Nuclear-quadrupole-resonance investigation of copper in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$

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The NQR spectra of Cu in the $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system at room temperature have been measured and analyzed. When Pr is substituted for Sm in $Sm_{1-x}Pr_xBa_2Cu_3O_7$, there are no significant structural changes. However, the electric charge distributions in the vicinity of both the Cu(2) and Cu(1) sites are quite different due to the influence of Pr atoms, which modify the quadrupole interaction. This work provides information on the normal-state properties of high-T_c superconductors.

I. INTRODUCTION

Superconductivity at about 90 K has been observed in $RBa_2Cu_3\ O_{7-y}$ ($R=$Y and the other rare earths except Ce, Pr, Pm, and Tb) compounds which crystallize in the orthorhombic structure with space group *Pmmm* (Refs. 1 and 2) at room temperature. Among the $RBa_2Cu_3O_{7-y}$ (RBCO) compounds $PrBa_2Cu_3O_{7-y}$ is intriguing because of the absence of superconductivity as well as a metallic state, though it is orthorhombic and isostructural to the superconducting RBCO compounds.[3,4] They have attracted increasing interest in studying the effect of Pr doping in RBCO compounds.[2,4-8] For each system of $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds, T_c decreases with increasing Pr content x, and the larger the ionic size difference of R and Pr ions, the less T_c decreases and hence the larger the critical Pr concentration of superconductivity. It is well known that superconductivity is closely correlated to the fine structure of the CuO_2 sheet and its environment, but so far the local microscopic information on the $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$ compounds has been poor. It can be investigated by the nuclear quadrupole resonance (NQR) as well as nuclear magnetic resonance (NMR) in which the nucleus is used as a probe of the electric and magnetic interactions in the system at the microscopic level through its coupling with the lattice.[9-12]

There are many NQR and NMR measurements for ^{63}Cu, ^{65}Cu, ^{17}O, and ^{89}Y in the high-T_c superconductors.[13-18] Among them, most experiments have been devoted mainly to the $YBa_2Cu_3O_{7-y}$ (YBCO) compounds to elucidate their superconducting mechanism as copper ions are responsible for superconductivity. The Cu NQR technique has been employed to study the charge distribution and the paramagnetic fluctuations of the R^{3+} ions in the high-T_c superconductors $RBa_2Cu_3O_{7-y}$ (Ref. 19) and in the insulators $RBa_2Cu_3O_6$.[20] There is a striking difference in the pattern of the Cu NQR frequency ν_Q in the two sets of materials; namely, ν_Q is almost the same in all the O_6 systems, but it decreases, for both Cu(1) and Cu(2) sites, in the O_7 materials as one passes from systems containing lighter rare-earth atoms to those containing heavier rare-earth atoms. The precise reason as to why ν_Q is the same in all the O_6 systems is not clear at present.[20] For the O_7 materials, the observed R dependence of ν_Q, which decreases with an increase of the 4f-electron number, has been found to come from the change in the contribution of the ionic charges outside the Cu(2) ion due to the volume change, so that the on-site charge at the Cu(2) sites is estimated to be almost R independent.[19] Recently, a NQR study of copper in $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ has been reported by Markandeyulu *et al.*,[7] which shows that the NQR frequency of Cu(2) in $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ is 31.5 MHz, greater than that in $LuBa_2Cu_3O_7$ (less than 30.4 MHz). This suggests strongly the influence of Pr atoms which modify the quadrupole interaction at the Cu(2) site. As a part of our program of NMR and NQR studies in high-T_c materials, we have carried out a NQR investigation of Cu in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ at room temperature for determining the underlying trends and for signs of deviations occurring from the general picture for the case of light rare-earth ion Sm, to provide local microscopic information on the normal-state properties of high-T_c superconductors. This also provides us with another system like $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ in which the R ion is a rare-earth ion, but with significantly different structural parameters and bond lengths due to Sm being a light rare-earth ion while Lu being a heavier one.

II. EXPERIMENTS

The samples of $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ with x between 0 and 0.3 were prepared following a standard procedure of solid-state reaction. All samples are superconductors whose T_c decreases rapidly with increasing Pr content, which is coincident with earlier reports.[2,5] NQR experiments were carried out using a conventional pulsed NMR spectrometer. The Cu NQR frequency-swept spectra were obtained from the Fourier transform of the spin echo as a function of frequency, measured point by point in the range from 19 to 35 MHz in zero external magnetic field at room temperature. Each frequency-swept spectrum was averaged with the same shots, whose value was over 30 000 for the Pr-doped compounds according to the signal-to-noise ratio of their resonance spectra.

