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Evidence for strong-coupling effects in the thermal conductivity of superconducting lead

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We have measured the temperature dependence of the thermal conductivity κ and the electrical resistivity ρ of a lead single crystal between 1.7 and 10 K. Between T_c and 5 K the data agree well with a recent theory by Beyer Nielsen and Smith on electronic thermal conductivity in strong-coupling superconductors. Below 5 K, however, heat conduction by electrons as well as by phonons is important. The temperature dependence of the lattice thermal resistance is obtained and is analyzed in terms of resistance contributions for phonon-boundary and phonon-electron scattering. Our results provide strong support for the Beyer Nielsen and Smith theory.

The low-temperature thermal conductivity κ of high-purity lead has been the subject of various experimental and theoretical investigations.[1–8] Experimentally, the thermal conductivity in the superconducting state is observed to decrease below $T_c = 7.18$ K towards a minimum near $T/T_c \simeq 0.7$. Below this temperature, κ again increases and a pronounced thermal-conductivity maximum develops between 2 and 3 K. The position and magnitude of this maximum is found to be sample dependent. At still lower temperature the thermal conductivity decreases rapidly.

In pure normal metals heat transport takes place mainly through the conduction electrons while heat conduction via phonons is generally small due to strong phonon-electron coupling. The traditional interpretation of the thermal conductivity data on superconducting lead, therefore, ascribes the initial decrease in κ below T_c to a decreasing electronic contribution as a result of the opening of the superconducting energy gap. The increase in κ below $T/T_c \simeq 0.7$ on the other hand is thought to result from a dramatic increase of the lattice contribution to the heat conduction due to the progressive weakening of the phonon-electron scattering. Ultimately, the phonon mean free path will be limited by scattering from defects as well as by sample boundaries, and the thermal conductivity then decreases and the superconducting metal has thermal properties that are similar to those of insulators.

An alternative explanation for the observed maximum in the thermal conductivity has recently been proposed by Beyer Nielsen and Smith.[9] These authors have derived a kinetic equation for thermal conductivity in strong-coupling superconductors which includes electron-phonon scattering as well as scattering from ordinary and magnetic impurities. For very high-purity lead their solution of the kinetic equation shows a thermal conductivity which initially decreases below T_c because of the rapid increase in the gap and the strong energy dependence of the electron-phonon scattering rate. Below $T/T_c \simeq 0.7$, however, the electronic thermal conductivity is found to increase again largely as a result of the reduction in the phonon population. At $T \simeq 0.25 T_c$ the calculated thermal conductivity reaches a maximum value which depends on the sample purity but may be twice the value at T_c. On further reduction of the temperature the behavior is dominated by the exponential freezing out of the number of quasiparticles, and the electronic contribution to the heat transport is completely negligible for $T < 1$ K. The solution of the kinetic equation for a range of impurity-scattering relaxation times, furthermore, showed that the position and magnitude of the conductivity maximum was a sensitive function of sample purity with the conductivity maximum decreasing in magnitude and shifting to higher temperatures as the electron scattering rate increases. From the calculations of Beyer Nielsen and Smith it, therefore, appears that heat transport in pure superconducting lead in the temperature range 1 K to $T_c = 7.2$ K might be attributed entirely to the conduction electrons.

In order to test this idea and to determine the relative contributions from phonons and electrons to the heat transport in a pure strong-coupling superconductor, we have measured the thermal conductivity of a high-purity lead single crystal between 1.7 and 10 K. Because the theoretical calculations show that the electronic component to κ can be determined only if the electron impurity-scattering time is known, we also measured the electrical conductivity of our sample in the same temperature range.

The single crystal was grown by the Czochralski method from a nominally 99.9999% pure lead melt in the form of a cylinder with a 5 mm diameter and a length of about 10 cm. The specimen was prepared in the form of a parallelepiped with dimensions $1.3 \times 0.8 \times 33$ mm^3 by a very smooth elecron spark erosion. After mounting the thermometers, consisting of sliced 100-Ω Allen-Bradley carbon resistors wrapped in silver foil, and the heater (a small manganin-wire coil), the sample was mounted on a sample holder in the same manner as shown previously.[8] In a fixed position, the sample was then annealed at room temperature for several weeks. The procedure to measure the thermal conductivity is standard and was also described in Ref. 8. For subsequent measurements of the electrical resistivity, four leads were attached to the sample using a room-temperature curing silver-epoxy mix.

