

Optical phonons in T^* -structure $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$

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We report Raman and far-infrared spectra of a ceramic compound with T^* structure. We perform an eigenmode analysis and show the displacement patterns of all modes. As T^* may be looked upon as a hybridization of the T and T' structures, it has twice as many modes as either T or T' . This enrichment in the spectra is observed experimentally. The similarity in the structures between T , T' , and $\text{YBa}_2\text{Cu}_3\text{O}_7$ and T^* is the basis for our mode assignment.

I. INTRODUCTION

A detailed knowledge of the lattice vibrations of high- T_c superconductors has proven to be important in advancing the understanding of the mechanism of high- T_c superconductivity. Numerous optical and neutron-diffraction studies of phonons have been performed to this effect, e.g., in $\text{YBa}_2\text{Cu}_3\text{O}_7$.^{1,2} Raman and far-infrared spectroscopies have yielded frequencies of the optically active modes at $\mathbf{k} = 0$, while with neutron scattering the entire Brillouin zone has been studied. The motivation of these studies is the determination of phonon frequencies, the development of material-characterization techniques, and the investigation of the electron-phonon interaction. In the $\text{YBa}_2\text{Cu}_3\text{O}_7$, the electron-phonon interaction has, in fact, been found to be significant, although the coupling strengths measured so far are not large enough to explain the high transition temperatures in these materials.^{3,4} Neutron-scattering experiments have not yet achieved sufficiently high resolution to study the wave-vector dependence of the coupling constants, which would presumably resolve this issue.

The superconductor studied here, $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$, was discovered recently by Akimitsu *et al.*⁵ When prepared under high oxygen pressure, this material becomes a hole-type superconductor with $T_c = 37$ K.⁶ Given the role the phonons play in the high- T_c superconductors, it is important to know the mode frequencies and understand their assignments to eigen-vectors of the primitive cell. The assignment for newly discovered structures may be based on a comparison to materials already known or to theoretically calculated eigenfrequencies. In this paper, we present results of a Raman and far-infrared study of a compound with T^* structure and compare the obtained mode frequencies with those of the T and T' structures, of which the superconductor families La_2CuO_4 and Nd_2CuO_4 are respective examples. As we shall see, the primitive cell in the T^* structure, which has twice the volume of the primitive cells of either T or T' , can be regarded as a hybridization of T and T' ; this helps the assignment of the modes con-

siderably, and we find that many of the experimentally observed modes nearly coincide with the ones already known in La_2CuO_4 and Nd_2CuO_4 . Furthermore, there is a number of additional Raman-active modes, which we shall presently discuss.

II. SAMPLES AND EXPERIMENTAL DETAILS

Ceramic samples of $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$ were prepared according to the prescription in Ref. 7 but annealed only at atmospheric pressure; hence the sample did not show signs of superconductivity in the Meissner effect. The composition was determined to be $x = 0.25$ and $y = 0.4$ by chemical analysis.

The Raman spectra were excited with the 530.9-nm line of a krypton-ion laser, dispersed with a DILOR x - y multichannel-spectrometer and detected with a charge-coupled device (CCD). Averaging times were 10 min for an incident laser power of 2–3 mW on a point focus. The samples were mounted on the cold finger of an evacuated cryostat. A special software program eliminated the spikes characteristic of CCD's.

The far-infrared-reflectivity measurements were carried out on a Bruker-113v Fourier-transform interferometer in the 30–650- cm^{-1} spectral range. A He-cooled germanium bolometer was used as a detector.

