

Different Pr³⁺ environments in Pr_{1.85}Ce_{0.15}CuO₄: A Raman crystal-field excitation study

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Low-temperature Raman scattering of crystal-field (CF) excitations within the Pr³⁺ ground-state ³H₄ multiplet of the compound Pr_{1.85}Ce_{0.15}CuO₄ suggests the presence of more than one CF environment for the Pr³⁺ ions. The Raman spectra were similar to spectra obtained in inelastic neutron-scattering experiments. The analysis of the Raman spectra for Pr_{1.85}R_{0.15}CuO₄ samples with R=Pr, La, Y, Ce, and Th indicates three different environments for Pr³⁺. One is associated with charge transfer caused by the replacement of Pr³⁺ by the tetravalent ions Ce⁴⁺ or Th⁴⁺. A second is almost identical to that observed in Pr₂CuO₄. The third is attributed to either an orthorhombic distortion or to sites of smaller lattice volume. The Nd- and Nd(Ce)-based compounds are also discussed.

I. INTRODUCTION

Crystal-field (CF) studies in high-temperature superconductors (HTS's) are extremely interesting, particularly for Ln₂CuO₄ (Ln = La, Pr, Nd) compounds, in which superconductivity is induced by a doping process. In the La-based compounds a divalent dopant (Sr²⁺ or Ba²⁺) oxidizes the CuO₂ planes, leaving holes as supercurrent carriers.¹ In contrast, doping of the Nd- and Pr-based compounds with tetravalent Ce or Th reduces the CuO₂ planes, giving rise to electron carriers.² The effective charge in the CuO₂ planes, *seen* by the rare earth (*R*) via the CF electrical potential, may be strongly affected by the doping process, and experiments sensitive to CF effects should detect the induced changes.

Results of inelastic neutron-scattering (INS) experiments in the electron-doped compounds Ln_{2-x}Ce_xCuO₄ (Ln=Nd, Pr) and their parent compounds (*x*=0) have been reported by several groups.³⁻¹¹ Although there is agreement on the observed CF spectra, analysis of the data leads to different sets of CF parameters. Furthermore, any of these sets yield a good fit of the anisotropic temperature dependence of the magnetic susceptibility.¹² Including a molecular field at the *R* site did not solve the problem.⁹ A difficulty in analyzing the INS data is that only a few clear CF transitions are observed, and these may not be enough to determine the five CF parameters.¹⁰ We recently reported on Raman experiments in Pr₂CuO₄,¹³ showing that the observed CF excitations agreed fairly well with those observed in the INS experiments. Here we report on Raman CF excitations in the electron-doped (*n*-type) Pr_{1.85}Ce_{0.15}CuO₄.

II. EXPERIMENTAL DETAILS

The Raman data were taken between 10 K and 293 K. The samples were platelike single crystals of Pr_{1.85}Ce_{0.15}CuO₄ having their *c* axis perpendicular to the large face. The samples were not subjected to reducing thermal treatments; hence, all our measurements were taken in the normal state. The crystals were grown from a nominally stoichiometric mixture of the respective oxides, using PbO- and CuO-based fluxes in Pt crucibles. The Pb content was less than 1% of the copper content.¹⁴ The Raman measurements were performed in backscattering geometry; the experimental details are given elsewhere.¹³

For comparison with the single-crystal data, polycrystalline samples of Pr_{1.85}R_{0.15}CuO₄ (*R*=Ce, Th, La, and Y) were also studied. These samples were prepared by heating a nominally stoichiometric mixture of the corresponding oxides in air at 1080 °C for 24 h. Successive re-grinding, pressing into pellets, and sintering was done until a single phase was detected by x-ray diffraction. X-ray powder diffraction measurements were performed using a Rigaku R200 diffractometer and rotating anode generator with Cu *K*α radiation. The lattice constants were calculated from the experimental data using a Rietveld profile refinement program.¹⁵ A tetragonal unit cell with atomic positions of the *T'* structure (SG *I4/mmm*) was used for the calculations. The results are shown in Table I.

