

T_c reduction in Sr-substituted $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ investigated by $^{63,65}\text{Cu}$ nuclear quadrupole resonance

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We report $^{63,65}\text{Cu}$ nuclear quadrupole resonance (NQR) spectra of Sr-substituted $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ at room temperature. The chemical pressure effect associated with Sr substitution leads to the results that the planar Cu(2) NQR signals are shifted to higher frequencies and the chain Cu(1) NQR signals are shifted to lower frequencies. With Sr substitution, the $^{63,65}\text{Cu}$ NQR linewidths increase significantly for both the Cu(2) plane site and Cu(1) chain site, and a new Cu NQR peak appears, which we expect, originates from partial oxygen disorder in the CuO_x chain layers. We expect that T_c reduction with Sr substitution in Y123 is due to carrier inhomogeneous distribution and localization caused by the partial oxygen disorder in the CuO_x chain layers, or the suppression of the resonant tunneling between the CuO_2 planes.

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I. INTRODUCTION

The pressure dependence of the transition temperature T_c of copper oxide high-temperature superconductors (HTSC's) is of fundamental interest for elucidating the microscopic mechanism of the superconductivity. It is generally believed that one of the key parameters controlling the T_c values is the charge carrier concentration in the CuO_2 planes, and it is postulated that the application of high pressure leads to the change of carrier concentration resulting in the pressure dependence of T_c .¹ However, some groups suggest that an additional variable, perhaps the effective pairing interaction, might be important.^{2,3} Such an effective pairing interaction might be shown by the scaling relationship between T_c and the buckling angle of the CuO_2 planes.^{4,5} The above two effects might play important roles in the description of T_c in the case of the external pressure or the internal pressure (chemical pressure).

The external pressure effect on T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123) has been extensively studied and the widely accepted result is the pressure enhanced carrier transfer from the CuO_x chain layers to the CuO_2 planes.¹ A similar result has also been observed in $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124) and behaves as a frequency shift in nuclear quadrupole resonance (NQR) experiments.⁶ Meanwhile, many groups⁷⁻¹⁶ focus on the divalent Sr^{2+} -doped $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ superconductors, where the chemical pressure effect can be studied due to the smaller-radius ion Sr^{2+} substitution for Ba^{2+} . Structural refinements of a variety of samples in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ system suggest that the decrease of T_c for increasing chemical pressure might be due to the decrease of the relaxation of the Ba/Sr layer strain.⁷⁻⁹ In another aspect, the thermoelectric power (TEP) study for $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ implicates a charge redistribution between the CuO_x chains and CuO_2 planes.¹⁰ Our internal friction study suggests that Sr-substitution results in a modification of the dynamic behavior of the carriers.¹¹ Then it is important for further research to study

the chemical pressure effect on the charge carrier behavior in detail.

NQR experiment provides a powerful tool for probing the local electronic and magnetic properties on the selected atom site. The electronic information in HTSC's can be obtained by the measurement of NQR frequency ν_Q at the copper sites, which is very sensitive to the local charge density. In this work, we performed $^{63,65}\text{Cu}$ NQR measurements on a series of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ powder samples with x varying from 0 to 0.6. Our experiments provide more information about the microstructure modification and the change of local carriers due to Sr^{2+} substitution.

II. EXPERIMENTAL

Ceramic samples of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ with $x=0, 0.02, 0.05, 0.1, 0.2, 0.4$, and 0.6 were prepared using the standard solid state reaction method.¹¹ All samples were examined to be single phased by powder x-ray diffraction using Cu K α radiation. The superconducting transition temperatures T_c determined by the standard four-probe dc resistivity measurements for $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ with $x=0, 0.02, 0.05, 0.1, 0.2, 0.4$, and 0.6 are 91, 90, 88, 85, 83, 80, and 78 K, respectively. NQR experiments were performed on a Bruker AVANCE (DSX) 400 high-power pulsed Fourier transform nuclear magnetic resonance (NMR) spectrometer, and experimental details were described in an earlier paper.¹⁷

III. RESULTS AND DISCUSSIONS

The superconducting transition temperature T_c is shown for each sample in Fig. 1. We can see clearly that T_c drops rather quickly. This is different than the result of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$, where T_c increases slightly or is nearly independent of Sr content.¹²⁻¹⁶ This difference will be discussed in detail later.

