Josephson Plasma Resonance and Phonon Anomalies in Trilayer $Bi_2Sr_2Ca_2Cu_3O_{10}$

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The far-infrared (FIR) c axis conductivity of a Bi2223 crystal has been measured by ellipsometry. Below T_c a strong absorption band develops near 500 cm^{-1}, corresponding to a transverse Josephson plasmon. The related increase in FIR spectral weight leads to a giant violation of the Ferrell-Glover-Tinkham sum rule. The gain in c axis kinetic energy accounts for a sizable part of the condensation energy. We also observe phonon anomalies which suggest that the Josephson currents lead to a drastic variation of the local electric field within the block of closely spaced CuO_2 planes.

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The transition from a normal metal to a superconductor (SC) below the critical temperature, T_c, is accompanied by a redistribution of spectral weight (SW) from finite frequencies in the normal state (NS) into a δ function at zero frequency in the SC state that represents the loss-free response of the SC condensate. For classical SC's the energy gap determines the frequency range over which the SW of the δ function is collected, so that noticeable changes occur only for $\omega \lesssim 6\Delta$ [Ferrell-Glover-Tinkham (FGT) sum rule] [1]. Recently, it was claimed that the FGT sum rule is partially violated for the c axis response of the high-T_c (HTSC) cuprate compounds $Tl_2Ba_2CuO_{6+x}$ (Tl2201), $La_{2-x}Sr_xCuO_4$ (LaSr214), and $YBa_2Cu_3O_{6.6}$ (Y123) [2]. It was found that the SW loss in the far infrared (FIR) below T_c is smaller than the SW of the δ function at zero frequency, which is independently determined from the imaginary part of the conductivity. However, the change of the FIR-SW in the SC state is small and hard to measure experimentally. Nevertheless, due to its important implications, this report has attracted considerable attention. It implies that a very large frequency scale is involved in the SC pairing and seems to rule out any conventional mechanism that relies exclusively on low-frequency bosons like phonons. Instead, it supports models where a decrease in the c axis kinetic energy below T_c provides a significant contribution to the SC condensation energy [3,4].

These far reaching implications call for further experiments on a compound where the related SW transfer is larger and therefore more easily identified. The most promising candidates are multilayer HTSC compounds, which contain more than one CuO_2 plane per unit cell. For the bilayer systems Y123 and $Bi_2Sr_2CaCu_2O_8$ (Bi2212) it has already been shown that a sizable absorption peak develops below T_c in the FIR range. Evidence has been presented that its SW is mostly electronic in origin and that it belongs to the SC condensate [5–9]. This can be understood in terms of the interlayer-tunneling model [3] which assumes that the CuO_2 planes are weakly coupled by the Josephson currents in the SC state. For bilayer compounds this results in two kinds of Josephson junctions with different longitudinal plasma frequencies [10]. Their out-of-phase oscillation gives rise to a transverse Josephson plasma resonance (t-JPR) which has been assigned to the absorption peak that develops below T_c. This model, termed Josephson superlattice model (JSM) in the following, successfully describes the anomalous FIR c axis response of Y123 and Bi2212 [5–9]. Nevertheless, it is not commonly accepted, and it is disputed whether the SW of the absorption band belongs to the SC condensate [11]. It has also been recently suggested that the absorption peak in the underdoped Y123 may result from the hopping between the CuO_2 planes assisted by the spin fluctuations [12].

In this manuscript we present ellipsometric data of the c axis dielectric response of the trilayer compound $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi2223). We show that a strong absorption band develops below T_c in the FIR. It leads to a clear increase of the SW in the FIR below T_c corresponding to a giant violation of the FGT sum rule. We quantify the associated change in kinetic energy and show that it can account for a substantial part of the SC condensation energy. We also show that the electronic mode and the associated phonon anomalies can be qualitatively described with the JSM.

