# Polarized Raman measurements of $Y_{1-x}Pr_xBa_2Cu_3O_7$

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We report polarized Raman measurements on small single crystals embedded in $Y_{1-x}Pr_xBa_2Cu_3O_7$ polycrystalline pellets. The measurements show two-mode behavior in the Cu-O bending mode of the $CuO_2$ planes ($B_{1g}$ mode). The increase in frequency with $x$ of the Ba-Ba stretching mode and the chain copper–apical oxygen Cu(1)–O(4) stretching mode is consistent with hole localization on Ba sites due to Ba $5d$–O $2p$ covalency. This localization may be related to the suppression of superconductivity in this compound, which increases with increasing $x$.

## I. INTRODUCTION

Among the $LBa_2Cu_3O_7$ compounds that are isostructural to $YBa_2Cu_3O_7$, where $L$ is a lanthanide element, (abbreviated $L$ 1:2:3), only $PrBa_2Cu_3O_7$ is nonmetallic and nonsuperconducting. $PrBa_2Cu_3O_7$, like $YBa_2Cu_3O_7$, has features that are thought to be essential for high-temperature superconductivity such as $CuO_2$ planes, Cu-O linear chains, and the stoichiometric oxygen content in the unit cell. Thus, Pr 1:2:3 has been studied with the hope of better understanding the mechanism of superconductivity. The solid solution system $Y_{1-x}Pr_xBa_2Cu_3O_7$ is particularly interesting since, if prepared properly, a single-phase 1:2:3 structure is obtained, and yet superconductivity is gradually suppressed as the Pr concentration increases. The mechanism for suppression of superconductivity is not well understood. We have recently reported Ba core-level shifts in x-ray photoemission spectroscopy measurements[1] on $Y_{1-x}Pr_xBa_2Cu_3O_7$ and $YBa_2Cu_3O_{7-y}$ samples. From these shifts we suggested that, as $x$ and $y$ increase, holes may become localized at Ba sites due to Ba $5d$–O $2p$ covalency. This localization of holes would lead to a suppression of superconductivity in both of these systems.

In this paper, we report Raman measurements of $Y_{1-x}Pr_xBa_2Cu_3O_7$ and find that the results are consistent with our earlier suggestion.[1] The Raman measurements were performed using a focused laser beam on single crystals embedded in samples of ceramic $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x$ = 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0) with $x(zz)\bar{x}$ and $z(xx)\bar{z}$ polarizations.[2] Five modes are expected,[2] $4A_{1g}+B_{1g}$ in tetragonal notation. Only the $4A_{1g}$ are allowed in $x(zz)\bar{x}$ polarization, but all five modes are allowed in $z(xx)\bar{z}$ polarization. Our measurements of the Pr 1:2:3 give results similar to previous work.[3-5] However, our $z(xx)\bar{z}$ polarization measurements show two-mode behavior[6] in the Cu-O bending mode ($B_{1g}$ mode) of the $CuO_2$ planes. The Ba-Ba stretching mode (Ba-$A_{1g}$ mode) and the apical oxygen stretching mode [O(4)-$A_{1g}$ mode] are observed to in-

crease in frequency as $x$ increases, in agreement with the previous result.[5] We note that the increase in frequency of the Ba-$A_{1g}$ and O(4)-$A_{1g}$ modes may be related to hole localization on Ba sites due to Ba $5d$–O $2p$ covalency.[1]

## II. EXPERIMENT

Details of sample preparation and characterization are described elsewhere.[1] In brief, x-ray diffraction, resistivity, magnetization, and x-ray photoemission spectroscopy show that all samples are essentially single phase with little impurity. An iodometric titration method determined the oxygen content to be 6.90±0.03, independent of Pr concentration $x$. The Raman measurements were done in back-scattering geometry with the laser beam focused on single crystals embedded in the ceramic samples. Two different polarizations, $x(zz)\bar{x}$ and $z(xx)\bar{z}$, were measured. The measurements were done at room temperature, using an Instruments SA micro-Raman system and a 5145-Å laser source.

