Anomalies of the infrared-active phonons in underdoped YBCO

as an evidence for the intra-bilayer Josephson effect

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The spectra of the far-infrared $c$-axis conductivity of underdoped YBCO crystals exhibit dramatic changes of some of the phonon peaks when going from the normal to the superconducting state. We show that the most striking of these anomalies can be naturally explained by changes of the local fields acting on the ions arising from the onset of inter- and intra-bilayer Josephson effects.

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The essential structural elements of the high-$T_c$ superconductors are the copper-oxygen planes which host the superconducting condensate. Many experiments, and also some theoretical considerations, suggest that these planes are only weakly (Josephson) coupled along the $c$ direction. Studies of the $c$-axis transport and those of the microwave absorption revealing Josephson plasma resonances, have established that Josephson coupling indeed takes place for planes (or pairs of planes) separated by insulating layers wider than the in-plane lattice constant.

It is not fully understood why the coupling is so weak and it is debated whether this is related to the unconventional ground state of the electronic system of the planes causing a charge confinement and/or to the properties of the insulating layers. In this context, it is of interest to ascertain whether the closely-spaced copper-oxygen planes of the so-called bilayer compounds, like YBa$_2$Cu$_3$O$_y$, are also weakly (Josephson) coupled.

In this paper we show that the far-infrared spectra of the $c$-axis conductivity of underdoped YBa$_2$Cu$_3$O$_y$ with $6.4 \leq y \leq 6.8$ may provide a key for resolving this interesting issue. The spectra exhibit, beside a spectral gap that shows up already at temperatures much higher than $T_c$, two pronounced anomalous features. Firstly, at low temperatures a new broad absorption peak appears in the frequency region between 350 cm$^{-1}$ and 550 cm$^{-1}$. The frequency of its maximum increases with increasing doping; for optimally doped samples this feature disappears. Secondly, at the same time as the peak forms, the infrared-active phonons in the frequency region between 300 cm$^{-1}$ and 700 cm$^{-1}$ (in particular their strength and frequency) are strongly renormalized. This effect is most spectacular for the oxygen bond-bending mode at 320 cm$^{-1}$, which involves the in-phase vibration of the plane oxygens against the Y-ion and the chain ions. For strongly underdoped YBa$_2$Cu$_3$O$_{6.5}$ with $T_c \sim 50$ K, this mode loses most of its spectral weight and softens by almost 20 cm$^{-1}$. Although the additional peak, and the related changes of the phonon peaks (phonon anomalies), start to develop above $T_c$, there is always a sharp increase of the peak magnitude below $T_c$. Similar effects have also been reported for several other underdoped bilayer compounds (see, e.g., Refs. [4,12]) and for hole-doped ladders in Sr$_{14-x}$Ca$_x$Cu$_{24}$O$_{41}$ [13].

Van der Marel et al. have suggested that the additional peak around 450 cm$^{-1}$ could be explained using a phenomenological model of the dielectric response of superlattices with two superconducting layers (a bilayer) per unit cell. The model involves two kinds of Josephson junctions: inter-bilayer and intra-bilayer. As a consequence, the model dielectric function exhibits two zero crossings corresponding to two longitudinal plasmons: the inter-bilayer and the intra-bilayer one. In addition, it exhibits also a pole corresponding to a transverse optical plasmon. Van der Marel et al. pointed out that the additional peak in the spectra of underdoped YBCO may just correspond to the latter plasmon. Very recently, they have confirmed their suggestion by more quantitative consideratios regarding the doping dependence of the peak position [14]. The details of the spectacular anomaly of the 320 cm$^{-1}$ phonon mode, however, cannot be explained within the original form of their model.

In the following we report a theoretical analysis of the additional peak and the phonon anomalies. We have extended the model of van der Marel et al. by including the four phonons at 280, 320, 560, and 630 cm$^{-1}$ in such a way that the extended model can account not only for the peak but also for the most striking phonon anomalies. The important new feature is that we take into account local electric fields acting on the ions participating in the above mentioned phonon modes. As we show below, the phonon anomalies are then simply due to dramatic changes of these local fields as the system becomes superconducting.

