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Optical conductivity of CuO$_2$ infinite-layer films

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The infrared conductivity of CaCuO$_2$, SrCuO$_2$, and Sr$_{0.85}$Nd$_{0.15}$CuO$_2$ infinite-layer films is obtained from reflection measurements by taking into account the substrate contribution. SrCuO$_2$, and Sr$_{0.85}$Nd$_{0.15}$CuO$_2$ exhibit extra-phonon modes and structured bands in the midinfrared, not found in stoichiometric CaCuO$_2$. These features mirror those observed in the perovskitic cuprates, thus showing that the polaronic properties of High-$T_c$ superconductors are intrinsic to the CuO$_2$ planes.

Keywords: A. high-$T_c$ superconductors, thin films D. optical properties

Since the early observations by photoinduced absorption, it has been pointed out that the injection of charges into the parent compounds of High-$T_c$ cuprates produces unexpected features in the infrared absorption of the $a$ – $b$ planes. These features, similar to those previously observed in other polar materials like AgBr and attributed to polarons, include extra-phonon lines (PILM’s, PhotoInduced Local Modes), and a broad band centered between 1000 and 1500 cm$^{-1}$. Afterwards, Infrared Active Vibrations (IRAV) similar to the PILM’s, together with bands peaked around 1300 cm$^{-1}$ and named $d$ or $J$, have been observed in a variety of chemically-doped cuprates. Both kinds of bands have been shown to survive in their metallic phase. The IRAV, or PILM, peaks have been attributed to local vibrations of clusters of atoms distorted by the injected charges, which self-trap under a strong coupling with the polar lattice. The $d$ band at higher energies is then straightforwardly explained in photoexcited hopping of those charges, in agreement with the polaronic models of the optical conductivity, and with the observation of a fine structure at low doping.

In connection with the present debate on the role of polarons in High-$T_c$ superconductivity, it may be crucial to determine whether the above infrared bands are originated in the CuO$_2$ planes, where superconductivity takes place, or in the surrounding crystal structures (often pictorially indicated as the “out-of-plane stuff”). According to some authors, the polaronic transport in High-$T_c$ cuprates should only involve the Cu-O chains, where present. This point of view is supported, for instance, by the absorption spectra of Y$_2$Ba$_4$Cu$_{6+n}$O$_{14+n}$, where a strong $d$ band is observed when the radiation is polarized along the chains. In other systems like La$_{2-x}$Sr$_x$CuO$_{4+y}$ and Bi$_2$Sr$_2$CaCu$_2$O$_y$, small polarons with heavy masses are invoked to describe the observed periodic displacements of the apical oxygens relative to the Cu-O planes. On the other hand, the infrared observation of local modes and/or polaron-like $d$ bands in compounds so different as Y$_2$Ba$_4$Cu$_{6+n}$O$_{14+n}$, Bi$_2$Sr$_2$YCuO$_8$, La$_2$CuO$_{4+y}$, and Nd$_{2-x}$Ce$_x$CuO$_{4+y}$ suggests that the polaronic phenomena involve directly the CuO$_2$ planes, independently of the presence of chains or apical oxygens.

In the present work we address this problem by measuring the optical conductivity of the simplest crystal structures which contain CuO$_2$ planes, the infinite-layer (IL) films of general formula (Ca,Sr)$_{1-x}$Nd$_x$CuO$_2$. A stoichiometric IL film consists of an infinite stack of CuO$_2$ planes separated by layers of alkaline-earth ions. The samples here prepared and measured are doped by reduction or by substitutions at the sites of the alkaline-earth ions, then no out-of-plane structures are present. Any doping-induced spectral feature can be originated only in the CuO$_2$ planes.