III. EXPERIMENTAL RESULTS

Figure 1 shows typical Raman spectra in the low-energy region for *ZX* polarization in Pr₂CuO₄ and in

TABLE I. Refined values of lattice parameters (\AA) for $\text{Pr}_{1.85}\text{R}_{0.15}\text{CuO}_4$ ($R=\text{Pr, La, Y, Ce, Th}$). The ionic radius (\AA) is given beside each R .

	$\text{Pr}^{3+}(1.09)$	$\text{La}^{3+}(1.15)$	$\text{Y}^{3+}(0.93)$	$\text{Ce}^{4+}(1.01)$	$\text{Th}^{4+}(0.95)$
a	3.959(1)	3.963(1)	3.954(1)	3.9616(1)	3.967(1)
c	12.236(3)	12.257(3)	12.185(3)	12.1536(3)	12.186(3)

three different samples of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. Similar spectra were obtained from different regions of the samples, and also for samples with lower nominal Ce concentrations ($0.05 \leq x \leq 0.15$). It is clearly seen that Ce doping broadens the spectra, developing multiple features in which at least three peaks may be identified. For XX and ZZ polarization the CF excitations are forbidden according to the selection rules of the Raman process.¹³ Figure 2 shows the Raman spectra of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ for different polarizations. These data suggest that the multiple-peak structure observed for the ZX polarization between 100 and 175 cm^{-1} corresponds to the CF excitation between the ground state Γ_4 and the first excited Γ_5 state. Moreover, Figure 3 shows greater thermal broadening for the multiple-peak structure than for the A_{1g} phonon mode, characteristic of faster relaxation for the CF excitations.¹³

Figure 4 shows the Raman spectra for $\text{Pr}_{1.85}\text{R}_{0.15}\text{CuO}_4$ ($R=\text{La, Y, Ce, and Th}$) and Pr_2CuO_4 polycrystalline samples. The electron-doped (n -type) compounds ($R=\text{Ce}^{4+}, \text{Th}^{4+}$) show basically the same multiple-peak structure, but less resolved, as that observed in single crystals and attributed to CF excitations. In contrast, the undoped compounds ($R=\text{La}^{3+}, \text{Y}^{3+}$) show a single narrow peak at $\sim 153 \text{ cm}^{-1}$ for La and a relatively broad peak at $\sim 156 \text{ cm}^{-1}$ for Y. In both, this peak is very close to that observed in Pr_2CuO_4 at $\sim 155 \text{ cm}^{-1}$.

IV. ANALYSIS AND DISCUSSIONS

In a recent letter on Raman experiments¹³ we showed that the CF excitations at 156, 540, and 690 cm^{-1} (Ref. 16) in Pr_2CuO_4 were very close to the CF transitions

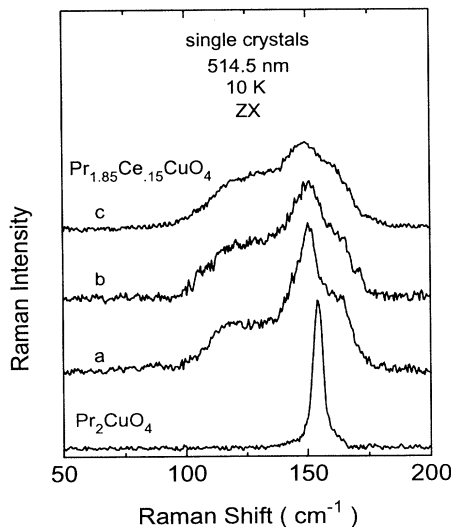


FIG. 1. Low-energy crystal-field Raman excitations for Pr_2CuO_4 and three different samples of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.

observed in INS experiments.⁹ In this work as well, the multiple-peak structure observed between 100 and 175 cm^{-1} for $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (see Fig. 1) shows basically the same features observed in INS experiments for the same energy interval (12–22 meV).⁹ Thus, we conclude that the origin of the multiple-peak spectra is the same in both experiments and may be associated with the presence of Pr^{3+} having different CF environments, coexisting within the area of the focusing laser spot ($\sim 100 \mu\text{m}$ diam.). But we should mention that while the INS experiment¹¹ showed two nearly resolved peaks at ~ 653 and $\sim 710 \text{ cm}^{-1}$ for the Ce^{4+} -doped compound, our Raman experiments failed to detect these transitions.

