PHYSICAL REVIEW VOLUME 127, NUMBER 6 SEPTEMBER 15, 1962

Lattice Conductivity of Copper Alloys*

P. LINDENFELD AND W. B. PENNEBAKER†
Rutgers University, New Brunswick, New Jersey

(Received May 11, 1962)

Measurements have been made at liquid helium temperatures of the thermal conductivity of nine specimens of copper containing germanium, aluminum, gallium, or indium impurities. The residual resistivities varied from 0.3 to 12.5 $\mu\Omega$-cm. The results for the lattice conductivity K_g of all specimens lie close to a single curve on a graph of $K_g/\rho_0 T$ against T/ρ_0.

Numerical calculations of the lattice conductivity have been made, using Pippard's theory of the dependence of the electron-phonon interaction on the electronic mean free path. The theory agrees well with our results and those of others if it is assumed that the longitudinal and transverse modes interact with the electrons nearly independently of each other. In the purer specimens the lattice conductivity is dominated by the transverse modes. The change in lattice conductivity between different specimens is seen to be the result of the change in the electron-phonon interaction without the necessity of assuming a large dislocation resistance. It is shown that dislocations do not cause a significant thermal resistance in annealed specimens.

I. INTRODUCTION

THE lattice thermal conductivity of metals is known to vary rapidly with impurity content at low temperatures.[1] Because the origin of the variation has been in doubt, the separation of the various resistive components has been subject to considerable uncertainty. We have measured the thermal conductivity of a series of copper alloys and have been able to show that the variation of the lattice conductivity K_g from specimen to specimen is correlated with the change in the residual electrical resistivity ρ_0. For all our specimens the data are close to a single universal curve on a graph of $K_g/T\rho_0$ against T/ρ_0. This agrees with the prediction of the theory developed by Pippard[2] for the dependence of the electron-phonon interaction on the electronic mean free path.

The theory has been used previously by Zimmerman[3] to describe the lattice conductivity of silver alloys with high residual resistivities. He made the assumption that the interaction of the transverse modes with the conduction electrons is the same as that of the longitudinal modes. We assume instead that the transverse and longitudinal modes interact with the electrons nearly independently of one another. We obtain good agreement between theory and experiment, leading to the conclusion that in the purer specimens the conductivity is predominantly due to the transverse modes.

Our measurements are described in Sec. II. In Sec. III we calculate the lattice conductivity as a function of electronic mean free path and temperature with the help of Pippard's theory, and in Sec. IV we compare the predictions of the theory with the experimental results. In Sec. V we consider the resistance caused by dislocations, which has been conjectured to be the cause of the variation of the lattice conductivity.[1] We show that dislocation scattering is not present in our specimens to a measurable extent.

II. EXPERIMENT

Apparatus

The low-temperature part of the apparatus is shown in Fig. 1. The stainless steel liquid-helium reservoir has a bottom made of tellurium copper to which are attached a vapor-pressure bulb and a "thermal station" which puts the electrical leads into good thermal contact with the reservoir. The thermal station consists of a copper ring with thick, insulated copper wires glued into tight-fitting holes. Each of these wires forms part of the path of a lead on its way from the top of the Dewar to the specimen. An insulating binding post and a specimen

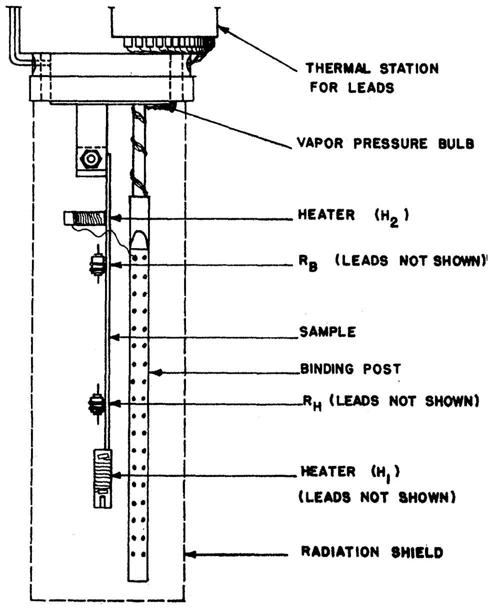

FIG. 1. Specimen assembly.

---

* Supported by the National Science Foundation and the Rutgers Research Council. This paper is based on a Ph.D. thesis submitted by W. B. Pennebaker to Rutgers University.

† RCA Fellow, 1959–1961. Present address: IBM Research Center, Yorktown Heights, New York.

[1] For a review see P. G. Klemens, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7, p. 1.

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

[3] J. E. Zimmerman, J. Phys. Chem. Solids 11, 299 (1959).

clamp are attached to the bottom of the vapor-pressure bulb.

Heater H_1 provides the temperature gradient along the specimen. The leads to it are made of niobium, so that no heat is developed in them below their superconducting transition temperature. Heater H_2 allows the average temperature of the specimen to be raised. The thermometers are 68-Ω, 1/10-Wt, Allen-Bradley resistors, glued into tight-fitting copper sleeves. Copper wires soldered to the sleeves attach the thermometers to the specimen and serve as both thermal and electrical contacts. Nonsuperconducting bismuth-cadmium solder[4] is used at the specimen to insure that the same geometrical factor can be used for the calculation of the thermal and electrical conductivities.

The following features of the external system deserve mention: Valves are arranged so that either the bath or the vapor-pressure bulb can be connected to the manometer. While the bath is being pumped down, the manometer is connected to the bath and the valve to the bulb is closed. This keeps the amount of liquid in the bulb nearly constant and allows equilibrium to be established quickly at each new temperature. In order to prevent an overpressure in the bulb during warmup a safety valve is used, consisting of a small mercury-filled U-tube with traps on each side, connected between the bath and the bulb.

