SPECTROSCOPY OF INFRARED-ACTIVE PHONONS IN HIGH-TEMPERATURE SUPERCONDUCTORS

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For a large variety of superconducting materials both experimental and theoretical lattice dynamical studies have been performed to date. The assignment of the observed infrared- and Raman-active phonon modes to the particular lattice eigenmodes is generally accepted (for a reviews see Ref. [1-5]). We will concentrate here upon the analysis of the changes of the infrared-phonon parameters (frequency and linewidth) upon entering the superconducting state which, as will be shown, may provide information on the magnitude of the superconductivity-related gap and its dependence on the superconducting transition temperature T_c.

Effects of the superconductivity-induced infrared-phonon renormalization were studied experimentally most intensively for $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$ (n = 0, 1, and 2) superconductors with a double CuO_2-layer in each primitive cell. An interesting feature of the materials with single-CuO chains as structural element (n = 0 and 1) is the possibility to gradually modify their superconducting properties by varying the oxygen content; this allows to study the effects of a reduced T_c in detail even for materials of the same crystallographic structure. For n = 2, however, the presence of the double-CuO chains fixes the oxygen content and, correspondingly, T_c. Another possible way to investigate the effects of phonon renormalization and their connection to superconductivity is to study ion-substituted superconductors knowing the effects of the ions on the superconducting properties of materials from independent measurements.

Superconductivity-induced phonon self-energy effects or so called phonon anomalies were found rather soon after discovery of YBCO superconductors [6, 7]. For a number of reasons they were studied most intensively by means of Raman spectroscopy mainly because the sample requirements are easier to fulfill for Raman then for infrared spectroscopy or neutron-scattering experiments. Pronounced changes (up to 10 cm^{-1}) of the frequencies and the linewidths of the oxygen-related mode at about 340 cm^{-1} were found upon cooling below the superconducting transition temperature (note that even larger effects have been reported for the $Tl_2Ba_2Ca_2Cu_3O_{10}$ superconductor [8]). It is clear qualitatively
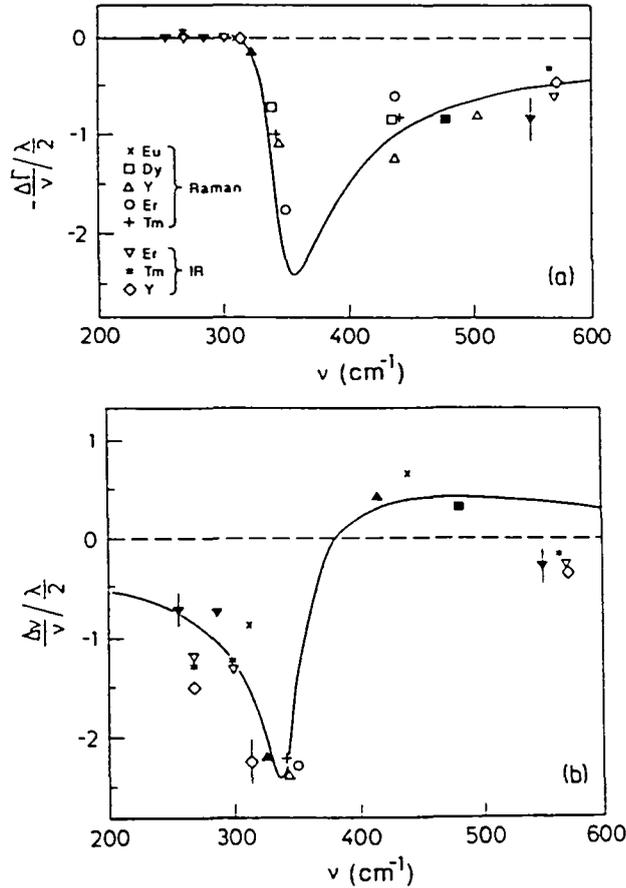
Figure 1: Calculated (after Zeyher and Zwicknagl [10]) imaginary (a) and real (b) parts of the phonon self-energies for a superconducting energy gap at $2\Delta = 316$ cm^{-1} and an impurity scattering rate $1/(2\Delta\tau) = 1$ (solid lines). Points are the experimental data (after Ref. [11-15] for Raman- as well as infrared-active (after Ref. [16]) phonons. Open points refer to ^{16}O and full - to ^{18}O substituted materials.

