Raman spectroscopy in high-temperature superconducting materials

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If the conventional phonon-mediated pairing is responsible for the high-temperature superconductivity of the Cu oxides, then a strong enhancement of the Raman activity at frequencies close to twice the superconducting gap can be expected. For other pairing mechanisms this effect is absent.

The pairing mechanism for the reported high-temperature superconducting Cu oxides is unclear at present. The first class of systems $(La_{1-x}M_x)_2CuO_4$ (M: Ca, Sr, Ba) originally investigated by Bednorz and Müller,[1] reaches temperatures in the 30–40 K range and exhibits the isotope effect for oxygen.[2,3] Moreover, the phonon spectra of this class of substances show a significant renormalization due to the coupling of the electronic constituents of the Cooper-pairs to high-frequency oscillations of the light O atoms (breathing modes) in the CuO_6 octaeders.[4] An Eliashberg calculation, taking into account these (breathing) modes, indicates the existence of strong-coupling phonon-mediated superconductivity in this first class of substances.[5]

A second class of superconductors, characterized by $MBa_2Cu_3O_7$ (M stands for Y and the lanthanids), reaches higher critical temperatures in the 90 K range and beyond. No isotope effect is reported[2,3] and no Eliashberg calculation motivates the critical involvement of phonons in the superconductivity of these systems.[6,7] Proposals for other pairing mechanisms has been put forward, but the situation seems unclear at present.[6,7] It is in no way evident, that the phonon mechanism which seems to explain the phase of the first class of materials, should not work for the other one.

It is therefore of great importance to establish further criteria for phonon-mediated superconductivity. In this Brief Report we present the renormalization of the phonon modes due to polarization effects, yielding an enhanced Raman activity in the superconducting phase close to the (real) quasiparticle creation threshold of twice the superconducting gap 2Δ. In the case of nonphonon-mediated superconductivity this effect is absent.

For the first class of systems, gap values are reported from electron tunneling[8] and from far-infrared transmission methods[9] to be of the order of characteristic phonon frequencies ω.[5] Thus, there exist relevant phonons with $2\Delta/\omega \sim 1$, whereas in usual superconducting systems this ratio is much smaller than one. This gives rise to a remarkable phenomenon: When the phonon frequency is of the order of or greater than two gap values, then real quasiparticle-antiquasiparticle production sets in, strongly enhancing the phonon polarization $\Pi(\omega)$ in the vicinity of $\omega \sim 2\Delta$. This renders strong contributions to the phonon renormalization corresponding to enhanced Raman activity for frequencies $\Omega = [\omega_0^2 - 2\omega_0\Pi(\Omega)]^{1/2}$, where ω_0 is the bare phonon frequency and Π is the (Coulomb screened) phonon polarization.

Figure 1 qualitatively shows the expected superconductivity related effect on the phonon dispersion (Raman signal). The bare and rather sharp phonon dispersion with energy slightly above 2Δ is shown in Fig. 1(a). If the full interaction with the superconducting electron gas is taken into account in Fig. 1(b), the phonon mode splits into a sharp mode below 2Δ and a broadened mode centered somewhat above the bare phonon energy.

The physical interpretation of this effect is quite evident: The phonon couples to the electronic charge density and the resulting phonon-charge density mixture exhibits a low-energy and high-energy branch. Only the branch

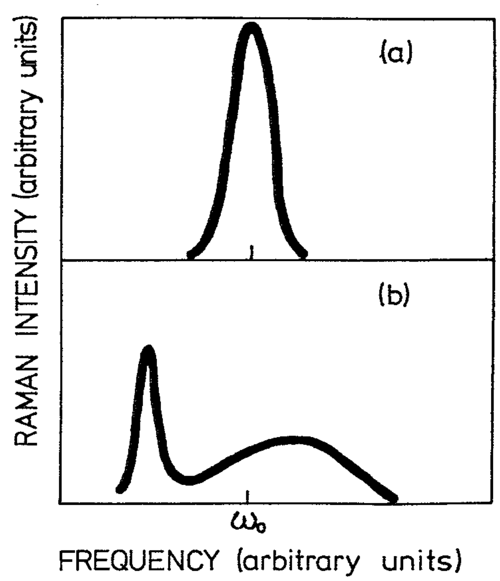

FIG. 1. Schematic representation of the Raman shift for (a) sharply peaked bare phonon, and (b) dressed phonon from (a) in the superconducting state.

above 2Δ is broadened since the electron-hole excitation is impossible below $\omega \sim 2\Delta$. The whole effect is strongly enhanced at $\omega \sim 2\Delta$ as a consequence of the diverging polarizability.

In the following we shall report calculations of the lowest-order phonon polarization $P^{(2)}$ for $T \neq 0$, which are applied for the renormalization of the phonon propagator.[10–14] This result is then used to predict a strong enhancement of the Raman activity, here referred to as resonant Raman scattering (RRS) via the effect discussed above.

The calculation is based upon a model often used in the Eliashberg theory of strong coupling superconductivity.[15,16]

(i) Quasiparticle (electron-hole) propagators G are represented in the Nambu notation[15,16]

$$G(k,i\omega_n) = \frac{(i\omega_n) + \tau_3\epsilon_k + \tau_1\Delta}{(i\omega_n)^2 - \epsilon_k^2 - \Delta^2 + i\delta} ,$$

where $\epsilon_k = (k^2 - k_F^2)/2m_{\rm el}$ and 1, τ_1, τ_3 are the Pauli matrices and the gap is assumed to be constant, $\Delta_k = \Delta$.

