# Infrared transmission study of crystal-field excitations in Al- and Sr-doped $Pr_{1+x}Ba_{2-x}Cu_3O_6$

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Absorption bands corresponding to the crystal-field excitations in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (where $y \sim 0$) have been observed by Raman scattering and infrared transmission spectroscopy. These excitations are assigned to transitions occurring from the two lowest-energy levels of the $^3H_4$ multiplet to the excited multiplets $^3H_5$, $^3H_6$, $^3F_2$, and $^3F_3$ of $Pr^{3+}$ ions located in their $D_{4h}$-symmetry sites. The spectra exhibit additional bands consistent with the presence of $Pr^{3+}$ ions in the $C_{4v}$-symmetry Ba sites, as well as various defects associated with disorder. This analysis confirms that the phenomenological crystal-field parameters follow the trends reported in $NdBa_2Cu_3O_6$ and $SmBa_2Cu_3O_6$. A spectral splitting of the $\Gamma_5$ levels is observed at low temperature and indicates Pr-Cu exchange interaction. Al doping results in the expected inversion of the $\Gamma_5$-$\Gamma_1$ symmetry sequence of the quasitriplet ground state, in accordance with the magnetic-susceptibility anisotropy measurements.

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## I. INTRODUCTION

The magnetic and electronic properties of $Pr_{1+x}Ba_{2-x}Cu_3O_{6+y}$ clearly differ from those of the other $RE_{1+x}Ba_{2-x}Cu_3O_{6+y}$ (RE—rare earth) compounds. Namely, the antiferromagnetic (AFM) ordering of the $RE^{3+}$ sublattice occurs at $T_N$ ranging between 12 ($y = 0$) and 17 K ($y = 1$) in $Pr_{1+x}Ba_{2-x}Cu_3O_{6+y}$, whereas this Néel temperature is an order of magnitude lower in $NdBa_2Cu_3O_6$ and $SmBa_2Cu_3O_6$.[1,2] Moreover, the $PrBa_2Cu_3O_7$ samples do not superconduct and the increase of the Pr concentration leads to a drastic reduction of the critical temperature in the superconducting $RE_{1-x}Pr_xBa_2Cu_3O_7$ systems.[3] Nevertheless, it has been argued that $PrBa_2Cu_3O_7$ superconducts at a critical temperature of roughly 90 K, if the sample is almost free of Pr in Ba site defects.[4,5] These defects are difficult to detect by neutron or x-ray-diffraction measurements since Pr and Ba have the same neutron-scattering length and close atomic numbers. It has been established that the particular properties of Pr-based materials are either caused by the enhanced oxygen-mediated interaction between the $Pr^{3+}$ ions and their neighboring $Cu(2)^{2+}$ ions,[6,7] or by the crystal disorder associated with the chemical Pr/Ba substitution.[4,5] Recently, the resistivity and the thermopower measurements performed in $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $SmBa_{2-x}Pr_xCu_3O_7$ compounds revealed that their electrical conductivity is less affected by possible Pr-4*f*/O-2*p* orbital hybridization than by the presence of Pr in Ba sites,[8] which is responsible for a decrease of the charge-carrier density.[9] On the other hand, the inelastic neutron-scattering (INS) measurements show that the Nd/Ba substitution gives arise to an effective ferromagnetic coupling between the $Cu^{2+}$ ions of the Cu(2)O(2,3) planes and the Cu(1)-O(1) chains in $Nd_{1+x}Ba_{2-x}Cu_3O_{6+y}$.[10] Such magnetic reordering leads to a significant drop of $T_N$ in the nonstoichiometric compounds and is adverse to the formation of the superconducting state in the highly oxygenated materials.

Recently, infrared transmission spectroscopy has been successfully used in the characterization of the crystal-field (CF) interaction at the regular RE sites located between the two adjacent conducting planes in $NdBa_2Cu_3O_6$ and $Sm_{1+x}Ba_{2-x}Cu_3O_6$ ($x = 0.01$, 0.03, 0.05, and 0.11).[11,12] In spite of the infrared inactive $D_{4h}$-symmetry site of the rare earth ions, the *f*-*f* transitions become infrared active due to the loss of the inversion center resulting from in-chain oxygen excess and RE/Ba substitution. In addition to complementing the results obtained by the INS techniques,[13,14] the infrared transmission measurements in $NdBa_2Cu_3O_6$ and $Sm_{1+x}Ba_{2-x}Cu_3O_6$ have provided a precise description of the CF excitations in the 1000–10 000 $cm^{-1}$ range and a clear indication of Nd/Ba and Sm/Ba substitutions. These investigations, including the superposition model and the density-functional theory based calculations, allow a detailed understanding of thermodynamical properties such as magnetic susceptibility and specific heat. The INS studies of $PrBa_2Cu_3O_{6+y}$ available in the literature led however to con-

flicting analysis.[15–18] Although all groups agree with the theoretically "quasitriplet" ground state of $Pr^{3+}$, separated by the energy gap of several hundreds of $cm^{-1}$ from the $^3H_4$ multiplet,[19] the detailed CF splitting strongly depends on the sample composition and the growing process.