We show in Fig. 2 the Cu NQR spectra for a series of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ samples in the frequency range 18–25 MHz. For the sample with $x=0$, the two main peaks at 22.23 and 20.55 MHz are the NQR signals of copper on

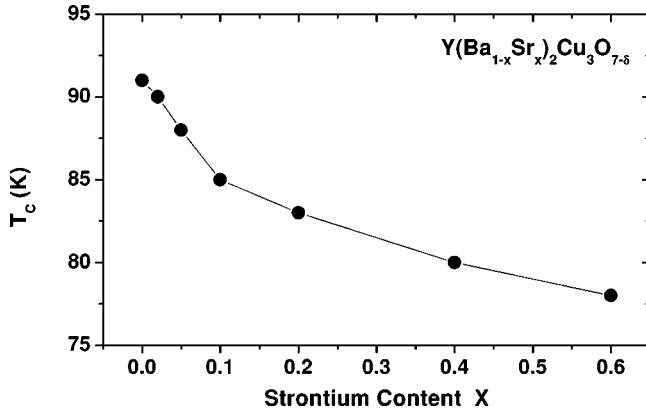


FIG. 1. The superconducting transition temperatures for different Sr concentrations in $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$.

the chain site $^{63}Cu(1)_4$ and $^{65}Cu(1)_4$ with fourfold oxygen coordinate, respectively. With increasing Sr content, these $^{63}Cu(1)_4$ and $^{65}Cu(1)_4$ NQR spectra are shifted toward lower frequencies, and the linewidths increase.

The Cu NQR spectra in the frequency range 25–34 MHz are given in Fig. 3. The spectrum of undoped $YBa_2Cu_3O_{7-\delta}$ in this range mainly shows two NQR peaks at 31.20 and 28.87 MHz, which have been assigned to $^{63}Cu(2)$ and $^{65}Cu(2)$ in the CuO_2 plane, respectively. We note that 31.20 MHz $^{63}Cu(2)$ peak has a trace of small peak around 30 MHz, which has been observed elsewhere^{17–19} and attributed

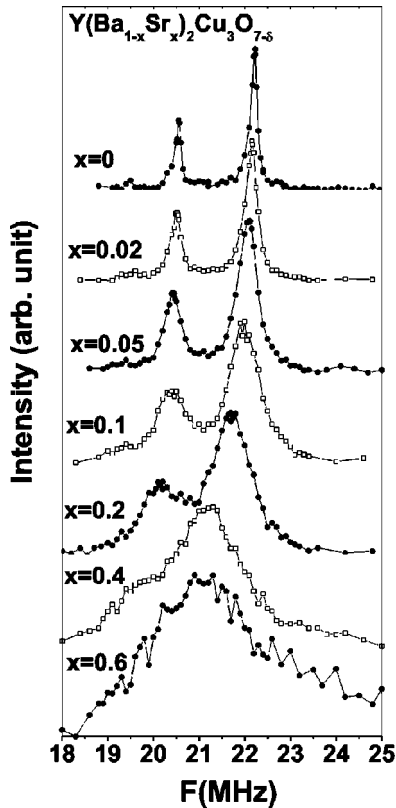


FIG. 2. $^{63,65}Cu(1)$ NQR spectra of $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ ($x = 0, 0.02, 0.05, 0.1, 0.2, 0.4, \text{ and } 0.6$) at room temperature. Results have been normalized to nearly equal ^{63}Cu peak height.