The thermometers were calibrated against the vapor pressure of helium with the $T58$ scale.[5] Above the lambda point, the vapor pressure bulb was measured with a mercury manometer; at lower temperatures the pressure in the main helium reservoir was measured with a butyl-phthalate manometer. In the first run, two of the calibration points were used to calculate the constants in the equation[6] $1/T^* = a^2 \log R + b^2/\log R + 2ab$ for each thermometer, and correction curves of $T_1^* - T$ and $T_2^* - T_1^*$ vs T_1^* were used for interpolation. The same thermometers were used in each run, and the same constants a and b used in the calculation of T^*. There were shifts in the correction curves from run to run, but the shapes of the curves remained similar, and in the later runs five calibration points were sufficient to determine the correction curves.

TABLE I. Specimen characteristics.

Sample	Approximate impurity concentration	Residual resistivity ($\mu\Omega$ cm)
1	1/16% Ge	0.301
2	1/8% Ge	0.600
3	1/4% Ge	1.08
4	1% Ge	3.38
5	2% Ge	6.14
6	4% Ge	12.5
6*H*	4% Ge	12.9
Al	1.6% Al	2.10
Ga	2.5% Ga	3.03
In	3% In	1.51

Specimens

The specimens were made of 99.999% pure copper (American Smelting and Refining Company) with alloying elements each at least 99.99% pure. The materials for each specimen were melted in a crucible of reactor grade graphite in an induction furnace and outgassed for 5 min under vacuum. The melt was then vibrated for $\frac{1}{2}$ h in a helium atmosphere. The specimens were cast in a split mold in the same furnace and were at least 3 in. long, of rectangular cross section 1/8 by 1/32 in. They were annealed in helium-filled Vycor tubes at 700°C for at least 22 h. Specimen 6 was cleaned and reannealed at 900°C for 4 days and then called 6*H*. Each specimen consisted of a few large crystal grains.

The characteristics of the specimens are shown in Table I. The impurity percentage given in the table is the atomic percentage calculated from the weights of the ingredients and will be incorrect if some material was lost during the casting process. In particular, some indium was apparently lost.

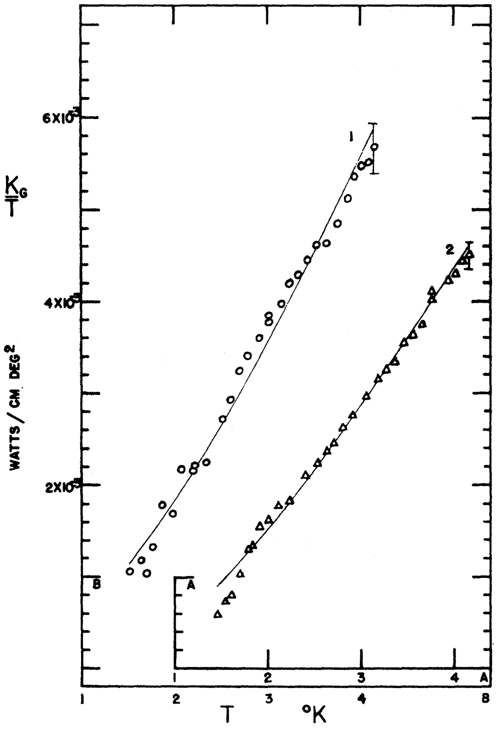

FIG. 2. Lattice conductivity divided by temperature for specimens 1 and 2.

---

[4] J. F. Cochran, D. E. Mapother, and R. E. Mould, Phys. Rev. **103**, 1657 (1956).

[5] F. G. Brickwedde, H. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Research Natl. Bur. Standards **64A**, 1 (1960).

[6] J. R. Clement, in *Temperature, its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1955), Vol. 2, p. 382.

Results

Measurements of the residual electrical resistance R_0 were made during each run. For some specimens R_0 was measured at 1.2 and 4.2°K. No variations of R_0 with temperature were observed. The electronic thermal conductivity was assumed to follow the Wiedemann-Franz law so that $K_e=(L_0T/R_0)(L/A)$, where L_0 is the Lorenz number 2.445×10^{-8} V²/deg², L is the distance between thermometers, and A the specimen area. The lattice conductivity K_g could then be calculated from the relation

$$K_g/T=(L/A)(Q/T\Delta T-L_0/R_0),$$

where Q is the power developed in heater H_1, ΔT is the temperature difference between the thermometers, and T is their average temperature.

The geometrical factor L/A was measured to about 2%. An error in this factor is seen to affect all points for a given specimen equally. The quantities Q, R_0, and T are known to about 0.1%. The temperature differences ΔT were generally between 0.1 and 0.2°K, and are estimated to be known to 0.2%. The uncertainty in the total thermal conductance $Q/T\Delta T$ is estimated to be 0.3%.

The results are shown in Figs. 2 to 7. Figures 2 and 3 show the data for the specimens with germanium impurity on graphs of K_g/T against T. The errors indicated at the end of each curve are those calculated from the estimated uncertainties in the conductance and do not include the uncertainty in the geometrical factor L/A. The percentage errors are larger for the purer

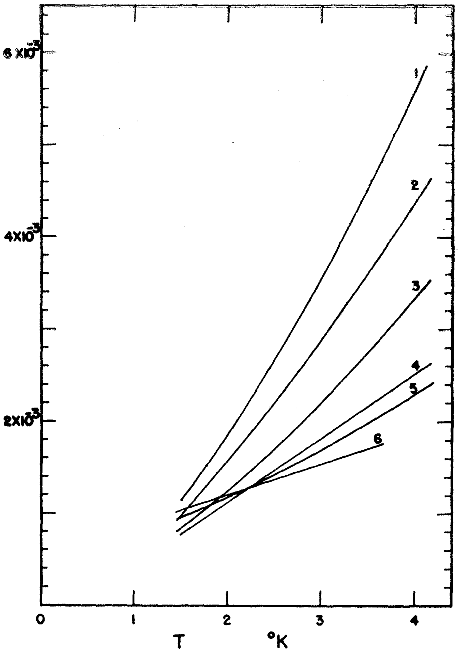

FIG. 4. Comparison of lattice conductivities for the specimens with germanium impurity.

