

Two-dimensional plasmon in nonstoichiometric La_2NiO_4

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(Received 2 March 1987)

The infrared reflectivity spectra of a single crystal of La_2NiO_4 and their dependence on temperature and data analyses are reported. A plasmon mode is found in the basal plane, whereas no plasmon mode is found to propagate along the tetragonal axis. The two-dimensional electronic properties of this crystal, which is isostructural with $(\text{Ba}_x\text{La}_{1-x})_2\text{CuO}_4$, which shows high- T_c superconductivity, are discussed.

The recent discovery¹⁻⁶ of high- T_c superconductivity in $(\text{Ba}_x\text{La}_{1-x})_2\text{CuO}_4$ —also called Ba-La-Cu-O—will require considerable effort to understand the origin of the phenomenon. A preliminary stage consists in the characterization of the electronic properties of oxides with the K_2NiF_4 structure at the microscopic scale. Superconductivity is known to exist also in cubic or pseudocubic oxidic perovskite structures, but at much lower temperatures. One of the questions one may ask, therefore, is whether the two-dimensional (2D) character of the K_2NiF_4 structure plays a dominant part in the occurrence of superconductivity in the Ba-La-Cu-O phases. Jorgensen *et al.*⁷ suggest that the 2D character of the structure plays a dominant role in explaining the transition to the superconducting state. The mechanism they propose is based upon a Peierls-type instability driven by an electron-phonon coupling to a 2D conduction band which would exhibit a large density of states near the Fermi energy because of the associated Van Hove singularity. If such a Peierls-type instability is present but controlled by doping to prevent a transition to an insulating state at low temperature, this may favor the onset of superconductivity which needs similar ingredients.⁷

The results of infrared reflectivity experiments performed with a single crystal of La_2NiO_4 , chosen as model of the Ba-La-Cu-O phase, are reported. Our crystal choice was dictated by two considerations. (i) The Ba-La-Cu-O system is isostructural with La_2NiO_4 and its electronic properties are expected to be similar, at least to a large extent. (ii) To our knowledge, single crystals of La_2CuO_4 and related compositions are not yet available in the world, whereas the growth of large samples of La_2NiO_4 ($20 \times 6 \times 6$ mm) has been achieved with success in our laboratory by Dembinski, Bassat, Coutures, and Odier, by the floating-zone technique.⁸ The availability of single crystals is obviously necessary to characterize the 2D properties. Previous investigations about the 2D character of the electronic properties of La_2NiO_4 yielded results that are unsatisfactory to some extent. Honig and Buttrey⁹ did report an anisotropy of the resistivity, but limited to only one order of magnitude. No anisotropy of the magnetic susceptibility has been reported at room temperature. However, χ_\perp displays an anomaly at 210 K, while χ_\parallel does not.¹⁰

Experiments have been performed in the wave-number

range 20–4500 cm^{-1} with the aid of a Bruker IFS 113 infrared Fourier spectrometer. The infrared reflection spectra of a 6-mm-diam single-crystal plate of tetragonal La_2NiO_4 for the electric field of the electromagnetic radiation polarized parallel and perpendicular to the tetragonal axis are shown in Fig. 1 at room temperature and 810 K. A giant anisotropy is straightforwardly visible. The $\text{E} \parallel \hat{c}$ spectrum does not show any signature of a plasmon

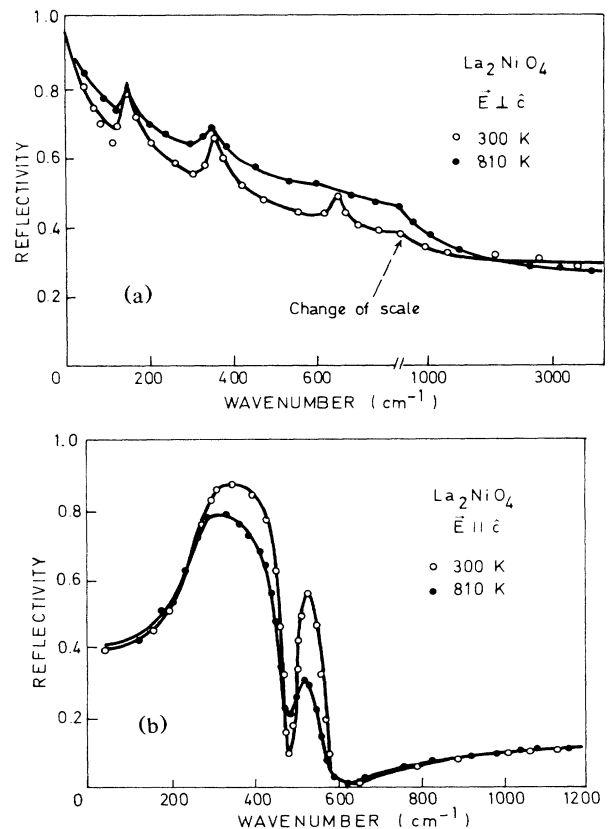


FIG. 1. Temperature dependence of infrared reflectivity for the electric field of the electromagnetic radiation polarized (a) perpendicular and (b) parallel to the c axis. Symbols represent experimental data, and full curves are best fit of Eq. (1) to the data.

