

## Raman study of $R_{2-x}Ce_xCuO_4$ ( $R = Pr, Nd, Sm$ ): Resonance effects

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We present resonant Raman scattering results of  $T'$ -phase cuprates  $R_{2-x}Ce_xCuO_4$  with  $R = Pr, Nd, Sm$  and  $x$  from 0 to 0.175. The two modes appearing in  $zz$  polarization show a different resonant behavior: whereas the allowed  $A_{1g}$  is nonresonant in pure compounds and decreases towards the uv in doped ones, the forbidden mode  $A^*$  resonates towards uv in Nd and Sm samples with  $x \neq 0$ , while for Pr compounds its evolution is similar to that of the  $A_{1g}$ . We assign the  $A^*$  mode to a locally modified  $A_{2u}$  mode, due to oxygen relaxation around  $Ce^{4+}$ . The resonance of this mode is interpreted in terms of electronic-band-structure calculations as involving transitions from  $O(1)p_z + O(2)p_z$  to empty cerium states, while the  $A_{1g}$  decrease in the blue is attributed to light absorption due to the metallic character of doped samples.

The family of  $R_{2-x}Ce_xCuO_4$  compounds ( $R = Pr, Nd, Sm, Eu$ ) has attracted the interest of condensed matter physicists since the discovery that, for cerium doping around  $x = 0.15$ , and after a thermal treatment in a reducing atmosphere, they show  $n$ -type superconductivity.<sup>1</sup> All members of this family crystallize in the tetragonal structure  $T'$ , which differs from the  $T$  structure of the  $La_{2-x}M_xCuO_4$  family only in the position of the "out-of-plane" oxygens,  $O(2)$ .<sup>1</sup> [We shall denote by "in-plane" oxygens or  $O(1)$  those in the  $CuO_2$  layer.]

Four Raman-active modes are expected in the pure compounds:  $A_{1g}, 2E_g, B_{1g}$ .<sup>2-4</sup> Since the doping does not change the global symmetry, it is expected that the same analysis holds for the doped compounds. The  $A_{1g}$  mode arises from the  $z$  vibration of  $R$  and has a frequency of  $220\text{--}230\text{ cm}^{-1}$ ; the  $B_{1g}$  and one of the  $E_g$  modes are mainly due to  $O(2)$  and have frequencies of  $300\text{--}340$  and  $460\text{--}500\text{ cm}^{-1}$ , respectively.<sup>5</sup> The rare-earth  $E_g$  mode has been identified in  $Pr_2CuO_4$  at  $165\text{ cm}^{-1}$  (Ref. 6) and in  $Nd_{1.85}Ce_{0.15}CuO_4$  at  $122\text{ cm}^{-1}$  (Ref. 7). Our  $xz$  spectrum in  $Nd_{1.85}Ce_{0.15}CuO_4$  shows, besides a feature at  $120\text{ cm}^{-1}$ , another one at  $172\text{ cm}^{-1}$ . Neither of these peaks can be unambiguously attributed to the Nd  $E_g$  mode, since recent inelastic neutron data<sup>8</sup> show the presence of Nd crystal-field excitations at  $123$  and  $167\text{ cm}^{-1}$ , together with modes of phononic origin between  $125$  and  $130\text{ cm}^{-1}$ . Only the  $A_{1g}$  mode should be observed in  $zz$  polarization. However, a strong feature,  $A^*$ , appears in the  $zz$  spectrum of all cerium doped samples around  $585\text{ cm}^{-1}$ , with nearly perfect  $A_{1g}$  symmetry. The appearance of the  $A^*$  mode in the  $zz$  spectrum of  $Pr_2CuO_4$  (Ref. 6) excludes the presence of cerium as the unique explanation for the activation of the mode. A broad band composed of several peaks is also detected in that region in the spectrum of  $Nd_2CuO_4$  for in-plane polarization and attributed to the  $O(1)$  breathing mode against  $Cu$ ,<sup>9</sup> which

might be activated by the presence of oxygen vacancies or due to strong electron-phonon interaction with charge-transfer excitations, as in other cuprates.<sup>10</sup> Both  $A_{1g}$  and  $A^*$  modes show some intensity dependence on the exciting energy in all compounds.