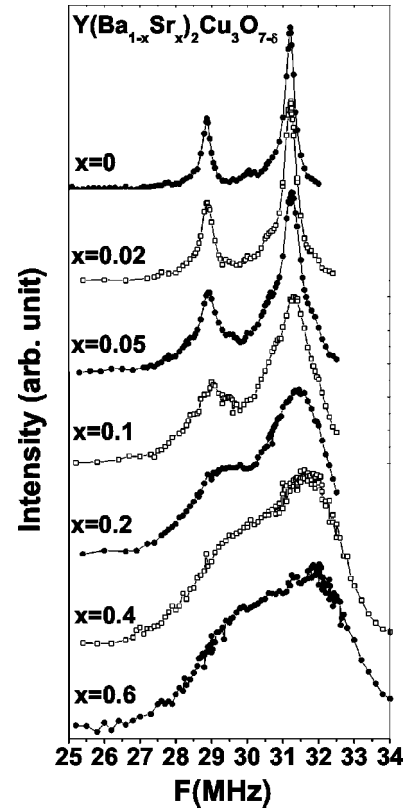


FIG. 3. $^{63,65}Cu$ NQR spectra of $Y(Ba_{1-x}Sr_x)_2Cu_3O_{7-\delta}$ ($x = 0, 0.02, 0.05, 0.1, 0.2, 0.4, \text{ and } 0.6$) in the frequency range 25–34 MHz at room temperature. Results have been normalized to nearly equal ^{63}Cu peak height.

to the Cu NQR signals accompanying the local lower oxygen content.¹⁸ During the Sr substitution, the $^{63,65}Cu(2)$ NQR spectra are shifted toward higher frequencies and linewidths increase, and a new Cu NQR shoulder peak appears at the lower frequency side of the Cu(2) signal.

Usually, the NQR frequency ν_Q is related to the electric field gradient (EFG) by

$$\nu_Q = \frac{eQV_{zz}}{2h} \sqrt{1 + \frac{1}{3}\eta^2},$$

where eQ is the nuclear electric quadrupole moment, V_{zz} the maximum principal component of the EFG tensor, and η the asymmetry parameter defined as $\eta = (V_{xx} - V_{yy})/V_{zz}$ with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Both theoretical calculation and experimental results indicate that the NQR frequency ν_Q of the planar copper is proportional to the charge density at the Cu site in the CuO_2 planes.^{20–24} At the same time, some theoretical and experimental results show that carrier density dependence of NQR frequency ν_Q is also roughly valid for the fourfold coordinated Cu(1) site.^{17,24,25}

With Sr substitution in Y123, the planar Cu(2) NQR spectra are shifted to higher frequencies, and the chain Cu(1) NQR spectra are shifted to lower frequencies, which is similar to the case for Sr substituted Y124.¹⁶ This result of NQR frequency ν_Q shift suggests that holes increase on the Cu(2) site and decrease on the Cu(1) site. In addition, the Cu(2) and

Cu(1) NQR frequency shifts are caused by the chemical pressure effect since this long range effect associated with small ion Sr substitution leads to the change of EFG at Cu sites on both CuO_2 planes and CuO_x chains which contributes to the frequency shift. Then NQR frequency ν_Q shift in our work indicates that the chemical pressure enhances the carrier transfer from the CuO_x chain layers to the CuO_2 planes. Such enhancement due to the Sr substitution in the single crystal $\text{YBa}_{1.92}\text{Sr}_{0.08}\text{Cu}_3\text{O}_7$ has been suggested by Horvatic *et al.*²⁶ This result is similar to the case for the external pressure. It has been reported that the application of external pressure to cuprate superconductors induces hole transfer from Cu(1) to Cu(2) in Y123 (Ref. 1) and Y124,^{13,14} which results in the increase of superconducting transition temperature T_c . The enhancement of hole transfer is also seen by the increase of NQR frequency $\nu_Q[\text{Cu}(2)]$ and decrease of $\nu_Q[\text{Cu}(1)]$ under external pressure in Y124.⁶ It is well known that CuO_2 planes play the key role to the development of the superconductivity and hole density is an important factor for high T_c . Then the T_c reduction by Sr substitution in Y123 is not due to the modification of average carrier density investigated by the present NQR experiment. In another aspect, we note that the NQR line widths of Cu(1) and Cu(2) increase with Sr substitution. The site disorder in the (Ba/Sr)O layers caused by Sr substitution may partly contribute to the increase of line widths. In Y124, Sr substitution shows little effect on T_c . A natural inference is that the site disorder in (Ba/Sr)O layers caused by Sr substitution affects T_c much less.¹⁶ We expect that it is also true in Y123, i.e., the effect of (Ba/Sr)O layers disorder on T_c is also less prominent in Y123.

