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PHONON SELF-ENERGIES AND THE GAP OF HIGH-TEMPERATURE SUPERCONDUCTORS

C. Thomsen, M. Cardona, B. Friedl, C.O. Rodriguez, I. I. Mazin and O.K. Andersen

Max-Planck-Institut für Festkörperforschung,
Heisenbergstr. 1, D-7000 Stuttgart 80, Federal Republic of Germany

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We report quantitative evidence from Raman scattering for the applicability of strong-coupling theory for phonon self-energies to high-T_c superconductors. Positive and negative shifts of optical phonon frequencies in the superconducting state of $RBa_2Cu_3O_{7-\delta}$ fall near a universal curve when plotted vs. phonon energy. This curve is the phonon self-energy shift obtained from strong-coupling theory by Zeyher and Zwicknagl, with $2\Delta/k_BT_c = 5.2$. The appropriate electron-phonon coupling constants ($\lambda = 0.02$ and 0.01 for the 340 and 440-cm^{-1} modes) were calculated *ab initio*.

Mechanisms for high-temperature superconductivity have been proposed in abundance. The fact that the isotope effect on T_c is small[1,2] cast doubts on the phonon mechanism. The results of tunneling spectroscopy,[3] on the other hand, indicate that phonons do play a role in high-temperature superconductivity. There are also experimental indications that the electron phonon interaction is rather strong (e.g. specific heat,[4] thermal conductivity[5]). Moreover the experimental estimates for the gap lead to relatively large values of $2\Delta(0)/k_BT_c$ (≥ 5) which is consistent with strong-coupling theory. Consequently, the frequency of the gluing boson if any, should be in the region of phonon frequencies. We report here on a series of Raman measurements of the anomalous frequency shifts of lattice vibrations, which occur when cooling a superconductor below T_c. We found that the observed positive and negative shifts may be quantitatively explained by a conventional superconducting state, assuming a strong coupling for the gap formation ($2\Delta/k_BT_c \approx 5.2$). The appropriate electron-phonon coupling constants for scattering across the gap were calculated in the LDA [6] with the full-potential LMTO method.[7]

The anomalous softening of the optical mode at 340 cm^{-1} first reported by Macfarlane et al.[8] in ceramic samples of $YBa_2Cu_3O_{7-\delta}$, has been investigated thoroughly. Experiments performed on single crystals[9] show that the transition to the "soft" phonon is rather sharp, i.e. it occurs within ~20 K of T_c. Based on the polarization selection rules observed in light scattering it has been proven[10] that this mode has its eigenvectors in the CuO_2-planes thus highlighting the relevance of these planes for superconductivity. Upon application of the magnetic field $H(T) > H_{c2}(T)$ the softening reverses to its normal-state value.[11] Odd vibrational modes have also been observed[12] to soften when cooled below T_c. Non-superconducting $YBa_2Cu_3O_6$ and $PrBa_2Cu_3O_7$ both do not exhibit any anomalous shift in the 10 K - 300 K range.[13] Also, structural changes large enough to explain the observed frequency anomalies have not been observed in $YBa_2Cu_3O_{7-\delta}$.[14] A concurring effect that has been studied somewhat less is the change in linewidth of the anomalous mode:[15,16] Cooper et al.[15] have reported an increase in linewidth γ (HWHM) from 8 to 12 cm^{-1} from 90 to 10 K. Similar effects are known for a classical superconductor, Nb, where a transverse acoustic phonon is reported to soften and broaden below T_c.[17] Relative magnitudes of the frequency shift $\Delta\omega/\omega$ and linewidth increase, $\Delta\gamma/\omega$ are comparable to those in the high-T_c materials. ($\Delta\omega/\omega = 1.9\%$ and $\Delta\gamma/\omega = 0.8\%$ in Nb, $\Delta\omega/\omega = 2.0\%$ and $\Delta\gamma/\omega = 1.2\%$ in $YBa_2Cu_3O_{7-\delta}$). It is thus well established that some form of coupling of the lattice to the electronic system exists in the superconducting state of high-T_c superconductors.

