Energy Gaps and Kohn Anomalies in Elemental Superconductors

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The momentum and temperature dependence of the lifetimes of acoustic phonons in the elemental superconductors lead and niobium were determined by resonant spin-echo spectroscopy with neutrons. In both elements, the superconducting energy gap extracted from these measurements was found to converge with sharp anomalies originating from Fermi-surface nesting (Kohn anomalies) at low temperatures. The results indicate electron many-body correlations beyond the standard theoretical framework for conventional superconductivity. A possible mechanism is the interplay between superconductivity and spin- or charge-density-wave fluctuations, which may induce dynamical nesting of the Fermi surface.

Over the past half-century, a comprehensive framework based on the Bardeen-Cooper-Schrieffer formulation (1) has been developed for the interpretation of experimental data on superconductors. Although this framework has been challenged by the discovery of high-temperature superconductivity, it provides a remarkably successful description of the physical properties of conventional low-temperature superconductors (2). Even today, however, the prediction of two of the most important quantities characterizing a superconductor, the transition temperature and the energy gap at the Fermi level, from first principles presents a formidable challenge to theory because they depend exponentially on material-specific parameters such as the phononic and electronic densities of states and the electron-phonon coupling (3). We present neutron scattering data on the lifetimes of acoustic phonons in Pb and Nb (the two elements with the highest superconducting transition temperatures, \( T_c = 7.2 \) and 9.3 K, respectively) that shed light on the energy gap in conventional superconductors.

The energy gap can be directly determined in phonon lifetime measurements, because electron-phonon scattering is suppressed (and the phonon lifetimes are thus enhanced) for energies below the gap. Our data indicate a surprising relation between the superconducting gap and the geometry of the Fermi surface, which also leaves an imprint on the phonon lifetimes (4): For phonon wave vectors connecting nearly parallel segments of the Fermi surface, the electron-phonon scattering probability is enhanced, and lifetime extrema (termed Kohn anomalies) are generally expected. We have recorded hitherto unknown Kohn anomalies in both Pb and Nb and found that the low-temperature energy gap coincides with such an anomaly in both materials. This phenomenon has not been anticipated by the standard theoretical framework for conventional superconductors.

Both Kohn anomalies (5–8) and superconductivity-induced phonon renormalization (9) have been observed by inelastic neutron scattering. However, because the requisite energy resolution is difficult to obtain, these investigations have been limited to a few selected materials, and both effects have thus far not been studied accurately in the same material. The systematic investigation reported here was made possible by recent advances in resonant spin-echo spectroscopy with neutrons (10–12), which have enabled the determination of the lifetimes of dispersive excitations with \( \mu \)V energy resolution over the entire Brillouin zone. In brief, the spin echo is generated on a triple-axis spectrometer by using radio-frequency magnetic fields to manipulate the spin polarization of neutrons scattered from a crystal before and after the scattering event. The excitation lifetime is then extracted from the spin-echo decay profile.

The measurements were taken on high-purity Pb and Nb single crystals. The resulting spin-echo decay profiles for selected transverse acoustic phonons in Pb and Nb (Fig. 1) are well described by exponentials, corresponding to Lorentzian phonon spectral functions; deviations from Lorentzian line shapes were not found within the experimental error. The spin-echo decay rate (proportional to the phonon linewidth and inversely proportional to its lifetime) decreases upon lowering the temperature, reflecting the loss of the electron-phonon decay channel in the superconducting state. The nonzero decay rate at the lowest temperatures is due to instrumental limitations, which can be quantitatively determined on the basis of the phonon dispersion relations and the mosaic spreads of the single-crystal samples (13). The intrinsic Lorentzian phonon line-widths, \( \Gamma \), are extracted by fitting the decay profiles

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to exponentials (lines in Fig. 1) and correcting for this instrumental contribution.

