Far-infrared measurements of the phonon density of states of superconducting lead*

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Far-infrared measurements of the derivative of the reflectivity of lead and lead alloys in the superconducting state are presented. The derivative of the reflectivity contains detailed information about the phonon spectrum including peaks not observed by tunneling spectroscopy. The peaks are, in general, in good agreement with neutron measurements and include evidence of phonon lifetime effects at a phonon frequency of 2Δ.

We would like to report on high-resolution reflectance measurements of phonon-induced infrared absorption in superconducting lead. With an improved signal-to-noise ratio we are able to obtain the derivative of the experimental curves and in this way display more directly a quantity closely related to the phonon spectrum of lead in the superconducting state. In particular, our results are in better general agreement with a phonon density of states as determined by Stedman *et al.*[1] by inelastic neutron scattering rather than with the density of states of Rowell and McMillan found by an inversion of the tunneling characteristic of thin-film superconducting junctions.[2] We also find an anomaly in the phonon spectrum at a frequency of twice the gap energy. We interpret this in terms of an abrupt change in phonon lifetimes due to the onset of electron-phonon scattering at this energy.[3]

Phonon-induced far-infrared absorption in superconducting lead was first observed by Joyce and Richards[4] and explained on the basis of the phonon generation mechanism originally proposed by Holstein.[5] More complete calculations have been carried out by Allen[6] using the golden rule and BCS theory and by Swihart and Shaw[7] using a strong-coupling formalism following Nam.[11]

Both sets of calculations made use of Rowell and McMillian's tunneling data and reproduced fairly well the broad structure observed in the far-infrared experiments. Subsequent experiments by Gavini and Timusk[8] showed detailed structure not predicted by these calculations. In this work we wish to show that this structure results from a series of sharp features present in the phonon spectrum of lead in the superconducting state. These features are not present in the results of the tunneling density of states.

In discussing our results, we use Allen's theory rather than the more accurate calculations of Swihart and Shaw, since these are more straightforward and the resulting expressions are easily evaluated numerically.

In the Holstein process the energy of the absorbed photon is distributed between an electron-hole pair and a phonon. In a superconductor an energy of at least 2Δ must go to the electron-hole pair. Allen gives for the phonon contribution to the absorptivity, for the superconductor,

$$A_{S\,ph}(\omega,\Delta)=\phi_S(\omega)(4\pi/\omega\omega_p)\times\int_0^{\omega-2\Delta}d\Omega\,(\omega-\Omega)\,\alpha^2_{tr}(\Omega)F(\Omega)E(k)\,, \tag{1}$$

where ω_p is the plasma frequency,

$$k^2=1-\left(\frac{2\Delta}{\omega-\Omega}\right)^2\,,$$

and $E(k)$ is the complete elliptic integral of the second kind. For the normal metal,

$$A_{N\,ph}(\omega)=\phi_N(\omega)(4\pi/\omega\omega_p)\times\int_0^{\omega}d\Omega\,(\omega-\Omega)\,\alpha^2_{tr}(\Omega)F(\Omega)\,. \tag{2}$$

Here 2Δ is twice the superconducting energy gap, $\alpha_{tr}(\omega)$ is the electron-phonon coupling parameter relevant to transport properties, and $F(\omega)$ is the phonon density of states. The functions ϕ_S and ϕ_N are slowly varying in ω and are assumed here to be constant through the phonon region. The ratio ϕ_S/ϕ_B forms the only adjustable parameter we use.

We take into account the double gap of lead by adding contributions from each gap:

$$A_{S\,ph}(\omega)=A_{S\,ph}(\omega,\Delta_2)+0.65A_{S\,ph}(\omega,\Delta_1)\,, \tag{3}$$

where the weighting factor 0.65 is a typical value of the relative strengths of the two gaps as determined from tunneling by Blackford.[9]

For the value of $2\Delta_2$ we use the point of steepest slope on the absorption edge, determined from our experiment, and since we have not found any evidence for structure in our samples at $2\Delta_1$ we use an average value reported by Blackford for the splitting of the two gaps. These procedures yield 20.5 cm^{-1} and 23.5 cm^{-1} for $2\Delta_1$ and $2\Delta_2$, respectively, for all our samples.

