Raman study of crystal-field excitations in Pr_2CuO_4

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Raman measurements in a Pr_2CuO_4 single crystal show structures related to nine crystal-field (CF) excitations. They correspond to transitions within the $^3H_4$, $^3H_5$, and $^3H_6$ multiplets of Pr^{3+} ions in C_{4v} site symmetry. Satellites to these CF excitations are also observed and associated with the presence of an inequivalent Pr^{3+} site of lower symmetry. A set of CF parameters which describes the observed energy spectra is derived and compared to previous calculations. [S0163-1829(97)05133-3]

I. INTRODUCTION

It has been shown that Raman scattering is a powerful tool to study rare-earth crystal-field (CF) excitations in $R_{2-x}Ce_xCuO_4$ (R=Nd, Pr, x=0,0.15).[1–4] In the case of Pr_2CuO_4, where the Pr^{3+} ion site symmetry is C_{4v}, inelastic neutron scattering[5–8] has revealed four Pr^{3+} ion CF excitations around 145, 680, 710, and 2350 cm^{-1}, while Raman studies[3,4] have reported three CF excitations at 156, 540, and 690 cm^{-1} and two broadbands around 2210 and 2685 cm^{-1}. Based on these studies, different sets of CF parameters have been proposed.[3,5–8] However, since they were determined by fitting the energies of a relatively small number of detected transitions, mostly within the $^3H_4$ ground-state multiplet, there is no complete agreement on the predicted CF excitations and, in some cases, not even on their symmetry.

In this paper we present a CF Raman study of Pr_2CuO_4. The detection of several CF excitations in all three ^3H_J multiplets allows us to obtain a more reliable set of CF parameters.

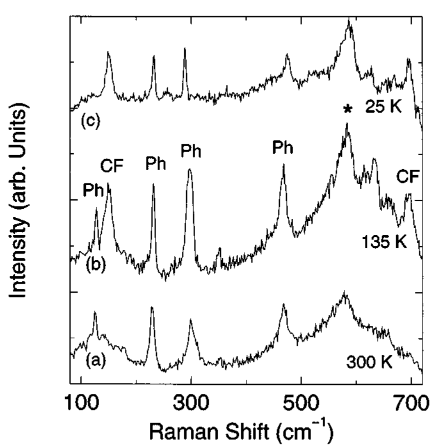

FIG. 1. Raman-active phonons (Ph) and CF transitions (CF) of Pr_2CuO_4 excited with the 4880 Å laser line at different temperatures. The incident and scattered polarizations are in the xz plane. The asterisk (*) indicates the 580 cm^{-1} local phonon mode.

II. EXPERIMENT

A Pr_2CuO_4 single crystal with a thickness of 80 μm along the z axis was grown using the top-seeded solution

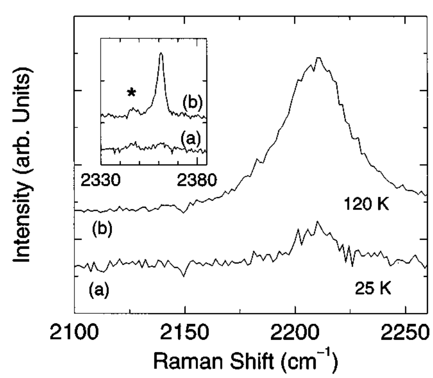

FIG. 2. Raman-active CF transitions in Pr_2CuO_4 in zz configuration measured with 4765 Å laser light. The inset shows CF transitions at 25 K in zz (a) and xz (b) configurations excited with the 4880 Å laser line. The line marked by (*) in spectrum (b) of the inset indicates a weak CF transition, which is attributed to an inequivalent Pr^{3+} site.