This paper deals with the IR transmission study of insulating $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ compounds, where $y \sim 0$, in the 2000–7000 $cm^{-1}$ range. For each sample, we report a systematic study of intermultiplet $f$-$f$ transitions from the two lowest levels of the $^3H_4$ ground-state multiplet to the $^3H_5$, $^3H_6$, $^3F_2$, and $^3F_3$ excited multiplets, in order to determine a reliable set of CF parameters. Also, our work focuses on the effects of the Pr/Ba substitution and the Al doping, and allows to reproduce the magnetic-susceptibility anisotropy.

## II. EXPERIMENTS

$Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ single crystals were grown in two different laboratories by the self-flux method,[20,21] using $Al_2O_3$ and MgO crucibles, respectively. Both samples, with initial oxygen contents equal to 6.35 (sample 1) and 6.24 (sample 2), were annealed in flowing argon at $T = 700\,^{\circ}C$ for 96 h, thus ensuring optimal oxygen reduction. Their tetragonal symmetry as well as their orientation were checked by Raman spectroscopy. The following lattice parameters : $a = 3.93$ Å, $c = 11.78$ Å for $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $a = 3.91$ Å, $c = 11.72$ Å for $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ were obtained by x-ray diffraction measurements at room temperature. Their nominal composition was determined by electron microprobe x-ray analysis using wavelength dispersive spectrometers (WDS—JXA 733 of JEOL). Samples were analyzed as grown prior to reduction, on natural shiny surfaces and also on optically polished surfaces to confirm previous results. Atomic concentrations were calculated supposing twelve atoms per unit cell.

Low-temperature Raman back-scattering studies were performed using a LABRAM-800 confocal system equipped with a nitrogen-cooled charge-coupled-device (CCD) detector and a 5 mW 633 nm He-He laser line polarized perpendicular to the $c$ axis, focused to a few microns spot diameter on the sample.

The infrared measurements were carried out with a fast-Fourier-transform interferometer (BOMEM DA3.002), using a quartz halogen lamp, an InSb detector, and a $CaF_2$ beam splitter. $1 \times 0.5 \times 0.1$ $mm^3$ $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ single crystals were mounted on the cold finger of a helium-cooled flow-through cryostat and 1 $cm^{-1}$ resolution transmittance spectra were recorded with the $ac$ plane perpendicular to the direction of the unpolarized incident beam.

The magnetic susceptibility of crystalline platelets were measured by using a superconducting quantum interference device magnetometer quantum design MPM-5S in the temperature range from 4.5 K to 300 K, with a 0.1 T static magnetic field oriented either parallel or perpendicular to the $CuO_2$ planes.

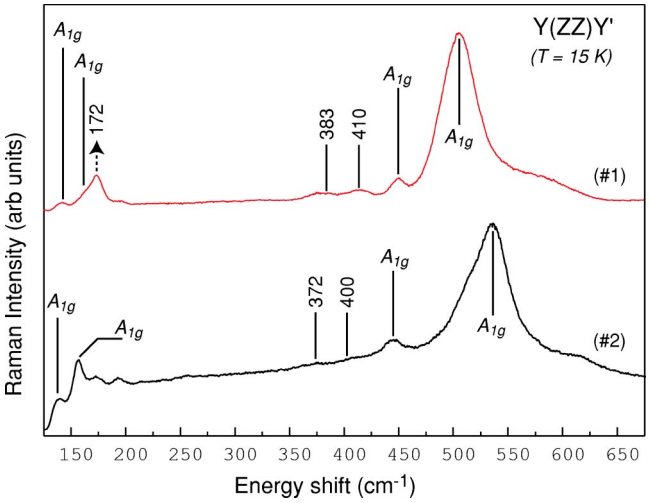



FIG. 1. Raman spectra of $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2), at $T = 15$ K, in the $y(zz)\bar{y}$ configuration.

## III. RESULTS

The Raman measurements of the $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and the $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2) crystals in the 125–625 $cm^{-1}$ range are presented in Fig. 1. These spectra are obtained in the $y(zz)\bar{y}$ configuration at $T = 15$ K. We identify four $A_{1g}$ phonons around 130, 170, 450, and 500 $cm^{-1}$ consistent with previous reports.[22,23] The additional peak observed at 172 $cm^{-1}$ in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ is due to the Al/Cu(1) substitution.[24] We associate the 383 and 410 $cm^{-1}$ lines in sample 1 and the 372 and 400 $cm^{-1}$ lines in sample 2 to the $f$-$f$ transitions occurring from the ground state to the 3rd and 4th excited level of the $^3H_4$ multiplet, respectively.

