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Cu nuclear quadrupole resonance study of site disorder and chemical pressure effects on $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$

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We report a zero-field Cu nuclear quadrupole resonance (NQR) study on the effects of nonmagnetic Sr substitution for high-T_c superconductors, $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ ($T_c = 82$–80 K, for $x = 0 - 0.4$), using a spin-echo technique. The site-disordering and chemical pressure effects associated with doping Sr were observed in the broadened, shifted Cu NQR spectra. Nevertheless, the site disorder did not significantly affect the homogeneity of Cu electron spin dynamics, in contrast to the in-plane impurity. The peak shift of the Cu NQR spectrum due to Sr was different between the chain- and the plane-Cu sites, more remarkably than those under a hydrostatic physical pressure, suggesting anisotropic or nonuniform local structural strains. The small decrease of T_c due to Sr can be traced back to either a cancellation effect on T_c between the disorder and the pressure, or an anisotropic or nonuniform chemical pressure effect on T_c.

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The role of imperfections in quantum many-body systems has attracted strong attention.[1,2] In high-T_c cuprate superconductors, an additional impurity potential is introduced through the in-plane or out-of-plane element substitution for the CuO_2 plane. There is a belief that site disorder does not cause serious damage to the electronic states of the CuO_2 plane. However, the reason why chemical pressure effect on T_c due to the element substitution is not the same as the physical (external) pressure one has been frequently ascribed to the randomness effect. How the site disorder changes the electronic states is poorly understood.

Here, we focus on the divalent Sr^{2+}-doped high-T_c superconductors, $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$. Since the stoichiometric and naturally underdoped $YBa_2Cu_4O_8$ (Y124) with $T_c = 82$ K has the exceptionally tight oxygen content, the Sr-doped Y124 is a suitable system to study the site-disordering effect on the electronic states. To be exact, one can expect two effects of Sr substitution for Ba in Y124 without change of oxygen content: (1) the chemical pressure and (2) the crystalline potential disorder. The substitution of Sr^{2+} ions causes no additional local (formal) charge in $Ba^{2+}O^{2-}$ layers. However, the size of Sr^{2+} ion is smaller than that of Ba^{2+} by about 10%,[3] so that the substituted Sr ions make local crystalline strains on the BaO layers. Thus, the Sr doping introduces crystalline potential disorder and chemical pressure to the lattice. Actually, the lattice constants shrink with doping Sr,[4] being in parallel to the physical pressure effect.[5]

The effect of hydrostatic physical pressure on the spin dynamics is similar to the carrier doping effect:[6–8] The physical pressure effects on T_c and on the pseudo-spin-gap temperature T_s agree with the carrier doping effects, i.e., with applying the physical pressure to Y124 ($T_c = 82$ K and $T_s \sim 160$ K at an ambient pressure $P = 0.1$ MPa), T_c increases[9] but T_s decreases,[8] as well as with doping Ca.[10,6] Here, the pseudo-spin-gap temperature T_s is defined as the maximum temperature of the planar $^{63}Cu(2)$ nuclear spin-lattice relaxation rate $^{63}(1/T_1T)$,[11] which is the wave-vector averaged dynamical spin susceptibility at a nuclear quadrupole resonance (NQR)/NMR frequency via a nuclear-electron coupling constant.[12] It is reported that the uniaxial pressure also increases T_c except along the c axis ($dT_c/dP_c \sim 0$, P_c is a pressure along the c-axis) from the thermal expansion coefficients of the lattice constants for powder Y124.[13]

The Sr doping, however, scarcely increases T_c for Y124,[4] or remarkably decreases T_c for $YBa_2Cu_3O_{7-\delta}$,[14–18] although the unit cell volume shrinks [for example, the unit cell volume of Y124 with Sr of $x = 0.3$ corresponds to that under an external hydrostatic pressure of about 2.4 GPa (Ref. 19)]. Hence, one can suspect that randomness affects the actual T_c. Nonmagnetic impurity Zn doping into the CuO_2 plane significantly decreases T_c in the hole-doped high-T_c cuprates.[20] However, there is a crucial difference between Zn^{2+} in the CuO_2 plane and Sr^{2+} in the BaO layer: The Zn^{2+} ion acts as a spin vacancy in the CuO_2 plane with site disorder, whereas the Sr^{2+} ion acts only as a site disorder in the CuO_2 plane without any vacancies. In terms of a single-band Hubbard model for the CuO_2 plane, the site disorder is descibed by the randomness or the modulation of transfer matrix elements t_{ij} (i and j are the labels of the nearest-neighbor Cu sites) in the kinetic energy of the conducting carriers $\Sigma_{i,j} t_{ij} c_i^\dagger c_j$ ($c_i^\dagger$ and c_j are the creation and the annihilation operators of an electron), which may cause a distribution of the local density of states of electrons.