The electrical resistance was measured with a four-probe technique using both a dc and an ac method. Below T_c the normal-state resistance was determined by placing the sample into the appropriate magnetic fields.

The thermal conductivity results are presented in Fig. 1. The curve shows the characteristic features for high-purity lead mentioned previously with the conductivity maximum occurring at $T \simeq 2.5$ K. The thermal conductivity at T_c is 4.11 W/cm K, while the ratio of the conductivity at the maximum to that at T_c is 1.32. Near 1.7 K the thermal con-

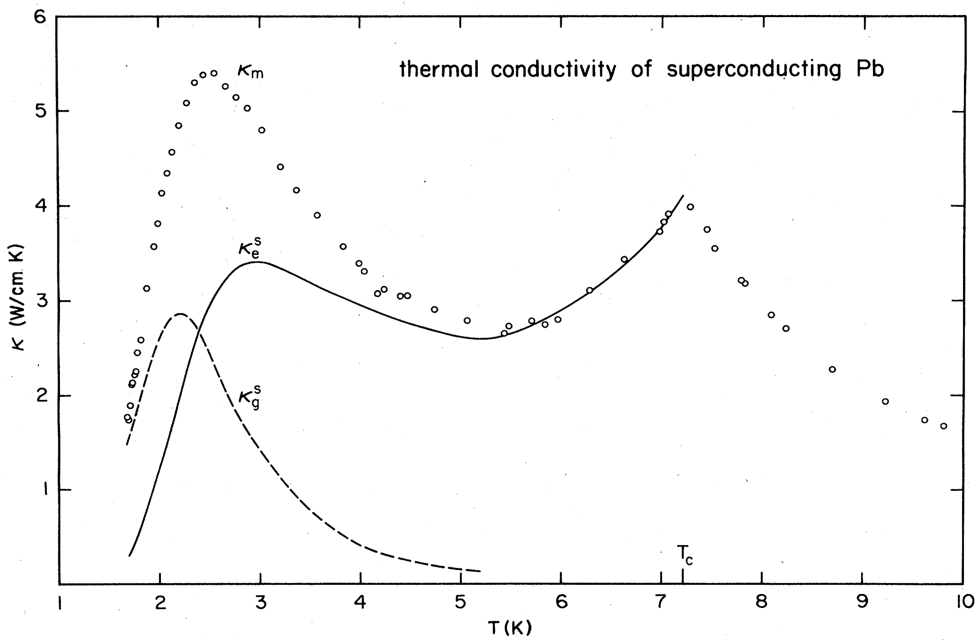

FIG. 1. Temperature dependence of the thermal conductivity of a high-purity lead crystal. κ_m, experimental data; κ_e^s, electronic component according to the theory of Ref. 9 with $c=0.073$ and $\kappa_e(T_c)=4.11$ W/cm K; κ_g^s, lattice thermal conductivity.

ductivity varies faster than T^3, the characteristic temperature dependence for heat transport by phonons in the boundary-scattering limit.

In its simplest form, the electrical resistivity of a pure metal can be written as $\rho=\rho_0+\rho_i$, where ρ_0 is the resistivity at $T=0$ and ρ_i the ideal resistivity. In the Grüneisen theory of electron-phonon scattering ρ_i varies at T^5 and our resistance measurements are in agreement with this temperature dependence. For magnetic fields above 0.05 T the normal-state resistance was corrected for magnetoresistance effects. The resistivity of our sample for $H=0$ is given by

$$\rho(T)=9.5\times10^{-10}+5.32\times10^{-13}\,T^5\ (\Omega\,\mathrm{cm}) \ . \tag{1}$$

This implies a ratio of room-temperature resistivity to residual resistivity of about 20 000. The size of the magnetoresistance effects and the scatter in the data is such, however, that the residual resistance cannot be determined to better than 50%.