The intrinsic wave vector ($q$)-dependent linewidths of the lowest-energy, transverse acoustic phonon mode $T_1$ of Pb along $q = (\xi, \xi, 0)$ is shown in Fig. 2A. At all temperatures, sharp anomalies in the phonon linewidths are seen at $\xi \sim 0.25$, 0.35, and 0.50 reciprocal lattice units (r.l.u.). Although the phonon spectrum of Pb has been studied extensively by conventional neutron spectroscopy, these particular features have not been recognized because of insufficient energy resolution. The same features also appear in the phonon dispersion relation (Fig. 2B): Maxima in the phonon linewidth coincide with characteristic S-shaped deviations from the $q$ linear dispersion, as stipulated by the Kramers-Kronig relation that holds for all excitations in solids. Artefacts associated with the new measurement method would generally not be Kramers-Kronig consistent and can thus be ruled out. This implies that phonons with the anomalous wave vectors shown in Fig. 2A are intrinsically unstable toward decay into other elementary excitations. In principle, the decay products can be either other phonons (generated, for instance, by anharmonic terms in the lattice potential) or electron-hole pairs (originating from Kohn anomalies). The features at $\xi \sim 0.35$ and 0.5 can be associated with Kohn anomalies because these wave vectors are known as nesting vectors of the Fermi surface. Indeed, Kohn anomalies have been observed at these wave vectors in the longitudinal phonon branch of Pb (5, 6, 13). The origin of the feature at $\xi \sim 0.25$ is more subtle because this wave vector does not match any known spanning vector of the Fermi surface. A possible origin is a three-phonon decay process previously observed in the spectrum of phonons in liquid helium, which are unstable because their phase velocity exceeds the velocity of sound (15, 16). Indeed, accurate measurements of the phonon dispersions in Pb (Fig. 2B) show that the phonon phase velocity exceeds the sound velocity around $\xi \sim 0.25$, presumably as a consequence of the dispersion anomaly at $\xi \sim 0.35$. This process has thus far not been observed in solids and deserves further investigation. Anharmonic terms in the lattice potential may also contribute to the anomaly.

We focused on the influence of superconductivity on the phonon linewidths below $T_c = 7.2$ K. As the superconductor is cooled below $T_c$, the electron-hole decay channel is closed (and $\Gamma$ is reduced) below the energy gap $2\Delta(T)$. This effect is observed at low wave vectors $\xi$ in Fig. 2A. In particular, $\Gamma$ approaches 0 for $T \ll T_c$ around $\xi = 0.32$ [corresponding to a phonon energy of 2.47 meV, below the low-temperature limit of $2\Delta \sim 2.7$ meV known from tunneling measurements (17)]. For lower energies around $\xi \sim 0.25$, however, $\Gamma$ remains nonzero even at the lowest temperatures, supporting the notion that the linewidth anomaly at this wave vector originates from the three-phonon down-conversion process discussed above and/or lattice anharmonicity and not from electron-hole pair production. We removed the contribution of this process for clarity and show only the phonon linewidth, $\Gamma_{e-p}$, directly attributable to the electron-phonon interaction (Fig. 3). As expected, $\Gamma_{e-p}$ exhibits a maximum because of the pileup of

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**Fig. 1.** Spin-echo decay profiles of transverse acoustic phonons at $q = (0.26, 0.26, 0)$, phonon energy $E = 2.32$ meV in Pb (top two curves) and $q = (0.11, 0, 0)$, $E = 2.06$ meV in Nb (bottom two curves) at selected temperatures. The spin polarization of the beam at the detector is plotted versus the spin-echo time $\tau$ (10, 11). The lines are the results of fits of exponentials (corresponding to Lorentzian spectral functions) to the data. (Inset) A conventional triple-axis scan through the phonon in Pb. Error bars indicate the statistical errors.

