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Analysis of infrared reflection spectra of oxides of the La_2CuO_4 high-T_c superconductor family in polarized light

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The temperature dependence of infrared reflection spectra of La_2NiO_4 single crystal in polarized light between 10 and 750 K is analyzed and compared to the results for an oriented sample of La_2CuO_4. In both compounds, the spectra are found to reflect the bidimensional character of this family of compounds with a plasmon restricted to the basal *a-b* plane. In the nickel compound, the plasma frequency increases with temperature according to a simple scheme of semiconducting behavior with thermal filling of an empty conduction band, consistent with the d^8 character of Ni. Conversely, in "metallic" La_2CuO_4 (d^9 character) the plasmon is found to shift little with temperature. The analysis of a number of results obtained with ceramics samples in superconducting and normal phases are reexamined under the light of these new data. The effective charges carried by the oxygen ions are also deduced from the splittings of polar modes into transverse and longitudinal components. Results confirm the strong anisotropy of the transition-metal-oxygen bonds with strong overlap in the basal plane related to the short bond lengths and much more ionic character along the tetragonal *c* axis.

I. INTRODUCTION

The analysis of infrared reflection spectra of high-T_c oxide superconductors, and their temperature dependence, may give information about at least four types of excitations, i.e., phonons, plasmon, superconducting gap, and possibly other narrow band and/or exciton gaps. This is the reason why extensive investigations[1-14] have been performed with this method over the last six months to help to understand the exciting physics of these conducting oxides discovered by Bednorz and Müller.[15] We will restrict ourselves and, in the first step, only examine compounds of the La_2CuO_4 family, the structure of which is much simpler than that of the Y-Ba-Cu-O family. Unfortunately, most measurements have been performed with ceramic samples for lack of a single crystal large enough. This is the reason why preliminary measurements performed with large single crystals of La_2NiO_4 were of importance. We found[16] considerable anisotropy of infrared reflection spectra. For light polarized parallel to the tetragonal *c* axis, the spectrum resembles that of an insulator, whereas the spectrum for the light polarized within the plane perpendicular to the *c* axis is dominated by a Drude-type free-carrier reflectivity. The plasmon background, however, does not screen the phonon modes completely. Results are shown in Fig. 1. The analysis of the lanthanum nickel-oxide single crystal also revealed that the electrical conductivity is strongly anisotropic, consistent with the bidimensional character of the plasma behavior.[16]

Another type of information that may be straightforwardly extracted from infrared reflectivity experiments with single crystals in polarized light concerns effective charges carried by each ion. The method was successfully applied to the analysis of many systems.[17-21] There are several ways to define the effective charge. In this method, we use the definition given below—the same as that which enters a rigid-ion model of lattice dynamics—which is useful because when divided by the chemical valence, the result is intermediate between 0 and 1, and is therefore easy to compare to ionicity.[17] This would not be so if, for example, one uses the Born or "transverse" effective charge, related to the present one by $e_T = Ze\sqrt{\epsilon_\infty}$. e_T includes contributions of the polarizable charged "shell". Equation (1) is based upon the simple concept that the splitting of polar vibrational modes into transverse optical (TO) and longitudinal (LO) components is due to the Coulombic field

$$\sum_j (\Omega_{j\mathrm{LO}}^2 - \Omega_{j\mathrm{TO}}^2)_\alpha = \frac{1}{\epsilon_v V} \sum_k \frac{(Ze)_{k\alpha}^2}{m_k} \quad . \tag{1}$$

ϵ_v is the dielectric constant of vacuum, V is the volume occupied by the k ions of mass m_k, and α denotes a direction of polarization. There are several unknowns in the right side of Eq. (1), the $(Ze)_k$'s, but only two equations, Eq. (1) and the electric neutrality of the crystal. The system, however, may be approximately solved in that case because the weight of the terms related to oxygen is by far dominant in Eq. (1). One thus finds an effective charge of oxygen, averaged over all sites, equal to only $-0.6e$ in the basal plane, whereas the effective charge is found twice as high along the tetragonal *c* axis. This result should be correlated with the very short Ni—O bond lengths in the basal plane and the large bond overlap that arises.[16] Utilizing the data deduced from the infrared measurements, we were thus able to reach conclusions about the bidimensional character of the system by using two independent methods.

When a system is so highly anisotropic, it is difficult to extract information from polycrystalline samples without ambiguity. This is the reason why published analyses of ceramics spectra of this family conclude in different ways.

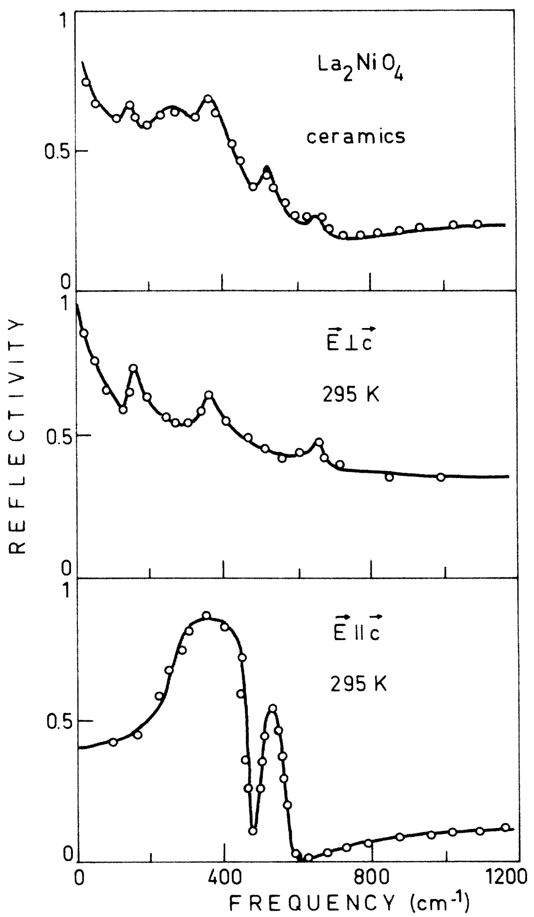

FIG. 1. Anisotropy of infrared reflection spectra of La_2NiO_4 single crystal compared to the spectrum of the ceramics at room temperature. Open circles represent experimental spectra and full curves represent the best fit of model Eq. (2) to the data with parameters given in Table I.