The T_c variation of the compound Y123 as a function of Sr substitution is different from that of Y124. With increasing Sr content, T_c clearly decreases in Y123, but increases slightly¹⁴ or is nearly independent of Sr constant^{12,13,15} in Y124. Furthermore, the T_c dependence of Sr content in Y123 and Y124 shows less consistent with the result for the external pressure where both compounds have a positive T_c dependence of the external pressure.^{1,6,13,14} Therefore, it is natural to consider that the different T_c dependence of Sr content in Y123 and Y124 is due to something caused by Sr impurity substitution, in addition to the modification of average carrier density and the site disorder in the (Ba/Sr)O layers discussed above. The microstructure studies reveal a clear scaling between T_c and the buckling angle of the CuO_2 planes.^{4,5,27} This provide an important way to study the intrinsic variable of T_c . The early powder neutron diffraction gives much detail microstructure information,⁷ from which we can obtain the buckling angles by our calculation. The buckling angle of CuO_2 planes for $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ series with $x=0, 0.25, 0.5, 0.625$, and for $\text{YBaSrCu}_3\text{O}_{7-\delta}$ with different oxygen content are shown in Figs. 4(b) and 4(a), respectively. The results for different oxygen content are consistent with the proportional relationship between T_c and the buckling angle of CuO_2 planes in the underdoping range, while the buckling angles of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ with Sr content show the opposite tendency along the \vec{a} axis and \vec{b} axis. The reason for these opposite results along \vec{a} axis

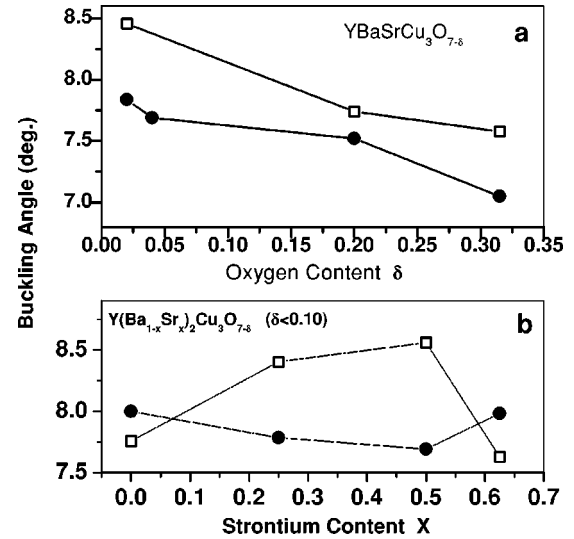


FIG. 4. The variations of the buckling angle of the CuO_2 planes with oxygen content for $\text{YBaSrCu}_3\text{O}_{7-\delta}$ (a) and with Sr content in $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$ (b). The buckling angles are calculated by the formula $\arccos a/(2 \times l_{\text{CuO}_2})$ (open square) and $\arccos b/(2 \times l_{\text{CuO}_3})$ (solid circle), where l_{CuO_2} and l_{CuO_3} are the bond length of CuO_2 and CuO_3 , respectively, a and b are the lattice parameters taken from Ref. 7.

and \vec{b} axis is not clear at present and we note that it has no relation to the orthorhombicity $[(b-a)/(a+b)]$ which is nearly constant as a variable of Sr content.⁷ Then no simple relation between T_c and the buckling angles can be obtained. This result made the discussion of T_c reduction from the aspect of buckling angles more difficult and no direct results can be given. Then we want to discuss the T_c reduction by Sr substitution in Y123 from another aspect.