Figure 5 shows, for the most highly resolved Raman spectra of Fig. 1(a), that the spectrum is equally well simulated by the superposition of either three or four Lorentzian lines having the appropriate energy positions, linewidths, and relative intensities. The simulations and calculated parameters are shown in the figure. Similar simulations were carried out for the spectra shown in Figs. 1(b) and 1(c) with approximately the same parameters.

It is thus clear that the multiple-peak structure observed in the Raman spectra for the Ce- and Th-based compounds may be associated with the presence of *three* different Pr^{3+} environments. The peak at $\sim 151 \text{ cm}^{-1}$ could be attributed to a Pr^{3+} site (site I) having an environment slightly perturbed from that in the pure compound Pr_2CuO_4 (see Fig. 1). This is supported by the nearly identical lattice parameters and Raman spectra

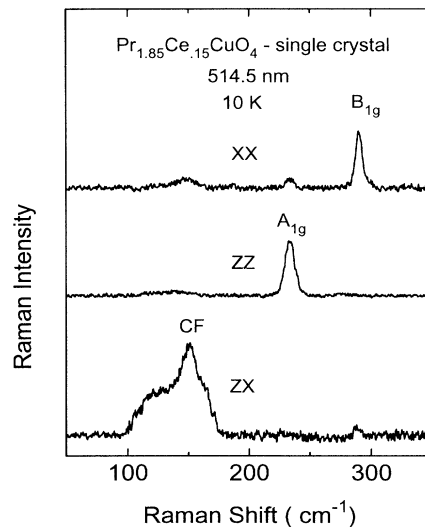


FIG. 2. Raman spectra of $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ for different polarizations.

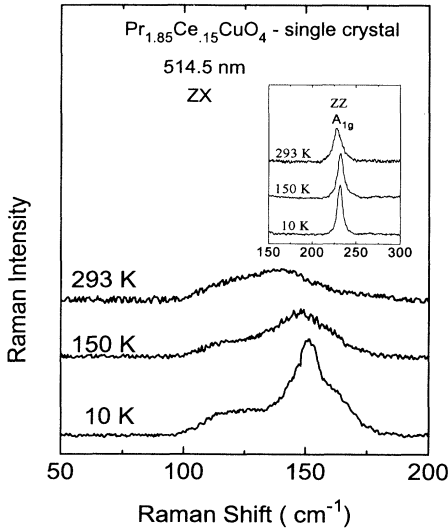


FIG. 3. Low-energy crystal-field Raman excitation for $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ as a function of temperature. The inset shows the temperature dependence of the A_{1g} phonon for the same sample.

obtained for Pr_2CuO_4 and La-doped compounds (see Table I and Fig. 4). The broad low-energy peak at $\sim 122 \text{ cm}^{-1}$ may arise from a Pr^{3+} environment (site II) that is strongly modified by the charge transfer caused by the substitution of a trivalent (Pr^{3+}) by a tetravalent (Ce^{4+} , Th^{4+}) ion (electron doping). The absence of this peak in the La- and Y-doped compounds supports this idea (see Fig. 4). Finally, the small high-energy shoulder at 163 cm^{-1} may be attributed to a third Pr^{3+} environment, whose origin may be twofold (sites IIIa and IIIb). First, the reduction in lattice volume caused by the substitution of Pr^{3+} by smaller ions (Ce^{4+} , Th^{4+} , and Y^{3+})