III. GROUP-THEORETICAL ANALYSIS AND EIGENMODES

We discuss first the crystal structure of the material under investigation. X-ray diffraction data have shown that Nd-Ce-Sr-Cu-O compounds have the so-called T^* structure (Fig. 1) that belongs to the space group D_{4h}^7 ($P4/nmm$). In contrast to the T - and T' -structure materials [both D_{4h}^{17} ($I4/mmm$)], they have neither Cu-O octahedra (T structure) nor sheets of simple Cu-O squares (T' structure). Instead, pyramids of oxygen form around the Cu atoms, similar to those in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.^{7–9} These Cu-O structural elements have lower symmetry than either octahedra or planes. The structure, how-

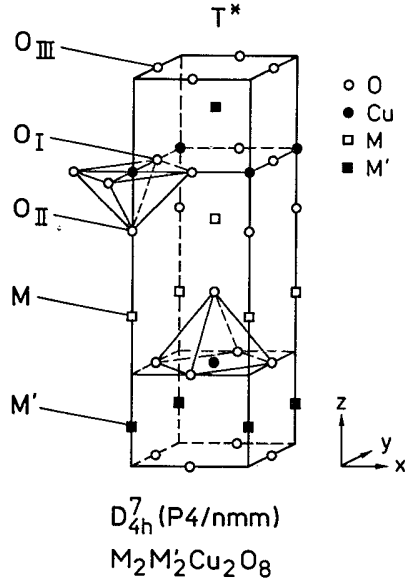


FIG. 1. Crystal structure of $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$. After parameters of Ref. 7.

ever, is able to retain a center of inversion by composing the primitive cell from two formula units (Fig. 1). It is interesting to note that the local environment of M and O_{II} is the same as that of La and the apex oxygen O_z in La_2CuO_4 (T), while that of M' and O_{III} is similar to that of Nd and O_{II} in Nd_2CuO_4 (T'). The $\text{Cu}-(O_1)_2$ planes are common to both. It is in this sense that T^* may be considered as a hybridization of the T and T' struc-

tures. The crystal point group for the T^* structure is the same as that for T and T' [D_{4h} ($4/mmm$)], although the space group is different. The T^* structure contains 14 atoms in a unit cell, and we expect twice as many vibrational modes T and T' structures, each of which has one formula unit per primitive cell. The vibrations of each nonequivalent atom can thus be classified into odd and even with respect to the inversion.

The site symmetry of all atoms is available from x-ray data.^{7,8} This allows us to make a detailed group-theoretical analysis of the long-wavelength, zone-center optical phonons.¹⁰ In the upper half of Table I, we give the mode symmetries next to the atoms to which they correspond and their Wyckoff site notation; in the lower half, we have grouped all modes according to their optical activity. For comparison, the corresponding information for the T and T' structures is also listed.¹¹

Since all crystal structures under consideration belong to the same point group, their optical phonons obey the same selection rules: Infrared-active phonons have $A_{2u}(z)$ and $E_u(x, y)$ symmetries, while the Raman active phonons have $A_{1g}(zz, xx + yy)$, $B_{1g}(xx - yy)$, and $E_g(xz, yz)$ symmetries. The $B_{2g}(xy)$ Raman modes are not present for any of these structures. Raman and infrared-active phonons belong to different irreducible representations of the D_{4h} point group, due to the presence of an inversion center, i.e., phonons cannot be simultaneously Raman and ir active.

It is seen from Table I that the number of both Raman and ir-active phonons is higher for the T^* -structure material. The incorporation of a second formula unit has

TABLE I. Comparative group-theoretical analysis of $k = 0$ phonon modes in the T , T' , and T^* structures. The Wyckoff site notation is given next to each atom.

