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Effect of Lattice Instabilities on Superconducting and Other Properties in TaC_x

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Tunneling measurements performed on TaC_x single crystals and recently published neutron-scattering data show that stoichiometric TaC is in the vicinity of a lattice instability. This leads to a strong dependence of many physical properties on carbon content. It is shown that TaC_x can be well described by a very simple model in which the band structure is considered composition independent while the vibrational spectrum strongly depends on carbon content. In particular, the effect of the anomalous phonon spectrum on superconductivity is discussed. Phillips's ideas about the relation between the instability and superconductivity are supported. The lattice instability is discussed in terms of a hard-sphere model. A consistent picture relating the unusual superconducting, electrical, and mechanical properties in TaC is found.

INTRODUCTION

Refractory carbides are very interesting materials, both from the scientific and the technical point of view. They combine metallic and covalent bonding, show extremely high melting points, and have high strength at elevated temperatures.[1]

The transition-metal carbides of group IV*B* (Ti, Zr, Hf) and V*B* (V, Nb, Ta) crystallize in the NaCl structure. Complete stoichiometry cannot be obtained, all carbides being carbon deficient. (By *M*C we do not denote a stoichiometric carbide, but rather one of unspecified composition.)

Within the group of fcc carbides, TaC (and to some extent also NbC) exhibit unusual properties. TaC_x is ductile for $x \approx 1$, while the other carbides are brittle. However, nonstoichiometric TaC_x is brittle, with a maximum in microhardness at $x = 0.83$, and exhibits a brittle-to-ductile transition at elevated temperature.[2] Moreover, TaC_x is a superconductor with a fairly high T_c ($\sim 10\,^\circ$K) for $x \approx 1$, but for $x \approx 0.8$ no superconductivity is found.[3]

Other properties such as Hall effect,[4] electronic specific heat,[5] and mechanical properties[2] also show a very strong dependence on composition. Previous discussions of the properties of the carbides have been mainly in terms of chemical bonding or electronic band structure. No consistent picture of the peculiarities of TaC, in particular the strong variation of several parameters with stoichiometry, has yet emerged. We will show that the composition dependence is related to an anomalous behavior of the phonon spectrum, indicating that stoichiometric TaC is near a lattice instability.

If this were the case, one would expect the phonon structure to be much more sensitive to changes in composition than the bare electronic band structure. One may therefore ask the question whether most of the x dependence of several properties of TaC could be explained by a strong x dependence of the phonon structure with a relatively slowly varying bare electronic structure. The x dependence of "electronic" properties such as electron specific heat, etc., would then be predominantly due to an x dependence of the electron-phonon coupling.

The strongest experimental evidence for TaC being near a lattice instability comes from recently published neutron-scattering experiments.[6] Strong structure is found in the optical- and acoustical-longitudinal-phonon dispersion relations at short wavelength.

Of all measurable quantities, one expects superconductivity to be particularly sensitive to vibrational anomalies. This has recently been discussed by Phillips,[7] who interpreted the anomalies in stoichiometric TaC as due to an overscreening of the ion-ion interaction by the electrons. He suggested that such instabilities play a dominant role in the occurrence of high T_c superconductivity. Under certain circumstances, such as in the case of TaC, the anharmonic forces stabilize the crystal structure and no static distortion occurs. In comparison, the A-15 compounds with high T_c are much closer to the instability, and under certain conditions static distortion occurs.[8] In the following we will use superconductivity to test a very simple model. The essential features of the model are: (i) The anomaly present in the vibrational spectrum of stoichiometric TaC gradually disappears when moving away from stoichiometry. (ii) Electronic properties, such as the band density of states $N(0)$, depend only weakly on stoichiometry. This model is not limited to superconductivity but allows us to relate the dependence on stoichiometry of many different physical parameters.

A discussion of the proposed model requires some knowledge of the vibronic structure and the electron-phonon interaction. Adequate information about the phonon density of states, in particular the low-frequency modes exhibiting strong elec-

tron-phonon coupling, can be obtained from electron-tunneling experiments.[9] We have, therefore, performed such an experiment.

