

Lattice thermal conductivity of copper alloys below 2 K*

J. L. Vorhaus and A. C. Anderson

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign,

Urbana, Illinois 61801

(Received 24 May 1976)

Thermal-conductivity measurements have been made between 0.06 and 2 K on copper samples containing 10-at.% Al. The data suggest that thermal phonons are resonantly scattered by dislocations at a frequency of $\approx 10^{11}$ Hz. The scattering of phonons by conduction electrons is in agreement with theory in both temperature dependence and magnitude. No unusual behavior has been observed in the thermal conductivity of CuAl, CuNi, or CuZn alloys near 0.5 K as had previously been reported.

I. INTRODUCTION

The thermal conductivities of copper alloys have been measured many times in several laboratories. The incentive for the present set of measurements perhaps can best be conveyed by a brief review of the literature and of our study of dislocations.

It has been demonstrated, using thermal conductivity and ballistic heat-pulse techniques, that dislocations in LiF behave like vibrating elastic strings, and that the lengths or resonant frequencies of the strings can be adjusted using γ -irradiation induced defects to pin the dislocations.¹ It has also been shown, using *measured* dislocation densities, that thermal phonons are much more strongly scattered by the localized modes than by the static strain fields of dislocations. This accounts for a factor of 10^2 – 10^3 difference between theory and experiment that previously had been reported; the data had been analyzed in terms of the wrong model. Other measurements gave evidence that a Peierls or undulating lattice potential energy experienced by the dislocations influenced the localized modes.¹⁻³

Measurements were carried out involving ionic, covalent, and fcc, bcc, and tetragonal metallic materials.¹⁻⁶ The metallic samples were always in the superconducting state so that the masking thermal conductance of the conduction electrons could be avoided. We wished to extend the measurements to normal metals to study any role the conduction electrons might play in the phonon-dislocation interaction. The electrons for example could serve to thermalize the phonons and/or damp the vibrating dislocations.

Experimentally, it is most convenient to measure the phonon or lattice conductivity κ_g in an alloy because alloying reduces the electronic contribution to the total thermal conductivity κ . Copper alloys have been chosen for this study since much experimental work has already been done on this system at low temperatures and since several in-

teresting features have been observed in κ_g for these alloys. The introduction of dislocations through deformation always reduces the magnitude of κ_g above ≈ 1 K and generally gives a temperature dependence close to $\kappa_g \propto T^2$. The scattering process responsible for this behavior is generally assumed to be related to the scattering of thermal phonons by the static strain fields surrounding the dislocations.⁷ Near 2–3 K, however, there is frequently said to be a kink or a change in the slope⁸⁻¹⁴ of a plot of κ_g vs T . This has been attributed to a reduction in phonon scattering which occurs when the wavelength of the dominant thermal phonons exceeds the separation between dislocations,^{10,11,14} see Sec. IV D, and/or to the presence of localized modes associated with the dislocations as discussed above.^{8,11,13} (A change in slope occurring for well-annealed samples has been attributed to a change, with temperature, of phonon scattering by conduction electrons,^{9,15} see Sec. IV A.) In brief, there is still some question as to the behavior of dislocations in copper (and other) alloys above ≈ 1 K.

At temperatures below ≈ 1 K the lattice thermal conductivity has been observed to have a negative temperature dependence, that is, κ_g decreases with increasing temperature.^{11,12,16} This is a very unusual behavior for κ_g in this temperature range and is indicative of an explicitly temperature-dependent phonon scattering cross section. Furthermore, some samples¹¹ exhibited a peak in κ_g near 0.5 K. The halfwidth of the peak was less than 0.5 K, or in other words less than the effective halfwidth of the thermal-phonon spectrum used to detect the peak. Thus the peak suggests the presence of a phase transition. Finally, there was some question as to the temperature dependence of the electron-phonon interaction in these alloys.¹¹

We wished to study the dislocation-phonon interaction in copper alloys below ≈ 2 K and at the same time to study the features mentioned above. The new ingredients introduced into the experiments

were an extension of the temperature range to lower temperatures by a factor of 10, and an explicit measurement of the dislocation densities within the samples.

The experimental technique is discussed in Sec. II, the data are presented in Sec. III, and the results are discussed in Sec. IV. A brief summary of the conclusions may be found in Sec. V.

II. EXPERIMENTAL TECHNIQUE

The samples were in two forms which, for convenience, will be referred to as plates and rods. Plates of ≈ 6 -cm length were cut from cold-rolled strips of Cu 0.05 cm thick by 2.5 cm wide containing either 30.8-at.% Zn, 10.7-at.% Al, or 3.4-at.% Ni.¹⁷ Some of these samples were annealed in vacuum at 800 °C to reduce the dislocation density. The mounting arrangement for the plates is shown in Fig. 1. A slotted copper bar was silver soldered at each end¹⁸ to provide an isotherm. The soldering was performed with the sample area immersed in water to prevent annealing. The top bar was thermally and mechanically attached to a dilution refrigerator with copper bolts,¹⁹ and an electrical heater was attached to the bottom bar. Resistance thermometers for measuring the temperature gradient were attached to 000-120 brass screws (≈ 0.07 cm diam) which were inserted into undersized tapped holes in the samples to improve electrical and thermal contact. For measuring the electrical conductivity, current leads were attached to the copper bars and potential leads were connected to the two brass screws.