The theory of this effect was worked out for optical, zone-center ($q = 0$) phonons by Zeyher and Zwicknagl.[18] They calculated the change of the self-energy, $\Delta\Sigma_\nu = \Delta\omega_\nu - i\Delta\gamma_\nu$, of the ν'th phonon mode due to scattering of pairs across the gap and obtained the result for the relative change:

$$\Delta\Sigma_\nu/\omega_\nu = \lambda_\nu f\left(\omega_\nu/(2\Delta)\right) , \qquad (1)$$

with the universal function of $\tilde{\omega} \equiv \omega_\nu/(2\Delta)$. In the weak-coupling (BCS) limit (see also Ref. [19])

$$f(\tilde{\omega}) \equiv \begin{cases} -2u/\sin 2u & \text{for } \sin u \equiv \tilde{\omega} < 1 \\ (2v - i\pi)/\sinh 2v & \text{for } \cosh v \equiv \tilde{\omega} > 1. \end{cases} \quad (2)$$

In Eq. (1), the electron-phonon coupling constant for the ν'th mode is defined as

$$\lambda_\nu \equiv 2N(0) \left\langle |g_{\nu kk}|^2 \right\rangle_{FS} / \omega_\nu \,, \quad (3)$$

in terms of the density of states per spin (in the normal state) and the average over the (normal state) Fermi surface (FS) of the electron-phonon matrix element squared. Since (in the BCS limit) scattering only occurs when the phonon-energy ω exceeds the gap 2Δ, the self-energy is real for $\tilde{\omega} < 1$. Moreover, since the interaction between the phonon and the gap-excitation makes them repel in energy, phonons with $\omega < 2\Delta$ soften ($f < 0$), and phonons with $\omega > 2\Delta$ harden (Re $f > 0$). From Eq. (2) it is easy to see that $f \to -1$ for $\tilde{\omega} \ll 1$, that $f \to -\infty$ for $\tilde{\omega} \to 1_-$, that $f \to +1 - i\infty$ for $\tilde{\omega} \to 1_+$, and that $f \to 0_+$ for $\tilde{\omega} \gg 1$. This means, that a low-frequency phonon softens by the relative amount λ_ν and that a phonon with frequency just above the gap hardens by the relative amount λ_ν. This only holds in the BCS limit. In the strong-coupling limit, the universal function $f(\tilde{\omega})$ now depends explicitly on T/T_c and on the impurity scattering time τ. The plots of $\Pi/N(0) \equiv 2f(\tilde{\omega})$ given, for instance, in Figs. 5 and 6 of Ref. 17b show a smearing of the BCS inverse-square-root singularity at $\tilde{\omega} = 1$, and a linewidth broadening also for $\tilde{\omega} < 1$. The softenings and broadenings are weakened. Impurity scattering makes the softening smaller than λ_ν for $\tilde{\omega} \leq 0.8$, and vanish for $\tilde{\omega} = 0$.

We obtained the electron-phonon coupling constants, Eq. (3), from an LDA frozen-phonon calculation[6] for the five Raman-active A_g $q = 0$ modes in $YBa_2Cu_3O_7$. This calculation consisted of 29 different self-consistent band-structure calculations corresponding to different A_g displacement patterns, $d(z_{Ba}, z_{Cu2}, z_{O2}, z_{O3}, z_{O4})$. The total energies, E, were fitted by the quadratic polynomial in the five variables, plus two cubic terms to account for a somewhat anharmonic coupling between the plane oxygen (O2 and O3). The eigenvectors, e_{ν_i}, of the full dynamical matrix $\partial^2 E/(\partial z_i \partial z_j \sqrt{M_i M_j})$, were used together with the energy bands ε_k relative to the Fermi energy to yield the self-consistently screened electron-phonon matrix elements $g_{\nu kk} = \sum_i (\partial \varepsilon_k / \partial z_i) e_{\nu_i} / \sqrt{(2\omega_\nu M_i)}$. These were evaluated at 147 k-points in the 1/8 Brillouin zone and, finally, integrated over the Fermi surface (for the equilibrium structure) using tetrahedral linear interpolation. The calculated frequencies for the 340 and 440-cm^{-1} modes were 335 and 400 cm^{-1}, respectively. As expected from Raman measurements,[10,13] these modes were found to be, respectively, out-of-phase and in-phase vertical movements of the plane oxygens. If the symmetry had been tetragonal, the first mode would have B_{1g} symmetry and the latter A_{1g} symmetry.[13] Now, the presence of the chain oxygen lowers the symmetry to orthorhombic and caused in the calculation a 20% mixing of the B_{1g} and A_{1g} tetragonal modes. As a result, the O3-atoms (above O1) vibrated more than the O2-atoms in the 440 cm^{-1}-mode, and the O2-atoms more than the O3-atoms in the 340 cm^{-1}-mode. In addition, the 440 cm^{-1}-mode was found to have 20% by-mixing of apical oxygen (O4).