With the aim of clarifying the origin of the  $A^*$  mode and its resonant behavior, as well as the differences in the spectra of Nd, Sm, and Pr compounds, we have studied the resonance effects on the  $zz$  spectrum as a function of cerium doping and  $R$  substitution. Previous resonance experiments in  $Nd_{1.85}Ce_{0.15}CuO_4$  can be found in Refs. 3 and 11. References 12 and 13 of the Y-Ba-Cu-O family contain, together with experimental data, an interpretation in the frame of electronic-band-structure calculations and/or optical data, as well as a discussion in terms of electron-phonon coupling contribution to the resonant behavior. For some results in other  $hT_c$  superconductors see for instance Ref. 14.

We have measured single crystals of  $R_{2-x}Ce_xCuO_4$  ( $R = Pr, Nd, Sm$ ;  $x = 0, 0.15$ ) and ceramic samples of  $Nd_{2-x}Ce_xCuO_4$  with  $x = 0.125, 0.135, \text{ and } 0.175$ . Sample preparation techniques are given elsewhere.<sup>15</sup> We used a Dilor XY spectrometer with intensified diode array detector. A Coherent argon laser was used for the region  $2.35\text{--}2.7\text{ eV}$  and the R6G in a dye laser for lower energies. The laser beam is focused onto the sample through a 50X objective. The laser power was always kept at low values (a few mW on the sample) to avoid sample damage. We used  $CaF_2$  or  $BaFCl$  as intensity standards in order to correct for instrumental efficiency and slight laser misalignments. No significant differences were found between measurements performed in reduced or unreduced samples.

In Fig. 1 we present room-temperature (RT) spectra of Nd, Sm, and Pr ( $x = 0.15$ ) single crystals for  $\lambda = 514.5$  and  $488\text{ nm}$ , and in Fig. 2 those of Nd compounds ( $x = 0, 0.125, 0.135, 0.175$ ) for  $\lambda = 514.5\text{ nm}$ . The results

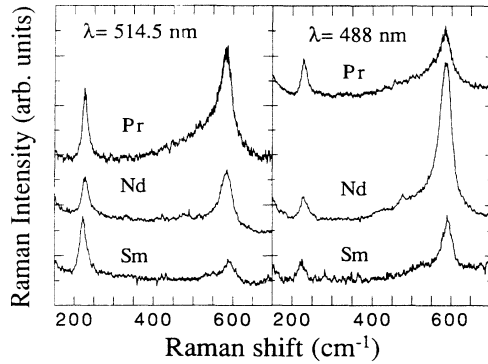


FIG. 1.  $zz$  Raman spectra of  $R_{1.85}\text{Ce}_{0.15}\text{CuO}_4$  for  $R = \text{Pr}$ , (top),  $\text{Nd}$  (middle), and  $\text{Sm}$  (bottom), taken at RT with the 514.5-nm (left) and the 488-nm (right)  $\text{Ar}^+$ -laser lines. The spectra are normalized to that of  $\text{BaFCl}$ .

are collected in Figs. 3 and 4, where we show the  $A_{1g}$  and  $A^*$  intensity dependence on exciting energy, as a function of the constituent  $R$  for  $x = 0$  and 0.15 (Fig. 3) and as a function of cerium doping for  $R = \text{Nd}$  (Fig. 4). The frequencies obtained for  $x = 0$  and 0.15 single crystals are given in Table I. Some considerations concerning experimental measurements and data presentation must be made: (i) We plot peak height intensities, since the values obtained by peak integration gave the same curves, except for a numerical factor that might depend on the compound. As concerns cerium doping dependence in Figs. 2 and 4, the use of integrated areas would enhance the  $A^*$  increase and partially reduce (but not suppress) the apparent decrease of  $A_{1g}$  upon doping. The qualitative trends are not modified. (ii) We assumed that the refraction index, reflection coefficient, and Raman activity of the standards used is dispersionless in the energy range studied.<sup>16</sup> We neither corrected for reflectivity nor for absorption dispersion of the sample, since the available experimental data with  $\mathbf{E}||c$  point towards fairly constant values in the 2–3 eV region.<sup>17</sup> (iii) In ceramic samples the spectra were taken by focusing the laser through a micro-

