other advantages good energy resolution and symmetry dependence. This may enable us to obtain information on the anisotropy of the gap from the A- and E-mode splittings. With the aid of theory, the electron-phonon coupling constant may be directly obtained. We may also be able to obtain information on the density of states in the vortex regime when H is large but not close to H_{c2}.

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Phonon Raman Scattering in Superconductors

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If a superconductor has a Raman-active phonon mode of low frequency (larger but of the order of magnitude of the superconducting energy gap 2Δ), we show that electron-phonon coupling leads to a complex bound excitation, also Raman active, with a discrete frequency lower than 2Δ and with intensity which can be appreciable. We propose that these are the lines found by Sooryakumar and Klein at approximately the energy-gap frequency in superconducting $2H$-$NbSe_2$.

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Recent experiments of Sooryakumar and Klein[1] on superconducting $2H$-$NbSe_2$ have detected, in addition to the ordinary Raman lines[2] at 234 and 248 cm^{-1}, and the Raman lines[3] induced by charge-density waves[4-7] (CDW) below $T_{CDW} \cong 33$ K at approximately 40 cm^{-1}, two additional peaks at approximately 16 cm^{-1} which are only present below the superconducting transition temperature $T_{SC} = 7.2$ K. These values seem to agree well with the superconducting energy gap, $2\Delta = 17.2 \pm 0.4$ cm^{-1}, as measured in a different sample by infrared transmission.[8] In addition, these new lines decrease in intensity and shift in frequency when large magnetic fields (~40 kG) are applied, which confirms the suspicion that they are closely related to the superconductivity of the material.

The fact that the spectrum shows well-defined sharp lines (as opposed to a less pronounced feature such as a shoulder or a broad band) clearly points out that they cannot be directly related to the excitation of superconducting quasiparticles. Their sharpness points to bosonlike excitations, such as a phonon, an exciton, or a magnon; the value of their Raman shift and the pronounced magnetic field dependence indicate that the superconductive properties of the sample must be directly involved.

We would like to suggest as a very likely explanation that the observed lines are a direct consequence of the interaction between $\vec{q}=0$ phonons of low frequency (the lines at approximately 40 cm^{-1}, caused by the CDW) and the superconducting electrons. In other words, it is an ordinary *phonon self-energy effect* in a superconductor when the phonon itself is Raman active.

A simple model calculation supports our hypothesis. We write a Hamiltonian

$$\mathcal{H}=\mathcal{H}_{BCS}+\mathcal{H}_{ph}+\mathcal{H}_{int}\,, \qquad (1)$$

which describes a Bardeen-Cooper-Schrieffer system[9] of interacting electrons, a single $\vec{q}=0$ phonon of frequency ω_0,

$$\mathcal{H}_{ph}=\hbar\omega_0 b^\dagger b\,, \qquad (2)$$

and an interaction term

$$\mathcal{H}_{int}=g\sum_{k\sigma}c_{k\sigma}^\dagger c_{k\sigma}(b+b^\dagger)\,, \qquad (3)$$

where $b^\dagger$ (b) creates (destroys) a phonon and $c_{k\sigma}^\dagger$ ($c_{k\sigma}$) is the creation (destruction) operator for an electron of wave vector k and spin σ.

Standard canonical-transformation methods[10] and a perturbation calculation which hybridizes the single-phonon state with an electron-hole pair (see Fig. 1) yield the complete one-phonon spectral function. For $\hbar\omega_0>2\Delta$ the phonon intensity is in general highly peaked about $\hbar\omega_0$, but with a continuous distribution which extends over the excited pair energy range, $\hbar\omega>2\Delta$. There is, in addition, a bound state of energy λ which splits off from the quasiparticle continuum: $\lambda<2\Delta$. The value of λ is given by the solution of the eigenvalue equation

$$\lambda^2=\hbar^2\omega_0^{\,2}-\frac{16\hbar\omega_0\Delta^2g^2\rho_0}{\lambda(4\Delta^2-\lambda^2)^{1/2}}\tan^{-1}\frac{\lambda}{(4\Delta^2-\lambda^2)^{1/2}}, \qquad (4)$$

where ρ_0 is the density of normal electron states per spin at the Fermi level. The phonon spectral density (residue) at λ can be easily calculated.[11,12] In Fig. 2, we show several examples of the complete phonon spectral density for various values of the energy gap 2Δ and for a coupling strength $g^2\rho_0/\hbar\omega_0=0.12$.

In Fig. 3, we have attempted a more detailed fitting of our calculation to the experiments of Sooryakumar and Klein.[1] In Fig. 3(a), we have taken their measured A_{1g} spectrum at 9 K ($T>T_c$) [their Fig. 1(b)], subtracted the constant back-

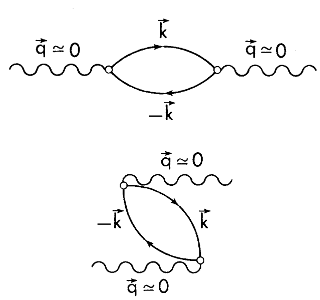

FIG. 1. The two processes leading to the formation of a phonon–quasiparticle-pair bound state.

