helium temperature. The two curves can also be used to find the added resistivity per atomic percent vacancies at room temperature (4.4 $\mu\Omega$ cm/at.% vac). In Table II

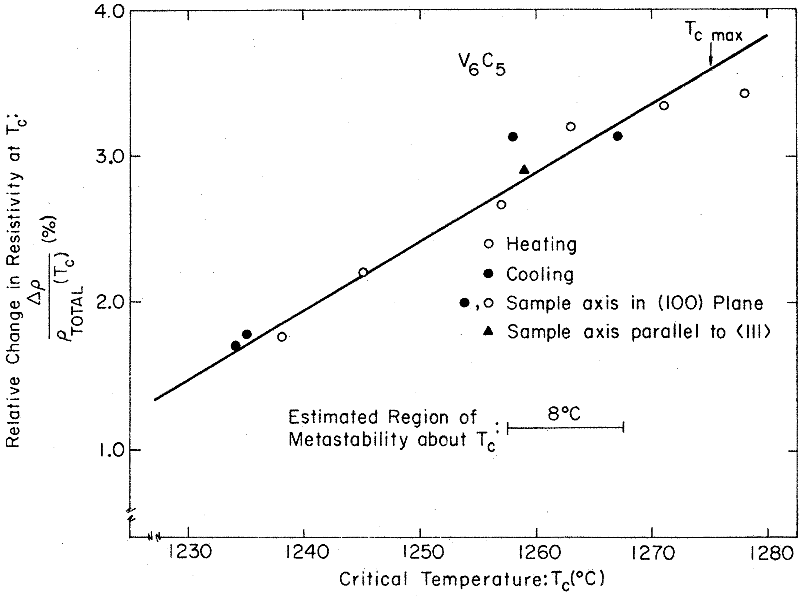

FIG. 5. Relative change in the electrical resistivity of V_6C_5 at T_c plotted as a function of critical temperature. $\Delta\rho(T_{c\,\max}) = 5.4 \pm 0.3$ $\mu\Omega$ cm or (3.6 ± 0.2)% of the total.

this value is compared with the values obtained for other pertinent solids. The added resistivities recorded for TaC and TiC were obtained from the variation of room-temperature resistivity with carbon content and are, therefore, subject to the restriction noted earlier. The generally higher added resistivities characteristic of all the carbide materials can be understood on the basis of the following likely possibilities: (1) A relatively high density of states near the Fermi level. (2) An effective charge on carbon vacancies which is greater than 1*e*. (3) A heavy effective mass in either the conduction band or an overlapping hole band. Although possibility (1) is generally accepted not to apply to TiC,[25] its large value of added resistivity per vacancy can easily be understood to result from its unusually low density of conduction electrons, as discussed by Williams.[2]

As we have already stated, the question of band-structure changes between ordered and disordered states is critical to this work. We have suggested that because of the noncubic nature of the V_6C_5 ordered state the existence of band-structure effects ought to be accompanied by an observable anisotropy in the resistivity. A search for anisotropy in V_6C_5 has been carried out and the result was negative. The resistivities of two samples cut along the ⟨100⟩ and the ⟨111⟩ directions appear in Fig. 7. The temperature dependence of the resistivity of both samples is nearly identical. This result contrasts sharply with the behavior of the resistivity of samples displaying anisotropic magnetic ordering effects.[26,27] Also, the size and shape of the change in resistivity of the ⟨111⟩ sample

TABLE II. Comparison of the scattering power of vacancies at room temperature (references in parentheses).

Compound	Added Resistivity per at.% vac. ($\mu\Omega$ cm/at.% vac.)	Conduction Electrons per Formula	Hall Mobility (cm^2/V sec)
$VC_{0.833}$	4.4		
$VC_{0.7}$		1.2 (22)	0.99 (22)
$TaC_{0.85-0.96}$	7.3[a]	2.2 (22)	0.71 (22)
$TiC_{0.92-0.97}$	16 (2)	0.08 (2)	15.80 (2)
Noble Metals	1.3 − 1.7 (23)	1.25 − 1.4 (24)	3.5 − 5.0[b]

[a] Computed from the data of Refs. 3 and 6.

