

Signatures of bilayer splitting in the c -axis optical conductivity of double layer cuprates

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We report on the infrared studies of the interlayer response for a series of $\text{YBa}_2\text{Cu}_3\text{O}_x$ high- T_c superconductors with Pr, Ni, and Zn dopants, as well as for the optimally doped crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$. These experimental results have motivated us to reexamine some of the long-standing issues in the interlayer electrodynamics of cuprates. Among them are the origins of the anomalous resonance specific to the conductivity of materials with more than one CuO_2 plane per unit cell, as well as the microscopic roots of the notorious “semiconducting” behavior seen in a variety of cuprates. Our data for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples indicate that the suppression of the superfluid density (and normal-state conductivity) with $\text{Y} \rightarrow \text{Pr}$ substitution occurs primarily due to changes in the electronic state of CuO_2 planes and not because of the fragmentation of Cu-O chains. We also show that the transverse Josephson plasma model proposed to explain the anomalous mode in the interlayer response is not fully consistent with the totality of the experimental data for double-layered materials. We discuss alternative/complimentary scenario assigning this feature of the c -axis conductivity to lifted degeneracy between bonding and antibonding bands associated with the two constituents of the CuO_2 bilayer (a so-called bilayer splitting effect).

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I. INTRODUCTION

Anomalous interlayer (c -axis) properties of high- T_c superconductors have been the focus of research ever since the first single crystals were synthesized.¹ Coexistence of “insulating” behavior seen in the c -axis resistivity with more conventional “metal-like” transport within the CuO_2 planes is one of the important indications for the breakdown of the Fermi-liquid theory in copper oxides.^{2,3} Closely related effects detected through the systematic examination of the interlayer infrared (IR) conductivity include the discoveries of the pseudogap⁴ and of the changes of the electronic kinetic energy.⁵⁻⁸ Yet another feature of the c -axis conductivity spectra, a broad resonance observed at $400\text{--}900\text{ cm}^{-1}$ only in bilayered systems,⁹⁻¹¹ has received a lot of attention re-

cently. The resonance has been interpreted in terms of the transverse Josephson plasmon enabled by two distinct types of interlayer barriers in cuprates with *two* CuO_2 planes per unit cell.^{12,13} An account of the changes in local electric fields that occur as a result of this effect permits accurate description of the exotic phonon features in the c -axis spectra.¹⁴ In this paper we report results for $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ ($\text{Bi}2212$), $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and for $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ samples doped with Ni and Zn. These data motivated us to revisit the issues pertinent to the differences between the interlayer conductivity of single- and double-layered high- T_c superconductors. In particular, we discuss a possible role of *bilayer splitting* in the formation of the unusual c -axis resonance. Possible relevance of the bilayer splitting effects to the interlayer electrodynamics was first analyzed by Chakraborty *et al.*¹⁵

This paper is organized in the following manner. In Sec. II we report on the experimental details of crystal preparation and reflectance measurements. Raw reflectivity data for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ single crystals are also discussed in this section. Section III is devoted to the analysis of the complex conductivity of Pr-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, as well as to the examination of the results for both Ni- and Zn-doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$. We also outline the common trends and distinctions in the interlayer response of cuprates with one and two CuO_2 layers per unit cell. Section IV is focused on one particular hallmark of the interlayer conductivity of double-layered high- T_c materials, namely the resonance occurring in the range between 400 cm^{-1} and 900 cm^{-1} , depending on doping regime. We first overview strengths and pitfalls of the Josephson transverse mode (JTM) interpretation of this resonance. Then we explore possible implications of the electronic structure of double-layered compounds in the development of the resonance anomaly. Conclusions and outlook are presented in Sec. V.

II. EXPERIMENT

We have investigated Pr substitution in YBCO series at two doping regimes: $\text{Pr}_{0.3}\text{Y}_{0.7}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($T_c=60\text{ K}$, $\Delta T_c=3\text{ K}$) and $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ($T_c=40\text{ K}$, $\Delta T_c=3\text{ K}$) grown at UCSD in ZrO_2 crucibles by the self-flux method. To optimize the oxygen content near $\delta=0.05$ value, the raw Pr-doped crystals were annealed at $420\text{--}450^\circ\text{C}$ for ten days in oxygen atmosphere. Details of crystal-growth method are described elsewhere.¹⁶ Temperature dependence of dc resistivity revealed a sharp transition to the superconducting state. Infrared measurements on these crystals have been carried out at UCSD. Individual crystals were less than $40\text{--}70\mu\text{m}$ thick and had typical in-plane dimensions of about 1 mm^2 . For the purpose of c -axis reflectance measurements we assembled a mosaic of several samples to achieve a total thickness of about 1 mm . The same procedure was used to investigate the interlayer response of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ crystals grown at CRIEPI. Single crystals of $\text{YBa}_2\text{Cu}_{2.997}\text{Zn}_{0.003}\text{O}_{6.6}$ and $\text{YBa}_2\text{Cu}_{2.99}\text{Ni}_{0.01}\text{O}_{6.6}$ have been studied at McMaster. The latter samples, grown at UBC, had typical dimensions $5\times 1\text{ mm}^2$ on the ac face. Larger area has allowed us to carry out IR measurements for individual crystals. Near normal incidence reflectance $R(\omega)$ was measured in the frequency range $20\text{--}48\,000\text{ cm}^{-1}$ ($\approx 2\text{ meV--}6\text{ eV}$) for Pr-doped compounds and in the range $20\text{--}8\,000\text{ cm}^{-1}$ for both Ni- and Zn-doped samples. To obtain the absolute value of $R(\omega)$ specimens were coated *in situ* with gold or aluminum in the optical cryostat and the spectra of the metal-coated sample were used as reference. This procedure yields reliable absolute values of $R(\omega)$ and minimizes the impact of diffuse reflectance in the case of mosaic samples.¹⁷