## III. RESULTS AND DISCUSSION

Figure 1 shows Raman spectra for $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples with $x(zz)\bar{x}$ polarization. The four expected $A_{1g}$ Raman modes are observed and are labeled 1, 2, 4, and 5 in order of increasing frequency (mode 3 is the $B_{1g}$ mode discussed later). Table I shows the peak frequencies. Peaks above 600 cm$^{-1}$ are due to small concentration $BaCuO_2$ impurities. The $B_{1g}$ mode is not allowed in $x(zz)\bar{x}$ polarization but can be seen in $z(xx)\bar{z}$ polarization, and it is shown, on an expanded scale, in Fig. 2. The $B_{1g}$ mode ($\sim$ 340 cm$^{-1}$, hence labeled 3) involves out-of-phase bending motion[2,7] of the $CuO_2$ planes. The mode decreases in frequency by $\sim$ 40 cm$^{-1}$ as $x$ increases from 0 to 1, in agreement with previous work.[3-5] This decrease in frequency could be due to longer Cu—O bond length of $CuO_2$ plane. However, the $A_{1g}$ mode at $\sim$ 440 cm$^{-1}$ (mode 4), which involves the motion of the oxygen atoms of one $CuO_2$ plane against those of the immedi-

ately adjacent $CuO_2$ plane,[7] is hardly affected by the change in the Cu—O bond length (Table I). Therefore, an explanation of these frequency changes based on the bond-length argument must be treated with caution.

We observe resolved two-mode behavior[6] in the $\sim 340$ cm$^{-1}$ mode for samples of $x=0.6$ and 0.8 (Fig. 2). In fact, for $x=0.2$ and 0.4, the linewidths of this mode are significantly broader than those of $x=0.0$ and 1.0 samples suggesting two-mode behavior as well. Figure 3 shows the peak frequency of this mode as function of $x$. Two-mode behavior as well as one-mode behavior is seen in true mixed crystals in the x-ray crystallographic sense (i.e., crystals with intermediate lattice constants of the parent crystals).[6] The cause for two-mode behavior of the $\sim 340$ cm$^{-1}$ mode may be related to degeneracy lifting

TABLE I.  The peak frequencies in cm$^{-1}$ of the four $A_{1g}$ modes in $Y_{1-x}Pr_xBa_2Cu_3O_7$. The modes are numbered corresponding to Fig. 1. The two-mode behavior for mode 3, the $B_{1g}$ mode, is shown in Figs. 2 and 3.

| $x$ | No. 1 | No. 2 | No. 4 | No. 5 |
|-----|-------|-------|-------|-------|
| 0.0 | 118.0 | 149.4 | 441.6 | 506.4 |
| 0.2 | 116.0 | 147.6 | 439.2 | 508.0 |
| 0.5 | 120.0 | 146.6 | 442.4 | 511.2 |
| 0.8 | 119.2 | 148.2 | 444.0 | 510.8 |
| 1.0 | 126.4 | 149.6 | 440.0 | 524.4 |

of vibrational motion of $CuO_2$ planes due to Pr doping for Y. In this case, the $\sim 145$-cm$^{-1}$ ($A_{1g}$ mode of the Cu in the planes[7]) and $\sim 440$-cm$^{-1}$ modes might also be expected to exhibit two-mode behavior, since these involve motion of atoms in the $CuO_2$ planes as well. However, for various $L$ 1:2:3 both of these modes vary in frequency
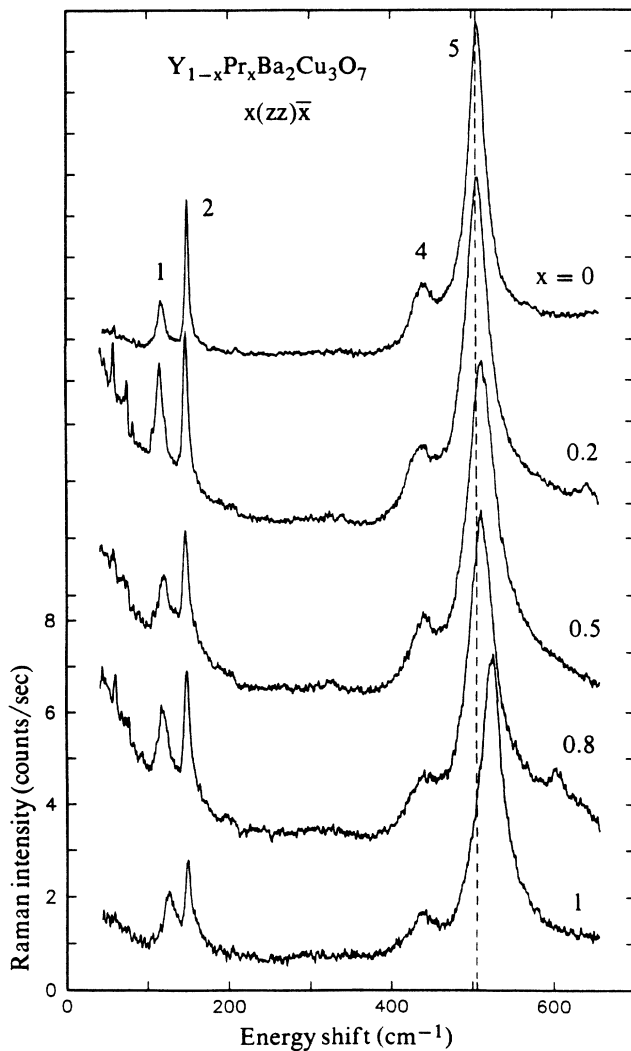