Figure 2 shows the infrared transmission spectra obtained at $T = 10$ and 78 K in the 2225–2825 $cm^{-1}$ range, where the $^3H_4 \rightarrow {}^3H_5$ transitions occur. In sample 1, five $f$-$f$ transitions are observed at 2260, 2285, 2346/59, 2580, and 2665 $cm^{-1}$ at $T = 10$ K, with a satellite absorption band at $T = 78$ K associated with the double feature at 2346/59 $cm^{-1}$. In sample 2, six CF excitations at 2250, 2273, 2242/56, 2557, 2667, and 2806 $cm^{-1}$ are observed. We note the presence of two additional absorption bands at $T = 78$ K, whose energies are located 10 $cm^{-1}$ above the 2242/56 and 2557 $cm^{-1}$ levels. Around 2290 and 2450 $cm^{-1}$, the vertical arrows point out two weak absorption bands in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$, while the filled circles designate regions where defects have been observed in $NdBa_2Cu_3O_6$ and $Sm_{1+x}Ba_{2-x}Cu_3O_6$.[11,12] Between 4100 and 5300 $cm^{-1}$, in Figs. 3(a) and 3(b), the $^3H_4 \rightarrow {}^3H_6$ transitions are presented. CF excitations are associated with the absorption bands observed at 4293, 4332, 4504, 4615, 4811, 4989, 5067, and 5105 $cm^{-1}$ in sample 1, and at 4287, 4336, 4499, 4611, 4808, 5012, 5060, and 5114 $cm^{-1}$ in sample 2.

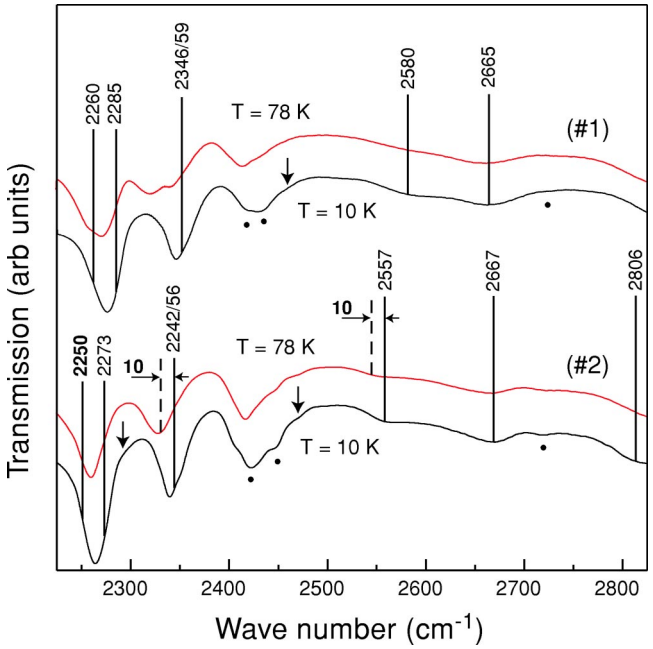
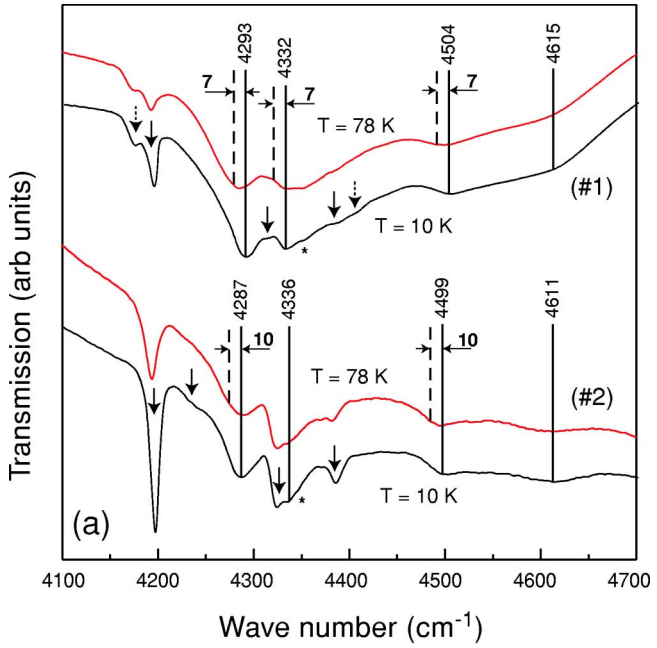



FIG. 2. IR transmission spectra at $T=10$ and 78 K, across $ac$-oriented platelets of $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2) in the 2225–2825 cm$^{-1}$ range. Vertical lines and vertical arrows indicate $Pr^{3+}$ CF excitations associated with $D_{4h}$- and $C_{4v}$-symmetry sites, respectively. (●) designates absorption bands also observed in $NdBa_2Cu_3O_6$ (Ref. 11) and $Sm_{1+x}Ba_{2-x}Cu_3O_6$ (Ref. 12).