that if the phonon energy $h\nu_{ph}$ is larger than the magnitude of a given superconducting gap 2Δ, one expects an additional broadening of the phonon at low temperatures because new decay channels appear due to the possibility to break a superconducting pair. When $h\nu_{ph} < 2\Delta$ one expects, on the other hand, the phonon to narrow because of the reduction in the density of states in the gap and hence in the number of decay channels. At the same time phonons exhibit frequency hardening or softening depending on their position relative to the superconductivity-related gap. Of course, phonons with energies close to the gap value 2Δ should react most sensitively to the transition from normal to the superconducting state. For even-parity Raman-active phonons all the features mentioned above were calculated quantitatively by Zeyher and Zwicknagl [9, 10] in the framework of weak BCS as well as conventional strong-coupling theory.

In Fig. 1 experimental results are shown for the superconductivity-induced changes of the phonon linewidth (a) and frequency (b) for single-chain YBa$_2$Cu$_3$O$_7$, i.e., changes of the phonon parameters ($\Delta\Gamma$ and $\Delta\nu$ between T$_c$ and T $\approx$ 0). The solid lines in the figure are the results of the calculations under the assumption of a single isotropic gap. The only adjustable parameter in these calculations (except, of course, of the magnitude of the superconducting gap 2Δ which was assumed to be 316 cm^{-1} $\approx$ 39.5 meV in Fig. 1) is the electron-phonon coupling constant which from the comparison of theoretical and experimental results was found to be 0.01-0.02 for the phonon branch. These values are in good

agreement with LMTO *ab-initio* calculations.

Note again that calculations presented in Fig. 1 were done for Raman-active modes. It is interesting that the self-energy effect of the odd-parity infrared-active modes could also be described by those calculations despite of the fact that for even-parity excitations different transitions are involved in the electron-phonon interaction (including intraband transitions). So, the superconductivity related gap and even the electron-phonon coupling constants seem to be rather similar for Raman- and infrared-active modes in $YBa_2Cu_3O_7$ [16]. The only infrared data points which do not fit into the general picture are the frequency variations of the high-frequency apical oxygen vibration at about 600 cm^{-1}: this mode exhibits a frequency softening in the superconducting state instead of the predicted hardening (see Fig. 1,b). It was shown recently, however, that this specific feature could consistently be explained theoretically by taking into account the interplane charge fluctuations of the double-plane system [17, 18].

Careful experimental investigations of various superconducting materials revealed a strong dependence of the superconductivity-induced phonon self-energy effects in $YBa_2Cu_3O_{7-\delta}$ on the oxygen content δ and the presence of impurities even for the samples within the so called 90K-plateau (see, e.g., Ref. [19, 20]). It is advantageous in this sense to investigate also the double-chain $YBa_2Cu_4O_8$ superconductor which is known to have an essentially fixed oxygen content because of the presence of the double CuO-chains.
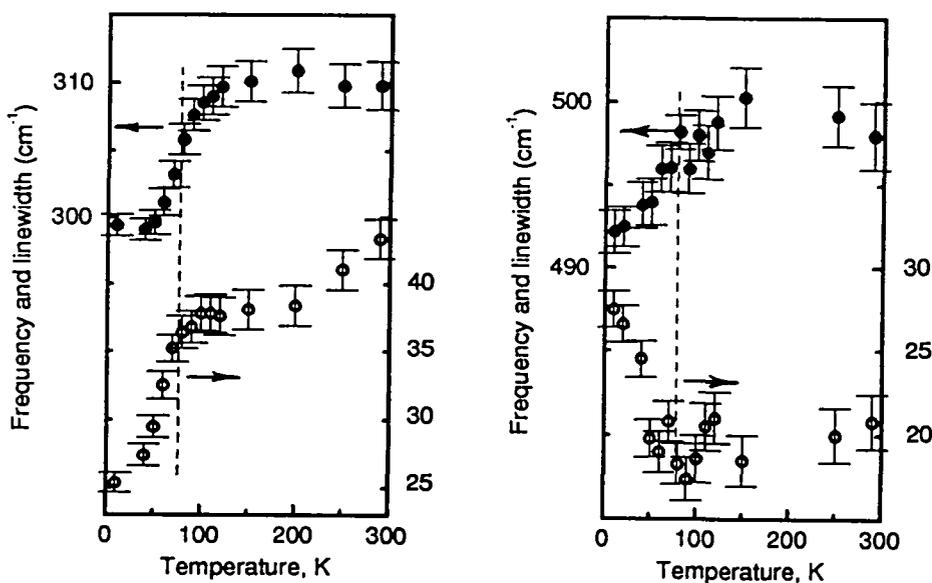

Figure 2: Temperature dependences of the frequencies (solid points) and linewidths (open points) of two oxygen-related modes of the double-chain $YBa_2Cu_4O_8$. The dashed vertical lines mark the T_c (after [25]).

