Influence of hydrogen on the thermal conductivities of superconducting Nb and Ta†

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The thermal conductivities of superconducting Nb and Ta have been measured in the temperature range 0.04–4 K with and without the presence of dissolved H or D. In Nb doped with D the phonon mean free path exhibits a minimum which occurs at the same temperature at which a deuterium-related anomaly has been observed in the specific heat. Phonon scattering caused by the addition of H to Nb or Ta is complicated by the presence of resonant scattering from dislocations produced by precipitation of the β-phase hydride.

I. INTRODUCTION

Anomalies have been reported in the superconducting-state specific heats of the transition metals V, Nb, and Ta.[1–3] These anomalies were originally attributed to the presence of a second superconducting energy gap.[4] However, more recent measurements of the specific heats of Nb,[5,6] V,[7] and Ta (Ref. 6) show a strong correlation between the occurrence of the anomalies and the presence of dissolved hydrogen. The fact that dissolved hydrogen might complicate the interpretation of the thermal behavior of the group-V*B* metals should not be totally unexpected, since it is known that hydrogen is highly soluble and mobile in all three metals.[8] But the over-all picture of the manner in which hydrogen influences these metals is not complete. In particular, it is not clear what detailed mechanism is responsible for the anomalous specific heats observed. Thus the present measurements on the thermal conductivity of superconducting Nb and Ta were undertaken in an effort to supplement the information obtained from specific-heat measurements reported in the preceding paper.[6] The same samples were used in both experiments so that a direct correlation between the two types of observations could be made.

We wished first to determine if phonons would be scattered resonantly by eigenstates associated with the specific-heat anomalies produced by the addition of H or D. If such eigenstates do exist, a minimum in the phonon mean free path may occur at nearly the same temperature T as the anomaly in the specific heat, C_A. The approximate temperature at which the scattering may occur can also be estimated from the maximum which appears in a plot of C_A/T vs T. Thus for H or D in Nb the resonances should occur near 0.7 and 0.1 K, respectively and for H in Ta resonant phonon scattering would occur $\lesssim 0.1$ K.[6] Second, it was hoped that measurements of the thermal conductivity might clarify questions as to the existence of a second superconducting energy gap in Ta. Previous thermal-conductivity measurements had suggested that a second gap is unlikely in Nb.[9,10]

II. EXPERIMENTAL DETAILS

The thermal-conductivity data were obtained using a technique which has been described previously.[10] Heat fluxes were used which produced fractional temperature differences of 10% or less across the samples, and the resulting data showed no dependence on the magnitude of the heat flux. No effort was made to null the magnetic field of the earth, since its effect on the lattice thermal conductivity of Nb had been shown to be negligible.[10]

The two Nb samples were rods of ≈ 1-cm^2 cross section and 7-cm length. Both polycrystalline rods were annealed and out-gassed at 2250 °C for ≈ 2 h in a high-vacuum induction furnace. Following this anneal, the Nb samples showed an electrical resistivity ratio of ≈ 100. Although this indicates that the Nb was not very pure, the impurities are felt to have no bearing on the present measurements. Phonon scattering from impurities at low temperatures would be significant only if there are localized states associated with the presence of the impurities in the Nb lattice. The surfaces of the samples were abraded with 27-μm airborne powder to reduce specular reflection of phonons. Thus a measurable boundary limited phonon mean free path was provided as a convenient reference. It had been shown that this sandblasting procedure does not introduce damage into the interior of Nb.[10] One Nb sample was bent to a radius of ≈ 12 cm to intentionally introduce a small dislocation density.

Following this preparation, thermal-conductivity measurements were made to establish the quality and condition of the samples. The unbent sample had a thermal conductivity comparable to that of the high-purity annealed single-crystal sample measured in Ref. 10 (see Fig. 1). The effect of bending the second sample was to lower the thermal conductivity in a manner similar to that seen in Ref. 10 and attributed in that work to the resonant scattering of thermal phonons by dislocations. These