mode, whereas an overdamped plasmon dominates the response in the plane perpendicular to c . This is true at any temperature in the investigated temperature range 300–810 K. We have fitted the infrared reflection spectra with the following dielectric function model:¹¹

$$\epsilon/\epsilon_\infty = \prod_j \frac{\Omega_{jLO}^2 - \omega^2 + i\gamma_{jLO}\omega}{\Omega_{jTO}^2 - \omega^2 + i\gamma_{jTO}\omega} - \frac{\Omega_p^2}{\omega(\omega - i\gamma_p)}. \quad (1)$$

The Ω_{jLO} 's represent the *decoupled* longitudinal optical (LO) mode frequencies, i.e., the moduli of the complex zeroes of the dielectric function in the absence of plasmons, the γ_{jLO} are decoupled LO mode dampings, and the TO subscripts refer to transverse optical modes. The second term is nothing but the usual Drude expression. Typical best fits of Eq. (1) to experimental data (dots) are shown by full lines in Fig. 1. The frequencies which yield the best fit to the experimental spectra displayed in Fig. 1 are plotted in Fig. 2. *No plasmon contribution is found for $\mathbf{E} \parallel c$.* In the plane perpendicular to the tetragonal axis, a plasma frequency Ω_p is found equal to 3850 cm^{-1} at room temperature. It reaches 4950 cm^{-1} at 810 K. In certain samples, the plasma frequency decreases slightly upon heating above a certain temperature which varies from sample to sample and depends on thermal treatments such as annealing. The temperature of this diffuse phase transition shifts with the nonstoichiometry of the sample.^{9,12} Such a behavior was observed in our previous study performed on ceramics samples.¹³ It is associated with a diffuse "semiconducting" to

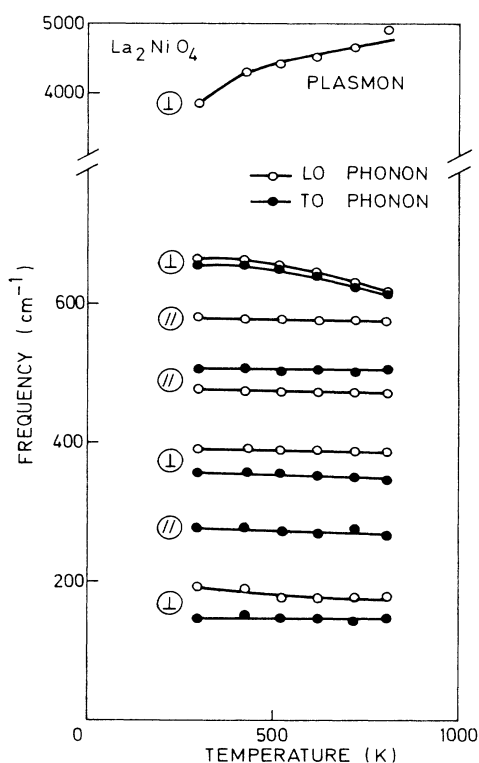


FIG. 2. Temperature dependence of plasmon and polar phonon frequencies.

"metal" change of regime. The temperature dependence of the plasma frequency was found to be consistent with that of the electrical conductivity.¹³ The level of plasmon energy reported in Ref. 13, however, was underestimated since it corresponds to a polarization averaged over all grains, and the weight of the contribution of grains with c oriented parallel to the electric field lowered the mean value. Figure 2 shows that such a change of regime is not visible in the single crystal we have investigated.

Because of the practical low-frequency limit of 20 cm^{-1} that can be reached with our experimental device, it is concluded that the anisotropy of the plasma frequency reaches at least a factor of 250. True 2D electronic behavior is therefore evidenced in this compound. This means that the plasma wave is restricted to the Ni-O-Ni planar network in the perovskite sheets perpendicular to

