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Infrared properties of $Y_{1-x}Pr_xBa_2Cu_3O_7$

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The infrared reflectance spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x=0$, 0.1, 0.2, 0.4, 0.5, 0.6, and 1.0) have been measured in the temperature range from 4.2 to 300 K. It is found that near the Ba mode there is an additional peak whose relative strength varies with increasing x, and whose position—unlike its strength—at 194 cm^{-1} does not depend on the concentration of Pr. We discuss these experimental phenomena and make tentative assignments of these modes.

Since the discovery of superconductivity in $YBa_2Cu_3O_{7-\delta}$, elemental substitution has been used to explore the mechanism of high-T_c superconductivity. Early results showed that the replacement of Y by the rare-earth elements except Ce, Tb, and Pr did not destroy superconductivity. $Y_{1-x}Pr_xBa_2Cu_3O_7$ has an orthorhombic perovskite structure, with its superconductivity gradually decreasing, with increasing x, until $x>0.5$, when it is no longer a superconductor.[1]

Various explanations have been given for such suppression of the superconductivity. Some physicists think that the valence of Pr in this system is 4+. When Y^{3+} is substituted with Pr^{4+},[2] the surplus electrons neutralize the holes, the carrier density decreases, and therefore T_c decreases gradually to zero with increasing x. Others believe that Pr is 3+ and causes the localization of hole, thus suppressing the superconductivity and the metal-insulator transition.[3] Yet a third approach suggests an intermediate valence of Pr between 3+ and 4+ based on a structure analysis of $Y_{1-x}Pr_xBa_2Cu_3O_7$.[4] We have systematically studied the infrared spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$, with $x=0$, 0.1, 0.2, 0.4, 0.5, 0.6, and 1.0. The experimental results yield additional insight in understanding the physical phenomena occurring in this material.

A series of $Y_{1-x}Pr_xBa_2Cu_3O_7$ samples was prepared with use of powdered $BaCo_3$, Y_2O_3, CuO, and Pr_6O_{11} starting materials with high purity. Appropriate amounts were mixed, ground, pressed into pellets, and sintered in air at 950 °C for 12 h and then cooled at 20 °C/h to room temperature. X-ray diffraction data show that all the samples used in this study are single phase with the 1:2:3 structure. In the range $0<x<0.55$, the compound is a superconductor whose T_c decreases with increasing x. For x larger than 0.55, the compound becomes an insulator. All the measurements of reflectance spectra are made on an Nicolet-200SXV Fourier-transform-infrared (FTIR) spectrometer with a gold mirror as a reference.

Figure 1 and 2 show the far-infrared reflectance spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$ with $x=0.1$, 0.2, 0.4, 0.5, 0.6, and 1.0, of which we note the following features.

(1) In $YBa_2Cu_3O_{7-\delta}$ the peak at 159 cm^{-1} is the Ba mode, which vibrates along the c axis. We find, in addition, another mode near it upon Pr substitution for Y. For small x ($x=0.1$), the Ba peak is higher than this additional peak. With increasing x, this peak increases in strength and eventually surpasses the Ba mode. The strength of this peak decreases with increasing temperature; at room temperature, only the Ba mode can be observed.

(2) In $YBa_2Cu_3O_{7-\delta}$, the peak at 194 cm^{-1} is identified as the vibrational mode of Y along the c axis. In $Y_{1-x}Pr_xBa_2Cu_3O_7$, the position of the above-mentioned peak does not depend on x. For $x<0.5$, its strength decreases with increasing x. However, for $x>0.5$, it increases with increasing x. This peak is weaker at higher temperatures; at room temperature, it can no longer be observed except for $x=1.0$.

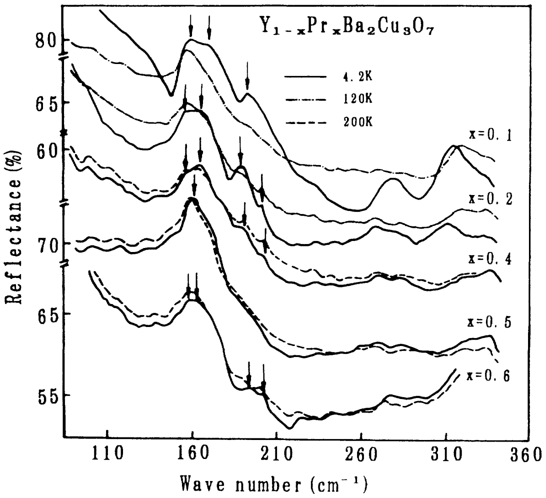

FIG. 1. Far-infrared reflectance spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$, with $x=0.1$, 0.2, 0.4, 0.5, and 0.6.