EXPERIMENTS

TaC single crystals of up to about 1 cm in size were embedded in Bakelite, mechanically and chemically polished, and subsequently electropolished in a H_2SO_4-ethanol mixture. The surface was then covered with an insulating varnish except for a small area (~ 0.1 mm^2) where the junction was formed. The oxide barrier was grown electrolytically. Only about 10–20% of the junctions showed good tunneling characteristics,[10] as judged from the residual conductivity at $V = 0$ in the superconducting state. Most junctions had weak link characteristics.

Since T_c is a strong function of x it is more significant to discuss $2\Delta/kT_c$ rather than the energy gap 2Δ. The BCS theory for a weak-coupling superconductor predicts that $2\Delta/kT_c = 3.53$. Initially, we observed anomalously small values of $2\Delta/kT_c$ (i.e., values as small as 2), but after electropolishing the surface and removing any material damaged during the mechanical polishing we obtained values of $2\Delta/kT_c$ in the range 3.4–3.6. Although this may still be somewhat depressed from the "true" value, it indicates that we are essentially measuring bulk properties. Anomalously small values of $2\Delta/kT_c$ have often been obtained in tunneling experiments performed on transition metals,[11] but it is believed that they do not represent bulk behavior. To sum up, we can say that TaC has a value of $2\Delta/kT_c$ typical of an intermediate coupling superconductor.

In order to obtain more detailed information about the electron-phonon coupling and the phonon density of states, we have measured the second derivative d^2I/dV^2 of the tunneling characteristic of a TaC-Au junction at 1.4 °K (Fig. 1). The structure is reproducible for junctions having $2\Delta/kT_c \sim 3.5$, but absent for junctions with unreasonably small gap values. The results presented in Fig. 1 are for a junction with the maximum obtainable stoichiometry ($x \approx 0.96$, $T_c = 8$ °K). Upon lowering x (and T_c), the intensity of the structure rapidly decays in agreement with a simple model which predicts the intensity to be of the order $(T_c/\Theta)^2$. McMillan and Rowell[9] have demonstrated how all parameters entering a strong-coupling theory of superconductivity can be obtained from such measurements. It is possible, however, to get some insight into what happens without carrying out the McMillan-Rowell gap-inversion procedure.

Although the structure in d^2I/dV^2 is not simply related to the phonon density of states, one expects strong structure in the vicinity of critical points in the phonon spectrum. The arrow in Fig. 1 indicates the cutoff energy of the acoustical phonons, and the bar shows the range of the optical phonons as determined by neutron-scattering experiments.[7] One notices a strong structure in the energy range of the acoustical phonons, the large energy separation between acoustical and optical phonons, and a very weak structure at the energy of the optical modes. The structure in the acoustical-phonon region is complex, indicating a complex phonon density of states.

DISCUSSION

It has been noticed earlier[3] that the strong variation of superconducting properties with composition

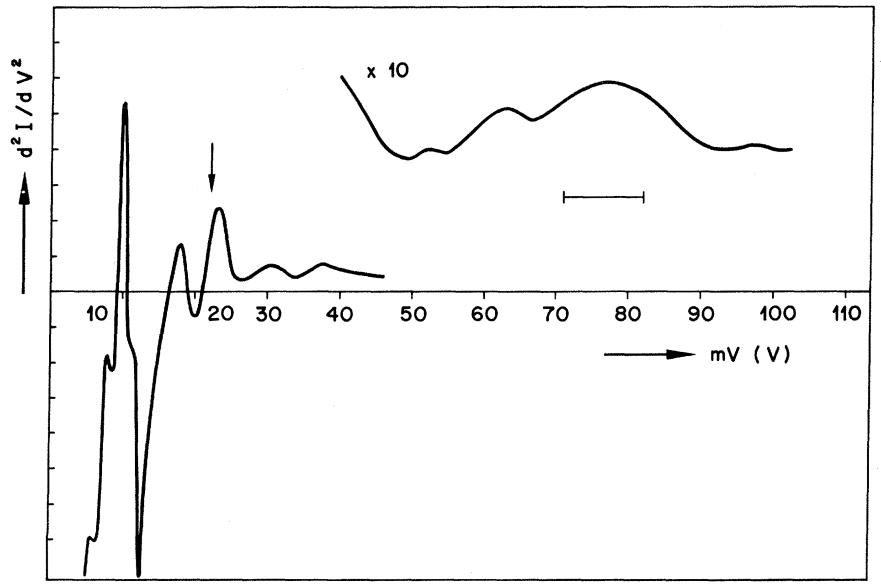

FIG. 1. Second derivative d^2I/dV^2 of the tunneling characteristic of a $TaC_{0.96}$–I–Au junction at $T = 1.3$ °K. One division corresponds to 1 part per 100 conductivity change per millivolt. The arrow marks the cutoff of the acoustical-phonon modes and the bar gives the energy range of the optical modes as obtained from a neutron-scattering experiment (Ref. 7) on a $TaC_{0.99}$ single crystal.