A Bi2223 single crystal of dimensions $6 \times 4 \times 0.5$ mm^3 was grown by the traveling solvent floating zone technique. The crystal contains more than 95% of Bi2223 with only a minor fraction of layer-intercalated Bi2212 [13]. The as grown crystal was underdoped with $T_c = 97$ K (midpoint) and $\Delta T_c = 7$ K. Subsequent to the optical measurements the same crystal was annealed for ten days in flowing oxygen at 500 °C (and then for three days in air at 700 °C) and rapidly quenched so it was nearly optimally doped with $T_c = 107$ K and $\Delta T_c = 3$ K (moderately underdoped with $T_c = 102$ K and

$\Delta T_c = 4$ K). The crystal surface was polished to optical grade. The high quality of the surface was confirmed by micro-Raman measurements. The ellipsometric measurements (see Ref. [7] for a description of the technique) have been performed at the infrared beam line of the synchrotron radiation source at ANKA in Karlsruhe, Germany and at NSLS in Brookhaven, U.S.A. A home-built ellipsometer attached to a "Bruker" IFS 66v/S FT-IR spectrometer has been used. The high brilliance of the synchrotron enables us to obtain accurate ellipsometric data in the FIR spectral range even on mm-sized samples.

Figures 1 and 2(a) show variation with temperature of the real part $\sigma_1(\omega)$ of the c axis optical conductivity of Bi2223 at the three different doping levels. The normal-state spectra are dominated by the contributions of several IR-active phonons; the one of the charge carriers is extremely weak. The main phonon bands are located at 97, 128 [14], 170, 211, 305, 360, 400, and 582 cm^{-1}. Except for the additional modes at 400 and 128 cm^{-1} the IR-active phonons of Bi2223 appear at similar frequencies as in Bi2212 [8,9]. In order to find the corresponding eigenvector patterns we have performed shell model calculations for the Bi-based compounds in the body centered tetragonal $I4/mmm$ structure. We obtained a set of parameters which allows us to reproduce simultaneously the structures, the experimental values of the c axis dielectric constants, and the frequencies of the IR-active modes in Bi2223, Bi2212, and Bi2201 [15]. For Bi2212 our assignment of the modes agrees well with the one given in Ref. [16]. The strongest modes at 582 and 305 cm^{-1} involve primarily vibrations of the apical O2 oxygen and the Bi-plane O3 oxygen, respectively. The eigenvector patterns of the modes at 360 and 400 cm^{-1} corresponding to the motion of the oxygens in the CuO_2 layers are shown in Fig. 3(a). The remaining four A_{2u} IR-active phonon modes at lower frequencies involve vibrations of the heavy ions and will not be further discussed here. Some additional weak modes at 276, 471, and 635 cm^{-1} are most likely related to the incommensurate modulation in the BiO and SrO layers [17].

In the NS the spectra exhibit hardly any noticeable changes, except for a sharpening of the phonons with decreasing temperature. Right below T_c, however, the spectra change appreciably. This is also illustrated in Fig. 2(a) which displays the difference $\sigma_1(T = 10\text{ K}) - \sigma_1(T = 120\text{ K})$. The most prominent feature is the broad absorption band around 500 cm^{-1} which appears below T_c and grows rapidly with decreasing temperature. Figures 1 and 2(a) show that the center of this band shifts towards higher frequencies with increasing doping. A similar absorption band has been previously identified in the bilayer compound Y123 where it has been attributed [5–7] to the t-JPR. The SW of this feature is very large in Bi2223 and gives rise to a considerable increase in the FIR-SW below T_c. Figure 2(b) shows the difference between the SW in the SC state at 10 K and the one in the NS at 120 K:

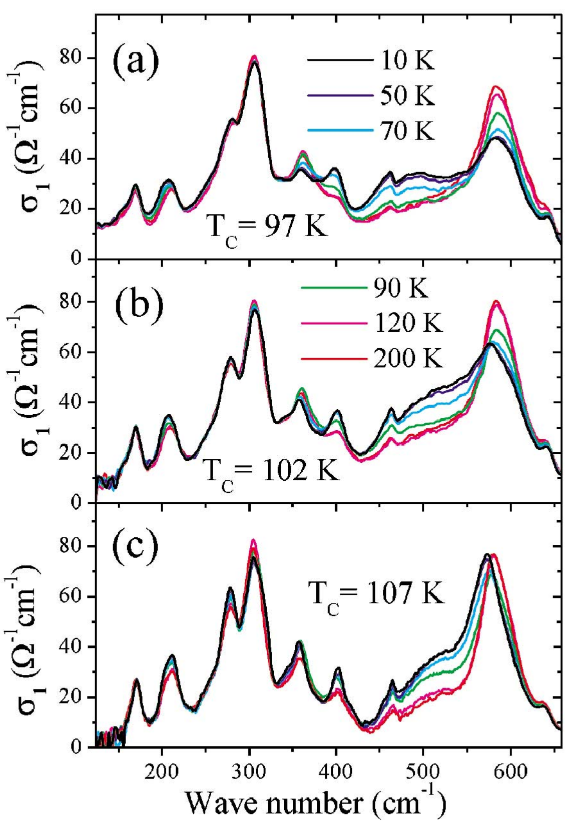

FIG. 1 (color). Real part, $\sigma_1(\omega)$, of the FIR c axis conductivity of Bi2223.

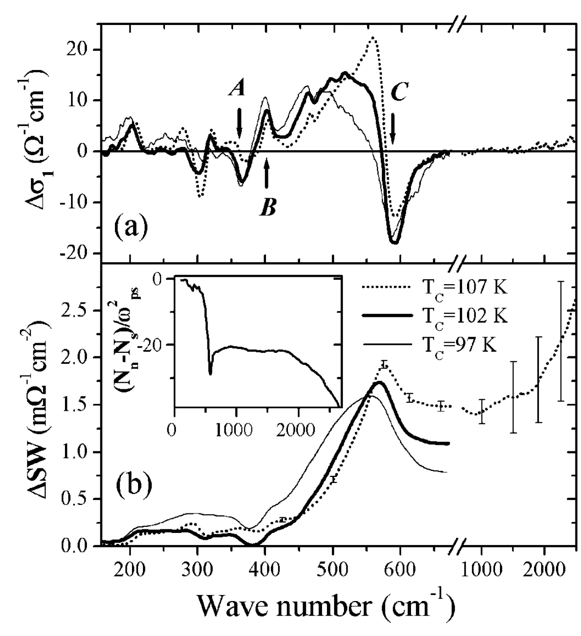

FIG. 2. Spectra of (a) $\Delta\sigma_1 = \sigma_1(10\text{ K}, \omega) - \sigma_1(120\text{ K}, \omega)$ and (b) $\Delta\text{SW}(\omega)$ [see Eq. (1)]. The phonon anomalies discussed in the text are denoted by A, B, and C. Inset: Upper limit of the quantity $(N_n - N_s)/\omega_{\text{ps}}^2$ defined in the text for Bi2223 with $T_c = 107$ K [$\omega_{\text{ps}} = 50\text{ cm}^{-1}$, error bars for $\Delta\text{SW}(\omega)$ are reckoned in].

$$\Delta\mathrm{SW}(\omega) = \int_{100\ \mathrm{cm}^{-1}}^{\omega} [\sigma_1(10\ \mathrm{K}, \omega') - \sigma_1(120\ \mathrm{K}, \omega')] d\omega'. \tag{1}$$