Let us briefly introduce the model. The dielectric function is written as

$$
\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \frac{i}{\omega - \omega_0} \sum_n \frac{j_n(\omega)}{E(\omega)},
$$

where $\varepsilon_\infty$ is the interband dielectric function at frequencies somewhat above the phonon range, $j_n$ are the induced currents, $\langle \rangle$ means the volume average, and $E$ is the average electric field along the $c$-axis.
The following currents have to be taken into account: the Josephson current between the planes of a bilayer, $j_{bl} = -i \omega \varepsilon_0 \chi_{bl} E_{bl}$, the Josephson current between the bilayers, $j_{int} = -i \omega \varepsilon_0 \chi_{int} E_{int}$, the current due to the oxygen bending mode at 320 cm$^{-1}$, $j_P = -i \omega \varepsilon_0 \chi_P E_{loc P}$, and the current due to the other three infrared-active modes involving vibrations of ions located between the bilayers (apical oxygens and chain atoms), $j_A = -i \omega \varepsilon_0 \chi_A E_{loc A}$. Here

$$
\chi_{bl} = \frac{\omega_{bl}^2 - \omega^2 - i \omega \gamma_{bl}}{\omega^2}, \quad \chi_{int} = \frac{\omega_{int}^2 - \omega^2 - i \omega \gamma_{bl}}{\omega^2},
$$

$$
\chi_P = \frac{S_P \omega_P^2}{\omega_P^2 - \omega^2 - i \omega \gamma_P}, \quad \chi_A = \sum_{\nu=1}^{3} \frac{S_\nu \omega_\nu^2}{\omega_\nu^2 - \omega^2 - i \omega \gamma_\nu}
$$

are the susceptibilities that enter the model. The plasma frequencies of the intra-bilayer and the inter-bilayer Josephson plasmons are denoted as $\omega_{bl}$ and $\omega_{int}$, respectively. We do not attribute any physical interpretation to the Lorentzian terms in Eq. (2) that are designed solely to account for the finite range of interest (i.e., from 200 cm$^{-1}$ to 700 cm$^{-1}$) in a Kramers-Kronig consistent way. The response of the phonons is described by Lorentzian oscillators as usual. Further, $E_{bl}$ is the average electric field inside a bilayer, $E_{int}$ is the average electric field between neighbouring bilayers, $E_{loc P}$ is the local field acting on the plane oxygens, and $E_{loc A}$ is the local field acting on the ions located between the bilayers. Note that by identifying $E_{loc P}$ with the field acting on the plane oxygens we have neglected the contributions of the other ions involved in the phonon (the Y-ion and the chain ions). This seems to be a reasonable approximation, since the contribution of the plane oxygens to the 320 cm$^{-1}$ mode is known to be dominant.

The electric fields $E_{bl}$, $E_{int}$, $E_{loc P}$, and $E_{loc A}$ can be obtained using the following set of equations:

$$
E_{bl} = E' + \frac{\kappa}{\varepsilon_0 \varepsilon_\infty} - \frac{\alpha \chi_P E_{loc P}}{\varepsilon_\infty},
$$

$$
E_{int} = E' - \frac{\beta \chi_P E_{loc P} + \gamma \chi_A E_{loc A}}{\varepsilon_\infty},
$$

$$
E_{loc P} = E' + \frac{\kappa}{2 \varepsilon_0 \varepsilon_\infty},
$$

$$
E_{loc A} = E',
$$

$$
- i \omega \kappa = j_{int} - j_{bl},
$$

$$
E(d_{bl} + d_{int}) = E_{bl} d_{bl} + E_{int} d_{int}
$$

containing two additional variables, $\kappa$ and $E'$. The former represents the surface charge density of the copper-oxygen planes which alternates from one plane to the other whereas $E'$ is the part of the average internal field $E$ that is not due to the effects of $\kappa$, $\chi_P$ and $\chi_A$. The terms in Eqs. (4) and (6) containing $\kappa$ represent the fields generated by charge fluctuations between the planes. The terms in Eqs. (4) and (5) containing the phonon susceptibilities represent the fields generated by the displacements of the ions. The values of the numerical factors $\alpha$, $\beta$, and $\gamma$ (1.8, 0.8, 1.4) have been obtained using an electrostatical model. While the feedback effects of the phonons on the electric fields have to be included in order to obtain the observed softening of the oxygen bending mode, they are not essential for explaining the spectral-weight anomalies. Equation (8) guarantees charge conservation. The distances between the planes of a bilayer and between the neighbouring bilayers are denoted by $d_{bl}$ ($d_{bl} = 3.3$ Å) and $d_{int}$ ($d_{int} = 8.4$ Å), respectively.

Figure 1(a) shows the experimental spectra of the $c$-axis conductivity of YBa$_2$Cu$_3$O$_{6.5}$ with $T_c = 53$ K from Ref. 14. Figures 1(b), 1(c), and 1(d) show the data for (b) $T = 300$ K, (c) $T = 75$ K and (d) $T = 4$ K together with the fits obtained by using the model explained above.