[b] Calculated with the help of Ref. 24 and the reported values of room-temperature resistivity.

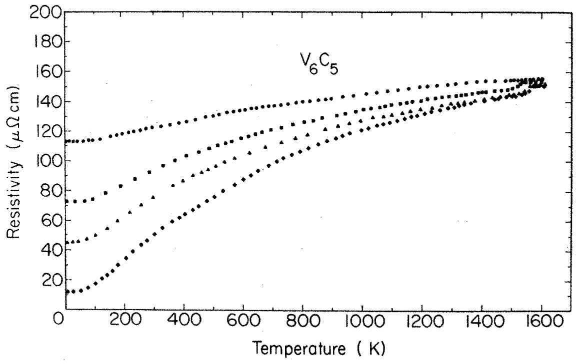

FIG. 6. Electrical resistivity of different V_6C_5 samples plotted as a function of temperature. The samples represented by the lower three curves (diamonds, triangles, and squares) all exhibited an optically observable domain structure. The sample represented by the upper curve (filled circles) was essentially a disordered sample. All curves were taken upon heating for samples cut from the Cambridge crystal.

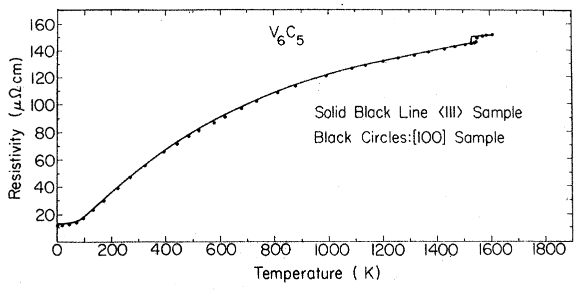

FIG. 7. Comparison of the resistivities of two V_6C_5 samples having their current axis along the ⟨111⟩ and ⟨100⟩ directions. The similarity between the two samples suggests that any anisotropy is small.

agree very closely with the results for ⟨001⟩ samples. (See the filled triangle in Fig. 5.)

The lack of observable anisotropy suggests that any energy gaps resulting from the formation of super zones are not in a position to affect the resistivity. A remaining possibility is that a discontinuous change in the carrier concentration occurs upon ordering or disordering without the appearance of a concomitant anisotropy. This possibility seems rather unlikely, especially in view of Takano's results[28] for the Hall coefficient of β-phase alloys. His measurements show a change in slope but no discontinuous jump of the Hall coefficient at T_c. There is also the possibility that the ordering process results in a change in the phonon spectrum which may cause the phonon-limited mobility [Eq. (8)] to change abruptly at the transition. Since little is known about the phonon spectra for VC_x we can not deal with this problem directly. One might suspect, however, that the existence of such an effect would lead to a marked difference in the behavior of V_6C_5 versus V_8C_7 since the two materials have unrelated ordered structures. This proposition will be examined in the following section.

VII. RESISTIVITY RESULTS: V_8C_7

The behavior of the resistivity near the transformation point in V_8C_7 is essentially identical to that of V_6C_5. The major exception is the size of the change which is as much as a factor of 4 larger in V_8C_7. The temperature dependence of the resistivity of a well-annealed sample of V_8C_7 appears in Fig. 8. As in V_6C_5, the resistivity change at the critical point is discontinuous, indicating a first-order transformation. Note also that the region of metastability ($T_{cH} - T_{cL}$) in the V_8C_7 transformation is more than three times larger than the corresponding region in V_6C_5 (cf. Fig. 3).