**Fig. 2.** (A) Linewidths of transverse acoustic phonons along $q = (\xi, \xi, 0)$ in Pb at selected temperatures. The data were obtained by correcting the measured spin-echo decay rates for instrumental effects (13). The gray symbols are the results of ab initio lattice-dynamical calculations, as described in the text. Error bars indicate the statistical errors. (B) Dispersion relation of the same phonon extracted from triple-axis data. (Inset) The phonon phase velocity ($E(q)$ computed from the data. The blue line in (B) and the black line in the (B) inset represent the experimentally determined sound velocity (29).
electronic density of states above $2\Delta(T)$, which moves to progressively higher energies upon cooling and closely tracks the energy gap determined in prior tunneling measurements (17) (Fig. 3 inset). Surprisingly, however, the superconductivity-induced maximum of $\Gamma_{e-p}$ merges with the Kohn anomaly as $T \to 0$. At $T = 0.5$ K, both anomalies are indistinguishable within the measurement error.

In order to explore whether the coincidence of $2\Delta(T\to0)$ and the Kohn anomaly in Pb is accidental, we performed similar experiments on phonons in Nb, an elemental superconductor with a different Fermi surface and phonon spectrum. Figure 4A shows the momentum-dependent linewidths of the transverse acoustic phonon branch along $(\xi, 0, 0)$ in Nb at temperatures above and below $T_c = 9.3$ K. The data above $T_c$ are in fair agreement with prior work (9), but they reveal several sharp features that have not been identified before. In part on the basis of ab initio lattice dynamical calculations, they can be identified as Kohn anomalies (see below). The existence of a Kohn anomaly at $\xi \sim 0.17$ persisting up to room temperature has been suggested on the basis of prior experimental work (7, 18). As described above for Pb, the linewidths are reduced below and enhanced above the gap for quasi-particle-pair production, $2\Delta(T)$, in the superconducting state, and the low-temperature electron-phonon linewidth shows the expected dependence on wave vector (or energy). Similar to the observation in Pb, the $2\Delta(T\to0)$ extracted from the low-temperature $\Gamma_{e-p}$ of Nb again coincides with the lowest-energy Kohn anomaly within the experimental error (Fig. 4B).

To help interpret these observations, we calculated the phonon dispersions and linewidths in the framework of ab-initio density functional perturbation theory in the local-density approximation (LDA) (13) on a very fine mesh of $q$ points in reciprocal space. The phonon frequencies were obtained by diagonalization of the dynamical matrices and the electron-phonon linewidths by Allen’s formula (19). The results are in reasonable overall agreement with the experimental data (Figs. 3 and 4). In particular, both the phonon frequencies and the linewidths associated with Kohn anomalies in the high-energy transverse acoustic phonons of Nb (Fig. 4A) and in the longitudinal phonon of Pb (13) are well described, indicating that the resolution of the calculations is sufficient to reproduce subtle structures in $q$ space.

The lowest-lying Kohn anomalies in the transverse-acoustic phonon branches of both Pb and Nb are, however, not reproduced by the calculations (Figs. 3A and 4, A and B). These anomalies therefore originate in factors not included in the calculations, such as the relativistic spin-orbit coupling, phonon nonadiabaticity (20), or many-body correlations beyond Allen’s formula (21, 22) or the LDA. Because the Kohn anomalies in Pb and Nb are of comparable strength, the spin-orbit coupling (which is much stronger in Pb than in Nb) cannot be responsible. Because of the large Fermi energies of both materials, nonadiabatic electron-phonon coupling effects should also be extremely weak.