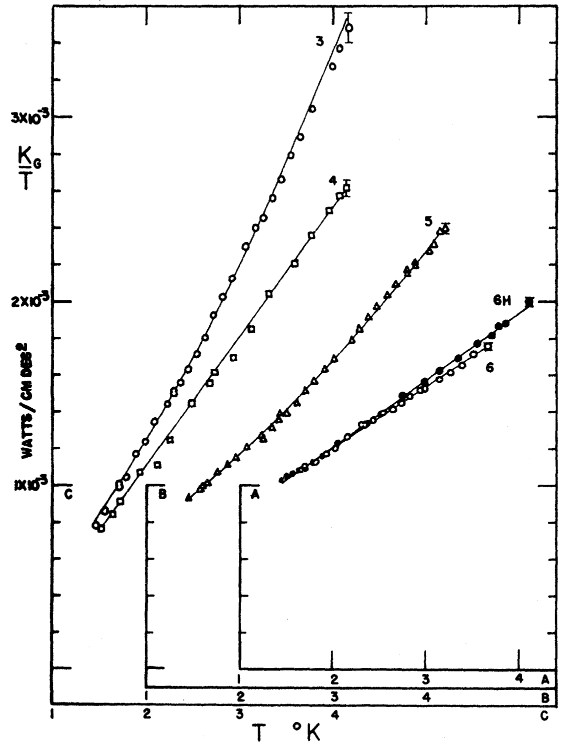

FIG. 3. Lattice conductivity divided by temperature for specimens 3, 4, 5, 6, and 6H.

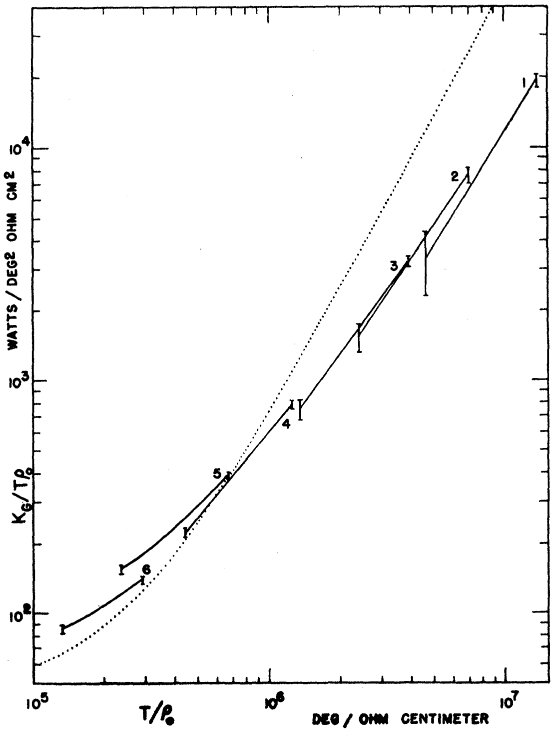

FIG. 5. Graph of K_g/ρ_0T against T/ρ_0 for the specimens with germanium impurity. The theoretical curve for $(K_L+K_T)T\Lambda_\epsilon$ from Fig. 9 is indicated by the dotted line.

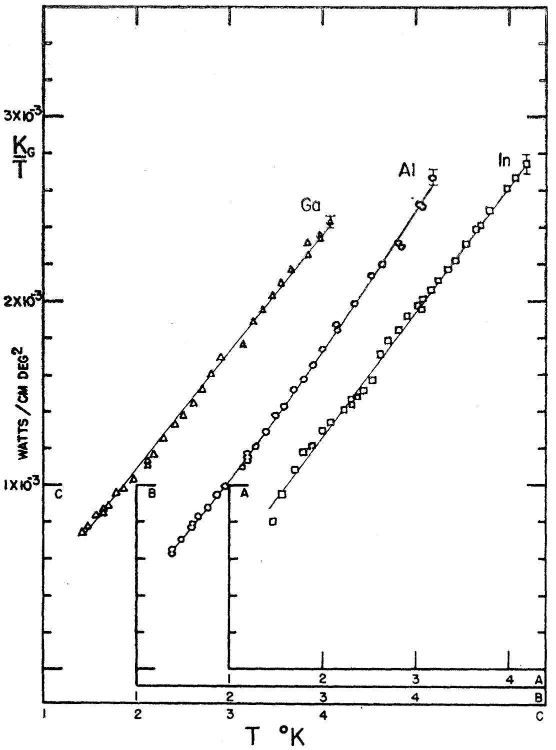

FIG. 6. Lattice conductivity divided by temperature for specimens with aluminum, gallium, and indium impurity.

specimens, because the lattice conductivity is for them a smaller fraction of the total. For example, at 4°K the lattice conductivity of specimen 1 is about 6% of the total conductivity.

On Fig. 4 the curves are plotted on one graph without the measured points in order to show their relation more clearly. If the lattice conductivity were proportional to T^2 (as expected from standard theory[1]), the curves would be straight lines through the origin. Instead, we see that the data seem to follow curved lines, although the temperature range is too small to draw this conclusion with certainty. If, however, straight lines are drawn through the data they are seen to have y intercepts which are negative for the purer specimens, increasing and becoming positive for the most impure specimens.

On Fig. 5 the data are plotted once more, this time on a logarithmic graph of $K_g/\rho_0 T$ against T/ρ_0. On this graph the data are seen to lie close to a single curve. The errors indicated on this graph are those in the conductivities and include the estimated errors of 2% in L/A.

The data for the specimens containing aluminum, gallium, and indium impurities are shown as K_g/T against T on Fig. 6. On Fig. 7 the data are replotted as $K_g/\rho_0 T$ against T/ρ_0. When plotted in this way, the data for these specimens as well as for those with germanium impurity lie close to a single, universal curve. The amount of impurity and the mass and valence of the impurity atoms seem to affect the lattice conductivity only through their effect on the residual electrical resistivity.

