The surface-plasmon absorption is readily apparent in graphs of ϵ_2 computed from ellipsometry data, and the resonant wavelength is observed to relax to progressively longer wavelengths as the age of the foil increases. This provides a sensitive measure of the formation of a surface corrosion layer as a function of time and environmental conditions. On the basis of computed values of ϵ_1, it is concluded that the Ag-vacuum resonant wavelength is approximately 3400 Å; in contrast, the resonant wavelength is always greater than or equal to 3450 Å after exposure of the foil to the atmosphere.

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Lattice Thermal Conductivity of Superconducting Niobium Carbide*

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The unusually low lattice thermal conductivity of the transition-metal carbides at low temperatures has been attributed to the scattering of phonons by conduction electrons. An experiment which confirms this interpretation is reported. Thermal conductivity measurements on single-crystal $NbC_{0.96}$ through its superconducting critical temperature (9.8°K) show that the lattice component of the thermal conductivity, K_{ls}, increases greatly below T_c because of decreased phonon-electron scattering. The maximum increase in lattice thermal conductivity from this effect occurs at 3°K with K_{ls}/K_{ln} equal to 160. The theories of Bardeen, Rickayzen, and Tewordt and of Klemens and Tewordt for the influence of electrons and point defects on lattice conductivity provide a quantitative interpretation of the effect. The best fit to the $NbC_{0.96}$ data is for $2\epsilon(o)/kT_c=4.0$. The behavior of $NbC_{0.96}$ is in contrast to that of $NbC_{0.76}$, which remains in the normal state throughout the temperature interval studied and shows no increase in thermal conductivity.

I. INTRODUCTION

PREVIOUS measurements[1,2] of the thermal conductivity of Groups IV and V transition-metal carbides have shown that strong phonon-electron scattering must be invoked to explain the low-temperature behavior of the lattice thermal conductivity. It was also noted, however, that the ordinary theory of phonon-electron scattering does not apply to carbide samples which are highly carbon deficient. Hence, some experimental demonstration of the above interpretation was sought.

In this paper, we report measurements on the thermal conductivity of superconducting niobium carbide which do demonstrate experimentally the existence of strong phonon-electron scattering in the transition-metal carbides. Use is made of the fact that some of the carbides have superconducting critical temperatures in the range of interest. Since electrons in the superconducting state do not scatter phonons, an increase in lattice conductivity below T_c is predicted and observed. A comparison of the data with the theories of Bardeen, Rickayzen, and Tewordt[3] (BRT) and Klemens and Tewordt[4] (KT) shows quantitative agreement for the effect of phonon-electron scattering and point-defect scattering on the lattice thermal conductivity.

II. EXPERIMENTAL

Two specimens of single-crystal niobium carbide, $NbC_{0.76}$ [5] and $NbC_{0.96}$,[6] were studied. The specimens, which crystallize in the rocksalt structure, are carbon

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[1] L. G. Radosevich and W. S. Williams, Phys. Rev. **181**, 1110 (1969).

[2] L. G. Radosevich and W. S. Williams (to be published).

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[5] This specimen has been characterized in (1).

[6] This specimen was obtained from Ventron Electronics Corporation, Alfa Crystals Division. The carbon-to-metal ratio of 0.96 was determined from measurements of the superconducting transition temperature T_c and comparison with data of Toth *et al.* See L. E. Toth, M. Ishikawa, and Y. A. Chang, Acta Met. **16**, 1183 (1968).

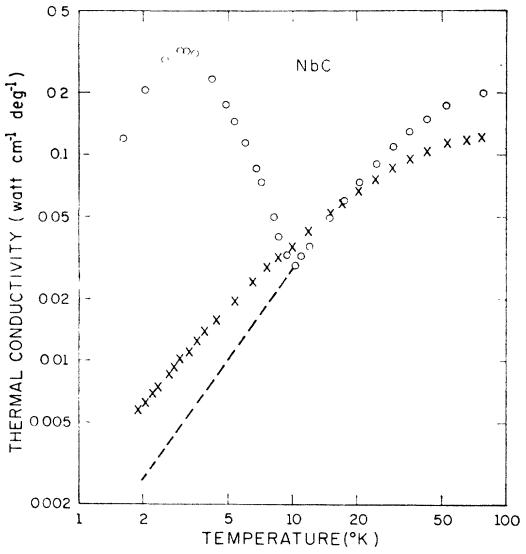

FIG. 1. Thermal conductivity versus temperature: open circles, $NbC_{0.96}$; crosses, $NbC_{0.76}$. The dashed line is an extrapolated curve which describes the normal-state behavior.

deficient with vacancy concentrations of 24 and 4%, respectively, in the fcc carbon sublattice. Thermal conductivity was measured using the longitudinal heat flow technique with Au-Fe thermocouples as temperature indicators. Details of the measurement have been reported.[1,2]

III. RESULTS

Figure 1 exhibits the thermal conductivity of $NbC_{0.76}$ and $NbC_{0.96}$ in the temperature range 1.65–78°K. The data for $NbC_{0.76}$ were reported in an earlier paper,[1] but to facilitate comparison with $NbC_{0.96}$ both sets of data are included.