In the charge-transfer model from the CuO chain to the CuO_2 plane, a charge distribution between the chain Cu(1) and the plane Cu(2) plays an important role in changing T_c.[21,22,5,17] From the structural analysis, however, the bond valence sums at Cu(1) and at Cu(2) are estimated to increase with doping Sr for Y124.[19] From the theoretical analysis based on band theory, the important role of an internal strain in the CuO_2 plane is emphasized.[23] Cu NQR can provide information on the charge distribution at each Cu site.

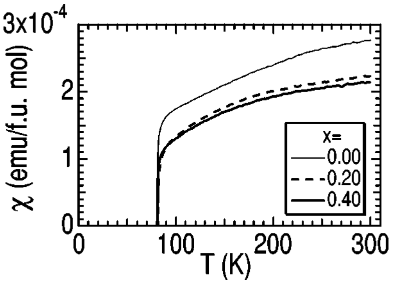

FIG. 1. The temperature and Sr-doping dependence of the static uniform susceptibility χ of $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ ($x=0$, 0.20, and 0.40). In contrast to Zn substitution for Cu, no Curie term is induced by Sr substitution for Ba.

In this paper, we report on Cu NQR measurements for $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$. We observed the site-disordering and chemical pressure effects in the broadened, shifted Cu NQR spectra. We found that the site disorder does not significantly affect the homogeneity of the electron spin dynamics of the CuO_2 plane, sharply in contrast to that due to the in-plane impurities.

The powdered samples were synthesized by a solid-state-reaction method with a hot-isostatic-pressing apparatus. From measurements of the *dc* magnetization with a superconducting quantum interference device (SQUID) magnetometer, the superconducting transition was observed at $T_c=82$, ~ 81, ~ 80.5, and ~ 80 K for $x=0.00$, 0.10, 0.20, and 0.40, respectively. While the previous study reported a somewhat increase in T_c with increasing Sr content,[4] our samples behaved conversely. Our samples were prepared through rather long-time heat-treatment under high oxygen partial pressure. We believe that the samples were purely single-phasic and free from structural defects, e.g., Cu-O single-chain. Synthesis and characterization of the samples will be reported elsewhere in details.

NQR measurements were carried out by a coherent-type pulsed spectrometer. The Cu NQR spectra were measured by integration of the Cu nuclear spin-echoes as the frequency is changed. The ^{63}Cu(2) nuclear spin-lattice relaxation curves $p(t)\equiv 1-M(t)/M(\infty)$ were measured by an inversion recovery technique, where the ^{63}Cu nuclear spin-echo intensity $M(t)$ was recorded as a function of time interval t after an inversion π pulse, in a $\pi-t-\pi/2-\pi$-echo sequence. The recovery curve $p(t)$ was analyzed by $p_{LD}(t)=p_{LD}(0)\times\exp[-(3t/T_1)_{HOST}-\sqrt{3t/\tau_1}]$, where $p_{LD}(0)$, $(T_1)_{HOST}$ and τ_1 are the fitting parameters. $p_{LD}(0)$ is a fraction of an initially inverted magnetization, $(T_1)_{HOST}$ is the nuclear spin-lattice relaxation time due to the host Cu electron spin fluctuations, and τ_1 is an impurity-induced nuclear spin-lattice relaxation time, which is originally called a longitudinal direct dipole relaxation time.[24] We regard τ_1 as just the measure of deviation from the single exponential function. An alternative analysis by a two-exponential function of $p_S\exp(-t/T_{1S})+p_L\exp(-t/T_{1L})$ (p_S, T_{1S}, p_L, and T_{1L} ($>T_{1S}$) are the fitting parameters) is possible, but it leaves our conclusions unchanged. We emphasize that the presented results are independent on the details of analysis.