Apart from some smaller changes related to the phonon anomalies it exhibits a steep increase between 400 and 550 cm^{-1}. Above 650 cm^{-1} and up to about 2000 cm^{-1} $\Delta\mathrm{SW}(\omega)$ remains essentially constant at $\Delta\mathrm{SW} = 800$, 1100, and 1400 $\Omega^{-1}\,\mathrm{cm}^{-2}$ for T_c of 97, 102, and 107 K, respectively. Such an apparent increase in the FIR-SW below T_c is certainly not expected for any conventional SC where the FIR-SW should be removed and transferred to the δ function at zero frequency. The FGT sum rule reads $(N_n - N_s)/\omega_{\mathrm{ps}}^2 = 1$ [1], where $N_n - N_s = -(120/\pi)\Delta\mathrm{SW}(\Omega_c)$(cutoff frequency $\Omega_c \gtrsim 6\Delta$), and ω_{ps} is the plasma frequency corresponding to the δ function. For highly anisotropic compounds like Bi2223 and Bi2212 ω_{ps} is extremely small [18]. Indeed, within the measured range ($\omega > 14\ \mathrm{cm}^{-1}$) we do not observe a noticeable change in ϵ_1 below T_c that would indicate a zero crossing at the screened plasma frequency $\omega_{\mathrm{ps}}/\sqrt{\varepsilon_\infty}$. With $\varepsilon_\infty \approx 12$ we thus obtain a solid upper limit of ω_{ps} of 50 cm^{-1}. The inset of Fig. 2(b) shows that our data on Bi2223 with $T_c = 107$ K result in a negative value of $(N_n - N_s)/\omega_{\mathrm{ps}}^2 \lesssim -20$ at $\Omega_c \gtrsim 650\ \mathrm{cm}^{-1}$. The data represent a striking manifestation of the violation of the FGT sum rule. They highlight the fact that a significant amount of SW is transferred from higher frequencies to the absorption band near 500 cm^{-1}. This result is independent of a particular model that is used to explain the origin of the band. We emphasize that within the JSM model the SW of the t-JPR belongs to the SC condensate just as much as the one of the δ function at zero frequency. For Bi2223 the SW of the t-JPR, however, exceeds the one of the δ function by more than 1 order of magnitude.

It is evident from Figs. 1 and 2(a) that the formation of the t-JPR is also associated with an anomalous temperature dependence of the phonon modes at 360, 400, and 582 cm^{-1} denoted by A, B, C in Fig. 2(a). Particularly interesting are the contrasting T dependences of the oxygen bond-bending modes at 360 and 400 cm^{-1} whose eigenvector diagrams are shown in Fig. 3(a). As shown in Fig. 3(b), the mode at 360 cm^{-1} loses a significant amount of its SW below T_c. A similar effect has been observed for the oxygen bond-bending mode in Bi2212. In clear contrast, the mode at 400 cm^{-1} (which is specific to the trilayer compound) gains in the SW in the SC state. In the following we show that this behavior, while surprising at first, is explained by the JSM.

As outlined in Refs. [6–9] the onset of the Josephson currents between the CuO_2 layers can lead to a significant change of the dynamical local electric field. A simple estimate can be obtained by considering a stack of homogeneously charged Josephson-coupled CuO_2 layers. A sketch is shown in Fig. 3(c) where $\kappa(\omega)$ denotes the charge density that alternates from one outer plane to the other. The Josephson currents $j_{bl}(\omega)$ and $j_{\mathrm{int}}(\omega)$ can be

