Small and large polarons in nickelates, manganites, and cuprates

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Abstract

By comparing the optical conductivities of La$_{1.67}$Sr$_{0.33}$NiO$_4$ (LSNO), Sr$_{1.5}$La$_{0.5}$MnO$_4$ (SLMO), Nd$_2$CuO$_{4-y}$ (NCO), and Nd$_{1.96}$Ce$_{0.04}$CuO$_4$ (NCCO), we have identified a peculiar behavior of polarons in this cuprate family. While in LSNO and SLMO small polarons localize into ordered structures below a transition temperature, in those cuprates the polarons appear to be large, and at low $T$ their binding energy decreases. This reflects into an increase of the polaron radius, which may trigger coherent transport.
La$_{2-x}$Sr$_x$NiO$_{4+y}$ (LSNO) and Sr$_{2-x}$La$_x$MnO$_4$ (SLMO) are isostructural to the high-$T_c$ superconductor La$_{2-x}$Sr$_x$CuO$_{4+y}$ (LSCO). Their parent compounds La$_2$NiO$_4$ and Sr$_2$MnO$_4$ are charge-transfer, antiferromagnetic insulators like La$_2$CuO$_4$. Nevertheless, neither LSNO, nor SLMO exhibit superconductivity. Both of them are even poor conductors: the former becomes metallic only for $x \sim 1$, in the latter no metallic phase has been observed yet. Recently, evidence for the formation of polarons (bipolarons) in LSNO (SLMO) and for their ordering below $\sim 220$ K ($\sim 250$ K) has been reported. \cite{1,2} In the cuprate families which show High-$T_c$ superconductivity, polaron formation induced by doping has been detected in several infrared experiments. \cite{3–6} However, no charge ordering has been observed by diffraction techniques in the superconducting materials, even if EXAFS data on BSCCO and LSCO have been interpreted in terms of charged stripes, possibly short-living. \cite{7}

In the present paper, a comparison is proposed among the infrared polaron bands in some nickelates, manganites, and cuprates, aimed at detecting any anomalous behavior in the latter compounds with respect to the other perovskites. Such comparison should be particularly meaningful at low temperature, where the superconducting transition takes place in cuprates only. The optical densities extracted from transmission measurements on polycrystalline La$_{1.67}$Sr$_{0.33}$NiO$_4$, Sr$_{1.5}$La$_{0.5}$MnO$_4$, and Nd$_2$CuO$_{4-y}$ (NCO) dissolved in a CsI matrix, as well as the optical conductivity obtained from the reflectivity of a single crystal of Nd$_{1.96}$Ce$_{0.04}$CuO$_4$ will then be compared with each other.

The experimental procedure has been reported previously. \cite{8} Once the optical conductivity $\sigma(\omega)$ (or the optical density $O_d \propto \sigma(\omega)$, see Ref. \cite{8}) of a doped charge-transfer insulator has been determined, it can be fitted to the following general expression:

$$
\sigma(\omega) = \sigma_{ph}(\omega) + \sigma_{IRA}(\omega) + \sigma_{pol}(\omega) + \sigma_{MIR}(\omega) + \sigma_{CT}(\omega).
$$

(1)

Here $\sigma_D(\omega)$ is the Drude conductivity from quasi-free carriers, $\sigma_{ph}(\omega)$ is the contribution of the extended TO phonons, $\sigma_{IRA}(\omega)$ that of the local modes induced by the self-trapped charges which distort the lattice, $\sigma_{MIR}(\omega)$ is the $T$-independent part of the midinfrared absorption (possibly due to states created by chemical doping in the charge-transfer gap), and
\( \sigma_{CT}(\omega) \) is the charge-transfer band. All those terms are usually reproduced by Lorentzians multiplied by \( 4\pi/\omega \).

