Infrared response of ordered polarons in layered perovskites

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Abstract

We report on the infrared absorption spectra of three oxides where charged superlattices have been recently observed in diffraction experiments. In La$_{1.67}$Sr$_{0.33}$NiO$_4$, polaron localization is found to suppress the low-energy conductivity through the opening of a gap and to split the $E_{2u}$-$A_{2u}$ vibrational manifold of the oxygen octahedra. Similar effects are detected in Sr$_{1.5}$La$_{0.5}$MnO$_4$ and in La$_2$NiO$_{4+y}$, with peculiar differences related to the type of charge ordering.
The layered perovskites of general formula $\text{La}_{2-x}\text{Sr}_x\text{MO}_4$, with $\text{M} = \text{Ni}, \text{Mn}, \text{and Cu}$, at $x=0$ (or at $x=2$ for $\text{M} = \text{Mn}$) are charge-transfer, antiferromagnetic insulators and have the same crystal structure. While the cuprate turns into a high-$T_c$ superconductor at a Sr doping $x = 0.06$, $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$ (LSNO) becomes metallic, not superconducting, at $x \sim 1$, and $\text{Sr}_{2-x}\text{La}_x\text{MnO}_4$ (SLMO) remains insulating at any $x$. Increasing effort is aimed at understanding how so different transport properties are related to the excitation spectrum of these materials. The optical conductivity of the perovskites has been extensively discussed in the literature since the discovery of high-$T_c$ superconductivity. Chemical doping is known to cause the insurgence of midinfrared bands (MIR) which, according to several authors, are responsible for the well-known ”anomalous Drude” behavior in the metallic phase. However, the origin of such midinfrared absorption is controversial. In cuprates like $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, the MIR band is made of two components: i) a broad band peaked at $\sim 4000 \text{ cm}^{-1}$, independent of $T$ and generally attributed to the electronic states produced by doping in the charge-transfer gap; ii) a component peaked at $\sim 1000 \text{ cm}^{-1}$, strongly dependent on temperature and showing phonon-like structures. The latter feature has been attributed to hopping polarons by some authors, to magnetic excitations by others. MIR bands were also observed in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+y}$ for various $x$ and $y$, and attributed to polarons. However, the calculated small-polaron optical conductivity $\sigma_{pol}$ was then found unable to describe the spectrum of $\text{La}_{1.84}\text{Sr}_{0.16}\text{NiO}_{4+y}$ at different temperatures.

An attempt to define the controversy on the polaronic nature of the above absorption features is made in the present paper by studying three layered perovskites where the existence of selftrapped charges has been established in diffraction experiments. Indeed, the photoexcitation of such charges will produce itinerant polarons whose characteristic infrared bands can be first studied here in a well defined environment. We also report on farinfrared observations which allow to identify the lattice deformations involved in the self-trapping of the charges.

Recently, evidence for polaronic stripes in the basal $a - b$ plane below a charge ordering
transition temperature $T_0 \simeq 240$ K in LSNO, and strong indications for bipolaronic ordered structures below $T_0 \simeq 220$ K in Sr$_{1.5}$La$_{0.5}$MnO$_4$, have been obtained by electron diffraction. Neutron scattering experiments on La$_2$NiO$_{4+y}$ (LNO) and Sr$_{1.5}$La$_{0.5}$MnO$_4$ have shown that charge and magnetic order are strictly related, as the polaron stripes act as charged walls which separate different antiferromagnetic domains. The formation of these walls at critical doping levels may lead to a suppression of the superconductivity, as observed in La$_{2-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ at $x \sim 1/8$.

Polycrystalline La$_2$NiO$_{4.2}$, La$_{1.67}$Sr$_{0.33}$NiO$_4$ and Sr$_{1.5}$La$_{0.5}$MnO$_4$, obtained as described in Refs. 9,10, have been finely milled, diluted in CsI (1:100 in weight), and pressed in pellets under vacuum. The intensity $I_s$ transmitted by the pellet containing the oxide and that, $I_{CsI}$, transmitted by a pure CsI pellet, were measured at the same $T$ by rapid scanning interferometers between 130 and 12000 cm$^{-1}$, after mounting both pellets on the cold finger of a closed-cycle cryostat. A normalized optical density defined as $O_d(\omega) = \ln[I_{CsI}(\omega)/I_s(\omega)]$ was thus obtained. In general, the optical density of a pellet will reflect only qualitatively the optical conductivity of the material. However, in the present case the reflectivity of the pellet is low, the perovskite dilution is high, and for the dielectric function of the oxide one has $\epsilon_1(\omega) >> \epsilon_2(\omega)$. Under these conditions, it can be shown that the above defined $O_d(\omega)$ is proportional to $\sigma(\omega)$, the optical conductivity of the pure perovskite, over the frequency range of interest here.

