

Investigation of Ta<sub>2</sub>C, Nb<sub>2</sub>C, and V<sub>2</sub>C for Superconductivity\*

A. L. GIORGI, E. G. SZKLARZ, E. K. STORMS, AND A. L. BOWMAN

*Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico*

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Previous investigators have reported that Ta<sub>2</sub>C and Nb<sub>2</sub>C became superconducting at 3.26 and 9.18°K, respectively. In this work, no superconducting transition was found in pure compounds of Ta<sub>2</sub>C and Nb<sub>2</sub>C for measurements down to 1.98°K, but when the metal phase was present, transition temperatures near to the reported transition temperatures were obtained. A sample of V<sub>2</sub>C, containing a slight excess of metal phase, was prepared and found to have a transition temperature of 4.7°K. However, when the sample was treated with boiling hydrochloric acid to preferentially leach out the metal phase, no superconducting transition was observed for measurements down to 1.98°K. In view of these results, and the similarity between the transition temperature of the metal and the *M-M*<sub>2</sub>C mixture, it appears that pure Ta<sub>2</sub>C, Nb<sub>2</sub>C, and V<sub>2</sub>C are not superconducting down to 1.98°K.

AS an extension of the work on the monocarbides of niobium and tantalum,<sup>1</sup> pure samples of Ta<sub>2</sub>C, Nb<sub>2</sub>C, and V<sub>2</sub>C were prepared and examined for superconductivity using susceptibility measurements. Hardy and Hulm<sup>2</sup> have reported that their samples of Ta<sub>2</sub>C and Nb<sub>2</sub>C became superconducting at 3.26 and 9.18°K, respectively, and that V<sub>2</sub>C was not superconducting down to 1.2°K. In this work, no superconducting transition was found in any of the pure compounds for measurements down to 1.98°K, but when the metal phase was present, transition temperatures near to the reported transition temperatures were obtained for Ta<sub>2</sub>C and Nb<sub>2</sub>C. This observation suggests that the earlier investigators were actually measuring the transition temperature of the carbon-saturated metal phase. The various samples used in this investigation are listed in Table I. They were prepared by heating a mixture of the pure elemental powders either by induction heating to the designated temperatures or by arc-melting. Previous experience with these systems has shown that samples prepared in this manner are of high purity.<sup>3-5</sup> The single-phase TaC<sub>0.48</sub> sample was analyzed and found to contain the following major impurities: O=230, N=10, Nb=850, and W=200, in ppm. The lattice constants for this sample were:  $a_0=3.1036$  Å and  $c_0=4.9367$  Å.

In the tantalum system, one can see that, for measurements down to 1.98°K, pure single-phase Ta<sub>2</sub>C was not superconducting, but when metal was present, a superconducting transition was observed. The slight difference in transition temperature of these samples as compared with that reported by Hardy and Hulm has not been completely explained. Perhaps the metal phase contained a different amount of quenched-in carbon due to different cooling rates employed.

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<sup>2</sup> G. F. Hardy and J. K. Hulm, *Phys. Rev.* **93**, 1004 (1954).

<sup>3</sup> E. K. Storms and N. H. Krikorian, *J. Phys. Chem.* **64**, 1471 (1960).

<sup>4</sup> E. K. Storms and R. J. McNeal, *J. Phys. Chem.* **66**, 1401 (1962).

<sup>5</sup> A. L. Bowman, *J. Phys. Chem.* **65**, 1596 (1961).

It should be realized, when examining the results from the niobium system, that because of the very narrow homogeneity range (NbC<sub>0.49</sub>-NbC<sub>0.50</sub>) single-phase Nb<sub>2</sub>C is very difficult to prepare. Therefore, a sample containing NbC was examined. This NbC phase is not superconducting at the composition in equilibrium with the Nb<sub>2</sub>C.<sup>1</sup> No transition was observed down to 1.98°K. The two arc-melted samples containing niobium metal, however, did show a transition at 9.2°K.

Although V<sub>2</sub>C had been reported as not superconducting, it was examined because in this system the metal phase can be chemically separated from the M<sub>2</sub>C phase. The V<sub>2</sub>C sample containing the metal

TABLE I. Transition temperatures and composition of Ta<sub>2</sub>C, Nb<sub>2</sub>C, and V<sub>2</sub>C samples.

Composition	Phases	$T_c$ (°K)	Method of preparation
TaC <sub>0.48</sub>	Ta <sub>2</sub> C	<sup>a</sup>	Heated at 1800°C
TaC <sub>0.4</sub>	Ta-Ta <sub>2</sub> C	2.8	Melted at 3400°C
TaC <sub>0.35</sub>	Ta-Ta <sub>2</sub> C	4.4	Heated at 2800°C
TaC <sub>0.25</sub>	Ta-Ta <sub>2</sub> C	4.34	Melted at 2900°C
NbC <sub>0.51</sub>	Nb <sub>2</sub> C-NbC	<sup>a</sup>	Heated at 2000°C
NbC <sub>0.48</sub>	Nb-Nb <sub>2</sub> C	9.2	Arc-melted
NbC <sub>0.4</sub>	Nb-Nb <sub>2</sub> C	9.2	Arc-melted
VC <sub>0.3</sub>	V-V <sub>2</sub> C	4.7	Arc-melted
VC <sub>0.44</sub>	V <sub>2</sub> C	<sup>a</sup>	V removed from the above sample with HCl

<sup>a</sup> No superconducting transition observed for these samples down to 1.98°K.

phase had a transition temperature of 4.7°K. However, after leaching out the metal phase with boiling HCl, no superconducting transition was observed for measurements down to 1.98°K.