We first discuss the behavior of $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system. It is instructive to examine the gross features of the reflectivity data of these materials in the context of what is known about Pr-free counterparts: $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (Refs. 4 and 9). Figure 1 presents the raw reflectance data $R(\omega)$ for all four compounds. We show only spectra collected at room temperature, at $T=T_c$ and 10 K for

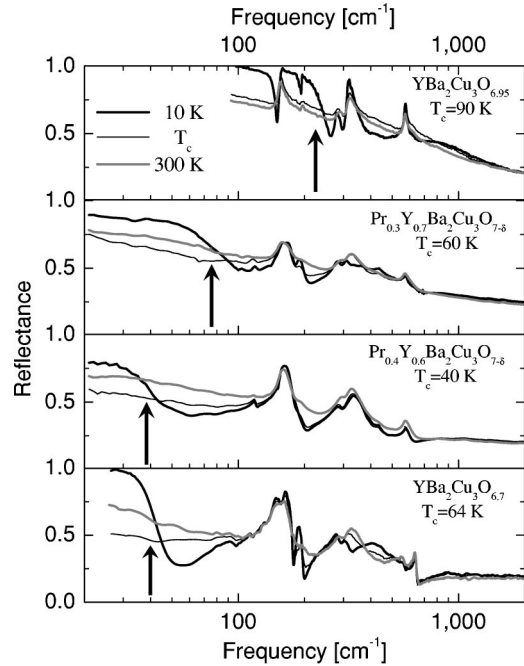


FIG. 1. Reflectance of $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ (from Ref. 9), $\text{Pr}_{0.3}\text{Y}_{0.7}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{Pr}_{0.4}\text{Y}_{0.6}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ (Ref. 9). Only room temperature T_c and 10 K data are shown. The arrows mark approximate position of the plasma edge in reflectance data at $T \leq T_c$.

clarity. The normal-state reflectance of all samples is dominated by optically active phonons in the region between 120 cm^{-1} and 700 cm^{-1} . Below this region there is a weak upturn towards $R \sim 1$ for $\omega \rightarrow 0$, expected for a rather poorly conducting system. The magnitude of $R(\omega, T_c)$ is the highest in the optimally doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ and has been shown to be systematically depressed with underdoping.^{9–11} This depression of the electronic background is apparent from a comparison of top and bottom panels in Fig. 1. Very similar effect can also be seen in the data for Pr-doped crystals: with increasing Pr content the electronic background in $R(\omega)$ is diminished and the phonon structure gains increasing prominence. At higher frequencies ($\omega > 700\text{ cm}^{-1}$) the reflectance is low (typically 20–25%) and shows little temperature and frequency dependence. In the superconducting state a plasma edge structure develops in the data for all crystals. Underdoping is known to suppress the ω position of the plasma edge.^{9,18} This trend is also followed by Pr-doped materials (Fig. 1). Thus a quick inspection of the raw $R(\omega)$ data indicates that the principal role of $\text{Y} \rightarrow \text{Pr}$ substitution is very similar to a reduction of carrier density through oxygen depletion of $\text{YBa}_2\text{Cu}_3\text{O}_x$.

III. INTERLAYER ELECTRONIC RESPONSE OF $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$

In order to quantitatively analyze the data we extracted the complex conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$ using Kramers-Kronig transformation of $R(\omega)$. Figure 2 shows the real part of the optical conductivity $\sigma_1(\omega)$ for all four compounds. Both Pr-doped samples reveal strongly reduced con-