If Eq. (1) is differentiated we get

$$\frac{d}{d\omega} A_{S\,ph}(\omega,\Delta) = \phi_S \frac{4\pi^2\Delta}{\omega\omega_p} \alpha^2_{tr}(\omega-2\Delta)F(\omega-2\Delta) + \phi_S \frac{4\pi}{\omega^2\omega_p} \int_0^{\omega-2\Delta} d\Omega\, \alpha^2_{tr}(\Omega)F(\Omega)\left[\Omega E(k) + \frac{\omega}{k^2}\left(\frac{2\Delta}{\omega-\Omega}\right)^2 [E(k)-K(k)]\right], \quad (4)$$

where $K(k)$ is an elliptic integral of the first kind. Since the second term is an integral over α^2_{tr} and the first varies directly with $\alpha^2_{tr}F$, structure in $dA/d\omega$ should arise mostly from the first term. Hence structure in the derivative of the experimental results should reflect in a direct way structure in $\alpha^2_{tr}F$.

In our experiments, we employed a far-infrared Michelson interferometer that feeds radiation via a light pipe to a conical nonresonant cavity whose walls hold the sample material. The sample is at 1.2 °K, and after an average of 100 reflections from the sample the light exits to a doped germanium bolometer. A magnetic field of about 3 kG was applied to drive the sample normal, and the signals from the superconducting and normal metals I_S and I_N were compared. The resulting spectrum is given by

$$S(\omega) = \frac{I_S}{I_N} \cong \frac{1-nA_S}{1-nA_N} \cong 1-n(A_S-A_N),$$

where n is the average number of reflections. This quantity depends weakly on the absorption and is given by

$$n = \frac{1}{A_0+A},$$

where A_0 is the absorption of the cavity in the absence of the sample absorption A. This cavity absorption is due to such things as the entrance and exit holes. For pure samples $A_0 > A$ and we can treat n as a constant.

The samples used in these experiments were either rolled foils of lead, lead-indium alloy, or evaporated films. The foils were annealed just below the melting point for 48 h under a hydrogen atmosphere and etched with an acetic-acid etch.[10] The films were evaporated in a vacuum of 10^{-7} Torr onto the stainless-steel wall of the cavity to a thickness of 30 μm. Typical resistances at 4.2 °K were 0.1, 0.03, and 0.45 $\mu\Omega$ cm for the lead films, the lead foils, and the lead-indium foils, respectively.

The signal-to-noise ratio for a single spectrum was usually 2000:1, and about ten spectra were averaged together to further reduce the noise. The root-mean-square noise expected in the derivative is 2% of the phonon peak height.

Figure 1 shows the derivative of the spectrum $ds/d\omega$ for pure lead and lead–0.5-at.%-indium foils. Also shown are calculated values for $ds/d\omega$ using Allen's theory with phonon density of states from neutron scattering and from tunneling. The densities of states used in the two calculations are shown in Fig. 2.

The two main features in the spectra, the broad transverse phonon peak centered at 63 cm^{-1} and the longitudinal one at 93 cm^{-1}, are clearly shown. The peaks all appear at somewhat higher frequencies than predicted. The shift is about 3 cm^{-1} compared to the neutron data and 4 cm^{-1} using tunneling data. These discrepancies are probably due to strong-coupling effects not taken into account in our simple calculations. The calculations of Nam,[11] which do include these effects but not the Holstein process, give peaks at higher frequencies. A proper combination of the two effects might produce the necessary shift.