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III. RESULTS AND DISCUSSION

Figure 1 shows the Cu NQR frequency-swept spectra for $Sm_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-y}$, as a typical example. The line profile is similar to that measured in the RBCO or YBCO compounds.[13–19] Cu nuclei experience a relatively large electric field gradient (EFG), which splits the nuclear spin levels. Two pairs of resonance signals are observed at high- and low-frequency sides, which are assigned to Cu(2) plane sites and Cu(1) chain sites, respectively. Each pair is composed of ^{63}Cu and ^{65}Cu on the same sites, because the ratio of the frequencies of the two lines is very close to the ratio of the quadrupole moments eQ of the two isotopes ($^{63}eQ/^{65}eQ = 1.081$)[12,21]. Also, their intensities are roughly in the ratio of the natural abundances of the two isotopes.

The variations of the Cu NQR spectra on Cu(1) and Cu(2) sites with Pr content in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ are shown in Figs. 2 and 3, respectively. For undoped $SmBa_2Cu_3O_{7-y}$, one is at 20.641 and 22.262 MHz (Fig. 2) and another is at 29.787 and 32.120 MHz (Fig. 3). The EFG becomes slightly larger than in Y-based compounds. The general behavior of our results is consistent with the earlier results reported by Kohori *et al.*[22] that two sets of signals are observed at 4.2 K: one at 21.0 and 22.4 MHz and another at 30.5 and 32.3 MHz. The difference in ν_Q is due to the temperature dependence of the EFG.

It is seen from Figs. 2 and 3 that Pr doping in $SmBa_2Cu_3O_{7-y}$ influences all NQR spectral parameters commonly used to characterize the resonance spectral line, namely, its position, width, shape, and intensity.[9–12] Compared with the Cu NQR spectra in the undoped compound $SmBa_2Cu_3O_{7-y}$, there are significant changes in the Cu NQR spectra at both Cu(1) and Cu(2) sites as a result of Pr doping. With increasing the Pr concentration, the resonances on Cu(1) sites are significantly shifted to lower frequency accompanying the evident splitting (Fig. 2), while the peak positions on Cu(2) sites are shifted down slightly and the width of the resonance is obviously broadening (Fig. 3). Furthermore, the intensity of NQR signals decrease with increasing Pr concentration. These results will be discussed in detail later.

It should be pointed out that the NQR signals observed

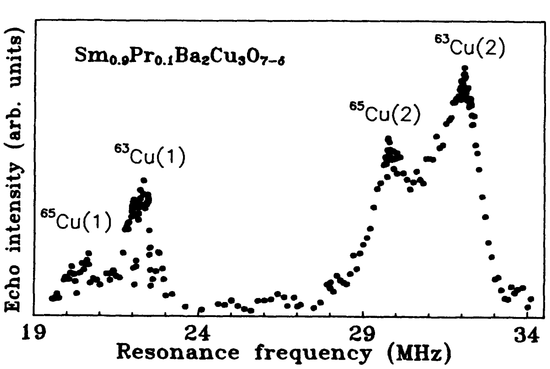

FIG. 1. Cu NQR frequency-swept spectra for $Sm_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-y}$ at room temperature.

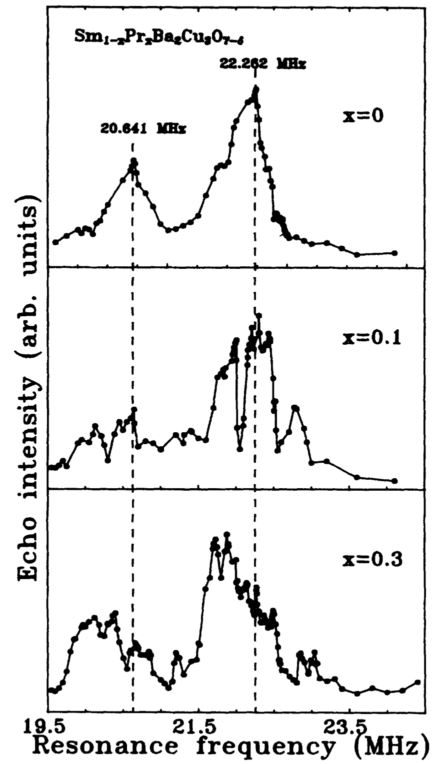

FIG. 2. Changes of Cu NQR spectra on Cu(1) sites with Pr content in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$. An observed pair of resonance lines, right one and left one, corresponds to two isotopes ^{63}Cu and ^{65}Cu, respectively.