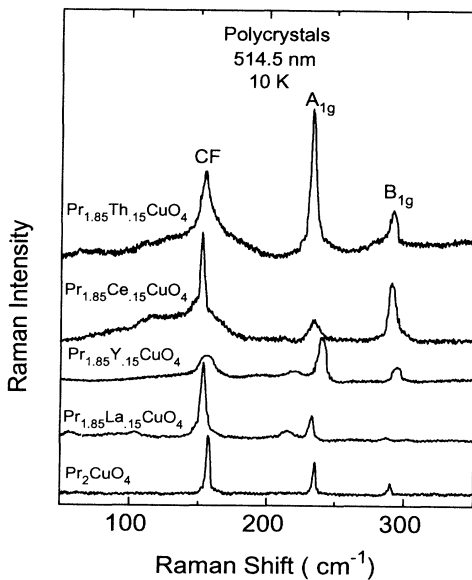


FIG. 4. Raman spectra of polycrystalline $\text{Pr}_{1.85}\text{R}_{0.15}\text{CuO}_4$ ($R=\text{La}, \text{Y}, \text{Ce},$ and Th) and Pr_2CuO_4 .

leads to a stronger local crystal electric field. The first excited Γ_5 CF level may then shift toward higher energy, giving rise to a single line at $\sim 163 \text{ cm}^{-1}$ [see Fig. 5(a)]. Second, Furusawa and Koyama¹⁷ observed in a transmission electron diffraction experiment the presence of an orthorhombic phase in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$. This would split the first excited Γ_5 CF level of Pr^{3+} , and the shoulder observed at $\sim 163 \text{ cm}^{-1}$ could then be attributed to the high-energy component of the split line, as shown in Fig. 5(b).

In order to account for these different possibilities we adopted the CF analysis (without molecular field), given in Ref. 9. The Hamiltonian describing the crystal field can be written

$$H_{\text{CF}} = \sum_{k,q} B_q^k C_q^k, \quad (1)$$

where C_q^k is the q th component of a spherical tensor of rank k , and the B_q^k are the corresponding CF parameters. For the lanthanide ions (Pr^{3+}) in the T' structure, the site symmetry is C_{4v} . Hence the nonzero CF parameters are B_0^2 , B_0^4 , B_0^6 , B_4^4 , and B_4^6 .¹⁸ Using the intermediate coupling approach and Eq. (1) (Ref. 19) for all 13 J multiplets of Pr^{3+} , we obtained the CF parameters and the level scheme that best fit the Raman CF excitations of Ref. 13 for the ground-state multiplet of Pr^{3+} in Pr_2CuO_4 . The resulting parameters and level scheme are shown in Table II and Fig. 6, respectively. For comparison, we give also the CF parameters and level scheme

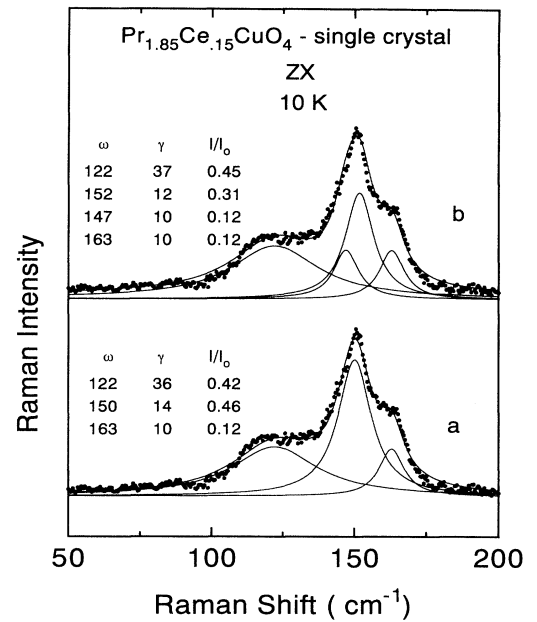


FIG. 5. Low-energy crystal-field Raman excitations for the sample of Fig. 1(a). The tables show the energy positions, ω (cm^{-1}), linewidths, γ (cm^{-1}), and relative intensities, I/I_0 , corresponding to (a) the simulation with three Lorentzian lines, and (b) the simulation with four Lorentzian lines. I is the Raman intensity for each site and I_0 the total Raman intensity between 100 and 175 cm^{-1} .