| T structure (D_{4h}^{17}) | | T' structure (D_{4h}^{17}) | | T^* structure (D_{4h}^7) | |
|---|-------------------------------|----------------------------------|--|--|---|
| Atom | Mode symmetry | Atom | Mode symmetry | Atom | Mode symmetry |
| Cu(2a) | $A_{2u} + E_u$ | Cu(2a) | $A_{2u} + E_u$ | Cu(2c) | $A_{1g} + E_g + A_{2u} + E_u$ |
| $O_p(4c)$ | $A_{2u} + B_{2u} + 2E_u$ | $O_p(4c)$ | $A_{2u} + B_{2u} + 2E_u$ | $O_I(4f)$ | $A_{1g} + B_{1g} + 2E_g + A_{2u} + B_{2u} + 2E_u$ |
| $O_z(4e)$ | $A_{1g} + E_g + A_{2u} + E_u$ | $O(4d)$ | $B_{1g} + E_g + A_{2u} + E_u$ | $O_{II}(2c)$ | $A_{1g} + E_g + A_{2u} + E_u$ |
| $M(4e)$ | $A_{1g} + E_g + A_{2u} + E_u$ | $M(4e)$ | $A_{1g} + E_g + A_{2u} + E_u$ | $O_{III}(2a)$ | $B_{1g} + E_g + A_{2u} + E_u$ |
| | | | | $M'(2c)$ | $A_{1g} + E_g + A_{2u} + E_u$ |
| | | | | $M(2c)$ | $A_{1g} + E_g + A_{2u} + E_u$ |
| Modes grouped according to their optical activity | | | | | |
| | | T structure (D_{4h}^{17}) | T' structure (D_{4h}^{17}) | T^* structure (D_{4h}^7) | |
| Acoustic | | $A_{2u} + E_u$ | $A_{2u} + E_u$ | $A_{2u} + E_u$ | |
| Raman active | | $2A_{1g} + 2E_g$ | A_{1g} (M only) + B_{1g} (O only) + $2E_g$ | $5A_{1g} + 2B_{1g}$ (O_I and O_{III} only) + $7E_g$ | |
| ir active | | $3A_{2u} + 4E_u$ | $3A_{2u} + 4E_u$ | $5A_{2u} + 6E_u$ | |
| Silent | | B_{2u} (O_p only) | B_{2u} (O_p only) | B_{2u} (O_I only) | |

as a consequence that displacements corresponding to *only* ir-active modes in the T and T' structures become Raman active as well in the T^* structure. This doubles the number of Cu and plane-oxygen modes. The two types of out-of-plane oxygen (O_{II} and O_{III}) and of heavy metal atoms (M and M') each now contribute four modes, yielding a total number of 42 modes, of which 39 are optical and 3 acoustic. In particular, we have in T^* $2A_{1g} + 2B_{1g} + 4E_g$ oxygen-related Raman modes, while in T and T' only $A_{1g} + E_g$ and $B_{1g} + E_g$ oxygen modes, respectively, are Raman active. Group theory thus predicts for the T^* structure a considerable enrichment of the Raman spectra. The number of ir-active modes, on the other hand, does not increase so dramatically, since Cu and plane-oxygen atoms do not contribute additional ir-active modes. Note that a silent mode [$B_{2u}(z)$] exists in all structures.

In Fig. 2 we show the displacement patterns or eigenvectors associated with each of the inequivalent atoms of the T^* structure. We have grouped the patterns according to site symmetry and only drawn elements of the primitive cell that participate in a particular mode. We note that modes of equal symmetry must mix, but those of different symmetry may not. The top row of Fig. 2 contains the 2c site (metal atoms and O_{II}), while 2(b) and 2(c) show the displacements of O_{III} and O_I . Note