The values of the parameters used are summarized in Table 1. Those used in computing the room-temperature spectrum have been obtained by fitting the measured complex dielectric function from Ref. 14 (with $\omega_{bl} = 0.0$ and $\omega_{int} = 0.0$). Those used in calculating the 4 K spectrum have also been obtained by fitting the data, except for $\varepsilon_\infty$, $\omega_P$, and the oscillator strengths of the phonons ($S_P$, $S_1$, $S_2$, $S_3$) which have been fixed at the room-temperature values. The appearance of the additional peak and the anomalies already at temperatures higher than $T_r$ may be caused by pairing fluctuations within the bilayers. Motivated by this idea, we have fitted the 75K spectra in the same way as the 4K ones allowing only the upper plasma frequency ($\omega_{bl}$) to acquire a nonzero value. We shall comment on this point below. Note that the low-temperature value of $\omega_{int}$ (220 cm$^{-1}$) is rather close to the one obtained from reflectance measurements (204 cm$^{-1}$ in Ref. 19) and that the screened value of $\omega_{bl}$ ($\sim 500$ cm$^{-1}$) falls into the frequency region of a broad peak in the loss function (Im(1/\varepsilon)) 15, which is a signature of a longitudinal excitation.
The values of the phonon frequencies are somewhat different from those which would result from a usual fit of the data (such as in Refs. [13][22][23]). This is because the susceptibilities of Eq. (3) represent response functions with respect to the local fields instead of the average field. In the absence of interlayer currents, the input frequencies would correspond to the TO-frequencies while the frequencies renormalized according to Eqs. (4)-(9) would correspond to the LO-frequencies instead of the average field. Our input frequency of the oxygen bending mode. It reproduces successfully: (i) the appearance of the additional peak, its position, broadening and magnitude; (ii) the loss of the spectral weight of the peak corresponding to the oxygen-bending mode and the pronounced softening of this mode; (iii) the loss of the spectral weight of the peaks corresponding to the apical oxygen modes at 550 cm\(^{-1}\) and 630 cm\(^{-1}\) and the increase of their asymmetry. The intrinsic frequencies of the latter modes have to be slightly increased in order to reproduce the noticeable hardening of these modes. The dotted lines in Figures 1(b), 1(c) and 1(d) represent the results obtained after omitting the phonons in the fitted expressions \(S_P = S_1 = S_2 = S_3 = 0.0\). It appears that the plasmon peak collects the lost part of the normal-state spectral weight of the phonons. This, however, only accounts for a part of its spectral weight. In the absence of the phonons and for small values of the residual conductivities the spectral weight of the \(\delta\) peak at \(\omega = 0.0\) is \(S_\delta = (\pi/2)\xi_0(d_{bl} + d_{int})\omega_b^2\omega_{bl}^2/(d_{bl}^2\omega_{bl}^2 + d_{int}\omega_b^2)\) and the spectral weight of the additional peak is \(S_p = (\pi/2)\xi_0(d_{bl}d_{int}/(d_{bl} + d_{int}))\omega_{bl}^2/(d_{bl}\omega_{bl}^2 + d_{int}\omega_b^2)\). For the values of the two plasma frequen-
cies given in Table 1 we obtain $S_d = 1700 \Omega^{-1} \text{cm}^{-2}$ and $S_p = 10000 \Omega^{-1} \text{cm}^{-2}$. Note that both $S_d$ and $S_p$ belong to the spectral weight of the superconducting condensate. This should be taken into account in discussing the sum rules as, e.g., in Ref. [27].

Our model allows us to explain the decrease of the spectral weight of the phonons when going from the normal to the superconducting state by using rather simple qualitative arguments. Neglecting the feedback effects of the phonons and the residual electronic background (represented by the Lorentzians in Eq. (2)), the electric fields $E_{bl}$ and $E_{int}$ are given by:

$$E_{bl} = \frac{(d_{bl} + d_{int})\varepsilon_{int}}{d_{bl}\varepsilon_{bl} + d_{int}\varepsilon_{int}} E, \quad E_{int} = \frac{(d_{bl} + d_{int})\varepsilon_{bl}}{d_{bl}\varepsilon_{bl} + d_{int}\varepsilon_{bl}} E,$$

(10)

where $\varepsilon_{bl} = \varepsilon_{\infty} - \frac{\omega_{bl}^2}{\omega^2}$ and $\varepsilon_{int} = \varepsilon_{\infty} - \frac{\omega_{int}^2}{\omega^2}$. The low-temperature spectra of $\varepsilon_{bl}$ and $\varepsilon_{int}$ are shown as the solid lines in Fig. 2. In the frequency range of the oxygen bending mode, $\varepsilon_{bl}$ and $\varepsilon_{int}$ have opposite signs and similar magnitudes and the same holds for $E_{int}$ and $E_{bl}$. As a consequence, the local field acting on the plane oxygens, which equals the average of the two fields $E_{int}$ and $E_{bl}$ (cf. Eqs. (4), (5), and (6)), can become rather small. The frequency range of the modes of the apical oxygens is close to the zero crossing of $\varepsilon_{bl}$. Consequently, the local field acting on the apical oxygens, $E_{int}$, is rather small in this frequency region. It is the decrease of the local fields when going from the normal to the superconducting state which is responsible for the spectral weight anomalies. The room- and low-temperature spectra of $E_{loc. p}$ shown in Fig. 2 illustrate the above considerations.