Analytical expressions for the contribution \( \sigma_{pol}(\omega) \) have been derived by Reik in the case of a small polaron which undergoes adiabatic hopping, and by Devreese et al. and Emin in the case of a large polaron extended over several lattice sites. For a small polaron one may write:

\[
\sigma_{pol}^{\text{small}}(\omega) \propto \left( \frac{n_p}{\omega} \Delta \right) \sinh(4E_p\omega/\Delta^2) \exp\left[ -(\omega^2 + 4E_p^2)/\Delta^2 \right]
\]

where \( n_p \) is the polaron concentration at \( T \), \( \omega \) is the photon energy, \( \Delta = 2\sqrt{2E_pE_{vib}} \), and \( E_p \) is the polaron binding energy. One may put in Eq. (2) \( E_{vib} = (1/2) \hbar \omega^* \) in the low-\( T \) limit, where \( \omega^* \) is a characteristic phonon frequency, and \( E_{vib} \sim kT \) in the high-\( T \) limit. All quantities are expressed in cm\(^{-1} \). For large values of \( E_p/\omega^* \), the maximum absorption will occur at \( \omega \simeq 2E_p/\hbar \). Hopping with simultaneous annihilation (for \( \omega < 2E_p/\hbar \)) or creation (for \( \omega > 2E_p/\hbar \)) of optical phonons causes the broadening of the polaron band. In turn, the large-polaron conductivity can be written as:

\[
\sigma_{pol}^{\text{large}}(\omega) \propto \left( \frac{n_p(T)}{\omega} \right) a^2(\omega - 3E_p) \left[ 1 + a^2(\omega - 3E_p) \right]^3
\]

where \( a \propto \sqrt{2mR} \), with \( m \)=polaron effective mass and \( R \)=polaron radius. One may notice that the dependence on temperature here comes from \( n_p(T) \). Moreover, the absorption in Eq. (3) has a threshold at \( 3E_p \), even if the large polaron may also perturb the far infrared phonon spectrum at frequencies much lower than \( E_p/\hbar \).

The experimental optical density \( O_d(\omega) \) is shown in Fig. 1 at low (20 K) and high (300 K) temperature for the polycrystalline sample \( \text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4 \), a powder where a charge/lattice modulation along the diagonals of the Ni-O squares on the \( a-b \) planes, with a period \( 3\sqrt{2}a \), has been observed below 250 K. The spectrum at 300 K in Fig. 1 shows a broad polaronic background superimposed to phonon peaks. It extends from the lowest frequencies to the charge-transfer (CT) band, peaked at 10200 cm\(^{-1} \). This polaronic continuum at \( \omega < 2E_p \) shows that the initial phonon states at high energies are populated. Thus, the energy
needed for the charge to move from its perturbed site to a neighboring, unperturbed, site is comparable with that of thermal excitations, and the polarons are mobile. This picture changes drastically at low $T$, as shown by the 20 K spectrum: here, a depopulation of the phonon states opens an energy gap in the background below $\sim 700 \text{ cm}^{-1}$, so that a midinfrared band peaked at $\sim 2000 \text{ cm}^{-1}$ shows up. Thus, at low $T$ the charges remain self-trapped until photons of suitable energy promote intersite hopping.

The formation of charged superstructures between 250 and 200 K, as reported in diffraction experiments, is confirmed by the behavior of the strong phonon band around 350 cm$^{-1}$ in the inset of Fig. 1. In our powder, this results from a superposition of the twofold $E_u$ bending of the in-plane Ni-O bond, and from the $A_u$ mode which displaces the Ni atom and both apical oxygens along the $c$-axis. In the pure nickelate, the three vibrations should be observed at approximately the same energy. In LSNO at 300 K, the charges induce random deformations of the octahedra which cause an inhomogeneous broadening of the peak. Below 250 K, the ordering transition induces regular deformations which give rise to the sharp phonon doublet shown in the inset.

