

Raman-scattering study of crystal-field excitations in Pr_2CuO_4

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Crystal-field transitions within the 3H_4 multiplet of Pr^{3+} in Pr_2CuO_4 were studied by Raman scattering as a function of temperature. We observed three crystal-field excitations at 156, 540, and 675 cm^{-1} . The peak at 156 cm^{-1} , assigned by other authors to the lowest E_g phonon mode, shows a thermal broadening of the linewidth, which is the signature for acoustic-phonon-relaxation processes between crystal-field levels. Our results are in excellent agreement with recent inelastic neutron-scattering experiments in Pr_2CuO_4 .

The study of crystal-field effects in high- T_c superconductors is important in order to characterize the local symmetry and charge distribution on the superconducting Cu-O planes. These data are helpful in understanding the three-dimensional long-range antiferromagnetic order of the rare-earth sublattice that coexists with the superconducting state,¹ and also in identifying correctly the Raman-active phonons. The parent compound, Pr_2CuO_4 , of the 2:1:4 electron-doped high- T_c superconductors $R_{2-x}M_x\text{CuO}_4$ (R =rare earth, M =Ce, Th) is particularly interesting because crystal-field excitations have been recently studied using inelastic neutron scattering.^{2,3} Also, crystal-field effects were studied in Gd^{3+} - and Er^{3+} -doped Pr_2CuO_4 by electron spin resonance.⁴ It has been shown that measurements by Raman scattering of trivalent rare-earth impurities (Nd^{3+} , Pr^{3+} , Eu^{3+} , etc.) in transparent crystals makes it possible to observe crystal-field excitations.⁵ However, similar data in opaque materials are more difficult to obtain, but is now possible because of the existence of very sensitive detectors. Recently, Jandl *et al.* have reported crystal-field excitations in the Raman spectra of Nd_2CuO_4 .⁶

In this paper we present Raman measurements of crystal-field excitations in Pr_2CuO_4 as a function of temperature. Platelike single crystals with the tetragonal c axis perpendicular to the large face were grown from PbO - and CuO -based fluxes. The lead content was less than 1% of the copper content. The Raman measurements were performed in a backscattering geometry for different orientations of the crystal c axis. The samples were mounted on the cold finger of a closed-cycle He refrigerator. In order to avoid spurious background from the cryostat window, we used an angle of incidence of about 20° , which is substantially reduced inside the crystal. To obtain the almost ZZ and ZX polarizations we mounted one of the samples with the c axis perpendicular to the plane of incidence. For the XX and XY polarizations a second sample was mounted with the c

axis parallel to the incident direction, and the a axis perpendicular to the plane of incidence. The 488 and 514.5 nm lines of an Ar ion laser were used to excite the spectra. The scattered light was analyzed with a Jobin Yvon T64000 triple spectrometer equipped with a cryogenic charge-coupled device camera. In all the measurements the spectral resolution was better than 4 cm^{-1} . A point focus of about $100\text{ }\mu\text{m}$ was used in order to avoid the heating of the samples.

Figure 1 shows the Raman spectra at 20 K for different polarizations of the incoming and scattered light. Pr_2CuO_4 has a D_{4h}^{17} space group with four active opti-

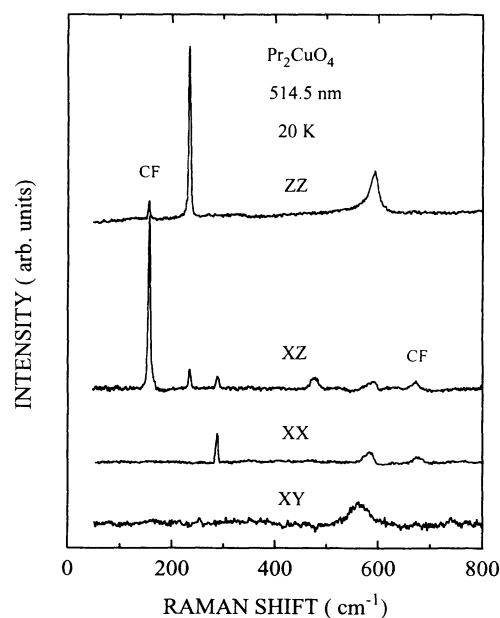


FIG. 1. Raman spectra of Pr_2CuO_4 at 20 K for various scattering configurations. The label CF indicates crystal-field excitations.