The infinite-layer (IL) structure (Ca,Sr)CuO$_2$ is thermodynamically unstable for most compositions under the usual solid state reactions. However, the corresponding epitaxial films have been successfully grown by Pulse Laser Deposition (PLD), Reactive Sputtering or Molecular Beam Epitaxy (MBE). Recently, good quality CaCuO$_2$ films were grown directly on NdGaO$_3$, (110) oriented, substrates. For the present experiment, three IL films were grown by PLD on SrTiO$_3$, a substrate more suitable for optical measurements than NdGaO$_3$. Details on the deposition procedure are reported elsewhere. The first sample was a CaCuO$_2$ film to be identified in the following as CCO. Since such a film cannot be deposited on bare SrTiO$_3$, we grew a SrTiO$_3$-SrCuO$_2$-CaCuO$_2$ heterostructure. The SrCuO$_2$ buffer layer, less than 5 nm thick, did not affect the infrared measurements. The CCO film had a thickness $d_f \approx 100$ nm and was grown under an O$_2$ partial pressure $p_O = 0.35$ mbar. Then, a film of nominal composition SrCuO$_2$ (SCO) with $d_f \sim 200$ nm was directly grown on SrTiO$_3$, under $p_O = 0.4$ mbar. In SCO films, an oxygen mobility much higher than in CCO may cause either the inclusion of excess oxygen ions, or the formation of oxygen vacancies in the CuO$_2$ planes during the growth or the cooling down of the film. In the present case, the oxygen pressure was...
kept very low during both phases of the film preparation, in order to obtain oxygen deficient CuO planes, i.e. a light electron doping. The resulting resistivity was $\rho \sim 10$ Ω cm at room temperature. In the following, the chemical formula of this film will then be written as SrCuO$_{2-y}$.

Finally, a Sr$_{0.85}$Nd$_{0.15}$CuO$_2$ (SNCO) film with $d_f \simeq 500$ nm was directly grown on SrTiO$_3$ under $p_O = 2 \times 10^{-3}$ mbar. Here, the Nd donors inject a large number of electrons in the CuO$_2$ plane, so that the room temperature resistivity falls to $\rho \sim 10$ mΩ cm. The structural properties of the three samples were studied by use of a θ-2θ diffractometer, by Scanning Electron Microscopy and by Energy Dispersive Spectroscopy (EDS). As shown in Fig. 1, all films have the c axis perpendicular to the surface and are single phase. A tiny amount of a $2\sqrt{2}a \times 2\sqrt{2}a$ superstructure was detected in the SNCO film, whose nominal composition was verified both by EDS and by measurements of the c lattice parameter.

The reflectivity measurements were performed in the frequency range 25-16000 cm$^{-1}$ for CCO, in the range 25-12000 cm$^{-1}$ for SCO and SNCO. The electric field of the radiation was polarized in the plane of the film.

The room-temperature reflectance $R(\omega)$ of the three samples is plotted by dots in Fig. 2. For sake of comparison, the reflectance of the bare SrTiO$_3$ substrate is also reported by dashed lines. The SrTiO$_3$ contribution dominates the farinfrared (FIR) reflectance of all samples, as the penetration depth of the incident radiation is much larger than $d_f$. However, several features can be attributed to the superimposed IL films. The CCO reflectance (top) shows a well defined charge-transfer band above 10000 cm$^{-1}$, while the MIR reflectivity follows that of the substrate. In the FIR region, a few absorptions appear around 230, 345, and 575 cm$^{-1}$. In the SCO reflectivity (middle), the charge-transfer band is reduced in intensity, while new absorption features arise in the MIR region. Moreover, further deviations from the substrate reflectance become evident in the FIR region. Finally, in the strongly doped SNCO, $R(\omega)$ is much different from that of the bare substrate at all frequencies. The CT band disappears, the absorption in the midinfrared grows considerably, while features similar to those of SCO are observed in the farinfrared.

The procedure described and tested in Ref. has
been followed to extract from the spectra of Fig. 2 the optical conductivity $\sigma(\omega)$ of the bare IL films. Shortly, the unknown dielectric function $\tilde{\varepsilon}_{IL}(\omega)$ has been modeled through a standard Drude-Lorentz expansion, while the dielectric function $\tilde{\varepsilon}_{\text{sub}}(\omega)$ has been extracted from reflectance and transmittance measurements. The reflectances of the film plus-substrate systems in Fig. 2 have then been fitted as described in Ref. 24, and the Drude-Lorentz parameters of $\tilde{\varepsilon}_{IL}(\omega)$ are thus determined. In CCO and SCO $\tilde{\varepsilon}_{IL}(\omega)$ is made up of Lorentzians peaked at $\omega > 0$, in SNCO it also includes a Drude term at $\omega = 0$. As shown in Fig. 2, the fits (solid lines) accurately reproduce the reflectance data of all samples.