Rods of CuAl alloy were made from the same

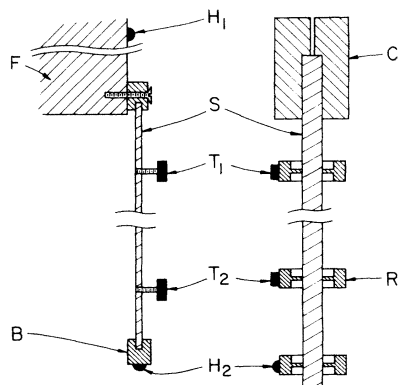


FIG. 1. Mounting arrangement for rod samples (right), and plate samples (left, edge view). S, sample; F, refrigerator; B, copper bar; C, copper collet; R, copper ring; H, electrical heaters; T, resistance thermometers. The distance between T_1 and T_2 was typically ≈ 4 cm. Heater H_1 was positioned so as to avoid temperature gradients between the sample and a magnetic thermometer. Superconducting leads were used on the heaters to provide thermal isolation.

cold-rolled strip, but recast into 0.4-cm-diam quartz tubes by induction heating under vacuum. The rods were passed through the induction coils several times to remove cavities, and the densities of the rods were measured as a final check. The rods were further vacuum annealed at 600 °C after removal from the quartz tubes, and then checked for homogeneity along their lengths using electrodeposition.

The mounting arrangement for the rods, Fig. 1, was similar to that used in Ref. 2. The top end was firmly gripped by a copper collet; the two resistance thermometers and the bottom heater were attached to separate annealed copper clamps. The thermometer clamps were used as potential probes in measurements of electrical conductivity.

Thermometer T_1 of Fig. 1 was uncalibrated and served to maintain that point on the sample at a constant temperature during a measurement by electronic regulation of power to heater H_1 . Temperatures before and after heat \dot{Q} was applied to H_2 were measured using T_2 . Thermometer T_2 was calibrated *in situ*²⁰ using a cerium magnesium nitrate magnetic thermometer²¹ calibrated against the vapor pressure of pure ^3He and checked against several superconducting fixed points.^{22,23} The resistance thermometers were modified Speer resistors,²⁴ although germanium thermometers were occasionally used at temperatures above 1 K. When carbon thermometers were used, both T_1 and T_2 were selected to be nearly identical in resistance versus temperature. Hence any residual, intrinsic drifts would tend to cancel.²⁴ Actually two Speer resistors (100- and 220- Ω nominal) were used at *each* position to provide optimum temperature resolution both above and below 0.2 K. The relative change in temperature of T_2 in measuring κ was $\Delta T/T < 10\%$, with occasional checks to be certain that the measured κ was independent of the ΔT used.

The calibration of T_2 was carried out in the following manner. Each pair of consecutive calibration points was used to obtain $n = d(\ln R)/d(\ln T) \approx \Delta R \bar{T} / \Delta T \bar{R}$, where \bar{R} and ΔR were the average and difference in resistance for a pair of points. The slope n was plotted versus $\ln \bar{R}$, and a smooth curve drawn through the points.²⁵

In measuring κ , the temperature T_0 of T_2 was measured *directly* with the magnetic thermometer with no heat applied to H_2 (Fig. 1). Then ΔR of thermometer T_2 was measured after heat was applied to H_2 , and \bar{R} was calculated. The graph of n vs $\ln \bar{R}$ gave a value for n , whence $\Delta T/\bar{T} = \Delta R/n\bar{R}$ and $\bar{T} = T_0(1 - \Delta R/2n\bar{R})^{-1}$. In brief, the temperature was determined essentially by the magnetic thermometer and the change in temperature by the resistance thermometer. This tech-

nique is of some importance since drift and certain other problems associated with carbon thermometers affect n less than R at a given temperature. Finally, $\kappa = \dot{Q}L/A\Delta T$, where L and A were the separation between thermometers and the cross sectional area of the sample, respectively.

The electrical resistance of each sample was measured with a standard four-terminal potentiometric method using the thermometer mounts as the potential probes. Hence, the geometrical factor was the same for the electrical and thermal measurements. The resistances were measured at less than 2 K and at 4.2 K. These two values agreed to within 0.1% for each sample.

Dislocations were intentionally added to some annealed samples by bending those samples about a radius directed perpendicular to the axis of the plate or rod.

The dislocation densities of the annealed or of the annealed and deformed CuAl samples were estimated from etch-pit counts. The etching technique was based on a procedure developed at the University of Virginia^{26,27} and is too lengthy to describe in detail.¹⁸ Briefly stated, the samples were sectioned by spark erosion at $\approx 45^\circ$ to all planes of symmetry and under minimum damage conditions. The surfaces were then mechanically/chemically polished and electropolished to provide a smooth, flat surface free of damage. Etching was done at -8 to -9°C for ≈ 1.5 sec using a modification of Livingston's solution.²⁶ The resulting pits remained for about a week if the samples were stored in an inert atmosphere. The pitted surfaces were photographed using a scanning electron microscope. The individual pits on a given grain had the same size, shape, and orientation.