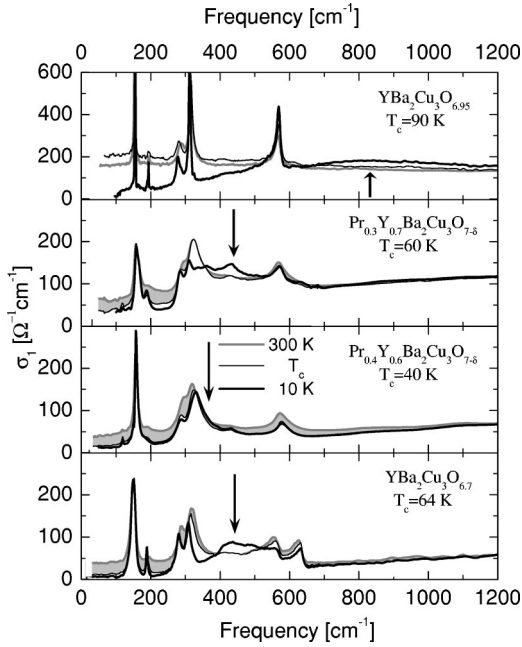


FIG. 2. The far-infrared optical conductivity $\sigma_1(\omega)$ extracted from the Kramers-Kronig analysis of reflectance data in Fig. 1. The arrows mark approximate position of the c -axis resonance. The gray areas represent the spectral weight that is removed from the low-frequency (pseudogap) region and transferred to higher frequencies, when lowering the temperature from 300 K to T_c .

ductivity compared to that of $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$. As temperature is lowered from room temperature to T_c , the conductivity of both Pr-doped crystals is suppressed with spectral weight shown in gray being transferred to high frequencies (beyond the cutoff of Fig. 2). This trend is characteristic of the c -axis response of cuprates in the pseudogap state. In fact, the functional form of the $\sigma_1(\omega)$ data in $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals is very similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ compound (bottom panel). An examination of the phonon modes in the data displayed in Fig. 2 readily confirms that the depressed electronic conductivity as well as signatures of the pseudogap state observed in Pr-doped crystals are *not* related to oxygen deficiency. Indeed, all oxygen-reduced $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples show a “double-peaked” phonon structure in the vicinity of 600 cm^{-1} . The phonon mode at 630 cm^{-1} is believed to be associated with the vibrations of apical oxygen neighboring an empty chain fragment, and is always found in oxygen-reduced $\text{YBa}_2\text{Cu}_3\text{O}_x$ samples.^{10,13,14} This well-established fact is exemplified in the bottom frame of Fig. 2. On the contrary, both Pr-doped materials studied here reveal only a 580 cm^{-1} mode similar to the peak seen in pristine $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$. This is consistent with the notion that both $\text{Pr} \rightarrow \text{Y}$ substitution and deoxygenation lead to substantial reduction of carrier density in the CuO_2 planes. Our findings parallel earlier ellipsometric results of Bernhard *et al.* (Ref. 19).

The superfluid density is also altered by Pr doping. To quantify this effect we have determined the plasma frequency of the superconducting condensate ω_s [related to the area under $\delta(0)$ peak in the $\sigma_1(\omega, 10\text{ K})$ spectra] from the

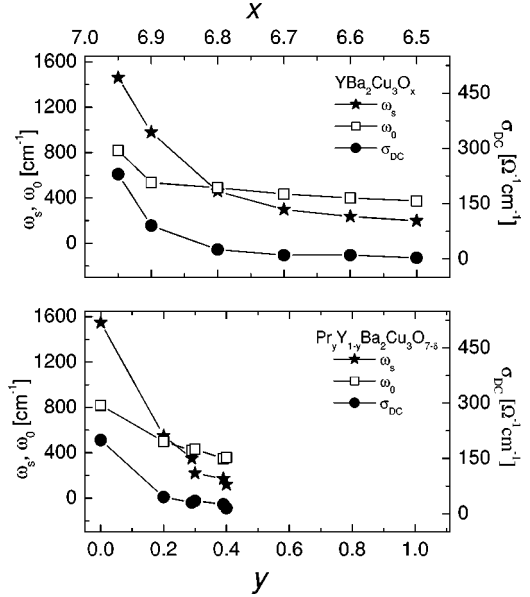


FIG. 3. The doping dependence of the superfluid density ω_s and of the frequency position of the c -axis resonance ω_0 (left axis) along with the doping dependence of $\sigma_1(\omega \rightarrow 0, T_c)$ (right axis). The top panel shows the data for $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Ref. 9) as a function of x , the bottom panel for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of y . The y range in the bottom panels corresponds to the x range in the top panel, as the effect of one oxygen atom is equivalent to the effect of two Pr atoms. The data for $y=0.3$ and 0.4 are from this work and for $y=0.2, 0.3$, and 0.4 from Ref. 19.

analysis of the imaginary part of the conductivity $\sigma_2(\omega)$, correcting the result for screening due to unpaired carriers, as described in Ref. 20. The data are summarized in Fig. 3 where we plot the doping dependence of ω_s and also of $\sigma_1(\omega \rightarrow 0, T \approx T_c)$. Since the doping effect of one oxygen atom is equivalent to the effect of two praseodymium atoms, the bottom panel is plotted over an extended doping range y that matches the doping range x in the top panel. Figure 3 shows that the depression of the electronic conductivity in $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals is accompanied by a rapid drop of the superconducting condensate density. A similar trend is universally found in cuprates and specifically in $\text{YBa}_2\text{Cu}_3\text{O}_x$ (Refs. 20 and 21).