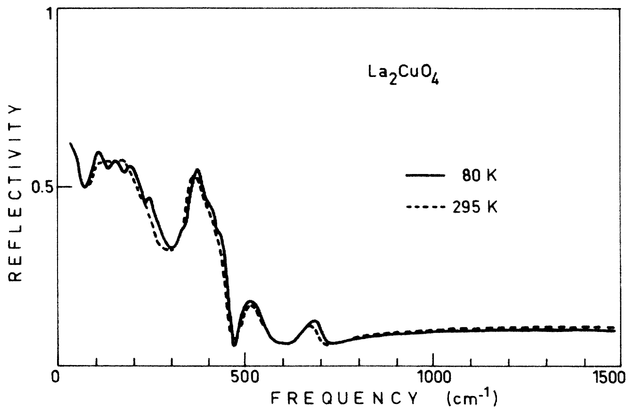

FIG. 2. Temperature dependence of the infrared reflection spectrum of La_2CuO_4 ceramics. Small additional modes characteristic of the orthorhombic distortion are resolved at low temperature.

In particular, the recognition of the plasma edge—an important parameter for modeling the physics of such systems—sometimes assigned to a dip between 0.5 and 1 eV or found by a Drude fitting procedure at much lower frequency, appears highly controversial. In La_2NiO_4, the spectrum of a ceramic sample (upper part of Fig. 1) analyzed before the availability of a single crystal appears dominated by the *a*-*b* plane spectrum, and the plasmon parameters may be deduced without too much inaccuracy in that case. Conversely, the infrared reflection spectrum of sintered La_2CuO_4 (Fig. 2) does not show any obvious plasma edge. The spectrum rather consists of phonon features with low reflectivity minima. The situation appears intermediate in $La_{1.85}Sr_{0.15}CuO_{4-y}$ ceramics with a composite spectrum. Phonon bands characteristic of the polarization parallel to the *c* axis are superimposed over a Drude profile corresponding to the polarization within the *a*-*b* plane where phonons are completely screened. It should be emphasized that the recent recognition and correct assignment[12,13] of spectral features in these ceramic samples have been made possible only after the availability of La_2NiO_4 single-crystal data and by analogy with them. Some aspects of these analyses, however, remain questionable in our opinion. The direct measurement with a single crystal clearly appears highly desirable if one wishes to extract unambiguous and accurate plasma parameters and deduce physical quantities like carrier concentration or effective mass. Accurate reflectivity measurements require rather large crystal plates (at least $5 \times 3 \times 1$ mm for measurements near normal incidence which ensure good polarization rates) and adequate samples were not available up to now to our knowledge. Recently, in our laboratory, Dembinsky succeeded in growing not properly single crystals but oriented samples of La_2CuO_4 which exhibit nice anisotropy in polarized light. The purpose of this paper is to report on the analysis of this new set of data obtained in oriented lanthanum copper-oxide samples, and more generally to discuss the plasmon-phonon coupled-mode spectra in conducting oxides of this family.

II. EXPERIMENT

Infrared reflectivity measurements have been performed with a Bruker IFS 113 rapid-scan Fourier spectrometer. Details about the experiment are reviewed in Ref. 22. The liquid-helium cryostat is equipped with polyethylene or thallium bromoiodine windows (identical to polarizer substrates) to cover the wave number ranges 20–300 cm^{-1} and 300–4000 cm^{-1}, respectively. Measurements at higher frequencies were performed with a grating Jobin-Yvon near-infrared and visible spectrometer equipped to work down to liquid-nitrogen temperature and which covers the wave number range 4000–28 000 cm^{-1} (0.5–3.4 eV).

Single crystals have been grown by using the floating zone technique with the aid of a CO_2 laser.[23] The growth is initiated from a germ fixed on an alumina rod and alimented by another rod of the sintered material. The starting La_2NiO_4 and La_2CuO_4 rods were obtained by solid-state reaction of La_2O_3 and NiO or CuO, or by mixing the nitrates $La(NO_3)_3$, $Ni(NO_3)_2$, $Cu(NO_3)_2$. Large high-quality La_2NiO_4 single crystals were grown with this method.[23] The growth of the copper compound appears more difficult. It was improved by adding CuO in excess together with a high pulling velocity. The best sample used in infrared reflection measurements consists of platelike single crystals as shown by scanning electron microscopy, all nearly oriented perpendicular to the c axis and embedded into a residue of CuO (a few percent).