The calculated coupling constants were:

$$\lambda_{340} = 0.02 \quad \text{and} \quad \lambda_{440} = 0.01 \,. \quad (4)$$

There are two reasons why $\lambda_{340} > \lambda_{440}$. The first is, simply, that λ_ν scales like $1/\omega_\nu^2$. The second reason is the approximate full symmetry (A_{1g}) of the 440 cm^{-1}-mode. In fact, Zeyher and Zwicknagl had argued, that self-energy effects for A_{1g} modes are zero, and had seen this as the reason why only the 340-cm^{-1} mode, which is the only non-A_{1g} mode of the five modes observed, showed self-energy effects in the Raman experiments. This is an oversimplification. Since λ_ν is the integral over the Fermi surface of the deformation potential squared $(\varepsilon'_{\nu k})^2$, it can only vanish if $\varepsilon'_{\nu k}$ vanishes at all points of the FS, that is, if the *shape* of the *adiabatic* FS does not change with the deformation. This is, for instance, the case for a one-band model with cylindrical symmetry because due to particle conservation, the Fermi level moves with the band. Now, the undeformed FS has the full crystal symmetry and, if deformation conserves this symmetry, the adiabatic FS can only deform little, because its volume must be conserved. This deformation is, however, not zero in general. For a deformation of *low* symmetry, the deformation of the adiabatic FS is, however, only constrained by this low symmetry. There is therefore a tendency for low-symmetry modes to have larger electron-phonon coupling constants. We should point out that the coupling constants for these modes are non-zero only for buckled CuO_2 planes. This may explain why the self-energy effects have not been observed for the corresponding vibrations in superconductors with flat CuO_2 planes (e.g. Tℓ and Bi families).

Zeyher and Zwicknagl had pointed out that a hardening should occur for phonons with energies just above the gap but, until now, this had not been observed, presumably because those phonons were all fully symmetric.

Our new experimental results for the 440 cm^{-1}-mode in $RBa_2Cu_3O_{7-\delta}$ fall in the range of predicted hardening. Furthermore, we have analyzed systematically the region of negative and positive self-energy by varying the phonon frequency. Exchanging lanthanides and the oxygen isotope we were able to determine systematic dependences of the self-energy on phonon frequency. Comparison with Zeyher and Zwicknagl's theory allows us to confine the gap to a narrow range of energies

and to infer an upper limit to the impurity scattering rate. The observed self-energy shifts agree quantitatively with the predictions of the theory using the LDA coupling constants Eq. (4).

Light-scattering experiments were performed on ceramic samples of $RBa_2Cu_3O_{7-\delta}$ (R = Eu, Sm, Tm, Y) and on a 90% isotope exchanged ($^{18}O \leftrightarrow {}^{16}O$, R = $Y(^{18}O)$ and $Y(^{16}O)$) sample. The oxygen content was monitored by thermogravimetry: $\delta \approx 0$ for all samples, which is an important point since the effects we study are sensitive to δ.[20] Transition temperatures were >90 K for all samples. A beam of 3 mW average power (wavelength = 5145 Å) was focussed to a point (~ 30 μm diameter) on the sample. Backscattered light, collected by a 50 mm f/1.4 lens was focussed onto the entrance slit of a DILOR xy triple monochromator with 1800 lines/mm holographic gratings and a charge-coupled device detector. No influence on the peak frequencies was noticed between 10 and 50 K when further reducing the exciting power thus ensuring that we obtained maximal shifts near 10 K.