cal modes ($A_{1g} + B_{1g} + 2E_g$). In agreement with Sugai, Kobayashi, and Akinitsu⁷ the strong and sharp $233 \text{ cm}^{-1} A_{1g}$ phonon can be observed for ZZ polarization (upper curve in Fig. 1). This mode corresponds to the z vibration of rare-earth ions in the $2:1:4 T'$ structure.⁸ The broadband centered at about 585 cm^{-1} has almost ZZ polarization but can also be observed, with reasonable intensity, in other polarizations. The origin of this structure is still controversial and it has been interpreted as a disorder activated oxygen local mode.⁹ We will show below that this peak superimposes to a crystal-field excitation at room temperature, giving an asymmetric structure. The XZ spectrum shows the in-plane oxygen vibration E_g mode at 474 cm^{-1} , and two peaks at 156 and 675 cm^{-1} which we will show to correspond to crystal-field excitations. The 156 cm^{-1} peak has been interpreted as the lowest frequency E_g phonon mode where the Pr^{3+} ions participate.⁷ The appearance of this E_g mode is somewhat controversial. In Nd_2CuO_4 and at room temperature this mode was found at 122 (Ref. 10) and 126 cm^{-1} .⁶ Jandl *et al.*⁶ interpreted the disappearance of this peak at low temperature as being due to the coupling with a very close crystal-field excitation at 119 cm^{-1} .¹¹ Finally, the XX spectrum shows the $287 \text{ cm}^{-1} B_{1g}$ phonon, related to the out-of-plane O vibration.

The $4f$ electron Pr^{3+} free-ion 3H_4 ground-state multiplet is ninefold degenerate. When the Pr^{3+} ion is placed in the C_{4v} site symmetry of Pr_2CuO_4 , the ground-state multiplet splits in five singlets ($2\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$) and two doublets ($2\Gamma_5$). Inelastic neutron-scattering measurements show at low temperature (30 K), a sharp and strong peak at 18 meV (145 cm^{-1}) and a broad peak at 88 meV (710 cm^{-1}).^{2,3} At higher temperatures a broader peak emerge at about 70 meV (565 cm^{-1}). Boothroyd *et al.*² also reported a broad feature at about 290 meV (2340 cm^{-1}), which was interpreted as an intermultiplet transition between the ground 3H_4 and the first excited 3H_5 multiplet. To fit the experimental results to a crystal-field Hamiltonian both authors used different approaches. Allenspach *et al.*³ used Russell-Saunders (RS) wave functions to fit their data obtaining the following level scheme: 0 meV (Γ_4), 18 meV ($\Gamma_5^{(1)}$), 77.6 meV (Γ_1), 82.4 meV (Γ_2), 84 meV ($\Gamma_5^{(2)}$), 87.7 meV (Γ_3), and 88.8 meV (Γ_3). On the other hand, Boothroyd *et al.*,² using the intermediate coupling approach and linear combinations of RS wave functions with the same J value, diagonalized the whole crystal-field Hamiltonian. They obtained a slightly different set of crystal-field parameters, which results in a different ordering for the higher energy levels of the ground-state multiplet. With these results in mind, we analyze our Raman data.

Figure 2 shows the XZ Raman spectra as a function of temperature for the low frequency region. We see that the 156 cm^{-1} peak starts to broaden at about 80 K , suggesting a crystal-field character. Following the neutron results, we attribute this peak to the transition from the fundamental Γ_4 level to the first Γ_5 excited level within the ground-state multiplet. The Raman selection rules are obtained from the direct product of the irreducible representations of the participating crystal-field levels, yielding: $\Gamma_4\Gamma_5 = \Gamma_5$ (E: xz, yz), where we also show the

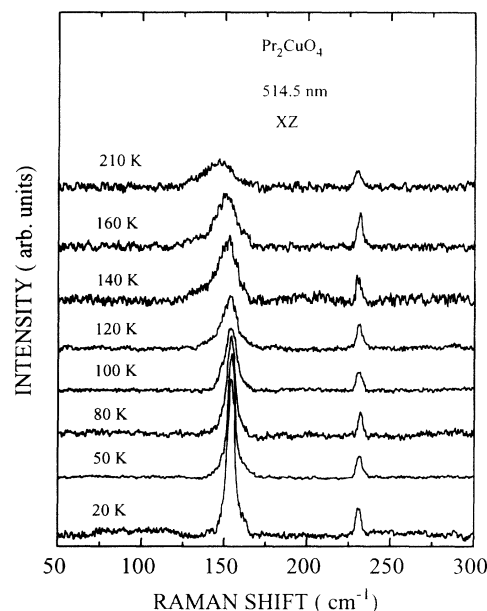


FIG. 2. Temperature dependence of the 156 cm^{-1} crystal-field transition, for XZ polarization. The peak at 233 cm^{-1} corresponds to the A_{1g} phonon.