The resistivity of a $VC_{0.84+}$ sample prepared by annealing a section of a V_6C_5 crystal in $VC_{0.843}$ powder is shown in Fig. 9. Amazingly enough, this sample exhibits a strong discontinuous change in resistivity at a temperature near the V_8C_7 critical point. One must conclude that the V_8C_7 ordered phase has been formed even though the composition is near $VC_{0.833}$ (V_6C_5). This preference for the V_8C_7 structure implies that the ordering energy for V_8C_7, v_{87}, must be larger than the corresponding energy associated with V_6C_5, v_{65}. This suggestion is supported by Emmons's DTA results,[17] which give $v_{87}/v_{65} = 1.88$. Emmons also notes a tendency for powders having compositions between $VC_{0.833}$ and $VC_{0.875}$ to show a change in enthalpy at the critical points for both V_8C_7 and V_6C_5. This observation is supported here by the existence of a vestigial V_6C_5 transformation in Fig. 9. The critical temperature for the V_6C_5

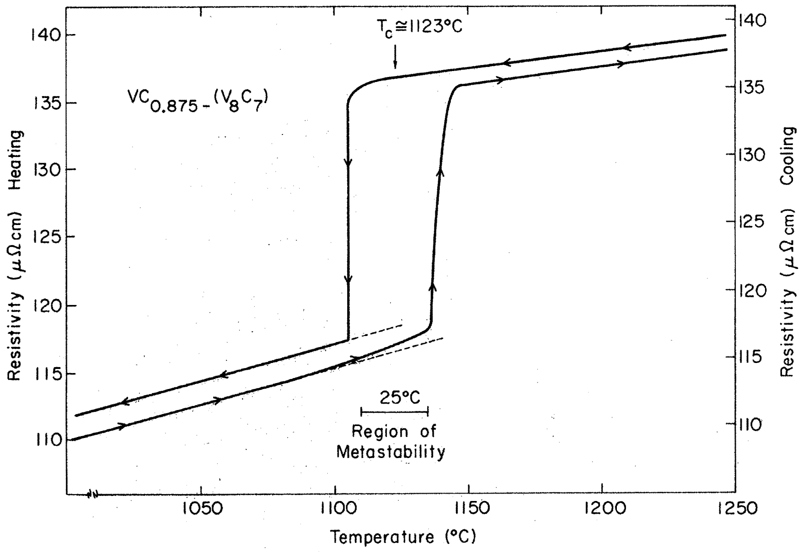

FIG. 8. Temperature dependence of the resistivity of a V_8C_7 sample prepared by annealing a section of the RIAS crystal (V_6C_5) in $VC_{0.875}$ powder. The negative curvature in the discontinuous portion of the heating curve is caused by a nonzero heating rate.

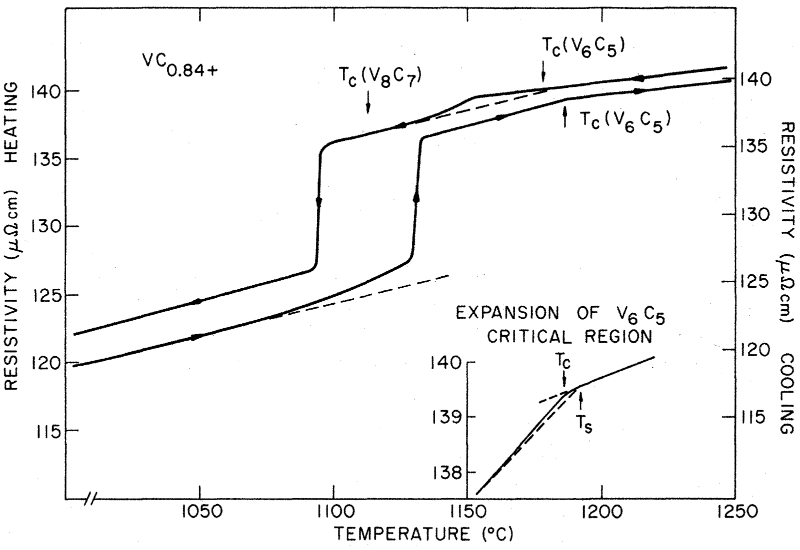

FIG. 9. Temperature dependence of a $VC_{0.84+}$ sample prepared by annealing a part of the RIAS crystal in $VC_{0.843}$ powder. Evidence exists for both V_8C_7 and V_6C_5 transitions.

transformation point is severely depressed, a condition which is expected for samples having compositions relatively far from $VC_{0.833}$. Apparently the situation in single crystals falls short of complete segregation into V_8C_7 and V_6C_5 phases, but a tendency in this direction is evident.