III. THEORY

The lattice thermal conductivity can be calculated from the kinetic relation[7]

$$K_g=\frac{1}{3}\int C_q v_q \Lambda_q d\mathbf{q}, \qquad (1)$$

where C_q, v_q, and Λ_q are the specific heat, the velocity, and the mean free path of phonons with wave number q. We limit our discussions to the case of free electrons in an isotropic metal without dispersion, and use for v_q the sound velocity and for $C_q d\mathbf{q}$ the Debye specific heat function.

The Pippard theory was initially developed to describe ultrasonic attenuation in metals and leads to expressions for the attenuation coefficients of longitudinal and transverse sound waves as functions of $q\Lambda_e$, where Λ_e is the electronic mean free path. We use the

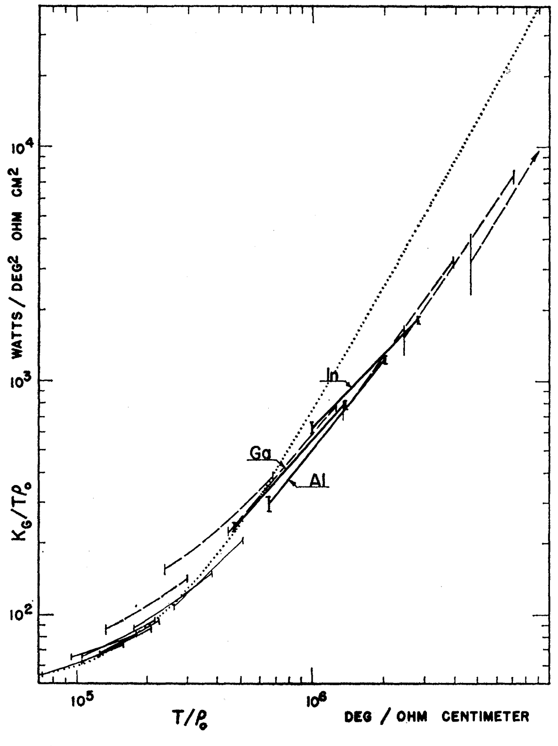

FIG. 7. Graph of $K_g/\rho_0 T$ against T/ρ_0 for the specimens with aluminum, gallium, and indium impurity. The broken lines are for the specimens with germanium impurity. The thin solid lines are for the silver-antimony specimens of Zimmerman (reference 3), scaled as described in the text. The theoretical curve for $(K_L+K_T)T\Lambda_e$ from Fig. 9 is indicated by the dotted line.

---

[7] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960).

reciprocals of the expressions for the attenuation coefficients for Λ_q in Eq. (1).

In Pippard's model the longitudinal modes interact with the conduction electrons because of the electric field of the space charge set up by the density variation of the lattice. As the electronic mean free path becomes short compared to the phonon wavelength, the increasing electron scattering helps the lattice to carry the electrons with it as it oscillates, and the space charge is reduced. When Λ_e becomes large the effect of electron scattering on the space charge is reduced, and the phonon mean free path approaches its value $\Lambda_{qp}{}^L$ in the pure metal (see Fig. 8).

The transverse waves cause no density variation and, thus, no space charge. The interaction with the electrons is through the current set up by the relative motion of the ions and electrons. This current causes a time-dependent magnetic field which induces an electric field. As before, the interaction is reduced for small values of $q\Lambda_e$. When Λ_e is large, the background of electrons, which travel out of phase with the wave and, thus, gain no net energy, shields the magnetic interaction, causing the phonon mean free path to rise again.

Pippard's expression for the mean free path for the longitudinal modes can be written

$$\Lambda_L=(Dv_L\tau/Nm)F_L(y)/y. \qquad (2)$$

Here N is the number of conduction electrons per unit volume, m the electronic mass, D the density of the metal, and v_L the longitudinal sound velocity. The variable y is equal to $q\Lambda_e$. The electronic relaxation time τ is equal to Λ_e/v_F, where v_F is the Fermi velocity. The function $F_L(y)$ is given by

$$y/F_L(y)=(y^2/3)[\tan^{-1}y/(y-\tan^{-1}y)]-1.$$

We now substitute Λ_L from Eq. (2) for Λ_q in Eq. (1), together with v_L for v_q and

$$C_q d\mathbf{q}=(k^4T^2/2\pi^2\hbar^3v_L{}^3)[x^4e^xdx/(e^x-1)^2],$$

where $x=\hbar\omega/kT$, to get for the conductivity of the longitudinal modes

$$K_L=\frac{Dk^3T^2}{6\pi^2Nm\hbar^2v_F}\int_0^\infty F_L(y)\frac{x^3e^xdx}{(e^x-1)^2}.$$

Since $y=(k/\hbar)(T\Lambda_e/v_L)x$, the integral is a function of $T\Lambda_e/v_L$.

As the electronic mean free path becomes large the function $F_L(y)$ approaches $6/\pi$. The corresponding conductivity is

$$K_L{}^0=(Dk^3T^2/\pi^3Nm\hbar^2v_F)J_3, \qquad (3)$$

where

$$J_3=\int_0^\infty x^3e^x(e^x-1)^{-2}dx=7.212.$$

Then

$$\frac{K_L}{K_L{}^0}=\frac{1}{J_3}\frac{\pi}{6}\int_0^\infty F_L(y)\frac{x^3e^xdx}{(e^x-1)^2}. \qquad (4)$$

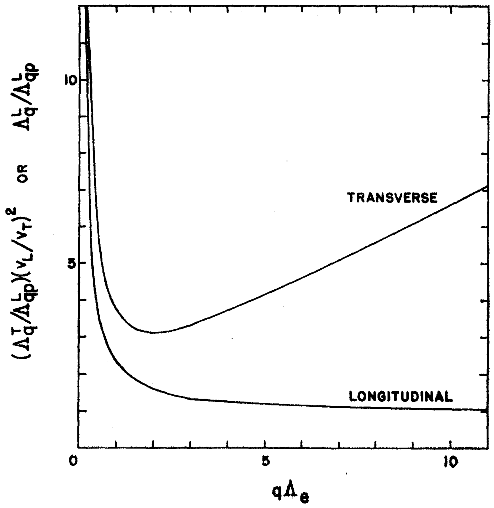

FIG. 8. Phonon mean free paths for the longitudinal modes ($\Lambda_q{}^L$) and for the transverse modes ($\Lambda_q{}^T$) as given by the Pippard theory. $\Lambda_{qp}{}^L$ is the value of $\Lambda_q{}^L$ in the pure metal.

