Scattering of thermal phonons by dislocations in superconducting lead and tantalum*

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Thermal-conductivity measurements on deformed superconducting samples of Pb and Ta have demonstrated the resonant scattering of thermal phonons from dislocations. The results are in good agreement with calculations based on the elastic-string model of localized modes associated with dislocations.

I. INTRODUCTION

Evidence for the presence of localized modes or resonances associated with dislocations has been observed in a number of low-temperature thermal-conductivity[1-3] and specific-heat[4] measurements. In addition, several models or theories of resonant dislocations have been developed, some of which will be discussed in Sec. II. In brief, no one model appears to be compatible with all of the thermal-conductivity data obtained thus far. Generally, the assignment of one or more parameters in a given model on the basis of one experiment is not consistent with the results of other experiments.

The present measurements on the thermal conductivity of superconducting Ta and Pb were undertaken in an explicit attempt to test two of the models. The resonant scattering of phonons observed near 1 K in Nb was most readily explained in terms of a model in which the dislocation vibrates within the undulating lattice or Peierls potential.[2] If this is a correct description, a similar scattering was to be expected near 1 K in the thermal conductivity of Ta (see Sec. II), which has a Peierls potential similar to that of Nb. Using a different model, Kronmüller[5] has predicted a dislocation resonance at 1.4×10^{10} Hz (≈ 0.14 K)[6] in Pb. In selecting Ta and Pb rather than other materials, we have the additional advantage that both are superconductors with high critical temperatures. Thus, the interpretation of experimental results is not compounded with the thermal conductance or phonon scattering caused by normal-state electrons. The experimental techniques used in the present work have been described elsewhere.[2]

The experimental results are presented in Sec. III and are compared with previous measurements on Pb and Ta. The results are compared with the models developed for resonant dislocations in Sec. IV. These models, in addition, are tested with data obtained from previous measurements on other materials. But first we present a separate, brief review of these several models so that their salient features will not be obscured by a discussion of experimental results.

II. MODELS OF RESONANT DISLOCATIONS

The resonant dislocation is a localized lattice mode which can absorb a phonon of frequency ν and then reradiate this quantum of energy in some direction other than the incident direction. To a thermal transport measurement, the phonon appears to have undergone an elastic collision with an attendant decrease in thermal conductance.

The most widely used model of dislocation resonance is the elastic-string concept.[7-9] The dislocation is treated as an elastic band stretched between pinning points that are a distance L apart. The dislocation then exhibits a natural resonance with frequency ν inversely proportional to L,

$$\nu \approx v/3L \ , \tag{1}$$

where v is the velocity of transverse phonons. The width of the resonance (in the materials of present interest) is assumed to be determined by phonon radiation.[10] There is evidence that this radiation-damping picture is quantitatively correct, at least when the dislocations are driven to relatively large motional amplitudes in acoustic or dc stress-strain measurements.[11,12]

The frequency or temperature dependence of a phonon lifetime limited by dislocation scattering has been presented elsewhere[1,13] and will not be duplicated here. Instead we use the results of Ref. 13 to obtain the phonon mean free path l limited by scattering from resonant dislocations of density N. If a minimum in l occurs at temperature T_{min} due to resonant scattering, the phonon mean free path at temperature T_{min} is given by

$$l \approx 3\times10^{12}\, T_{min}/Nv \tag{2}$$

for an exponential distribution of loop lengths L (N, l, and v are expressed in cm).

If the loop lengths were all identical, then, roughly,

$$l \approx 2\times10^{11}\, T_{min}/Nv \ . \tag{3}$$

The resonant scattering will be dominant over the nonresonant or static-strain-field scattering below

a temperature of ≈ 10 K.[1] It should be noted that for an exponential distribution of loop lengths, the resonant peak in the scattering occurs at a frequency that is a factor of ≈ 4 lower than that calculated from Eq. (1) using an *average* loop length L.