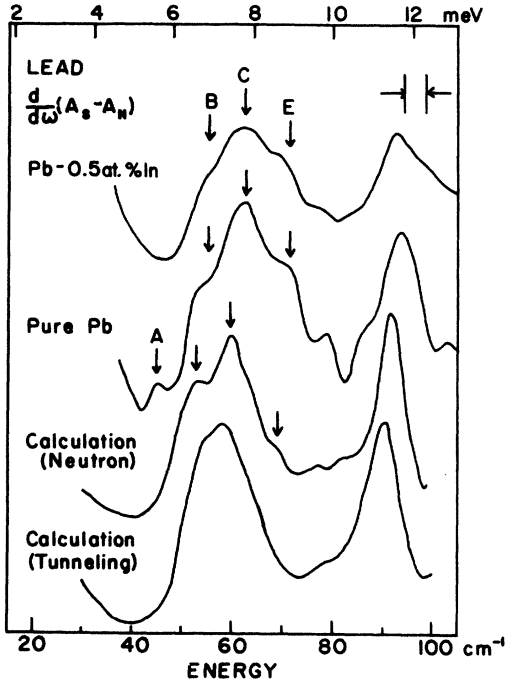

FIG. 1. Experimental and theoretical curves for the derivative of the difference between the far-infrared absorption in the normal and superconducting states of lead. The theoretical curves are computed from two densities of states for the phonons, derived from neutron and tunneling spectroscopy, respectively. Our experiments agree with the neutron-derived density of states.

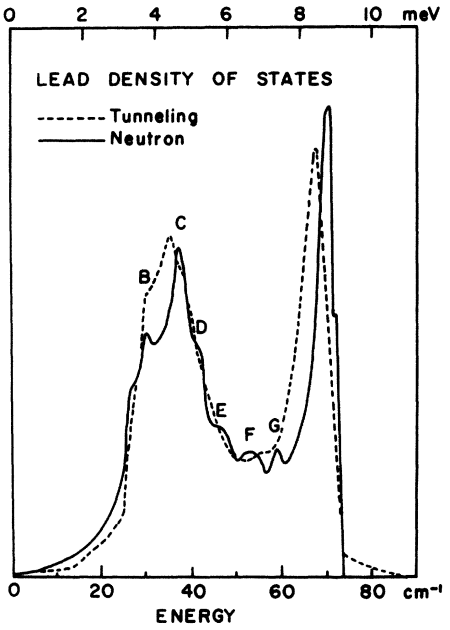

FIG. 2. Density of states used for the calculations derived from two sources. Note the sharp peaks in the neutron results. Our far-infrared measurements show several of these peaks as well.

Of more interest is the appearance of smaller peaks on each side of the main transverse peak labeled B and E. These peaks are predicted by the calculation with the neutron density of states and correspond to similarly labeled peaks in $F(\omega)$, but not by the tunneling data. A similar association can be made for the peaks F and G, though less reliably since structure in this region and at higher frequencies is influenced by the age of the sample, probably because of oxidation.

We would particularly like to point out the feature marked A. Its frequency of 46 cm^{-1} corresponds quite accurately to $4\Delta_2 = 47$ cm^{-1}, and it is found in all our pure-lead samples. Figure 1 shows, however, that the structure is absent when the sample is alloyed with indium. We interpret this structure as due to a change in the phonon density of states at a frequency where the phonons can create electron-hole pairs. In the far-infrared spectra such a feature is expected to occur at a frequency 4Δ in good agreement with our experiment. It can also be seen that the impurity scattering in the sample containing indium is strong enough to smooth out the discontinuity. The discontinuity arises from an abrupt change in lifetime of phonons of frequency 2Δ. Below this frequency their lifetime and mean free path are very long.[12] Above 2Δ, scattering due to electron-phonon interaction sets in and, in view of the strong peak in the electron density of states at 2Δ, there is a strong change in the imaginary part of the phonon self-energy. This leads to a change in the real part, i.e., a frequency shift which in turn results in a discontinuity in the density of states.