Pippard's expression for the attenuation coefficient of the transverse modes was generalized by Blount[8] and Steinberg,[9] whose results can be put in the following form for the range of our experiments [where $\omega^2\tau^2\ll1$ and $(\omega_p{}^4/q^4c^4)\omega^2\tau^2g\ll1$; ω_p is the plasma frequency]:

$$\begin{aligned}\Lambda_T&=(Dv_T\tau/Nm)(F_T(y)/y),\\ y&=(1-g)F_T(y),\\ g&=(3/2y^2)\{[(y^2+1)/y]\tan^{-1}y-1\}.\end{aligned} \qquad (5)$$

The conductivity K_T of the transverse modes can now be calculated by substituting Λ_T from Eq. (5) for Λ_q, and v_T for v_q in Eq. (1), to get the expression

$$\frac{K_T}{K_L{}^0}=\frac{2}{J_3}\frac{\pi}{6}\int_0^\infty F_T(y)\frac{x^3e^xdx}{(e^x-1)^2}. \qquad (6)$$

Analogously to the previous case the integral is a function of $T\Lambda_e/v_T$.

The integrals of Eqs. (4) and (6) were evaluated numerically on the IBM 650 computer of the Rutgers Computation Center. The results of the integration are given in Table II.

Figure 9 shows graphs of $(K_L/K_L{}^0)T\Lambda_e$, $(K_T/K_L{}^0)T\Lambda_e$, and their sum against $T\Lambda_e$. Since $K_L{}^0$ is proportional to T^2 and Λ_e is inversely proportional to ρ_0, the graphs are similar to graphs of the conductivities divided by ρ_0T against T/ρ_0.

It is seen that K_L is proportional to T for small $T\Lambda_e$, and becomes proportional to T^2 as it approaches $K_L{}^0$. This behavior has been described previously by Zimmerman,[3] and our expression for the conductivity of the longitudinal modes [Eq. (4)] is equivalent to his. The

---

[8] E. I. Blount, Phys. Rev. **114**, 418 (1959).

[9] M. S. Steinberg, Phys. Rev. **111**, 425 (1958).

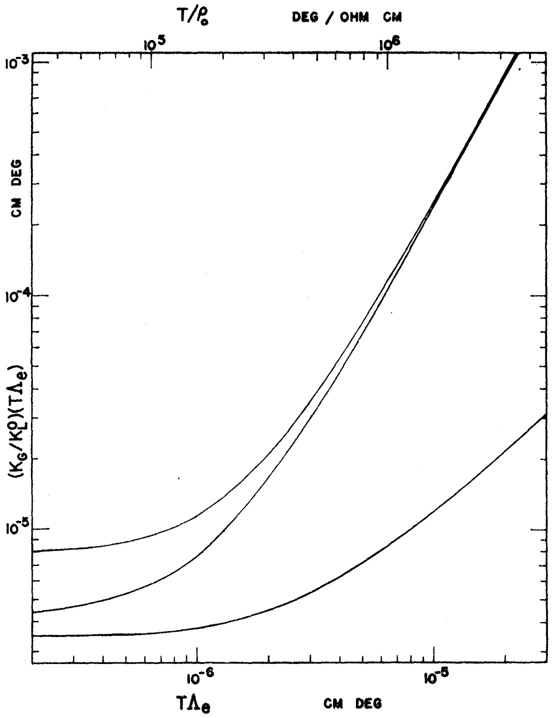

FIG. 9. Graphs of $(K_L/K_L{}^0)(T\Lambda_e)$ (lower curve), $(K_T/K_L{}^0)(T\Lambda_e)$ (middle curve), and their sum.

conductivity of the transverse modes behaves quite differently. For small $T\Lambda_e$ the transverse and longitudinal waves interact with the electrons to the same extent, but, as $T\Lambda_e$ becomes larger, K_T rises more rapidly and approaches a cubic dependence on the temperature. If we make the assumption that the different modes contribute to the conductivity independently of each other, so that $K_g=K_L+K_T$, we see that the conductivity will approach K_T and will continue to rise beyond $K_L{}^0$ as $T\Lambda_e$ increases.[10]

IV. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

The theoretical curve for the total lattice conductivity from Fig. 9 is indicated on Figs. 5 and 7 by dotted lines. ($T/\rho_0=15.4\times10^{10}T\Lambda_e$ deg/Ω-cm for copper.[11]) It should be emphasized that there are no adjustable parameters in the theory. The agreement of the experimental data with the theory is therefore quite remarkable. Agreement with the theoretical curve for longitudinal waves only is obviously much worse.

As T/ρ_0 increases the experimental data are seen to fall further and further below the theoretical curve. It might be thought that in this region scattering of electrons by phonons becomes important, so that the Wiedemann-Franz law no longer gives the correct separation of the electronic and lattice conductivities. The electronic conductivity in pure copper has been measured by Berman and MacDonald[12] and found to be $1/K_e=\rho_0/L_0T+AT^2$ with $A=2.55\times10^{-5}$ cm/deg W. Even if the scattering of electrons by phonons were larger by a factor of twenty in our specimens, our results would not be measurably affected.[13]

An important assumption in the theoretical description of Sec. III is that the longitudinal and transverse phonons can be considered independently. A strong phonon-phonon interaction would tend to make the mean free path of the transverse phonons equal to that of the longitudinal ones. While our results indicate that the assumption of complete independence is much better than that of complete mixing of the modes, some mixing may be expected as the temperature gets higher and as the mean free path of the transverse modes becomes much larger than that of the longitudinal modes. Differences between theory and experiment may also result from anisotropy and from the departure of the Fermi surface from sphericity.

