Evidence for Large Gap Anisotropy in Superconducting Pb from Phonon Imaging

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We report the first ballistic phonon images of superconducting Pb. Unusual absorption lines are observed for phonon wave vectors in {111} planes. We show that a highly anisotropic energy gap can lead to sharply defined directions of phonon attenuation. Overhauser and Daemen [Phys. Rev. Lett. **61**, 1885 (1988)] postulated a spin-density-wave ground state for Pb that leads to directions of strongly reduced gap. By applying their idea to the actual Fermi surface of Pb, we predict phonon attenuation directions consistent with the data.

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Lead is a conventional superconductor with not-so-conventional properties. Anomalies in the lattice dynamics, specific heat, and acoustic attenuation have puzzled researchers for several decades. According to BCS theory, the specific heat of a superconductor decreases in proportion to the number of thermally excited quasiparticles [1]. The predicted exponential behavior is observed in superconductors such as Sn or In; however, at low temperatures the electronic specific heat of Pb deviates strongly [2,3] from the expected form, $\exp[-\Delta_0/k_B T]$, where $\Delta_0 = 1.35$ meV is the zero-temperature superconducting gap measured by tunneling experiments [4]. Ultrasound attenuation experiments [5] in Pb also indicate a much larger concentration of quasiparticles than predicted from the measured value of Δ_0.

These deviations from the BCS predictions at low temperatures led the experimenters to hypothesize a highly anisotropic gap for Pb [2]. However, detailed calculations including the strong-coupling nature of Pb predict less than 10% gap anisotropy [6]. While nonconventional d-wave superconductors have highly anisotropic superconducting gaps [7], no one has suggested that Pb is other than a conventional s-wave superconductor.

Overhauser and Daemen [8,9] proposed a remarkable answer to this puzzle: the electronic ground state of Pb possesses a spin density wave (SDW) structure, which is not included in the BCS and strong-coupling calculations. They showed that the SDW's would lead to a large anisotropy in the superconducting gap of Pb. Their theory explained the anomalous temperature dependencies of the specific heat and acoustic attenuation assuming a critical temperature for the SDW's of about 660 K. Chen and Overhauser [10] further showed that such an electronic ground state would explain the highly anomalous phonon dispersion observed in Pb. An attempt to observe spin-dependent neutron scattering yielded a null result [11], which indicates the SDW's are longitudinally polarized.

If indeed the energy gap is anisotropic, how would one measure it? Conventional gap measurements involve a particular crystal surface or propagation direction and are not easily adaptable to angular scanning. In fact, tunneling measurements [12] have shown a 10%–15% anisotropy in the gap, but only for a limited set of tunneling directions. In this paper we introduce ballistic phonon imaging as a directional probe of the superconducting state. Indeed, by measuring the transmission of phonons through the bulk of a single crystal of high purity Pb, we observe a striking anisotropy in the phonon transmission.

For a superconductor, phonons with energies $h\nu$ greater than $2\Delta_0$ rapidly break Cooper pairs and are strongly absorbed. For this reason, the ballistic phonons observed in our experiment certainly have energies less than $2\Delta_0 = 2.70$ meV. Phonons with $h\nu < 2\Delta_0$ can nevertheless scatter from thermally excited quasiparticles. Narayanamurti *et al.* [13] were the first to show the ballistic propagation and scattering of phonons in superconducting Pb ($T_c = 7.2$ K). Hauser, Gaitskell, and Wolfe [14] reported the first images of phonons in a superconductor, Nb.

Figure 1 shows a time-resolved phonon image of the longitudinal acoustic (LA) phonons in an undoped crystal of Pb [15]. Brightness is proportional to the phonon transmission through the 1-mm-thick crystal at $T = 1.8$ K. The detector is a small, $5 \times 10\ \mu\text{m}^2$, superconducting-Al bolometer evaporated on one face of the crystal. This bolometer is electrically insulated from the sample by a 50-nm layer of SiO and is biased at a temperature near its superconducting transition [14]. The phonons are produced by a focused Ar^+ laser beam (10-ns cavity-dumped pulse) incident on the opposite face. A 250-nm film of copper was deposited on this face so that the optical excitation produces a Planckian distribution of acoustic phonons with frequencies in the several-hundred-GHz range [16]. To produce the image in Fig. 1 the laser beam is scanned across a (110) face of the crystal. The center of the image corresponds to propagation along the [110] direction.