If one fits Eq. (1) to the data of Fig. 1, with $\sigma_{pol}(\omega)$ given by the small-polaron Eq. (2), one gets the dashed curves plotted in Fig. 1. Except for the very far infrared, where the transmittance of the CsI matrix is poor, the absorption spectrum is well reproduced by the model, where Lorentz oscillators at 3200 cm$^{-1}$ and at 13500 cm$^{-1}$ have been introduced for $\sigma_{MIR}(\omega)$ and $\sigma_{CT}(\omega)$, respectively. The 300 K fit yields a polaron bandwidth $\Delta = 1233 \text{ cm}^{-1}$ and $2E_p = 1945 \text{ cm}^{-1}$, in excellent agreement with the high-$T$ prediction $\Delta = 2\sqrt{2E_p kT}$ which gives $2E_p = 1900 \text{ cm}^{-1}$ The 20 K fit in turn yields $2E_p = 2000 \text{ cm}^{-1}$ and, from the low-$T$ expression $\Delta = 2\sqrt{E_p \omega^*} = 1050 \text{ cm}^{-1}$, one finds $\omega^* = 275 \text{ cm}^{-1}$.

If in the perovskite one replaces Ni by Mn, one finds effects similar to those of Fig. 1, suggestive of an even stronger charge-lattice interaction. In Fig. 2 one can see the optical density of $\text{Sr}_{1.5} \text{La}_{0.5} \text{MnO}_4$, a sample where commensurate charge/magnetic superlattices similar to those of $\text{La}_{1.67} \text{Sr}_{0.33} \text{NiO}_4$ have been detected by electron diffraction, and by neutron scattering. In SLMO, however, the superlattices are attributed to the ordering
of small bipolarons. At 300 K, a deep absorption minimum is already present at 750 cm$^{-1}$, pointing toward low polaron mobilities even at room temperature. Here, the broad background observed in LSNO at 300 K should then appear at much higher temperatures. However, the behavior at low $T$ is not qualitatively different, as the minimum in Fig. 2 further deepens, through a transfer of spectral weight towards higher energies. At $T < 100$ K a polaron-like peak is left, which is peaked at a much higher energy than in Fig. 1 and can be attributed to the bipolaronic superstructure found out below $\sim 220$ K. Such a charge ordering is confirmed here again by splittings in the intense $E_u-A_u$ manifold (inset of Fig. 2). At room temperature, a broad absorption peak with a few shoulders is observed, suggestive of disordered octahedra deformations. Between 250 and 200 K, three lines appear at 346, 388, and 433 cm$^{-1}$. The detection of a triplet suggests that two charges on a single site remove both the twofold degeneracy of the Mn-O bending mode and the accidental degeneracy between this mode and the $A_u$ vibration.

Let us now consider the infrared spectrum of a cuprate like NCO, the parent compound of the e-doped high-$T_c$ superconductor Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ (NCCO). The infrared $a-b$ plane reflectivity of both insulating (NCO) and metallic (NCCO) single crystals has been extensively studied, and found to exhibit polaronic contributions centered at $\sim 1000$ cm$^{-1}$. Here, we have measured the infrared transmission a Nd$_2$CuO$_{4-y}$ (NCO) pellet prepared in the same way as the perovskites of Figs. 1 and 2 to facilitate the comparison. The structure of NCO differs slightly from that of LSNO and SLMO, as in the former perovskite the apical oxygens are displaced on the walls of the tetragonal cell.

The optical density $O_d$ of the NCO pellet, where extra charges are introduced by oxygen deficiency, is shown in Fig. 3. The farinfrared absorption shows the four TO phonon peaks of the $a-b$ plane, which partially hide the three TO modes polarized along the $c$-axis. Indeed, the frequencies of these latters are very close to those of the first, second, and fourth $a-b$ mode, respectively. At low $T$ one may also notice a few shoulders on the TO phonons, the IRAV modes induced by doping. In the midinfrared, where in single crystals one distinguishes two peaks centered at $\sim 1000$ cm$^{-1}$ ($d$ band) and at $\sim 3500$ cm$^{-1}$ (MIR band),
respectively, Fig. 3 shows a broad absorption delimited by a gap below $\sim 800 \text{ cm}^{-1}$. If one now compares the optical densities of Fig. 3 with those of the Ni, Mn oxides in Figs. 1 and 2, one remarks that their temperature behavior is different. Indeed, in the Ni, Mn oxides the gap between the phonon region and the polaron band **deepens** as $T$ lowers. On the contrary, in the reduced cuprate the intensity of the background slightly increases at low $T$, so that the gap at $\sim 800 \text{ cm}^{-1}$ tends to be partially filled. In other words, the few polaronic charges present in NCO seem to increase their mobility at low temperature, instead of localizing as observed in LSNO and SLMO.

