FIG. 16. Quantum yield extrapolated to zero thickness Y_0 for diffuse reflectance and $\Delta E_p = 0.001$ eV.
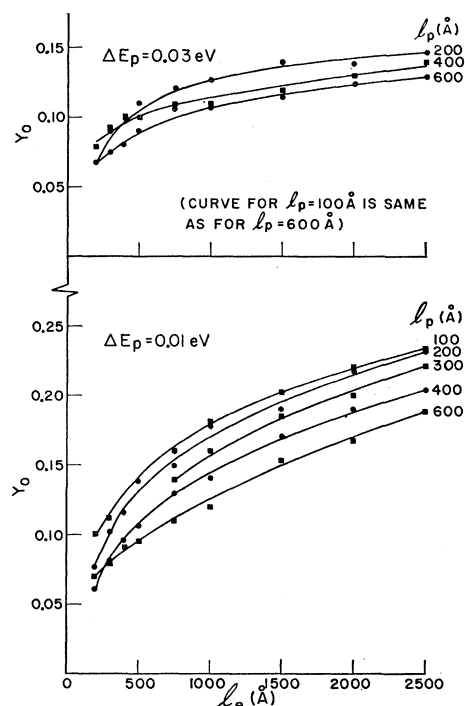

FIG. 17. Quantum yield extrapolated to zero thickness Y_0 for diffuse reflectance with ΔE_p values of 0.01 and 0.03 eV.

Scattering of Electrons by Vacancies in Nonstoichiometric Crystals of Titanium Carbide*

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A study has been made of the influence of carbon vacancies on the resistivity of titanium carbide, a refractory hard metal. Crystals were obtained with vacancies in concentrations of from 3 to 20%. The vacancies were introduced into the fcc carbon sublattice of the rock salt structure of TiC by controlling the C/Ti ratio during crystal growth. The vacancy concentration in some crystals was further reduced by preferential vaporization of Ti at high temperatures and in others by addition of ~1% boron to release carbon to the lattice through the formation of TiB_2 precipitates. Measurements were then made of resistivity as a function of vacancy concentration at 77 and 298°K. On some samples, the Hall coefficient was also measured. The resistivity shows a monotonic increase with increasing vacancy concentration and has a large residual value, whereas the Hall coefficient is relatively independent of vacancy concentration but increases at low temperatures. The data are analyzed using Matthiessen's rule and the Bloch-Grüneisen formula and interpreted using Mott's band model for transition metals. A value for the added resistivity per atomic percent carbon vacancies in TiC was obtained: $16\mu\Omega$ cm. This value is an order of magnitude larger than that for the noble metals. A four part explanation is offered: TiC has a smaller number of conduction electrons per atom, the scattering probability is higher in TiC because of the high density of states in a d-like band overlapping the s-like conduction band, the screening of a vacancy is less effective because of the smaller number of conduction electrons, and the effective charge of a vacancy is probably greater than $1e$. The room-temperature resistivity of stoichiometric TiC, as inferred in the analysis, is $70 \pm 10\ \mu\Omega$ cm.

1. INTRODUCTION

FUNDAMENTAL investigations of the properties of the refractory hard metals are hampered by the

difficulty of obtaining pure and well-characterized samples. A survey of data on the room-temperature resistivity of titanium carbide indicates that fourteen different investigators have obtained values ranging from 35 to 250 $\mu\Omega$ cm. The rather surprising lack of agreement for the value of this simple quantity was one
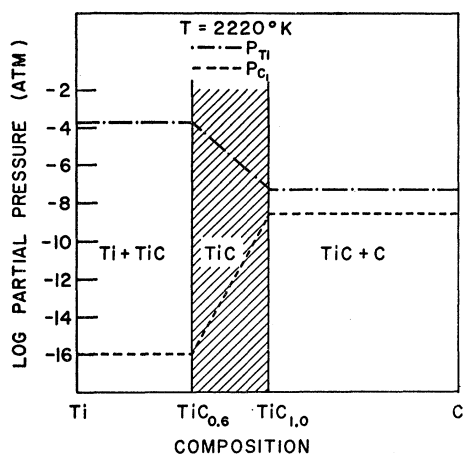
FIG. 1. Simplified pressure-composition diagram for the Ti-C system. NaCl-structure phase, TiC_x, is shown as shaded area. Figure shows that $P_{Ti} > P_C$ throughout the composition range ($T = 2200°K$).

of the principal motivations of the present work. It was suspected that the typically high and uncertain concentrations of lattice vacancies in TiC might account for the observed spread in resistivity values.