In Fig. 3, a new NQR shoulder peak at the lower frequency side of Cu(2) signals appears for each ^{63}Cu and ^{65}Cu nucleus with Sr substitution, located the about 30.6 MHz for ^{63}Cu nucleus. This shoulder peak indicates that a possible new kind of copper site with different chemical environment appeared when Sr was substituted for Ba in Y123. We mention that this new peak has not been observed in the NQR spectra of Sr substituted Y124.¹⁶ Furthermore, we expect that this new peak in Sr substituted Y123 might reveal the underlying mechanism for different T_c response to Sr substitution in Y123 and Y124. The occurrence of similar extra peak has been observed when Ba^{2+} atoms were substituted by trivalent rare earth as in $\text{Pr}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$ (Ref. 25) or in $\text{LaBa}_2\text{Cu}_3\text{O}_{6+x}$,²⁸ and it is attributed to fivefold oxygen coordinate copper in the chains. The presence of extra oxygen atoms located on the O(5) sites is due to the charge compensation. Such fivefold oxygen coordinate Cu(1) also could be a consequence of the presence of CO_3 groups near the chains.²⁹ However, the presence of extra oxygen doping cannot be invoked in our samples as no charge compensation is necessary when Ba^{2+} atoms are substituted by Sr^{2+} . We must mention that no high oxygen pressure was used in the sample synthesis here, otherwise the oxygen content of samples will increase and then fivefold oxygen coordinated Cu(1) sites could be present in Sr substituted Y123.³⁰ The

new peak in our experiment is neither due to fivefold oxygen coordinated Cu(1), nor due to Cu(2) just located above threefold oxygen coordinated Cu(1),²⁸ as no clear change of the threefold Cu(1) NQR signals has been found in our NQR spectra. Above deduction is also consistent with the result that the orthorhombicity is nearly constant as Sr content varies.

Then we attribute the new copper NQR peak to other kind of structure modification. The neutron diffraction measurements show a progressive structural deformation, deviation of the position of chain layer O(4) from the \vec{b} axis with Sr substitution.⁷ Consequently, it will lead to the structural disorder in the CuO_x chain layer. Such structural disorder will contribute to the broadening of NQR spectra both for two copper isotope Cu(1) peaks and Cu(2) peaks in addition to the contribution of site disorder in (Ba/Sr)O layers discussed above. O(4) site disorder might also contribute to the new NQR peak at the lower frequency side of the Cu(2) signal.

The effect of the CuO_x chain layer on the electronic property has been studied by angle resolved photoemission spectra (ARPES), which demonstrates a definite hybridization in the one-electron spectra of chains and planes.³¹ Then the partial oxygen disorder caused by Sr substitution will affect the electronic property of the CuO₂ planes. The natural results are the carrier inhomogeneous distribution and partial localization. Consequently, the superconducting transition temperature T_c decreases. We note that no such oxygen disorder in the chain layers was found in Sr substituted Y124. Then no such additional oxygen disorder effect contributes to T_c dependence of Sr substitution in Y124. Maybe this is the reason why T_c is suppressed with Sr substitution in Y123 and less shifted in Y124. T_c reduction due to such oxygen disorder might also be understood from another aspect. The partial oxygen disorder in the chain layers reduce \vec{c} axis

carrier transport more efficient than that in plane. Then T_c reduction for Sr substituted Y123 might be better derived from the scenario of the resonant tunneling mechanism,³² in which the resonant tunneling between the CuO₂ planes will be suppressed by the oxygen disorder in the chain layers, and consequently T_c decreases. At present, the results of Sr-substituted Y123 polycrystal show that in plane resistivity is less sensitive to Sr content for high Sr concentration.¹⁰ A further \vec{c} axis resistivity measurement will be needed to test the above speculation.

IV. CONCLUSION

We found that a new Cu NQR shoulder peak appeared in Sr substituted YBa₂Cu₃O_{7- δ} (Y123) and it is related to partial oxygen disorder in the CuO_x chain layers. The chemical pressure effect associated with Sr substitution leads to the results that the NQR spectra for planar Cu(2) and chain Cu(1) are shifted toward opposite directions with Sr substitution which evidences the enhancement of carrier transfer from Cu(1) to Cu(2). We expect that T_c reduction with Sr substitution in Y123 is due to the carrier inhomogeneous distribution and partial localization in the CuO₂ planes caused by partial oxygen disorder in the CuO_x chain layers, or the suppression of the resonant tunneling between CuO₂ planes.

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