In Fig. 1 we show the frequencies of the 340 and 440 cm^{-1} modes of $RBa_2Cu_3O_{7-\delta}$, R = Y (a) and R = Tm (b) as a function of temperature. We recognize the by now well known anomalous *softening* of the mode at 340 cm^{-1} by $\Delta\omega \simeq -8.0 \pm 0.5$ cm^{-1} for R = Y (We define here $\Delta\omega = \omega(T = 10\text{K}) - \omega(T = 90\text{K})$ from experimental peak frequencies ω_{max}; lattice anharmonicity effects are not significant in this region.) Also plotted in Fig. 1a) is the frequency of the 440 cm^{-1}-mode which shows substantial *hardening* below T_c compared to the rather continuous behavior between 300 K and T_c. The hardening amounts to $\Delta\omega = +4.0 \pm 0.5$ cm^{-1}, which is a new result. It is seen even more clearly in Fig. 1b) for R = Tm where it amounts to $\Delta\omega = +5.5 \pm 0.5$ cm^{-1}, nearly equal in magnitude to the softening of the mode at 338 cm^{-1} with $\Delta\omega = -7.5 \pm 0.5$ cm^{-1}. We have found similar frequency anomalies for the corresponding modes in R = Sm, Eu and $Y(^{18}O)$. The absolute magnitudes of the shifts vary and will be discussed below.

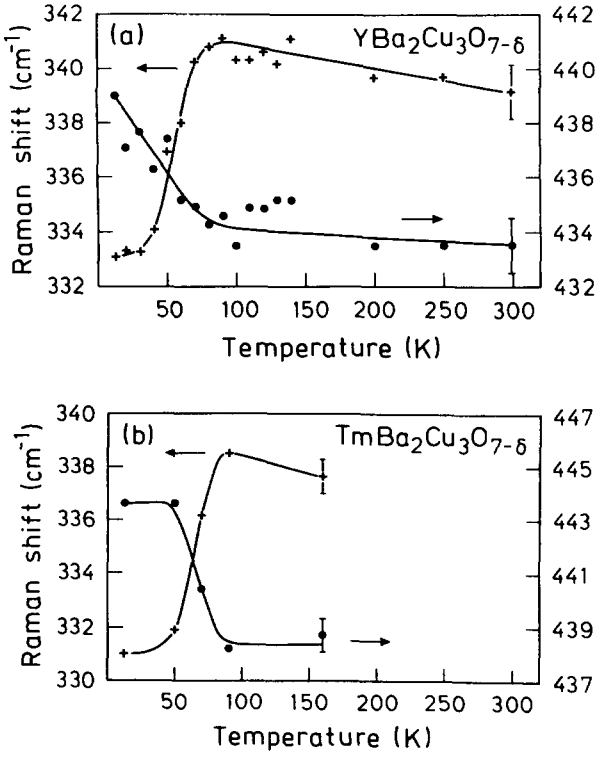

Fig. 1 Anomalous phonon-frequency hardening and softening measured in $RBa_2Cu_3O_{7-\delta}$ (a) R = Y, (b) = Tm. Note the discontinuities in the frequency changes below T_c.

In Fig. 2 we have plotted the relative experimental frequency shifts as a function of the eigenfrequency of a particular mode. In the case of the B_{1g}-like mode we used the *bare* phonon frequencies $\omega_\nu = \omega_{max} - \gamma/q$ as obtained by fits to Fano lineshapes, q being the asymmetry parameter[13]; the A_{1g}-like modes were fitted to a Lorentzian. Two groups of data points are seen; positive shifts come from the A_{1g}-like mode, negative ones from the B_{1g}-like mode with frequencies ω_ν depending roughly linearly on the ionic radius of the rare earth[21,22] [ω (T = 90 K) = 308.8 and 437.2 cm^{-1}, $\Delta\omega/\omega$ = −0.81 and 0.34% (Eu)[23]; 322.8 and 416.8 cm^{-1}, $\Delta\omega/\omega$ = −1.75 and 0.55% ($Y^{18}O$); 323.4 and