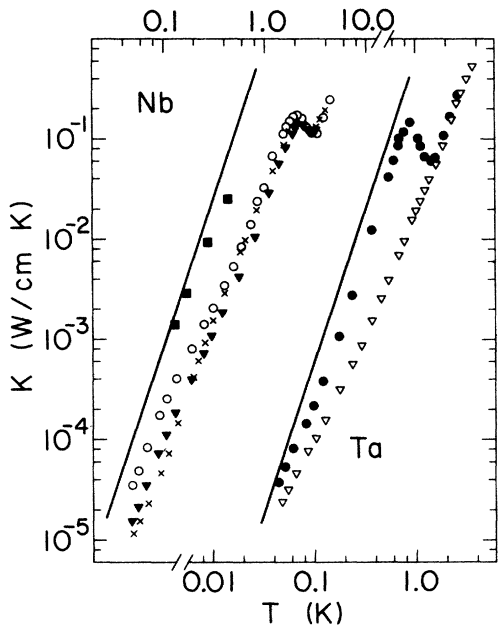

FIG. 1. Thermal conductivity of superconducting Nb (top temperature scale) and Ta (bottom temperature scale). The straight lines represent the lattice thermal conductivity calculated on the assumption that nonspecular reflection of phonons occurs at the sample surfaces: ■, annealed and out-gassed Nb; ×, Nb with D intentionally added; ▾, Nb with H intentionally added; ○, Nb with H removed; ●, annealed and out-gassed Ta; ▽, Ta with H intentionally added.

data were not included in Fig. 1 for the sake of clarity. In brief, the initial thermal conductivities of both samples were well known and understood.

The Ta sample was a polycrystalline rod about 8 cm long with a diameter of 0.64 cm. This sample was annealed and out-gassed at 2100 °C for ≈3 h. Following the anneal, the sample had an electrical resistivity ratio of ≈100. The surface of the rod was sandblasted with 27-μm airborne powder to prevent specular reflection of phonons. The thermal conductivity was then measured; see Fig. 1. A slight resonant scattering of phonons by dislocations was evident near 0.15 K.[11] Hence again thermal transport in the sample was well characterized initially.

Since the specific-heat measurements[6] had indicated an isotope effect in the observed anomalies, thermal-conductivity measurements were made with H alone or with D alone diffused into the samples. In both cases the gas was diffused into the metal in the same way. The sample was first heated to 700 °C in a vacuum furnace to dissolve the oxide coating on the surface. The furnace was then pressurized with H_2 or D_2 which had been passed through a Pd purifier. The furnace was next allowed to cool while the pressure was adjusted to keep the concentration of H or D in the sample constant.[8] The sample was oxidized at ≈100 °C so as to seal the H or D inside. The H or D could be removed from the samples by repeating the above process, but with H_2 or D_2 absent from the furnace.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Some of the thermal-conductivity data for the Nb and Ta samples are shown in Fig. 1. These data represent the total measured thermal conductivity κ in the superconducting state due to both phonons and electrons. Because of the relatively high superconducting transition temperatures of these metals, the Nb data below ≈3.0 K and the Ta data below ≈1.5 K represent thermal conduction contributed principally by phonons. Above these temperatures, electrons dominate the thermal conductivity. It is the phonon conductance which is of interest here. The straight lines in Fig. 1 were calculated assuming a boundary-limited phonon mean free path[12] l with $\kappa = 0.71 l T^3$ W/cm^2 K^4 for a Debye temperature of 274 K in Nb,[13] and $\kappa = 0.75 l T^3$ W/cm^2 K^4 for a Debye temperature of 265 K in Ta.[14]

The phonon mean free path resulting from scattering caused by mechanisms other than boundaries

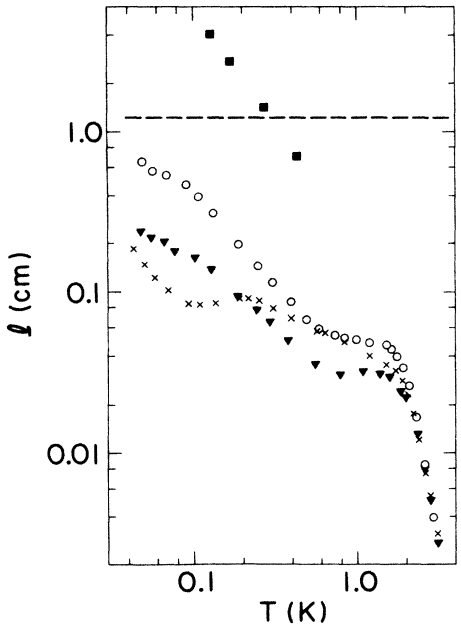

FIG. 2. Phonon mean free paths in Nb limited by scattering mechanisms other than the sample surfaces. The symbols refer to the same samples as in Fig. 1. The phonon mean free path attributed to boundary scattering is indicated by the dashed line. Electrons dominate the scattering above ≈2 K. The additional scattering caused by the introduction of D can be seen roughly by comparing the (×) and (○) data.