Although the curves for all specimens fall close to a universal curve on a graph of K_g/ρ_0T vs T/ρ_0, there are small discontinuities between the curves for different specimens. The differences between the curves could be caused by so many differences in the electronic and lattice properties that it seems fruitless to try to account for them in detail. The free electron model does predict some changes with electron concentration, and we will return to a consideration of the changes after showing

TABLE II. Numerical integration results.[a,b]

$T\Lambda_e$ (cm deg)	I_1	I_2
10^{-8}	2471	1493
10^{-7}	247.3	150.9
7×10^{-7}	37.34	30.99
9×10^{-7}	29.92	28.41
10^{-6}	27.36	27.77
1.2×10^{-6}	23.58	27.25
1.5×10^{-6}	19.89	27.59
2×10^{-6}	16.30	29.57
3×10^{-6}	12.90	35.58
4.5×10^{-6}	10.78	46.20
6×10^{-6}	9.786	57.44
10^{-5}	8.666	88.23
10^{-4}	7.336	79.38

[a] $I_1=\frac{\pi}{6}\int_0^\infty F_L(y)\frac{x^3e^xdx}{(e^x-1)^2}$; $I_2=\frac{\pi}{6}\int_0^\infty F_T(y)\frac{x^3e^xdx}{(e^x-1)^2}$.

[b] $v_L=5.01\times10^5$ cm/sec, $v_T=2.27\times10^5$ cm/sec (American Institute of Physics Handbook, McGraw-Hill Book Company, New York, 1957).

---

[10] Previous attempts to interpret measurements of the lattice conductivity of copper by assuming different interactions for the longitudinal and transverse modes were made by R. W. Morse, Bull. Am. Phys. Soc. **3**, 203 (1958) and by T. Olsen, J. Phys. Chem. Solids **12**, 167 (1959).

[11] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).

[12] R. Berman and D. K. C. MacDonald, Proc. Roy. Soc. (London) **A211**, 122 (1952).

[13] Increases in the coefficient A with residual electrical resistivity have been observed by several investigators. See, for example, A. M. Guénault, Proc. Roy. Soc. (London), **A262**, 420 (1961). The form of the Pippard theory which is described here does not account for these observations.

that the model accounts quite closely for changes in the lattice conductivity between different solvents.

In Sec. III it was shown that $(K_L/K_L^0)(T\Lambda_e/v_L)$ is a universal function of $T\Lambda_e/v_L$, and that a similar expression holds for the transverse case. We can change the variables by using Eq. (3) for K_L^0, $\Lambda_e\rho_0 = mv_F/Ne^2$, $v_F = (\hbar/m)(3\pi^2N)^{1/3}$ and the relationship between the Debye temperature θ and the sound velocity, which shows that θ is proportional to $v_Ln^{1/3}$, where n is the number of atoms per unit volume. We can also substitute the atomic weight A (proportional to D/n) and the valence $b=N/n$. The variables of the universal function can then be written as $(K_g/\rho_0T)(b^{2/3}/A\theta)$ and $(T/\rho_0)(b^{2/3}n^{1/3}\theta)^{-1}$.

The curves measured by Zimmerman[3] on silver-antimony alloys have been scaled by the factors appropriate for silver and plotted as thin solid lines on Fig. 7. The agreement with the theoretical curve is seen to be excellent, and considerably better than that shown in reference 3.

Comparisons with older data are more difficult. The lattice conductivity was usually assumed to vary as T^2, and the coefficient of T^2 was determined from the slope of a straight line fitted to a plot of K/T vs T. Extrapolation of these lines to absolute zero occasionally resulted in apparent discrepancies with the Wiedemann-Franz law which could be positive or negative. We can now ascribe these apparent discrepancies to the assumption of an incorrect temperature dependence. The coefficients of T^2 which are quoted in the literature must then be regarded as average slopes over a limited temperature interval of graphs of K_g/T vs T. We have attempted a rough comparison with the theory of plotting $(1/K_g)T^2 = W_eT^2$ at 3°K vs ρ_0. The resulting curve is shown in Fig. 10 with experimental points from published data for copper alloys. The agreement is quite good. Again we see, however, that the lattice conductivity of the purer specimens is smaller than expected from the theory.

Figure 10 is drawn for copper as the solvent, but the coordinates can be scaled as indicated above. The results of Sladek[14] on indium-thallium alloys have been multiplied by the appropriate factors and plotted on the same graph. The points fall in the same region as those for copper alloys.

The available results on other solvents (silver,[3,15] gold,[16] tin,[17] and lead[18]) are not shown on Fig. 10. Most of the measurements, when scaled, fall in the same region as the points for copper alloys, with somewhat increased scatter.

The success of the scaling factors in accounting for differences between different solvents makes it interesting to see whether they can also explain some of the differences between different solutes. An increase in valence can be seen to push a curve upward and to the left and might help to bring the curve for specimen 6 more nearly in line with those for the other specimens. The effect may be larger than expected from the change in the ratio of electrons to atoms, because the electronic specific heat is known to rise much more rapidly[19] for small solute concentrations than expected from the free electron model. Changes in θ are known to be small in this system for our concentration range.[19]

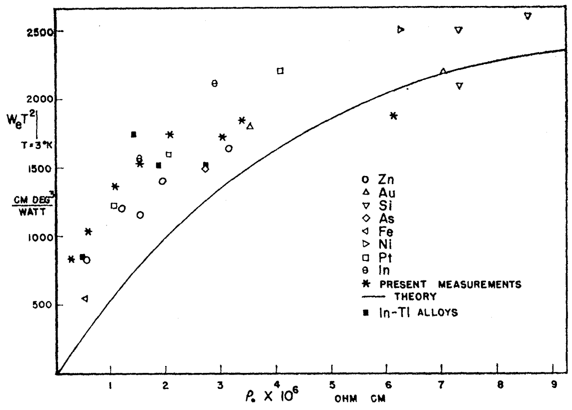

FIG. 10. Lattice conductivities at 3°K for a number of copper alloys, and for indium-thallium alloys (scaled as described in the text). The sources are as follows: W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Australian J. Phys. **10**, 454 (1957)–Zn, Au; W. R. G. Kemp and P. G. Klemens, *ibid.* **13**, 247 (1960)–Si; G. K. White and S. B. Woods, Can. J. Phys. **33**, 58 (1955)–Fe; P. G. Klemens, R. J. Tainsh, and G. K. White, *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1961)–Pt; J. E. Zimmerman (private communication)–Zn, Ni; P. Lindenfeld and W. B. Pennebaker, (unpublished measurements)–In, Si; reference 22–As; reference 14–In-Tl. See also reference 26. A similar diagram has been constructed by G. K. White (to be published). We would like to thank Dr. White for sending us a copy of his manuscript.