Schoenflies notation for the irreducible representation of the crystal-field excitation in C_{4v} local symmetry and the allowed Raman tensor components. Figure 1 shows that the 156 cm^{-1} peak obeys these selection rules. In Fig. 2 we can also see the $233 \text{ cm}^{-1} A_{1g}$ phonon due to imperfect polarization.

Figure 3 shows the XZ Raman spectra as a function of temperature in the 500 to 780 cm^{-1} region. The relative broad peak at 675 cm^{-1} shows a temperature dependence of the linewidth similar to that found for the 156 cm^{-1} crystal-field line. This peak may involve at least two very close transitions from the lower Γ_4 state: $\Gamma_4 \rightarrow \Gamma_5^{(2)}$ [$\Gamma_4\Gamma_5 = \Gamma_5$ (E: xz, yz)] and $\Gamma_4 \rightarrow \Gamma_2$ [$\Gamma_4\Gamma_2 = \Gamma_3$ (B_1 : xx, yy)], estimated to appear at 677 and 664 cm^{-1} , respectively.³ Figure 1 shows that this transition can also be observed for XX polarization. Figure 3 also shows at about 540 cm^{-1} a broad feature, emerging above 100 K . We assign this peak to a crystal-field transition from the first excited state $\Gamma_5^{(1)}$ to several higher energy levels, particularly involving the $\Gamma_5^{(1)} \rightarrow \Gamma_5^{(2)}$ transition, expected to appear at 532 cm^{-1} (Ref. 3) with the selection rule: $\Gamma_5^{(1)}\Gamma_5^{(2)} = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4$. We observe this peak for ZZ and XZ polarization. The temperature dependence of the intensity is easily accounted by the temperature dependence of the Boltzmann population factor of the $\Gamma_5^{(1)}$ excited level. Near room temperature (280 K spectrum) this peak collapses with the 585 cm^{-1} phonon structure in a very broad asymmetric peak.

Figure 4 shows the linewidth of the 156 and 675 cm^{-1} crystal-field excitations as a function of temperature. For comparison, we also show the linewidth of the A_{1g} phonon. For the 156 cm^{-1} peak we used a Lorentzian fit, and for the 675 cm^{-1} we plotted the measured full width at half maximum. Two fundamental mechanisms con-

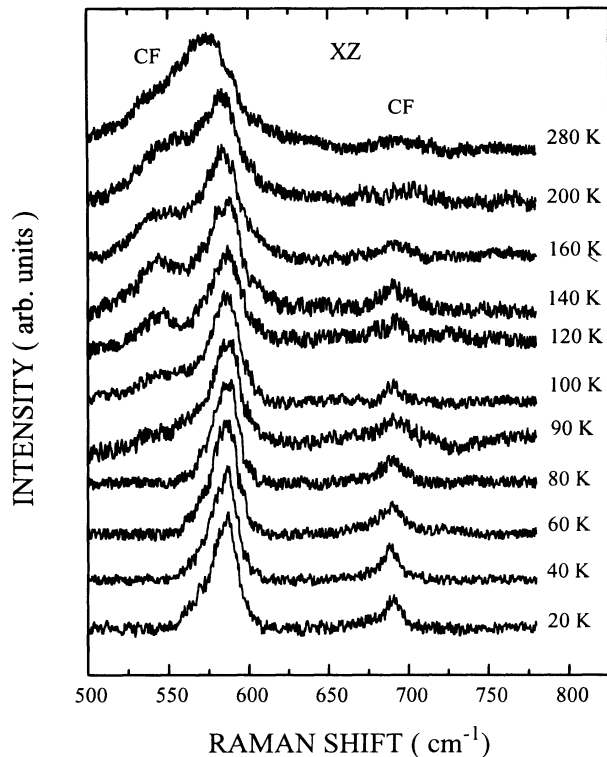


FIG. 3. Temperature dependence of the Raman spectra for the 675 and 540 cm^{-1} crystal-field structures, for XZ polarization. The label CF indicates crystal-field excitations. The broadband at 585 cm^{-1} is usually attributed to a disorder activated oxygen local mode (Ref. 9).