A dislocation which behaves as an elastic band may also produce another form of phonon scattering when the fundamental frequency of the dislocation ($v/3L$) is much less than the incident phonon frequency.[14] The phonons essentially produce traveling waves on the dislocation. This interaction is independent of frequency and depends on the angle of incidence between phonon and dislocation. The situation is analogous to the excitation of Rayleigh waves on the surface of a solid caused by acoustic waves incident from the bulk. The computation is complicated and has been carried out explicitly only for LiF,[14] for which

$$L \approx 3\times 10^{6} T^{0.4}/N \ . \tag{4}$$

We do not know how l varies with the properties of the material. Presumably this mean free path will merge at low temperature or frequency with that caused by the standing wave modes [see Eq. (1)].

Another possibility is that an eigenmode is associated with the intrinsic structure of the dislocation. This would apply especially to thermal transport measurements where the dislocation remains in thermal equilibrium with the lattice at a very low temperature and thus has the smallest possible vibrational amplitude. For example, the dislocation may oscillate within the Peierls potential, which is the undulating potential energy that the dislocation experiences as a function of position in the lattice.[15,16] In this case, there would be no traveling waves nor distribution of resonant frequencies. An expression for a discrete resonance has not been derived, so as an approximation we will use

$$\nu_0 \approx (1/2\pi)\,(\sigma_P/\rho b^2)^{1/2} \ , \tag{5}$$

where σ_P is the Peierls stress, ρ is the mass density, and b is the Burgers vector. The width of the resonance should be determined by phonon radiation, so the phonon mean free path at the resonant frequency or temperature would be given roughly by Eq. (3).

A tunneling mode also is possible in principle. In this case, the dislocation tunnels between two configurations having classically the same potential energy. This degeneracy is lifted by tunneling, and a phonon of energy $h\nu$ (h = Planck's constant) equal to the energy splitting could be absorbed and reradiated. Again, there are unknown parameters involved. Only limited evidence for a tunneling mode has been observed.[17]

Another possible scattering mechanism is the relative oscillation of the partials of a dissociated dislocation.[5] The frequency of resonance is nearly proportional to the energy of the stacking fault connecting the partials, and it depends on the type of dislocation. A resonance has been predicted in Pb, as well as in certain other metals, based on the expected form of dissociated dislocations in the fcc lattice. We would expect the minimum phonon mean free path produced by this type of resonance to be given by Eq. (3).

Variations on these models are also possible. It has been suggested that impurity atmospheres may modify the resonance.[18] This, however, adds another adjustable parameter, which we wish to avoid. It is also possible to discuss the dislocation in terms of a kink model.[19] For a high density of kinks, the dislocation again behaves like an elastic band. For a lower density of kinks, ν_0 decreases and l increases. Again a parameter is introduced—the kink density—which is difficult to ascertain experimentally. This density should, of course, remain constant at the temperature and the vibrational amplitudes of thermal-transport measurements. We have also ignored, for the present, the possible difference in phonon scattering caused by edge and screw dislocations.

It is not intended that this review be exhaustive, but rather that it provide a reasonably complete sampling of mechanisms of dislocation resonances for comparison with experimental data.

III. EXPERIMENTAL RESULTS

Two polycrystalline Ta samples were cut from the same 0.639-cm-diam rod. Mass-spectrographic analysis of the rod gave 100 ppm (atomic) W, 40 ppm Mo, and 80 ppm Nb. All other elements were $\lesssim 1$ ppm. The samples were annealed and outgassed at ≈ 2000 °C for 0.5 h in high vacuum. The electrical residual resistivity ratio was then 100. Thus, the purity of our samples was not very good. However, the lattice conductivity at low temperature is not strongly affected by point defects. The sides of the samples were abraded with 27 μm airborne powder to ensure that phonons which struck the sides were not specularly reflected.[2] One sample was measured without further treatment. The other was intentionally bent at one end to introduce dislocations, and the thermal conductivities of both ends were measured separately during the same run. It is quite likely that a small amount of strain was also introduced into the "unbent" end of this sample since the sample was of finite length. No attempt was made to shield either the Ta or Pb superconducting samples from