In order to verify this unexpected behavior in a more doped sample, and to check whether it can be ascribed to the $a - b$ plane, we have also studied a single crystal of Nd$_{2-x}$Ce$_x$CuO$_4$. This latter is expected to be more heavily doped than NCO, but its Ce concentration ($x=0.04$) is much lower than that reported for the insulator-to-metal transition ($x=0.12$). Fig. 4 shows the $a - b$ plane optical conductivity $\sigma(\omega)$ of the above NCCO crystal. The solid lines are extracted by Kramers-Kronig transformations from the normal-incidence reflectivity $R(\omega)$, as measured from 75 through 20000 cm$^{-1}$. The latter has been accurately extrapolated to zero frequency by fitting the reflectivity to a model Drude-Lorentz dielectric function, then by reconstructing the missing part of $R(\omega)$ through the fitting parameters. At high frequency, the extrapolation has been based on existing NCO data up to 40 eV. In Fig. 4, the $\sigma(\omega)$ thus obtained exhibits at 300 K the expected insulator-like behavior and a $d$ band peaked at $\sim 1000 \text{ cm}^{-1}$. The latter, partially superimposed to a broad midinfrared band, can be fitted by the large polaron model of Eq. (3), with the characteristic threshold at $3E_p$, here found out at $\sim 500 \text{ cm}^{-1}$. One may notice that around $E_p \simeq 170 \text{ cm}^{-1}$, the 300 K curve shows a broad absorption that has been also observed in previous experiments on the same compound. All of the four $E_u$ phonons of NCCO exhibit Fano-like lineshapes, possibly due to interactions with the polaronic background, as it will be discussed in detail in a separate paper. The resulting fit, in excellent agreement with the measured $\sigma(\omega)$, is shown by a dashed line in Fig. 4.

As the temperature is lowered, the spectrum of Fig. 4 changes drastically. At 20 K, the $d$
band loses much of its intensity, its peak moves towards lower frequencies, while two peaks appear at the lowest frequencies here measured. The former is the narrow contribution at $\sim 100\,\text{cm}^{-1}$. The latter, which extends to the lowest frequencies here measured, suggests the appearance of a strong Drude-like contribution. Both features are insensitive to the choice of the extrapolation to zero frequency, as verified by comparing the results of the above procedure based on a Drude-Lorentz fit with a standard Hagen-Rubens approximation. The fit of the 20 K curve by the large polaron model of Eq. (3) places the $3E_p$ threshold at $300\,\text{cm}^{-1}$, so that $E_p$ here coincides with the sharp peak at $100\,\text{cm}^{-1}$. As the large-polaron radius is $R_p \approx (\alpha^2 m \omega^*)^{-1} \approx (E_p m)^{-1}$, where $m$ is the effective mass of a quasi-free electron, the softening here observed between 300 and 20 K suggests that $R_p$ increases at low temperature. As one also observes at the same $T$ the appearance of a Drude-like peak, one may speculate that the increase in the polaron size may trigger a coherent polaronic transport. The impressive transfer of spectral weight towards lower energies observed in NCCO at low temperature can be better appreciated in the inset of Fig. 4, where the difference $\Delta \sigma(\omega)$ between the optical conductivities at 20 K and 300 K, once subtracted of the Lorentzian contributions from phonons and local modes, is plotted vs. $\omega$. One can see how the polaron band at $\sim 1000\,\text{cm}^{-1}$ looses weight at low temperature in favor of the peak at $\sim 100\,\text{cm}^{-1}$ and of a Drude peak centered at zero frequency. This behavior, just opposite to that of hopping small polarons in the nickelate and the manganite of Figs. 1 and 2, confirms and extends the result of Fig. 3. In the heavily doped cuprate the polarons are large, and at low temperature their radius increases so that coherent carrier states may become available, as shown by the insurgence of a strong Drude term. This surprising effect appears to be similar to an anomalous enhancement in the Drude optical conductivity observed at low temperature $^{22}$ in superconducting $\text{La}_2\text{CuO}_4$.66.