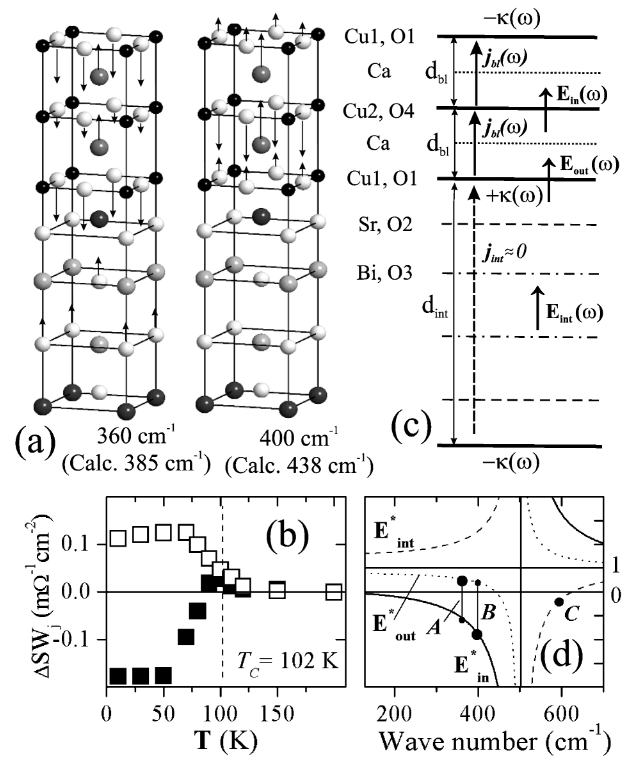

FIG. 3. (a) Calculated oxygen bond-bending A_{2u} eigenmodes of Bi2223. (b) Relative SW changes of the phonons at 360 cm^{-1} (solid squares) and 400 cm^{-1} (open squares) with decreasing temperature, $\Delta\mathrm{SW}_j = [\mathrm{SW}_j(T) - \mathrm{SW}_j(200\ \mathrm{K})]/\mathrm{SW}_j(200\ \mathrm{K})$. SW_j has been derived by fitting a sum of Lorentzian functions to the complex dielectric function. (c) Schematic representation of the model discussed in the text. The horizontal lines represent CuO_2 (solid), Ca (dotted), SrO (dashed), and BiO (dash-dotted) planes. (d) Frequency dependent variation of the normalized local electric field due to the Josephson currents as defined in the text: $E_{\mathrm{int}}^\star$ (dashed line), $E_{\mathrm{in}}^\star$ (solid line), and $E_{\mathrm{out}}^\star$ (dotted line). The local fields at the sites of the particular ions participating in the eigenmodes at 360, 400, and 582 cm^{-1} are indicated by A, B, and C, respectively.

described by using the local dielectric functions of the intratrilayer region and of the intertrilayer region, $\varepsilon_{tl}(\omega) = \varepsilon_\infty - \omega_{bl}^2/\omega^2$ and $\varepsilon_{\mathrm{int}}(\omega) = \varepsilon_\infty - \omega_{\mathrm{int}}^2/\omega^2$, respectively. Following the model of Ref. [6] the normalized local fields inside the spacing layer that separates the trilayers, $E_{\mathrm{int}}^\star$, inside the trilayer, $E_{\mathrm{in}}^\star$, and at the outer CuO_2 layers, $E_{\mathrm{out}}^\star$, are

$$E_{\mathrm{int}}^\star = \frac{E_{\mathrm{int}}}{\langle E\rangle} = \frac{(d_{tl} + d_{\mathrm{int}})\varepsilon_{tl}}{(d_{tl}\varepsilon_{\mathrm{int}} + d_{\mathrm{int}}\varepsilon_{tl})}, \tag{2a}$$

$$E_{\mathrm{in}}^\star = \frac{E_{\mathrm{in}}}{\langle E\rangle} = \frac{(d_{tl} + d_{\mathrm{int}})\varepsilon_{\mathrm{int}}}{(d_{tl}\varepsilon_{\mathrm{int}} + d_{\mathrm{int}}\varepsilon_{tl})}, \tag{2b}$$

$$E_{\mathrm{out}}^\star = \frac{(E_{\mathrm{int}}^\star + E_{\mathrm{in}}^\star)}{2}, \tag{2c}$$

where $\langle E\rangle$ is the average field, $d_{tl} = 2d_{bl}$. For $\omega_{\mathrm{int}} = 0$, $\omega_{bl} = 1250\ \mathrm{cm}^{-1}$, $\varepsilon_\infty = 4$, $d_{\mathrm{int}} = 12.0$ Å, and $d_{bl} = 3.4$ Å we obtain the result that is shown in Fig. 3(d). In the NS with $\omega_{\mathrm{int}} = 0$ and $\omega_{bl} = 0$ we have $E_{\mathrm{int}}^\star = E_{\mathrm{in}}^\star = E_{\mathrm{out}}^\star = 1$. Note the following: (i) In the frequency range of the bond-bending modes (360 to 400 cm^{-1}) E_{out} is positive but strongly suppressed in the SC state, whereas E_{in} acquires a large negative value; (ii) the value of E_{int} around the frequency of the apical oxygen mode (582 cm^{-1}) is also strongly suppressed with respect to the NS.