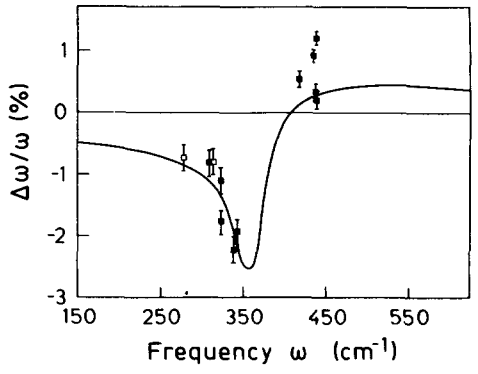

Fig. 2 Experimental (squares) and theoretical (curve) phonon self-energies (real part) in the $RBa_2Cu_3O_{7-\delta}$ system. Plotted is the relative shift in per cent vs. the phonon frequency ω (T = 90 K) for R = Eu, Sm, Tm, $Y^{16}O$, and $Y^{18}O$. The full squares are from this work, the open squares are ir-active modes from Ref. 11. The parameters taken for the theoretical curve were $2\Delta = 333$ cm^{-1}, $\tau^{-1} = 2\Delta$, and $\lambda = 0.02$.

438.6 cm^{-1}, $\Delta\omega/\omega = -1.1$ and 0.21% (Sm); 341.6 and 438.2 cm^{-1}, $\Delta\omega/\omega = -2.22$ and 1.23% (Tm); 344.2 and 434.6 cm^{-1}, $\Delta\omega/\omega = -1.93$ and 0.94% ($Y^{16}O$)]. Two infrared-active B_{1u} modes[12] at $\omega = 278$ and 314 cm^{-1} are also plotted. The qualitative features of the data points are increasingly negative shifts for increasing phonon frequency followed by a sudden jump towards positive shifts. Crudely speaking, we are tuning the unrenormalized phonon frequency through the region of the superconducting energy gap which may be assumed to be the same for all these materials (they have the same T_c). The curve is the result of strong-coupling theory[18] with the parameters: $2\Delta = 333$ $cm^{-1} = 5.2\ k_BT_c$ and $\tau^{-1} = 2\Delta$. For simplicity, *one* coupling constant, $\lambda = 0.02$, was taken. The curve follows the experimental points rather well. One might have obtained a fit of similar quality by using the mode-dependent λ-values, Eq. (4), together with $2\Delta = 360$ cm^{-1} and $\tau^{-1} = 0$. It seems impossible to get the theoretical curve to pass through both sets of data points around 440 cm^{-1}, unless one is willing to use mode-dependent gaps: $2\Delta_{340} \approx 340$ cm^{-1} and $2\Delta_{440} \approx 430$ cm^{-1}. For a gap which is not constant over the Fermi surface, this is in principle possible. Finally, we should note that the imaginary part of our self-energy is in accord with the 1.2% linewidth increase found by Cooper et al. for the 340-cm^{-1} mode and with the absence of a linewidth increase which our data show for ω_ν further away from the gap (R = Eu).[23]

An important qualitative consequence of the experiment is the fact that the gap is between ≈ 310 and ≈ 420 cm^{-1} independently of any concrete theoretical model, as long as the described physical mechanism is supposed. It *does not* necessarily mean that the electron-phonon coupling is the cause for electron pairing, but suggests that a BCS-like state is realized in the high-T_c superconductors. If all other modes couple to the electrons as strong as these two zone-center phonons, λ_{tot} would be around 0.6, which is definitely not enough to provide $T_c = 92$ K and a gap of $5.2\ k_BT_c$.

In conclusion, we have reported an experimental verification of a strong-coupling theory for high-T_c superconductors $RBa_2Cu_3O_{7-\delta}$. Positive and negative experimental phonon self-energies induced by superconductivity fall on a universal curve when the phonon energy is tuned in the gap region. We have determined the electron-phonon coupling constants from *ab initio* calculations and used them to compare the experimental results to solutions of the Eliashberg equations obtained by Zeyher and Zwicknagl. For a single gap of $2\Delta/k_BT_c = 5.2$ the experimental self-energies are reproduced quite accurately.

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