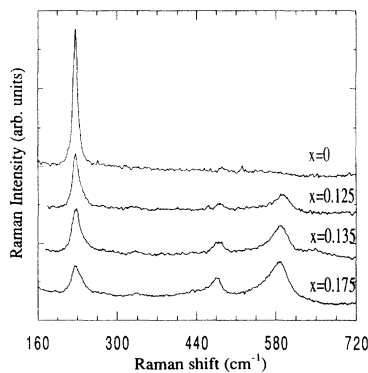


FIG. 2. Cerium doping dependence of the  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  spectrum for  $\lambda = 514.5 \text{ nm}$  taken with incident and scattered electric field parallel to a direction close to  $c$  axis. The  $x = 0$  sample is a single crystal and  $zz$  polarization is exact; all the other are ceramics. The spectra are normalized to that of  $\text{CaF}_2$ . See the text for a discussion on measurements on ceramic samples.

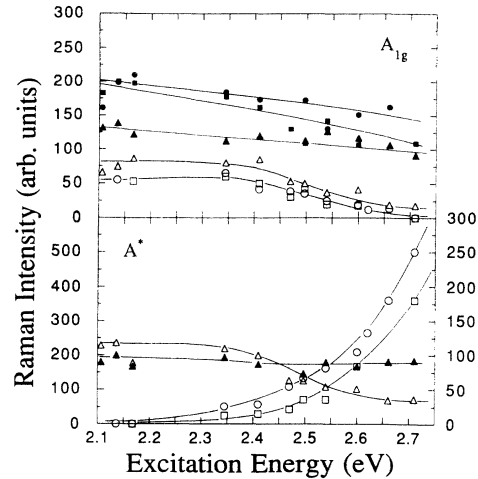


FIG. 3. Excitation energy dependence of the  $A_{1g}$  (top) and  $A^*$  (bottom) peak intensities of  $R_{2-x}\text{Ce}_x\text{CuO}_4$  single crystals for  $R = \text{Pr}$  ( $\Delta$ ),  $\text{Nd}$  ( $\circ$ ), and  $\text{Sm}$  ( $\square$ ). Filled symbols are for  $x = 0$ , and hollow symbols are for  $x = 0.15$ . The  $\text{Pr}$  data in the  $A^*$  figure refer to the right vertical scale; all the others refer to the left scale.

scope onto a single crystalline grain, with  $\mathbf{E}_i||\mathbf{E}_s$ . Different grains were tested until a spectrum characteristic of  $zz$  polarization was obtained. Of course, some degree of misorientation is usually present, as proved by the presence of the  $E_g$  mode in Fig. 2. In an approximative way, the degree of misorientation is estimated by comparing the relative intensities of the  $x = 0.175$  spectrum (showing the highest misalignment) to those of an  $x = 0.15$  single crystal. Then we find that the  $x = 0.175$  spectrum corresponds to a direction  $20^\circ$ – $25^\circ$  out of the  $z$  axis, which means that  $A_{1g}$  and  $A^*$  intensities are underestimated by 20%. Similar or smaller misorientations are present for the other ceramics. Even taking into account this correction, the integrated intensity of the  $A_{1g}$  mode decreases by  $\approx 50\%$  from  $x = 0$  to 0.175 samples. The important point is that, since  $A_{1g}$  and  $A^*$  have the