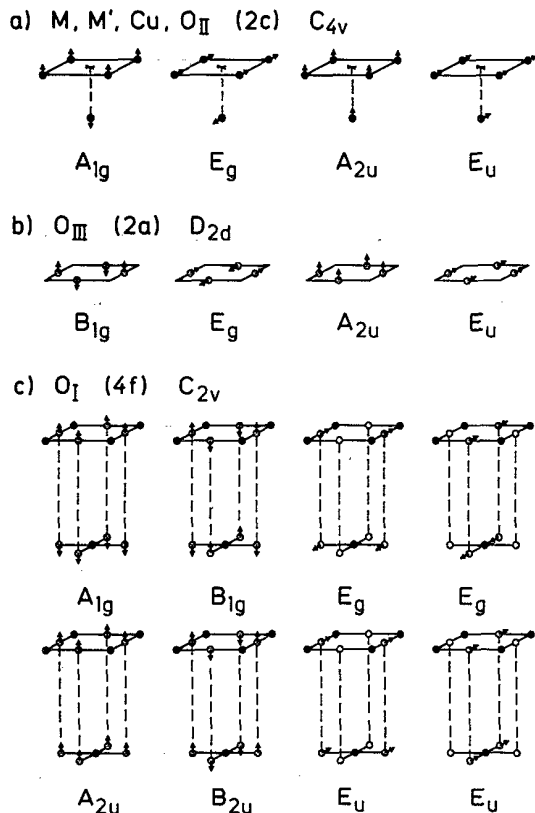


FIG. 2. Eigenmodes of the T^* structure at $k = 0$. Note that there are two formula units per primitive cell and, hence, considerably more modes than in the T and T' structures.

the presence of $A_{1g} + B_{1g}$ modes from oxygen (O_I) in the Cu- O_2 plane, as in $YBa_2Cu_3O_7$.¹ Neither of these modes exist in T or T' , and they arise from the doubling of the primitive-cell volume. The A_{1g} and B_{1g} modes of T and T' correspond to those depicted in 2(a) and 2(b). Also note the presence of two E_g and E_u modes each for the O_I eigenmodes. Because T^* has the $P4/nmm$ space group, different from that of $YBa_2Cu_3O_7$ ($Pmmm$), the number of Cu-O bond-stretching and -bending vibrations is the same for each of the two E_g and the two E_u modes, which would therefore be degenerate. Because of the O_I - O_I coupling they will mix and generate modes with in-phase and out-of-phase relative linear combinations of the patterns shown in Fig. 2. The silent mode (B_{2u}) has the typical displacement pattern in all tetragonal copper oxide superconductors.¹

IV. EXPERIMENTAL RESULTS AND MODE ASSIGNMENTS

We discuss first the even, Raman-active vibrations. Figure 3 shows the experimental spectra of $Nd_{2-x}Ce_xSr_yCuO_4$ at 77 K for two different relative polarizations. We find that the spectra may be divided roughly into two parts: a region at low frequencies ($\nu < 250$ cm^{-1}), which contains a number of modes forming a broad band and a high-frequency regime ($\nu > 300$ cm^{-1}), which should contain only oxygen-related vibrations. Furthermore, from the change in amplitude for parallel ($I_{||}$) and perpendicular (I_{\perp}) polarizations of incident and scattered light, one may discern fully symmetric (A_{1g}) modes from E_g and B_{1g} modes in ceramic materials. We use the depolarization ratio $\sigma_D = I_{\perp}/I_{||}$ for the assignment of the experimental frequencies to eigenmodes of the lattice. We find (Fig. 3) a particularly small σ_D for the modes at 137, 191, 375, and 452 cm^{-1} , which hence probably have A_{1g} symmetry.¹² The modes at 103, (158), 216, (318), and (485) cm^{-1} (weak modes in paren-

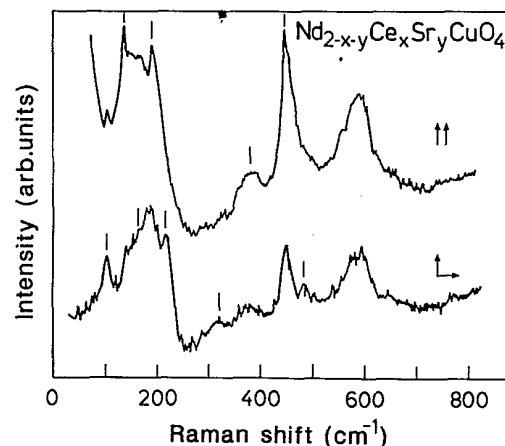


FIG. 3. Raman spectra of $Nd_{2-x-y}Ce_xSr_yCuO_4$ for parallel (upper curve) and crossed (lower curve) polarizations of the incident and scattered light at 77 K.

theses) have a rather large σ_D and probably are of E_g or B_{1g} symmetry. We cannot, on the basis of σ_D , decide the symmetry of the mode with the highest frequency (590 cm^{-1}).