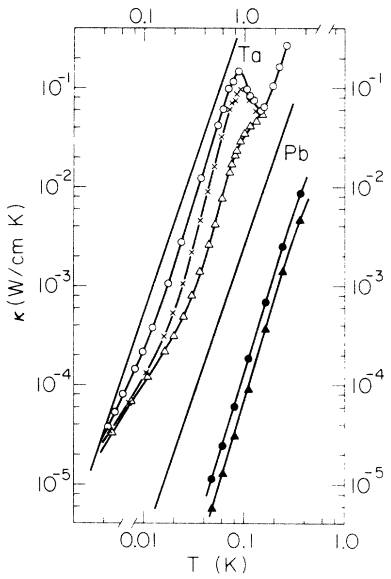

FIG. 1. The thermal conductivity of superconducting Ta (top temperature scale) and Pb (bottom temperature scale). Curves drawn through the data are intended as an aid to the eye. The straight lines represent the lattice thermal conductivity calculated on the assumption that no specular reflection of phonons occurs at the sample surfaces. ○, annealed Ta; ×, "annealed" end of bent Ta sample; △, sample of Ta intentionally bent; ●, "annealed" end of Pb sample; ▲, sample of Pb intentionally bent.

the magnetic field of the earth, since this precaution has been shown previously to be unnecessary.[2,20,21]

The Ta data are displayed in Fig. 1. The solid line represents the lattice thermal conductivity, assuming phonons are scattered only by sample boundaries.[22] (For a Debye temperature of 262 K, $\kappa = 0.77 l T^3$ W/cm^2 K^4.) The effect of strain on reducing κ is readily apparent. Previous measurements[23,24] on Ta extending down to ≈ 0.2 K gave $\kappa \propto T^3$ below 1 K with a phonon mean free path $l \leq d$, the sample diameter, which is in agreement with the present data for this same temperature range. Above 1 K in Fig. 1, the phonon conduction is first reduced due to scattering by electrons; then, above ≈ 1.6 K, the thermal conduction of the electrons becomes dominant. The electronic contribution can be subtracted to give just the lattice thermal conductance.[25]

The phonon mean free path in the Ta samples is shown on Fig. 2. The effect of boundary scattering has been subtracted using the phonon equivalent of Matthiessen's rule.[26] The abrupt decrease in l near 1 K is due to electron scattering, as mentioned above.[25] The reduction in l near ≈ 0.2 K with increasing strain is readily seen.

After completion of the thermal-conductivity measurements, the dislocation density in the bent end of the deformed sample was estimated from etch-pit counts. The sample was cut by spark erosion so that both the plane of the cut and the normal to this plane were oriented at $\approx 45°$ to the axis of the sample. One surface thus exposed was electropolished to remove spark-erosion damage,[27] heated in air at 300 °C for 20 h to decorate dislocations lying near the surface, and finally etched to produce the pits.[28] The etch patterns were similar to those previously published for Ta.[28] The count was 3×10^7 cm^{-2}, which is accurate to a factor of ≈ 2. A *lower* limit on the dislocation density introduced by deformation could be obtained from the radius of curvature of the bend.[29] This gave a density of $> 3\times10^6$ cm^{-2}.

The polycrystalline Pb sample was a 0.687-cm-diam rod of nominal 99.999% purity. The sample was annealed in vacuum at 150 °C for 8 h and handled carefully thereafter. The sides were abraded with 27 μm airborne powder. One end of the sample was intentionally bent at room temperature to introduce dislocations, and the thermal conductivity of each end was measured separately during the same run. The sample was cooled to liquid-He temperatures as soon as possible after it was intentionally strained.

In preparing the Pb sample, we could draw on the experience of earlier researchers. It is very difficult to produce a strain-free sample of Pb suitable for thermal-conductivity measurements. High-purity Pb will deform under its own weight.

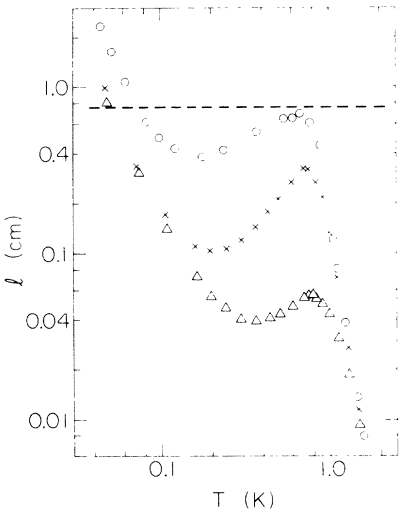

FIG. 2. Phonon mean free path in Ta limited by scattering mechanisms other than the sample surface. The symbols are the same as in Fig. 1. The mean free path attributed to nonspecular reflection of phonons from the abraded surface of the sample is indicated by the broken line.