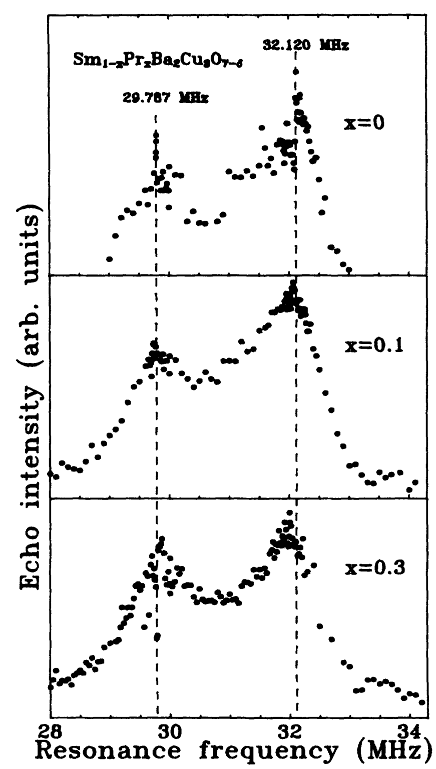

FIG. 3. Changes of Cu NQR spectra on Cu(2) sites with Pr content in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$. An observed pair of resonance lines, right one and left one, corresponds to two isotopes ^{63}Cu and ^{65}Cu, respectively.

by us in the $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ system does not come from those Cu(2) sites in which there are Pr atoms as the nearest neighborhood and whose signals are outside our detected frequency regions. This would leave some Cu(2) atoms unobservable because of local antiferromagnetic ordering. It has been reported that the end compound $PrBa_2Cu_3O_7$ is insulating and was found in recent muon-spin-resonance (μSR) experiments to exhibit plane-Cu antiferromagnetic order, in which Cu(2) atoms carry magnetic moment which orders antiferromagnetically at about 285 K.[4] The frequency-swept spectra were obtained over the frequency range 18–130 MHz at 1.4 K in zero external field for $PrBa_2Cu_3O_7$, which shows that no signal was found near the Cu(2) NQR frequency of 32 MHz in present Sm-Pr-Ba-Cu-O, but two broad spectra were observed for frequencies around 21 and 80 MHz.[4] The broadening of the resonance peak in Pr-doped material, as compared with that in $SmBa_2Cu_3O_{7-y}$, could be due to the influence of the moments associated with Pr atoms and/or the Cu(2) atoms in their vicinity. A number of new NQR signals resulting from changes in Cu coordination environments accompanies the electronic structure changes due to Pr doping. The superposition of those signals would lead to a broadening of the NQR peak.

The ν_Q on Cu(2) sites deserves to be commented upon when compared with that in other $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$. It is well known that the NQR frequency spectra provide useful information on the microscopic charge distribution, since signals from the inequivalent sites, such as Cu(1) and Cu(2) sites having different coordination, can be resolved in the NQR spectra according to the difference of the local EFG.[20] The ν_Q for ^{63}Cu or ^{65}Cu ($I=\frac{3}{2}$) are related to the components of the local EFG tensor by the equation