$O_d(\omega)$ is shown in Fig. 1 at five different temperatures for the polycrystalline sample La$_{2-x}$Sr$_x$NiO$_{4+y}$ with $x=0.33$, a powder where a charge/lattice modulation along the diagonals of the Ni-O squares on the $a - b$ planes, with a period $3\sqrt{2}a$, was observed below 240 K. The spectrum at 300 K in Fig. 1 shows a broad continuum of states with phonon peaks superimposed, which extends from the lowest frequencies through the charge-transfer (CT) gap, which is peaked at 10450 cm$^{-1}$. On the opposite side, $O_d$ decreases at low frequency. Then, the broad background which at high $T$ partially shields the phonons cannot be attributed to conventional Drude absorption, consistently with the low dc conductivity of this LSNO sample [$\rho (300$ K) $\sim 1$ $\Omega$cm, $\rho (100$ K) $\sim 10^2$ $\Omega$cm]. As $T$ is lowered, an
energy gap opens in the background below $\sim 700 \text{ cm}^{-1}$. At 100 K the absorption does not change any more and a well defined midinfrared band appears. The strong dependence on $T$ of this band up to 3000 cm$^{-1}$ or more, is suggestive of polaronic absorption. Photons in the midinfrared range excite adiabatic polaron hopping from a perturbed site to neighboring, unperturbed sites. \[16\] The transition rate is peaked approximately at twice the polaron binding energy $E_p$. \[17\] The broadening at $\omega < 2E_p$ is due to hopping with simultaneous annihilation of optical phonons, that at $\omega > 2E_p$ to hopping with creation of phonons. In some cuprates such vibronic lines have been resolved at low doping. \[3\] At room temperature, the strong absorption at $\omega < 2E_p$ in Fig. 1 shows that the initial phonon states at high energies are populated. Thus, the energy needed for the charge to jump from site to site is comparable with that of thermal excitations, and polarons are mobile. At lower temperatures, a depopulation of the highest phonon states opens the energy gap shown in Fig. 1 and prevents thermally activated hopping, so that the charges remain selftrapped. Then, the infrared spectra of Fig. 1 provide evidence for polaron localization between 250 and 200 K in LSNO. This does not necessarily imply that polarons are ordered below those temperatures. Evidence for an ordering transition will be discussed further on, in connection with the far-infrared spectrum.

As already done in previous infrared investigations of the LSNO system, we have also compared our data with the model optical conductivity for a small polaron, \[17\]

$$\sigma_{pol} \propto (1/\omega \Delta) \sinh(4E_p \omega / \Delta^2) \exp[-(\omega^2 + 4E_p^2)/\Delta^2]$$  \[1\]

where $\omega$ is the photon energy and $\Delta = 2 \sqrt{2E_p E_{vib}}$. One may put $E_{vib} = (1/2) \omega^*$ 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$^{-1}$. The total optical conductivity will be given by \[3\]:

$$\sigma(\omega) = \sigma_{ph}(\omega) + \sigma_{pol}(\omega) + \sigma_{MIR}(\omega) + \sigma_{CT}(\omega)$$  \[2\]

where Lorentzian lineshapes multiplied by $(\omega/4\pi)$ are used for the phonon contribution $\sigma_{ph}(\omega)$, for the $T$-independent part of the midinfrared absorption $\sigma_{MIR}(\omega)$, and for the
charge-transfer band \( \sigma_{CT}(\omega) \). For the present samples, as reported above, \( O_d(\omega) \propto \sigma(\omega) \) and one can fit Eqs. (1) and (2) to data in Fig. 1. The resulting curves at 300 and 20 K are plotted in Fig. 1 (b). The 300 K fit can be shown to be selfconsistent, as it yields independently the peak energy \( 2E_p = 1945 \text{ cm}^{-1} \) and the bandwidth \( \Delta = 1233 \text{ cm}^{-1} \). Using the high-\( T \) limit \( \Delta = 2\sqrt{2E_p kT} \), one gets \( 2E_p = 1900 \text{ cm}^{-1} \) in excellent agreement with the above determination. 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 \( \omega^* = 275 \text{ cm}^{-1} \). Here, both \( \Delta \) and \( \omega^* \) are likely to be overestimated. This is due to the misfit near the band edge, which could possibly be eliminated by a model where at least two different modes are involved in polaron formation.