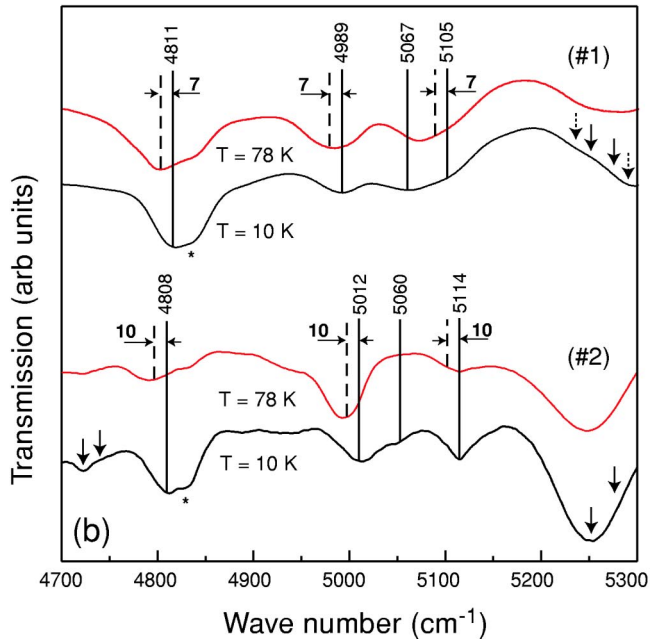




FIG. 3. $^3H_4 \rightarrow {}^3H_6$ CF transitions in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2), in the 4100–4700 cm$^{-1}$ (a) and 4700–5300 cm$^{-1}$ ranges. Vertical lines and vertical arrows indicate $Pr^{3+}$ CF excitations associated with $D_{4h}$- and $C_{4v}$-symmetry sites, respectively. The dashed arrows are associated with Al doping in sample 1, and (*) corresponds to local defects.

At $T=78$ K, the spectra exhibit additional bands with energies shifted $\sim 7$ cm$^{-1}$ and $\sim 10$ cm$^{-1}$ from bands measured at $T=10$ K. A far infrared study of polycrystalline $PrBa_2Cu_3O_6$ performed by Mukhin *et al.*[25] has indicated the presence of a weak and broad absorption band around 15 cm$^{-1}$ at $T<70$ K, attributed to electronic transitions between the low-energy CF levels of $Pr^{3+}$. The vertical arrows locate bands with larger intensity in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ and (*) designates defects. $^3H_4 \rightarrow {}^3F_2$ transitions, which cover the 5250–5850 cm$^{-1}$ range are shown in Fig. 4. These excitations are, respectively, ascribed to the bands observed at 5471, 5516/24, 5601, and 5614 cm$^{-1}$ in sample 1, and at 5471, 5517/28, 5598, and 5625 cm$^{-1}$ in sample 2. Finally, we assign the lines at 6527, 6630 cm$^{-1}$ in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and 6530, 6640 cm$^{-1}$ in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (Fig. 5) to the $^3H_4 \rightarrow {}^3F_3$ transitions.

## IV. DISCUSSION

We analyze our transmission measurements in terms of the CF interaction, which is the strongest perturbation of free-ion 4$f$ electron states of the $RE^{3+}$ in the cuprates. The CF Hamiltonian can be written as

$$H_{CF}=\sum_{k,q} B_{kq}[C_q^{(k)}+C_q^{(k)}], \qquad (1)$$

where the $C_q^{(k)}$ and $B_{kq}$ Wybourne operators correspond to the $q$th component of the spherical tensor operator of rank $k$ and the so-called CF parameters, respectively.[26] In the $D_{4h}$-symmetry regular site of $Pr^{3+}$, as well as in the $C_{4v}$-symmetry Pr/Ba substitution site in nonstoichiometric $Pr_{1+x}Ba_{2-x}Cu_3O_{6+y}$, only five CF parameters $B_{20}$, $B_{40}$, $B_{44}$, $B_{60}$, and $B_{64}$ are nonzero.[27] Following the standard procedure (for a recent survey of the CF data reported for the RE cuprates, see Refs. 27 and 28), their values are determined by solving numerically the *inverse secular problem*

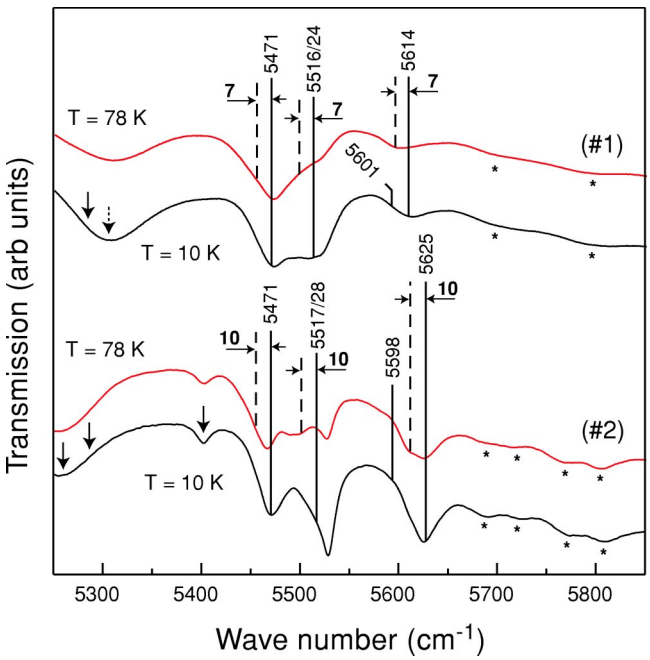



FIG. 4. IR absorption bands due to $^3H_4 \rightarrow {}^3F_2$ CF transitions from $Pr^{3+}$ ions in the regular site (lines) and the Pr/Ba site (arrows) in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2), in the 5250–5850 $cm^{-1}$ range. (*) designates defects.

