Lorenz Number for High-Purity Copper

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(Received May 13, 1960)

Following a recent report that the Lorenz number, $L=\lambda/\sigma T$, does not approximate to the theoretical value of $2.45\times10^{-8}W$ ohm deg^{-2} for very pure copper at the lowest temperatures, measurements have been made of thermal and electrical conductivities on copper of similar purity. Between 2 and 4°K, values of L are observed lying in the range 2.5_4 to $2.4_0\times10^{-8}W$ ohm deg^{-2}.

1. INTRODUCTION

RECENTLY Powell *et al.*[1] reported observations of the low-temperature transport properties of pure copper in both the annealed and cold-drawn conditions; this followed extensive earlier work by them[2] on commercial grades of copper. Their work on 99.999% pure copper (from the Central Research Laboratories of the American Smelting and Refining Company) generally confirmed the behavior of the electrical resistivity and thermal conductivity observed by Berman and MacDonald[3] and by White[4] on slightly less pure samples. However, a most striking feature of their work was the observation that as the temperature approached 0°K (where impurity scattering becomes dominant) the value of the Wiedemann-Franz ratio or Lorenz number did not approach its theoretical value but a value about 25% lower. Denoting thermal and electrical conductivities, respectively, by λ and σ, and the corresponding resistivities by W and ρ, this ratio $\lambda/\sigma T\equiv L\equiv\rho/WT$ approached the value of about $1.85\times10^{-8}W$ ohm deg^{-2} [or (volt/deg)^2 if preferred] rather than 2.45×10^{-8}. This is in sharp contrast to previous experimental observations on pure metals and to the theoretical predictions of electronic transport theory (see reviews of Klemens[5] and Blatt[6] and discussion below), so that we have felt obliged to extend our earlier work on copper to samples of the same high degree of purity as those used by Powell *et al.*[1]

2. BACKGROUND

In a metal an electric field or a temperature gradient causes an electron drift which is restricted only by the collisions which the electrons make with imperfections in the lattice, whether they be static defects or lattice vibrations. When the electron distribution function is disturbed from its equilibrium value, the rate of return to equilibrium—by collision processes—may be expressed in terms of a relaxation time τ. The Boltzmann equation expresses the equilibrium situation and may yield the solutions[5]

$$\sigma=\frac{e^2}{12\pi^3}\int\frac{\tau v^2 dS}{|\mathrm{grad}_{\mathbf{k}}E|},\quad \lambda=\frac{k^2T}{36\pi}\int\frac{\tau v^2 dS}{|\mathrm{grad}_{\mathbf{k}}E|},$$

where dS is an element of the Fermi surface ($E=\zeta$) in $\mathbf{k}$ space, v is the electron velocity and k is the Boltzmann constant. Obviously, if the relaxation time is the same for both the electric and thermal transport, then

$$\frac{\lambda}{\sigma T}=\frac{\pi^2}{3}\left(\frac{k}{e}\right)^2=L.$$

This limiting value of L which is due to Sommerfeld (see, e.g., Froehlich[7]) is thus a constant independent of band structure or relaxation time.

Regarding relaxation, Froehlich[7] has pointed out that equilibrium can be reached in two ways: either by processes changing the direction of motion of an electron but not changing its energy significantly, or by processes changing energy but not direction—the so-called "horizontal" or "vertical" movements on the Fermi surface.[5,6] "Vertical" movement is, however, ineffective in producing electrical resistance. Hence the relaxation times for electrical and thermal conduction are strictly equal only if "vertical" movement is absent. The effective scattering by lattice waves at high temperatures and by impurities at low temperatures is large-angle and elastic, so that τ is the same for the different transport processes; therefore we expect

$$L=\frac{\pi^2}{3}\left(\frac{k}{e}\right)^2\simeq2.45\times10^{-8}W \text{ ohm deg}^{-2}$$

for $T>\theta$ and for $T\ll\theta$.

Turning to the experimental picture, what has low temperature research revealed? Observations on copper,[3] sodium,[8] the alkali metals,[9] magnesium,[10] the

