

## Effect of Composition on the Superconducting Transition Temperature of Tantalum Carbide and Niobium Carbide\*

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Tantalum carbide and niobium carbide samples with carbon-to-metal molar ratios varying from 0.754 to 0.987 for tantalum carbide and from 0.70 to 0.977 for niobium carbide were examined for superconductivity. Both niobium and tantalum carbides were found to be superconducting with transition temperatures which vary with composition. The major conclusion is that the highest temperature is reached for the stoichiometric composition and any deviation therefrom results in a lowering and eventual disappearance (less than 1.05°K) of  $T_c$ .

**SUPERCONDUCTIVITY** among carbides of niobium and tantalum has been the subject of contradictory communications. In these, the superconducting transition temperatures  $T_c$  reported for niobium carbide varied from 6.0°K<sup>1</sup> to 10.3°K,<sup>2,3</sup> while tantalum carbide was repeatedly reported to be normal at temperatures as low as 1.20°K.<sup>1,4</sup> Meissner<sup>3</sup> reported tantalum carbide to be superconducting at 9.4°K. However, since he used the resistance method and did not give any crystallographic data, it was not clear whether the superconductivity was due to filaments of some tantalum carbide or the compound itself. The results of the present investigation not only show that superconductivity occurs in both niobium and tantalum carbides but also explains the various transition temperatures previously reported.

Our major conclusion is that the highest temperature is reached for the stoichiometric composition and any deviation therefrom results in a lowering and eventual disappearance (less than 1.05°K) of  $T_c$ . The rate at

which this lowering occurs with deviation from stoichiometry is quite unprecedented. It is larger than one would expect from any corresponding variation of the valence electron concentration.<sup>5</sup>

Table I and Fig. 1 show the variation with composition of the superconducting transition temperature of tantalum and niobium carbides. The data were obtained by susceptibility measurements. Tantalum carbide samples were prepared by heating mixtures of the elemental powders in graphite crucibles at 1850°, under vacuum of 10<sup>-5</sup> mm. of Hg for six 1½-hour periods. The material was ground to a powder after each heating.<sup>6</sup> Niobium carbide samples were prepared in a similar manner at approximately 2000°, with heating times varying from 2 to 24 hours. These carbides have a wide homogeneity range,<sup>7,8</sup> and deviation from the molar ratio of 1:1 is easily obtained. The composition can be

TABLE I. Transition temperatures and composition of tantalum and niobium carbide samples.

Composition	$T_c$ (°K)	Composition	$T_c$ (°K)
TaC <sub>0.987±0.01</sub>	9.7	NbC <sub>0.977±0.002</sub>	11.1
TaC <sub>0.981±0.01</sub>	9.0	NbC <sub>0.975±0.02</sub>	11.1
TaC <sub>0.979±0.01</sub>	9.4	NbC <sub>0.968±0.02</sub>	10.6
TaC <sub>0.978±0.01</sub>	8.8	NbC <sub>0.918±0.01</sub>	7.3
TaC <sub>0.968±0.01</sub>	7.5	NbC <sub>0.885±0.01</sub>	3.2
TaC <sub>0.938±0.01</sub>	6.4	NbC <sub>0.881±0.01</sub>	4.2
TaC <sub>0.910±0.01</sub>	4.75	NbC <sub>0.878±0.01</sub>	3.5
TaC <sub>0.878±0.01</sub>	3.20	NbC <sub>0.829±0.01</sub>	1.05
TaC <sub>0.848±0.01</sub>	2.04	NbC <sub>0.79±0.01</sub>	a
TaC <sub>0.754±0.01</sub>	a	NbC <sub>0.76±0.01</sub>	a
		NbC <sub>0.75±0.01</sub>	a
		NbC <sub>0.70±0.01</sub>	a

\* No superconducting transition observed for these compositions down to 1.05°K.

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<sup>1</sup> G. F. Hardy and J. K. Hulm, *Phys. Rev.* **93**, 1004 (1954).

<sup>2</sup> B. T. Matthias and J. K. Hulm, *Phys. Rev.* **87**, 799 (1952).

<sup>3</sup> W. Meissner and H. Franz, *Z. Physik* **65**, 30 (1930).

<sup>4</sup> W. T. Ziegler and R. A. Young in *Proceedings of the International Conference on Low-Temperature Physics, Oxford, England 1951*, edited by R. Bowers (Oxford, 1951), p. 124.

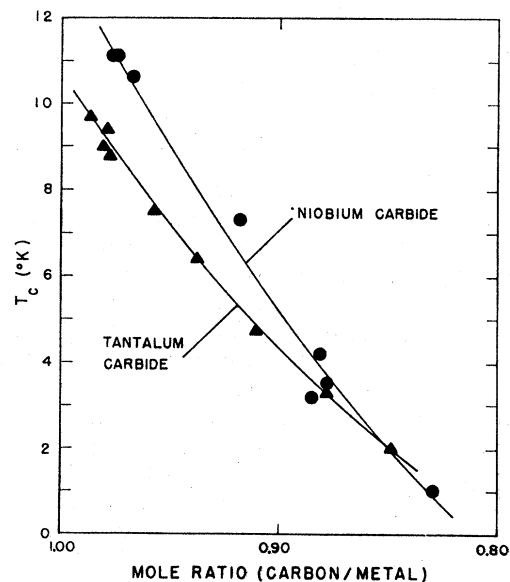


FIG. 1. Variation of the transition temperature  $T_c$  with carbon-to-metal ratio.