III. RESULTS

The temperature dependence of infrared reflection spectra of La_2NiO_4 for the electric field of the electromagnetic radiation polarized parallel and perpendicular to the tetragonal c axis are shown in Figs. 3 and 4, respectively. Spectra have been fitted with the following dielectric function model:

$$\epsilon/\epsilon_\infty=\prod_j \frac{\Omega_{j\mathrm{LO}}^2-\omega^2+i\gamma_{j\mathrm{LO}}\omega}{\Omega_{j\mathrm{TO}}^2-\omega^2+i\gamma_{j\mathrm{TO}}\omega}-\frac{\Omega_p^2}{\omega(\omega-i\gamma_p)}\ , \qquad (2)$$

in which the usual Drude term has been added to the expression which describes the phonon modes according to Maxwell's equations (see e.g., Ref. 22). The upper parts of Figs. 3 and 4 display the imaginary parts of the dielectric response which correspond to TO excitations, and the imaginary parts of the inverse dielectric function (LO excitations) calculated with the parameters which yield a best fit to reflectivity data. Good agreement is achieved with this simple model which assumes only two adjustable parameters per mode (LO or TO phonon, plasmon), as shown in the lower parts of Figs. 3 and 4. Note that whereas TO modes are the poles of Eq. (2), once the Drude term is added, the $\Omega_{j\mathrm{LO}}$'s are no longer the complex zeros but instead are decoupled LO phonon modes. As indicated in the Introduction, results show a dominant broad plasma background in the basal plane and its absence for the polarization parallel to the tetragonal c axis. The second point which should be emphasized concerns the temperature dependence of the plasma frequency which increases rapidly with temperature. This is qualitatively observable by the increase with temperature of the reflectivity level in the whole spectral range and quantitatively confirmed by the Drude fit. Another signature of this temperature dependence is the fact that LO phonon modes interfere strongly with the plasma background in the Fano sense to such a degree that phonon features appear as "holes" instead of peaks. This is true at room temperature and above but the effect is minimized at low temperatures and the coupled LO phonon mode profiles appear much more "symmetric" with the decrease of the plasma contribution (which shifts down to as low as 519 cm^{-1} at 80 K for example) with which they couple.

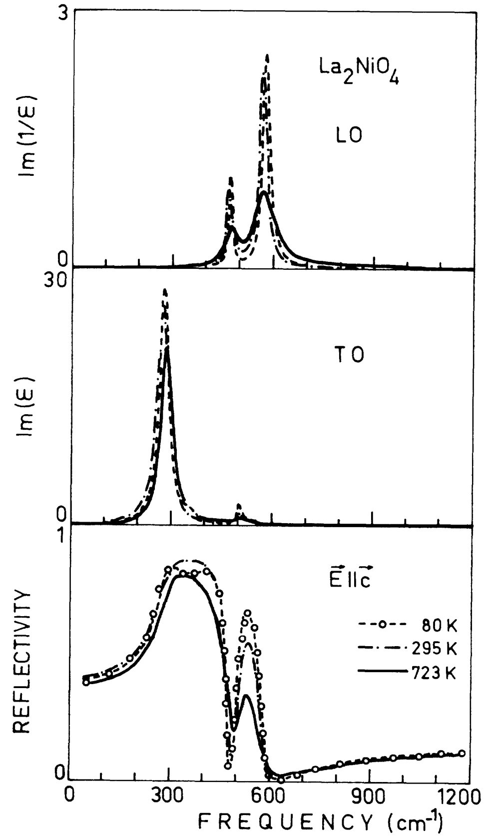

FIG. 3. Temperature dependence of infrared reflection of La_2NiO_4 single crystal for the electric field of the infrared radiation polarized parallel to the tetragonal c axis. Typical best fit of Eq. (2) to experimental spectrum (open circles) is shown at 80 K. Note the third small mode at 340 cm^{-1} predicted by group theory for this polarization, resolved at low temperature only. No Drude contribution is needed at any temperature.

The analyses of infrared reflectivity data of La-Cu-O ceramics samples and their Sr-substituted derivatives published during the last six months appear very controversial. One of the reasons for the discrepancies is the bump around 0.5 eV.[3,6,7,9,11] Among other original results presented in this paper, the observation of a similar feature in the La_2NiO_4 single-crystal spectrum *but limited to the polarization within the basal plane* should be noted. Geserich, Scheiber, and Renker[9] and Tajima *et al.*[11] assigned the high-frequency tail of the 0.5 eV bump to the plasma edge. Conversely, Herr *et al.*[7] argued that the spectrum is decidedly non-Drude-like and assigned the 0.44 eV broad feature to an electronic excitation. Authors of reflectivity spectra in the infrared, visible, and ultraviolet ranges encountered problems to fit their spectra with a sum of phonon modes plus a Drude term only. To fit their spectrum, Orenstein *et al.*[6] assumed that a fraction of the plasma oscillator strength is "consumed" in an optically allowed transition at 0.45 eV across the gap. In addition, their starting formula was

$$\epsilon=\epsilon_\infty-\frac{\Omega_p'^2}{\omega(\omega+i\gamma)}\ , \qquad (3)$$

where Ω_p' *is not a complex zero of the dielectric function* as any longitudinal mode should be according to Maxwell's equations. Their $\epsilon_\infty^{-1/2}\Omega_p'$ that was found equal to 0.9 eV, which is equivalent to Ω_p in Eq. (3), coincides with the high-frequency edge of a bump at 0.5 eV, in accordance with assignments in Refs. 9 and 11. Taking into account the bidimensional character of the infrared properties set in an earlier paper,[16] Schlesinger, Collins, Shafer, and Engler[12] simulated the infrared spectra of a hypothetical single crystal of $La_{1.85}Sr_{0.15}CuO_4$ with a plas-