As there are no reported lattice-dynamical calculations for the T^* structure, we let ourselves be guided by known assignments in related compounds. We have listed in Table II the frequencies of Raman-active modes of the T and T' structures, all modes that should also be present in T^* . For the assignment of the additional Raman-active modes (Cu and O_I ; see Table I), we use the frequencies of $\text{YBa}_2\text{Cu}_3\text{O}_7$, since it has, like T^* , Cu-O pyramids.

The low-frequency broad structure apparently consists of a number of contributions that are not narrow enough to separate into individual peaks. We expect at least six modes with frequencies below $\sim 250 \text{ cm}^{-1}$, namely those of the three metal ions with $A_{1g} + E_g$ symmetries. In addition, there may be some low-lying oxygen bonding vibrations. Recent structural data⁸ showed an ordering of the heavy cations in a similar T^* -structure compound; however, it is clear from the stoichiometry of the sample investigated here that Nd^{3+} must occupy both M and M' positions. The additional occupation by divalent Sr^{2+} and tetravalent Ce^{4+} should broaden vibrations related to the heavy cations considerably. From the T - and T' -phase investigations we expect the M (A_{1g}) vibrations to be near 230 cm^{-1} ; the E_g vibrations have been calculated to be near 100 and 160 cm^{-1} .^{13,14}

The Cu modes ($A_{1g} + E_g$), on the other hand, are expected to remain relatively sharp. In analogy with $\text{YBa}_2\text{Cu}_3\text{O}_7$, we expect the A_{1g} eigenmode of Cu at $\sim 150 \text{ cm}^{-1}$. Taking also into account the depolarization characteristics, we thus assign the low-frequency peaks as follows (see Table II): Cu and M, M' A_{1g} at frequencies 137 and 191 cm^{-1} ; Cu and M, M' E_g at 158 and

103 cm^{-1} . Experimentally, we cannot make a distinction between the M and M' modes and thus we assign them together. The similarity of the respective A_{1g} frequencies in the T and T' phases justifies the approach. We note that the metal-ion E_g vibrations have not been seen in the T and T' phases.

We also predict one O_{II} vibration in the low-frequency region; corresponding to the strong E_g apex-oxygen mode of O_z in La_2CuO_4 at 230 cm^{-1} . From the depolarization behavior, we may identify it with the peak at 216 cm^{-1} in our sample.

We now turn to the high-frequency portion ($\nu > 300 \text{ cm}^{-1}$) of the spectra. From the masses involved, we infer that all peaks in this region are related to oxygen vibrations. The strongest peak, at 452 cm^{-1} with A_{1g} character, is most likely the fully symmetric vibration of O_{II} . It corresponds to the apex-oxygen stretch and is usually found to be strong. As it occurs at 429 cm^{-1} in La_2CuO_4 , we believe the assignment to the 452-cm^{-1} peak in the T^* phase to be reasonable, in particular, since the Cu- O_{II} distance^{7,8} is 10% smaller than that in La_2CuO_4 .

Having assigned the O_{II} vibrations, we are now left with six modes of O_I and O_{III} ; their assignment will be tentative. Only two of them, the vibrations of O_{III} , have a counterpart in the T' phases. The strong E_g vibration, in (Ce-doped) T' structure at 480 cm^{-1} , may correspond to the peak at 485 cm^{-1} . The B_{1g} frequency of O_{III} is expected to be around 330 cm^{-1} , and we indeed find a weak but broad structure at $\sim 318 \text{ cm}^{-1}$. The remaining oxygen vibrations we compare to the corresponding ones in $\text{YBa}_2\text{Cu}_3\text{O}_7$, which also has the Cu-O pyramids as structure elements. The second B_{1g} mode should have nearly the same frequency as that of O_{III} and comes from O_I ; thus the two modes of B_{1g} symmetry will probably

