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ANOMALOUS LATTICE SPECIFIC HEAT OF SUPERCONDUCTORS*

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(Received April 25, 1961)

Bryant and Keesom[1] have discovered that the lattice specific heat of indium is significantly less in the superconducting than in the normal state. A similar effect has been detected in niobium by Boorse, Hirshfeld, and Leupold.[2] Daunt and Olsen[3] have proposed to account for the difference in terms of a temperature dependence of the zero-point energy in the superconducting state. But according to the second law of thermodynamics, a physical system can only take on heat by means of an increase in its entropy, or disorder. If the high-frequency lattice oscillators remain in their ground states, their quantum numbers do not change and they cannot directly contribute any disorder to the system. Their energy is indeed temperature dependent because of their interaction with the low-lying electron excitations,[4] but this interaction energy is customarily included as part of the electron excitation energy and must not be counted twice. Thus the zero-point energy does not constitute a new and independent source of heat, but instead simply contributes to the "renormalization" of the single-electron excitation energies. In any case, it cannot produce a specific heat anomaly at very low temperatures ($T \ll T_C$) because of the "freezing-out" of the electrons in the superconducting state.[5]

The purpose of the present note is to emphasize that the specific heat anomaly is clear and unmistakable evidence for an anomalous dispersion in the phonon spectrum of the superconducting state. Although a more complete report is in preparation, we shall also indicate here the a priori basis of such a dispersion, and show that it gives a good quantitative account of the data. In addition we propose several straightforward experimental tests of the theory.

Consider a constant shift upwards of $\Delta\omega$, in the range of the angular frequencies involved. The specific heat of any given lattice mode is $kf(\hbar\omega/2kT)$, where k and $2\pi\hbar$ are Boltzmann's and Planck's constants, T is the temperature, ω is the angular frequency of the oscillator, and

$$f(x) = (x/\sinh x)^2. \tag{1}$$

The fractional decrease in the total lattice specific heat is

$$\Delta C_S/C_S = T_S/T, \tag{2}$$

where

$$T_S = 0.556\hbar\Delta\omega/k, \tag{3}$$

and it is assumed that $T \gg T_S$. The numerical factor is one half of the ratio of the sum of the inverse cubes of the integers to the sum of the inverse fourth powers. To first order in the anomaly, the lattice specific heat in the superconducting state is

$$C_S = \alpha T^3 - BT^2, \tag{4}$$

where the coefficient of the T^2 anomalous term is $B = \alpha T_S$.

Figure 1 shows the data of Bryant and Keesom[1] divided by T^2 and replotted vs T. The slope of the lines is not adjusted but is instead fixed by the value computed by Chandrasekhar and Rayne[6] from their measurements of the elastic constants of indium. The dashed line passing through the origin represents the Debye specific heat in the

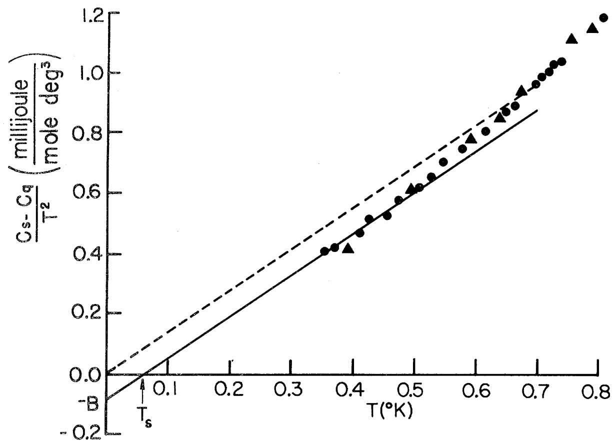

FIG. 1. Specific heat divided by the square of temperature vs absolute temperature, for the superconducting state of indium. (The nuclear quadrupole specific heat C_q is subtracted from the measured total.) The solid line is shifted downwards by the dispersion resulting from the self-energy process of Fig. 2.

absence of the dispersion. It is seen that the displaced line, which contains only one adjustable parameter, its displacement, gives a fit at the very low temperatures which could hardly be excelled by any temperature dependence other than that of Eq. (4). The vertical and horizontal intercepts are $B = 0.09$ millijoule mole^{-1} deg^{-3} and $T_S = 0.065$°K, which inserted into Eq. (3) give $\Delta\omega = 1.6 \times 10^{10}$ sec^{-1}, or a frequency shift of 2.5×10^9 cycles per sec. At the higher temperatures (0.55°K< T < 0.85°K) the difference between the heavy line and the experimental points is fitted well by the exponential $ae^{-bT_c/T}$, where T_c is the transition temperature of 3.37°K and the coefficients are $a = 7.3$ and $b = 1.43$. These values can be compared with the predictions[7] of the BCS theory of $a = 8.5$ and $b = 1.44$. The good agreement with the BCS exponent is consistent with the similar agreement with BCS theory in the temperature dependence of ultrasonic attenuation found by Morse and Bohm[8] for indium. Turning to the niobium anomaly, we find that the data are not fitted quite as well by our T^2 dependence. If we assume, however, that the corrections referred to in reference 2 will lower the lowest temperature points the most, the fit becomes satisfactory.