cannot be explained by a corresponding change in valence-electron concentration. In the first part of this section we discuss the superconductivity of TaC_x in terms of theories by McMillan[12] and Hopfield,[13] and show that our model leads to an understanding of the composition dependence. The only parameter which is considered composition dependent within the model is Θ_A, an appropriately averaged phonon frequency.

The electron-phonon coupling constant λ is proportional to an average $\langle 1/\omega^2 \rangle$, as defined in Ref. 12, and thus is mainly determined by the acoustical modes. This is also reflected in the relative intensity of the structure in d^2I/dV^2 (Fig. 1). We conclude, therefore, that the optical modes are unimportant for the electron-phonon coupling and we will neglect them in the further discussion. For simplicity we will approximate the acoustical modes by a Debye temperature Θ_A.

We can obtain an estimate for Θ_A from the cutoff frequency of the acoustical modes, either from our tunneling data or from the neutron-scattering experiments, where one has to consider the lowering of Θ_A caused by the anomaly in the longitudinal-acoustic-phonon (LA) dispersion relation. We take $\Theta_A = 210\,^\circ\mathrm{K}$ and apply McMillan's formula[12]:

$$T_c = \frac{\Theta_A}{1.45} \exp\left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right) . \qquad (1)$$

Since TaC has a fairly low electronic density of states, we take the Coulomb pseudopotential μ^* to be 0.1. Stoichiometric TaC has $T_c = 10.6\,^\circ\mathrm{K}$ (extrapolated from Ref. 3) leading to $\lambda = 0.925$; i.e., TaC is a moderately strong-coupling superconductor.

Hopfield[13] has shown that the electron-phonon coupling constant λ can be written as

$$\lambda = \eta/A\,\langle \Theta^2 \rangle \quad , \qquad (2)$$

where A is the atomic number, $\langle \Theta^2 \rangle$ an average squared phonon frequency, and η a parameter mainly dependent on atomic properties. Although the application of Hopfield's theory to binary systems is not straightforward, we try to give an estimate for η_{TaC} by

$$\frac{\eta_{TaC}}{\eta_{Ta}} \approx \frac{\lambda_{TaC}}{\lambda_{Ta}} \left(\frac{\Theta_A^{TaC}}{\Theta^{Ta}}\right)^2 . \qquad (3)$$

With $\lambda_{Ta} = 0.657$ and $\Theta^{Ta} = 258\,^\circ\mathrm{K}$,[13] we find $\eta_{TaC} \approx 0.93\eta_{Ta}$, i.e., $\eta_{TaC} \approx \eta_{Ta}$. Since η depends mainly on the screened atomic potential, this shows that the atomic potential of Ta in TaC and Ta is about the same and implies a rather weak ionicity.

η does not change appreciably between Ta and TaC and thus we may also expect η to be constant for TaC_x as x is varied. The strong x dependence of T_c should then arise entirely from the x dependence of the phonon spectrum.

Next we discuss the effect of a variation of Θ_A on T_c. Due to the lack of data for the x dependence of the phonon spectrum we relate the x dependence of Θ_A to the x dependence of the lattice constant l in a simple Grüneisen picture: The linear dependence of l on x implies dependence of Θ_A on x. Thus we have

$$\Theta_A(x) = \Theta_A + (1-x)B ,$$

with $\Theta_A = 210\,^\circ\mathrm{K}$.

Using $\lambda(x) \sim 1/\Theta^2(x)$ and Eq. (1), we can fit the constant B to the observed x dependence of T_c. Figure 2 shows the fit obtained with $B = 600\,^\circ\mathrm{K}$. The experimental d^2I/dV^2 curves show an x dependence that is consistent with the above value of B. However, as x is decreased, the structure rapidly becomes weaker and broader [the intensity is expected to be of order $(T_c/\Theta_A)^2$] and no exact value of B can be derived.