The tendency of the V_8C_7 transformation to become sharper as the $VC_{0.875}$ composition is approached is clearly indicated by Figs. 10 and 11. Figure 11 provides the clearest evidence of this behavior because the situation in these carbon-rich samples is not complicated by a tendency to form V_6C_5 order. Also, the tendency of the critical temperature to reach a maximum value at the

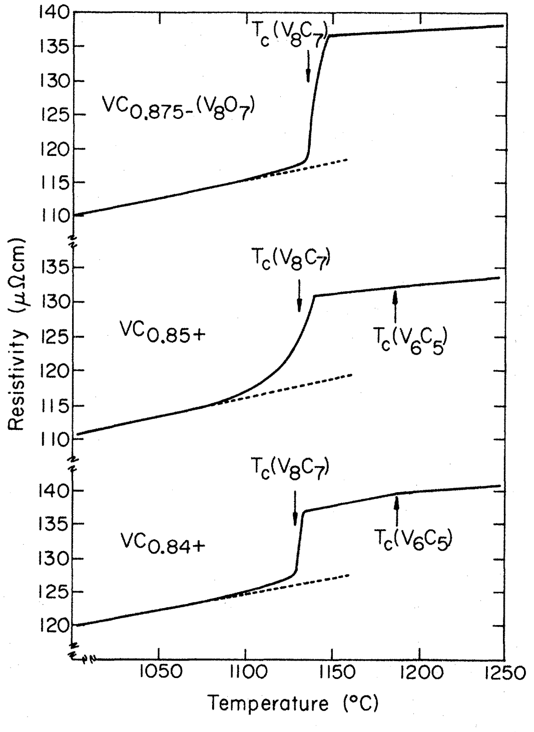

FIG. 10. Temperature dependence of the resistivities of several samples approaching the $VC_{0.875}$ (V_8C_7) composition from the carbon-deficient side. All curves were taken upon heating on samples prepared from the RIAS crystal.

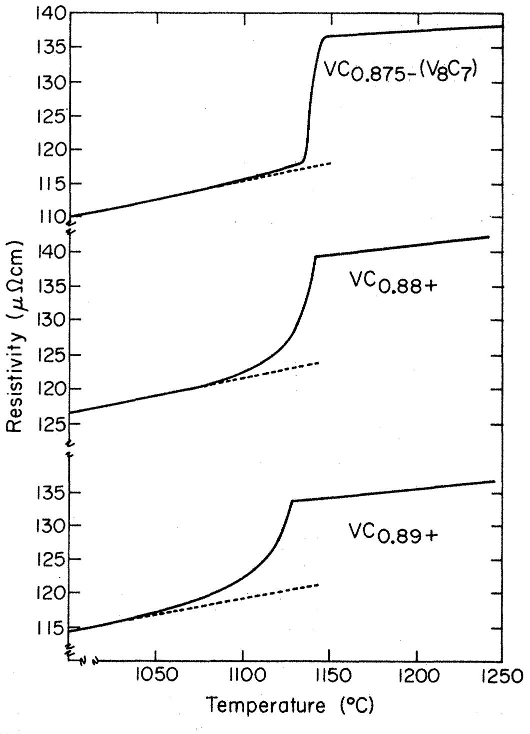

FIG. 11. Temperature dependence of the resistivities of several samples approaching the $VC_{0.875}$ (V_8C_7) composition from the carbon-rich side. All curves were taken upon heating on samples prepared from the Alfa crystal.

composition of V_8C_7 can be seen in Figs. 10 and 11. In addition, there is some evidence that the change in critical temperature with composition appears stronger in Fig. 11 (carbon-rich side) than in Fig. 10 (carbon-deficient side). This behavior is consistent with the assumption that a maximum exists in T_c because the ordering energy v_{87} has a maximum at the ideal composition. Then the local maximum in T_c caused by the ordering potential must be imposed upon the parabolic background predicted by theory[19] having a maximum at the *AB* composition ($VC_{0.5}$).