Generally, suppression of both the interlayer conductivity and superconducting condensate in underdoped $\text{YBa}_2\text{Cu}_3\text{O}_x$ can be attributed to two separate processes. Indeed, in oxygen deficient samples either the suppression of carrier density within the CuO_2 planes or the reduction of hopping amplitude between the planes due to defects in the chain layer can in principle result in decline of both $\sigma_1(\omega)$ and ω_s . The data for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ lead us to a surprising conclusion: destruction of chains separating bilayers in $\text{YBa}_2\text{Cu}_3\text{O}_x$ appears to be essentially *irrelevant* for the interlayer dynamics. The phonon structure seen in $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ crystals clearly testifies that our samples are fully oxygenated and thus the sole structural impact of Pr is to mildly enhance the separation within the CuO_2 bilayers. Nevertheless Pr substitution has striking consequences for the electronic transport and initiates trends both in the in-plane^{22,23} and in the c -axis conductivity remarkably similar to underdoping of

CuO₂ planes by oxygen reduction. These results establish that the interlayer transport, at least in YBa₂Cu₃O_x series, is determined primarily by the electronic state of the CuO₂ planes, whereas structural aspects associated with fragmenting Cu-O chains seem to be playing only a minor role in the *c*-axis response.

Finally, we briefly comment on yet another feature common to electrodynamics of both oxygen deficient YBa₂Cu₃O_x samples and Pr_yY_{1-y}Ba₂Cu₃O_{7-δ} crystals. In both classes of materials we observe a resonance mode at ≈400 cm⁻¹. This structure is evident in the conductivity of Pr_{0.3}Y_{0.7}Ba₂Cu₃O_{7-δ} and is reminiscent of similar structure shown in the bottom frame of Fig. 2. With increase of Pr content up to *y*=0.4 value the resonance mode is nearly completely suppressed and only a weak structure is observed in the 400 cm⁻¹ region. The resonance mode observed both in oxygen-depleted YBa₂Cu₃O_x samples and in Pr_{0.3}Y_{0.7}Ba₂Cu₃O_{7-δ} crystals is strongest in the 10 K spectrum but is also noticeable in the data sets at *T*≈*T*_{*c*}. In the following section we will overview existing interpretations of this resonance and offer yet another approach to understand it in terms of a so-called bilayer splitting effect. The latter scenario assigns this feature to lifted degeneracy between bonding and antibonding bands associated with the two constituents of the CuO₂ bilayer.

IV. THE *c*-AXIS RESONANCE IN THE INTERPLANE CONDUCTIVITY OF DOUBLE-LAYERED CUPRATES

A. Principal experimental results

In this section we focus on the analysis of the resonance mode observed in the interlayer conductivity of bilayer cuprates. Detailed studies of the resonance in underdoped YBa₂Cu₃O_{6.5} and YBa₂Cu₃O_{6.6} revealed that this mode emerges at *T*<150 K and acquires ≈50% of the oscillator strength at *T*>*T*_{*c*} (Refs. 9 and 14). The frequency position of the *c*-axis resonance in YBa₂Cu₃O_x shows strong composition dependence: the mode systematically hardens from 375 cm⁻¹ in YBa₂Cu₃O_{6.5} to nearly 900 cm⁻¹ in YBa₂Cu₃O_{6.95} and YBa₂Cu₃O_{6.99} phases (Fig. 3). In the latter two compounds this feature is found *only* in the superconducting state conductivity; underdoped YBa₂Cu₃O_x crystals as well as Pr_yY_{1-y}Ba₂Cu₃O_{7-δ} materials reveal the anomalous feature already in the normal state. Notably, the doping dependence of the superfluid density in YBa₂Cu₃O_x reveals much more rapid decrease with *x* compared to the hardening of the *c*-axis mode (Fig. 3).

In Fig. 4 we summarized a large body of experimental data, including results from this work, which unambiguously show that the anomalous *c*-axis resonance is indeed specific to double-layer cuprates. Panels on the left-hand side of the diagram present conductivity for the single-layered systems including results on the superconductors with critical temperature in excess of 90 K, such as Tl₂Ba₂CuO_{6+x} (Tl2201) (Refs. 5 and 24) and HgBa₂CuO₄ (Hg1201) (Ref. 25). We also present results for hole doped La_{1.875}Sr_{0.125}CuO₄ (Ref. 20) and for its electron doped counterpart Nd_{1.85}Ce_{0.15}CuO₄ (Ref. 26). In all of these compounds $\sigma_1(\omega, T \ll T_c)$ spectra