tribute to the broadening of the crystal-field levels due to the electron-phonon interaction. One is the nonradiative decay between crystal-field levels within the same multiplet with the emission and absorption of acoustical phonons (direct process). The other one is the transition between crystal-field levels due to inelastic scattering of phonons (Raman process).^{12,13} Taking into account both contributions we fitted the linewidth of the sharp peak at 156 cm^{-1} to the following expression:

$$\gamma = \gamma_0[p(156 \text{ cm}^{-1}) + 1] + A(T/\Theta_D)^7 \int_0^{\Theta_D/T} dx x^6 e^x / (e^x + 1)^2 \quad (1)$$

where the first term corresponds to the direct process and the second to the Raman process. $p(156 \text{ cm}^{-1})$ is the Bose statistical factor for the energy of the transition, γ_0 the residual linewidth at zero temperature, Θ_D is the Debye temperature, and A is a constant containing the electron-phonon matrix elements between the Γ_4 and $\Gamma_5^{(1)}$ levels. Since these levels are well separated in energy from the excited levels in the ground-state multiplet, we can neglect the contribution from these excited levels to the linewidth of the 156 cm^{-1} peak. Using $\Theta_D = 361 \text{ K}$,¹⁴ the best fit was obtained for $\gamma_0 = 5.1 \pm 0.2 \text{ cm}^{-1}$ and $A = 323 \pm 10 \text{ cm}^{-1}$. The continuous line in Fig. 4 shows the result of this fitting. We want to mention that it was not possible to fit these data with

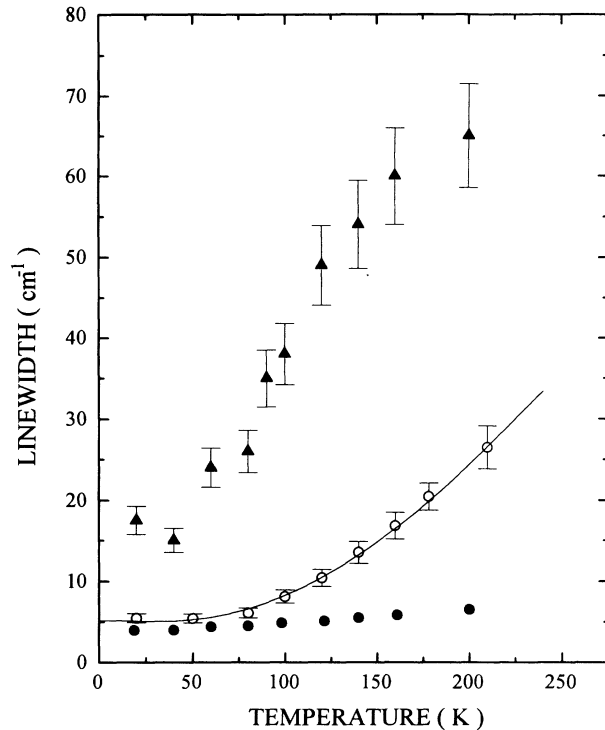


FIG. 4. Temperature dependence of the linewidth for the 156 (open circles) and 675 (full triangles) cm^{-1} crystal-field excitations. The continuous line is the best fit of the linewidth for the 156 cm^{-1} crystal-field peak (see text). The full circles correspond to the 233 cm^{-1} A_{1g} phonon.

the standard third-order anharmonic decay of one optical phonon into two acoustical phonons, according to the Klemens formula.¹⁵ We did not fit the linewidth of the 675 cm^{-1} peak involving the direct and Raman relaxation processes, because as we mention above this peak may contain two unresolved transitions. On the other hand, the first term in Eq. (1) will be much more complicated due to several direct relaxations terms between nearby adjacent excited crystal-field levels.

Finally, it is worth mention that neutron-scattering experiments predicts the observation of a Raman line at 290 meV (2340 cm^{-1}), corresponding to a transition between the ground state and first excited multiplet.² We failed to observe this transition in our Raman experiments. We believe that this was due to the fact that neutron-scattering experiments already show an extremely broad peak for this transition.

In conclusion, temperature dependent Raman-scattering measurements in Pr_2CuO_4 revealed electronic crystal-field excitations within the $\text{Pr}^{3+3}H_4$ ground-state multiplet split in a C_{4v} local symmetry. Our results were found to be in very good agreement with inelastic neutron-scattering measurements. We show in particular that the peak at 156 cm^{-1} , attributed in the literature to the lowest frequency E_g phonon mode, is now unambiguously associated to a crystal-field transition. This illustrates the importance of Raman studies as a function of temperature for a correct assignment of the observed

peaks in the Raman spectra. It is worthwhile to mention that unlike neutron-scattering experiments the Raman technique requires only small crystals, making this technique very useful for crystal-field studies in high- T_c superconductors. We are currently performing similar

measurements in the 2:1:4 Ce-doped high- T_c superconductors.

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