Fig. 3. The room-temperature optical conductivity of the CaCuO$_2$ infinite-layer film is reported by a solid line, and compared with the far-infrared $\sigma(\omega)$ of a Ca$_{0.86}$Sr$_{0.14}$CuO$_2$ single crystal (dashed line), as extracted from the reflectivity data of Ref. 26. $E$, $B$, and $S$ label the external mode, the CuO$_2$ bending, and the CuO$_2$ stretching, respectively.

The real part $\sigma(\omega)$ of the optical conductivity, as obtained from $\tilde{\varepsilon}_{IL}(\omega)$, is reported in Fig. 3 (solid line) for the CCO sample. It exhibits three phonon lines at 230, 345 and 573 cm$^{-1}$ corresponding to the TO external mode ($E$), to the bending ($B$) and stretching ($S$) mode of the CuO$_2$ planes, respectively. The symmetric phonon lineshapes and the sharp charge-transfer band at 10500 cm$^{-1}$ confirm that this CCO film is stoichiometric, even if a weak midinfrared absorption in the 1500 cm$^{-1}$ region may be attributed to a tiny amount of oxygen defects (see below). No infrared data on pure CaCuO$_2$ crystals are available to check our procedure, due to the above mentioned instability of this compound. In Fig. 3, the far-infrared $\sigma(\omega)$ extracted from the reflectivity of a single crystal of Ca$_{0.86}$Sr$_{0.14}$CuO$_2$ is then reported for comparison. Therein, the three TO phonon peaks are centered at 230 ($E$), 360 ($B$), and 583 cm$^{-1}$ ($S$). The agreement between the spectrum of the single crystal and that of the IL film confirms the reliability of the present analysis. The slight shifts of the $B$ and $S$ phonon peaks of Ca$_{0.86}$Sr$_{0.14}$CuO$_2$ with respect to the corresponding peaks of CaCuO$_2$ can be attributed to an average expansion of the CuO$_2$ lattice in the former compound, in presence of the large Sr impurities.²⁴

Fig. 4. The room-temperature optical conductivities of the IL films SrCuO$_{2-y}$ (top) and Sr$_{0.85}$Nd$_{0.15}$CuO$_2$ (center) are compared with that of a single crystal of Nd$_4$CuO$_{4-y}$ at 20 K (bottom, from Ref. 5). $E$, $B$, and $S$ label the external mode, the CuO$_2$ bending, and the CuO$_2$ stretching, respectively. The dots indicate the local modes $\nu_1$ and $\nu_2$. The arrows mark the features resolved in the spectrum of the slightly-doped SCO, and assigned to overtones and combinations of $\nu_1$ and $\nu_2$ (see text).

On the top of Fig. 4, $\sigma(\omega)$ is reported between 200 and 3000 cm$^{-1}$ for the slightly electron-doped film SrCuO$_{2-y}$. Major changes are evident with respect to the stoichiometric CCO of Fig. 3. The bending mode transfers spectral weight to a softer vibration centered at $\nu_1 = 305$ cm$^{-1}$, while the stretching mode at 573 cm$^{-1}$ is nearly replaced by a strong peak at $\nu_2 = 480$ cm$^{-1}$. The two IRAV’s (indicated by dots in the Figure) are not related to the replacement of the out-of-plane Ca by Sr, as confirmed by the phonon spectrum of Ca$_{0.86}$Sr$_{0.14}$CuO$_2$. The dots indicate the local modes $\nu_1$ and $\nu_2$.
in Fig. 3. On the other hand, IRAVs are predicted to appear on the low-energy side of the corresponding extended phonons (on both sides for very strong coupling) and whenever self-trapped charges are distorting the \( \text{CuO}_2 \) planes. The polaronic character of the SCO spectrum is confirmed by the insurmountable above 1000 cm\(^{-1} \) of a \( d \) band with resolved phonon-like structures. This effect has been theoretically predicted and already observed in perovskite cuprates at low doping. Therein, however, the line spacing within the polaron band is narrower than in the IL film of Fig. 4, consistently with the higher number of vibrational modes available in the perovskite structure. The band structure should be based on the local modes of the distorted clusters, not on the extended phonons of the unperturbed lattice. Indeed, the frequencies of the features indicated by arrows in Fig. 4, and obtained by a fit to a sum of Lorentzian, correspond to the following series of overtones and combinations of the two IRAVs \( \nu_1, \nu_2 \): 2\( \nu_1 \) (observed at 635 vs. 610 cm\(^{-1} \)), 2\( \nu_1+\nu_2 \) (1100 vs. 1090 cm\(^{-1} \)), 3\( \nu_2 \) (1450 vs. 1440 cm\(^{-1} \)), 2\( \nu_1+2\nu_2 \) (1630 vs. 1570 cm\(^{-1} \)), 4\( \nu_2 \) (1950 vs. 1920 cm\(^{-1} \)), 5\( \nu_2 \) (2350 vs. 2400 cm\(^{-1} \)). The excellent agreement here reported also implies that the eventual anharmonic shifts are not much larger than the experimental uncertainties. One may also notice that the combination \( \nu_1+\nu_2 \) and the overtone 2\( \nu_2 \), expected around 785 and 960 cm\(^{-1} \) respectively, are missing. Indeed, both these lines should appear in the region where the reflectivity of \( \text{SrTiO}_3 \) rapidly drops, and the sensitivity of our procedure for reconstructing \( \sigma(\omega) \) is poor.