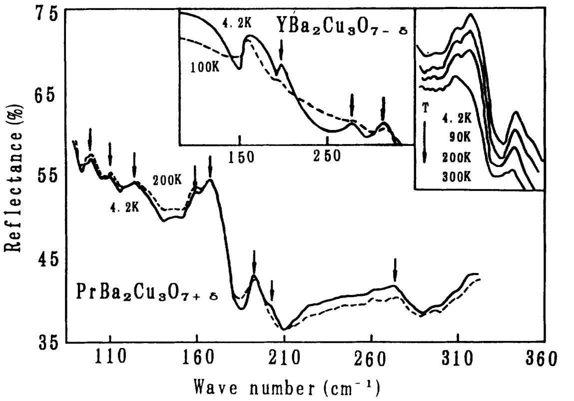

FIG. 2. Far-infrared reflectance spectra of $Pr_xBa_2Cu_3O_{7+\delta}$. The inset on the left is the far-infrared reflectance spectra of $YBa_2Cu_3O_{7-\delta}$.

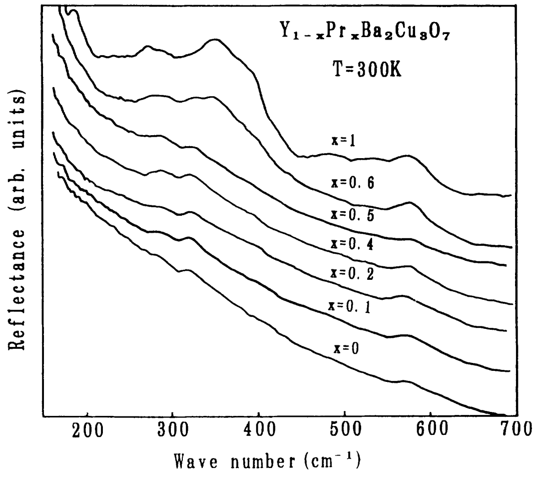

FIG. 3. Midinfrared reflectance spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$ for various values of x at room temperature.

(3) The number of phonon modes in the reflectance spectra increases with increasing x, except for $x=0.5$. For $x=0.2$, 0.4, 0.6, and 1.0, the additional peak at 202 cm^{-1} can always be observed. For $x=0.4$ and 0.5, there are some inconspicuous structures in the region below 150 cm^{-1}, which become clearly identifiable peaks at 100, 110, and 125 cm^{-1} for $x=1.0$. For $x=0.5$, the spectrum undergoes a sudden change, so that neither the additional peak near the Ba mode nor the peaks at 194 and 202 cm^{-1} can be observed.

Figure 3 shows the spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$ between 150 and 700 cm^{-1} for various values of x at room temperature. The curves for $x<0.5$ are found to be similar; the curves for $x=0.6$ and 1.0 are also similar to each other. The positions of the reflection peaks of $Y_{1-x}Pr_xBa_2Cu_3O_7$ for various values of x are listed in Table I.

In $YBa_2Cu_3O_{7-\delta}$, the peaks at 570, 280, and 318 cm^{-1} have been identified as the Cu(1)-O(1) c-axis stretch mode and the Cu(2)-O(3) and Cu(2)-O(2) out-of-plane bending modes, respectively.[5] For $x=1.0$, we find three more weak peaks at 395, 480, and 530 cm^{-1}, which are the Cu-O modes in the a-b plane.

The lattice dynamics shows that $YBa_2Cu_3O_7$ possesses 21 infrared-active modes: $7\ B_{1u}+7\ B_{2u}+7\ B_{3u}$. Since the c-axis resistance is much larger than that in the a-b plane, the carriers move only in the a-b plane and screen the vibrational modes B_{2u} and B_{3u},[6,7] which vibrate in the a-b plane; therefore, only mode B_{1u}, which vibrates along the c axis, can be observed in the spectra of $YBa_2Cu_3O_{7-\delta}$.[5]

Because $PrBa_2Cu_3O_{7+\delta}$ is not a superconductor, the modes in the a-b plane are not screened so that there should be 21 modes; however, only 13 modes are observed. The missing modes may be too weak, or too close to other modes, to be observed.