where the CF levels deduced from the experimental data are taken to be the eigenvalues of the CF Hamiltonian.[29]

Regarding the $D_{4h}$-symmetry site, our CF analysis has been performed in two steps. First, we have restricted the fitting procedure to the 13 (sample 1) and 14 (sample 2) bands that present a satellite absorption at $T=78$ K, using the CF parameters obtained for the regular site of $Nd^{3+}$ in $NdBa_2Cu_3O_6$ as an initial estimate.[11] We conjecture that these satellite lines correspond to transitions occurring from the first excited level of the $^3H_4$ multiplet located at $\sim 10$ $cm^{-1}$ above the ground state. We have then successively included the energies of the bands close to the levels predicted by the previous fit in the calculation. This procedure was iterated for each multiplet till the criterion of convergence was satisfied. The final best-fit parameters for the regular $D_{4h}$-symmetry sites are given in Table I for each sample. Their corresponding CF levels are reported in Table II for the multiplets $^3H_4$, $^3H_5$, $^3H_6$, $^3F_2$, and $^3F_3$. The standard deviations between the calculated energies and the CF levels observed by Raman and IR transmittance measurements are 4.06 and 4.33 $cm^{-1}$ for $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$, respectively. The free-ion levels, which vary with the CF parameters in the fitting procedure, are 0, 2123, 4340, 4793, and 6141 $cm^{-1}$ for $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and 0, 2119, 4337, 4808, and 6148 $cm^{-1}$ for $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2). These values are close to the free-ion levels of $Pr^{3+}$ in $Pr_2CuO_4$.[30]

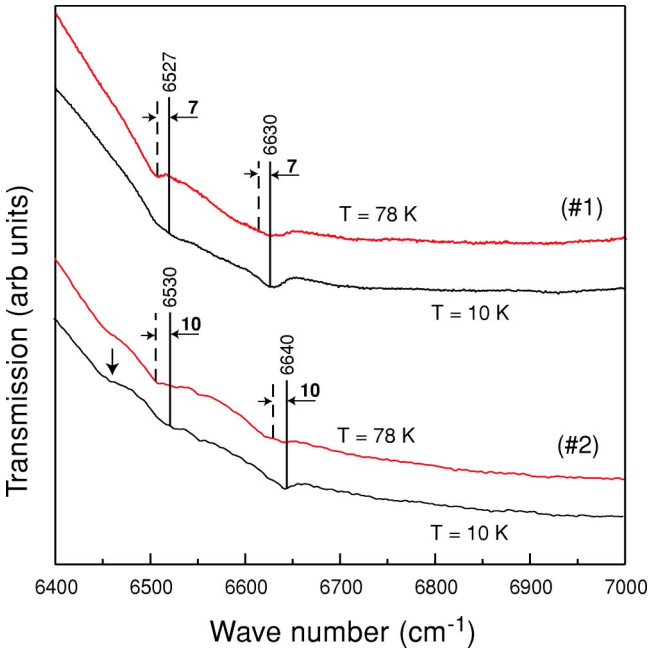



FIG. 5. IR absorption bands due to $^3H_4 \rightarrow {}^3F_3$ CF transitions from $Pr^{3+}$ ions in the regular site (lines) and the Pr/Ba site (arrows) in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2) in the 6400–7000 $cm^{-1}$ range.

Since the Pr/Ba substitution depends on the crystal growing process, the spectral weight of the bands relative to the presence of $Pr^{3+}$ in the Ba sites can drastically vary with the sample origin. According to Muroi and co-workers[31,32], a small amount of Sr seems to favor the Pr/Ba substitution, thus leading to stronger spectral absorption bands in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$. This feature allows us to ascribe the lines pointed by a vertical arrow in Figs. 2–5 to the irregular $C_{4v}$-symmetry site of Pr. In the two last columns of Table II, the energy of these transitions are compared to the calculation performed for the $C_{4v}$-symmetry site, using the previously determined free-energy levels and the CF parameters reported in the 6th column of Table I. Presuming that the variation of $B_{kq}$ across the RE series is smooth, we have derived this set from a former study of $SmBa_2Cu_3O_6$, reported in the 7th column of Table I.[12]