The curves for the specimens with indium, gallium, and aluminum impurity (Fig. 7), which may be assumed to differ only because of the differences in the value of A are seen to vary in the direction indicated by the scaling factors.

The slope of the curve for the indium specimen of Fig. 7 is smaller than that of the neighboring curves. This behavior is similar to that of one of the specimens measured by Zimmerman. He was able to remove the discrepancy by making a more homogeneous specimen. The behavior of our specimen may be related to the fact that some indium was apparently lost from the melt.

V. DISLOCATIONS

In Sec. III we have shown that our results are in accord with Pippard's theory, indicating that the only important resistive mechanism in the lattice conductivity of our specimens is the electron-phonon interaction. There has been considerable speculation that

---

[14] R. J. Sladek, Phys. Rev. **91**, 1280 (1953).

[15] W. R. G. Kemp, P. G. Klemens, A. K. Sreedhar, and G. K. White, Proc. Roy. Soc. (London) **A233**, 480 (1956).

[16] J. A. Birch, W. R. G. Kemp, and P. G. Klemens, Proc. Phys. Soc. (London) **71**, 843 (1958).

[17] M. Garfinkel and P. Lindenfeld, Phys. Rev. **110**, 883 (1958).

[18] P. Lindenfeld, Phys. Rev. Letters **6**, 613 (1961).

[19] J. A. Rayne, Phys. Rev. **110**, 606 (1958).

dislocations add to the resistivity significantly, even in annealed specimens,[1] and we now examine this possibility in more detail.

The theory of the effect of dislocations on the lattice thermal conductivity has been discussed by Klemens,[20] who has shown that the thermal resistivity corresponding to a dislocation density N_d is

$$W_d = CN_d/T^2. \tag{7}$$

This result makes it very difficult to distinguish resistance caused by dislocations from that caused by electrons by observations of the temperature dependence of the conductivity. Calculations of the proportionality constant C are uncertain, but two different experimental determinations have been made which agree quite well with each other. The first is by Lomer and Rosenberg[21] who measured the lattice conductivity of a series of copper-zinc alloys as a function of strain, and obtained electron microscope measurements of the dislocation density of two of their strained specimens of copper with 30% zinc. They arrive at a value for C of 3×10^{-8} $\mathrm{W}^{-1}\ \mathrm{cm}^3\ \mathrm{deg}^3$. This value is compatible with that of Kemp, Klemens, and Tainsh,[22] who correlated their measurements of the heat conduction of two copper alloy specimens with studies of the release of stored energy by Clarebrough, Hargreaves, and West.[23] Further confidence in the quoted value of C is gained from the fact that electron microscope measurements of dislocation density as a function of strain in pure polycrystalline silver by Bailey and Hirsch[24] agree very well with Lomer and Rosenberg's results on dislocation density vs strain as deduced from measurements of lattice conductivity.

None of the measurements quoted here give any information on the dislocation density in annealed alloys. The electron-microscope measurements of Lomer and Rosenberg, would, in principle, be able to give such information, but measurements were made on specimens strained 9.3 and 16.5%, and any extrapolation to zero strain is not likely to be meaningful.

In order to find out whether the dislocation densities in annealed alloys might be large enough to cause a measurable contribution to the thermal resistance, we have made some electron microscope studies which we reported on briefly before.[25] Electron micrographs of strained alloy specimens were similar to those of Bailey on pure silver. The pictures from annealed specimens, on the other hand, showed too few dislocations for meaningful measurements of dislocation density. The dislocation density was certainly too small for Eq. (7) with Lomer and Rosenberg's value for C to predict a detectable dislocation resistance.

It is possible to rule out significant dislocation resistance in annealed specimens even without a knowledge of the proportionality constant C. In order to account for the observed increase in lattice resistance in specimens containing a few percent of impurity the number of dislocations removed by annealing would have to be of the same order of magnitude as those remaining. This possibility is ruled out by the electron microscope evidence.

The most direct evidence that dislocations are not responsible for the increase in resistance with impurity comes from recent measurements on lead alloys[18] which show that the increase in resistance is very much smaller in the superconducting state than in the normal state. Since the electron-phonon interaction is known to decrease rapidly in the superconducting state as the temperature is lowered, this result is in accord with the discussion of Sec. III.

The evidence cited in the previous paragraphs shows conclusively that dislocations play a negligible role in the heat conduction of annealed specimens. There remained, however, some contradictory evidence which it seemed worthwhile to investigate. Several experiments[26] showed that the lattice conductivity was increased by high-temperature annealing, and the increase was attributed to the removal of dislocations. We, therefore, cleaned our most impure specimen (No. 6) and reannealed it at 900°C for four days. We found that the lattice conductivity changed by a small amount, and that the change could be accounted for within the experimental error by the change in the residual resistivity of the specimen.

VI. CONCLUDING REMARKS

The theory outlined in Sec. III accounts well for the observed change in the lattice conductivity with impurity. It is necessary to assume that the transverse and longitudinal phonons interact with the electrons nearly independently of each other. This assumption will become poorer at higher temperatures and in materials of lower residual resistivity. We do, in fact, observe that at the larger values of T/ρ_0 of our measurements the agreement between theory and experiment becomes worse. It would be desirable to investigate the additional thermal resistance in the purer specimens by making measurements over a wider range of temperature and residual resistivity. It is likely that further information can be gained in this way about the interaction of the phonons with each other and with the electrons.