TABLE II. Pr^{3+} crystal-field parameters B_q^k (meV) in $\text{Pr}_{2-x}\text{Ce}_x\text{CuO}_4$ ($x=0.0, 0.15$).

B_q^k	Pr_2CuO_4		$\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$			
	INS ^a	Raman ^b	Site I	Site II	Site IIIa	Site IIIb
B_0^2	-28	-30	-30	-17	-35	-29
B_2^2	0	0	0	0	0	4
B_0^4	-301	-275	-285	-297	-250	-275
B_0^6	26	21	25	41	19	21
B_4^4	228	228	228	228	228	228
B_4^6	224	224	224	224	224	224

^aFrom Ref. 9.^bFrom Ref. 13.

obtained from INS experiments.⁹

Starting with the parameters obtained from the Raman spectra (second column in Table II), we varied B_0^2 , B_0^4 , and B_0^6 until the peaks shown in Fig. 5 were obtained. These calculations were carried out bearing in mind that only a small splitting of the transition at 690 cm^{-1} ($\sim 88\text{ meV}$) is allowed by INS experiments.¹¹ The new parameters are shown in columns 3 – 6 of Table II and the energy levels in columns 3 – 6 of Fig. 6. We note that the energy level scheme for site II (see Fig. 6) has a Γ_2 and a Γ_5 level at $\sim 664\text{ cm}^{-1}$, close to the peak at $\sim 653\text{ cm}^{-1}$ observed in INS.¹¹

We now comment on the INS experiments in $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.⁹ The INS spectra show broad peaks with no resolved structure, in contrast to $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$. Using the intermediate coupling approach we calculated the level scheme for the Nd^{3+} ground state in Nd_2CuO_4 with the set of CF parameters given in Ref. 9. Introducing relative changes in the CF parameters similar to those for the different Pr^{3+} environments in $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ (see Table II), we found a Nd^{3+} level scheme compatible with the INS spectra observed for $\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$.^{5,9,11} The main effect of the CF parameters for site II (see Table II) is to intro-