The calculations of Beyer Nielsen and Smith for the electronic thermal conductivity are presented in terms of a parameter c which is inversely proportional to the impurity scattering time τ_{imp}. For their model electron-phonon scattering the relationship is

$$c=[\hbar/(0.15k_B\,T_c\tau_{\mathrm{imp}})] \ . \tag{2}$$

If we estimate τ_{imp} from the residual resistivity through a Drude model we find that for our sample $c\simeq0.2$. This implies that the thermal-conductivity curve appropriate for our samples is between curves labeled D and C in Fig. 2 of Ref. 9. For such a curve the ratio $\kappa_e^s(T)/\kappa_e(T_c)$ at the maximum is about 0.7 and is, thus, almost a factor of 2 smaller than the experimental value. In order to explain the observed magnitude of the thermal conductivity maximum entirely through electronic heat conduction requires a residual electrical resistivity for our sample an order of magnitude smaller than what we observed. Such a value lies outside the experimental uncertainty for the resistivity. We, therefore, conclude from this comparison of experiment and calculation that in our case the thermal conductivity near the maximum must be determined approximately equally by electron as well as phonon heat transport.

The measured thermal conductivity κ_m should then be expressed in terms of an electronic component κ_e and a lattice component κ_g so that

$$\kappa_m(T)=\kappa_e(T,c)+\kappa_g(T) \ . \tag{3}$$

In annealed lead samples the lattice thermal conductivity in turn is dominated by phonon-electron scattering and at very low temperatures by phonon scattering from sample boundaries so that in terms of the respective thermal resistances we can write

$$(\kappa_g^s)^{-1}\equiv W_g^s=W_b+W_{\text{ph-}e} \ . \tag{4}$$

For lead the boundary scattering can be written as[8]

$$W_b=(0.341/\Lambda_b)(1/T^3)\ \ (\mathrm{cm\,K/W}) \ , \tag{5}$$

where Λ_b is a boundary scattering parameter (in cm) that describes the effective phonon mean free path.

Any analysis of the thermal conductivity of a superconductor such as lead and any test of theories for the electronic component to heat transport is hampered by our poor understanding of $\kappa_g^s(T)$. We can, however, make some qualitative comments concerning the expected temperature dependence of κ_g^s. The normal-state lattice thermal conductivity κ_g^n is known to be small. Through work with lead alloys, Montgomery[6] estimated that $\kappa_g^n=1.3\times10^{-3}\,T^3$ and $\kappa_g^n(T_c)$ would thus amount to only 2% of $\kappa_m(T_c)$. It is then reasonable to expect κ_g^s to also be small near T_c so that $\kappa_m(T)\simeq\kappa_e^s(T)$ in that temperature region. As the temperature is lowered, the phonon mean free path should increase and κ_g^s is expected to rise.

It was shown by Odoni, Fuchs, and Ott,[2] that $\kappa_m(T)$ of high-purity lead samples with dimensions similar to those of our specimen show a T^3 temperature dependence near 1.2 K. At that temperature there seems no doubt that the thermal conductivity is entirely phonon dominated. In the low-temperature region for our sample we should, therefore, expect κ_g^s to show a T^3 or weaker temperature dependence. In our analysis we have thus assumed that the electronic contribution is as calculated by Beyer Nielsen and Smith, and we then obtain for $\kappa_g^s(T)$ the expression

$$\kappa_g^s(T)=\kappa_m^s(T)-\{[\kappa_e^s(T,c)]/\kappa_e^n(T_c)\}[\kappa_m(T_c)-\kappa_g^n(T_c)] \quad , \tag{6}$$

where $\kappa_e^s(T,c)/\kappa_e^n(T_c)$, is the electronic thermal-conductivity ratio calculated in Ref. 9. For our analysis we have set $\kappa_g^n(T_c)=0$.