A wide homogeneity range is characteristic of the cubic transition-metal monocarbides. Titanium carbide, for example, exhibits the NaCl structure from $\sim 11\%$ C to 20% C by weight.[1] The lower extreme of this range corresponds to a concentration of vacancies in the fcc carbon sublattice of ~ 50 at.%. The vacancy concentration is determined by the relative amounts of metal and carbon reacted together to form the compound. These concentrations are much higher than those produced by quenching or irradiating a normal metal.

The presence of such a large concentration of vacancies would be expected to affect various physical properties such as diffusion, yield stress, thermal conductivity, and electrical resistivity. Since the relation between carbon content and yield stress for TiC has already been studied,[2] the present investigation was aimed at studying the influence of carbon vacancies on the electrical resistivity. It was found that scattering of electrons by vacancies dominates the resistivity of typical TiC crystals.

2. CONTROL OF VACANCY CONCENTRATION IN CRYSTALS

TiC single crystals grown by the arc-Verneuil process were obtained from Union Carbide Corporation, Linde Division. Crystals with various carbon to titanium ratios were produced at Linde by reacting differing relative amounts of Ti and C powders and using the reacted powders in crystal growth. The compositions of the crystals were determined chemically by Linde. Oxygen and nitrogen levels were found to be $<0.02\%$

by weight and no metallic impurities were detected spectroscopically. A description of the substructure of these crystals has been published.[3]

Since the lowest vacancy concentration in the crystals received was 3%, ways were sought to reduce this concentration further. High-temperature free-surface vaporization to preferentially remove titanium was one method selected. Consideration of the free energy of formation of TiC[4] and the heats of sublimation of Ti and C[5] shows that there is no crossover in the partial pressures (more correctly, the fluxes) of Ti and C in the pressure-composition diagram (see Fig. 1) and hence no region of congruent vaporization or constant boiling.[6] Rather, throughout the diagram, the partial pressure of Ti exceeds that of C.

These considerations apply to gas-solid equilibrium; for the purpose discussed above, a nonequilibrium, free-surface (Langmuir) vaporization is required to permanently remove titanium from the solid. The equilibrium data can be applied to nonequilibrium vaporization only if the vaporizing species and their vaporization coefficients are known. Mass spectrometer studies have been made of the equilibrium vaporization of TiC by Chupka et al.,[7] and of the free-surface vaporization of a similar compound, TaC, by Williams and Schissel.[8] These results suggest that in the free-surface vaporization of TiC the vapor species are monatomic Ti and C with similar vaporization coefficients. Hence, from the equilibrium diagram and from the kinetic theory relation between flux and pressure, it follows that a solid sample of titanium carbide undergoing free-surface vaporization at 2220°K will lose titanium ~ 10 times faster than it loses carbon. The composition of the solid will consequently shift toward the carbon-rich side of the diagram.

To test this prediction, a crystal of TiC was heated to $\sim 2200°K$ inside the induction coil of an ultrahigh vacuum furnace.[9] The temperature was maintained for four days, then gradually reduced for four more days. As discussed below, resistivity measurements showed that the titanium to carbon ratio of this crystal was affected by the heat treatment as predicted. Another sample, similarly prepared, yielded similar results.