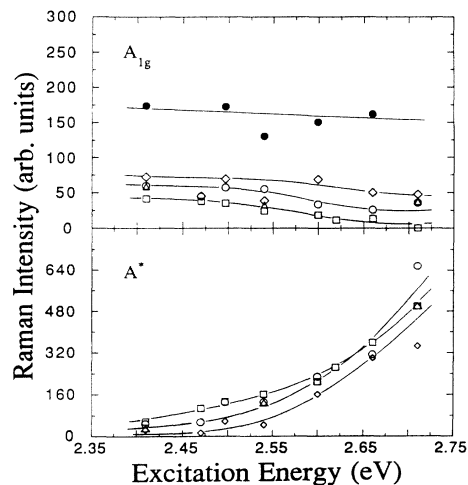


FIG. 4. Excitation energy dependence of the  $A_{1g}$  (top) and  $A^*$  (bottom) intensities of  $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$  as a function of  $x$ :  $\bullet$ ,  $x = 0$ ;  $\diamond$ ,  $x = 0.125$ ;  $\Delta$ ,  $x = 0.135$ ;  $\square$ ,  $x = 0.15$ ; and  $\circ$ ,  $x = 0.175$ .

TABLE I.  $RT$  frequencies (in  $cm^{-1}$ ) of the  $A_{1g}$  and  $A^*$  modes of  $R_{2-x}Ce_xCuO_4$  single crystals ( $R = Pr, Nd, Sm$ ;  $x = 0, 0.15$ ).

$R$	$x$	$A_{1g}$	$B_{1g}$	$E_g$	$A^*$
Pr	0	228.5	303	459.5	576
Nd	0	227	329	483	
Sm	0	221.5	334.5	496.5	
Pr	0.15	228	303	460	583
Nd	0.15	229	333	475	585
Sm	0.15	225	340	485	594

same symmetry and for both modes  $zz$  activity is strongest, we can measure their resonance by selecting them from the spectra taken "in parallel."

We now comment on the results in more detail: The  $A^*$  mode presents a clear resonance towards the uv in Nd and Sm compounds, while it is enhanced towards the red in the Pr,  $x = 0.15$  compound. Within experimental error, no resonance is observed in the  $A^*$  mode in  $Pr_2CuO_4$ . From Fig. 4 we conclude that the energy of resonance does not depend on  $x$ , at least in the range studied. On the other hand, the  $A_{1g}$  mode shows similar dependence on exciting light for all three Nd, Sm, and Pr compounds with the same cerium content (Fig. 3). However, this evolution depends on  $x$ , as shown in Fig. 4: While its intensity is nearly constant in the pure compounds (with a smooth decrease towards the blue), it decreases and even vanishes at high energies as cerium is introduced, this trend being more pronounced for increasing values of  $x$ .

We shall first discuss which is the origin of the  $A^*$  mode, among the several plausible models. There is a common agreement about several facts: The high energy of the mode and its polarization point towards a mode involving oxygen displacement along the  $c$  axis. Thus, this mode cannot, in spite of the frequency coincidence, be explained by the breathing of O(1) in the  $CuO_2$  plane, for the latter involves oxygen displacement in  $x$  and  $y$  directions. The LO  $A_{2u}$  phonon, though Raman forbidden, was a good candidate for the  $A^*$  mode. It could have been activated by the disorder introduced by cerium doping. However, its frequency is too low,<sup>18,19</sup> and, also, it is difficult to justify the activation in the cerium-free sample  $Pr_2CuO_4$ . Finally, it has been proposed that some of the O(2) could move to a position such as the apical site in the  $T$  structure<sup>11</sup> and that this displacement would occur preferably near a  $Ce^{4+}$ , due to its smaller ionic radius (0.92 Å) compared, for instance, to that of  $Nd^{3+}$  (0.995 Å). The  $A^*$  mode would be the stretching of this apical oxygen against Cu and Ce and would have the correct polarization. The difference between the  $A^*$  frequency and that of the apical oxygen stretching in  $T$ -phase cuprates [about 400  $cm^{-1}$  (Ref. 20)] could be due to a shorter Cu-O distance in the  $T'$  compound. However, the transition from  $T'$  to  $T$  is favored by the presence of larger ions, such as  $Sr^{2+}$ , and not of smaller ones, as  $Ce^{4+}$ . This has been convincingly established by x-ray-absorption near-edge structure (XANES) experiments in  $T$ ,  $T'$ , and  $T^*$  compounds,<sup>21</sup> which show that small tetravalent ions,