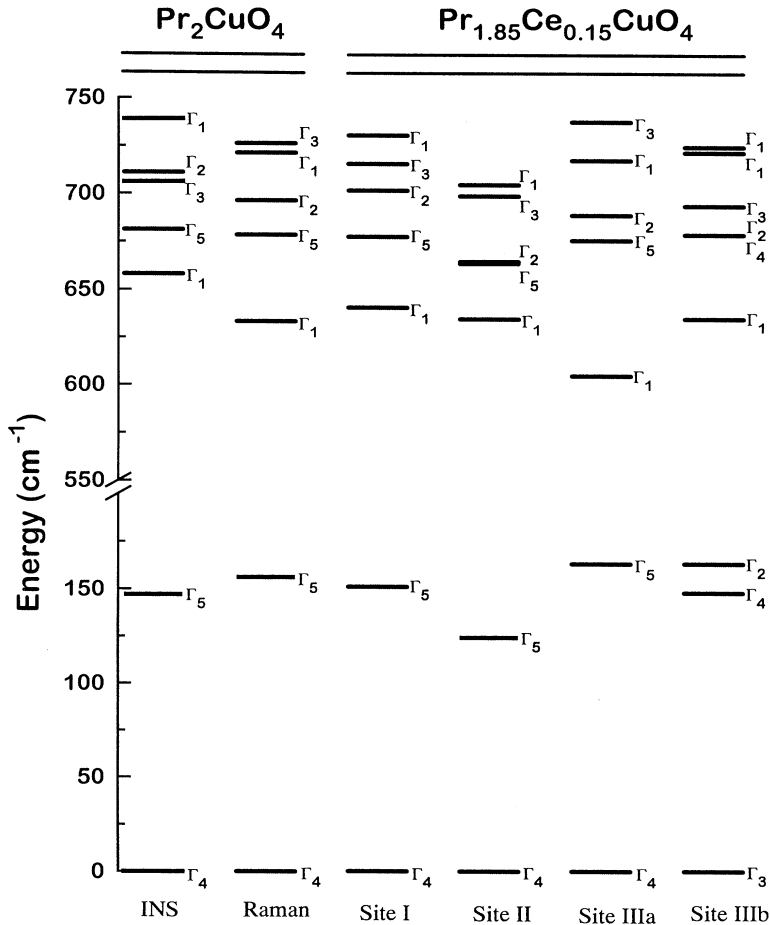


FIG. 6. CF ground-state level scheme for Pr^{3+} in Pr_2CuO_4 (Raman and INS) and $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ sites (I, II, IIIa, and IIIb).

duce a shift of the first Γ_5 excited state of Pr³⁺ from ~ 155 to ~ 124 cm⁻¹ (see Fig. 6). A similar relative change of the CF parameters for Nd³⁺ results also in a shift of the first Γ_7 excited state from ~ 116 to ~ 71 cm⁻¹. This agrees with the observation of a first excited level at ~ 92 cm⁻¹ (11.5 meV) in INS experiments in Nd_{1.85}Ce_{0.15}CuO₄.^{5,9,11}

Loong and Soderholm¹⁰ analyzed their INS data for Pr₂CuO₄ and report a different set of CF parameters and level scheme for the Pr³⁺ ground state ³H₄. They attribute the 710 cm⁻¹ peak, observed in Raman experiments at ~ 690 cm⁻¹,¹³ to a transition between a Γ_3 ground state and a Γ_4 excited state. However, the Raman selection rules for a CF excitation between these two levels forbids this transition. Rather, for the level scheme given in Fig. 6, this peak is associated with a transition between the Γ_4 ground state and the Γ_5 and Γ_2 excited states, allowed by the Raman selection rules.¹³ Furthermore, Loong and Soderholm¹⁰ found a broad single peak for the first CF excitation in Pr_{1.85}Ce_{0.15}CuO₄, contrary to the multiple structure observed by us and Refs. 9 and 11.

Recently Martins *et al.*²⁰ measured electron spin resonance (ESR) of Gd³⁺ in Pr_{2-x}Ce_xCuO₄ and found that the second-order $|b_{20}|$ CF parameter of Gd³⁺ decreases by about 23% upon doping. We therefore expect a similar reduction in the second-order $|B_0^2|$ CF parameter of Pr³⁺.²¹ It is interesting to note that the absolute value of a second-order CF parameter weighted among different sites, $\langle B_0^2 \rangle = \sum (I/I_0)_i B_{0i}^2$, where i ranges over the vari-

ous sites, gives $|\langle B_0^2 \rangle| \simeq 23\text{--}25$ meV. This is about 22% smaller than the value for Pr₂CuO₄, in good agreement with the ESR results, though Gd³⁺ has an S ground state for which CF effects are observed only via spin-orbit coupling with the excited states.

V. CONCLUSIONS

In summary, we have shown that in as-grown Pr_{1.85}Ce_{0.15}CuO₄, there is more than one CF environment for the Pr³⁺ ion. The CF excitation spectra observed in Raman and INS experiments for the electron-doped Pr_{1.85}Ce_{0.15}CuO₄ compound can be interpreted in terms of *three* different Pr³⁺ CF environments. The CF parameters for these sites describe well the observed Raman and INS spectra; however, as they were obtained in a simple way, they should be used with caution. One of these sites may be attributed to charge transfer associated with the doping process. Calculations from first principles will be needed in order to estimate the amount and localization of charge transfer that would account for the change in the CF parameters.

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