Previous measurements found $l \ll d$.[21,30-32] That is, no boundary scattering was observed unless the sample was rolled to a thickness of 7×10^{-3} cm and then annealed.[21] Also, strained Pb recovers slowly from deformation if left at room temperature.[32] It has been shown, however, that strain produced in Pb *at* liquid-He temperatures results in the same temperature dependence of the thermal conductivity as a sample strained at room temperature.[32] Thus, we deformed our sample at room temperature, realizing there would be some relaxation of strain before the measurements began. The sample was stored at 77 K after removal from the cryostat and prior to a dislocation count.

The Pb data are shown in Fig. 1. Also shown is the thermal conductivity calculated assuming only nonspecular reflection from the surfaces.[22] (For a Debye temperature of 105 K, $\kappa = 3.4lT^3\,\mathrm{W/cm^2\,K^4}$.) The effect of strain is quite obvious. The temperature dependence of the conductivity is close to T^3, as noted by previous authors.[21,30-32] The phonon mean free paths calculated from these data and corrected for boundary scattering are shown in Fig. 3. The dashed curve is obtained by subtracting (using Mattheissen's rule) the "annealed" or background mean free path of the unstrained sample from that of the bent sample. This emphasizes the fact that intentionally bending the sample only decreased the magnitude of l independent of temperature, and that therefore the annealed portion was also strained a lesser amount.

After completion of the thermal conductivity measurements, the dislocation density was estimated from etch-pit counts. The sample was parted by spark erosion (as was done for the Ta sample), electropolished to remove surface damage,[33] and etched.[33] For the bent part, $N\approx 6\times10^7$ cm^{-2}, while in the annealed region, $N\approx 2\times10^7$ cm^{-2}. These values are accurate to within a factor of ≈ 2. The increase in etch-pit count in the bent portion agrees with the decrease in l of Fig. 3 with increased strain. The *minimum* density in the bent part calculated from the radius of curvature[29] was $>10^6$ cm^{-2}.

IV. DISCUSSION

The phonon mean free path l of the deformed Ta sample (Fig. 2) cannot be explained in terms of the static-strain-field scattering of sessile dislocations. Not only is the temperature dependence wrong, but a density of dislocations in excess of 10^{11} cm^{-2} would be required, as compared to the measured etch-pit count of $\approx 3\times10^7$ cm^{-2}.[1] One might try to match the measured temperature dependence by assuming a special dislocation array,[34,35] but this would necessitate an even greater density of dislocations.

The temperature dependence l is suggestive of the presence of resonant scattering. Using Eqs. (1)–(3), a dislocation density of $\approx 10^8$ cm^{-2} and an average loop length L of $\simeq 10^{-6}$ cm would be required to explain the data if there were an exponential distribution of loop lengths, or of $\approx 10^7$ cm^{-2} if all dislocations exhibited the same frequency of resonance. It should be emphasized again that Eqs. (2) and (3) are intended to give only rough estimates. Comparing these values to the measured etch-pit density of $\approx 3\times10^7$ cm^{-2} suggests that eigenmodes associated with dislocations do exist in the deformed Ta.

If the resonances were caused by a Peierls potential, we find from Eq. (5) and a value of $\sigma_P \simeq 3\times10^9$ dyn/cm^2 [16] that $\nu_0 \simeq 7\times10^{10}$ Hz. A minimum in l should then appear near 0.7 K,[6] which is in rough agreement with the temperature of the minimum in Fig. 2. This minimum, however, appears to shift with strain, which would not be expected for a dislocation constrained to a Peierls potential trough. Thus, the nature of the dislocations, at least in deformed samples, appears to be more accurately described by the string model.

The phonon mean free path l in the Pb sample (Fig. 3) cannot be due to the static-strain field of dislocations. Not only is the temperature dependence wrong, but a dislocation density in excess of 10^{10} cm^{-2} would be required, as compared to the measured etch-pit density of $\approx 2\times10^7$ cm^{-2} for the undeformed sample.[1] Since there is also no evidence for phonon scattering from grain boundaries in Pb,[21] we will assume that a resonant phonon-dislocation interaction occurs.