The three resolved \( E_{2u} \) modes of the \( a-b \) plane, out of the four predicted by theory, are found at 20 K (300 K) at 175, 235, 695 (670) \text{ cm}^{-1}. Two \( A_{2u} \) modes polarized along the \( c \)-axis, out of the three predicted, are observed at 300 \text{ cm}^{-1} \) as a weak shoulder, and at 501 (501) \text{ cm}^{-1} \) as a well resolved peak. The above assignment is based on previous determinations [18,19] in La\(_2\)NiO\(_4\) single crystals. As the temperature is lowered, major changes are observed in the phonon spectrum of Fig. 1. The \( E_{2u} \) stretching mode at 670 \text{ cm}^{-1} \) hardens regularly as the lattice contracts, an effect already observed, [7] while both low-energy \( E_{2u} \) modes, which are shielded by the polaronic continuum above 250 K, spring up at lower \( T \)'s.

The most interesting effect of temperature involves the absorption feature around 350 \text{ cm}^{-1} \) (see inset). This peak includes the double degenerate \( E_{2u} \) bending mode of the in-plane Ni-O bond, and the \( A_{2u} \) mode which displaces the 4 basal oxygens relative to the Ni atom and to both apical oxygens. Those two phonons, observed by neutron scattering in La\(_2\)NiO\(_4\) at 347 and 346 \text{ cm}^{-1} \), respectively, [14] are quasi-degenerate due to the high symmetry of the oxygen octahedron which surrounds the Ni atom. [20] Any distortion of the oxygen square, as produced by a selftrapped charge, will remove the twofold degeneracy along the \( a \) and \( b \) axes of the \( E_{2u} \) phonon, any axial distortion will remove the degeneracy between \( A_{2u} \) and \( E_{2u} \). [21] This process is clearly monitored in the inset of Fig. 1. Above 250 K, due to disorder
and to polaron mobility, random splittings result in a broad absorption. At 200 K a sharp
doublet appears with peak frequencies at 341 and 382 cm$^{-1}$, while the band narrows. This
abrupt change yields evidence for spatial ordering of the octahedra distortions. [22] Indeed,
no structural (i.e. tetrahedral-orthorombic) transition would produce such a large splitting
in the bending mode (see the results reported in Ref. [23] for La$_{2-x}$Sr$_x$CuO$_4$.) Moreover,
the occurrence of structural transitions in doped La$_2$NiO$_4$ has been explicitly excluded by
high-resolution neutron diffraction. [19]

The Sr-free compound La$_2$NiO$_{4+y}$ (LNO) exhibits incommensurate charge and magnetic
ordering in neutron scattering experiments. At $y=0.125$ the polaronic structures are related
to the ordering of the out-of-plane oxygens. [11] Superlattice peaks which increase in intensity
by a factor of 4 below 230 K [19] have been also observed in a sample with $y=-0.13$. These
results show that incommensurate charge ordering may occur in LNO for various oxygen
nonstoichiometries. The absorption spectrum of La$_2$NiO$_{4.2}$ is reported in Fig. 2. Polaronic
features similar to those of LSNO are observed therein, even if important differences are
found. In Fig. 2, a gap in the polaronic continuum is partially open at room temperature.
It deepens as $T$ lowers, before stabilizing at 100 K. A "freezing" in the polaronic peaks was
observed at the same temperature by neutron scattering [19]. One may notice that in Fig.
2 the gap opens more gradually with temperature than in LSNO, and that no midinfrared
peak can be clearly identified. At 20 K (300 K) the phonon spectrum includes $E_{2u}$ peaks at
165, 235 (230), 665 (650) cm$^{-1}$, and $A_{2u}$ peaks at 300 (300), 505 (505) cm$^{-1}$. The $A_{2u}$-$E_{2u}$
manifold at $\sim 350$ cm$^{-1}$ (see the inset of Fig. 2) exhibits an inhomogeneous broadening
above 200 K, suggestive of random octahedra deformations. At lower $T$ a doublet can be
identified, much less resolved than the one associated with the ordering of charges in Fig. 1.

Finally, we report in Fig. 3 the optical density of Sr$_{1.5}$La$_{0.5}$MnO$_4$, a sample where
charge/magnetic superlattices similar to those of La$_{1.67}$Sr$_{0.33}$NiO$_4$ have been detected by
electron diffraction [10] and by neutron scattering. [12] In SLMO, however, the superlattices
are attributed to small bipolarons. [10] The spectra of Fig. 3, which to our knowledge
represent the first infrared observations in the family of strontium manganate, show that
here the charge-lattice coupling is much stronger than in LSNO. At 300 K, a deep absorption minimum is already present at 750 cm\(^{-1}\), pointing toward low polaron mobilities even at high temperatures. However, as \( T \) is lowered, a loss of spectral weight is observed below 4000 cm\(^{-1}\), the energy range which in LSNO corresponds to (single) polaron absorption. At low temperature (\( T < 100 \) K) a peak is left at \( \sim 4000 \) cm\(^{-1}\), namely at twice the energy of the corresponding peak in Fig. 1. According to the Holstein model, if \( E'_p \) is the polaron binding energy measured in SLMO, and \( U < 2E'_p \) is the repulsion energy between two charges on the same site, the infrared absorption of small bipolarons is expected to be peaked at \( 4E'_p - U \).\[17\] As for LSNO \( E_p \approx 1000 \) cm\(^{-1}\), \( 4E'_p - U \approx 4E_p \), so that \( E'_p > E_p \) in agreement with the above statement that the charge-phonon coupling in SLMO is larger than in LSNO.