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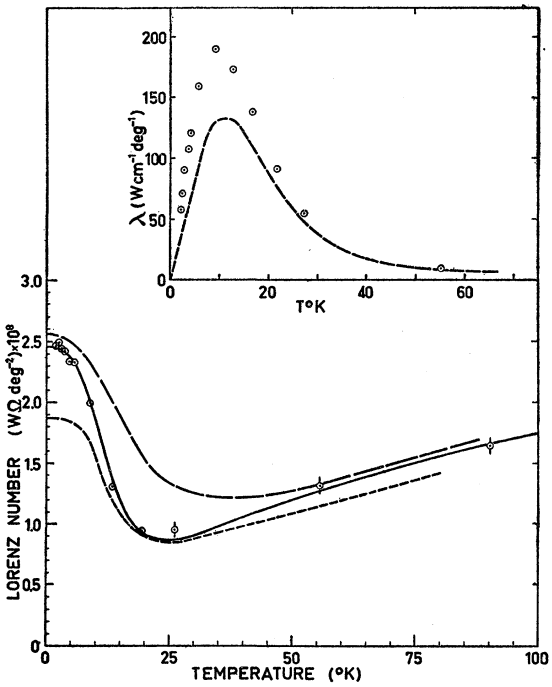

FIG. 1. The Lorenz number, $L=\rho/WT$, for pure annealed copper. Inset shows thermal conductivity, λ. Dashed curve, Berman and MacDonald (see reference 3); dotted curve, Powell, Roder, and Hall (see reference 1); ⊙ experimental points; solid curve, a curve calculated assuming $L=(\rho_0+\rho_i)/(W_0+W_i)T$ with $\rho_0=0.87\times10^{-9}$ ohm cm; $W_0=\rho_0/2.45\times10^{-8}T$, ρ_i and W_i from earlier work (see references 3 and 11).

transition elements[10,11] have all seemed to confirm this theoretical prediction. For some specimens of rather limited purity, it has been evident that $\lambda/\sigma T>2.45\times10^{-8}$ at liquid helium temperatures, but this finds a ready explanation in the presence of an appreciable component of heat conduction due to the lattice. Such a component only becomes appreciable when conduction by electrons is reduced far below that for a pure metal, by the presence of impurities. Thus prior to the report of Powell *et al.*[1] no evidence had been presented suggesting that as $T\rightarrow0$, L should have a value *less than* its theoretical value, and for the relatively pure samples of good metallic conductors it has appeared that L does approximate closely to this value.

3. EXPERIMENTAL METHOD

Details of the cryostat, in which electrical and thermal conductivities can be measured on the one specimen down to 2°K, have been given before.[12] The copper specimen used was from a $\frac{3}{4}$-in. diameter rod from the same source as that of Powell *et al.*, namely the American Smelting and Refining Company; their spectrographic analysis showed less than 1 ppm each of Fe, Sb, Se, and less than 2 ppm of Te, As. For our purposes, 0.030-in. diameter wire was rolled and drawn from this rod and then annealed at 530°C *in vacuo* for some hours. Care was taken to avoid contamination and the residual resistivity of $\rho_0\simeq0.87\times10^{-9}$ ohm cm (see value of $\rho_0\simeq1.01\times10^{-9}$ ohm cm reported by Powell *et al.*[1]) confirms the purity of the resulting wire. The annealed wire was cut into three parts, the center part of about 8 cm being mounted in the cryostat with nonsuperconducting solder and with a thin glass frame (of very low heat conductivity) assisting to support the rather thin and soft specimen. The electrical resistivities of the two end pieces, each about 1 meter long, were also measured in liquid helium in order to test for uniformity in the case of any contamination. Their residual resistivities differed by less than 3%, each being close to 0.8×10^{-9} ohm cm. This latter value of ρ_0 corresponds to a residual resistance ratio, R_4/R_{294}, of about 5×10^{-4}.

The total electrical resistance, at liquid helium temperatures, of each of these wires was only about 12×10^{-6} ohm, and of the actual sample in the cryostat was only 2×10^{-6} ohm. To measure this, a galvanometer amplifier[13] with a maximum sensitivity of 60 cm/μv and random error of about ±1% was used. However, a rather high-measuring current ($\geqslant100$ ma at liquid helium temperatures) is still required and this may produce undesirable heating effects. Later, as a check, the outer brass and copper jackets were removed from the cryostat so that the sample could be immersed directly into liquid helium and its resistivity determined with a reasonably heavy (500 ma) measuring current under completely isothermal conditions. It then showed a resistivity of $0.86_5\pm0.01\times10^{-9}$ ohm cm, compared with values in the range $0.88\pm0.02\times10^{-9}$ ohm cm determined earlier.

4. RESULTS

No detailed study of the temperature dependence of the ideal electrical resistivity was made, as the specimens were of too low a total resistance for an accurate investigation. However, at temperatures near 30, 55, 90, and 294°K values agreed quite well with earlier determinations.[4,11] For example, at 294°K and 90°K, respectively, the measured resistivity was 1.67_5 and $0.27_5\times10^{-6}$ ohm cm.