Our CF analysis of $Pr^{3+}$ is based on 22 and 23 observed $f$-$f$ transitions that involve the five lowest multiplets $^3H_{4-6}$ and $^3F_{2-3}$. The INS studies of $PrBa_2Cu_3O_{6+y}$ provide more limited data since they have been restricted to the transitions within the $^3H_4$ ground-state multiplet.[15,18,33] The experimental CF levels obtained for $y \sim 1$ have been determined at 0, 32, 363, 403, 524, 645, 686, and 847 $cm^{-1}$ and at 0, 12, 27, 508, 547, 669, and 786 $cm^{-1}$ by Soderholm *et al.*[15] and Hilscher *et al.*,[18] respectively. The ground-state CF splitting magnitudes reported by Boothroyd *et al.*[33] and Hilscher *et al.*[18] are very close. The only data available for $y \sim 0$ have been published by Hilscher *et al.*[18], locating the CF levels of the $^3H_4$ multiplet at 0, 14, 27, 492, 522, 608, and 678 $cm^{-1}$. The differences between various CF analysis performed by INS is due to discrepancies in the broadband assignments. For example, bands around 400 $cm^{-1}$ have been assigned to CF excitations by Soderholm *et al.*,[15] whereas a similar

TABLE I. $Pr^{3+}$ ion CF parameters (in $cm^{-1}$) for $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1), $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2), $NdBa_2Cu_3O_6$ (Ref. 11), and $SmBa_2Cu_3O_6$ (Ref. 12). Given in brackets are the mean errors associated with the fitting parameters.

| $B_{kq}$ | $D_{4h}$-symmetry site | | | | $C_{4v}$-symmetry | |
|---|---|---|---|---|---|---|
| | Sample 1 (fit) | Sample 2 (fit) | $NdBa_2Cu_3O_6$ | $SmBa_2Cu_3O_6$ | This work | $SmBa_2Cu_3O_6$ |
| $B_{20}$ | 567(3) | 633(3) | 380(28) | 282(5) | −730 | −227 |
| $B_{40}$ | −2763(5) | −2741(6) | −2956(34) | −2481(12) | 46 | 24 |
| $B_{44}$ | 1470(5) | 1466(5) | 1664(25) | 1307(10) | −350 | −331 |
| $B_{60}$ | 603(4) | 618(5) | 526(15) | 321(12) | −115 | −427 |
| $B_{64}$ | 2283(4) | 2233(5) | 2021(10) | 1931(6) | 982 | 624 |

TABLE II. $f$-$f$ transitions observed in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (sample 2), at $T=10$ K, and the predicted energies obtained from a fit of the CF Hamiltonian. The CF levels for $D_{4h}$ and $C_{4v}$ are associated with the $Pr^{3+}$ ion located in the regular site and the Ba site, respectively.

| Multiplet | Sample 1 $D_{4h}$-symmetry site | | | Sample 2 $D_{4h}$-symmetry site | | | Sample 2 $C_{4v}$-symmetry site | |
|---|---|---|---|---|---|---|---|---|
| | Expt. ($cm^{-1}$) | Theory ($cm^{-1}$) | Sym. (Ref. 44) $i\ \Gamma_i$ | Expt. ($cm^{-1}$) | Theory ($cm^{-1}$) | Sym. (Ref. 44) $i\ \Gamma_i$ | Obs. ($cm^{-1}$) | Calc. ($cm^{-1}$) |
| | 0 | 0 | 3 | 0 | 2 | 5 | 0 | 3 |
| | 7 | 6 | 5 | 10 | 11 | 3 | | 83 |
| | 383 | 394 | 2 | 372 | 378 | 2 | | 122 |
| $^3H_4$ | 410 | 401 | 1 | 400 | 389 | 1 | | 208 |
| | | 609 | 5 | | 614 | 4 | | 292 |
| | | 614 | 4 | | 618 | 5 | | 411 |
| | | 827 | 1 | | 830 | 1 | | 525 |
| | 2260 | 2249 | 1 | 2250 | 2239 | 1 | | 2085 |
| | 2285 | 2288 | 2 | 2273 | 2272 | 2 | | 2086 |
| | 2346/59[a] | 2359 | 5 | 2342/56[a] | 2355 | 5 | | 2112 |
| | | 2404 | 4 | | 2410 | 4 | | 2138 |
| $^3H_5$ | 2580 | 2581 | 5 | 2557 | 2560 | 5 | | 2225 |
| | 2665 | 2660 | 3 | 2667 | 2666 | 3 | 2295 | 2288 |
| | | 2803 | 5 | 2806 | 2803 | 5 | | 2369 |
| | | 2858 | 2 | | 2863 | 2 | 2470 | 2476 |
| | 4293 | 4294 | 5 | 4287 | 4290 | 5 | 4196 | 4193 |
| | 4332 | 4340 | 3 | 4336 | 4349 | 3 | 4231 | 4231 |
| | | 4448 | 1 | | 4442 | 1 | | 4261 |
| | 4504 | 4505 | 2 | 4499 | 4501 | 2 | 4323 | 4324 |
| $^3H_6$ | 4615 | 4608 | 5 | 4611 | 4605 | 5 | 4385 | 4378 |
| | | 4696 | 4 | | 4682 | 4 | | 4464 |
| | 4811 | 4803 | 3 | 4808 | 4795 | 3 | | 4509 |
| | 4989 | 4993 | 5 | 5012 | 5003 | 5 | | 4630 |
| | 5067 | 5066 | 1 | 5060 | 5074 | 1 | 4725 | 4735 |
| | 5105 | 5105 | 4 | 5114 | 5106 | 4 | 4739 | 4747 |
| | 5471 | 5459 | 1 | 5471 | 5461 | 1 | 5255 | 5255 |
| $^3F_2$ | 5516/24[a] | 5533 | 5 | 5517/28[a] | 5533 | 5 | 5279 | 5279 |
| | 5601 | 5597 | 3 | 5598 | 5602 | 3 | | 5374 |
| | 5614 | 5614 | 4 | 5625 | 5625 | 4 | 5404 | 5400 |
| | 6527 | 6534 | 5 | 6530 | 6539 | 5 | 6460 | 6464 |
| | 6630 | 6621 | 3 | 6640 | 6631 | 3 | | 6482 |
| $^3F_3$ | | 6799 | 2 | | 6793 | 2 | | 6590 |
| | | 6909 | 5 | | 6912 | 5 | | 6607 |
| | | 7173 | 3 | | 7173 | 3 | | 6614 |