The assignment of the phonon peaks observed in Fig. 3 can be easily obtained by a comparison with the isostructural powder of Fig. 1. The TO normal modes polarized in the \( a - b \) plane of \( \text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_4 \) at 20 K (300 K) are resolved at 190 (190), 230 (230), 645 (625) cm\(^{-1}\), those along the \( c \)-axis at 285 (280) and 510 (505) cm\(^{-1}\). Both lowest-energy \( E_{2u} \) phonons are here resolved at room temperature, due to the absence of a polaronic background at such frequencies. The Mn-O stretching mode shifts considerably with temperature (+20 cm\(^{-1}\) between 300 and 20 K) with no remarkable discontinuities. Here again, the ordering process of the charges detected by diffraction probes is monitored by splittings in the intense \( E_{2u} \)-\( A_{2u} \) manifold. At room temperature, a broad absorption peak with a few shoulders is observed, suggestive of disordered octahedra deformations. Between 250 and 200 K, consistently with the bipolaron ordering transition at \( \sim 220 \) K reported by Bao \textit{et al.}\[10\], three lines appear at 346, 388, and 433 cm\(^{-1}\). The detection of a triplet indicates 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 \( A_{2u} \) vibration. In this system, a full breaking of the octahedral symmetry is then produced at the sites where charges localize.

In conclusion, we have shown that the infrared spectra of three layered perovskites are fully consistent with the observation in the same systems, by diffraction probes, of charged superlattices. The reported presence of polarons (bipolarons) in Ni-based (Mn-based) per-
ovskites reflects into a partial (full) splitting of the $E_{2u}-A_{2u}$ manifold related to the three-dimensional symmetry of the oxygen octahedra. Below the temperatures where the polarons (bipolarons) build up superlattices, the broad distribution of splittings collapses into a well resolved doublet (triplet). The self-trapped charges can be photoexcited, thus producing a midinfrared band that is reasonably fitted by a small-polaron optical conductivity. In LSNO the band is peaked at $\sim 2000 \text{ cm}^{-1}$, in SLMO at $\sim 4000 \text{ cm}^{-1}$. The genesis of the band is here observed. It forms through the opening of a gap in the polaronic background, which clears up the far-infrared range as polarons localize at low temperature. In bipolaronic $\text{Sr}_{1.5}\text{La}_{0.5}\text{MnO}_{4}$ the gap is already open at 300 K, consistently with the stronger charge-lattice coupling predicted for this system.

The present results may also help to interpret the spectra of the Cu-based perovskites, where midinfrared bands similar to those reported here are observed at low doping. These bands have two components, of which that at lower frequency ($\sim 1000 \text{ cm}^{-1}$) has been associated with polaron hopping by different authors. This band survives in the metallic phase, where it is superimposed to a Drude-like absorption, and can be related to the periodic charged distortions detected in several cuprates by extended x-ray absorption fine structure.

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FIGURES

FIG. 1. (a) The optical density $O_d$ of polycrystalline La$_{1.67}$Sr$_{0.33}$NiO$_4$ at five temperatures from 300 K (dotted line) to 20 K (solid line). The region of the $E_{2u} - A_{2u}$ manifold (see text) is reported in the inset by using the same symbols. (b) The data at 300 and 20 K (solid lines) are fitted by use of Eqs. (1) and (2) (dashed lines).

FIG. 2. The optical density $O_d$ of polycrystalline La$_2$NiO$_4$ at five temperatures from 300 K (dotted line) to 20 K (solid line). The phonon assignment is as in Fig. 1. The region of the $E_{2u} - A_{2u}$ manifold (see text) is reported by using the same symbols in the inset, where the curves have been slightly scaled vertically for the reader’s convenience.

FIG. 3. The optical density $O_d$ of polycrystalline Sr$_{1.5}$La$_{0.5}$MnO$_4$ at five temperatures from 300 K (dotted line) to 20 K (solid line). The region of the $E_{2u} - A_{2u}$ manifold (see text) is reported in the inset by using the same symbols.