---

[20] P. G. Klemens, Proc. Phys. Soc. (London) **A68**, 1113 (1955).

[21] J. N. Lomer and H. M. Rosenberg, Phil. Mag. **4**, 467 (1959).

[22] W. R. G. Kemp, P. G. Klemens, and R. J. Tainsh, Phil. Mag. **4**, 845 (1959).

[23] L. M. Clarebrough, M. E. Hargreaves, and G. W. West, Proc. Roy. Soc. (London) **A232**, 252 (1956).

[24] J. E. Bailey and P. B. Hirsch, Phil. Mag. **5**, 485 (1960).

[25] P. Lindenfeld and W. B. Pennebaker, *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, Toronto, 1961).

[26] W. R. G. Kemp and P. G. Klemens, Australian J. Phys. **13**, 247 (1960).

ACKNOWLEDGMENTS

We are indebted to Dr. P. R. Weiss for considerable help with the interpretation and application of the theory. The suggestion that the interaction of the electrons with the transverse modes, as described by Pippard, might account for our results was made by Dr. R. W. Morse. We have had many helpful conversations with Dr. B. Serin and Dr. E. A. Lynton.

The electron microscope investigation was done at the Materials Research Laboratory of Rutgers University. We are grateful to Dr. S. Weissmann for help with the interpretation of the pictures, and to Dr. M. Hirabayashi for instructing us in the use of the instrument.

The apparatus was constructed by C. Leathem and A. Siemons.

PHYSICAL REVIEW VOLUME 127, NUMBER 6 SEPTEMBER 15, 1962

Pressure Dependence of the Curie Temperature of Ferromagnetic Metals

S. H. Liu
Thomas J. Watson Research Center, International Business Machines Corporation, Yorktown Heights, New York

(Received March 26, 1962; revised manuscript received June 11, 1962)

It is shown that according to the indirect exchange theory of ferromagnetic metals the pressure dependence of the Curie temperature is related to certain properties of the conduction electrons. A number of experiments are suggested to further our understanding of the problem.

IN 1954, Patrick[1] reported the results of his measurements on the pressure dependence of the Curie temperature of several ferromagnets. These results have not been satisfactorily explained. The difficulty lies in the uncertainty of the conventional theory of ferromagnetism in making quantitative calculations since everything hinges on the size of the "exchange integral", a quantity so difficult to calculate that it is almost impossible to draw any dependable conclusion about its pressure dependence. Furthermore, many recent calculations all bear out the fact that the exchange integral is not enough to explain the ferromagnetism in transition elements.[2] In rare-earth metals the direct exchange should be extremely weak, because the magnetic $4f$ shells of different ions have little or no overlap. Hence, the magnetic interaction in these metals must come from an entirely different origin. It is generally believed that the indirect exchange mechanism via the conduction electrons is responsible for the magnetic interaction in these metals. The theory of indirect exchange as given by Ruderman and Kittel[3] and others[4–6] involves a set of parameters which characterize the properties of the conduction electron system and the strength of the electron-ion coupling. These parameters can be deduced from other experimental data. Therefore, it is possible to obtain a self-consistent theory of all the properties of the electron-ion system. This paper discusses the pressure dependence of the Curie temperature of gadolinium from the point of view of the indirect exchange theory. It shows that the pressure effect implies certain properties of the conduction electron wave function. Although the present knowledge of the electronic properties of the material is not sufficient to give a complete explanation, it is possible to assign reasonable upper and lower bounds to the relevant quantities.

In the indirect exchange theory, one assumes the total Hamiltonian of the electron-ion system to be

$$H=\sum_i \frac{p_i^2}{2m^*}+\sum_j I(\mathbf{r}_i-\mathbf{R}_j)\mathbf{s}_i\cdot\mathbf{S}_j, \tag{1}$$

where the first term is the kinetic energy of the conduction electrons in the effective mass approximation and the second term is the exchange interaction between the conduction electrons and the ions. $\mathbf{R}_j$, $\mathbf{S}_j$ are the position and spin of the jth ion, $\mathbf{r}_i$,$\mathbf{s}_i$ the position and spin of the ith electron, and $I(\mathbf{r}_i-\mathbf{R}_j)$ is the strength of the exchange interaction. The electron is described by a Bloch function $\phi_{\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{\mathbf{k}}(\mathbf{r})$, where $u_{\mathbf{k}}(\mathbf{r})$ is periodic in the lattice. The Bloch function is normalized in a large volume V, the volume of the sample, so the matrix element of the exchange interaction can be written as

$$(1/N)\mathbf{s}_i\cdot\mathbf{S}_j I_{\mathbf{k}\mathbf{k}'}\exp[i(\mathbf{k}-\mathbf{k})\cdot\mathbf{R}_j], \tag{2}$$

where

$$I_{\mathbf{k}\mathbf{k}'}=N\int \phi_{\mathbf{k}'}^*(\mathbf{r})I(\mathbf{r})\phi_{\mathbf{k}}(\mathbf{r})d\mathbf{r}. \tag{3}$$

N is the total number of ions in V. In the second-order perturbation theory the interaction between the spins can be expressed by the spin Hamiltonian[3–5]

$$H_s=\sum_{i\neq j}\sum_j J(R_{ij})\mathbf{S}_i\cdot\mathbf{S}_j, \tag{4}$$

---

[1] L. Patrick, Phys. Rev. **93**, 384 (1954).

[2] A. J. Freeman and R. E. Watson, Phys. Rev. **124**, 1439 (1961), and the references cited therein.

[3] M. A. Ruderman and C. Kittel, Phys. Rev. **96**, 99 (1954).

[4] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).

[5] K. Yosida, Phys. Rev. **106**, 893 (1957).

[6] A recently published derivation of the theory by the author [Phys. Rev. **123**, 470 (1961)] is incorrect.