The bright band of phonon flux in the phonon image is due to LA phonons that have propagated ballistically (without scattering) from the source to detector. The concentration of phonons in the horizontal $(1\bar{1}0)$ plane is due to an effect known as phonon focusing [17] and is well predicted from the known elastic constants of Pb. The image

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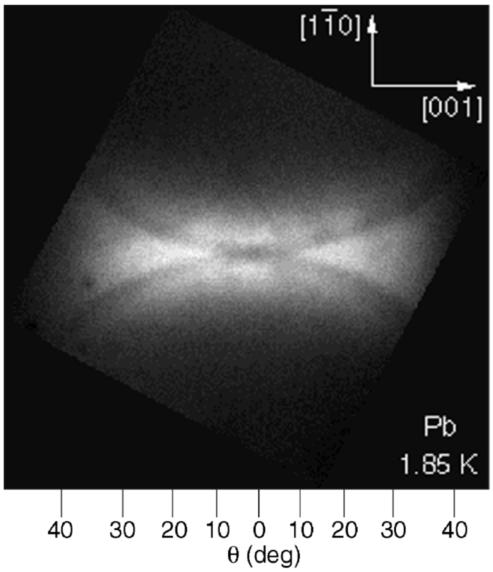

FIG. 1. Phonon image in Pb at 1.85 K using a 100-ns gate 500 ns after the excitation pulse, corresponding to the LA phonon velocity. The [110] direction is the twofold symmetric axis in the center of the image. The original data have been rotated to match the crystallographic orientation drawn in the inset. The full width of the figure is ±45° from [110].

is resolved in time to separate the LA from the transverse phonons [18].

The striking result in Fig. 1 is the pattern of dark lines crossing in the [110] direction. We believe that these sharp dips in phonon flux are due to highly selective phonon scattering by quasiparticles. The absorption lines correspond closely to LA phonons with *wave vectors* in {111} planes. The absorption lines are curved rather than straight because phonon wave vector and group velocity in an anisotropic medium are generally not collinear due to phonon focusing [17].

A vertical scan through the center of the image, Fig. 2a, quantitatively shows the magnitude and sharpness of the absorption dip. We have fit these data to the function

$$I = I_0 \exp(\Theta^2/2\sigma_0)[1 - (I_{\rm att}/I_0)\exp(\Theta^2/2\sigma_s)], \quad (1)$$

where the Gaussian function with width $\sqrt{\sigma_0}$ is an empirical representation of the unattenuated phonon flux, and the Gaussian function with width $\sqrt{\sigma_s}$ is used to model the scattering profile. In order to quantify the magnitude of attenuation along [110], we have defined an attenuation coefficient $\alpha = -(1/\ell)\ln(I_{\rm att}/I_0)$, where $\ell = 1$ mm is the phonon propagation distance. For this particular scan, $\alpha = 0.53$ mm^{-1}, and the full width at half maximum of the scattering profile is 4.6°.

The temperature dependence of the attenuation coefficient α, plotted in Fig. 2b, is a valuable indicator of the physical processes involved. The attenuation along [110] *increases* with increasing temperature [19]. This is the correct sign if the phonon scattering is due to thermally activated quasiparticles; however, the slope of the temperature dependence, when plotted versus 1/T, is 6 times lower