Etch-pit counts were generally reproducible within the same grain, but varied from grain to grain because of the orientation of the surface and the variation in susceptibility to pitting of the various orientations. Counts made on different surfaces cut from the same sample agreed to within a factor of 2 or 3. Within this accuracy, we will assume that the dislocation density encountered by phonons is the same as the etch-pit density.

The annealed CuAl plates had a grain size of $\approx 10^{-2}$ cm and a dislocation density of $\approx 10^8$ cm $^{-2}$. The annealed CuAl rods had a grain size of $\approx 10^{-1}$ cm and a dislocation density of $\approx 10^7$ cm $^{-2}$. Bending an annealed rod increased the density to $\approx 10^8$ cm $^{-2}$. An attempt was made to obtain a density less than 10^7 cm $^{-2}$ in the rods by means of a longer higher-temperature (800 $^\circ\text{C}$) anneal. However, these samples issued audible pinging noises while lying quiescently at room temperature. This sound may have been caused by the relief of internal stresses related to the differential thermal contraction of

the randomly oriented grains. In any event, the dislocation density remained at $\approx 10^7$ cm $^{-2}$.

The change in electrical resistivity caused by 10^8 dislocations/cm 2 was too small to be detected²⁸ and so could not be used as a check on the etch-pit count. It was observed that, within the scatter of the data, bending an annealed plate did not change κ_g . From the radius of curvature of the bend, a dislocation density of 3×10^7 cm $^{-2}$ would be expected²⁹ as a lower limit. This is consistent with an etch-pit count of $\approx 10^8$ cm $^{-2}$ both before and after bending.

III. EXPERIMENTAL RESULTS AND PROBLEMS

Thermal-conductivity measurements were made on 11 samples of CuAl, four samples of CuZn, and two samples of CuNi. Only the CuAl data will be discussed explicitly. The CuZn was difficult to anneal, even when shielded, without loss of Zn from the Cu matrix. The CuNi was avoided because of the possibility that magnetic effects might obscure interpretation of the low temperature data. There was no significant difference between the thermal conductivity data for the CuZn and CuNi when compared with that for the CuAl.¹⁸

A portion of the CuAl data are presented in Fig. 2 in the form κ/T vs T . Assuming the validity of the Wiedemann-Franz law at these low temperatures permits one to obtain the lattice component of the total thermal conductivity, $\kappa_g = \kappa - LT\rho_0^{-1}$, where L is the Lorenz number (2.445×10^{-8} W Ω/K^2) and ρ_0 is the residual electrical resistivity. There is, however, a problem associated with this procedure. The term $LT\rho_0^{-1}$ is theoretical and per-

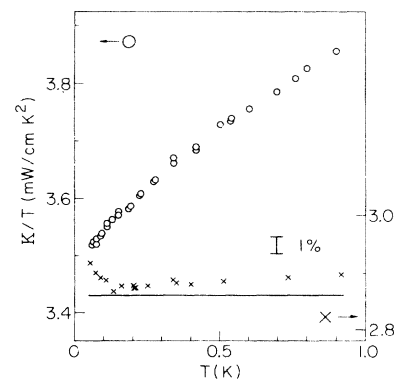


FIG. 2. Total thermal conductivity κ , divided by temperature T , for two CuAl samples. \times , cold rolled plate, as received; \circ , annealed plate. The horizontal line is the electronic contribution for both samples as deduced from measurements of the electrical resistivity using the Wiedemann-Franz law. As emphasized in the text, correction for a suggested error in the He vapor pressure temperature scale could lower all the data on this figure by as much as $\approx 0.8\%$.

tains to the absolute temperature. The data on the other hand are obtained using a temperature scale based on the vapor pressure of liquid helium (T_{58}), and this scale may be $\approx 0.4\%$ in error relative to the absolute scale.³⁰ A correction of this magnitude would lower all the data of Fig. 2 by $\approx 0.8\%$. But then the data points at $T < 1$ K for the highly strained, as received sample would straddle the horizontal line representing L/ρ_0 . In brief, within the accuracy of the temperature scale, the thermal conductivities of the as received samples at $T \leq 0.6$ K may be due entirely to electrons in which case a κ_g could not be extracted. (For $T \leq 0.1$ K there does seem to be a slight rise in κ/T above the value L/ρ_0 by $\approx 1\%$.) As no correction to T_{58} has been universally adopted, we will continue to use T_{58} and will comment on any influence such a correction would have on our interpretation of the data.

In none of our data (including that for CuNi or CuZn) did we observe the unusual temperature dependence of κ reported in Refs. 11, 12, and 16 and discussed in Sec. I. This is demonstrated in Fig. 3. Thus it may be concluded that such behavior is not intrinsic to these alloys.

Subtraction of the electronic contribution from κ gives the lattice component κ_g shown in Fig. 4 for several CuAl samples. The effect of correcting T_{58} would be to increase the temperature dependence at the smallest values of κ_g . Also shown is the range of values of κ_g reported^{8,10,12,15,31} for various well annealed CuAl (or CuNi) alloys at $T \geq 2$ K. The κ_g of both heavily deformed and annealed Cu-10-at.-%-Al samples of Ref. 11 are shown by the dotted lines. Rather good agreement exists between the two laboratories at $T \geq 1$ K.