The most striking feature of Fig. 1 is the large increase in the total thermal conductivity K below the superconducting transition temperature T_c for $NbC_{0.96}$. At 3°K, the ratio of K in the superconducting state to that in the normal state, K_s/K_n, is nearly 70. The normal-state behavior for $NbC_{0.96}$ below T_c was obtained by extrapolating the data in the range 10–15°K to lower temperatures. We believe that this extrapolation procedure is valid because the slopes of the $K(T)$ curves for the carbides change only slightly below 15°K.[1] The superconducting transition temperature for $NbC_{0.76}$ is less than 2°K and could not be observed with our apparatus.

A second feature of Fig. 1 is the dependence of the thermal conductivity on vacancy concentration. At temperatures below 20°K, the thermal conductivity is lower for the crystal with the lower vacancy concentration. This result is just the opposite of the behavior expected for scattering by point defects in lattice *or* electronic thermal conduction. (At higher temperatures, the presence of point-defect scattering is more apparent.[2]) Such behavior was observed in measurements of K for TiC_x as a function of x[1,2] and led us to invoke strong phonon-electron scattering to explain the low-temperature data. For NbC_x, as x is increased, the electronic density of states at the Fermi surface also increases, according to the specific-heat measurements of Toth *et al.*[6] Hence the scattering probability is increased, and the lattice conductivity is decreased. The electronic component K_e is still limited by vacancy scattering as is evidenced by measurements of the residual electrical resistivity.

IV. DISCUSSION

To discuss the behavior of K_e and K_l in detail and to compare the present results with theory, we have calculated the superconducting and normal components of the electronic thermal conductivity K_{es} and K_{en}. The electrical resistivity of $NbC_{0.96}$ changes only slightly, from 28.8 $\mu\Omega$ cm at 77°K to 26.7 $\mu\Omega$ cm at 10°K. Most of the resistance is therefore attributable to elastic electron-vacancy scattering, so that K_{en} can be calculated using the Wiedemann-Franz Law. Values of K_{es} were obtained from the BRT theory for the case of strong electron-defect scattering. The resulting smoothed curves are shown in Fig. 2. As is evident from Figs. 1 and 2, the normal state values of K_e contribute significantly to K for $NbC_{0.96}$ at low temperatures. This was not the case for $NbC_{0.76}$ where the residual resistivity 172 $\mu\Omega$ cm is much higher.

From the experimental data along with the calculated values of K_{es} and K_{en}, the superconducting and normal components of the lattice thermal conductivity, K_{ls} and K_{ln}, were determined. The smoothed curves are shown in Fig. 3 along with K_{ln} for $NbC_{0.76}$. Curve A is the superconducting component of the lattice thermal conductivity of $NbC_{0.96}$, and curves B and C are the

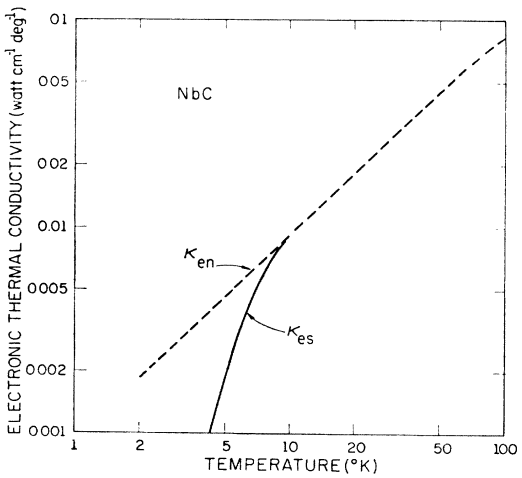

FIG. 2. Electronic thermal conductivity versus temperature of $NbC_{0.96}$ in the normal and superconducting states.