![Figure 2](image-url)

**FIG. 2.** The approximate dielectric functions of the intra-bilayer and the inter-bilayer regions, $\varepsilon_{bl}$ and $\varepsilon_{int}$ defined in the text (solid lines). The room- and low-temperature spectra of the local field $E_{loc. p}$ acting on the plane oxygens (dashed and dotted lines).

Our model is also capable of explaining the experimentally observed doping dependence of the additional peak and the anomaly of the oxygen bending mode. As the doping increases the peak shifts towards higher frequencies and it becomes broader and less pronounced (see Fig. 10 of Ref. [11] and Fig. 3 of Ref. [11]). Both these trends can be easily understood. The first one is due to the progressive increase of the plasma frequencies with hole doping, which is related both to the increase of the condensate density and to the reduction of the charge confinement [14]. The second one is due to the fact that the broadening is proportional to the residual background conductivities which increase with increasing doping. In addition, the size of the spectral gap $(2\Delta_{\max})$ decreases with hole doping [14] and eventually falls below the energy of the transverse optical plasmon around optimum doping. The phonon anomaly appears in the same range of doping as the additional peak. For $y$ around 6.8, the spectral weight from the high-frequency side of the phonon peak moves into the additional peak (see Figs. 10 (a) and (b) of Ref. [11]) as the temperature is lowered. For $y$ around 6.6 we find the most pronounced anomaly (see the experimental data of Fig. 1). For even lower doping levels the additional peak and the phonon merge together forming a single highly-asymmetric structure (see Fig. 3 (d) of Ref. [11]). These trends can be understood using arguments similar to those presented above (see the discussion related to Fig. 2) and can be well reproduced using the model. This is demonstrated in Fig. 3 which displays the experimental spectra of the c-axis conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_y$ with (a) $y = 6.4 (T_c = 25 \text{K})$ and (b) $y = 6.8 (T_c = 80 \text{K})$ from Ref. [15] together with the fits (Fig. 3(c) and 3(d), respectively).

We discuss next the peculiar temperature dependence of the additional peak and the phonon anomalies. The proximity of the onset temperature of the anomalies and the onset temperature of the spin gap $(T^*)$ observed in nuclear magnetic resonance experiments has provoked several speculations [17, 12] that the anomalies are due to the coupling of the phonons to spin excitations. From the fact that we are able to fit the data for temperatures between $T_c$ and $T^*$ (see Fig. 1(c)) we infer that in this temperature-range the intra-bilayer plasmon is already developed. This suggests that many of the electronic and possibly also structural anomalies starting below $T^*$ (see, e.g., Ref. [24]) are caused by pairing fluctuations within the bilayers.

In summary, we have extended the phenomenological model of Van der Marel et al. involving inter-bilayer and intra-bilayer Josephson junctions by including phonons and local field effects.
FIG. 3. Experimental spectra of the c-axis conductivity of YBa$_2$Cu$_3$O$_y$ with (a) $y = 6.4$ ($T_c = 25$ K) and (b) $y = 6.8$ ($T_c = 80$ K) from Ref. [15]. (c) and (d) Fits of these spectra obtained by using the present model.

The model allows us to explain not only the additional broad peak around 450 cm$^{-1}$ but also the spectacular anomaly of the oxygen bending mode at 320 cm$^{-1}$ and the spectral weight anomalies of the apical oxygen modes at 550 and 630 cm$^{-1}$. Our results indicate that also the closely spaced copper-oxygen planes of underdoped bilayer cuprates are weakly (Josephson) coupled. These findings provide support for the conjecture [7] that the c-axis dynamics of the cuprates (at least the underdoped ones) is dictated by the unconventional properties of the ground state of the electronic system of the planes. We suggest that the onset of the anomalies at temperatures significantly higher than $T_c$ may be caused by pairing fluctuations within the bilayers.

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We have represented the ions by uniformly charged plane s perpendicular to the $c$-axis and expressed the additional electrical fields generated by the phonon displacements. The electrost atical calculations lead to expressions for the parameters $\alpha, \beta, \gamma$. The values of the charge densities of the planes have been estimated using the values of the effective ionic charges presented in Ref. [23]. In order to express the fields $E_{bd}$ and $E_{int}$, the boundaries between the intra- and inter-bilayer regions have to be specified. We have identified them with the charged planes corresponding to the oxygens. The use of this model may be partially justified by the fact that the electromagnetic skin depth is shorter than the wavelength, so that any pronounced cancellation of the fields generated by the phonons is not expected.

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