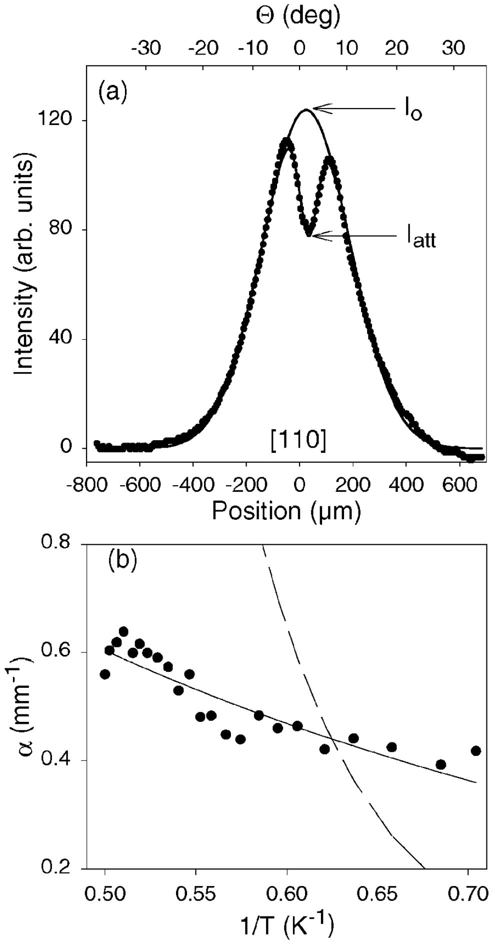

FIG. 2. (a) Solid dots are the measured phonon flux along a vertical line through the center of the phonon image in Fig. 1. The unattenuated flux is approximated with a Gaussian function of amplitude I_0. The thin line through the data points is the fit based on Eq. (1) in the text. (b) Temperature dependence of the phonon attenuation coefficient along [110]. The solid line shows an exponential fit using an energy gap of $\Delta_0/6$ and the dashed line uses Δ_0 with an arbitrary vertical displacement.

than that predicted from the $\exp(-\Delta_0/k_BT)$ dependence expected with $\Delta_0 = 1.35$ meV. This weak temperature dependence is roughly consistent with the low-temperature specific heat data suggesting a gap of $\Delta_0/4$ [2]. Clearly, the phonon attenuation associated with the absorption lines cannot be explained by activation of quasiparticles across the accepted gap of Pb.

Let us look more closely at the scattering kinetics. When a phonon with wave vector $\mathbf{q}$ is absorbed, a quasiparticle is deflected from wave vector $\mathbf{k}_i$ to $\mathbf{k}_f$ such that $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i \equiv \mathbf{dk}$. For phonons with $\nu = \Delta_0/h \approx 300$ GHz, the magnitude of the LA phonon wave vector $q = \omega/v_{\rm sound}$ is about 1/20 of the Fermi wave vector, implying that $\mathbf{dk}$ is nearly normal to the initial and final electron wave vectors. Our experiment shows that $\mathbf{q}$, and therefore $\mathbf{dk}$, lies in the {111} planes.

Imagine a narrow region in wave vector space where the gap is lowered from Δ_0 to $\Delta_{\rm min}$, as illustrated in Fig. 3. At 1.8 K, $k_BT = 0.15$ meV $\ll \Delta_0$ so there are many

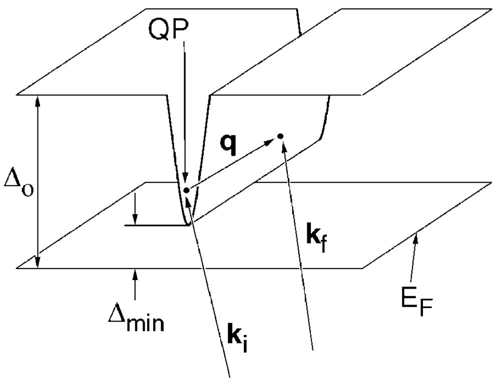

FIG. 3. Schematic representation of a region of reduced energy gap. Along the valley the gap is reduced to $\Delta_{\min} < \Delta_0$. Absorption of a low energy phonon, scattering the quasiparticle from $\mathbf{k}_i$ to $\mathbf{k}_f$, is restricted to phonons with $\mathbf{q}$ along the valley. Only a portion of the quasiparticle wave vectors are shown.

more thermally excited quasiparticles in this valley than in the Δ_0 regions. Phonons with energy less than about $\Delta_0 - \Delta_{\min}$ are restricted to scattering a quasiparticle from one region of lowered gap to another; i.e., the scattered quasiparticle remains in the valley and $\mathbf{dk}$ points along the line of lowered gap. Thus phonons with wave vectors pointing along this line will be more strongly absorbed. At low temperatures the absorption would be activated with the gap $\Delta_{\min}$, or if $\Delta_{\min} = 0$ the phonon absorption will have a polynomial temperature dependence. The small temperature range of our present experiments cannot distinguish these cases.