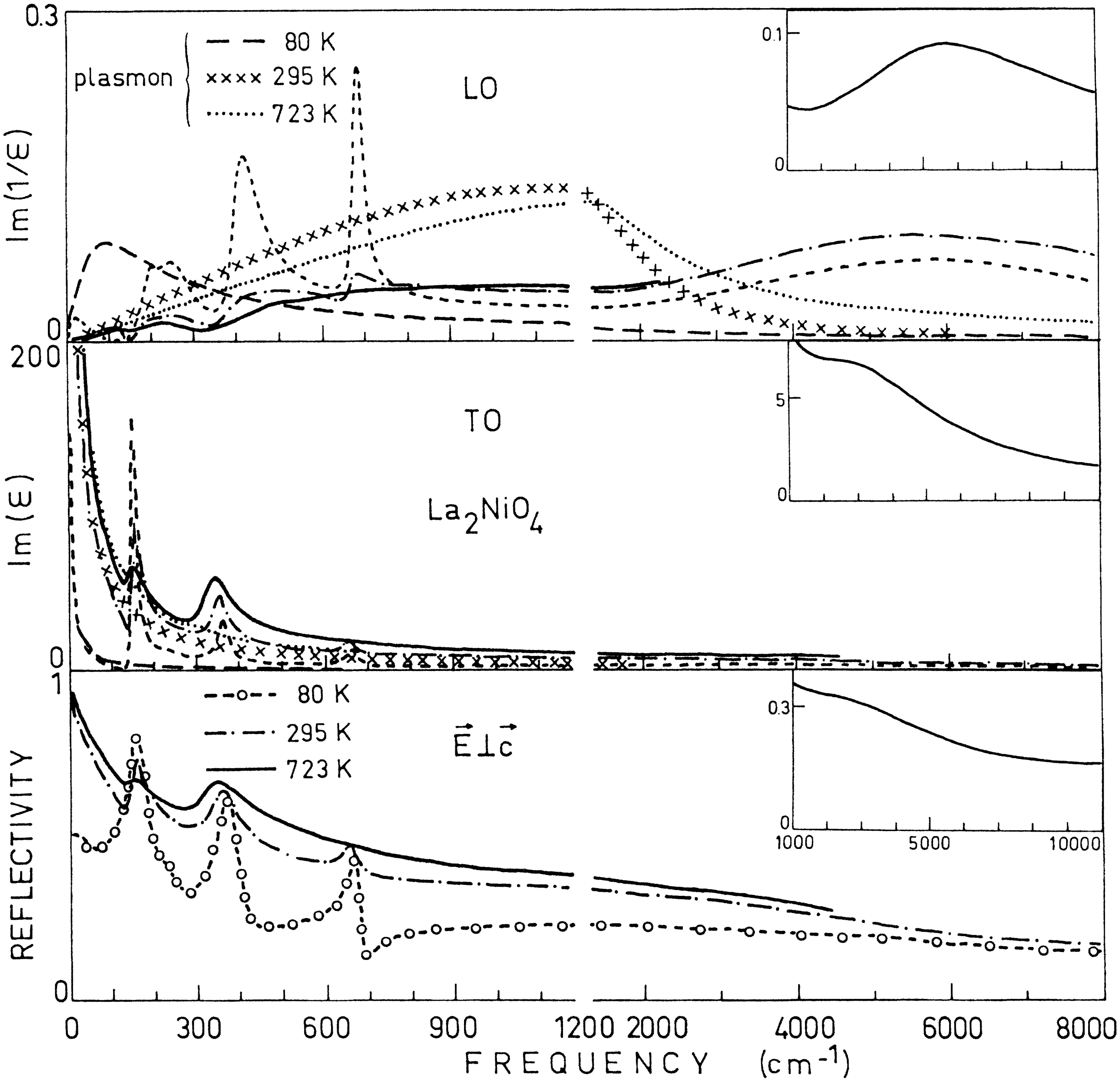

FIG. 4. Temperature dependence of infrared reflection spectra for the electric field of ir radiation within the basal *a*-*b* plane of La_2NiO_4. Upper parts show the temperature dependence of TO and LO modes obtained from the best fit of Eq. (2) to reflectivity data (see typical fit to the data represented by open circles at 80 K). The contribution of the plasmon alone is superimposed over the response of all coupled LO excitation. Due to Fano-type destructive interference, coupled LO phonons appear asymmetric at 80 K and even as holes instead of peaks at higher temperature. In addition, interferences with the upper "electronic mode" lower the plasmon response around 1000 cm^{-1}. Note that no specific coupling parameter is entered into Eq. (2) to produce such effects in an artificial way. Scale is changed at 1200 cm^{-1}. Insets detail the "electronic" mode at 295 K.

ma frequency of 0.5 eV in such a manner that the composite spectrum of the ceramics is reproduced correctly. Here, in the Ni compound, the best fit to the spectrum for the polarization within the basal plane is obtained with the Drude term and an "electronic mode" at 0.5 eV. The plasma frequency is found lower than the electronic mode at any temperature. The infrared reflection spectrum of La_2CuO_4 ceramics, at least in the normal state or above the superconducting gap, appears to depend little on temperature (see Fig. 2 and Ref. 3) even near the "plasma edge at 0.8 eV" assumed by certain authors.[7,11] More important is to realize that the *position of this edge does not appear to shift with the substitution of* Sr *on* La *sites.*[6,9,11,12] Conversely the reflectivity level at lower frequencies increases with strontium concentration in the whole spectral range, a fact that it is reasonable to relate to an increase of the carrier concentration, consistent with other measurements. One arrives at the conclusion that the band tail at 0.8 eV appears not related to the plasma edge which lies at lower frequency and is coupled with LO phonons. However, in highly conducting compounds with 15% of strontium, the plasma frequency reaches 0.9 eV