TABLE II. Frequency of Raman active phonon modes in ceramic $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$ at 77 K and their assignment. For a comparison, data for T -structure La_2CuO_4 (Ref. 15) and T' -structure $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (for $x = 0$ and in square brackets for $x = 0.15$, Refs. 13, 16, and 17), as well as for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Refs. 1 and 18) are also listed. Weak modes are given in parentheses. All frequencies are given in cm^{-1} .

| T structure | | | T' structure | | | YBa ₂ Cu ₃ O _{7-δ} | | | T* structure | | |
|----------------|-----------------|--------------|--------------|-----------------|-------------|---|-----------------|-----|--------------------|-----------------|-------|
| M | A _{1g} | 228 | M | A _{1g} | 230 [225] | Cu | A _g | 154 | Cu | A _{1g} | 137 |
| | | | | | | | | | M | A _{1g} | 191 |
| O _z | A _{1g} | 429 | O | B _{1g} | 344 [338] | O | A _g | 440 | M' | A _{1g} | 191 |
| | | | | | | | | | O _I | A _{1g} | (375) |
| M | E _g | 105 (calc.)* | O | E _g | 161 (calc.) | | | | O _{II} | A _{1g} | 452 |
| | | | | | | | | | O _{I,III} | B _{1g} | (318) |
| O _z | E _g | 230 | O | E _g | 494 [477] | O | B _{1g} | 340 | O _{I,III} | B _{1g} | |
| | | | | | | | | | M | E _g | 103 |
| | | | | | | Cu | B _{3g} | 140 | Cu | E _g | (158) |
| | | | | | | | | | M' | E _g | (158) |
| | | | | | | | | | O _{II} | E _g | 216 |
| | | | | | | O | B _{3g} | 303 | O _I | E _g | |
| | | | | | | O | B _{3g} | 526 | O _{III} | E _g | (485) |
| | | | | | | | | | O _I | E _g | |

*Reference 14.

mix. Then, the 318-cm^{-1} peak should originate from the in-phase relative displacement of O_I and O_{III} . The out-of-phase mode should be at higher frequencies (the corresponding ir-active A_{2u} mode in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ has a TO frequency of 516 cm^{-1}), but we cannot clearly identify it in the appropriate frequency range.

The A_{1g} O_I vibration should compare with the in-phase oxygen vibration in the Cu-O_2 planes in $\text{YBa}_2\text{Cu}_3\text{O}_7$ at 440 cm^{-1} . We find a weak A_{1g} -type peak at $\sim 375\text{ cm}^{-1}$ and tentatively identify it with the A_{1g} O_I eigenmode.

Finally, as already mentioned, the two E_g modes of O_I are also expected to mix, since there should exist a sizable restoring force between the in-plane pair of O_I atoms. A similar situation occurs in $\text{YBa}_2\text{Cu}_3\text{O}_7$, where these two modes lie^{1,18} at 303 and 526 cm^{-1} . In $\text{YBa}_2\text{Cu}_3\text{O}_7$, these modes are very weak and we do not expect related sizable peaks in the T^* phase either.

The feature in the Raman spectra which remains unassigned is the broad peak (width = 60 cm^{-1}) centered at $\sim 590\text{ cm}^{-1}$. It is too broad to be a single Raman line, if it stems from lattice vibrations, and should thus originate from a disorder- or defect-induced oxygen site. In fact, as we shall see later, there are also features in that frequency region in the ir spectra. An additional peak in the Raman spectra was also observed in the T' -phase compound $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ at 581 cm^{-1} with A_{1g} -like symmetry.¹³ It should be interesting to study this peak as a function of oxygen annealing pressure, which is a relevant parameter for the preparation of superconducting T^* -structure samples of this composition.

Let us discuss now the odd (infrared-active) phonons in T^* -structure $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$. The reflectivity spectra for two different temperatures are displayed in Fig. 4(a). A Kramers-Kronig transformation has been performed to obtain precise information on the frequencies of the infrared-active phonons of the sample [Fig. 4(b)]. Oscillator strengths were estimated from the relationship $S \approx \Gamma_{\text{TO}} \text{Im}[\epsilon(\nu_{\text{TO}})]/\nu_{\text{TO}}$. The high reflectivity in the low-frequency range indicates a high charge-carrier concentration in the Cu-O_2 planes of the material under investigation. The values of LO-phonon frequencies (plasmon-LO-phonon modes) obtained from $\text{Im}(-1/\epsilon)$ are also listed in Table III.