Daemen and Overhauser [9] pointed out that for Pb the candidate SDW wave vectors are $\mathbf{Q} = (2\pi/a)[211]$ or $(2\pi/a)[210]$, which satisfy the condition $|\mathbf{Q}| = 2k_F$ to within 98.7% and 90%, respectively. The dashed circles in Fig. 4a show the intersection of the $(2\pi/a)\{211\}$ planes with the Fermi surface of Pb in the spherical approximation. According to the predictions of Daemen and Overhauser, these intersection curves represent (in the spherical approximation) the locus of wave vector directions where the superconducting gap would be reduced by SDW's.

Of course, the actual Fermi surface of Pb is not spherical. Following Anderson and Gold's analysis of the de Haas–van Alphen data for Pb [20], we have calculated where the $(2\pi/a)\{211\}$ planes intersect the actual Fermi surface. The intersections are shown as the solid lines in Fig. 4a. The circles in the spherical approximation are distorted and break apart due to band gaps. Segments originating from adjacent circles overlap near the [111] directions, forming a triangular-shaped intersection of the $(2\pi/a)\{211\}$ planes and the actual Fermi surface. SDW theory suggests there are narrow valleys of lowered gap running along this "triangle."

In Fig. 4b, we plot in our experimental (110) plane the locus of directions connecting one point on the triangle to another. The intense well defined curves correspond to transitions tangential to a side of the triangle. These "intravalley" transitions involve phonons with $\mathbf{q}$'s in the

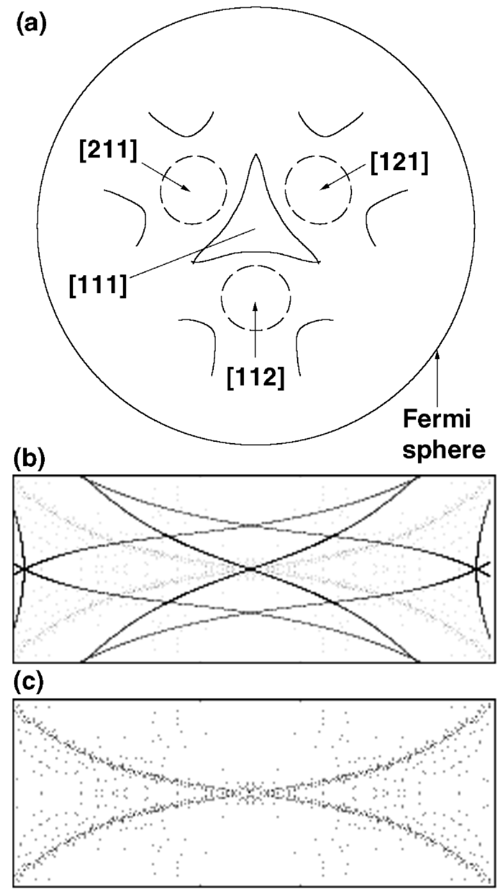

FIG. 4. (a) Lines of intersection between {211} planes and both spherical (dashed circles) and calculated (solid lines) Fermi surface in Pb around the [111] direction. (b) (110) observation plane corresponding to Fig. 1. Dark points indicate calculated propagation directions of phonons with $E = \Delta_0$ that can scatter a quasiparticle between any two points on the solid curves in (a). (c) Calculated propagation directions of phonons scattering quasiparticles from one side of the triangle in (a) to another side (intervalley scattering) only.

{211} planes. None of the intravalley curves matches the experimental absorption lines.

Almost hidden in the simulation in Fig. 4b is a diffuse collection of phonons with wave vectors nearly in {111} planes. This structure, isolated and amplified in Fig. 4c, is due to a transition from one side of the triangle to another; i.e., states $\mathbf{k}_i$ and $\mathbf{k}_f$ are in valleys of reduced gap associated with distinct SDW $\mathbf{Q}$'s (e.g., [211] and [121]). Because the Fermi surface is very flat near [111], these "intervalley" transitions involve phonons with $\mathbf{q}$'s almost exactly in {111} planes. These intervalley transitions match the experimentally observed absorption lines in Fig. 1. We also examined the possibility of [210] SDW's, but agreement with the data was less satisfactory.