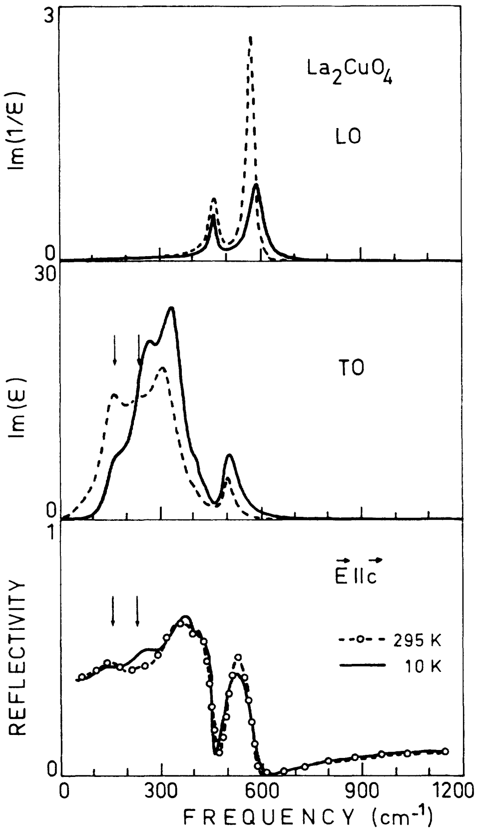

FIG. 5. Same as Fig. 3 for La_2CuO_4. Arrows denote residue of the other polarization.

and incidentally masks the electronic mode as shown in Ref. 12.

Results for an oriented sample of La_2CuO_4 are shown in Figs. 5 and 6. Although measurements in polarized light show small residue of spectral features of the other polarization in each spectrum, we consider they are worth discussing because they display strong similarities with those of the single-crystal spectra of the nickel compound. As in La_2NiO_4, the spectrum for the electric field polarized along the tetragonal c axis does not need any Drude term to be fitted at any temperature, whereas a weakly temperature-dependent plasmon is found in the basal plane, *with a frequency much lower than in* La_2NiO_4. Again the electronic mode near 0.5 eV is found in the basal plane only. The high-frequency dielectric constant measured along the c axis is found to be 4.1. These results contradict the assumptions of Sulewski, Noh, McWhirter, and Sievers[13] in their analysis of the La-Sr-Cu-O ceramics. They also contradict the assignments of the band tail near 0.8 eV to the plasma edge in La_2CuO_4 ceramics. The electronic mode at 0.5 eV in La_2CuO_4 has been recently proposed to correspond to a localized gap which originates from a strong electron-phonon interaction.[24]

IV. COMPARISON WITH Y-Ba-Cu-O SPECTRA

A controversy similar to that in lanthanum copper oxides exists about the interpretation of infrared reflection spectra of Y-Ba-Cu-O-type ceramics also. Certain authors[25] reported by infrared reflectivity spectroscopy the existence of an electronic mode at 0.37 eV in superconducting ceramic samples. Its absence in nonsuperconducting samples was interpreted as support of a superconductivity mechanism in which electron pairing would be mediated by excitons. Bozovic *et al.*[26] measured the optical transmission of superconducting oriented films and did not observe any absorption around 0.37 eV in any polarization. They concluded, therefore, that excitons do not seem to be an essential ingredient for the onset of superconductivity in this material. Drude fitting of the spectrum obtained for the electric field polarized within the conducting plane gave rise to a plasma frequency of 2.6 eV. Simultaneous measurements of Schlesinger, Collins, Kaiser, and Holtzberg[27] with a single crystal in the a-b plane were fitted with a similar plasma frequency of 3 eV and no mode at 0.37 eV. Such values are also similar to the ones reported earlier in ceramic samples in which the conductivity is large enough. In that case, the Drude profile screens the phonon within the conducting plane and dominates phonon modes that vibrate in the c direction perpendicular to that plane.[28,29] These results are to be compared with those of Genzel *et al.*[30] who reported 0.5 eV for the plasma frequency whereas Perkowitz *et al.*[31] found $\Omega_p = 0.05$–0.15 eV only. An ambiguity of a factor of 2 remains, however, depending on whether the prefactor $\epsilon_\infty^{-1/2}$ is incorporated into the result [see Eq. (3)] or not. More important is to realize that some authors of electron loss measurements have reported a plasmon energy as high as 24.6 eV.[32] Unpublished data by the various workers cited above seem rather to indicate a plasma frequency of 0.75–1 eV for the a-b plane. A clarification of the situation when large single crystals will be available appears highly desirable.

V. PLASMA BEHAVIOR, CARRIER EFFECTIVE MASS, AND ELECTRON-PHONON COUPLING

A simple basic view that prevails with regard to the understanding of the electronic properties of such compounds is based upon the fact that Ni^{2+} is a d^8 ion which implies a semiconducting band scheme. Charge carriers are related to the amount of Ni^{3+} created by doping and/or nonstoichiometry. Carriers may be equivalently understood in terms of formation of holes in oxygen sites. Cu^{2+} is a d^9 ion which assumes half-filled band and "metallic" behavior. It should be emphasized that, within the basal plane, this oversimplified band scheme model is confirmed by present experimental data. In semiconducting La_2NiO_4, the plasma frequency increases rapidly with temperature whereas a "metallic" behavior is found for La_2CuO_4 with little dependence on temperature. A weakly doped semiconducting behavior with much lower carrier concentration is reported for both compounds in the direction perpendicular to the basal plane. However, things might not be so simple. The plasma frequency is very low in La_2CuO_4, and the electrical conductivity is found consistently smaller in the copper than in the nickel compound at room temperature. (It has been recently pointed out that the Drude contribution may not fit the dc