The microscopic basis for the shift in the frequency of the phonons in the superconducting state is the well-known result of Bardeen and

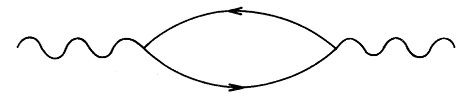

FIG. 2. Phonon self-energy Feynman diagram. The absorption of the phonon produces an electron-hole pair which can then re-create the phonon, resulting in a frequency shift. The same electron excitations are involved in both the real and imaginary parts of the frequecny shift. Thus the dispersion in the superconducting state is related to the ultrasonic attenuation in the normal state [Eq. (8) of the text].

Pines[9] and others that the frequency of a sound wave is very much dependent on the response of the conduction electrons. This is illustrated by the phonon self-energy Feynman diagram in Fig. 2. The phonon (represented by a wavy line) continually causes electrons to be excited out of their normal state. The electrons then act back on the phonon, changing its energy. (Time is imagined to flow from right to left.) The dispersion of the sound waves depends upon the real part of the matrix element corresponding to Fig. 2. We want to calculate the change in the real part when the metal passes from the normal to the superconducting state. It is useful, however, first to consider the imaginary part, which represents the damping calculated by Kittel,[10] and which can be written as $\omega/4\pi Q$, where ω is the angular frequency of the sound wave, and Q is a dimensionless number measuring the phonon mean free path in units of the wavelength. Kittel's result is

$$Q = \hbar^3 \rho c_S / (m^* C)^2, \tag{5}$$

where $2\pi\hbar$ is Planck's constant, ρ is the mass density of the metal, c_S is the velocity of sound, m^* is the electron effective mass, and C is the usual electron-phonon coupling constant.[11] It is clear that there is not only a contribution to the imaginary part of the phonon frequency, but that a real contribution must also result, from virtual excitation of the same type of electron states as contribute to the damping.

The general features of Kittel's formula have been verified by Morse and Bohm,[8] including the frequency independence of Q. They have also shown that at temperatures very much below the transition temperature the Kittel damping disappears completely. This result follows readily from an energy gap picture of superconductivity:

If the phonon energy is less than the gap, there is no continuum of excited states into which a transition can take place. But this same deficiency of states in the gap will also lead to a loss in the virtual excitations, and thereby produce a change in the real part of the phonon frequency. Introducing $\hbar\bar{\omega}_g$ as the effective energy gap within which the normal density of electron excitations per unit excitation energy ϵ, $\rho(\epsilon)$, is replaced by zero in the superconducting state, we can write the difference in the complex phonon self-energy between the normal and superconducting state as the following integral:

$$\hbar\left(-\Delta\omega - \frac{i\omega}{4\pi Q}\right) = 2\int_0^{\hbar\bar{\omega}_g} \frac{|H_q|^2 \rho(\epsilon)\epsilon}{(\hbar\omega)^2 - (\epsilon - i\delta)^2} d\epsilon. \quad (6)$$

H_q is the matrix element for the production of an electron-hole pair by the absorption of a sound wave of wave number q and is independent of ϵ, while δ is an infinitesimally small positive quantity. Since $\rho(\epsilon)$ vanishes for $\epsilon = 0$, we can use the Taylor series expansion $\rho(\epsilon) = \epsilon\rho'$, where ρ' is the derivative. [We now restrict our attention to values of q sufficiently large that the maximum value of ϵ for which $\rho(\epsilon) \neq 0$ is much larger than $\hbar\bar{\omega}_g$; i.e., we consider wavelengths considerably smaller than the coherence length.] Both $|H_q|^2$ and ρ' can now be taken outside the integral sign, and elementary integration yields

$$\Delta\omega + (i\omega/4\pi Q) = |H_q|^2\rho'(2\bar{\omega}_g + i\pi\omega). \quad (7)$$

We verify that insertion of the usual expressions for H_q and ρ' reduces the imaginary part of this equation to Eq. (5). The real increase in the sound-wave frequency in the superconducting state can now conveniently be compared with the imaginary part, giving us our basic equation,

$$\Delta\omega = \bar{\omega}_g/(2\pi^2 Q). \quad (8)$$

This is a type of dispersion relation, relating the dispersive behavior of the metal to its absorptive properties.