Overhauser has proposed [21] that the dominance of intervalley over intravalley scattering is the result of different coherence factors for the two scattering processes. This difference is similar to the difference between the coherence factors for ultrasound attenuation and spin relaxation [1]. The validity of this interpretation is dependent on the SDW theory explaining an intravalley scattering that is over 2 orders of magnitude smaller than intervalley scattering.

In conclusion, we have observed sharp absorption lines for ballistic phonons in superconducting Pb, a unique and striking effect in phonon imaging experiments. Figure 3 shows how such anisotropies in phonon transmission can be associated with narrow valleys in the superconducting gap. A family of 12 [211] SDW's provides an attractive explanation of this phenomenon, but further theoretical and experimental support is required to test this hypothesis. Presently we have no other explanation of the sharp absorption lines and their temperature dependence.

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[1] See, for example, M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, Inc., New York, 1996), 2nd ed.

[2] B. J. C. Van Der Hoeven, Jr. and P. H. Keesom, Phys. Rev. **137**, A103 (1965).

[3] Anomalies in specific heat or ultrasonic attenuation are often ascribed to impurities or defects in the crystals. However, the specific-heat anomaly was observed in a 99.9995% pure sample and doping with In brought the specific heat more in line with the isotropic-gap expectations (see Ref. [2]).

[4] I. Giaever, H. R. Hart, Jr., and K. Megerle, Phys. Rev. **126**, 941 (1962).

[5] W. A. Fate, R. W. Shaw, and G. L. Salinger, Phys. Rev. **172**, 413 (1968).

[6] A. Bennett, Phys. Rev. **140**, A1902 (1965).

[7] D. J. Van Harlingen, Rev. Mod. Phys. **67**, 515 (1995).

[8] A. W. Overhauser and L. L. Daemen, Phys. Rev. Lett. **61**, 1885 (1988).

[9] L. L. Daemen and A. W. Overhauser, Phys. Rev. B **39**, 6431 (1989).

[10] X. M. Chen and A. W. Overhauser, Phys. Rev. B **39**, 10 570 (1989).

[11] A. W. Overhauser and T. M. Giebultowicz, Phys. Rev. B **47**, 14 338 (1993).

[12] B. L. Blackford and R. H. March, Phys. Rev. **186**, 397 (1969); G. I. Lykken *et al.,* Phys. Rev. B **4**, 1523 (1971).

[13] V. Narayanamurti *et al.,* Phys. Rev. B **18**, 6041 (1978).

[14] M. R. Hauser, R. Gaitskell, and J. P. Wolfe, Phys. Rev. B **60**, 3072 (1999).

[15] Sample is 99.9999% pure Pb grown by Metal Crystals & Oxides, Ltd., United Kingdom.

[16] For a local source with $T = 20$ K, the Planck maximum occurs at $2.8k_B(20\text{ K}) = 5\text{ meV} = h(1.2\text{ THz})$. However, it is likely that mass defect scattering in the sample limits the frequency of ballistically propagating phonons to several hundred GHz. Given $V_L = 2.46 \times 10^5$ cm/s and $\tau^{-1} = (5.05 \times 10^{-41}\text{ s}^3)\nu^4$ for isotope scattering in Pb, a 470 GHz phonon has a mean free path equal to the sample width of 1 mm.

[17] J. P. Wolfe, *Imaging Phonons* (Cambridge University Press, Cambridge, England, 1998).

[18] There are no caustics in heat flux for the LA phonons. Observation of transverse modes shows sharp caustics but no obvious absorption lines.

[19] By adjusting the electrical bias, the detector is operable over a temperature range from 1.4 to 2.0 K.

[20] J. R. Anderson and A. V. Gold, Phys. Rev. **139**, A1459 (1965).

[21] A. W. Overhauser (private communication).