[a]The doublet energies are approximated by their average value in the fitting procedure.

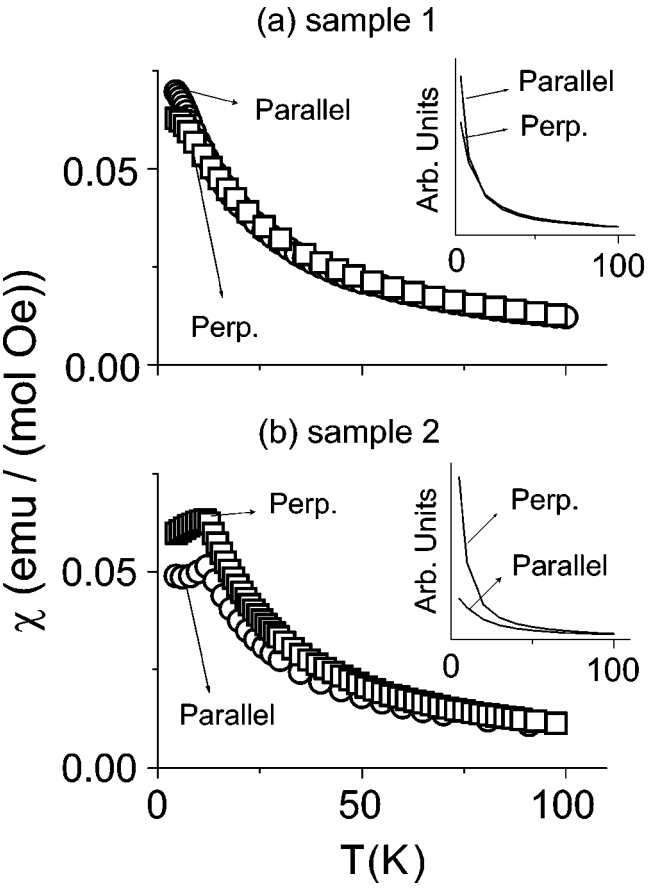



FIG. 6. Magnetic-susceptibility measurements of $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6.35}$ (sample 1) and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Cu_{2.74}O_{6.24}$ (sample 2) parallel ($\parallel$) and perpendicular ($\perp$) to the $ab$ plane. Insets: calculations performed with the CF parameters reported in the 2nd and 3rd columns of the Table I.

$Q$-dependence study indicated that these peaks are mainly of phonon origin—though a very small magnetic contribution may underlie the phonon contribution.[18]

The comparison of the above-mentioned investigations of the CF interaction in $PrBa_2Cu_3O_{6+y}$ is hampered by several additional factors. First, the Pr substitution in the Ba site strongly depends on the sample preparation and is difficult to quantify. Second, the structural as well as the magnetic data including the CF excitations are more sensitive to oxygen content in comparison to the remaining members of the $REBa_2Cu_3O_{6+y}$ family.[18,33,34] Third, $Al^{3+}$ and $Mg^{2+}$ ions contaminate the single crystals grown in $Al_2O_3$ (sample 1) and MgO (sample 2) crucibles by the flux technique.