This leaves electron correlation effects beyond the LDA as the most likely mechanism responsible for the low-energy Kohn anomalies. It seems reasonable to assume that the same correlations are also responsible for the observed coincidence of $2\Delta(T\to0)$ with the same anomalies. Because the anomalies persist to temperatures above 100 K, superconducting fluctuations are unlikely to be directly responsible. We note, however, that the formation of spin or charge density waves driven by electron correlations has been predicted for Pb and other elemental metals (23). Although extensive searches for static
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Density waves in simple metals have been unsuccessful, it is conceivable that fluctuations characteristic of such states dynamically enhance the nesting properties of the Fermi surface and hence the propensity for Kohn anomalies in the phonon spectrum. Indeed, experiments on charge-density-wave materials such as NbSe$_2$ have revealed Kohn anomalies (8) and Fermi-surface “pseudogaps” (24, 25) in the extended fluctuation regime at temperatures well above the onset of static density-wave order. Detailed theoretical work is required to assess whether interference between density-wave and superconducting correlations can limit the growth of the superconducting gap and lead to the observed convergence of both energy scales at low temperatures.

Our experiments on two different elemental superconductors demonstrate that the low-temperature limit of the superconducting energy gap coincides with low-lying Kohn anomalies in transverse acoustic phonons. Because both superconductors exhibit different lattice structures, phonon spectra, Fermi surfaces, and superconducting gaps, this coincidence cannot be accidental. Although its origin is presently unclear, a specific scenario to explore in future theoretical work is the interplay between density-wave and superconducting correlations. Lastly, we point out a possible analogy to research on high-temperature superconductors, where an anomalous coherence of the superconducting gap with a weakly temperature-dependent pseudogap has recently been reported in some regions of momentum space (26–28).

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Synthesis of Macroyclic Copolymer Brushes and Their Self-Assembly into Supramolecular Tubes

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We report on an efficient route to design large macrocyclic polymers of controlled molar mass and narrow dispersity. The strategy is based on the synthesis of a triblock copolymer ABC, in which the long central block B is extended by two short A and C sequences bearing reactive antagonist functions. When reacted under highly dilute conditions, this precursor produces the corresponding macrocycle by intramolecular coupling of the A and C blocks. Chloroethyl vinyl ether was selected as the monomer for the central block B, because it can be readily derivatized into brushlike polymers by a grafting process. The corresponding macrocyclic brushes were decorated with polystyrene or randomly distributed poly(styrene) and polyisoprene branches. In a selective solvent for the polystyrene branches, the macrocyclic brushes self-assemble into cylindrical tubes of up to 700 nanometers.

The interest in cyclic macromolecules began more than 50 years ago with the theoretical prediction of the effect of chain cyclization on polymer properties (I, 2) and the discovery of naturally occurring macrocycles such as DNA (3). Recently, the self-assembly of proteins into nanorods for the fabrication of advanced materials has been reported (4). Because of their very limited availability, large polymer macrocycles remain a fascinating curiosity for theoreticians and physicists and a challenging area for synthetic chemists (5).

Macroyclic polymers were first obtained from macromolecules systems exhibiting ring-linear chain equilibria (6). In such systems, low-to-medium molar mass macrocycles are obtained generally in admixture with linear chains, although a more selective approach has been recently reported by Grubbs (7).

The most appropriate method for the synthesis of cyclic polymers with controlled size and narrow dispersity was first proposed by Casassa (8) more than 40 years ago. It is based on the end-to-end chain coupling of linear α,ω-difunctional chains in highly dilute conditions. Coupling of α,ω-dianionic polymers with difunctional agents has been the most extensively used ring closure approach (9–11); however, cyclization yields for large macrocycles are generally low, and fractionation procedures are required to remove residual linear chains and polycondensates (12). An alternative route is based on the end-to-end coupling of α,ω-heterodifunctional linear chain (13). Cyclization is performed under high dilution by selective activation of one polymer end, which reacts intramolecularly with the second chain end. Higher cyclization yields have been reported but molar masses of the macrocycles remain limited. A more selective approach was proposed by Tetzuka (14) that involves the precyclization of linear chains bearing ionic end groups. However, only very low molar mass macrocycles have been synthesized.

The preparation of large macrocyclic polymers and copolymers is thus limited (12) by (i) the difficulty to get pure α,ω-difunctional high molar mass precursors, (ii) the drastic decrease of the end-to-end ring closing efficiency when in-