Figure 1 shows the uniform spin susceptibility χ for the powdered samples, which were measured using a SQUID magnetometer under an external magnetic field of 1 T. Obviously, no Curie term is observed, sharply in contrast to the Zn doped Y124.[25] The site disorder does not induce a local moment. The small decrease of χ with doping Sr cannot be accounted for by the diamagnetic susceptibility χ_{core} of core electrons of Sr^{2+} ions, because of the estimated $\chi_{core}=-(2.16-2.02)\times 10^{-4}$ (emu/f.u.-mol) for $x=0-0.40$ [$\chi_{core}=34x-216$ (10^{-6} emu/f.u.-mol) for $x=0-2$]. The origin of the decrease is not clear at present.

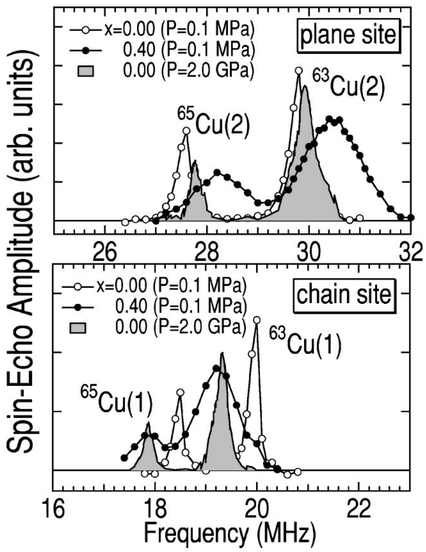

FIG. 2. The ^{63,65}Cu NQR frequency spectra of the plane Cu(2) (a) and the chain Cu(1) (b) for $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ of $x=0.00$ (open circles) and $x=0.40$ (closed circles) at an ambient pressure ($P=0.1$ MPa). For comparison, the Cu NQR spectra (shaded area) of pure Y124 under a hydrostatic physical pressure ($P=2.0$ GPa) are also reproduced from Ref. 7.

Figure 2 shows ^{63,65}Cu NQR spectra of the plane Cu(2) (a) and of the chain Cu(1) (b) for $x=0.00$ (open circles) and $x=0.40$ (closed circles) at $T=4.2$ K. For comparison, the shaded ^{63,65}Cu NQR spectra for a pure Y124 under a hydrostatic physical pressure of $P=2.0$ GPa are reproduced from Ref. 7. With doping Sr, the Cu(2) NQR spectra are shifted to higher frequencies, whereas the Cu(1) NQR spectra are shifted to lower frequencies. Since the directions of these shifts are in parallel to those under the hydrostatic pressure, a charge transfer from the chain to the plane may occur with doping Sr, similarly to the external pressure effect.[26,7] However, one should note that the degree of shifts of the Cu(2) NQR spectra is quite different from that of Cu(1) between the Sr-doping and the hydrostatic pressure effects.[26,7] This difference indicates that compression due to the internal pressure of Sr is different from that due to the hydrostatic pressing. A local strain model as in Ref. 23 may account for the shifts of the Cu NQR spectra.

NQR frequency indicates the deviation of charge distribution from cubic symmetry around the nuclear site, which is quite sensitive to the local crystal structure. Both the linewidths of Cu(1) and Cu(2) are broadened by Sr doping, indicating the enhancement of randomness of the crystalline potential due to Sr in BaO layer. For such a broadened spec-

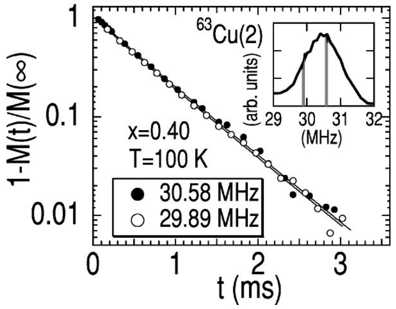

FIG. 3. The frequency dependence of the recovery curve of the ^{63}Cu(2) nuclear spin-echo $M(t)$ at 30.58 MHz (closed circles) and at 29.89 MHz (open circles) for $x=0.40$ at 100 K. The solid curves are the least-squares fitting results using Eq. $p_{LD}(t)$ (see the text). The inset shows the ^{63}Cu(2) NQR spectrum and the corresponding hot spot regions (shaded area) excited by the rf pulse in the measurement of the recovery curve.

trum, one would expect an inhomogeneous local density of electron states and an inhomogeneous electron spin dynamics.