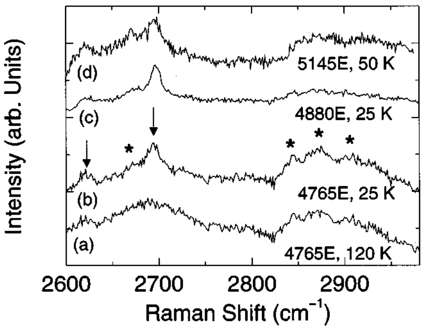

FIG. 3. Raman-active CF transitions in Pr_2CuO_4 indicated by arrows in (b). The spectra were excited in zz configuration. The peaks marked by (*) indicate weak CF transitions, which are attributed to an inequivalent Pr^{3+} site.

growth method.[9] Raman-backscattering measurements were performed using a closed-cycle refrigerator, different Ar^+ ion laser lines, and a multichannel spectrometer equipped with a CCD camera. The polarizations of incident and scattered light were in the xz plane. The laser power was roughly 15 mW, focused to a 50 μm diameter spot on the sample. Under these conditions we found in Nd_2CuO_4 that the sample temperature is raised by about 10 K.[10] The CF excitations were detected with at least two laser lines in order to avoid possible misinterpretation due to luminescence. The typical experimental uncertainty of measured frequencies is ± 2 cm^{-1}.

III. RESULTS AND DISCUSSION

As a consequence of the C_{4v} site symmetry of the Pr^{3+} ion in Pr_2CuO_4, the ninefold degenerate $^3H_4$ ground-state multiplet splits into five singlets and two doublets ($2\Gamma_1$, Γ_2, Γ_3, Γ_4, $2\Gamma_5$). The $^3H_5$ multiplet splits into five singlets and three doublets (Γ_1, $2\Gamma_2$, Γ_3, Γ_4, $3\Gamma_5$), while the $^3H_6$ multiplet splits into seven singlets and three doublets ($2\Gamma_1$, Γ_2, $2\Gamma_3$, $2\Gamma_4$, $3\Gamma_5$). Four Raman-active phonons (A_{1g}, B_{1g}, and 2 E_g) are expected in Pr_2CuO_4, which has the D_{4h}^{17} space group.

In Fig. 1 we show the temperature evolution of phonons (marked by Ph) and CF excitations (marked by CF) in the frequency range from 100 to 700 cm^{-1}. The peaks at 232, 289, and 475 cm^{-1} correspond to the A_{1g}, B_{1g} and high-energy E_g phonons of Pr_2CuO_4,[11,12] respectively. At room temperature we observe an excitation around 125 cm^{-1}, which we assign to the Pr E_g phonon mode. At 135 K this mode has shifted to 127 cm^{-1}, while the lowest $^3H_4$ intramultiplet CF excitation appears at 154 cm^{-1}. Upon further lowering of the temperature, this E_g phonon decreases in intensity and can no longer be detected at 25 K. We found the same behavior for the low-frequency (Nd) E_g phonon in Nd_2CuO_4 and attributed it to phonon-CF interaction.[1] Two peaks observed at low temperatures at 154 and 695 cm^{-1} are assigned to CF excitations, in agreement with Sanjurjo *et al.*[3] and Sanjuán and Laguna.[4]

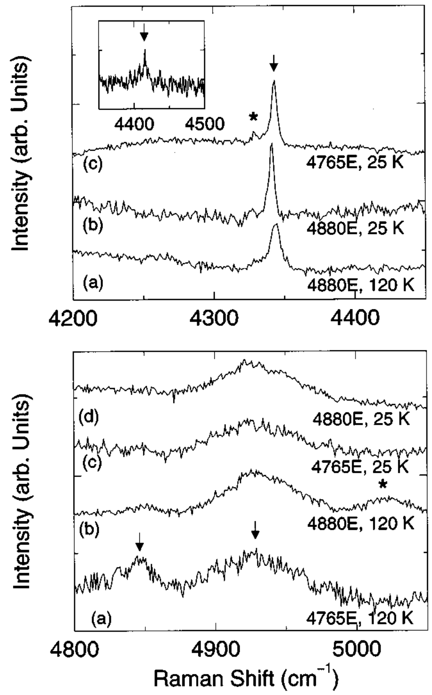

FIG. 4. Raman-active CF intermultiplet transitions in Pr_2CuO_4 (arrows) excited with different laser lines at different temperatures. The spectrum shown in the inset was recorded in xz configuration, all other spectra were measured in zz configuration. Peaks labeled by (*) represent weak CF transitions originating from an inequivalent Pr^{3+} site.