such as  $Ce^{4+}$ , prefer the eightfold coordination typical of  $T'$  structure. We note that in  $T^*$ -NdCeSrCuO the stretching of the apical oxygen is observed at 450  $cm^{-1}$ , with the simultaneous presence of the forbidden  $A^*$  mode.<sup>22</sup>

We propose a model that is consistent with all present observations and may explain the resonance effects. First, we note that the similarity in the frequency of the mode in Nd, Sm, or Pr compounds implies that its configuration is the same in all three cases, in spite of the differences in resonance behavior. From Fig. 2, it is also clear that its intensity is enhanced by cerium doping.

The most important structural effect of cerium doping is associated to its charge. The presence of an extra positive charge, together with the smaller radius of  $Ce^{4+}$ , can produce an inward relaxation of the oxygens surrounding cerium, giving rise to a local distortion of the  $T'$  structure. We think that the  $A^*$  mode is the local mode that involves the  $z$  displacement of these oxygens, in a manner very similar to the  $A_{2u}$  mode that consists mainly of the antiphase vibration of O(2) and O(1). The smaller cerium-oxygen distances can explain the higher frequency of the  $A^*$  mode, compared with that of the  $A_{2u}$  mode.<sup>19</sup> This model explains the frequency, polarization, and cerium dependence of the mode. The problem of its appearance in  $Pr_2CuO_4$  still remains. Here, we would like to relate this question with the absence of superconductivity in  $PrBa_2Cu_3O_{6+x}$ . Two possible explanations have been given (see Ref. 23 for a discussion). The first one claims a mixed-valence state (between 3 and 4) for Pr. The second one suggests that the nonsuperconductivity is due to strong hybridization of Pr  $4f$  states, either with O  $2p$  states or with conduction states close to  $E_f$ . Probably, the same reason that prevents superconductivity in this hole-doped material is helping it in electron-doped  $Pr_2CuO_4$ . We cannot decide from our Raman experiments which is the Pr valence. However, the presence in  $Pr_2CuO_4$  of a small proportion of localized  $Pr^{4+}$ , whose charge and ionic radius are similar to that of  $Ce^{4+}$ , might induce almost identical local distortion and mode activation as a light cerium doping does. From the relative intensities of the  $A^*$  and  $A_{1g}$  modes in  $Pr_2CuO_4$  and  $Nd_{2-x}Ce_xCuO_4$  we estimate the hypothetical  $Pr^{4+}$  concentration to be about 5%. We note that such a small concentration might be difficult to detect by other techniques but enough to activate local modes. Part of the XANES experiments of Ref. 21 were interpreted as due to the presence of localized  $Pr^{4+}$  or  $Tb^{4+}$  in  $T^*$  compounds, in concentrations of up to 20%. The presence of some  $Pr^{4+}$  ions may be related to the fact that slightly smaller  $x$  is needed to maximize  $T_c$  in  $Pr_{2-x}Ce_xCuO_4$  than in  $Nd_{2-x}Ce_xCuO_4$  or  $Sm_{2-x}Ce_xCuO_4$ .<sup>24</sup>