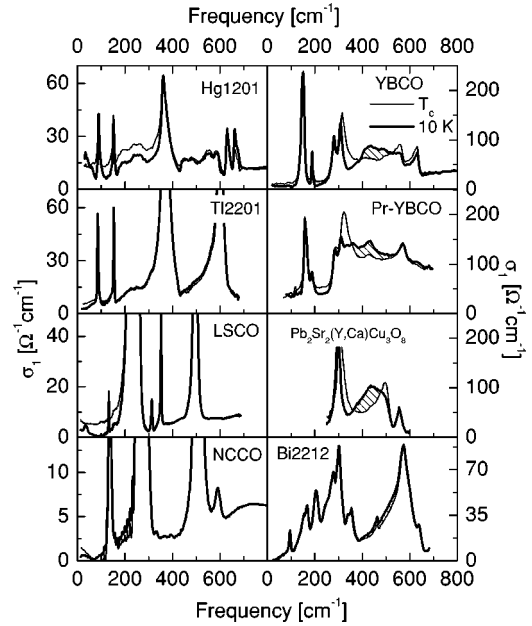


FIG. 4. Interlayer conductivity $\sigma_1(\omega)$ of single-layer (left panels) and double-layer cuprates (right panels) at *T*_{*c*} and *T*≪*T*_{*c*}. Experimental data: HgBa₂CuO₄ (Hg1201), Ref. 25; Tl₂Ba₂CuO_{6+x} (Tl2201), Refs. 5 and 24; La_{2-x}Sr_xCuO₄ (LSCO), Ref. 20; Nd_{2-x}Ce_xCuO₄ (NCCO), Ref. 26; YBa₂Cu₃O_{6.6} (YBCO), Ref. 9; Pr_yY_{1-y}Ba₂Cu₃O_{7-δ}, this work; Pb₂Sr₂(Y/Ca)Cu₃O₈, Ref. 27; and Bi₂Sr₂CaCu₂O_z (Bi2212), this work. In single-layered systems the $\sigma_1(\omega, T \ll T_c)$ spectra are suppressed compared to $\sigma_1(\omega, T_c)$ data, in accord with type-II coherence factors relevant to the response of superconductors in the extreme dirty limit. Crossing between normal and superconducting data (shaded areas) is apparent in the conductivity spectra for several different classes of double-layered materials.

are suppressed compared to the normal-state conductivity $\sigma_1(\omega, T_c)$. This effect is in accord with type-II coherence factors relevant for superconducting transition. On the contrary all double-layered materials in the right-hand panels systematically show crossing between the conductivity data above and below *T*_{*c*}. This latter behavior is incompatible with type-II coherence factors in the *extreme* dirty superconductor, relevant to the *c*-axis conductivity of cuprates.¹³ Recent data for a triple-layered Bi₂Sr₂Ca₂Cu₃O₁₀ also show similar crossing effect²⁸ suggesting that this behavior is likely to be a common property of all multilayered cuprates.

The resonance mode discussed above is sensitive to impurities. In Fig. 5 we plot the raw reflectance spectra (left panels) along with the conductivity data (right panels) for a clean YBa₂Cu₃O_{6.6} as well as the results for both YBa₂Cu_{2.997}Zn_{0.003}O_{6.6} and YBa₂Cu_{2.99}Ni_{0.01}O_{6.6} single crystals. Both Ni and Zn impurities are believed to substitute Cu atoms in the CuO₂ planes. Figure 5 shows that either type of impurities appears to significantly reduce the oscillator strength of the *c*-axis resonance. At the same time, the frequency position of the mode *hardens* in both Ni- and Zn-doped samples compared with the data for pristine YBa₂Cu₃O_{6.6}. Hauff *et al.* examined the behavior at high levels of Zn doping and found that 1.3% of Zn is sufficient to eliminate the anomalous *c*-axis resonance with simultaneous

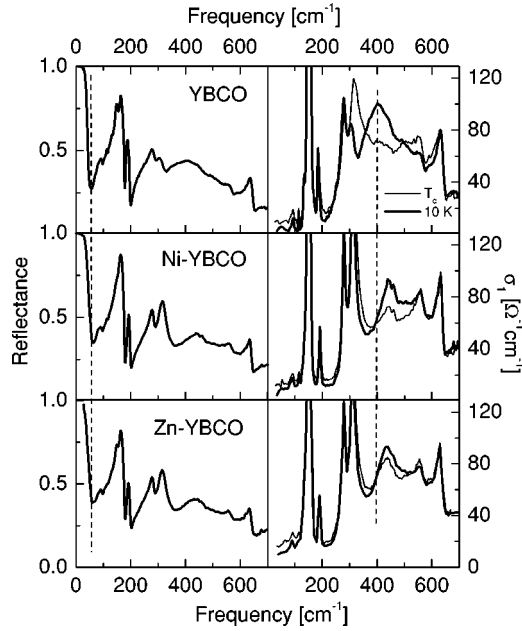


FIG. 5. Interlayer response of $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ (Ref. 9), $\text{YBa}_2\text{Cu}_{2.99}\text{Ni}_{0.01}\text{O}_{6.6}$, and $\text{YBa}_2\text{Cu}_{2.997}\text{Zn}_{0.003}\text{O}_{6.6}$. Left panels display the reflectance data $R(\omega)$ and right panels the corresponding optical conductivity $\sigma_1(\omega)$. In Ni- and Zn-doped samples the c -axis resonance in the conductivity shifts to higher energies and its oscillator strength is suppressed. On the other hand, the superfluid density is virtually the same in all samples as indicated by the location of the plasma edge in the c -axis reflectance.