TABLE I. Calculated and measured CF levels (in cm^{-1}) of Pr^{3+} in Pr_2CuO_4. The theoretical values were calculated using the CF parameters shown in Table II.

	$^3H_4$			$^3H_5$			$^3H_6$	
	Theory	Expt.		Theory	Expt.		Theory	Expt.
Γ_3	-3		Γ_4	2360		Γ_3	4343	4343
Γ_5	154	154	Γ_5	2367	2363	Γ_1	4403	
Γ_1	670		Γ_2	2420		Γ_5	4416	4416
Γ_4	684		Γ_1	2523		Γ_2	4561	
Γ_5	696	695	Γ_3	2697	2696	Γ_5	4624	
Γ_2	721		Γ_5	2767	2772	Γ_4	4899	
Γ_1	751		Γ_2	2769		Γ_3	4929	4928
			Γ_5	2803		Γ_1	4983	
						Γ_5	5004	5004
						Γ_4	5062	

TABLE II. Pr^{3+} CF parameters in Pr_2CuO_4 (in cm^{-1}) obtained by fitting the CF Hamiltonian to the experimental data. The values are compared to those of other works.

CF parameter	Ref. 5	Ref. 6	Ref. 7	Ref. 8	Ref. 3	This work
B_{20}	−129	−226	−555	−567	−242	−235(13)
B_{40}	−2025	−2428	−2003	−1703	−2218	−2287(29)
B_{44}	1783	1839	1550	1546	1839	1864(14)
B_{60}	105	210	550	435	169	32(32)
B_{64}	1395	1807	1992	1849	1807	1519(19)

According to inelastic neutron-scattering data, the Pr^{3+} CF ground state in Pr_2CuO_4 is a singlet of Γ_3 symmetry and the first excited state, which we observe at 154 cm^{-1}, is a Γ_5 doublet.[8] At low temperature one therefore expects to observe transitions from the ground state to other Γ_3 levels in zz polarization and transitions to Γ_5 states in xz polarization. At higher temperatures, where the Γ_5 level at 154 cm^{-1} becomes thermally populated, one expects to see additional transitions in zz geometry from this level to higher Γ_5 levels.

Figure 2 presents Raman spectra in zz polarization of an excitation at 2209 cm^{-1}. Its strengthening at 120 K (b) compared to 25 K (a) indicates that it corresponds to a $\Gamma_5 \rightarrow \Gamma_5$ transition from the level at 154 cm^{-1} to a level of the $^3H_5$ multiplet at 2363 cm^{-1}. The inset of Fig. 2 confirms the Γ_5 symmetry of this level by its observation in xz symmetry as a transition at 25 K from the Γ_3 (0 cm^{-1}) $^3H_5$ ground state. A weak excitation is also observed around 2348 cm^{-1} in both xz and zz configurations, possibly due to an inequivalent Pr^{3+} site of lower symmetry.

In Fig. 3 several CF transitions are displayed for different temperatures and exciting laser lines. The excitation at 2696 cm^{-1} appears stronger at low temperature and must thus be attributed to a transition from the Γ_3 (0 cm^{-1}) ground state to a Γ_3 level of the $^3H_5$ multiplet, while the weaker excitation at 2618 cm^{-1} is tentatively associated with a transition from the Γ_5 level at 154 cm^{-1} to a Γ_5 level (2772 cm^{-1}) of the $^3H_5$ multiplet. We also observe a CF excitation around 2670 cm^{-1} and a band of excitations between 2850 cm^{-1} and 2950 cm^{-1}, which are assigned to an inequivalent Pr^{3+} site.