The SW of a given phonon mode is determined by the local field at the ions participating in the mode and by the mode polarizability. The trends (i) account for the anomalies of the bending modes. Concerning the in-phase mode at 360 cm^{-1}, the pattern of the local field is in agreement with the eigenvector pattern above T_c (E_{out} and E_{in} are parallel) but not below T_c (E_{out} and E_{in} are antiparallel). In addition, the magnitude of E_{out} is strongly suppressed below T_c. Both effects lead to the observed decrease of the SW of the mode in the SC state. For the out-of-phase mode at 400 cm^{-1} the situation is reversed; that is, the two patterns are not in agreement above T_c whereas they are in accord below T_c. In addition, the magnitude of E_{in} increases below T_c. Both effects contribute to the SW increase of the mode below T_c. We emphasize that these results are rather robust against a change of the relative amplitudes of the ionic displacements which will affect only the relative contribution of the above mentioned effects. Finally, point (ii) allows one to understand why the SW of the apical oxygen mode at 582 cm^{-1} decreases below T_c: E_{int} decreases below T_c and so does the SW. These phonon anomalies clearly reflect a transition from a state exhibiting confinement (incoherent intratrilayer conductivity) into a state where the CuO_2 planes are Josephson coupled. They demonstrate that in the SC state the local electric field can exhibit enormous variations within the unit cell; even its sign can change between the inner and outer layers of the trilayer. We are not aware of any other model which would allow one to describe these phenomena in so much detail.

Having shown that the JSM provides an excellent description of the additional absorption band and the phonon anomalies, we evaluate the change in the c axis kinetic energy of the charge carriers, ΔH_c, which is related to the growth of the t-JPR. In a recent paper [9] ΔH_c in Y123 and Bi2212 has been estimated according to $\Delta H_c = E_J$, where E_J is the coupling energy of the intrabilayer Josephson junction. This approach, however, ignores the changes upon entering the SC state due to the single particle tunneling and thus may overestimate the value of ΔH_c. The more rigorous sum-rule approach [4] is appropriate only for single-layer materials but not for the bi- or trilayer ones [9]. In the mean time some of us have derived [19] a version of the sum rule that is valid for multilayer compounds with fully insulating blocking layers such as Bi2212 or Bi2223. For trilayer cuprates it reads

$$\Delta H_c = \frac{2\hbar^2 a^2}{\pi e^2}\frac{(2d_{bl} + d_{\mathrm{int}})}{d_{bl}^2}\Delta \mathrm{SW}(\Omega_c), \qquad (3)$$

where a is the in-plane lattice constant. Using the results shown in Fig. 2(b) we obtain $\Delta H_c \approx 0.06$, 0.08, and 0.11 meV for $T_c = 97$, 102, and 107 K respectively. The condensation energy of Bi2223 is not known. Remarkably, however, our results for ΔH_c are comparable to the condensation energy of 0.13 meV obtained by specific heat measurements for optimally doped Bi2212 [20].

In summary, our data of the c axis dielectric function of Bi2223 provide clear evidence that the transverse Josephson plasma resonance is a universal feature of the multilayer HTSC cuprate compounds. They show unambiguously that the spectral weight of the plasmon is electronic in origin and arises from high frequencies beyond the FIR range. The related transfer of the spectral weight gives rise to a significant change in c axis kinetic energy of the charge carriers which can account for a sizable part of the condensation energy. We also observe phonon anomalies which suggest that the Josephson currents lead to a strong variation of the dynamical local electric field even between the inner and outer CuO_2 planes of a trilayer.

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