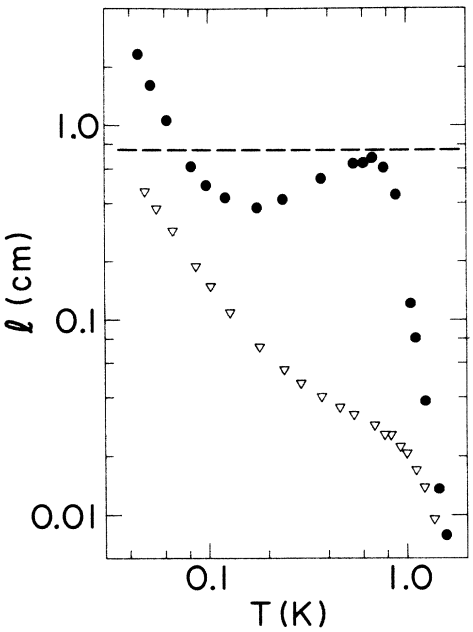

FIG. 3. Phonon mean free paths in Ta limited by scattering mechanisms other than the sample surfaces. The symbols refer to the same samples as in Fig. 1. The phonon mean free path attributed to boundary scattering is indicated by the dashed line. Electrons dominate the scattering above ≈ 1 K.

was obtained by first subtracting the calculated electronic thermal conductivity from the data of Fig. 1.[15] Then the effect of boundary scattering was eliminated by using a phonon equivalent of Matthiessen's rule and the boundary-limited phonon mean free paths described above.[10] The resulting mean free paths represent scattering from "internal" sources only, and are shown in Fig. 2 for Nb and in Fig. 3 for Ta. Above ≈ 1 K for Ta, and above ≈ 2 K for Nb, the phonons are scattered by electrons.[16]

The consequences of adding 3000-ppm (atomic) H to Nb are readily apparent in Fig. 2. Resonant scattering of phonons seems to occur near 0.8 K. This agrees well with the temperature at which the specific-heat anomaly caused by the addition of H was located, as discussed in Sec. I. Unfortunately, phonons are also resonantly scattered from dislocations in Nb, and this interaction also produces a minimum in l near 0.8 K.[10] The presence of H in Nb may enhance the dislocation scattering by increasing the density of dislocations through the formation of β-phase hydride as the sample is cooled in the cryostat. Since the β phase differs by $\simeq 10\%$ in molar volume from that of the high-temperature α phase, additional dislocation loops are generated to relieve the stresses produced as the β-phase precipitates.[17]

We attempted to distinguish between these two scattering mechanisms, dislocations and interstitial H, by out-gassing the H at a temperature of 700 °C as described in Sec. II. This procedure should have left the dislocations in the lattice, but should have removed the H.[17] The mean free path in the out-gassed condition is shown on Fig. 2, and it may be noted that l has indeed been increased somewhat. But whether this increase is due to the removal of H scattering centers or to a slight reduction in the density of dislocations can not be determined.

The situation is less confused with the addition of 3000-ppm (atomic) D to the Nb samples. The data from the unbent sample are shown in Figs. 1 and 2; the other, bent sample, gave very similar results. There is a depression in l near 1 K which again might be associated with dislocations produced by the β-phase precipitate. There is also a distinct depression near 0.1 K which may be compared with the specific heat anomaly near 0.1 K discussed in Sec. I and attributed to the addition of D to Nb. Outgassing the D removes this low-temperature depression in l, indicating that the depression is directly associated with the presence of D in the metal. Thus it appears that the eigenstates related to interstitial D are evident in both the thermal conductivity and the specific heat of Nb.