$$\nu_Q=(eV_{zz}Q/2h)(1+\eta^2/3)^{1/2} ,$$

where V_{zz} is the component along the principal axis and the asymmetry parameter is given by $\eta=(V_{xx}-V_{yy})/V_{zz}$. Since the eQ value is constant for given ^{63}Cu or ^{65}Cu, the change in ν_Q reflects the change in the EFG produced by the charges of the d shell of the Cu ion itself and the surrounding lattice ions. In the high-T_C superconductors $RBa_2Cu_3O_{7-y}$, ν_Q at the Cu(2) sites related to the charge distribution has been found to decrease monotonously toward the heavy end of the rare-earth element. It is 33.5 MHz for $NdBa_2Cu_3O_{7-y}$ and 30.5 MHz for $YbBa_2Cu_3O_{7-y}$. The observed R dependence of ν_Q, which decreases with an increase of the $4f$ electron number, has been explained as the change in the contribution of the ionic charges outside the Cu(2) ion due to the volume change, so that the on-site charge at the Cu(2) sites is estimated to be almost R independent.[19] In $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$, we have observed a slight change of ν_Q with Pr concentration, monotonically decreasing with increasing x (Fig. 3). Similar results in $Y_{1-x}Pr_xBa_2Cu_3O_{7-y}$ have been reported by Reyes *et al.*[23] They also found that the symmetries of EFG's remain essentially unchanged for both copper sites over the range of Pr concentrations studied. It is noted that the ^{63}Cu NQR frequencies on Cu(2) sites in all $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ samples are almost around 32 MHz (Fig. 3). This means that they do not undergo significant structural changes when Pr is substituted for Sm. This result is consistent with the x-ray-diffraction patterns which show that all samples (for all values of x) exhibit the YBCO structure with orthorhombic symmetry. The shifts of the NQR peak with Pr concentration suggests the influence of Pr atoms which modify the quadrupole interaction at the Cu(2) sites, which demonstrates that the electric charge distributions in the vicinity of the Cu(2) sites are quite different. This is most likely dominated by differences in the hybridization and occupancy of the electronic wave functions. A gradual broadening of the peaks also implies a wide distribution of ν_Q associated with small variations of the local electric charge at Cu(2) due to Pr doping. This tendency of the peak position to change in $Sm_{1-x}Pr_xBa_2Cu_3O_{7-y}$ samples is different from that in $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_7$, which shows that the NQR frequency of Cu(2) in $Lu_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ is 31.5 MHz, greater than that in $LuBa_2Cu_3O_7$ (less than 30.4 MHz).[7] Since the ionic size difference of Lu and Pr ions is larger, which could cause a larger lattice distortion, we think the changes in ν_Q mainly result from the contribution of the surrounding lattice ions because a change in the degree of symmetry of the near-neighbor coordination gives rise to a variation in the EFG. It would be expected that the lattice contribution to the EFG becomes smaller as the symmetry of the coordination becomes like a cubic.[12] Shimizu *et al.*[14] have obtained a universal relation between $^{63}\nu_Q$ and the calculated lattice contribution to the EFG at Cu sites for a number of cuprates. Our results approximately fall on their curves; we expect a lattice contribution close to that of $YBa_2Cu_3O_7$ since the chains are full in both compounds. On these grounds and in the absence of a more accurate description of the EFG in these systems, we speculate that the change in $^{63}\nu_Q$ is mainly due to the decreased hole concentration on the plane as x is increased in $Sm_{1-x}Pr_xBa_2Cu_3O_7$.

As mentioned above, when Pr is substituted for Sm in $Sm_{1-x}Pr_xBa_2Cu_3O_7$, there are no significant structural changes, but the electric charge distributions in the vicinity of the Cu(2) sites are quite different as a result of the influence of Pr atoms, which modify the quadrupole interaction. It should be pointed out that in addition to the contribution from the quadrupole interactions, there is an extra contribution from the hyperfine interaction between the nuclear spin and Sm or Pr magnetic moment on both Cu(1) and Cu(2) sites. The ratio of the resonance frequencies at the peak is precisely the same as the ratio of the nuclear quadrupole moments of the two isotopes ^{63}Cu and ^{65}Cu. This clearly implies that there is no static magnetic field at the Cu(2) sites in $SmBa_2Cu_3O_{7-y}$ at room temperature. However, the ratio of the NQR frequencies of two isotopes at the Cu(2) site decreases to 1.071 rapidly even when the position of the ^{63}Cu NQR peak is still shifted down for the $x=0.3$ compound, which deviates from the value of 1.081. This result may suggest that the immediate neighborhood of Pr atoms may have a moment since Pr atoms themselves have a magnetic moment. A similar result is obtained on the Cu(1) site in addition to the peak splitting (Fig. 2). Although the variation of the resonance peak is small compared to the linewidth, the consistent behavior observed across the range of Pr concentrations suggests that it is intrinsic to the system. The peak splitting on the Cu(1) site means that there exist several inequivalent Cu(1) sites, indicating the strong influences of Pr doping on the Cu(1) coordinating. In the Pr-doped compounds, the partial substitution of Pr for Sm does not induce structural distortion, but has an effect on the electric charge redistributions in the vicinity of both Cu(1) and Cu(2) sites. These results illustrate the importance of the interplay between superconductivity and magnetism in the high-T_c cuprates. Further work is needed to clarify this aspect.

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