Figure 3 shows results at higher resolution for a very pure evaporated film. In the same diagram a calculation is shown which uses a double gap and a neutron-determined density of states of Stedman *et al.* The peaks B and C appear split by 3 cm^{-1}, consistent with the prediction of the calculation. The anomaly at 4Δ is also split by the same amount, consistent with our interpretation. This double-gap splitting observed in the films is not wholly attributable to higher resolution, but is presumably due to preferential orientation in the films, whereas in the apparently more isotropic foils only one gap is seen. The large peak between the transverse and longitudinal branches is not predicted by either density of states, but a recent Born–von Karman fit to the neutron data does predict a peak here, in agreement with our data.[13]

In conclusion, we would like to summarize the main results of our experiments. First, it seems that the density of states, $F(\omega)$, derived from neutrons is more realistic than the $\alpha^2F(\omega)$ obtained

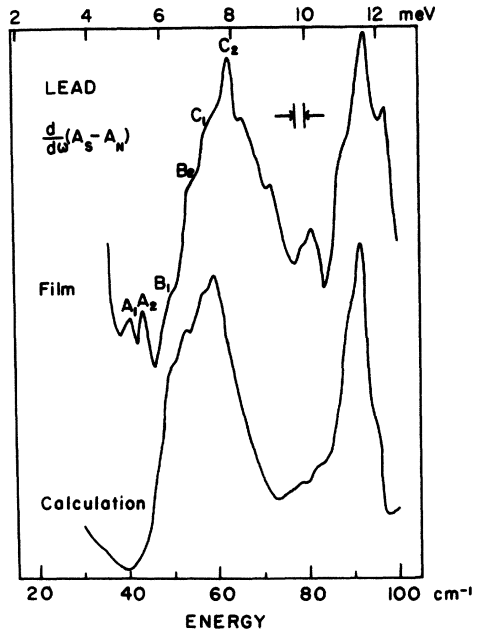

FIG. 3. Derivative of the absorption difference for an evaporated film and a calculation from the neutron density of states assuming two energy gaps. Note the evidence for the double-gap structure resulting in the splitting of the peaks into two components. The peaks A_1 and A_2, we suggest, arise from phonon lifetime effects at a phonon frequency of 2Δ.

from tunneling, which appears to have too little fine structure. The reasonably good agreement between experiment and the simple calculation also shows that $\alpha_{tr}(\omega)$ is essentially smooth in the frequency region of interest. This has been suggested by Allen.[6] Second, we would like to stress the observation of the anomaly at 4Δ. The area under the peaks is approximately 1% of the total of two transverse branches. From this value we can estimate the phonon width at 2Δ using as a guide a recent calculation by Schuster.[14] We estimate this way that in lead, phonons in the gap region have a width 2Γ of 12% of their energy. The recent measurements of Axe and Shirane[15] on niobium give a value of 5% for the width in the gap region, in good agreement with our estimate for lead, if the 2.5-fold increase in electron-phonon coupling is taken into account.

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[1]R. Stedman, L. Almqvist, and G. Nilsson, Phys. Rev. 162, 549 (1967).
[2]W. L. McMillan and J. M. Rowell, Phys. Rev. Lett. 14, 108 (1965).
[3]V. M. Bobetic, Phys. Rev. 136, A1535 (1964).
[4]R. R. Joyce and P. L. Richards, Phys. Ref. Lett. 24, 1007 (1970).
[5]T. Holstein, Phys. Rev. 96, 535 (1954).
[6]P. B. Allen, Phys. Rev. B 3, 305 (1970).
[7]J. C. Swihart and W. Shaw, Physica 55, 678 (1971).
[8]A. Gavini and T. Timusk, Phys. Rev. B 3, 1049 (1971).
[9]B. L. Blackford and R. H. March, Phys. Rev. 186, 397 (1969).
[10](70–80)% glacial acetic acid, (20–30)% hydrogen peroxide.
[11]S. B. Nam, Phys. Rev. 156, 487 (1967).
[12]B. C. Dynes and V. Narayanamurti, Phys. Rev. B 6, 143 (1972).
[13]E. R. Cowley, Solid State Commun. 14, 587 (1974).
[14]H. G. Schuster, Solid State Commun. 13, 1559 (1973).
[15]J. D. Axe and G. Shirane, Phys. Rev. B 8, 1965 (1973).