The phonon mean free path l in the dominant phonon approximation could be extracted from the data by use of

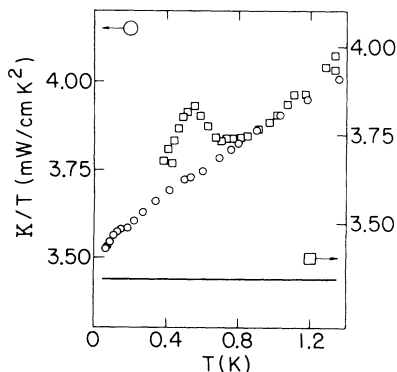


FIG. 3. Total thermal conductivity κ divided by T for two annealed CuAl samples. \circ , present data; \square , data from Ref. 11. The solid line represents the electronic contribution to κ/T for both samples.

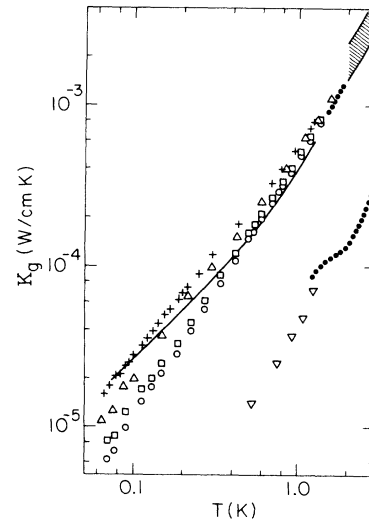


FIG. 4. Lattice thermal conductivity κ_g of several CuAl samples. ∇ , cold rolled plate; \circ , annealed plate; \square , annealed and bent plate; $+$, Δ , annealed rods (results from other annealed rods fell between these two sets of data). The dotted curves represent data above ≈ 1 K from Ref. 11 for an annealed sample and a deformed sample. The shaded area represents a composite of several measurements taken from the literature. The solid curve is a calculated κ_g assuming the phonons are scattered only by electrons.

$$\kappa_g = 0.572 l T^3 \quad (1)$$

in units of W/cm K. But we are primarily interested in the effect of dislocations on l . Therefore we take the *difference* in the experimental thermal resistivities κ_g^{-1} of two samples to find the increase in resistivity associated with the greater number of dislocations in one of the samples. This to a large extent avoids the problem associated with determining the magnitude of other scattering sources such as the conduction electrons. From Eq. (1) we thus obtain the phonon mean free path which would exist if *only* the additional dislocations were present to scatter phonons, and this result is plotted in Fig. 5. The difference in dislocation densities is, in each case, $\approx 10^8$ cm⁻² within a factor of 2. Although the slope of each curve is rather uncertain at the higher temperatures, it appears there is a minimum in l near 1.0 K at a magnitude of $l \approx 10^{-2}$ cm.

The data for the annealed rods of Fig. 4 can now be corrected for phonon scattering by the residual density of dislocations. Assuming that l varies inversely with the density of dislocations, a value of $l \approx 0.3$ cm at 0.1 K is obtained from Fig. 5 for a measured dislocation density of $\approx 2 \times 10^7$ cm⁻². The correction is $\approx 17\%$ at 0.1 K, and is smaller at higher temperatures. Hence the data for these samples represent to a good approximation the

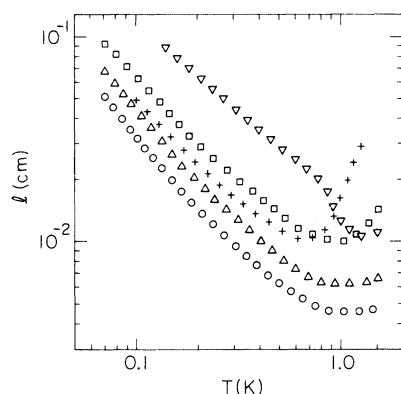


FIG. 5. Phonon mean free path l associated with a dislocation density of $\approx 10^8 \text{ cm}^{-2}$. The points do not represent experimental data. $\nabla \square \circ$, three independent determinations using six samples. $\circ \Delta +$, three determinations involving the same sample to emphasize the scatter present in the data.

lattice thermal conductivity when phonons are scattered *only* by electrons.

IV. DISCUSSION

A. Electron-phonon interaction

The lattice thermal conductivity as limited by electron scattering of phonons should vary as T^2 at high temperatures and as T at sufficiently low temperatures.^{15,32,33} The expected behavior (from Ref. 33), for CuAl alloys assuming a spherical Fermi surface is shown by the solid curve in Fig. 4. Recalling that the data for the annealed rods should be corrected upwards by $\geq 17\%$ at $T \leq 0.1$ K to account for the residual dislocations, we note that the theoretical curve lies low by only $\approx 20\%$ and has the correct temperature dependence throughout the range of measurements. (A correction for T_{58} , if applicable, would partially cancel the effect of removing the scattering caused by the residual dislocations.)

Occasionally $\kappa_g^{-1} T^2$ is plotted versus alloy composition to expose the dependence of κ_g on electron concentration.^{11,34} Instead of κ_g varying smoothly with composition, a cusplike behavior is usually obtained near the value representing the pure host metal. We cannot contribute to this question except to note that alloy data for $T \leq 1$ K are not appropriate for the analysis since κ_g does not vary as T^2 . It should also be noted that the typical plot of κ/T vs T for annealed alloys should *not* extrapolate to L/ρ_0 (even if the temperature scale is corrected) for data obtained at $T \leq 1$ K since κ_g varies as T^n , $n < 2$. At sufficiently low temperatures this should also be true for deformed samples since the cross section for phonon scattering

by dislocations is expected to decrease (see Sec. IVD).