It is difficult to calculate from the residual resistivity the correct c parameter. In view of this and because of the substantial error in the residual resistivity it seemed more appropriate to determine c by insisting that near the low-temperature end of our experiment the computed lattice conductivity should have a T^3 temperature dependence. For $c=0.073$ (curve c in Fig. 2 of Ref. 9) this condition is approximately satisfied and the electronic component as well as the resulting lattice conductivity are shown in Fig. 1. The lattice conductivity has a maximum value of 2.86 W/cm K near 2.2 K. As Fig. 1 shows, the electronic component for this (and smaller) value of c follows the experimental points very well from T_c to the minimum in κ_m near 5.5 K. This implies that the lattice conductivity in this temperature region is too small for us to determine. In the low-temperature region $\kappa_g^s/T^3 \simeq 0.33$ W/cm K^4. From Eq. (5) this yields a boundary scattering parameter $\Lambda_b=1.1$ mm which is, thus, comparable to the lateral dimensions of our sample. We can now use (4) to determine in a limited temperature range $W_{\text{ph-}e}$ or alternatively $\kappa_{\text{ph-}e}=(W_{\text{ph-}e})^{-1}$ which is the component of lattice thermal conductivity that is limited by phonon-electron scattering. The result is shown as curve a in Fig. 2.

We have attempted a similar analysis for the thermal conductivity measurements on high-purity lead by Mezahov-Deglin.[7] His results show the same general features for the thermal conductivity in the superconducting state that we observe. The main difference appears to be in the low-temperature region. Our measurements vary as T^n with n larger than three while most of his results on well annealed samples that had cross-section areas larger than ours appear to show a T^3 temperature dependence that extends close to the thermal-conductivity maximum. For samples that are strained, the conductivity maximum shifts to higher temperatures and for a severely deformed sample the conductivity shows a T^3 region up to about 1.2 K and a much stronger temperature dependence above this value. The best samples investigated in that work had resistance ratios somewhat higher than the value for our sample although, as in our case, the uncertainties are large and the appropriate c parameter is very difficult to estimate. To estimate $\kappa_{\text{ph-}e}$ from his data we, therefore, again let $c=0.073$. The magnitude and general form of $\kappa_{\text{ph-}e}$ that we obtain for his highest-purity samples is shown as curve b in Fig. 2, and is seen to be similar to $\kappa_{\text{ph-}e}$ for our sample.

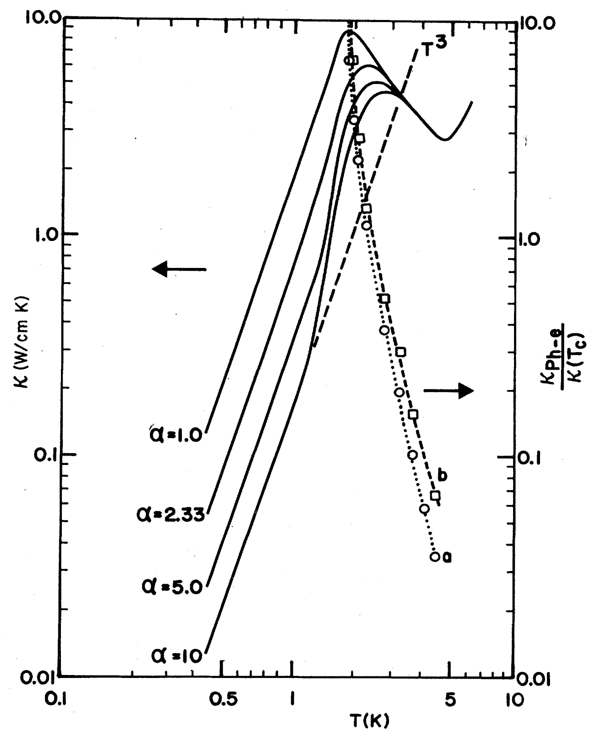

FIG. 2. Temperature dependence of κ for high-purity lead according to Eq. (7) for a range of boundary-scattering parameters α. For all curves the electronic contribution was obtained from Ref. 9 with $c=0.073$ and $\kappa(T_c)=4.2$ W/cm K, and the lattice thermal resistance from phonon-electron scattering was assumed to have the form of curve b. For large values of α the curves show a kink near 1.5 K which reflects the onset of heat conduction by the conduction electrons. Curves a and b are the lattice conductivity limited by phonon-electron scattering. a, this work; b, Ref. 7.