FIG. 1.  Raman spectra for $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples with $x(zz)\bar{x}$ polarization. Four $A_{1g}$ modes are allowed in this polarization and are labeled as shown. The dashed line, near mode 5, is a guide for the eye. The Raman intensity of only the bottom spectrum is given. The other spectra have similar intensities (also in Fig. 2).
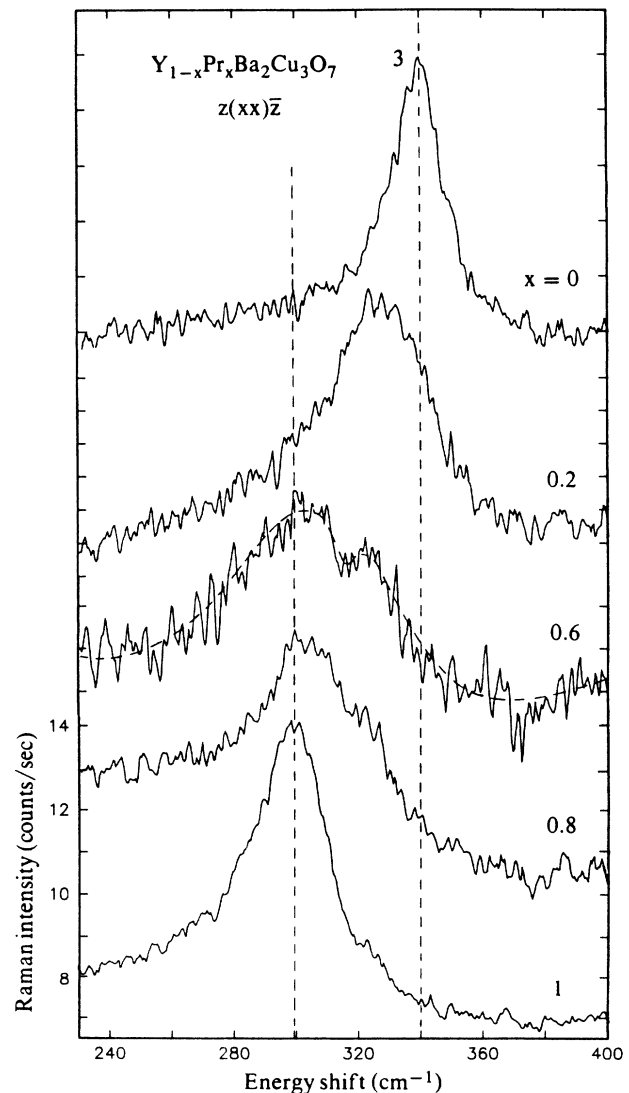


FIG. 2.  Raman spectra for $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples with $z(xx)\bar{z}$ polarization emphasizing just the 300-cm$^{-1}$ region of the $B_{1g}$ mode (mode 3).
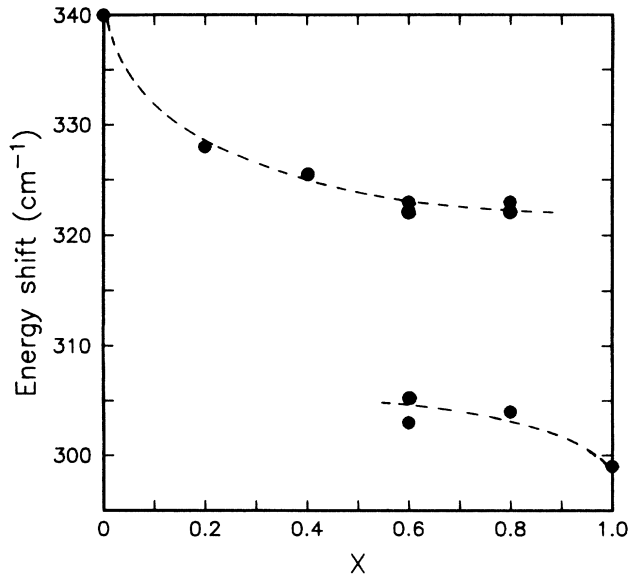
FIG. 3. The $\sim$340-cm$^{-1}$ mode (mode 3) peak frequency vs Pr concentration $x$. The spectral data from Fig. 2 and other measurements are plotted. Two-mode behavior is clearly seen for $x$=0.6 and 0.8 samples, and is indicated in the $x$=0.2 and 0.4 samples by larger linewidths. The dashed lines are guides for the eye.