B. Dislocation-phonon interaction: Static

The theory of the scattering of phonons by the static strain fields of dislocations was treated by Klemens³⁵ and more recently and in greater detail by Kogure and Hiki.³⁶ The original scattering cross section obtained by Klemens was increased³⁷ somewhat arbitrarily by a factor of 15, and it is the adjusted value which is usually cited in the literature.³⁸ We will adopt as a theoretical value for copper alloys

$$\kappa_g = 3 \times 10^8 T^2 N^{-1} \quad (2)$$

in units of W/cm K, where N is the dislocation density. This lies within a factor of 2 of Klemens's original derivation adjusted by the factor of 4 as argued by Ackerman.³⁸ It is also within a factor of 2 of the Kogure-Hiki result quoted for Cu when it is recognized that fast thermalization of phonons by conduction electrons should allow the shortest l (of the three phonon modes) to dominate κ_g . Equation (2) gives for κ_g a magnitude which is a factor of 10 larger than presented by Ackerman.³⁸ The Ackerman result, although apparently consistent with theory, reflects a continuing attempt to match calculations with experimental data at higher temperatures.³⁷

A mean free path related to phonon scattering by static strain fields can be obtained from Eq. (2). In units of cm,

$$l = 5.2 \times 10^8 N^{-1} T^{-1}. \quad (3)$$

Indeed l of Fig. 5 below 1 K varies roughly as T^{-1} . However to explain these data in terms of static strain field scattering would require, from Eq. (3), a dislocation density of $N \approx 10^{11} \text{ cm}^{-2}$ as compared to a measured density (difference) of $\approx 10^8 \text{ cm}^{-2}$. Even if Ackerman's value were adopted, the discrepancy would still be a factor of $\approx 10^2$. Thus the data of Fig. 5 would appear not to be associated with static strain field scattering.

The κ_g for the as received, highly strained sample of Fig. 4 is sufficiently small that electron scattering of phonons is negligible. Only dislocations scatter the phonons. The data follow roughly a T^2 behavior. A dislocation density of $N \approx 6 \times 10^{12} \text{ cm}^{-2}$ would be required to bring agreement between the data and Eq. (2), or $N \approx 6 \times 10^{11} \text{ cm}^{-2}$ to give agreement with Ackerman's result. We will return to a discussion of the highly deformed samples in Sec. IVD, as it is possible that another mechanism is contributing to the scattering.

C. Dislocation-phonon interaction: Dynamic

As discussed in Sec. I, a resonant interaction may occur between thermal phonons and a localized phonon or excitation associated with a dislocation. This interaction can be a factor of 10^2 – 10^3 stronger than for the static strain field, depending on the temperature (phonon-frequency) range in which the resonance falls. From Fig. 5, it appears that a resonant interaction occurs in CuAl near 1 K ($\approx 10^{11}$ Hz) and that at the resonance a dislocation density of 10^8 cm^{-2} produces a phonon mean free path of $\approx 10^{-2}$ cm. This resonant frequency and the scattering cross section are similar to those observed in several pure metals (Sec. I).

A number of models of dislocation excitations have been proposed. That which has been discussed most widely in the literature is the elastic string model of Granato and Lücke.³⁹ From this model a phonon mean free path can be deduced for the CuAl alloy.¹⁸ If all the dislocation resonances fall at the same frequency, the mean free path at resonance is⁴⁰

$$l \approx 3 \times 10^5 T_{\min} / N \quad (4)$$

in units of cm, where T_{\min} is the temperature for which l is a minimum. If the dislocations have a statistical (exponential) distribution of vibrating loop lengths and resonant frequencies,

$$l \approx 10^7 T_{\min} / N. \quad (5)$$

For our samples Eqs. (4) and (5) would give $N \approx 3 \times 10^7$ cm^{-2} for a single resonant frequency, or $N \approx 10^9$ cm^{-2} for an exponential distribution. These are to be compared to a measured density of $N \approx 10^8$ cm^{-2} .

For an exponential distribution, the average dislocation loop length would be ≈ 100 Å for a resonance near 1 K. It seems unlikely that an exponential distribution could exist with an average length this small, and so the resonant frequencies may be peaked around a value of $\approx 10^{11}$ Hz. Acoustic measurements are often indicative of a much larger average loop length,³⁹ $\approx 10^{-4}$ cm. In the present case, however, the dislocations undergo the smallest possible vibrational amplitude since they are in thermal equilibrium with the lattice at $T \approx 1$ K. Hence the dislocation motion would be dominated by the weakest of lattice potentials and pinning points.

The width of the resonance in Fig. 5 is much broader than observed previously in superconducting metals,^{2,3} although as already noted the resonant frequencies are very similar. It is known from previous work that the apparent width in $l \propto \kappa_g T^{-3}$ is influenced by processes which ther-

malyze the phonons, processes such as phonon scattering from damaged surfaces of samples or phonon scattering by electrons.^{2,41} Thus, phonons "outside" the resonance experience an effective, reduced mean free path. In a sense the electrons play the role of the N -processes encountered at much higher temperatures.