VIII. ANALYSIS OF $V_8C_7 \rightleftarrows VC_{0.875}$ RESULTS

One can obtain the limiting size of the resistivity change at the V_8C_7 critical point from Fig. 12, which gives the relative change in resistivity as a function of the critical temperature for heating, T_{cH}. As was done for V_6C_5, one may obtain the maximum critical temperature $(T_{cH})_{\max}$ from an extrapolation of a curve of residual resistivity versus T_c to low resistivity. Such a procedure gives $(T_{cH})_{\max} = (1136.5 \pm 2)$ °C or $T_c = (1124 \pm 15)$ °C. This result compares favorably with the value of 1100 °C obtained from an electron-microscope study of $VC_{0.87-0.90}$ by Billingham and Lewis.[14] The relative change in resistivity corresponding to the value of $T_{cH} = 1136.5$ *C* is (Fig. 12)

$$\frac{\Delta\rho(T_c)}{\rho_{\text{total}}(T_c)} = 14.7 \pm 1.0\%$$

or

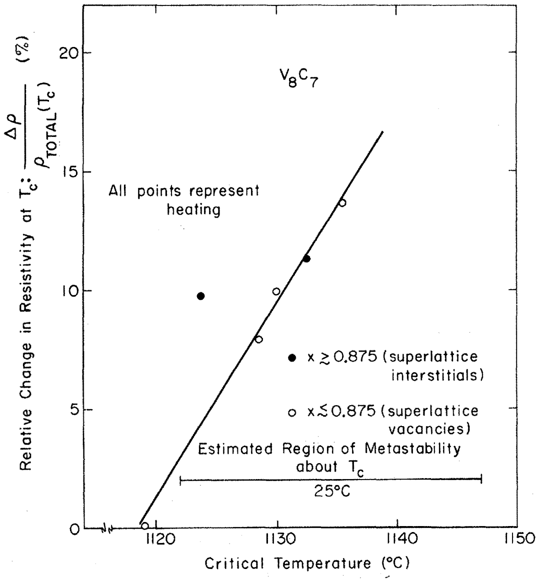

FIG. 12. Relative change in the resistivity at T_c of samples displaying V_8C_7 order as a function of critical temperature for heating, T_{cH}. $\Delta\rho(T_{c\,\max}) = 20.1 \pm 1.4$ $\mu\Omega$ cm or $(14.7 \pm 1.0)\%$ of the total.

$$\Delta\rho(T_c) = 20.1 \pm 1.4\ \mu\Omega\,\text{cm}.$$

In order to develop possible explanations for this resistivity change being four times larger than that in V_6C_5, it is necessary to consider Fig. 13. Here, the resistivity of several samples displaying a V_8C_7 transformation is shown. There is a great similarity between these curves and those for V_6C_5 (Fig. 6). Notice, however, that the difference between sets of curves is less temperature dependent than is the corresponding difference for V_6C_5. Notice, also, that the set of curves lies generally below those for V_6C_5. No direct relation such as Eq. (6) exists in this case because the samples in Fig. 13 can be expected to have different values of $m^*R(T)$ resulting from the wide variation in composition between them. There is as well a considerable composition difference between V_6C_5 samples and V_8C_7 samples. The scattering power of defects and phonons as well as the value and temperature dependence of $m^*R(T)$ can readily be affected by this difference in carbon content. As mentioned at the end of Sec. VII, one must also consider the possibility that the ordering process alters the scattering power of phonons and defects. The dissimilarity of the ordered structures of V_6C_5 and V_8C_7 should cause a difference in order-induced effects in the two solids. Such behavior would certainly contribute to the observed difference between $\Delta\rho(T_c)$ for V_6C_5 and V_8C_7. Despite all of these possibilities for a difference, the behavior of both materials retains great similarity. The results for V_8C_7 like those for V_6C_5 imply that vacancies provide strong scattering centers for electrons at low temperatures, but become of lessening importance as temperature increases.