Excitations from the $^3H_4$ ground-state multiplet to the $^3H_6$ second excited multiplet are shown in Fig. 4. The temperature behavior of the lines at 4343 and 4928 cm^{-1} allows us to identify them as Γ_3 (0 cm^{-1}) $\rightarrow \Gamma_3$ transitions, while the line observed at 4850 cm^{-1} corresponds to a Γ_5 (154 cm^{-1}) $\rightarrow \Gamma_5$ transition to a level at 5004 cm^{-1}. An excitation at 4416 cm^{-1}, observed in xz geometry and shown in the inset of Fig. 4 corresponds to a CF transition from the Γ_3 ground state (0 cm^{-1}) to a Γ_5 level. The weak satellite at 4328 cm^{-1} and the excitation observed around 5025 cm^{-1} in resonance with the 4880 Å laser line are again attributed to an inequivalent Pr^{3+} site.

Altogether nine CF transitions have been observed in Pr_2CuO_4 by Raman scattering. The symmetries and energies of the corresponding CF levels are summarized in Table I. In the following analysis, which proceeds along the lines described previously[2] for Nd_2CuO_4, the CF Hamiltonian is written in terms of irreducible tensor operators C_{kq} as $H_{CF}=\sum_{k,q}B_{kq}C_{kq}$ with five nonzero CF parameters (B_{20}, B_{40}, B_{60}, B_{44}, B_{64}) to account for the C_{4v} symmetry of the ideal Pr^{3+}-ion crystal site.[13] The values of these parameters are determined by fitting the energies and symmetries of the eigenvalues of the CF Hamiltonian to the CF levels deduced from the observed Raman-active CF transitions. The fit includes the lowest seven CF multiplets. Free-ion energies of the four lowest multiplets were also included into the fitting routine as unknowns. In Table II the best-fit CF parameters determined from our intermultiplet data are displayed and compared to those obtained by other groups, mostly from fits to CF excitations within the ground-state manifold. As an application of these rather precise CF parameters we have calculated the magnetic susceptibility of Pr_2CuO_4 vs temperature, which is shown (open circles) in Fig. 5. The agreement with experiment (solid lines)[14] is improved compared to previous results (dashed lines).[15] The CF parameters could be further tested in Zeeman studies, which are very sensitive to the CF wave functions and thus to the multiplet mixing.[16] Such studies should highlight the significance of the differences between the parameter sets of Table II. Preliminary Raman measurements of cerium-doped Pr_2CuO_4 show an enhanced intensity of those CF transitions which we associate with inequivalent sites. Further investigations concerning their physical origin are in progress.

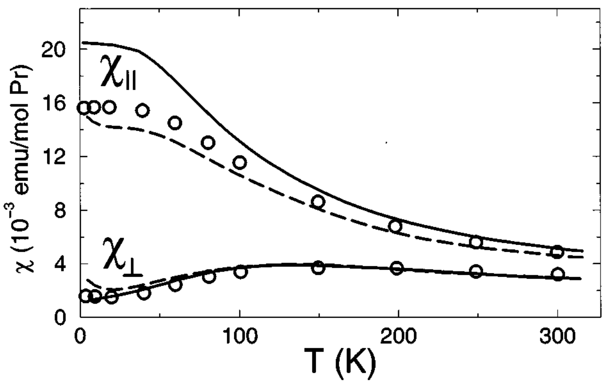

FIG. 5. Magnetic susceptibility of Pr_2CuO_4 as a function of temperature: experimental (Ref. 14) (—) and calculated previously (Ref. 15) (- - -), (○) calculated with the CF parameters of this work.

IV. CONCLUSIONS

Using Raman spectroscopy, we have determined a large number of Pr^{3+} intermultiplet CF excitations from levels of the $^3H_4$ ground-state multiplet to levels within the $^3H_5$ and $^3H_6$ multiplets in Pr_2CuO_4. A set of CF parameters that predicts the observed excitation energies and their symmetries has been derived. An inequivalent site of lower symmetry, probably due to local distortions, has also been observed.

ACKNOWLEDGMENTS

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