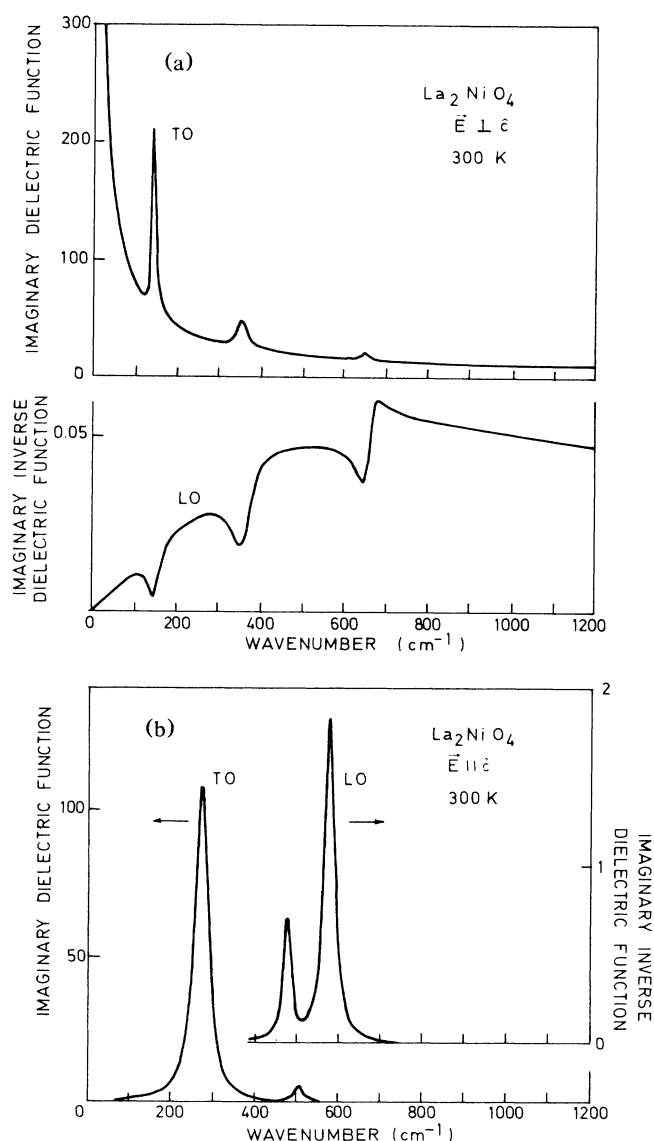


FIG. 3. Infrared response of TO and coupled LO modes at room temperature for the vibrations into (a) the basal plane and (b) perpendicular to it.

the tetragonal axis. We measured the anisotropy of resistivity by a four-probe method in the same sample and found a factor $\rho_{\parallel}/\rho_{\perp}$ of $\sim 10^2$. Both measurements are therefore consistent with each other. At this stage one should realize that a hypothetical sample of stoichiometric La_2NiO_4 would not exhibit high electrical conductivity in the basal plane. The actual chemical composition of the single crystal we have studied turns out to be $\text{La}_{1.9}\text{Ni}_{10.96}^{2+}\text{Ni}_{0.04}^{3+}\text{O}_{3.87}$. The La-to-Ni ratio has been deduced from a chemical analysis and the rate of Ni^{3+} from magnetic susceptibility measurements.

Another way to characterize the anisotropy of the chemical bonding is to calculate the effective charge Ze carried by the ions. The sum

$$\sum_k \frac{(Ze)_k^2}{m_k} = \epsilon_v V \sum_j (\Omega_{j\text{LO}}^2 - \Omega_{j\text{TO}}^2)_a \quad (2)$$

may be evaluated from the knowledge of the splittings of polar modes into TO and decoupled LO mode frequencies which yield the best fit to reflectivity data.¹⁴ In Eq. (2), ϵ_v is the dielectric constant of the vacuum, α denotes a polarization, and the k sum is over all atoms of mass m_k in the elementary volume V . We cannot evaluate the effective charge of the individual ions since we have only two equations [Eq. (2) and the electric neutrality $\sum_k (Ze)_k = 0$] and at least three unknowns for each polarization. A crucial point nevertheless is that the sum in Eq. (2) calculated for the modes which vibrate parallel to the \mathbf{c} axis is found to be 4.8 times higher than for those polarized perpendicular to it. Since the weight of the oxygen ions is dominant in the left-hand side of Eq. (2) because of their low mass, we arrive at the result that $Z_{0\parallel}$ is found to

be more than *two times higher* than $Z_{0\perp}$. This anisotropy is consistent with (i) the shorter Ni—O bond length of 1.94 Å in the basal plane, compared to 2.27 Å along the \mathbf{c} axis, and (ii) the anisotropic thermal factors found for axial oxygens of the NiO_6 octahedra.¹⁵

The imaginary part of the dielectric function (TO modes) and the imaginary inverse dielectric response (coupled plasmon-LO phonon modes) calculated with Eq. (1) and the parameters which yield the best fit to reflectivity data, are shown in Fig. 3. Whereas the spectrum for $\mathbf{E}\parallel\mathbf{c}$ displays the usual phonon mode response for both directions of propagation, the spectrum of LO modes for $\mathbf{E}\perp\mathbf{c}$ is typical of the Fano-Breit-Wigner-type interference between the overdamped plasma background ($\gamma_p/\Omega_p \sim 5$) and LO phonon discrete states. The asymmetric profiles in the spectrum of LO excitations contrast markedly with the Lorentzian line shapes of TO excitations which fit the reflectivity data. Note that the Ω_p plasma frequency which enters the Drude term is strongly shifted toward high energies with respect to the maximum of the plasmon response. The results of Fig. 2 do not indicate any tendency at softening of the polar modes at the Brillouin zone center in the temperature range investigated. The situation in such a layered-related-perovskite structure thus appears markedly different from that of strontium titanate doped with niobium, for example, in which the electron-phonon coupling associated with the zone-center ferroelectric mode has been suggested to play a part in the onset of superconductivity.¹⁶

Fruitful discussions with Dr. D. Jérôme are gratefully acknowledged.

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