As discussed in the earlier work on copper, the thermal resistivity W may be expressed as a sum of impurity and ideal resistivities, W_0 and W_i, respectively. Analysis of our results indicated that the thermal resistivity could be expressed as $W=A/T+BT^n$ where $n\simeq2.3$ for $T<40$°K. The magnitude of the second term in this equation, which we call the ideal thermal resistivity, agrees quite well with that obtained previously for annealed samples.[1,3,4] Our sample was of slightly higher purity than in previous work; A was 0.035_1 cm deg W^{-1} as compared with 0.059 for the

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sample of Powell *et al.*[1] This difference is also reflected in the maximum value of heat conductivity (see inset figure), which is about $190W$ cm^{-1} deg^{-1} for our sample and about $135W$ cm^{-1} deg^{-1} for their annealed sample.

The important factor is, however, the comparison of the thermal and electrical resistivities. The values of $L=\rho/WT$ are shown in Fig. 1, together with curves obtained by Berman and MacDonald[3] and by Powell *et al.*[1] The third curve shown is that calculated from existing data on the "ideal" resistivities for copper,[11] and from the known residual resistivity of our specimen, i.e., from the equation $L=(\rho_0+\rho_i)/(W_0+W_i)T$, assuming $\rho_0=0.87\times10^{-9}$ ohm cm, $W_0=\rho_0/2.45\times10^{-8}T$. The experimental points below about 4°K indicate that at the lowest temperatures L lies between 2.4 and $2.5\times10^{-8}W$ ohm deg^{-2}, not differing more than 2% from the theoretical Sommerfeld value of 2.45×10^{-8}.

Note that only at very low and at high temperatures should L approach the Sommerfeld value. At intermediate temperatures, where scattering is not elastic, and hence where relaxation times are not the same for thermal and electrical resistivity, L will fall below this value. The temperature at which L is a minimum, and hence the minimum value of L, decrease with increase in purity. Allowing for the differing purity of our sample and that of Berman and MacDonald, the temperature variation of L is consistent.

5. CONCLUSION

In agreement with the theory, it appears that this specimen of high purity copper exhibits the same value of the Wiedemann-Franz-Lorenz ratio at liquid helium temperatures as do less pure copper samples, and as do many specimens of other metallic elements, namely $L\simeq2.45\pm0.05\times10^{-8}W$ ohm deg^{-2}. The reason for a departure from this pattern in the experiments of Powell *et al.*[1] seems obscure; perhaps it arises from spurious heating effects.

PHYSICAL REVIEW VOLUME 119, NUMBER 6 SEPTEMBER 15, 1960

Possibility of the Existence of Attractive Forces Between Dislocations of Like Sign

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(Received April 8, 1960)

It is concluded that two moving dislocations of the same sign and on the same slip plane can sometimes attract rather than repel one another (and two of unlike sign repel rather than attract each other). This reversal over the usual behavior will occur at velocities where the kinetic energy in the displacement field of an isolated moving dislocation is larger than the strain energy in the same field.

IT is usually considered that dislocations of like sign repel each other and those of unlike sign attract each other. We wish to point out that, at high dislocation velocities, the reverse situation may occur. A consideration of the energy of a moving dislocation shows under what circumstances like dislocations can attract and unlike repel. The energy of a uniformly moving dislocation can be divided into two parts, a potential energy associated with the strains existing in the elastic displacement field and a kinetic energy associated with the velocity of these elastic displacements. Let E_1 and E_2 represent these two energies. In general the values of E_1 and E_2 will increase monotonically as the velocity of the dislocation increases. Now consider the following thought experiment. Let two dislocations which originally are widely separated each be given a velocity V_0 with respect to the crystal lattice and set into motion towards each other so that ultimately they will meet. If it is assumed that energy is conserved, the dislocations will pass through each other and eventually regain the original velocity V_0 when they again are widely separated. The criterion as to whether the forces between these dislocations are attractive or repulsive simply is the following: If at the moment of meeting the velocity V_1 of the dislocations is greater than the original velocity V_0, the forces must be attractive. If the velocity V_1 is smaller, the forces are repulsive. (We assume, of course, that the initial energy is sufficiently great that the two dislocations can meet in the repulsive case.)

If linear elasticity theory is applicable and energy loss by the radiation of sound waves neglected, the solution of the displacement field of two moving dislocations is simply the sum of the displacements of each dislocation considered alone. Hence when two unlike dislocations collide, the displacements and stresses go to zero and the potential energy at the moment of impact is zero. The velocity of the displacements does not go to zero for unlike dislocations, but is double the velocity of the displacements of an isolated, uniformly moving dislocation with the velocity V_1. Since kinetic energy goes as the square of the displacement velocity one has

$$4E_2(V_1)=2[E_1(V_0)+E_2(V_0)], \quad (1)$$