Another method used to reduce the carbon vacancy concentration in TiC crystals was to heat them in contact with boron. The reaction $TiC + 2B = TiB_2 + C$ has been investigated by Brewer and Haraldsen[10] and

[1] M. Hansen, Constitution of the Binary Alloys (McGraw-Hill Book Company, Inc., New York, 1958), 2nd ed., p. 384.
[2] W. S. Williams, J. Appl. Phys. 35, 1329 (1964).
[3] W. S. Williams and R. D. Schaal, J. Appl. Phys. 33, 955 (1962).
[4] G. L. Vidale, G. E. Space Science Laboratory Report No. R61SD010, 1961 (unpublished).
[5] D. R. Stull and G. C. Sinke, Thermodynamic Properties of the Elements (American Chemical Society, Washington, D. C., 1956), pp. 68 and 210.
[6] A. W. Searcy, W. S. Williams, and P. O. Schissel, J. Chem. Phys. 32, 957 (1960).
[7] W. A. Chupka, J. Berkowitz, C. F. Giese, and M. A. Inghram, J. Phys. Chem. 62, 611 (1958).
[8] W. S. Williams and P. O. Schissel (unpublished work).
[9] W. S. Williams, Rev. Sci. Instr. 32, 743 (1961).
[10] L. Brewer and H. Haraldsen, J. Electrochem. Soc. 102, 399 (1955).

the writer,[11] and it has been established that the di-
boride of titanium is more stable than the carbide. Thus,
a TiC crystal exposed to boron at high temperatures
will suffer conversion as indicated. If the amount of
boron added is small ($\leq 1\%$), the boride phase will
form a lamellar precipitate, coherent with the TiC
matrix and lying along {111} planes. (The appearance
of such crystals was described previously by the writer,[12]
although at that time it was believed that the pre-
cipitates were graphite.) Carbon atoms released by the
reaction can fill vacant lattice sites and reduce the
resistivity. The measurements confirmed this expecta-
tion. A secondary effect is a partial short-circuiting of
the TiC matrix by the lower resistivity of TiB_2.[13] This
effect can account for only a small fraction of the ob-
served change in resistance because of the low concen-
tration of TiB_2 ($<1\%$).

3. MEASUREMENTS OF RESISTIVITY AND HALL COEFFICIENT

Resistivity and Hall coefficient measurements were
made on samples cleaved from four TiC single crystals
with various carbon/titanium ratios. Resistivity meas-
urements only were made on several other TiC crystals
from various sources and with different heat treatments.
Direct-current techniques were employed and readings
were taken at 77 and 298°K. Room-temperature
resistivity measurements were made with the sample
in four orientations. Two different current values and
both directions for each current were used for each
orientation and the results averaged. In each Hall
measurement, three values of current and three of
magnetic field were used (see Fig. 2), and for each
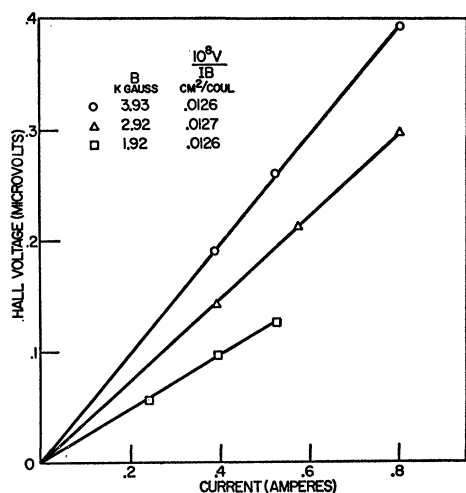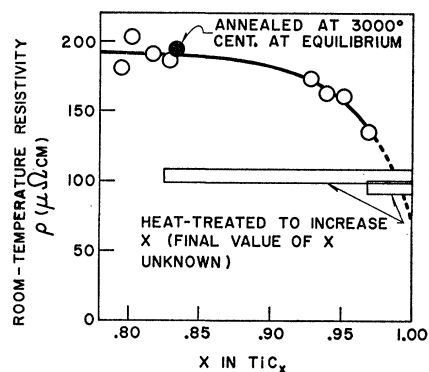combination of field and current values the readings

FIG. 3. Room temperature resistivities for TiC
crystals of various C/Ti ratios (values of x).

were taken for both current directions and both
magnetic field directions. Measurements were made on
two samples from each crystal and averaged. Hall
voltages ($\sim 0.1\ \mu V$) were read directly on a Keithley
model 149 millimicrovoltmeter. In the resistivity meas-
urements, probe voltages were measured with a Rubicon
6-dial potentiometer (least count 0.01 μV) with the
Keithley amplifier used as a null detector. The over-all
uncertainty of each tabulated resistivity and Hall
coefficient is estimated to be $\pm 5\%$. The principal
uncertainty is in the crystal dimensions, which are
irregular due to chipping and step formation during
cleavage and slight curvature from the presence of
subgrain boundaries.