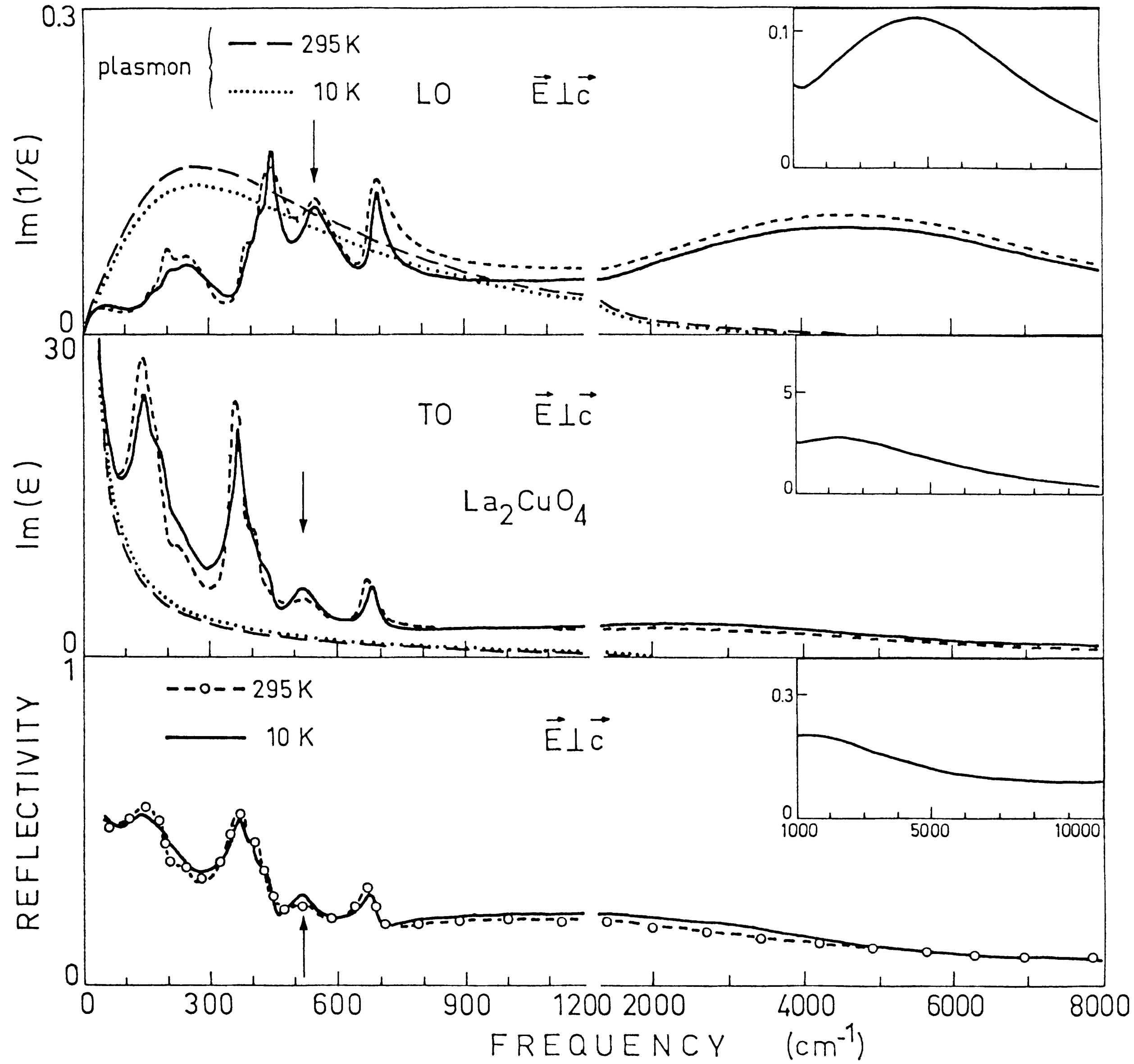

FIG. 6. Same as Fig. 4 for La_2CuO_4. The arrows denote a residue of the other polarization.

conductivity due to a frequency dependence of the relaxation time of the plasmon.) This situation also raises the problem of the carrier effective mass. In similar studies of other transition-metal ions with octahedral oxygen environment, we have found plasma frequencies of the same order of magnitude.[19,33] The example of a single crystal of strontium titanate reduced under hydrogen to ensure a carrier concentration of the order of magnitude of 10^{20} cm^{-3}, is shown in Fig. 7. Here the plasma edge decreases with increasing temperature (see the discussion in Ref. 34). To explain this unusual behavior, Eagles[35] suggested an increase of the effective mass from $6m_e$ at 0 K up to $22m_e$ at room temperature. Note that Nb-doped or reduced strontium titanate becomes a superconductor below 0.7 K. The effective mass in reduced rutile TiO_2 was found to be equal to $(8-10)m_e$.[33] In Ba-La-Cu-O, Michel, Er-Rakho, and Raveau[36] reported an approximate value for the effective mass of $10m_e$. This order of magnitude is confirmed by thermoelectric power measurements.[37] Seebeck coefficients in La-(Sr)-Cu-O do not vary much with temperature at least between liquid nitrogen and room temperature.[38-40] These results imply little variation of carrier concentration above liquid-nitrogen temperature consistent with results for the plasmon in the basal plane of La_2CuO_4. Conversely, the Hall coefficient appears to vary more than the Seebeck coefficient and this raises the problem of the determination of carrier concentration from such data. Similar results are found in Y-Ba-Cu-O.[41] In this compound, decrease of the Seebeck coefficient below 90 K is clearly related to the onset of superconductivity. The large effective masses and strong electron-phonon coupling it implies, seem to be, therefore, a characteristic common to those oxides. It is intimately connected with the concept of polaron also known to play