As to the origin of the additional mode near the Ba mode at about 165 cm^{-1}, one may consider several possi-

TABLE I. Dependence of the position of peaks of $Y_{1-x}Pr_xBa_2Cu_3O_{7+\delta}$ on the concentration x. The upper part is for $T=4.2$ K, the lower part for 300 K.

	$x=0$	0.1	0.2	0.4	0.5	0.6	1.0
$T=4.2$ K							100
							110
							125
	159	160	157	157	160	157	158
		172	165	165		163	167
	194	194	193	193		194	194
			202	202		202	202
$T=300$ K	280	285	285	285	280	280	270
	318	320	320	325	325	320	
						345	350
							395
							480
							530
	570	570	570	575	575	575	580

bilities. It may be the Pr B_{1u} mode; since the peak at 194 cm^{-1} in $YBa_2Cu_3O_{7-\delta}$ has been identified as the Y B_{1u} mode and Pr is heavier than Y, the Pr B_{1u} mode is expected to shift to low wave numbers. Another possibility is a Ba double-mode behavior: With increasing x, the density of carriers decrease and so does the screening effect to vibrational modes in the *a-b* plane; hence some infrared-active modes in the *a-b* plane can be observed as x increases. It can therefore be assumed that the mode at $\sim 165\ \mathrm{cm}^{-1}$ is the Ba mode in the *a-b* plane. In the case of complete substitution of the rare earth Sm, Gd, or Eu for Y, their B_{1u} mode is at about 175 cm^{-1}.[8] Since Pr is heavier than Y, but lighter than these three elements, the 165-cm^{-1} mode seems too small to be assigned as the Pr B_{1u} mode; therefore, it is more reasonable to interpret it as the Ba mode in the *a-b* plane.

For values $x < 0.5$, the peak at 194 cm^{-1} is the Y B_{1u} mode, whose strength decreases with increasing x. But, for values $x > 0.5$, there are two possibilities for the origin of the 194-cm^{-1} mode: One is the Pr B_{2u} or B_{3u} mode vibrating in the *a-b* plane; another is the Pr B_{1u} mode. Usually, the phonon mode related to superconductivity is not at the Γ point; for example, it is the X point for the superconductor $La_{2-x}Sr_xCuO_4$,[9] and such phonons are softened. The phonons observed in infrared spectra are located at the Γ point, which depends on the structure rather than the superconductivity. Both $YBa_2Cu_3O_{7-\delta}$ and $PrBa_2Cu_3O_7$ possess orthorhombic structure, and their infrared spectra look quite similar; the only difference is that there are more phonon modes in $PrBa_2Cu_3O_7$. The experiments have shown that the reflection spectra of $YBa_2Cu_3O_{7-\delta}$ and $YBa_2Cu_3O_6$ have very different features,[5] because of their different crystallographic structures. In semiconducting $YBa_2Cu_3O_6$, the Y E_u mode vibrating in the *a-b* plane is at 194 cm^{-1}, but we cannot assign the 194-cm^{-1} mode in $PrBa_2Cu_3O_7$ to the Pr B_{2u} or B_{3u} mode since $YBa_2Cu_3O_6$ is in a tetragonal phase rather than an orthorhombic phase. So we think that one of the modes at 194 and 202 cm^{-1} is the Pr B_{1u} mode and another is the Pr B_{2u} or B_{3u} mode. Pr is not only found as a trivalent ion (in PrF_3), but also a tetravalent one (in PrO_2). Thus, if the 194-cm^{-1} mode is a Pr B_{1u} mode, the valence of Pr in the compound should be 4+: Since $f \propto \sqrt{K/m}$ and Pr is heavier than Y, the valence of Pr should be larger than 3+.

We have systematically studied and, in this paper, presented the infrared spectra of $Y_{1-x}Pr_xBa_2Cu_3O_7$, with $x=0$, 0.1, 0.2, 0.4, 0.5, 0.6, and 1.0. Comparing with $YBa_2Cu_3O_{7-\delta}$, we think the additional mode at $\sim 165\ \mathrm{cm}^{-1}$ is another Ba mode that vibrates in the *a-b* plane. For $x < 0.5$, the mode at 194 cm^{-1} is the Y B_{1u} mode, while for $x > 0.5$ it is probably the Pr B_{1u} mode and the Pr B_{2u} or B_{3u} mode, with $x = 0.5$ being the critical concentration.

It should be pointed out that it is difficult to distinguish the phonon modes in different directions in an unoriented ceramic sample. To verify these assignments, further work with oriented ceramic or single-crystal samples of $PrBa_2Cu_3O_7$ will be required.

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