The measured resistivity at room temperature is
shown as a function of carbon content in Fig. 3. The
two bars refer to crystals for which only the initial
value of the carbon/titanium ratio x was known. After
heat treatment to vaporize Ti and increase x, only an

FIG. 2. Typical Hall effect results for TiC crystals.

[11] W. S. Williams, J. Phys. Chem. **65**, 2213 (1961).
[12] W. S. Williams, J. Appl. Phys. **32**, 552 (1961).
[13] W. S. Williams and R. T. Dolloff, Bull. Am. Phys. Soc. **4**, 228 (1959).

TABLE I. Resistivity and Hall coefficient values for TiC crystals
of various C/Ti ratios ($\pm 5\%$ uncertainty on all values).

% Carbon by weight	x in TiC_x	Resistivity ($\mu\Omega$ cm) ρ_1'	ρ_2'	Hall coefficient (10^{-4} cm³/C) $-R_1$	$-R_2$
18.9	0.928	161	173	22.4	15.5
19.1	0.939	151	163	26.4	15.0
19.6	0.969	125	136	34.2	16.6
>19.6	>0.969	83.5	95.7	31.7	15.0
(after heat treating)					
16.61	0.794	175	181		
16.8	0.803	197	203		
17.02	0.816	184	191		
17.23	0.829	180	187		
17.3	0.833		195		
19.3	0.951		161		
>17.2	>0.826	91.0	103 (after heat treating)		
[a](composition unknown)			155		
[b](composition unknown)			⎰197 (before heat treating) ⎱148 (after heat treating)		
(boron treated)		64	120		
		60	105		

[a] From Semi-Elements, Inc.
[b] From Horizons, Inc. (Other crystals from Union Carbide Corporation
Linde Division.)

TABLE II. Results of analysis of Hall and resistivity data using Matthiessen's rule and Bloch-Grüneisen formula with $\theta = 734°K$.[a]

x in TiC$_x$	N_v	μ_1'	μ_2'	μ_0	μ_1	μ_2	$1/\mu_0$	ρ_1	ρ_2	ρ_{01}	ρ_{02}
0.928	0.073	13.79	8.96	13.92	1256	25.00	0.0719	1.77	62.0	159.2	111.2
0.939	0.061	17.48	9.20	17.80	955	18.99	0.0562	2.76	79.0	148.2	84.2
0.969	0.031	27.35	12.21	28.00	1405	21.65	0.0357	2.44	76.6	122.1	59.3
>0.969	<0.031	38.00	15.80	39.10	1328	26.45	0.0256	2.39	57.1	81.1	38.6

[a] μ's in cm^2/V-sec, ρ's in $\mu \Omega$ cm.

upper bound of $x=1$ was available. The solid datum point refers to a crystal that was annealed in an *equilibrium* environment just under the melting point and cooled slowly to reduce the concentration of *thermal* vacancies. No change occurred in the resistivity. This result demonstrates that the concentration of thermal vacancies is much less than the chemically determined value, $1-x$.

The complete resistivity and Hall measurement results are the first four lines presented in Table I. Most of the results are for Linde crystals, but studies made on samples from two other sources revealed similar resistivity values. The principal feature is a monotonic decrease in resistivity with decreasing vacancy content and no significant change in the room-temperature Hall coefficient. The large residual resistivity at 77°K also supports the idea that vacancy scattering is important in these samples.

4. ANALYSIS OF DATA

The object of the analysis is to separate vacancy effects from the intrinsic scattering of electrons by phonons. Matthiessen's rule expressed in terms of mobilities[14] states that this separation can be made through the addition of reciprocal mobilities. We have

$$1/\mu_i' = 1/\mu_i + 1/\mu_0 \quad (i=1,2), \tag{1}$$

where μ_i' = effective mobility, μ_i = intrinsic mobility (temperature-dependent), μ_0 = mobility associated with vacancy scattering (temperature-independent), and the
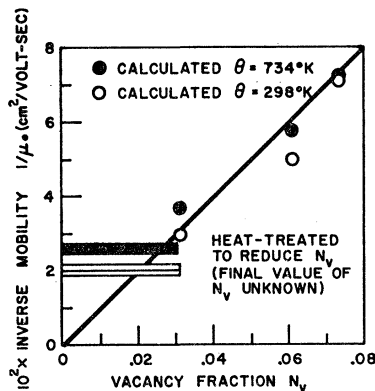