Between 1 and 3 K the character of the thermal-conductivity curves of high-purity lead is strongly affected by phonon-boundary scattering. This is illustrated in Fig. 2. For the curves shown the total thermal conductivity is written as

$$\kappa(T)=\kappa_e(T,c)+[(\alpha/T^3)+W_{\text{ph-}e}]^{-1} \quad . \tag{7}$$

The electronic component was obtained for $c=0.073$, and we used curve b of Fig. 2 for $W_{\text{ph-}e}$ with $\kappa(T_c)=4.2$ W/cm K. For large values of α—that is, samples with small cross sections or with internal phonon-scattering centers—the thermal conductivity is small and follows a T^3 law to almost 1.4 K. Beyond that temperature heat conduction by electrons becomes significant and near 2.5 K phonons and electrons contribute approximately equally to the heat transport. As the phonon mean free path is increased by either increasing the sample diameter or by annealing a large diameter sample, significant deviations from a T^3 behavior set in at progressively higher temperatures while the thermal-conductivity maximum shifts to lower temperatures.

The available experimental data seem in general agreement with these results. For example, our sample has $\alpha \simeq 3.6$ (cm K^4/W) and we would expect a faster than T^3 temperature dependence for our lowest-temperature points in agreement with the measurements. For some of the samples of Mezahov-Deglin, on the other hand, $\alpha \simeq 1$ and, again in agreement with experiments, a nearly cubic temperature dependence for the low-temperature side of the thermal-conductivity maximum is suggested by Fig. 2. For the curves in Fig. 2 a constant c parameter and, hence, a constant electron mean free path l was assumed. In general, changes in Λ_b will be accompanied by changes in l, and will, thus, also lead to changes in the electronic component to the heat transport. Changes in l can, furthermore, affect the matrix elements for phonon-electron coupling so that $\kappa_{\text{ph-}e}$ will in general vary with sample quality. Our simple analysis is, however, capable of reproducing most of the features of thermal-conductivity curves on high-purity superconducting lead and the results provide strong support for the work of Beyer Nielsen and Smith. The results of Fig. 2 suggest a more reliable way of obtaining the electronic component κ_e^s and of verifying directly the exponential temperature dependence of κ_e^s near $T_c \simeq 0.25$. Measurements between 0.8 and 2 K of the thermal conductivity of high-purity lead wires with diameters less than $\frac{1}{2}$ mm should show an initial T^3 temperature dependence while above about 1.3 K a much more rapid temperature dependence should be observed. Thermal resistance from phonon-electron scattering is negligible below about 2 K, so that the deviation of the experimental data above 1.3 K from an extrapolated T^3 behavior should yield the magnitude and initial temperature dependence of κ_e^s as well as the appropriate c parameter.

Our analysis suggests that in high-purity samples the phonons contribute only about 5% to the total heat conductivity at $T/T_c \simeq 0.7$ while near the thermal-conductivity maximum phonon heat transport predominates in samples with a large phonon mean free path while electronic conduction predominates if the phonon mean free path is short. It is suggested that a more detailed examination of the theory of Beyer Nielsen and Smith should be possible through thermal-conductivity measurements between 0.8 and 2 K on small diameter high-purity lead crystals.

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[1]W. J. de Haas and A. Rademakers, Physica **7**, 992 (1934).
[2]J. K. Hulm, Proc. R. Soc. London, Ser. A **204**, 98 (1956).
[3]J. H. P. Watson and G. M. Graham, Can. J. Phys. **41**, 1738 (1963).
[4]J. Bardeen, G. Richayzen, and L. Tewordt, Phys. Rev. **113**, 982 (1959).
[5]V. Ambegaokar and L. Tewordt, Phys. Rev. B **134**, 805 (1964).
[6]H. Montgomery, Proc. R. Soc. London, Ser. A **244**, 85 (1958).
[7]L. P. Mezahov-Deglin, Zh. Eksp. Teor. Fiz. **77**, 733 (1979) [Sov. Phys. JETP **50**, 369 (1979)].
[8]W. Odoni, P. Fuchs, and H. R. Ott, Phys. Rev. B **28**, 1314 (1983).
[9]J. Beyer Nielsen and H. Smith, Phys. Rev. Lett. **49**, 689 (1982).