(ii) Electron-phonon vertices are parametrized by $g\tau_3$, where g is some electron-phonon coupling constant which need not be small.

(iii) Due to Migdal's theorem,[15,16] the full vertex function can be approximated by the bare vertex $g\tau_3$ and a perturbation expansion in the kinematic ratio $(m_{\rm el}/M_{\rm ion})^{1/2} \sim 10^{-2}$ can be derived.

(iv) For the full phonon propagator D this expansion yields

$$[D(k,i\omega_n)]^{-1} = [D_0(k,i\omega_n)]^{-1} - \Pi(k,i\omega_n) , \quad (1)$$

where

$$D_0(|k| \sim \omega_0/c, i\omega_n) = 2\omega_0/[\omega_0^2 - (i\omega_n)^2 + i\delta]$$

is the bare phonon propagator and the polarization Π is given in lowest order, including Coulomb screening

$$\Pi = g^2(1 - V_c P)^{-1} P , \quad (2)$$

$$P^{(2)}(q,i\omega_n) = -k_B T \int \frac{d^3k}{(2\pi)^3} \sum_{m=-\infty}^{\infty} \mathrm{Tr}[\tau_3 G(k+q, i\omega_n + i\omega_m)\tau_3 G(k, i\omega_m)] . \quad (3)$$

In (2), V_c stands for the Coulomb potential.

By taking the traces and performing the frequency summation via extension of the contour of the Poisson formula to infinity, one obtains in the dynamic screening range ($|q| \sim 0$) after analytic continuation to real frequencies

$$P^{(2)}(\omega) = 4 \int \frac{d^3k}{(2\pi)^3} \frac{\Delta^2}{(\epsilon_k^2 + \Delta^2)^{1/2}(\omega^2 - 4\Delta^2 - 4\epsilon^2)} \tanh[\tfrac{1}{2}\beta(\epsilon_k^2 + \Delta^2)^{1/2}] , \quad (4)$$

where $\beta = (k_B T)^{-1}$ and $\Delta \sim \Delta_{T=0}(1 - T/T_c)^{1/2}$ from the Bardeen-Cooper-Schrieffer (BCS) theory is assumed. The integral in (4) can be solved by substituting $d^3k/(2\pi)^3 \sim N(0)d\epsilon$, where $N(0)$ is the density of electron states at the Fermi surface. It is given by $[x = a\sinh(\epsilon/\Delta)]$

$$P^{(2)}(\omega) = -8N(0)\Delta^2 \int_0^\infty dx \frac{\tanh[\frac{1}{2}\beta\Delta\cosh(x)]}{4\Delta^2[\cosh(x)]^2 - \omega^2} . \quad (5)$$

The dimensionless phonon-electron and Coulomb coupling strength can be parametrized by $\lambda = 2g^2 N(0)/\omega_0$ and $\mu = V_c N(0)$. These variables, however, should not be confused with the dimensionless coupling parameters of the Eliashberg theory,[15,16] where the coupling strength is weighted over the phonon spectrum and the momentum ranges. Only in the case of a strongly peaked (Einstein) spectrum the λ parameters coincide.

Numerical studies show that the resonant Raman frequency Ω becomes larger when λ is decreased and μ is increased. For $2\Delta < \omega_0$, $\Omega \leq 2\Delta$; whereas for $2\Delta\omega_0$, $\Omega \leq \omega_0$. The results show that inclusion of Coulomb screening improves the convergence of Ω toward its saturation values 2Δ and ω_0. In any case, one should be able to observe a strong peak of the Raman activity in the superconducting phase at frequency shifts close to 2Δ due to the diverging polarizability $P(2\Delta)$, as can be seen from (5). This requires the existence of phonon modes in this range as well as electron (hole)-phonon coupling; both are necessary conditions for the conventional pairing mechanism.

If one assumes gap values of 50–400 cm^{-1}, corresponding to 6–48 meV, enhancement of the Raman energy shift should occur at about twice that value. Raman spectra are published for transparent materials with the K_2NiF_4 structure, such as Sr_2TiO_4.[17] Furthermore, there are two Raman studies on $La_{1.85}Sr_{0.15}CuO_{4-\delta}$; (i) in the 50–500 cm^{-1} frequency shift range at temperatures 6–300 K,[18] and (ii) in the 50–900 cm^{-1} frequency shift range at temperatures 44–300 K.[19] Both groups record no significant change in the Raman spectrum of the superconducting phase up to frequency shifts of 500 cm^{-1}. At 666 cm^{-1} a broad peak appears at low temperature, an effect which has been ascribed to a planar breathing mode.[19] Hence, so far no clear signature of a resonant enhancement of the Raman spectrum, even for the first class of materials of the $(La_{1-x}M_x)_2CuO_4$ type has been observed. Whether the absence of this effect can be explained by nonexisting phonon modes at 2Δ is unclear at present.

For the second class of superconductors experimental results are more promising.[20] By subtracting the normal-state Raman intensity from the superconducting state one, a significant enhancement of the Raman activity has been observed in the frequency range of 30–100 meV. It is reasonable to interpret this increased Raman activity as an indication for a resonance effect close to twice the superconducting gap and, thus, as a criterion for phonon-mediated superconductivity of the $YBa_2Cu_3O_7$ system.

In conclusion, it can be said that inelastic light scattering is a phenomenon worth investigating for high-temperature superconductors due to its significance for the consolidation of a phonon-mediated pairing hypothesis. For a definite answer, more experimental evidence is necessary.

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