In the heavily doped film \( \text{Sr}_{0.85}\text{Nd}_{0.15}\text{CuO}_2 \) (middle of Fig. 4), the \( E \) phonon is shielded by a broad Drude absorption with \( \sigma(0) = 130 \ \Omega^{-1}\text{cm}^{-1} \) (in good agreement with the above dc determination of \( \rho \)) and with \( \Gamma = 500 \ \text{cm}^{-1} \). The \( B \) and \( S \) modes are barely discernible, while the two IRAVs and the \( d \) band are more intense than in SCO. The \( d \) band is also less resolved, but shows the peak \( \nu_1+\nu_2 \) at 800 cm\(^{-1} \). This strong combination band, not seen in the SCO spectrum, is observed in heavily doped NCO, probably due to the smaller penetration depth of the radiation. The overall \( \sigma(\omega) \) of NCO is impressively similar to those previously reported for the perovskitic cuprates. As an example, in the bottom of Fig. 4 we plot \( \sigma(\omega) \) for an electron-doped single crystal of \( \text{Nd}_2\text{CuO}_{4-y} \) (NCO) at 20 K. The local modes of NCO associated with the modes \( B \) and \( S \) of its \( \text{CuO}_2 \) planes correspond to the IRAVs of the SCO IL film. The behaviors with frequency of their \( d \) bands are also very similar. On the other hand, the evolution with temperature of those bands seems to be different. Both in \( \text{Nd}_2\text{CuO}_{4-y} \) and \( \text{La}_2\text{CuO}_{4+y} \), the IRAVs and the \( d \) band are barely detectable at room temperature and reach their maximum intensity at a “polaron freezing” temperature \( T_0 \sim 150 \text{ K} \). In the SCO and NCO infinite-layer films here investigated, preliminary measurements show that the optical conductivity does not change appreciably when lowering the temperature, suggesting a \( T_0 \geq 300 \text{ K} \).

In conclusion, the present work first reports on the optical conductivity of \( \text{CuO}_2 \) infinite-layer films. In a \( \text{CaCu}_2\text{O}_2 \) film used as stoichiometric reference, \( \sigma(\omega) \) just shows the three TO phonons and a sharp charge-transfer band in the near infrared. Two \( \text{SrCu}_2\text{O}_2 \) films have been electron-doped, one (SCO) by a few oxygen vacancies, the other (NCO) by substitution of 15% Sr ions by Nd ions. In both cases the extended phonons and the charge-transfer band loose much of their intensity, while new features appear. These consist of a pair of IRAV modes in the far infrared, and of a broad band above 1000 cm\(^{-1} \). In the slightly-doped film, the latter has been resolved in phonon-like peaks whose energies correspond to overtones and combinations of the two IRAVs. In the strongly doped film, \( \sigma(\omega) \) reproduces faithfully that of electron-doped \( \text{Nd}_2\text{CuO}_{4-y} \), a cuprate which contains out-of-plane oxygens. Remarkable correspondences can also be found with the spectra reported in the literature for hole-doped compounds with apical oxygens and chains.

The similarities here reported between the spectra of infinite-layer compounds and those of different perovskitic cuprates provide conclusive evidence that the polaronic excitations observed in High-\( T_c \) superconductors do not depend on the existence of chains, apical oxygens or other “out-of-plane stuff”, but are intrinsic to the \( \text{CuO}_2 \) planes. This result removes a common objection to the possibility that polarons are directly involved in the mechanism of High-\( T_c \) superconductivity.

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