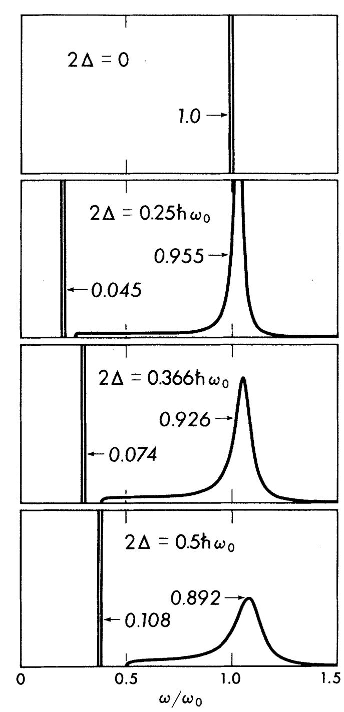

FIG. 2. The phonon spectral density for the coupled modes. In these examples the coupling constant is $g^2\rho_0=0.12\hbar\omega_0$ and the value of the superconducting energy gap is indicated. The spectral weights of the bound state and the continuum are shown.

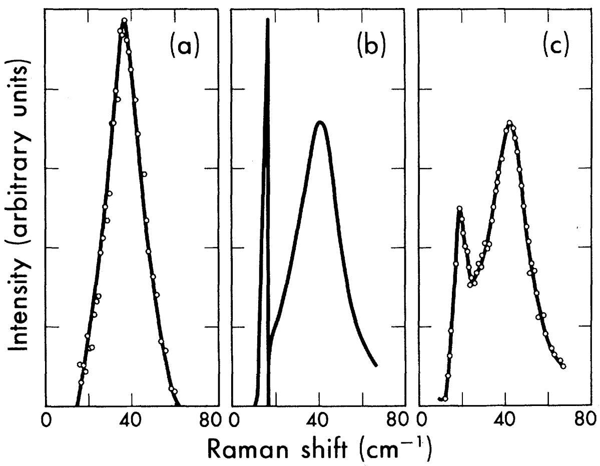

FIG. 3. The spectrum for an inhomogeneously broadened phonon fitted to the experimental data of Ref. 1. (a) The experimental A_{1g} spectrum at $T=9$ K and the fitted spectral curve (background subtracted). (b) The theoretical spectrum at $T=0$ for a coupling constant $g^2\rho_0=0.08\hbar\omega_0$, linear in the frequency. (c) The experimental A_{1g} spectrum at $T=2$ K (background subtracted).

ground, and fitted the curve. If that is considered the inhomogeneously broadened spectrum of the original line, and we assume that the coupling constant $g^2\rho_0$ is proportional to the frequency of the phonon ($g^2\rho_0=0.08\hbar\omega_0$), the resulting spectrum from our calculation is shown in Fig. 3(b). This is to be compared with the experimental data of Fig. 3(c) (where a similar constant background subtraction has been performed). Comparison between theory and experiment is satisfactory.

In conclusion, several points obtained from our calculations are worth remarking:

(1) A phonon–quasiparticle-pair bound state always exists in our model; its energy λ is smaller than 2Δ.

(2) For the most common values of phonon frequency, energy gap, and coupling strength ($\hbar\omega_0 \gg 2\Delta$; $g^2\rho_0 \sim 0.2\hbar\omega_0$) the bound state appears at $\lambda \simeq 2\Delta$ with vanishing small spectral strength and is thus unobservable.

(3) The spectral intensity of the bound state is only appreciable when $\hbar\omega_0$ is of the same order of magnitude as 2Δ. This explains why the effect has been observed in $NbSe_2$, a CDW superconductor, and not in other superconductors[13] (ordinary Raman-active phonons, if they exist, have usually frequencies from ten to one hundred times the energy-gap frequency). In particular an incommensurate CDW renders some low-frequency phonon modes Raman active by "folding" the Brillouin zone; this makes the effect observable.

(4) If the low-frequency mode $\hbar\omega_0 \gtrsim 2\Delta$ is strongly coupled to the electrons, the bound-state energy may be considerably smaller than 2Δ. For strong enough coupling it may even become negative, i.e., the superconducting crystal becomes unstable against spontaneous lattice distortions.

(5) For CDW superconductors we expect the coupling parameter $g^2\rho_0$ to be relatively small, smaller than typical superconducting coupling constants.[9] This is due to two effects: The phonons involved are low-frequency phonons,[14] and the relevant coupling strength gets considerably reduced by the CDW coherence factors.[15]

(6) For reasonable values of the parameters (see Fig. 2) we have obtained bound states close to 2Δ and with appreciable spectral intensity.

(7) These coupled phonon-quasiparticle modes could also be responsible for the peculiarities of the observed infrared absorption spectrum.[8]

(8) These modes are in principle also observable in a non-CDW superconductor[13] with a soft Raman-active mode, regardless of the origin of that active mode.

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