It is now desirable to see if Eq. (8) yields a reasonable value for Q. For our present purposes, we can approximate the effective gap by the actual energy gap, $\hbar\bar{\omega}_g \approx \hbar\omega_g \approx 4kT_c$. Sum rule arguments indicate that this is probably an overestimate, but not by more than 50%.[12] With this sort of accuracy understood, we can write

$$Q \approx 0.11\, T_c/T_s, \quad (9)$$

from which we obtain for indium, $Q \approx 5.8$. Equation (5) enables us to go further, and deduce the mean electron-phonon coupling strength. From the Debye temperature[6] of 111.3°K we infer $c_s \approx 0.83 \times 10^5$ cm/sec, while the normal state specific heat of indium[1] gives m^* equal to 1.21 times the free electron mass. We find $C \approx 7.9$ ev, which happens to be just equal to the Sommerfeld-theory Fermi energy. This result is not unreasonable for a metal with a complicated energy band structure sensitive to lattice changes, and indicates that a given percentage elastic strain must change the individual single-electron energies in about the same proportion. Since all superconductors do not necessarily have such large deformation potentials, it is clear that the specific heat anomaly cannot always be expected to appear. Furthermore, the lowest shear mode, with which the anomaly is primarily associated, has a longitudinal admixture for nonsymmetry directions. The resulting longitudinal deformation potential and electric field could in some cases interfere destructively with the shear coupling constant for the low-energy electron excitations. Therefore, it is clearly not feasible to predict a priori which superconductors will exhibit the anomaly. Nevertheless, it is possible to measure the quantity Q directly from ultrasonic absorption (for the lowest velocity mode averaged over propagation directions) and thereby employ Eq. (9) to predict the value of T_s. This would yield a quantitative prediction of the heat anomaly in advance of actual thermal measurements. Conversely, it would be highly desirable to have a check on the present considerations by means of an actual ultrasonic measurement of Q for indium (and, of course, also niobium for which $T_s \approx 0.2$°K and $Q \approx 5$). Such a measurement has already been made on the (001) shear wave in tin,[13] yielding $Q \approx 60$. Assuming that this is representative of the other propagation directions, we can predict that the specific heat anomaly is an order of magnitude smaller in tin than in indium. A further indication of an especially strong coupling of the shear waves to the electrons in indium is the strong temperature dependence found by Simmons and Slichter[14] in the nuclear quadrupole resonant frequency.

An alternative ultrasonic experimental check on the present considerations would be a direct measurement of the dispersion in the superconducting state, rather than of the attenuation in the normal state. Wavelengths λ smaller than the coherence length ξ_0 are required, because of the general principle that the bulk elastic constants must give a correct description of sound waves for $\lambda > \xi_0$. (The very small normal-superconducting difference in the elastic constants results in turn from the fact that the transition energy depends parametrically on the lattice strains and forms only an extremely small fraction of the total ground-state energy.) Since the coherence length can be estimated for indium at $\xi_0 = 6300$ A, the minimum frequency for detecting appreciable dispersion is about 1.3×10^9 cycles per second. As a consequence of this minimum frequency, the lattice specific heat must return to its undisplaced Debye value in the limit $T \rightarrow 0$. That is, if it were possible to extend the measurements to such low temperatures, the points in Fig. 1 would leave the solid line and rejoin the dashed line.

It should also be noted that the constant frequency shift follows from Eq. (6) only for $\omega \ll \bar{\omega}_g$. At higher frequencies a more complicated dispersion results, leading for $\omega \gg \bar{\omega}_g$ to a very small shift [reduced by the order of $(\bar{\omega}_g/\omega)^4$]. Consequently, inelastic neutron scattering or the Mössbauer effect, for example, does not offer a feasible alternative method of detecting the dispersion.

An additional experimental test of Eq. (8) is suggested by Pippard's[15] study of the effect of the electron mean free path l on the ultrasonic attenuation. He finds that the Kittel damping is reduced by a factor proportional to l/λ for $l < \lambda$, in agreement with similar studies by Kittel,[10] Mason,[16] and Morse.[17] This suggests that if a metal showing the heat anomaly were heavily enough doped with an alloying impurity to reduce significantly the coherence length (as would be indicated by a decrease in the superconducting skin depth), then the anomaly would disappear.

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*Research supported in part by the Air Force Office of Scientific Research and by the Office of Naval Research.

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