The specific heat of Ta containing $\approx 1\%$ (atomic) H exhibited an anomaly near or below 0.1 K.[6] However, the thermal coupling between this anomalous heat capacity and the lattice was very weak, giving an internal thermal relaxation time of ≈ 1 sec for the sample. Thus the scattering of phonons by these eigenstates would also be weak, and an associated anomaly might not be expected in the thermal conductivity of Ta. The phonon mean free path for this H-doped sample is shown in Fig. 3 and indeed there is no suggestion of a minimum, or even an inflection, at or below 0.1 K.

The data of Fig. 3 suggest, however, that addition of H to Ta does produce a depression in l near 1 K, the details being masked by electron scattering at higher temperatures. It was surmised that this additional scattering was produced by resonant or vibrating dislocations. In Ta the resonant frequency of dislocations has been observed to increase with increasing strain.[11] Thus the minima in the two sets of data in Fig. 3 could both be attributed to dislocations even though they lie at different temperatures. The occurrence of a larger density of dislocations in the H-doped sample than in the annealed sample is believed to be related to the formation of the β-phase hydride, as was discussed in the case of H in Nb.

To test for the presence of dislocations the doped Ta sample was cut by spark erosion, then electropolished and etched to provide etch pits.[11] The density of etch pits was counted to obtain an estimate

of the dislocation density. Assuming a one-to-one correspondence between etch pits and dislocations the result was $\approx 10^8$ dislocations cm^{-2}. With this density and the phonon scattering cross section per dislocation reported in Ref. 11, a phonon mean free path of $l = 0.03$ cm is obtained at the minimum if it is assumed that the minimum in l lies near 1 K. This calculated value of $l = 0.03$ cm is seen to be in good agreement with the measured l near 1–2 K in Fig. 3 for the H-doped sample. We conclude therefore that the additional phonon scattering caused by the diffusion of H into Ta is associated with dislocations, and that no scattering related to the interstitial H itself is observed.

These results on Ta also reinforce our belief that dislocations were likewise produced in Nb by the β-phase precipitate and were at least partially responsible for the depression near 1 K in the H-doped sample. We did not choose to destroy the Nb samples in order to obtain an estimate of the dislocation density.

The data for the undoped Ta sample of Fig. 3 may be used to search for the anomalous or additional electron scattering of phonons which might be associated with a second superconducting energy gap. (This procedure has already been used for Nb in Ref. 9.) Specific-heat measurements on this sample exhibit a feature in the range 0.2–0.7K which can not be attributed to phonons,[6] nor can this feature be associated with the small fraction of normal-state electrons characteristic of a single superconducting energy gap in this carefully annealed sample.[15] One might ask if this additional heat capacity could be caused by normal electrons associated with a second energy gap, although the temperature dependence is not particularly indicative of this. If all electrons in Ta contributed a similar heat capacity, the ratio of s-state to d-state electrons required to produce the additional heat capacity would be ≈ 0.02. This density of normal s-state electrons would cause phonon scattering with a resulting mean free path[16] of $l \approx 6 \times 10^{-3}\ T^{-1}$ cm K assuming s and d electrons have a similar phonon scattering cross section. The measured mean free path in the annealed undoped sample is about two orders of magnitude greater than this near 0.6 K. This result does not prove that a second superconducting energy gap is absent in Ta, but it is clear that a second gap need not be assumed to satisfactorily explain the thermal conductivity data.

IV. CONCLUSIONS

The introduction of H or D into Nb and Ta caused a reduction in the mean free paths of thermal phonons in the superconducting state within the temperature range of the measurements, 0.04–4 K.

In Nb doped with H it could not be determined if the phonon scattering was caused by dislocations produced by precipitation of the β-phase hydride or by the eigenstates associated with interstitial H, since both have resonances at about the same temperature or thermal frequency.[6,10] With Nb doped with D, on the other hand, resonant scattering of thermal phonons did occur at the same temperature as the anomaly in the specific heat produced by interstitial D.[6] This observation is consistent with the suggestion that the anomalies in the specific heat of H- or D-doped group VB metals are related to a discrete set of energy levels associated with interstitial motion.[6]

In Ta doped with H it was shown that phonons were scattered by dislocations produced during precipitation of the β-phase hydride. No scattering by the H interstitial itself was observed. This is consistent with the very weak interaction between the H-related eigenstates and the lattice phonons which has been observed in specific-heat measurements.[6] No evidence was found in annealed undoped Ta for a second superconducting energy gap.

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