In brief, the string model seems capable of explaining the data of Fig. 5 if sufficient thermalization of the phonons occurs.

Other models have been proposed. Kronmüller⁴² has suggested an excitation involving the relative oscillations of the partials formed by a dissociated dislocation. For pure Cu, Kronmüller predicts a frequency of 0.3×10^{11} Hz, and the frequency would be lower for a CuAl alloy.⁴² This is to be compared with our observed value of $\approx 10^{11}$ Hz. The dislocation might oscillate within a valley of the undulating lattice (Peierls) potential or undergo a quantum-mechanical tunneling motion,³ but there are not as yet good theoretical models of these mechanisms with which to compare the data.

It is possible that a solute atmosphere influences a dislocation resonance. From the present data we note that the apparent resonance is qualitatively independent of whether a medium dislocation density has been obtained by annealing a highly strained sample or by deforming a highly annealed sample. In the latter case the sample was at times cooled immediately (≈ 1 h) to low temperatures after bending. Hence either the Al diffuses very rapidly at room temperature, or enhanced solute atmospheres do not form around dislocations in CuAl. It has been suggested that rapid diffusion of Al in Cu can occur at room temperature after deformation.⁴³ A definitive test would require deforming the sample at low temperature. (See note added in proof.)

Kusunoki and Suzuki⁸ report evidence from measurements above 1.6 K for a dislocation resonance in Cu plus 15-at.% Al. If we apply the same treatment to their data as used in the present paper, a set of curves similar to Fig. 5 is obtained. The resonance (minimum in l) falls near 2.5–3.0 K, or $(2.5\text{--}3.0) \times 10^{11}$ Hz, for dislocation density differences ranging from 3.6×10^9 cm^{-2} to 5.8×10^{10} cm^{-2} . These densities were deduced by Kusunoki and Suzuki from the measured deformation. All the data are consistent with $lN \approx 10^6$ near the minimum, which agrees with the value obtained from Fig. 5. Thus one would be inclined to conclude that the resonant frequency is simply increased with the larger Al concentration, or possibly that the apparent difference in frequency only reflects the difficulty in making the measurements.⁴⁴ It may be noted that it becomes increasingly difficult to identify a resonance as the temperature is increased since the scattering due to static strain

fields increases with T while the cross section for dynamic scattering (at the resonance) decreases with increasing T . Indeed other laboratories fail to observe a resonance near 3 K in CuAl samples of similar composition,^{14,31} although the measured temperature dependence of κ_g is often¹⁰⁻¹² somewhat faster than T^2 . That is, independent of sample history, a plot of l vs T decreases monotonically with increasing T contrary to the resonant-like behavior reported by Kusunoki and Suzuki. The several laboratories do agree that there is a change in slope of κ_g vs T near 2-3 K as mentioned in Sec. I.

It is of interest to compare the results of Fig. 5 with the work of Bevk,⁴⁵ even though the measurements were made above 1.5 K. Bevk reported a 2% increase in the specific heat of pure Cu with severe deformation. Interpreting this in terms of the string model gave the correct dislocation density and an upper limit on the average resonant frequency of $\approx 10^{11}$ Hz. (Essentially the same conclusion would be obtained for either a single resonant frequency or an exponential distribution.) If the change in specific heat is indeed related to dislocation excitations, only the string model would appear to fit the data. Oscillations in a Peierls potential, tunneling, etc., would produce Einstein or Schottky anomalies in the specific heat. These conclusions for pure Cu may not, however, extrapolate to CuAl alloys.¹³

D. Dislocation-phonon interaction: Large dislocation density

The character of the scattering of phonons by the static strain fields of dislocations is expected to change when the phonon wavelength becomes large compared to the average separation between dislocations, $\approx N^{-1/2}$. The temperature dependence of κ_g should deviate from T^2 , with the result that κ_g becomes relatively larger (less scattering) at $T < T_B$, where^{11,46}

$$T_B \approx 3 \times 10^{-6} \sqrt{N}. \quad (6)$$

We can test for this behavior using the data of Fig. 2. The data for the as received sample break from a straight line on the κ/T -vs- T plot and rise toward the value of κ/T limited by electron scattering at 0.1-0.2 K. It is not certain that this break is real, but it is certain that there are no breaks at higher temperatures. From Eq. (6) this fact would give $N \leq 10^9 \text{ cm}^{-2}$. All estimates of dislocation densities in severely cold worked Cu alloys have been near 10^{11} - 10^{12} cm^{-2} . Thus either the reduction in phonon scattering below T_B does not occur, or some other mechanism is scattering the phonons and hence obscuring the expected behavior.⁴⁷ A candidate for the other mechanism is, of course, resonant scattering near ≈ 1 K.

The change in temperature dependence that should occur near T_B might account for the "kink" or change in slope of κ/T vs T often reported near 2-3 K (Sec. I).¹¹ An average and reasonable dislocation density of $N \approx 10^{12} \text{ cm}^{-2}$ would place the kink near 3 K as observed. The kink should move to lower temperatures as N decreases, but this seems not to be observed and in fact would be obscured by the similar temperature dependence of the scattering by electrons which would then begin to dominate κ_g . Explanation of the kink in terms of T_B would still require an additional scattering mechanism, such as resonant dislocation scattering, to maintain κ_g small below T_B as observed in Fig. 2.