There are basically three band-structure calculations for pure or Ce-doped  $Nd_2CuO_4$ , whose results are quite similar, except for the binding energies of O(2).<sup>25-27</sup> Within our model, resonance of the  $A^*$  mode may arise from transitions between oxygen and empty  $4f$  or  $5d$  cerium states. That cerium states are involved is clear from the absence of resonance in  $Pr_2CuO_4$ . The nature of the oxygen states depends on which calculation is fol-

lowed. In Ref. 25, while nonplanar O(2) have large binding energies in  $T'$  structure, planar O(1) lie close to  $E_f$  and are shifted from empty cerium states by 2 or 3 eV. On the other hand, in Ref. 27 the  $p_z$  orbitals of the O(1)-O(2) chains couple to produce a pair of bonding-antibonding states, the antibonding state being close to  $E_f$ . We suggest that this state can couple strongly to the modified  $A_{2u}$  mode ( $A^*$ ) thus explaining the strength of the resonance and why it affects mainly the  $A^*$  mode. The question arises as to why those electronic transitions that result in such a huge resonance are not observed in the  $z$  component of the dielectric constant. This problem was also found in  $\text{YBa}_2\text{Cu}_3\text{O}_6$ ,<sup>13</sup> where a resonance of the  $zz$  component of the  $A_{1g}$  mode at  $472\text{ cm}^{-1}$  could not be explained in terms of the dielectric constant and was attributed to the large deformation potential derived from strong modulation of the O(4) $p_z$ +Cu(1) $d_{3z^2-r^2}$  band by the motion of O(4). A similar explanation could apply to our case: Instead of Cu—O bonds, the  $T'$  structure has O(1)—O(2) chains along the  $c$  axis. The suggested initial state for the resonance, O(1) $p_z$ +O(2) $p_z$ , would be greatly affected by O(1) and O(2) motion in the  $A^*$  mode, leading to a strong electron-phonon matrix element, that could overwhelm the weakness of the dipolar transition to the upper (cerium) states, which is not strong enough to be detected in the dielectric constant.

The nondependence of the resonance energy on cerium doping can also be understood from band-structure calculations: A rigid band behavior upon cerium doping seems to be justified, merely shifting the Fermi level up ( $\Delta E_f \approx 0.26\text{ eV}$  for  $x=0.25$ ) (Ref. 25) and introducing empty cerium states in the conduction band. A possible shift of these cerium states with increasing doping, if present, would be difficult to detect, since the variation range of  $x$  is small.

Since we lack calculations for Pr compounds, it is difficult to explain the differences observed in resonance

phenomena. However, smaller binding energies are expected in this case due to the larger distances. Since the  $A^*$  mode is nonresonant in  $\text{Pr}_2\text{CuO}_4$  and its evolution with excitation energy in  $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$  is completely analogous to that of the  $A_{1g}$  mode, we suggest that the enhancement of the  $A^*$  mode towards the red is not a resonant phenomenon, but for the same reason, associated with cerium doping, this causes the decrease of the  $A_{1g}$  towards the uv. From Fig. 3 we may conclude that this decrease is not an antiresonance effect between  $A_{1g}$  and  $A^*$  modes, since in Pr compounds both modes show a similar trend. The participation of the rare-earth states can also be discarded, since no resonance effects appear in pure compounds. A possible explanation for the intensity decrease for increasing excitation energy might be the screening effects arising from conduction electrons introduced by cerium doping. The enhancement of this feature with increasing doping levels is an argument in favor of the preceding explanation. The lack of systematic experimental data on the optical absorption and reflectivity of doped samples in the 2–3-eV region with  $E_{||c}$ , as in our  $zz$  measurements, prevents a definite attribution of the  $A_{1g}$  decrease to light absorption or reflection.

In summary, we have studied the  $zz$  Raman spectrum of Pr, Nd, and Sm cuprates with  $T'$  structure as a function of rare-earth substitution and cerium doping. We propose a model for the activation of the forbidden mode  $A^*$  as an oxygen local mode caused by oxygen relaxation around  $\text{Ce}^{4+}$ . From the resonance curves, we conclude that cerium states are involved in the resonance of the  $A^*$  mode, while the  $A_{1g}$  decrease towards uv is probably a consequence of the metallic character of doped samples.

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