Finally, an over-all picture of the behavior of the vanadium-carbon system can be formulated with the data which we have obtained on composition and residual resistivity. The NMR study performed by Froidevaux and Rossier[12] on vanadium carbide clearly indicates that some degree of order exists for nearly all compositions. Furthermore, Billingham and Lewis[14] have shown that the vanadium-carbon system prefers either the hexagonal (V_6C_5) or the cubic (V_8C_7) ordered structure over the range $VC_{0.75}$–$VC_{0.90}$. This tendency to form order over a broad range of composition is also demonstrated by our results appearing in Fig. 14. Nearly the entire composition range corresponds to one or the other of the ordered phases. Only a small region of disorder exists between the regions of order. The disordered sample appearing in Fig. 6 is part of this disordered region. Its disorder, therefore, results from its composition and not from its thermal history. The kinetics of the transformation is such

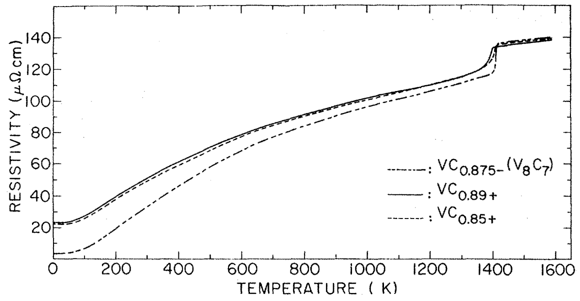

FIG. 13. Resistivities of several samples displaying a V_8C_7 transition as a function of temperature.

that no sample having the ideal composition ($VC_{0.833}$) can be quenched to the disordered state.

IX. ORDERING KINETICS

Our continuing investigation of the ordering kinetics of vanadium carbide has led us to conclude that the actual situation is more complicated than our earlier results indicated.[1] The usual assumption that the resistivity of a quenched sample approaches its equilibrium value exponentially in time appears to be an oversimplification for vanadium carbide. The behavior of the resistivity of a V_6C_5 sample upon isothermal reordering is illustrated in Fig. 15. It may be observed that as reordering proceeds the rate at first increases and then decreases. This general behavior was true of nearly all samples, both V_6C_5 and V_8C_7. Although it may be possible to understand these results in a variety of ways, an appealing interpretation appears in a discussion by Sato[29] of Takagi and Oguchi's[30] calculation of ordering kinetics for *AB* alloys in the Bragg–Williams approximation. These calculations predict a departure from simple exponential behavior and in fact indicate that the ordering rate along an isothermal path should at first increase and then decrease.

Another feature of the ordering kinetics is apparent from Table III. The characteristic reordering time (time for $1/e$ of the change to occur) is a sensitive function of the temperature differential $T_{cL} - T_0$, where T_{cL} is the lower limit of the metastable disordered state and T_0 is the temperature at which isothermal ordering takes place. If the system is rapidly quenched to a reordering temperature well below the critical point, T_{cL}, the ordering process can occur as much as 100 times faster than if the reordering took place near T_{cL}. The work of Takagi and Oguchi[30] suggests an explanation. Their calculations show that the ordering rate is near minimum for any isothermal path near T_c and that a maximum rate exists only for a temperature which is distinctly below T_c.

X. DISCUSSION

Our results for the resistivity of the ordered phases of vanadium carbide, V_6C_5 and V_8C_7, indicate that the scattering of electrons by vacancies forms the dominant contribution to the low-temperature resistivity and, therefore, supports earlier conclusions[1-7] regarding the role of vacancies in this and other transition-metal carbides. We have shown further that the contribution of vacancies be-