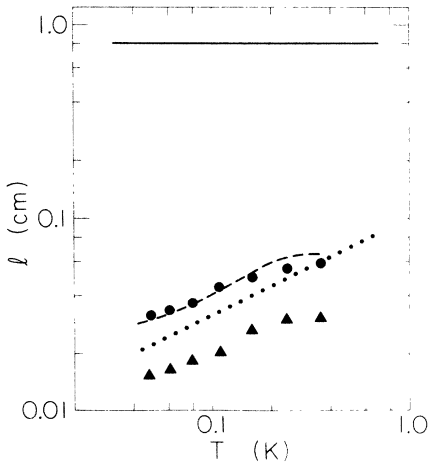

FIG. 3. Phonon mean free path in Pb limited by scattering mechanisms other than the sample surfaces. The symbols are the same as in Fig. 1. The line near the top of the figure is the calculated mean free path due only to nonspecular reflection from the sample surface. The other curves are discussed in the text.

The temperature dependence of l in Fig. 3 suggests that the standing-wave resonance of Eq. (2) occurs at a temperature below 0.04 K. Using the explicit expression for the temperature dependence of the thermal conductivity from Ref. 8 and the expression $N = 6 \times 10^7$ cm^{-2}, we obtain the dotted line shown in Fig. 3. It is important to note here that there are *no* adjustable parameters in this calculation; the loop length L does not influence the high-temperature (frequency) scattering. There is good agreement with the data, which suggests that dislocations in Pb behave as elastic bands that are not strongly influenced by a Peierls potential. This, of course, is consistent with the observation that Pb is readily deformed by its own weight at room temperature. The good agreement also suggests that the phonon mean free path associated with the "traveling-wave" scattering mechanism must be greater for Pb than the value given by Eq. (4), or, in other words, that scattering by this mechanism is not dominant. Using Eq. (1), we obtain for the average loop length of an exponential distribution of loop lengths the lower limit of $L > 3 \times 10^{-6}$ cm.

There is no evidence for a resonance near 0.14 K (see Fig. 3) that was predicted by Kronmüller for a dissociated dislocation in Pb.[5] This observation plus the observation of a phonon-dislocation resonant scattering near 0.2 K in deformed Al,[3] which has a rather large stacking-fault energy,[36] indicates that this mechanism does not dominate the dynamic interaction of phonons with dislocations.

The phonon-scattering resonances in Al and in Nb did not shift as a function of strain or of impurity content.[2,3] This suggests that a Peierls potential was present. Also, in LiF the assumption of the existence of a Peierls potential was consistent with the phonon-scattering data.[1] On the other hand, the shift of the resonance with strain in Ta (Fig. 2) and with γ irradiation in LiF suggests that the elastic-band model, with a changing number of pinning points, is also appropriate. In addition, the string model appears to be required by the specific-heat measurements on Cu,[4] since the heat capacity associated with a Peierls-well oscillation (Einstein oscillator) or tunneling state (Schottky anomaly) cannot be made to fit those data. A picture consistent with the above remarks would be a dislocation which is dominated by the Peierls potential for the crystal in question until pinning points (impurities, defects, or dislocation intersections) become sufficiently numerous to influence the dynamic behavior. Thus, the minimum resonant frequency in a thermal measurement would normally be determined by the Peierls potential. Indeed, just such a picture was suggested to explain the results of γ irradiation on the resonance of dislocations in LiF.[1]

The average loop lengths required ($L \simeq 10^{-6}$ cm) when the elastic-string model is fitted to thermal data (Refs. 1–4, plus the present work) is smaller than usually deduced from acoustic measurements.[9] Again, it should be remarked that in thermal measurements the magnitude of vibration is as small as possible, and hence the weakest pinning point (or Peierls potential) will control the resonance.

V. CONCLUSION

The thermal conductivities of deformed samples of superconducting Ta and Pb have been measured between 0.04 and 1.5 K. The phonon mean free paths obtained from these measurements are limited in both metals by the presence of resonant scattering attributed to vibrating dislocations. Comparison of the data with a number of models for resonant dislocations suggests that both the magnitude and temperature dependence of the scattering can best be explained in terms of the elastic-string model of a dislocation.

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