depression of the superfluid density.²⁹ Smaller concentrations of dopants studied here render the strength of the c -axis condensate virtually unaffected. Insensitivity of the superfluid density to small concentrations of either Ni or Zn can be readily seen in raw reflectance data. Indeed, the plasma edge in the c -axis reflectance is virtually unaffected by minute inclusions of both Ni and Zn.

Recently, Kojima *et al.* reported on sensitivity of the c -axis resonance to magnetic field applied parallel to CuO_2 planes.³⁰ In this geometry magnetic field introduces Josephson vortices which have a strong impact on the magnitude of the interplane superfluid density.^{31,32} A novel effect discovered by Kojima *et al.* in a double-layered $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ material is a field induced enhancement of the oscillator strength of the c -axis resonance. This effect is stronger when experiment is performed under zero-field cooling condition. Although the magnitude of the 400 cm^{-1} resonance is strongly affected by modest magnetic field of 7 T, there is no noticeable shift of the peak position in the in-field spectra.

B. Understanding the c -axis resonance

As pointed out above, the absorption structure in the c -axis conductivity found exclusively in double-layered or multilayered materials cannot be directly attributed to superconducting gap¹³ since (in the extreme dirty limit) type-II coherence factors prohibit increase of $\sigma_1(\omega, T \ll T_c)$ over the normal-state value.³³ In this context the JTM model developed by van der Marel and co-workers^{12,13} is especially ap-

pealing since it naturally accounts for the crossing of the conductivities probed above and below T_c . Assuming that a double-layered cuprate can be viewed as a stack of Josephson junctions with alternating weaker and stronger links the complex impedance $z(\omega)$ can be written as^{12,13}

$$\frac{z(\omega)}{4\pi i/\omega} = \frac{1}{\epsilon(\omega)} = \frac{x_A}{1 - \frac{\omega_{p,A}^2}{\omega^2 + i\gamma_A\omega}} + \frac{x_B}{1 - \frac{\omega_{p,B}^2}{\omega^2 + i\gamma_B\omega}}, \quad (1)$$

where $\omega_{p,A}$ and $\omega_{p,B}$ are the plasma frequencies associated with weaker and stronger “links,” γ_j are dampings, and x_j are the relative volume fractions of the two subcells in a crystal ($x_A + x_B = 1$) (Ref. 34). In the superconducting state $\gamma_A = \gamma_B = 0$ and assuming there is no dissipation due to unpaired carriers Eq. (1) reduces to

$$\epsilon(\omega) = \frac{(\omega^2 - \omega_{p,A}^2)(\omega^2 - \omega_{p,B}^2)}{\omega^2(\omega^2 - \omega_0^2)}, \quad (2)$$

where

$$\omega_0 = \sqrt{x_B\omega_{p,A}^2 + x_A\omega_{p,B}^2}. \quad (3)$$

The form of Eq. (2) implies that in addition to the usual (superconducting) transverse mode at $\omega = 0$ with the strength $\rho_s = (\omega_{p,A}\omega_{p,B}/\omega_0)^2$, a new transverse mode at the frequency ω_0 develops in the conductivity spectra. The oscillator strength ρ_0 of this latter mode is given by

$$\rho_0 = \frac{(\omega_{p,B}^2 - \omega_{p,A}^2)^2}{\frac{\omega_{p,A}^2}{x_A} + \frac{\omega_{p,B}^2}{x_B}}. \quad (4)$$

This framework of the transverse Josephson mode has been used to interpret the anomalous c -axis resonance in the conductivity of double-layered cuprates.^{12,13}

The model of van der Marel *et al.* is elegant and physically transparent. Moreover it has been extremely successful in (self-consistently) explaining both the additional peak in c -axis conductivity and phonon anomalies.¹⁴ Although the general framework of the model [Eq. (1)] is not in question, it appears that some microscopic details are inconsistent with experimental observations reported here. In particular the Josephson nature of the current inside the bilayer appears to be most problematic. To explain the appearance of the peak at temperatures above T_c Gruninger *et al.* had to invoke the idea of preformed pairs, i.e., superconducting fluctuations (without long-range order) at temperatures higher than T_c . Such fluctuations have indeed been observed above T_c (Refs. 36 and 37), but as pointed out by Timusk and Homes³⁸ no experimental evidence exists for preformed pairs at such high temperatures at which the mode begins to develop in the c -axis data.