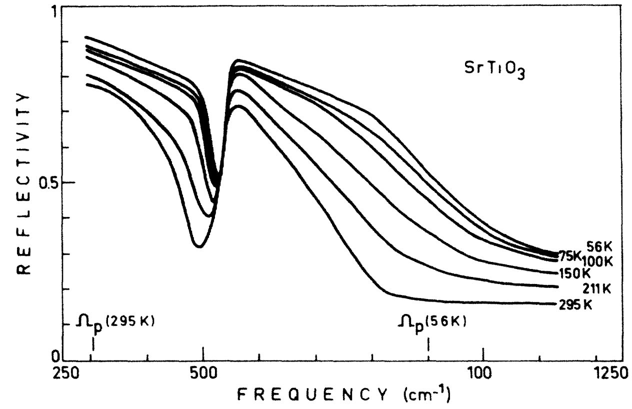

FIG. 7. Temperature dependence of strontium titanate reduced under hydrogen. Note the up-shift of coupled-plasmon-LO-phonon-mode edges with decreasing temperature, whereas the TO mode edge at 550 cm^{-1} consistently does not shift with temperature.

an important role in transition-metal oxides. Direct evidence of the importance of electron-phonon coupling in La$_2$CuO$_4$ has been recently reported by photoinduced infrared-active vibrational modes.[24]

Accurate data about free carriers appear to be of importance, first because they constitute the "bath" in which Cooper pairs will be formed. In addition, such low values of plasma energy may imply strong electron-phonon coupling. Most recent isotopic effect measurements in La$_{1.85}$Sr$_{0.15}$CuO$_4$ and YBa$_2$Cu$_3$O$_7$ as well, although results are smaller than expected from the Bardeen-Cooper-Schrieffer (BCS) prediction, also conclude in favor of an important role played by phonons in the electron-pairing mechanism.[42,43] It has been recently shown by NMR spectroscopy that ^{17}O mainly exchanges with oxygens of the "chains" parallel to the *b* axis.[44] Recent results in the bismuth compounds relativize the importance of such chains and confirm the essential role play by CuO$_2$ square planes, common to all high-T_c superconductors. If one therefore admits that isotopic substitutions in Y-Ba-Cu-O thus mainly affect oxygens that would play little role in the superconductivity mechanism supposed to be restricted to the basal *a*-*b* planes, then a small isotopic effect in Y-Ba-Cu-O would not rule out a strong electron-phonon coupling mechanism. Let us recall that most recent analyses of infrared reflection spectra of Y-Ba-Cu-O report a value of $2\Delta/k_B T_c$ that reaches 8.[45] Several authors have calculated the band structure of copper compounds of this family.[46,47] The Fermi level is found to lie within upper antibonding valence bands. Most recent calculations[47] found large and positive values for the effective mass at the top of the valence band which is found nearly flat near some Brillouin-zone-boundary points in Y-Ba-Cu-O. This is consistent with the fact that the conduction in this metal is mostly by holes as found in most cases by thermoelectric power measurements.[37-39] X-ray and ultraviolet photoemission spectroscopy measurements also indicate a marked tendency at localization in these unusual "metals." A narrower valence band is found in La$_2$CuO$_4$ compared to La$_2$NiO$_4$ thus indicating more localized carriers in the former compound.[48] In other words, the dispersion of the bands seem to be flatter in La-Cu-O and this is consistent with a large effective mass.

VI. PHONON MODE ASSIGNMENT

The complete phonon dispersion curves of La$_2$NiO$_4$ have been measured by neutron scattering with a large $5\times5\times20$ mm single crystal.[49] Phonon dispersion curves have been fitted by Reichardt with a rigid-ion model with electron screening in the basal plane.[50] Results allow unambiguous assignment of infrared-active modes. Within the basal plane and in La$_2$NiO$_4$ we find four TO mode frequencies, 656, 351, 224 (weak mode observed at low temperature only), and 151 cm^{-1}, that are assigned as follows: (1) Ni-O stretching mode, (2) vibration of all cations against all anions, (3) motion of sheets containing Ni against intermediate sheets of oxygens, and (4) the motion of La against NiO$_6$ octahedra, respectively. This is consistent with group theory predictions. Corresponding modes are found in the copper sample at 671, 363, 220, and 163 cm^{-1}, respectively. Spectra obtained at low temperature reveal additional weak modes, for example at 402 and 433 cm^{-1}, that are assigned to the lifting of degeneracy related to the small orthorhombic distortion with respect to the tetragonal symmetry. For the polarization parallel to the *c* axis the lowest-frequency main TO mode [275 cm^{-1} in La$_2$NiO$_4$, and found at 320 cm^{-1} in our La$_2$CuO$_4$ sample but most likely expected only at 240 cm^{-1} in a single crystal (see footnotes in Table I) at room temperature] consists of the vibration of all cations against all oxygens while the upper mode (503 cm^{-1} in La$_2$NiO$_4$, 501 cm^{-1} in La$_2$CuO$_4$) involves motions of oxygens with respect to nickel or copper, in opposite phase in two consecutive planes.