Two remarks should be made concerning the value of B: (a) The value of B implies a Grüneisen constant about an order of magnitude larger than usual, if B is thought to arise from a pure volume effect. (b) Toth *et al.*[5] have found the low-tem-

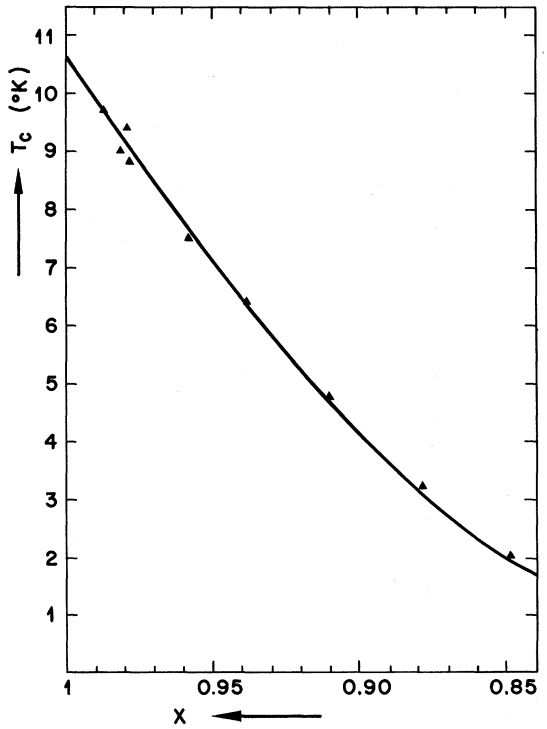

FIG. 2. Dependence of T_c on composition in TaC_x. Data points are from Ref. 3. The solid line is calculated using McMillan's formula, assuming Θ_A to be a linear function of x and keeping all other parameters fixed.

perature specific heat Θ to be much larger and to decrease slightly when moving away from stoichiometry.

In our case B does not represent an over-all property of the phonon spectrum but is defined by the phonon modes important for the electron-phonon interaction. The following model gives the same magnitude of B as found in the fit: The anomaly in the LA mode at $x = 1$ has disappeared at $x = 0.8$; the rest of the phonon spectrum is only weakly x dependent. This is consistent with the results of Toth *et al.*[5] Their heat-capacity experiment is sampling the low-frequency part of the phonon spectrum only, and is insensitive to the LA anomaly.

It is interesting to note that the x dependence of λ obtained in the above analysis can account for most of the x dependence of the electronic specific heat[5])Fig. 3). Data points in Fig. 3 are from Refs. 5 and 16. The band density of states at the Fermi surface thus depends only weakly on x. We obtain for one spin direction

$$N_b(0) = 0.36 \text{ states/eV atom.}$$

Hopfield's parameter η[13] corresponds to the product $N_b(0)\langle J^2\rangle$ in the McMillan theory.[12] The fact that $N(0)$ and η are nearly constant implies also that McMillan's electron-phonon matrix element $\langle J^2\rangle$ is nearly constant.

In the previous section it was shown that the composition dependence of T_c and of the electronic specific heat, at least in the range $1 > x > 0.8$, can be accounted for by a linear dependence of an averaged phonon frequency on carbon content. The bare electronic structure of TaC seems to depend only weakly on carbon content. This has, of course, consequences in the band-structure description of TaC . In particular, the charge transfer, which in theoretical calculations has turned out to be very model dependent, is rather small. (Many references concerning this point are given in Ref. 1.) Qualitatively, TaC seems to be a true defect structure, where the main effect of the carbon is to stabilize the fcc structure.

We have now arrived at a rather simple and consistent picture of the intriguing variety of properties in TaC. For the understanding of many experimental results, a detailed knowledge of the complex and complicated band structure is not required. Band-structure effects can be treated by composition-independent parameters such as $N(0)$. It is the vibrational spectrum which has to be discussed in detail and which is, in the case of a fcc metal, rather simple.

Up to now we have not discussed the nature and cause of the instability. It is hard to envisage how a Kohn anomaly[15] could produce such a large effect on the dispersion relation. It seems more likely that an understanding of the effect requires a strong-coupling theory of the dielectric function. In such a theory a distinction between a generalized Kohn anomaly and an overscreening effect, as proposed by Phillips,[7] would be merely a matter of semantics. However, at present the detailed nature of the effect has to be considered as not understood.