Further complications with the JTM interpretation of the data are indicated by the lack of correlations between the $\omega = 0$ Josephson resonance and the additional mode that are

readily expected within the JTM scenario. Indeed, the results displayed in Fig. 5 clearly show that the plasma edge in the superconducting reflectance is unchanged in the regime where only small concentrations of Ni or Zn are introduced in $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$, implying $\omega_{p,A} = \text{const}$. However within the JTM picture this mode is expected to harden since the c -axis resonance shows a clear shift to higher frequencies. Therefore, experiments for both Ni- and Zn-doped samples do not provide support for an interdependence between the two structures expected within the JTM picture [Eqs. (3) and (4)]. In fact, the resonance structure in both Ni- and Zn-doped samples is weaker compared to that of pristine $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ sample. Similar problem occurs when comparing the data plotted in Fig. 2 for $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ crystal and for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ material with $T_c = 40$ K. In this latter system we failed to find a straightforward scaling relationship expected from Eqs. (3) and (4) between the frequency position of the c -axis resonance (ω_0) and its oscillator strength (ρ_0). Analogous inconsistency emerges in the high magnetic-field data: the 400 cm^{-1} anomaly gains spectral weight without apparent change of the frequency position as discussed above.³⁰ Therefore, for all these reasons we conclude that the so-called “ 400 cm^{-1} ” peak in the optical conductivity of bilayer cuprates cannot be of Josephson, i.e., superconducting origin.

Formally, superconductivity *is not* a necessary precondition for the emergence of the additional transverse resonance.¹³ Indeed Eq. (1) produces a finite frequency peak even when both γ_A and γ_B are kept nonzero. As shown by Timusk and Homes³⁸ the primary effect of finite damping (that can originate from a normal component in the conductivity at $T < T_c$) is to broaden the ω_0 resonance and to smear out the corresponding features in reflectance. This finding prompted Timusk and Homes to propose a different view point on the structure characteristic for the interlayer conductivity of all double- and triple-layered cuprates studied to date.³⁸ In their opinion long-lived magnetic spin excitations will promote current path within a pair of (antiferromagnetically coupled) CuO_2 layers. Namely, in order for a hole to hop from one CuO_2 plane to the other it needs to undergo a spin flip, which is achieved by scattering of charge carriers off the so-called “ 41 meV ” peak seen in neutron scattering. However as pointed out by these authors, this model has a problem explaining the opposite magnetic-field dependencies of the neutron peak and the resonance mode in the optical conductivity.

Searching for alternative/complementary interpretations of the resonance mode we wish to point out one common feature of the electronic structure of all double-layered materials, which has recently received a lot of attention. Indeed, bilayer splitting is inevitable in this class of compounds if individual CuO_2 layers forming such a bilayer interact with each other. Transitions between these split bands can give rise to an alternative current path inside the bilayer and can give rise to a structure in the interlayer conductivity.¹⁵ Various aspects of bilayer splitting have been discussed in the literature^{15,39–45} and recently some of them were experimentally verified in a number of angular-resolved photoemission spectroscopy (ARPES) measurements of Bi2212. (Refs. 46–

49). The magnitude of the bilayer splitting is the largest in the $(\pi,0)$ and $(0,\pi)$ regions of the Brillouin zone (BZ) and is of the order of $40\text{--}80\text{ meV}$ ($320\text{--}640\text{ cm}^{-1}$) in Bi2212, according to ARPES results. Note that this particular region of the BZ determines the interlayer conductivity of cuprates because of directionality of the c -axis matrix elements.^{15,40}

A transition between the bands associated with the two constituents of a bilayer is permitted if both of the following conditions are satisfied: (i) final states are available in the vicinity of $(\pi,0)$ and $(0,\pi)$ regions; (ii) quasiparticles (QP) in bilayer bands are not overdamped. The first condition can be fulfilled if an energy gap develops in the $(\pi,0)$ and $(0,\pi)$ regions. Systematic ARPES studies of the evolution of the Fermi surface with temperature and doping in Bi2212 system suggest that a gap (pseudogap) in this part of the BZ develops only below T_c in the optimally doped materials and at $T < T^*$ in the underdoped compounds. This is in agreement with the temperature/doping trends of the c -axis resonance which appears in the optimally doped compounds only in superconducting state but becomes visible in underdoped systems already in the pseudogap state. As far as the QP precondition is concerned, existing ARPES measurements give no clear indications for well-defined quasiparticle peaks in the pseudogap state. At the same time, a detailed analysis of the in-plane carrier dynamics in both $\text{YBa}_2\text{Cu}_3\text{O}_x$ and Bi2212 systems reveals significant depression of the in-plane scattering rate $1/\tau(\omega)$ in the pseudogap state.^{52–54} While the gross features of $1/\tau(\omega)$ spectra are common for both $\text{YBa}_2\text{Cu}_3\text{O}_x$ and Bi2212 compounds, the depression of $1/\tau(\omega)$ appears to be much more prominent in the former group of materials. Specifically, the scattering rate analysis of the IR data for $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ suggests that $1/\tau(\omega) \approx \omega$, which indicates that QP excitations are no longer overdamped in this system in the pseudogap state.⁵² Therefore both conditions essential for the observation of the interband structure in the c -axis conductivity of $\text{YBa}_2\text{Cu}_3\text{O}_x$ appear to be fulfilled.