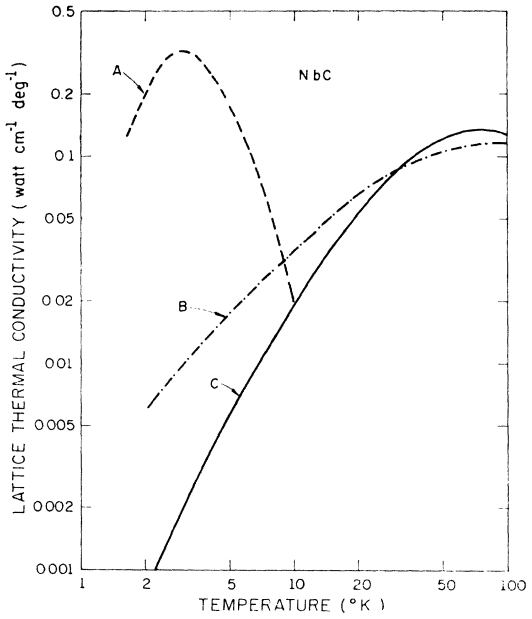

FIG. 3. Lattice thermal conductivity versus temperature: A, superconducting $NbC_{0.96}$; B, normal $NbC_{0.76}$; C, normal $NbC_{0.96}$.

normal lattice components of $NbC_{0.76}$ and $NbC_{0.96}$, respectively. In the superconducting state, the calculated value of the phonon mean free path at 1.65°K is close to the smallest dimension of the sample. Hence, boundary scattering of phonons lowers K_{ls} below the conductivity maximum. In the temperature region 3–9.8°K, the increase in K_{ls} of $NbC_{0.96}$ is due to decreased phonon-electron scattering with $K_{ls}(3°K)/K_{ls}(9.8°K) = 17$ and $K_{ls}(3°K)/K_{ln}(3°K) = 160$. The latter ratio demonstrates that phonon-electron scattering is indeed a strong scattering mechanism in the carbides.

The large ratio of K_{ls}/K_{ln} below T_c suggested a comparison with the theory of the thermal conductivity of superconductors by Bardeen, Rickayzen, and Tewordt.[3] BRT have calculated the effect of electrons on the lattice conductivity below T_c. The BRT theory, which is based on the BCS theory of superconductivity,[7] predicts that in the weak-coupling limit, the ratio K_{ls}/K_{ln} should be a universal function of T/T_c. For $NbC_{0.96}$, T_c/θ_D equals 0.0162, and the weak-coupling approximation should be valid. This result is supported by low-temperature measurements of the electronic heat capacity of $NbC_{0.98}$,[8] which closely follow the values calculated for the BCS weak-coupling case.

Curve C of Fig. 4 shows the BRT result for K_{ls}/K_{ln} as a function of T/T_c for $2\epsilon(0)/kT_c$ equal to 4. The quantity $2\epsilon(0)$ is the gap energy at $T=0$. If the ratio $2\epsilon(0)/kT_c$ is reduced to the BCS value of 3.5, K_{ls}/K_{ln} will be lowered. Since the gap energy for $NbC_{0.96}$ has not yet been measured, the value of $2\epsilon(0)/kT_c$ is treated as a parameter. Finally, curve C is not extended below $T/T_c = 0.4$ because boundary scattering begins to dominate at low temperatures, and the theory is inapplicable.

In addition to boundary scattering, point-defect scattering can also affect K_{ls}/K_{ln}. Klemens and Tewordt[4] have shown that point defects can significantly reduce K_{ls}/K_{ln}, which was calculated on the basis of only phonon-electron scattering. The effect is more pronounced at lower reduced temperatures where the phonon-electron scattering in the superconducting state is greatly decreased. For the carbides, it has been shown[2] that the main contribution to the scattering coefficient comes from force-constant differences rather than mass differences. In the KT notation, α for $NbC_{0.96}$ equals 1.8×10^{-5} for mass-defect scattering and 2.8×10^{-3} for scattering due to force-constant differences. The coefficient α measures the scattering strength and concentration of point defects. Curve B of Fig. 4 is the calculated value of K_{ls}/K_{ln} for $\alpha = 2.8\times10^{-3}$ and $2\epsilon(0)/kT_c = 4.0$. The latter ratio gives the best visual fit to the smoothed data, curve A. Since 4.0 is the upper limit of