Fig. 4. Inverse mobility associated with scattering of conduction electrons by carbon vacancies as related to concentration of vacancies.

subscripts 1 and 2 refer to 77.3 and 298°K, respectively. When $\mu_0 \cong \mu_i$, as in the present case for $i=2$, Matthiessen's rule does not hold exactly. However, the deviation will be small if the changes in elastic constants, lattice constant, and electronic structure are small.[14] These conditions apply here. Let $A \equiv \mu_2/\mu_1$; then we have

$$\mu_2 = \frac{1-A}{1/\mu_2' - 1/\mu_1'}, \quad \mu_1 = \frac{\mu_2}{A}, \quad \mu_0 = \frac{1-A}{1/\mu_1' - A/\mu_2'}. \tag{2}$$

The mobility ratio A for a normal metal can be obtained approximately from the Bloch-Grüneisen expressions, $r_i = \mu_i/\mu_\theta$ and $r = 1.056(T/\theta)F(\theta/T)^{15}$; the function $F(\theta/T)$ is tabulated.[15] The value of θ (Debye temperature) is taken as 734°K, a value obtained by Bernstein[16] from elastic constant measurements on TiC crystals. The resulting mobility ratio is $A = 0.0199$. The primed (effective) mobilities are given by the one-carrier relation between resistivity ρ, and Hall coefficient R, and mobility $\mu = |R|/\rho$. An argument for conduction in a single s-like band in TiC has been given by Piper.[17] We have then for the resistivities

$$\rho_i = |R_i|/\mu_i, \quad \rho_{0i} = |R_i|/\mu_0$$

and

$$\rho_i' = \rho_i + \rho_{0i} \quad (i=1,2). \tag{3}$$

Thus, the quantities μ_1', μ_2', μ_0, μ_1, μ_2, ρ_1, ρ_2, ρ_{01}, and ρ_{02} can be calculated from the measured quantities ρ_1', ρ_2', R_1 and R_2. The residual resistivity ρ_{0i} is a function of temperature because the carrier concentration changes with temperature, as shown by the behavior of the Hall coefficient. The mobility associated with vacancy scattering μ_0 is taken as temperature-independent.

A tabulation of the results of these calculations is given in Table II; there are two principal results. As shown in Fig. 4, $1/\mu_0$ depends linearly on the vacancy fraction N_v, where $N_v = 1-x$. Second, a value is inferred for the intrinsic resistivity of stoichiometric TiC at room temperature of $70 \pm 10 \mu\Omega$ cm. The results are not sensitive to the choice of Debye temperature (see Fig. 4). This conclusion is fortunate because it is not clear what Debye temperature is appropriate. The small number of conduction electrons means that the

[14] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960), p. 434.

[15] D. K. C. MacDonald, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. XIV, p. 171.

[16] B. Bernstein (to be published).

[17] J. Piper, J. Appl. Phys. **33**, 2394 (1962).

radius of the Fermi surface will be small, leading to a Debye temperature for the acoustical phonons involved in the resistivity that is much lower than that calculated from the elastic constants. But since TiC has two atoms per unit cell, there will be an optical branch to the frequency spectrum, and the optical phonons, which are more energetic, will be important in determining the intrinsic mobility, as in InSb and other compound semiconductors.[18]

5. HALL COEFFICIENT

The relative constancy of the measured Hall coefficient with respect to x is somewhat curious, since there is evidence that added carbon atoms contribute additional conduction electrons: an explanation can be based on Mott's band model used in connection with the transition metals and applied by Piper[17] to TiC. Conduction is primarily in an s band with a small density of states, but the presence of an overlapping d band of low mobility and high density of states affects the transport properties. In connection with the Hall coefficient, conduction electrons added as x increases are mostly taken up by the d band and do not substantially increase the electron concentration n in the one-carrier expression $R = 1/nec$. Hence, R is insensitive to changes in x.