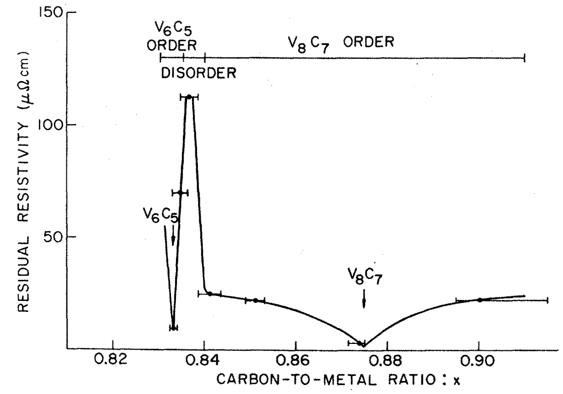

FIG. 14. Residual resistivity of single-crystal vanadium carbide as a function of composition. A strong tendency to form order over a broad range of composition is indicated. The classification of the type of order in each region was determined according to whether the material exhibited a transformation at the V_6C_5 or V_8C_7 critical point. In addition those samples falling within the V_6C_5 region displayed the optically observable domains characteristic of the hexagonal-ordered structure.

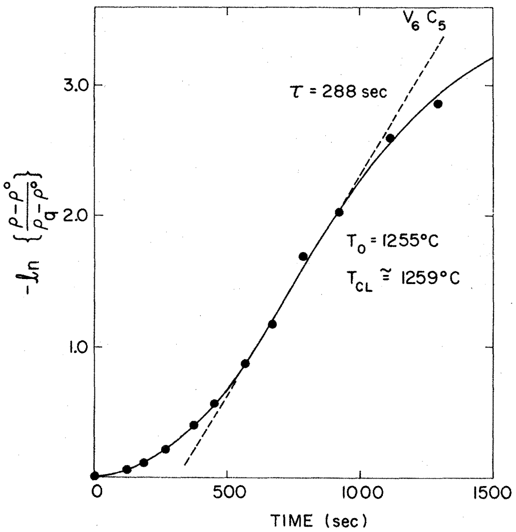

FIG. 15. Isothermal change in the resistivity of V_6C_5 (near ideal composition) at a temperature T_0 immediately below the critical temperature for cooling, T_{cL}. ρ_q is the resistivity after quenching; ρ^0 is the equilibrium resistivity at T_0.

TABLE III. A comparison of ordering time as a function of composition and temperature.

Material	Resistivity ($\mu\Omega$ cm)	Reordering temperature: T_0 (°C)	Critical temperature for cooling: T_{cL} (°C)	$T_{cL}-T_0$ (°C)	Characteristic reordering time (sec)
		Samples displaying V_6C_5 order			
V_6C_5	9.5	1255	1259	4	288
V_6C_5	12	1233	1251	18	~15
		Samples displaying V_8C_7 order			
V_8C_7	3.2	1105	1110	5	510
$VC_{0.85+}$	22.1	1071	1106	35	6

comes of lessening importance as temperature increases. These conclusions are represented graphically in Fig. 16. We present the resistivity of an essentially disordered sample of $VC_{0.83}$ (solid line) which has a behavior quite representative of other nonstoichiometric group IV and V transition-metal carbides. By subtracting the resistivity of a nearly perfectly ordered V_6C_5 sample (broken line), we obtain an estimate of the contribution of vacancy scattering to the resistivity of the disordered solid (dashed line). Therefore, the lower two curves in Fig. 16 approximate the additive contributions of vacancy scattering and phonon scattering to the resistivity of the disordered solid. At low temperature the vacancy term is dominant. We believe that the decline in the vacancy contribution with increasing temperature is most likely produced by a decrease in the Hall coefficient and/or the effective mass since such behavior is common in the transition-metal carbides.[15,31] However, there is the possibility that changes in the band structure with temperature also contribute to the reduction in the vacancy resistivity by decreasing the scattering power of vacancies as temperature increases. We are directing our future efforts toward a measurement of the Hall coefficient and the effective mass of vanadium carbide in order to resolve the mechanism controlling the temperature dependence of the vacancy contribution. Preliminary measurements of the Hall coefficient of V_8C_7 indicate that there is a reduction in $R(T)$ in going from helium temperature to room temperature of the required magnitude.