We therefore reach an impasse in interpreting data from the highly strained samples at $T \leq 1$ K. The data are consistent with the static strain field scattering being reduced below $T_B \approx 3$ K plus additional resonant scattering from dislocations near 1 K. But the situation is sufficiently complex⁴⁸ that no definitive analysis appears possible.

E. Dislocation-electron interaction

Conduction electrons are believed to damp or hinder the motion of dislocations.⁴⁹ Hence the resonant motion of a dislocation should be more highly damped in a metal than in a dielectric or superconductor where the damping at low temperatures is entirely by phonon radiation. Increasing the damping increases l near the minimum in the resonance and broadens the resonance as observed in l . Increasing the damping in the calculation a sufficient amount to fit the breadth of the curves in Fig. 5 would require not only a damping due to electrons orders of magnitude larger than deduced from other types of measurements, but would require a dislocation density (difference) much larger than observed from etch-pit counts. Thus the breadth of the resonance is probably related to the thermalizing effect provided by the conduction electrons as discussed in Sec. IV C. The scattering cross section or strength of the resonant dislocation-phonon interaction is then consistent with the value deduced from radiation damping [Eqs. (4) and (5)] indicating that at low temperatures the electron damping is of the order of or smaller than radiation damping at 10^{11} Hz as would be deduced from other measurements.⁴⁹

V. SUMMARY

The anomalous behavior of the lattice thermal conductivity of CuAl, CuZn, and CuNi alloys reported in the literature has been shown not to be intrinsic to these materials. The scattering of thermal phonons by conduction electrons in CuAl

at $T < 1$ K is in good agreement with theory. In CuAl, a resonant interaction appears to exist between thermal phonons and dislocations. The resonant frequency is $\approx 10^{11}$ Hz. In highly strained samples no conclusion can be reached as to the origin or origins of the phonon scattering below ≈ 1 K. One major problem is the uncertainty in the T_{58} temperature scale presently in use.

Note added in proof. The rapid formation of a solute atmosphere has been demonstrated by

P. Charsley and M. H. S. Rahim [Phys. Status Solidi A 34, 533 (1976)].

ACKNOWLEDGMENTS

We are very grateful to W. E. Nixon for his advice concerning the etch pitting of CuAl alloys. We thank I. D. Ward and J. B. Woodhouse for assistance with the scanning electron microscope, G. DePasquali for the use of an induction furnace, and R. J. Linz for discussions.

*Research was supported in part by the NSF under Grant No. DMR-72-03026. This paper is based on a dissertation submitted by J. L. Vorhaus in partial fulfillment of the requirements for the Ph.D degree at the University of Illinois, Urbana, Ill.

¹A. C. Anderson and M. E. Malinowski, Phys. Rev. B 5, 3199 (1972).

²A. C. Anderson and S. C. Smith, J. Phys. Chem. Solids 34, 111 (1973).

³S. G. O'Hara and A. C. Anderson, Phys. Rev. B 10, 574 (1974).

⁴M. P. Zaitlin and A. C. Anderson, Phys. Rev. B 10, 580 (1974).

⁵S. G. O'Hara and A. C. Anderson, J. Phys. Chem. Solids 35, 1677 (1974).

⁶S. G. O'Hara and A. C. Anderson, Phys. Rev. B 9, 3730 (1974).

⁷See, for example, H. M. Rosenberg, *Low Temperature Solid State Physics* (Oxford U.P., London, 1963), and papers cited therein.

⁸M. Kusunoki and H. Suzuki, J. Phys. Soc. Jpn. 26, 932 (1969).

⁹M. A. Mitchell, P. G. Klemens, and C. A. Reynolds, Phys. Rev. B 3, 1119 (1971).

¹⁰A. D. W. Leaver and P. Charsley, J. Phys. F 1, 28 (1971).

¹¹R. J. Linz, T. K. Chu, A. C. Bouley, F. P. Lipschultz, and P. G. Klemens, Phys. Rev. B 10, 4869 (1974).

¹²A. Kapoor, J. A. Rowlands, and S. B. Woods, Phys. Rev. B 9, 1223 (1974).

¹³Y. Kogure and Y. Hiki, J. Phys. Soc. Jpn. 39, 698 (1975).

¹⁴T. K. Chu, J. Appl. Phys. 46, 5101 (1975).

¹⁵P. Lindenfeld and W. B. Pennebaker, Phys. Rev. 127, 1881 (1962).

¹⁶A. C. Bouley and D. H. Damon, Bull. Am. Phys. Soc. 21, 104 (1976).

¹⁷Materials Research Corp., Orangeburg, N. Y. 10962. Our mass spectrographic analyses indicated that the samples contained ≈ 5 ppm (atomic) each of Fe, Ni, and Mg. The impurities were not distributed homogeneously and may have remained embedded in the etched surfaces.

¹⁸For details see J. L. Vorhaus, Ph.D. thesis (University of Illinois, Urbana, Illinois, 1976) (unpublished).