At low temperatures the Hall coefficient increases, indicating a decrease in n. It is then easy to see why the resistivity of a TiC crystal changes only slightly on immersion in liquid nitrogen: the concentration of carriers decreases but the intrinsic mobility increases by approximately the same amount.

6. CONCENTRATION DEPENDENCE OF VACANCY SCATTERING

The measured room-temperature resistivity ρ_2' of TiC crystals decreases with increasing x in TiC_x as shown in Fig. 3. The relation between ρ_2' and x is not linear. However, the analysis described above using Matthiessen's rule leads to the conclusion (see Fig. 4) that the inverse mobility term associated with vacancy scattering, $1/\mu_0$, increases linearly with vacancy fraction $N_v (=1-x)$. Since R_2 is independent of x, the vacancy-induced resistivity is also proportional to the concentration of vacancies at least up to 7% vacancies. At higher concentrations, Fig. 3 suggests that a saturation effect might occur. Some deviation from linearity would be expected when the vacancy concentration becomes high enough to permit interaction of perturbed charge distributions around the defects.

From the slope of the line in Fig. 4 and an average Hall coefficient at room temperature of 16×10^{-4} cm^3/C, one may calculate that the added resistivity per atomic percent carbon vacancies in TiC at room temperature is $16 \mu\Omega$ cm. This value is to be compared with the

corresponding value of 1.5 for noble metals determined experimentally by Simmons and Balluffi[19] and also predicted theoretically.[20] The larger value for TiC comes partly from the low number of conduction electrons in TiC compared with a noble metal: from the Hall coefficient we obtain ~ 0.08 electron/Ti atom for TiC. The incremental resistivity per vacancy is proportional to the reciprocal of the carrier concentration. Another contribution to the large value of resistivity per vacancy comes from the high density of states in the d band into which the conduction electrons from the s band can be scattered.

A third contribution comes from the slightly larger screening length, compared with a noble metal (a consequence of the smaller number of conduction electrons, see Ref. 4, p. 170). The potential around the vacancy will be substantially affected through the exponential shielding factor. Fourth, the effective charge of the carbon vacancy is possibly greater than $1e$, leading to an important increase in the coulomb term. The third and fourth contributions have been suggested by Cutler et al.[21] to account for the large residual resistance of cerium-deficient cerium sulfide.

7. COMPARISON WITH LITERATURE ON RESISTIVITY OF TiC

A variation of the resistivity of titanium carbide with carbon content has also been found by Münster and Sagel and reported by Bilz.[22] The measurements were made on vapor-deposited films of TiC. Bilz attributes Münster and Sagel's results to scattering of electrons by excess titanium. Although chemically an excess of combined titanium is indistinguishable from a deficiency of carbon, there is a difference in the physical model: the former condition would be associated with interstitial Ti and the latter with carbon vacancies. The decrease in the x-ray lattice constant with decreasing carbon to titanium ratio[23] shows that the second model is correct. The explanation is apparent on consideration of the relative atomic radii and the elastic strain energy appropriate to the two models.

One possible explanation for the large range of resistivity values in the literature is suggested by the present work: differing vacancy concentrations. Two other effects are also probably influential, especially for samples prepared by powder techniques. The presence of an intergranular iron film, acquired in ball milling for particle size reduction prior to hot-pressing, has been found by the writer to produce low resistivity values, whereas samples hot-pressed from magnetically separated powders show higher resistivities. Piper[17] has found that nitrogen doping can also lower the resistivity of TiC.

[18] H. Ehrenreich, Phys. Chem. Solids **2**, 131 (1957); **9**, 179 (1959).

[19] R. O. Simmons and R. W. Balluffi, Phys. Rev. **125**, 862 (1962).
[20] See Ref. 14, p. 344.
[21] M. Cutler, J. F. Leavy, and R. L. Fitzpatrick, Phys. Rev. **133**, A1143 (1964).
[22] H. Bilz, Z. Physik **153**, 338 (1958).
[23] P. Ehrlich, Z. Anorg. Chem. **259**, 1 (1949).