The bilayer splitting interpretation can qualitatively account for principal trends in the behavior of the c -axis resonance in the process of doping of $\text{YBa}_2\text{Cu}_3\text{O}_x$ with oxygen, as well as with different impurities. Strong enhancement of the resonance seen upon the increase of oxygen content from $x = 6.5$ to $x = 7$ may be prompted by the reduction of length of the unit cell along the c axis. Compression of the crystal along the c axis inevitably leads to stronger disparity between bonding and antibonding bands of the CuO_2 bilayer so that the energy of the transition is enhanced from 350 cm^{-1} in the $x = 6.5$ phase to nearly 900 cm^{-1} in the $x = 7$ sample. Suppression and eventual vanishing of this mode in the conductivity data of disordered (Ni- and Zn-doped) crystal may be understood in terms of rapid depression of QP lifetime within the CuO_2 planes. Indeed, in these latter materials the “QP precondition” is no longer satisfied so that the bilayer induced resonance in the $\sigma_1(\omega)$ spectra is strongly damped. Suppression of the c -axis structure in the Pr-doped $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$ crystals also may be connected with the QP lifetime. In addition to that, Pr doping appears to reduce the coupling within the bilayer thus restoring the degeneracy of bonding and antibonding bands. We therefore conclude that

the bilayer interpretation of the c -axis structure has certain merits over the alternative scenarios discussed above.

Note that the idea of bilayer splitting does not contradict van der Marel/Munzar approach to interpret unconventional line shape of several phonon modes. A “bilayer scheme” which we advocate here merely proposes an alternative microscopic nature of currents between individual CuO_2 planes. Existence of these currents is not in dispute and therefore the formalism developed by Munzar and collaborators is applicable.¹⁴ The new scenario immediately remedies the issues of the JTM description arising from an explicit connection of intrabilayer currents and of the resonance mode with superconducting pairing. Within the bilayer scheme the $\omega=0$ superconducting mode and the c -axis resonance originate from entirely different processes. Therefore the scaling relations preset by Eqs. (3) and (4) do not need to be followed. The onset of the resonance mode and of unconventional phonon line shapes is expected to occur below the pseudogap temperature promoting QP coherence. When superconductivity sets in at T_c the intrabilayer current acquires additional (Josephson) component, which results in a further increase in both the peak intensity and phonon anomalies in accord with the data.¹⁴

V. CONCLUSIONS AND OUTLOOK

The analysis of the interlayer conductivity of seven different families of high- T_c superconductors provides firm evidence for the existence of an additional electronic resonance in the response of materials with more than one CuO_2 plane per unit cell. We have examined the evolution of this mode in $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals doped with different impurities. We have found that the original interpretation of this prominent feature of the interlayer electrodynamics in terms of a transverse Josephson mode is not fully consistent with the totality of experimental data. In particular, we failed to observe expected scaling between the frequency position and the oscillator strength of this resonance. These results provoked search for alternative/complimentary interpretations of the resonance mode. We pointed out that the microscopic roots of this feature may be related to the electronic structure

of bilayered (multilayered) cuprates: interaction between constituents of the CuO_2 bilayer should lift the degeneracy between corresponding bands and give rise to a new current path between the CuO_2 planes inside the bilayer. All conditions required for the observation of these transitions in the interlayer conductivity appear to be satisfied. We therefore speculate that bilayer splitting may be an important factor defining the character of the interplane ac response of high- T_c cuprates. One implication of this scenario is that quasiparticles in bilayer split bands become well defined already in the pseudogap state since the c -axis resonance in underdoped materials is clearly visible well above the T_c . The idea of the existence of well-defined quasiparticles in the pseudogap state is at odds with conclusions emerging from ARPES studies indicating broad line shapes at $T > T^*$. In this context it is worth pointing out that bilayer splitting effect may be in part responsible for this broadening as recently discussed in Ref. 55. The analysis of doping trends reported here indicates that the magnitude of bilayer splitting is systematically enhanced with doping and appears to correlate with T_c both in $\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ materials.

The analysis of the data for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ in conjunction with the results for oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_x$ points to the fact that the “semiconducting” trends in the interlayer transport of these systems have little to do with fragmenting of the Cu-O chains. We conclude that it is the electronic state of the CuO_2 planes that is primarily responsible for strong depression of both interlayer conductivity and of the c -axis superfluid density in underdoped compounds.

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