¹⁹M. Suomi, A. C. Anderson, and B. Holmström, Physica (Utr.) 38, 67 (1968).

²⁰R. L. Cappelletti and M. Ishikawa, Rev. Sci. Instrum. 44, 301 (1973).

²¹A. C. Anderson, R. E. Peterson, and J. E. Robichaux, Rev. Sci. Instrum. 41, 528 (1970). The calibration of this magnetic thermometer has consistently reproduced to $\approx 1\%$ over a period of six years.

²²R. P. Hudson, H. Marshak, R. J. Soulen, and D. B. Utton, J. Low Temp. Phys. 20, 1 (1975).

²³R. J. Soulen, Jr., J. F. Schooley, and G. A. Evans, Jr., Rev. Sci. Instrum. 44, 1537 (1973); D. L. Martin, *ibid.* 46, 1670 (1975).

²⁴A. C. Anderson, in *Temperature*, edited by H. H. Plumb (Instrument Society of America, Pittsburgh, Pa., 1972), Vol. 4, Part 2, p. 773.

²⁵A. C. Anderson, J. H. Anderson, and M. P. Zaitlin, Rev. Sci. Instrum. 47, 407 (1976).

²⁶B. J. Hockey and J. W. Mitchell, Philos. Mag. 26, 409 (1972), and papers cited therein.

²⁷W. E. Nixon (private communication).

²⁸Z. S. Basinski, J. S. Dugdale, and A. Howie, Philos. Mag. 8, 1989 (1963).

²⁹A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford U.P., London, 1953), p. 29.

³⁰See, for example, T. C. Cetas and C. A. Swenson, in *Temperature*, edited by H. H. Plumb (Instrument Society of America, Pittsburgh, Pa., 1972), Vol. 4, Part 1, p. 57. We assume for the present paper that the vapor pressure scales for liquid ${}^4\text{He}(T_{58})$ and liquid ${}^3\text{He}(T_{62})$ are equivalent.

³¹P. Charsley, J. A. M. Salter, and A. D. W. Leaver, Phys. Status Solidi 25, 531 (1968).

³²J. E. Zimmerman, J. Phys. Chem. Solids 11, 299 (1959).

³³A. C. Anderson and S. G. O'Hara, J. Low Temp. Phys. 15, 323 (1974).

³⁴W. R. Kemp and P. G. Klemens, Aust. J. Phys. 13, 247 (1960).

³⁵P. G. Klemens, in *Solid State Physics*, edited by D. Turnbull and F. Seitz (Academic, New York, 1958), Vol. 7, p. 1, plus earlier papers cited therein.

³⁶Y. Kogure and Y. Hiki, J. Phys. Soc. Jpn. 38, 471 (1975).

³⁷See Ref. 32, p. 92.

³⁸M. W. Ackerman, Phys. Rev. B 5, 2751 (1972).

³⁹A. Granato and K. Lücke, J. Appl. Phys. 27, 583 (1956); A. V. Granato and K. Lücke, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1966), Vol. 4, p. 225.

⁴⁰An orientation factor in the theory has been set equal to unity as in our earlier papers. This factor is fairly complex, and might even be larger than unity for frequencies above the fundamental resonance. See Ref.

- 39 and T. Ninomiya, *J. Phys. Soc. Jpn.* 25, 830 (1968).
- ⁴¹See also M. P. Zaitlin, L. M. Scherr, and A. C. Anderson, *Phys. Rev. B* 12, 4487 (1975).
- ⁴²H. Kronmüller, *Phys. Status Solidi B* 52, 231 (1972). Parameters appropriate to CuAl are given in A. Howie and P. R. Swann, *Philos. Mag.* 6, 1215 (1961).
- ⁴³S. F. Antani and P. G. Klemens, *Phys. Rev. B* 11, 2771 (1975).
- ⁴⁴Another possible explanation is that two resonances do exist at ≈ 1 K and ≈ 3 K as suggested in Ref. 11.
- ⁴⁵J. Bevk, *Philos. Mag.* 28, 1379 (1973). Both metallic specific-heat terms in T and T^3 were observed to increase, but only the linear term was analyzed by Bevk. See also, Y. Hiki, T. Maruyama, and Y. Kogure, *J. Phys. Soc. Jpn.* 34, 725 (1973).
- ⁴⁶M. W. Ackerman and P. G. Klemens, *Phys. Rev. B* 3, 2375 (1971).
- ⁴⁷The possibility of an enhanced scattering cross section at large N due to coherent effects has been suggested by P. Grumer, *Z. Naturforsch. A* 20, 1626 (1965).
- ⁴⁸There is the added complication that the electronic thermal conduction must be subtracted from κ to obtain κ_g . With $\kappa_g \approx 10^{-2}\kappa$, it is important to know what to subtract. It has already been indicated that uncertainty in T_{58} contributes an uncertainty of $\approx 10^{-2}\kappa$. There is also the question whether the Wiedemann-Franz law is sufficiently precise. To an accuracy of $\approx 1\%$, it has been shown that inelastic electron scattering does not occur from resonant dislocations, see S. G. O'Hara and A. C. Anderson, *Phys. Status Solidi B* 67, 401 (1975).
- ⁴⁹A. V. Granato, *Phys. Rev. B* 4, 2196 (1971), and papers cited therein.