VII. EFFECTIVE CHARGES

Equation (1) allows us to approximately calculate the effective charge localized at the ionic sites, at least for oxygen the contribution of which is by far dominant in the right side of Eq. (1). This is a straightforward application of the principle of infrared spectroscopy which probes instantaneous dipole moments created by the vibrational motions of effective point charges. We find an effective charge of oxygen that is strongly anisotropic and appears to be only slightly dependent of the value that is attributed to one of both remaining unknowns in Eq. (1), Z_{La} and Z_{Ni}. For the direction of polarization along the *c* axis, values quite comparable to what is commonly measured[17] in transition-metal oxides are found, viz., an "ionic character" of 60% ($Z_{\parallel} = -1.2e$) in La$_2$NiO$_4$ and 50% in La$_2$CuO$_4$. Those values are found independent of temperature within experimental error. For the polarization within the basal *a*-*b* plane we have to eliminate the effect of screening by charge carriers. This is why *decoupled* LO mode parameters should be entered in the left-hand side of Eq. (1). This is done explicitly by utilizing the LO parameters obtained by fitting the dielectric function model Eq. (2) to reflectivity data. Results are $Z_{\perp} = -0.6e$ in La$_2$NiO$_4$ and $Z_{\perp} = -0.7e$ in La$_2$CuO$_4$, at

TABLE I. Typical oscillator parameters that yield best fit to the room-temperature data shown in Figs. 3–6. Frequencies and dampings are in cm^{-1} except in lines between parentheses when they are also given in eV units. Note that the oscillator strengths are not adjustable parameters but are deduced from the TO-LO splittings. Small additional modes due to the orthorhombic distortion of La_2CuO_4 are ignored in this comparison.

		La_2NiO_4					La_2CuO_4		
Ω_{TO}	γ_{TO}	Ω_{LO}	γ_{LO}	Strength	Ω_{TO}	γ_{TO}	Ω_{LO}	γ_{LO}	Strength
					$E \parallel c$				
275	39	472	20	14.5	320[a]	106	463	31	5^b
503	26	574	27	0.27	501	33	574	26	0.31
		$\epsilon_\infty=5.2$					$\epsilon_\infty=4.1$		
		$\epsilon_0=20$					$\epsilon_0=16.7^c$		
					$E \perp c$				
151	13	171	57	5.2	162	78	183	90	4.9
351	45	391	92	3.2	363	36	390	32	2
(224	62	243	82	1)[d]	220	75	250	90	1.9
656	32	665	33	0.34	671	35	683	45	0.22
3825	6000	6065	8000	8.4	4525	9700	6425	9200	4
(0.46	0.72	0.73	0.96		0.54	1.2	0.77	1.1 eV)	
		$\Omega_p=1542$	$\gamma_p=2300$				$\Omega_p=555$	$\gamma_p=1300$	
		(0.18	0.28				0.07	0.16 eV)	
		$\epsilon_\infty=5.6$					$\epsilon_\infty=4.1$		
		$\epsilon_0=22.8$					$\epsilon_0=21.8$		

[a] This frequency is overestimated due to the vicinity of modes of the other polarization at lower frequency (see also note below). In the absence of "forbidden" modes, a fit to the low-frequency reflectivity lowers that frequency down to 240 cm^{-1}.

[b] This oscillator strength is underestimated because lower-frequency "forbidden" modes denoted by arrows in Figs. 5 and 6 contribute to the dielectric response too. As a result of this smaller strength, the TO-LO splitting of this mode is minimized and the TO frequency shifted up as indicated above.

[c] ϵ_0 appears higher than the sum $\epsilon_\infty+\sum_j \Delta\epsilon_j$ because of the existence of "forbidden" modes (parameters ignored in this table) related to the residual polycrystalline character of our sample.

[d] These parameters correspond to the fit at 80 K. This mode is hardly revealed at room temperature.

room temperature. The average oxygen effective charge within the basal plane is renormalized from $-0.6e$ at room temperature up to $-0.7e$ at 80 K in the Ni compound. This increase of "ionic character" goes along with the decrease of carrier concentration. Conversely, no significant change of effective charge with temperature is found in the copper compound and this is consistent with the small dependence on temperature of the plasma frequency.

VIII. CONCLUSION

Results in single crystals reported here compared to those obtained in ceramics show that unambiguous conclusions can be deduced from the analysis of oriented samples in polarized light only. This is particularly true in this situation where physical properties are bidimensional. Several recently published works based on the analysis of ceramic samples appear very questionable. For example, the fact that phonon modes are screened more and more by charge carriers with the increase of carrier concentration[51] and therefore tend to disappear in infrared transmission spectra, seems to have been misinterpreted in Ref. 1. It is simply the addition of Sr that increases the carrier concentration. If the plasmon background gives rise to high infrared reflectivity, then results of these analyses might not be too inaccurate. But if phonon bands dominate the spectrum, then this means that the phonons are screened little and indicates that either they correspond to the polarization perpendicular to the a-b plane or that the Drude contribution is small.

Ionic effective charges measured within the basal plane and along the tetragonal c axis confirm the large anisotropy of the chemical bond in those systems. Another result worth mentioning is that the electronic mode observed at 0.5 eV in both Ni and Cu compounds is restricted to the basal plane. The La_2CuO_4 sample we have investigated is not superconducting because its carrier concentration is too small, as shown by the low plasma energy found in this sample. Large nonstoichiometries (lanthanum-deficient compound) are known to allow the onset of superconductivity in this compound.[52] Most recent determinations of the superconducting gap by infrared reflectivity give values as high as 400–500 cm^{-1} (50–60 meV) in Y-Ba-Cu-O samples.[45] Such high values compared to T_c are indicative of strong-coupling superconductivity. Indications of strong anomalies of breathing-type phonon branches for modes propagating in the (110) direction,[49,50] which just correspond to that of perfect nesting of the Fermi surface, were reported recently. Earlier, Weber[53] had suggested that nesting might be at the origin of superconductivity in La-Sr-Cu-O. Such indications of strong coupling of electronic charge carriers with oxygen breathing mode, the large carrier effective mass, added to recent indication of isotope effects in those materials, at least for La-Sr-Cu-O, all point towards a mechanism of superconductivity in which electron-phonon coupling seems to play an important role.

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