<sup>5</sup> B. T. Matthias, *Phys. Rev.* **92**, 874 (1953).

<sup>6</sup> Allen L. Bowman, *J. Phys. Chem.* **65**, 1596 (1961).

<sup>7</sup> Allen L. Bowman (to be published).

<sup>8</sup> E. K. Storms and N. H. Krikorian, *J. Phys. Chem.* **64**, 1471 (1960).

determined by chemical analysis or by examining the x-ray data for the lattice parameter.<sup>6,9</sup> From the data it appears that the tantalum carbide samples previously reported as not superconducting had C/Ta mole ratios lower than 0.84. Such a composition is to be expected for samples which have been arc-melted or heated to very high temperatures under vacuum due to the rapid vaporization of carbon under these conditions. It must be emphasized that true stoichiometry was not attained in the present work, and by reference to the phase diagrams<sup>7,8</sup> it is apparent that it cannot be attained at the temperatures used for preparation of samples. Carbides of higher carbon content can be prepared in the presence of excess carbon, and therefore transition temperatures higher than 9.7°K for tantalum

<sup>9</sup> E. K. Storms and N. H. Krikorian, *J. Phys. Chem.* **63**, 1747 (1959).

carbide and 11.1°K for niobium carbide may be attainable.

Now only vanadium carbide of the Group Va carbides remains as a nonsuperconductor. However, vanadium carbide with a molar ratio, C/V, higher than 0.88 cannot be obtained by the usual techniques.<sup>10</sup> It is very possible that this limitation prevents the occurrence of a superconducting transition rather than any fundamental difference between vanadium carbide and the other carbides of this group.

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<sup>10</sup> E. K. Storms and R. J. McNeal (to be published).

## Theory of the Anomalous Photovoltaic Effect of ZnS

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A theory to account for anomalies observed in the photovoltage of faulted ZnS crystals is proposed. The theory assumes that the spontaneous polarization of hexagonal ZnS causes internal fields in these crystals, with opposing fields in cubic and in hexagonal material. If one then considers a unit of one cubic and one hexagonal segment, these fields will cause differences in carrier concentration, and resultant differences in photovoltage at the two band-gap barriers in such a unit. The net photovoltages of such units will be additive along the crystal. It appears that the proposed theory can account for observed photovoltages, both as to their magnitude and their reversal of sign with wavelength.

### I. INTRODUCTION

A NUMBER of investigations on ZnS single crystals<sup>1-5</sup> have established the existence and a number of properties of a so-called "anomalous" photovoltaic effect. The main characteristics of this effect are that the photovoltage is much higher than the voltage corresponding to the band gap,<sup>1-5</sup> and that it reverses sign with wavelength of irradiation.<sup>2,4,5</sup> In the region of band-edge absorption (the region of interest in the present paper), the photovoltage is generally of one sign (negative, by convention<sup>2,4</sup>) until about 3300 Å, then becomes positive until about 3500 Å, and then becomes negative again.<sup>2,4</sup> At longer wavelengths, there can be still another reversal, with the photovoltage persisting to quite long wavelengths<sup>2</sup> ( $\gtrsim 10\,000$  Å), but this will not be considered here.

It has been established fairly well that this anomalous behavior takes place only in crystals which show at least some stacking disorder (i.e., changes in structure from cubic to hexagonal).<sup>1,3-5</sup> Early attempted explanations<sup>1,3</sup> therefore assumed a photovoltage at each structural reversal (estimated experimentally at 0.15 v per reversal<sup>3</sup>), with these voltages additive along the crystal. However, as was pointed out by Tauc, it is hard to understand such additivity, so that it seems better to assume that each structural "unit," i.e., a unit composed of one segment of cubic structure and one of hexagonal structure, contains opposing barriers (or potential gradients).<sup>6</sup> Each unit would here have one or more barriers with an increasing potential energy, and opposing barriers with a decreasing potential energy. In addition, one requires some asymmetry in this system, in order to prevent cancellation between the voltages associated with these opposing barriers.<sup>6</sup> The explanation of the effect proposed by Tauc<sup>6</sup> does provide appropriate barriers and asymmetry. However, Tauc<sup>6</sup> proposes that the barriers arise either from impurity gradients,

<sup>1</sup> S. G. Ellis, F. Herman, E. E. Loebner, W. J. Merz, C. W. Struck, and J. G. White, *Phys. Rev.* **109**, 1860 (1958).

<sup>2</sup> G. Cheroff and S. P. Keller, *Phys. Rev.* **111**, 98 (1958).

<sup>3</sup> W. J. Merz, *Helv. Phys. Acta* **31**, 625 (1958).

<sup>4</sup> A. Lempicki, *Phys. Rev.* **113**, 1204 (1959).

<sup>5</sup> G. Cheroff, R. C. Enck, and S. P. Keller, *Phys. Rev.* **116**, 1091 (1959).

<sup>6</sup> J. Tauc, *J. Phys. Chem. Solids* **11**, 345 (1959).