We have concluded a search for anisotropy in the resistivity of V_6C_5 and found no measurable effect. Although the situation is complicated by the existence of domains, we believe that the failure of V_6C_5 to show a measurable anisotropy indicates that our conclusions regarding the role of vacancies can be supported.

So far the contribution of impurities (> 500 ppm) in the vanadium carbide crystals used has not been discussed. The major impurities detected were other transition metals (Table I). These would enter the vanadium lattice substitutionally with a high binding energy and would probably not be affected by order-disorder transformations. Even if some strain energy were associated with a substitutional defect, segregation at domain boundaries would be unlikely because of the large energy for diffusion of the metal species in the carbides. Thus the Cr, etc., impurities in the samples studied probably supply a constant background of electron scattering but contribute less to the resistivity than vacancies and superlattice defects.

The remaining uncertainty in our interpretation of the role of vacancies is that of short-range order. Short-range order (sro), unlike long-range order (lro), does not fall to zero at T_c; rather, it possesses an exponentially decaying tail extending into the region above T_c. We believe that sro does exist in vanadium carbide above T_c. Indeed, we observe some evidence for the existence of a "memory" for superlattice orientation before and after disordering. (Individual domains which can be identified according to size, shape, and color when viewed under crossed polarizers seem to return to roughly the same appearance after being heated above T_c.) We are less certain about the effects of sro on the resistivity of disordered vana-

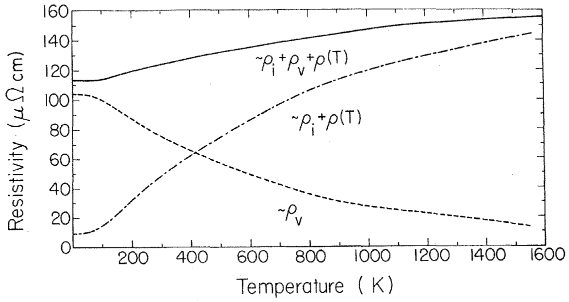

FIG. 16. Temperature dependence of the resistivity of an essentially disordered $VC_{0.83}$ sample (solid line) and a nearly perfectly ordered V_6C_5 sample (broken line) are presented. The difference in resistivity between these two samples (dashed line) approximates the contribution of vacancies to the resistivity of the disordered state.

dium carbide. The characteristic nonlinear variation of sro with temperature should produce a similar nonlinear effect on the resistivity, yet the behavior of the resistivity above T_c is perfectly linear. There does, however, appear to be a general tendency for the resistivity of better-ordered samples in Fig. 6 to lie below the resistivity of the disordered sample even above T_c. There are several possible alternative explanations, so the actual cause of this behavior is uncertain.

We have established the critical temperature for the disordering of the two ordered phases to be (1275 ± 8) °C (V_6C_5) and (1124 ± 15) °C (V_8C_7). These values are in general agreement with other results.[10,14,17] We have also shown that these temperatures are composition dependent and that they tend to reach maxima at the ideal compositions $VC_{0.833}$ and $VC_{0.875}$. Although we did not explore the region below $VC_{0.83}$, Billingham and Lewis[14] have shown that the critical temperature decreases rapidly as carbon is removed, falling to 900 °C at $VC_{0.78}$. Therefore, it is safe to assume that a maximum in T_c exists for $VC_{0.833}$ as well as for $VC_{0.875}$.

We might also note that a single-crystal sample of V_8C_7 was produced during the course of this work which had the lowest residual resistivity (3.17 $\mu\Omega$ cm) ever measured in a nonsuperconducting fourth- or fifth-group transition-metal carbide. Since there is good reason to believe that this sample was still not perfectly stoichiometric V_8C_7 (it was produced by annealing part of the RIAS crystal in $VC_{0.875}$ powder), there is hope for reducing this resistivity even further, perhaps by enough to make Fermi-surface measurements possible. Bachmann and Williams[32] have approached this same problem through the production of low-resistivity samples of tungsten carbide, but now an alternative path is suggested.

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