It was found that the self-energy effects experienced by the $B_{1u}(z)$ infrared-phonons of the double-chain $YBa_2Cu_4O_8$ are rather similar to those observed

for the single-chain $YBa_2Cu_3O_{7-\delta}$ and discussed above [21-23]. In Fig. 2 data are presented for the frequency and linewidth variation upon cooling of two phonon modes: the plane-oxygen vibration at 300 cm^{-1} and also the CuO-chain mode [24] at about 500 cm^{-1}. A pronounced narrowing of the former upon cooling below T_c and a broadening of the latter yielded boundaries for the magnitude of the superconducting gap: 310 $cm^{-1} \leq 2\Delta \leq 497$ cm^{-1} [22]. Note that similar to the single-chain $YBa_2Cu_3O_{7-\delta}$ a frequency softening of the high-frequency mode is evident. Remarkably, for both modes shown in Fig. 2 the softening starts at temperatures well above T_c – a fact which is still under discussion and may be related to the opening of the spin-related gap above T_c in *underdoped* superconductors (see [1, 26] and references cited therein).
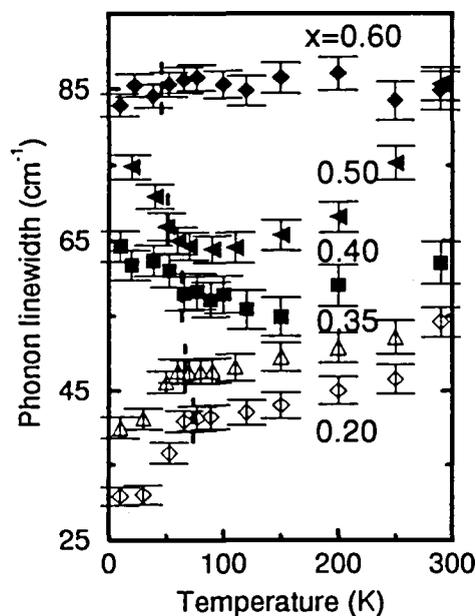

Figure 3: Temperature dependence of the full linewidth at the half-maximum of the plane-oxygen phonon of $(Pr_xY_{1-x})Ba_2Cu_4O_8$ superconductors with frequency about 300 cm^{-1}. The curves from top to bottom are offset vertically by 45, 25, 15, 10, and 0 cm^{-1}. The dashed vertical lines mark the T_c for each sample (after Ref. [27]).

Investigations of T_c-reduced (Pr- and Zn-substituted) double-chain $YBa_2Cu_4O_8$ yielded more information on the superconducting gap. Some of the results for $(Pr_xY_{1-x})Ba_2Cu_4O_8$ are shown in Fig. 3. A narrowing upon cooling of the phonon at 300 cm^{-1} for all materials with Pr-content $x < 0.35$ signals the presence of the gap at higher energies. For higher Pr-contents this mode starts to broaden below T_c. This has been interpreted as a result of the creation of a new decay channel for the plane-oxygen phonon and experimental evidence for the shift of the corresponding gap to lower energies across the phonon frequency [27].

Qualitatively similar results as regards to the effect of the reduction of T_c on the infrared-phonon self-energies were observed in the case of Zn-substituted $YBa_2Cu_4O_8$ [28]. An important experimental finding is that for both Pr- and Zn-

substitute different ions within the crystallographic structure) differs by factor of ten. As a comparison, there is no effect on the self-energies in the case of Sr substitution for Ba within a rather wide range of concentrations, which also does not influence the superconducting temperature T_c. All these facts provide convincing evidence that the discussed effects of the infrared-active phonon of $Y_2Ba_4Cu_{6+n}O_{14+n-\delta}$ are indeed superconductivity related.

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