The assignment of infrared-active phonons (Table III) is more difficult than that of the Raman phonons. We

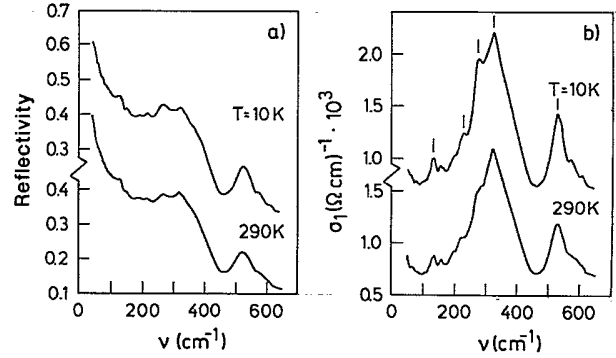


FIG. 4. Unpolarized reflection spectra (a) and dynamical conductivity (b) of $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$ at 10 and 290 K.

conjecture that the strongest modes observed in the spectra are due to $A_{2u}(z)$ vibrations as a consequence of the high planar charge-carrier concentration mentioned above, which should lead to screening of the modes with ion displacements in the planes^{11,13} (E_u modes). Furthermore, it is clear that the infrared-active phonons are more mixed than the Raman-active modes due to the requirement to keep the center of mass at rest in an optical vibration. This occurs automatically for the Raman-active modes even with only one equivalent atom. The relatively large oscillator strength S of the modes at 132 , 223 , 273 , 321 , and 524 cm^{-1} identifies them as being of $A_{2u}(z)$ symmetry; the small structures at 154 , 196 , 572 , and 606 cm^{-1} may belong to incompletely screened $E_u(x, y)$ modes. Indeed, as it can be seen from Table III, the frequencies of the A_{2u} modes agree well with the corresponding ones observed in T - and T' -structure materials. For a study of the E_u modes in $\text{La}_{2-x}\text{Dy}_x\text{CuO}_4$ (with T^* -structure), see Tajima *et al.*²⁰ For a more detailed assignment of both Raman and infrared-active phonons, measurements on single crystals of the compound are required.

V. CONCLUSIONS

We have reported the optical spectra of T^* -phase $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$ and made assignments of the experimentally observed phonon peaks to the theoretically performed eigenmodes of the lattice. Most modes could be identified based on comparison with structurally related compounds of the T and T' phases, which are the

TABLE III. TO (LO) frequencies, half-widths, and oscillator strengths of $A_{2u}(z)$ infrared-active phonons in a $\text{Nd}_{2-x-y}\text{Ce}_x\text{Sr}_y\text{CuO}_4$ ceramic at 10 K. Data for the T -structure $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x = 0.08$, Ref. 19) and the T' -structure $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ ($x = 0.15$, Ref. 13) are listed for comparison. Frequencies and half-widths are given in cm^{-1} .

| T structure | T' structure | | T^* structure | | | | |
|-------------------|-------------------|-----------------------|-------------------|-------------------|----------------------|-------------|--|
| ν_{TO} | ν_{TO} | (ν_{LO}) | ν_{TO} | ν_{LO} | Γ_{TO} | S | |
| | 134 | (144) | 132 | (145) | 8.5 | 0.36 | |
| 242 | | | 223 | (232) | ~ 20 | ~ 0.23 | |
| | 282 | (433) | 273 | (460) | ~ 51 | ~ 1.34 | |
| 342 | | | 321 | (288) | ~ 66 | ~ 1.57 | |
| 501 | 516 | (559) | 524 | (563) | 45 | 0.23 | |

building blocks of the T^* phase. Measurements on single crystals should complete the picture and clarify assignments where they have remained tentative.

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