One disturbing feature in all of the measurements was that the magnitude of the mutual inductance change, when the sample became superconducting, indicated that the entire sample became superconducting. This happened even when only a small amount of metal phase was present. When the V<sub>2</sub>C sample was examined metallographically, the vanadium metal phase was found to have deposited along certain crystal planes during cooling to give a Widmanstätten struc-

ture.<sup>6</sup> Thus a series of parallel metal platelets occurred in each crystal of V<sub>2</sub>C. Since the bulk sample was made up of many of these crystals, oriented in a random way, a continuous interlacing thread of metal could be produced. This could shield the nonsuperconducting V<sub>2</sub>C and cause the bulk effect. Niobium metal has been seen to deposit in the same way upon the cooling of Nb<sub>2</sub>C. In addition, this type of behavior is consistent

<sup>6</sup> C. S. Barrett, *Structure of Metals*, (McGraw-Hill Book Company, Inc., New York, 1952), Chap. 22, pp. 538-580.

with the phase diagrams of these systems.<sup>3,4</sup> Ta<sub>2</sub>C is presumed to behave in the same manner.

In view of these results, and the similarity between the transition temperature of the metal and the *M-M<sub>2</sub>C* mixture, it appears that the materials used in the previous investigation contained a slight amount of the metal phase, which was mistaken for the total sample because of the bulk effect, and that pure Ta<sub>2</sub>C, Nb<sub>2</sub>C, and V<sub>2</sub>C are not superconducting down to 1.98°K.

## Modulus and Damping of Copper after Plastic Deformation at 4.2°K

L. J. BRUNER\* AND B. M. MECS

*IBM Watson Laboratory, Columbia University, New York, New York*

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An investigation of the Bordoni dislocation relaxation peaks in copper has been carried out under experimental conditions which permit plastic deformation of specimens at 4.2°K, with measurement of their Young's modulus and internal friction upon subsequent warmup. Isochronal annealing at progressively higher temperatures in the interval from 100° to 360°K, taking data from 4.2°K after each anneal, shows (a) a pronounced reduction in height of both the major peak at 62°K and the minor peak at 28°K for annealing temperatures to 200°K, (b) a slow regrowth and shift to higher temperature of the major peak with annealing above 200°K, accompanied by continued diminution of the minor peak, and (c) a monotonic increase, through the full range of annealing temperatures, of the Young's modulus as measured at 4.2°K. A qualitative discussion of these results indicates that the interaction between point defects and dislocations is an essential feature of the dislocation relaxation process.

### I. INTRODUCTION

THE initial observation by Bordoni<sup>1</sup> of low-temperature internal friction peaks in plastically deformed metals has led to extensive investigation. The work done in this area prior to 1960 has been reviewed by Niblett and Wilks.<sup>2</sup> It is generally accepted that the low-temperature anelasticity displayed by cold-worked metals arises from the thermally activated displacement of dislocations in the crystal lattice. Several markedly different models for the dislocation relaxation process have, however, been presented.

One of these, developed by one of the present authors,<sup>3</sup> is based upon the thermally activated motion of paired partial dislocations between vacancy pinning points. This model, involving an interaction between point defects and dislocations, is substantially different from those of Seeger<sup>4</sup> and of Brailsford.<sup>5</sup> Here the essential parameters are related to intrinsic properties of dislocations comprising a network with fixed pinning points, either dislocation nodes or point imperfections.

The present work has been undertaken in an effort

to evaluate the relevance of point imperfections to the dislocation relaxation process. Our approach is based upon the assumption that it should be possible to exercise some control over the type and number of such imperfections at dislocation lines by initially cold working specimens at temperatures below which the imperfections can migrate. Then, upon warming in steps to progressively higher temperatures, the point defects present in the lattice migrate to sinks with the more mobile species moving first. It is presumed that dislocation lines constitute one type of available sink.

Interpretation of such an experiment rests first of all upon an understanding of the means by which point imperfections are generated in significant quantities by moving dislocations during cold work.<sup>6</sup> Furthermore, identification of the defect species migrating in a given temperature range depends upon the analysis of a wide variety of recovery experiments. These experiments record the irreversible variation of such parameters as electrical resistivity and release of stored energy; these changes occur upon annealing after low-temperature pretreatments including cold work, irradiation, and quenching. They appear as a series of steps or stages; the change associated with each extending over a relatively narrow range of annealing temperatures. The interpretation of these stages in terms of the

\* Present address: Department of Physics, University of California, Riverside, California.

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<sup>4</sup> A. Seeger, *Phil. Mag.* **1**, 651 (1956).

<sup>5</sup> A. D. Brailsford, *Phys. Rev.* **122**, 778 (1961).

<sup>6</sup> F. Seitz, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1952), Vol. 1, p. 43.