It is possible, however, to get some insight into why a lattice instability occurs at all, from consideration of a hard-sphere model of TaC. Rowcliffe and Hollox[16] have recently noted that in TaC the ratio of carbon to metal radii is close to the critical value of 0.59, where a transition to a more complicated crystal structure is expected. Compared to the nonsuperconducting IVB carbides with a smaller-radius ratio and contact between the metal ions, the crystal structure in TaC is more

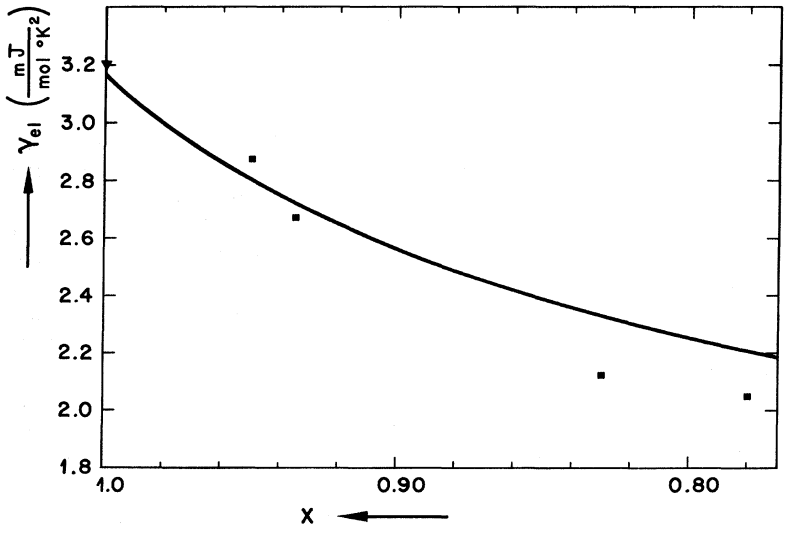

FIG. 3. Electronic specific heat as a function of carbon content in TaC_x. Data points are from Ref. 5, ■ and Ref. 14, ▼. The solid line represents const$[1+\lambda(x)]$, i.e., the x dependence one would expect with $N^b(0) = \text{const}$. Note the expanded scale.

open and the carbon has appreciably expanded the lattice.

This tempts us to go one step further and speculate that the main effect of the carbon is a volume effect. The result should then be the same whether we change the lattice constant by carbon content or by temperature. The data on mechanical properties presented in Ref. 16 suggest that this is qualitatively correct.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 5 1 MARCH 1972

Calculation and Measurement of the Electronic Part of the Thermal Conductivity of a Strong-Coupling Superconductor in Which Elastic Scattering of the Electrons Dominates*

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We have generalized the theoretical expression for the electronic contribution K_{es} to the thermal conductivity in strong-coupling superconductors to include elastic scattering of the electrons. In the limit where the elastic scattering dominates, the resulting expression for K_{es} is equivalent to that of Bardeen, Rickayzen, and Tewordt except for a change in the energy-gap width; the renormalization function Z_s does not explicitly appear. We have made measurements of the thermal conductivity of quench-condensed lead films which are in very good agreement with the theory, with no adjustable parameters.

I. INTRODUCTION

The electronic contribution K_e to the thermal conductivity K in superconductors has been of interest for many years.[1] It is known that the temperature dependence of K_e is qualitatively affected by the important scattering mechanisms near the transition temperature T_C. If the electrons are scattered mainly by static lattice imperfections, the theory of Bardeen, Rickayzen, and Tewordt (BRT)[2] should be applicable for weak-coupling superconductors (those in which the coupling between the electrons and the phonons is relatively weak). This theory has been well verified by experiments on weak-coupling superconductors, for instance aluminum.[3] The theory predicts that K_{es}/K_{en} is a universal function of the reduced temperature T/T_C, where K_{es} and K_{en} are the electronic contribution to K in the superconducting and normal states, respectively. This predicted function has a continuous first derivative at T_C.

If the electrons are scattered mainly by the phonons near T_C, the theory of Tewordt[4] should apply. In this case, the first derivative of K_{es}/K_{en} is predicted to have a marked discontinuity at $T/T_C = 1$. The size of this discontinuity, 1.6, is in reasonable agreement with experimental data for the weak-coupling superconductor tin, and for the fairly weak-coupling superconductor indium, but is in