Due to the over determination of the inverse secular problem we were able to determine a set of reliable phenomenological CF parameters of $Pr^{3+}$ in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$. The comparison of our results with the $NdBa_2Cu_3O_6$ and $SmBa_2Cu_3O_6$ parameters (Table I) shows that the absolute value of $B_{kq}$ tends to increase with the radial charge distribution $R_{4f}(r)$. As previously mentioned by Nekvasil,[35] these coefficients are generally higher than the CF parameters calculated for other RE oxides,[36] thus confirming the stronger contribution of CF interactions to the energy of the system. Also, the values of $B_{20}$ for $D_{4h}$-symmetry sites in samples 1 and 2 (Table I) compare reasonably well with the theoretical value of 425 $cm^{-1}$, calculated for the ideal $PrBa_2Cu_3O_6$ structure using the density-functional based method.[11,12,37] The difference between our best-fit parameters and those reported by Hilscher *et al.*[18] (e.g., $B_{20}=-317$ $cm^{-1}$, $B_{40}=-2787$ $cm^{-1}$, $B_{44}=1098$ $cm^{-1}$, $B_{60}=864$ $cm^{-1}$, and $B_{64}=1446$ $cm^{-1}$) is mainly ascribed to the misinterpretation of some of the above mentioned broad features in the INS spectra.

It is also interesting to note the energy splitting of the doubly degenerate $\Gamma_5$ levels at $T=10$ and 78 K. Particularly evident for the 2242/56 and 5517/28 $cm^{-1}$ features in Figs. 2 and 4, this phenomenon persists at $T=78$ K, far above the AFM ordering of the Pr sublattice. This band splitting is ascribed to an exchange interaction of the $4f$ electrons with the magnetically ordered Cu sublattice.[2] Moreover, the perfect isotropy of the low-temperature in-plane magnetization measurements, reported in the following, excludes the symmetry lowering as an alternative mechanism for the observed $\Gamma_5$ level splitting.

As for the effects of the Al doping, they manifest themselves by two remarkable features. Due to their localization in the Cu(1)O(1) chains,[38] near the Ba site, the $Al^{3+}$ ions are responsible for additional weak absorption peaks in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$, as indicated by the dashed vertical arrows in Figs. 3(a) and 3(b). We conjecture that these satellite absorption bands arise from $Pr^{3+}$ ions occupying $C_{4v}$-symmetry Ba sites perturbed by neighboring $Al^{3+}$ ions. On the other hand, the CF excitations associated with the $D_{4h}$-symmetry site of $Pr^{3+}$ in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ are shifted by 10–20 $cm^{-1}$ in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ (Figs. 1–5). These shifts are associated with differences in the contribution of the long-range electrostatic interaction to $B_{20}$, which affects the high-order parameters only marginally.[39] In Table II the calculation of the CF levels reveals that the $\Gamma_5$-$\Gamma_1$ symmetry sequence of the quasitriplet ground state is reversed in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ as compared to $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$. As previously mentioned by Hilscher *et al.*,[18] this reversal modifies the magnetic-susceptibility anisotropy at low temperature. In order to check this hypothesis and to further test the reliability of our theoretical approach, we have calculated the magnetic susceptibility using the CF parameters obtained for each sample. In addition to the AFM transition around $T_N=12$ K, the susceptibility measurements parallel (circles) and perpendicular (squares) to the $ab$ plane show that $\chi_\parallel > \chi_\perp$ in $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6.35}$ and $\chi_\perp > \chi_\parallel$ in $Pr_{0.93}Ba_{1.93}Sr_{0.13}Cu_{2.74}O_{6.24}$ [Figs. 6(a) and 6(b)]. Such reversal of the magnetic anisotropy is qualitatively reproduced by the calculations [inset of Figs. 6(a) and 6(b)] that do not include Pr-Pr anisotropic exchange and Pr-Cu interactions.[2,20,40–42] In Fig. 6(b), it is noted that the Pr sublattice in sample 2 magnetically orders at $T_N(\mathrm{Pr}) \sim 12$ K. This value corresponds to the Néel temperature measured in polycrystalline low oxygenated materials.[17] As expected,[43] the data reported in Fig. 6(a) show that the Al substitution of Cu(1) in the chains suppresses $T_N(\mathrm{Pr})$ in sample 1.

## V. CONCLUSION

Using infrared transmission technique, we have detected 23 $f$-$f$ transitions that involve the five lowest multiplets $^3H_4$, $^3H_5$, $^3H_6$, $^3F_2$, and $^3F_3$ multiplets of the $Pr^{3+}$ ions in regular $D_{4h}$-symmetry sites in Al- and Sr-doped $Pr_{1+x}Ba_{2-x}Cu_3O_6$. A CF analysis of these transitions gives a good account of the experimental data including the magnetic-susceptibility anisotropy reversal. Regarding the $4f$ electrons radial charge distribution, our phenomenological CF parameters obtained for $Pr_{1.05}Ba_{1.88}Cu_{2.39}Al_{0.34}O_{6+y}$ and $Pr_{0.93}Ba_{1.93}Sr_{0.13}Mg_{0.05}Cu_{2.74}O_{6+y}$ follow the trends observed in $NdBa_2Cu_3O_6$ and $SmBa_2Cu_3O_6$. Additional absorption bands whose relative intensity and energy fluctuate as a function of the crystal stoichiometry are detected. We assign these bands to the presence of $Pr^{3+}$ ions in the irregular $C_{4v}$-symmetry sites resulting from Pr/Ba substitution.

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