by only a small amount[3] (also see Table I) so that two-mode behavior, even if present, would be unobservable. Temperature dependences of Raman spectra of various $L$ 1:2:3 show that the $\sim$ 340-cm$^{-1}$ mode decreases in frequency below $T_c$,[8,9] implying that this mode might be related to superconductivity. Therefore, two-mode behavior of the 340-cm$^{-1}$ line of $Y_{1-x}Pr_xBa_2Cu_3O_7$ might be related with the suppression of superconductivity in the compound. On the other hand, it is possible that the two-mode behavior is a general phenomenon, which can be found in any mixed $L$ 1:2:3 system regardless of superconductivity.

From the $x(zz)\bar{x}$ polarization data (Fig. 1 and Table I) the Ba-$A_{1g}$ mode ($\sim$115 cm$^{-1}$) and apical oxygen O(4)-$A_{1g}$ mode ($\sim$500 cm$^{-1}$) are seen to increase in frequency with increasing Pr concentration, in agreement with previous work.[5] The $\sim$ 500-cm$^{-1}$ mode, which is assigned to the apical oxygen O(4) stretching against a stationary chain copper Cu(1), should *decrease* in frequency if

it follows the usual bond-length arguments, since the Cu(1)—O(4) bond length is *longer* for higher values of $x$.[10,11] Contrary explanations have been given[5] for the increase in frequency of this mode, which are based on the assumption that the Cu(1)—O(4) bond length shortens as $x$ increases. However, frequency changes of the $\sim$ 340-cm$^{-1}$ and $\sim$ 500-cm$^{-1}$ modes seem to correlate well with the estimated ionic radius of the rare earth for various $L$ 1:2:3.[3,5]

An increase in the frequency of the Ba-$A_{1g}$ mode (mode 1) and the O(4)-$A_{1g}$ mode (mode 5) could be due to charge transfer between Ba and surrounding oxygen [predominantly the apical O(4)] atoms as suggested from our x-ray photoemission spectroscopy measurements.[1] This mechanism implies strong electron-phonon coupling in the modes involving motion of Ba and surrounding oxygen atoms. Indeed, Cooper et al.[12] show that the $\sim$115-cm$^{-1}$ mode and the $\sim$340-cm$^{-1}$ mode exhibit asymmetric Fano line shapes indicative of strong electron-phonon coupling. The assignment of these modes by Cooper et al. is different from ours. However, Mascarenhas et al.[13] clearly identify the $\sim$145-cm$^{-1}$ mode as the $A_{1g}$ mode of the copper atoms in the CuO$_2$ planes, from copper-isotope-shift data. This is another piece of evidence that Ba atoms may play an important role in determining superconductivity via charge transfer between Ba and neighboring oxygen atoms.

In conclusion, we have observed the Raman spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$ using $x(zz)\bar{x}$ and $z(xx)\bar{z}$ polarizations. The effect of Pr substitution is prominently seen in modes involving CuO$_2$ planes ($\sim$340 cm$^{-1}$), Ba ($\sim$115 cm$^{-1}$), and apical oxygen O(4) ($\sim$500 cm$^{-1}$). Two-mode behavior is seen for the $\sim$340-cm$^{-1}$ mode, whose average frequency decreases with increasing Pr concentration. The small frequency variation of other modes involving the motion of the CuO$_2$ planes in various $L$ 1:2:3, precludes the observation of the two-mode behavior of those modes. We note that the increase in frequency of the $\sim$115-cm$^{-1}$ mode and $\sim$500-cm$^{-1}$ mode as $x$ increases could be related to the possibility of hole localization on Ba sites as $x$ increases.

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