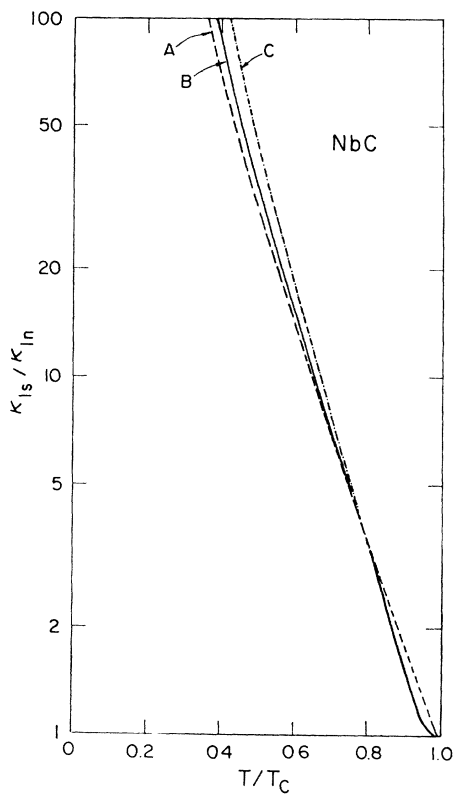

FIG. 4. Ratio of the lattice thermal conductivity in the superconducting and normal states versus reduced temperature: A, derived data of $NbC_{0.96}$; B, BRT calculated curve including point-defect scattering for $NbC_{0.96}$; C, BRT calculated curve. Curves B and C are shown for $2\epsilon(0)/kT_c = 4.0$.

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BRT theory, the value of $2\epsilon(0)/kT_c$ for $NbC_{0.96}$ is fairly closely determined by the present results. Curves for the choice $2\epsilon(0)/kT_c=3.5$ and 3.7 were also calculated. With the inclusion of point-defect scattering, known to be present here, these values are clearly too low to fit the data.

The value of 4.0 for $2\epsilon(0)/kT_c$ corresponds to a value of the zero-temperature energy gap of 0.0034 eV. This value is subject to some uncertainty. First, it must be noted that K_{ln} was derived from an extrapolated curve, and this procedure introduces an estimated uncertainty of $\pm 10\%$ into K_n. Second, for the special case of the carbides, the applicability of the BRT theory must be further examined. Although $NbC_{0.96}$ appears to satisfy the weak-coupling limit treated by BRT, a second factor must also be considered. In the BRT theory, the electron mean free path is assumed to be longer than the dominant phonon wavelength. Studies of the carbides indicate that for high vacancy concentrations, λ_e is small compared to an average phonon wavelength at low temperatures. This result alters the frequency dependence of the phonon relaxation time.[9] Resistivity measurements indicate, however, that the electron mean free path λ_e in $NbC_{0.96}$ is much greater than λ_e for $NbC_{0.76}$, and thus the ordinary theory of phonon-electron scattering may apply to $NbC_{0.96}$. This result is consistent with the observed higher slope value of $\ln K$ versus $\ln T$ for $NbC_{0.96}$. In Fig. 3, the slope of curve C for $NbC_{0.96}$ is slightly greater than 2 in the low-temperature region. This result is in contrast to the data for the other carbides which always gave slope values between 1 and 2. A slope value greater than 2 suggests that the ordinary theory of phonon-electron scattering is applicable to $NbC_{0.96}$ since this theory predicts a slope of 2. When combined with the boundary scattering, the slope will lie between 2 and 3. A similar behavior was noted for TiC specimens with higher carbon contents.[1,2] The uncertainty in K_{ln} for $NbC_{0.96}$ due to extrapolation of the data below T_c should not alter any of the above qualitative remarks, however. The above discussion thus suggests that the largest uncertainty in $2\epsilon(0)$ arises from the need to extrapolate K_n below T_c.

[9] A. B. Pippard, Phil. Mag. **46**, 1104 (1955).

The value of $2\epsilon(0)/kT_c$ for niobium metal is 3.64 from the work of Carlson and Satterthwaite.[10] This value was obtained by fitting the k_e data to the theory of Kadanoff and Martin.[11] Kadanoff and Martin modified the BRT treatment of k_e for the case of strong electron-phonon scattering. This modification is not required for the carbides because the electron scattering is defect-controlled and, hence, elastic. Niobium metal also differs from its carbide in the fact that heat is transported primarily by electrons in the former. Hence, as the superconducting transition of niobium is reached from above, the measured thermal conductivity initially *decreases*, since electrons in the superconducting state cannot carry thermal energy. In niobium carbide, the measured thermal conductivity *increases* below T_c as electrons are removed as phonon scatterers. The values of T_c for Nb and NbC are similar, 9.3 and 9.8°K, respectively. At temperatures considerably below T_c (centered at approximately 2°K) a "phonon bump" appears in K versus T for Nb. The effect is smaller than in $NbC_{0.96}$, but has the same origin. Other examples of the enhancement of lattice conductivity below the superconducting transition temperature are discussed by Mendelssohn and Rosenberg.[12]

To summarize our results, we have shown that measurements of the thermal conductivity of superconducting niobium carbide demonstrate experimentally the existence of strong phonon-electron scattering in materials of this type. The results are in reasonable agreement with theory for the effect of electrons and point defects on the lattice conductivity in the superconducting state.

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[10] J. R. Carlson and C. B. Satterthwaite (to be published).
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