In conclusion, the infrared region of all the perovskitic oxides here examined is dominated by polaronic effects. Nevertheless, while the optical conductivities of the nickelate LSNO and of the manganite SLMO are easily interpreted in terms of charge localization and ordering at low temperature, in excellent agreement with the electron diffraction ex-
periments, $\sigma(\omega)$ in the low-doping cuprate NCO shows that the fraction of mobile charges increases slightly as the temperature decreases. In a Ce-doped NCCO single crystal, whose midinfrared absorption is well fitted by a large-polaron model with a polaron binding energy which decreases at low temperature, a peak appears in the extreme farinfrared at 20 K suggesting the onset of a Drude-like behavior. This result shows that at temperatures that are typical of the superconducting transition in more doped cuprates, the normal-state conductivity of a semiconducting member of the family may become metallic due to an increase in the average polaron radius. It can be emphasised once again that such optical behavior is opposite to that displayed by the small polarons in the perovskites of Ni and Mn, which indeed are poor metals and do not exhibit superconductivity.

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FIGURES

FIG. 1. The optical density $O_d$ of polycrystalline La$_{1.67}$Sr$_{0.33}$NiO$_4$ is reported at 300 K and 20 K (solid lines), and fitted to Eq. (1) by use of the small-polaron conductivity of Eq. (2) (dashed lines). The region of the $E_u - A_u$ manifold is reported in the inset at five different temperatures (the dotted line refers to 300 K, the solid one to 20 K).

FIG. 2. The optical density $O_d$ of polycrystalline Sr$_{1.5}$La$_{0.5}$MnO$_4$ is reported at 300 K (dashed line) and 20 K (solid line). The region of the $E_u - A_u$ manifold is reported in the inset at five different temperatures (the dotted line refers to 300 K, the solid one to 20 K).

FIG. 3. The optical density $O_d$ of polycrystalline Nd$_2$CuO$_{4-y}$ at 300 K (dashed line) and 20 K (solid line).

FIG. 4. The $a - b$ plane optical conductivity $\sigma(\omega)$ of a single crystal of Nd$_{1.96}$Ce$_{0.04}$CuO$_4$ at 300 K and 20 K (solid lines) is fitted to Eq. (1), with $\sigma_{pol}(\omega)$ given by the large-polaron model of Eq. (3) (dashed lines). In the inset, the difference $\Delta \sigma(\omega)$ between the optical conductivities at 20 K and 300 K, once subtracted of the contributions from phonons and local modes, is plotted in units $10^3 \Omega^{-1} \text{cm}^{-1}$ vs. $\omega$ in cm$^{-1}$.
Optical density vs. Energy (cm$^{-1}$) for Sr$_{1.5}$La$_{0.5}$MnO$_4$ at different temperatures: T = 300 K, 250 K, 200 K, 100 K, and 20 K.
Optical density

Energy (cm$^{-1}$)

T = 20K, 300K

Nd$_2$CuO$_{3.97}$

Fig3J$^{sup97}$
Nd$_{1.96}$Ce$_{0.04}$CuO$_4$

$\sigma$ (Ω$^{-1}$ cm$^{-1}$)

Energy (cm$^{-1}$)

$\Delta\sigma$

T = 20 K
300 K

Fig4Jsup97