Several investigations of the resistivity of approximately stoichiometric hot-pressed TiC have been reported[24–27] in the last decade: the average of these four results is 62 $\mu\Omega$ cm, and an uncertainty of ± 10 $\mu\Omega$ cm includes them all. From the present experiment, the value of the intrinsic resistivity of stoichiometric TiC is estimated to be 70 ± 10 $\mu\Omega$ cm, a value consistent with the results quoted. As with pure transition metals, the resistivity of TiC is high.

Linde TiC single crystals low in both nitrogen and iron, similar to the ones used in the present work, were used in an investigation by Hollander.[28] He found a room temperature resistivity of 212 $\mu\Omega$ cm. Piper[17] measured resistivities and Hall coefficients on several TiC crystals from the same source and obtained values similar to the ones reported here.

8. COMPARISON WITH RESULTS ON TaC

Tantalum carbide is isomorphic with respect to titanium carbide. Since the present work was begun, two publications have appeared describing measurements of the resistivity of TaC and the effect of lack of stoichiometry. These studies were carried out on tantalum wires that had been carburized by interaction with hydrocarbon vapor.

Eckstein and Forman[29] determined the temperature dependence of the resistivity of TaC in the range 1800 to 3400°K. They found a linear relation: $\rho = 102 + 0.0178T$ $\mu\Omega$ cm, indicating a residual resistivity of 102 $\mu\Omega$ cm. They suggest that variations in carbon content might account for the lack of literature agreement on the resistivity of TaC.

Cooper and Hansler,[30] who studied the influence of carbon content on the resistivity of TaC, found a linear dependence of resistivity on x in TaC_x from $x = 0.86$ to 0.98. They determined values of x by x-ray measurement of lattice constant and use of the empirical relation between these two quantities established by Bowman.[31] (For titanium carbide, a similar procedure is not possible because of the insensitivity of the lattice constant to changes in carbon content in the range of interest.)

These results on tantalum carbide strongly support the present conclusion that the resistivity of available titanium carbide crystals is dominated by scattering of electrons by carbon vacancies.

9. MAGNETIC DISORDER SCATTERING

Another mechanism that is known to produce a large residual resistivity is magnetic disorder scattering. This effect results from perturbations in the superexchange field connecting conduction electrons with unpaired electrons on atoms. Such behavior occurs in certain dilute solid solutions and in ferromagnetic and antiferromagnetic materials above their magnetic transition temperatures, i.e., whenever there is disorder in the atomic magnetic moments. These effects have been reviewed extensively by Coles.[32]

Although there is no evidence that TiC has a disordered antiferromagnetic structure, such has been attributed[32] to β-Ti to account for its large residual resistivity.[33] Some compounds having the rock-salt structure are known to be antiferromagnetic (e.g., NiO, CoO). Hence, it is conceivable that rock-salt structure TiC is in a disordered antiferromagnetic state at all temperatures and that its high residual resistivity is a consequence. This explanation does not include the observed variation of resistivity with carbon content. Since the vacancy-scattering hypothesis is sufficient and well-supported, it is favored.

Note added in proof. The intrinsic mobility of electrons in TiC is high ($\mu_2 \sim 1000$ cm^2/V-sec from Table II), so the high resistivity is primarily a consequence of the low carrier concentration ($n \cong 0.08$ electrons/Ti atom). Since $n_{Ti} \gg n_{TiC}$ and yet $\rho_{Ti} \cong \rho_{TiC}$, it follows that $\mu_{Ti} \ll \mu_{TiC}$. The mobility difference could be explained by assuming that the d-band density of states at the Fermi level in TiC is much less than in Ti; i.e., that the Fermi level of stoichiometric TiC is near a minimum in the density of states curve. A similar conclusion about TiC has been reached by R. G. Lye from a recent study of the Seebeck coefficient of TiC (unpublished).

[24] F. W. Glaser and W. Ivanick, J. Metals 4, 387 (1952).
[25] G. V. Samsonov, Zh. Techn. Fiz. 26, 716 (1956) [English transl.: Soviet Phys.—Tech. Phys. 1, 695 (1956)].
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[32] B. R. Coles, Advan. Phys. 7, 40 (1958).
[33] S. L. Ames and A. D. McQuillan, Acta Met. 2, 831 (1954).