Figure 3 shows a semi-logarithmic plot of the ^{63}Cu(2) nuclear spin-echo recovery curves $p(t)$ at 30.58 MHz and at 29.89 MHz in the broadened spectrum of $x=0.40$ at $T=100$ K. The inset figure shows the broadened ^{63}Cu(2) NQR spectrum, where the shaded areas represent the hot spot regions excited by the first $\pi/2$ pulse at the respective frequencies for the measurement of the recovery curves. The excited region is estimated from the pulse strength ν_1 of the first $\pi/2$ pulse, e.g., $\nu_1 \sim 63$ kHz from the relation of $2\pi\nu_1 t_w=\pi/2$ using the time duration of the first $\pi/2$ pulse, $t_w \sim 4$ μs. In contrast to our naive expectation, the recovery curves are nearly the same single exponential function, being independent of the frequency. The lattice imperfections broaden the static NQR spectra, nevertheless it does not affect the homogeneity of the Cu spin dynamics in the CuO$_2$ plane. That is, the homogeneous spin dynamics is observed in the inhomogeneously broadened Cu NQR spectrum.

Figure 4 shows the Sr-doping dependence of the ^{63}Cu(2) nuclear spin-lattice relaxation rate $(1/T_1)_{HOST}$ and of the extra relaxation rate $1/\tau_1$ in a log-log plot. The magnitude of $(1/T_1)_{HOST}$ for $x>0$ is slightly smaller than that for $x=0$ over a temperature range of 4.2–300 K. The smaller $(1/T_1)_{HOST}$ than that for $x=0$ was also observed for the chain ^{63}Cu(1) (not shown here). With doping Sr, the extra relaxation rate $1/\tau_1$ is slightly increased. Although the small increase of $1/\tau_1$ is only an indication of the site disorder effect on the homogeneity of Cu electron spin dynamics, the increased $1/\tau_1$ for $x=0.40$ is one or two orders of magnitude smaller than that for 1–2% Zn- or Ni-doped Y124.[27–30] Since there is no Curie term in the uniform susceptibility in Fig. 1, the physical origin of τ_1 must not be paramagnetic impurities. The overall feature of Cu nuclear spin-lattice relaxation is not changed so much by the Sr doping. The host Cu spin dynamics is robust and still unique. The robust electronic state for the site disorder may be a remarkable characteristic of the two-dimensional electron system confined within a CuO$_2$ plane, which may indicate a "quantum protectorate."[1]

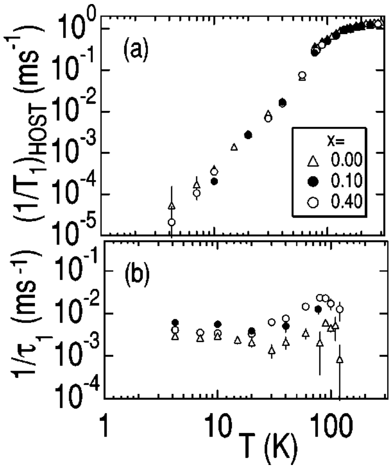

FIG. 4. The temperature and Sr-doping dependence of $(1/T_1T)_{HOST}$ (a) and $1/\tau_1$ (b) estimated from the ^{63}Cu(2) nuclear spin-echo recovery curves.

Figure 5 shows the Sr-doping effect on the pseudo spin-gap behavior of $(1/T_1T)_{HOST}$. The pseudo-spin-gap temperature T_s slightly decreases with doping Sr, similarly to the physical pressure effect.[8] The slight suppression in the magnitude of $(1/T_1T)_{HOST}$ with doping Sr is similar to that with the in-plane Zn doping.[28,30] For the high-T_c cuprates, the Cu(2) $1/T_1T$ is approximately expressed by an antiferromagnetic spin susceptibility. The site disorder suppresses slightly the host antiferromagnetic spin susceptibility. Thus, we found that with doping Sr, the inhomogeneity in the Cu spin dynamics, the suppression of the host Cu antiferromagneic spin correlations and the decrease in T_c are small.

From these results, one can infer two possibilities for the Sr-doping effect on the spin dynamics and T_c. One is the cancellation mechanism between the disorder and pressure effects. The original effect of the site disorder may be so large as to induce a large $1/\tau_1$ and a large decrease of T_c. But, the Sr chemical pressure may increase the carrier density, as the hydrostatic physical pressure, which decreases $1/\tau_1$ and raises T_c. As a result, the Sr doping may retain a slight decrease of T_c and less inhomogeneity in the spin dynamics. The other is the anisotropic or nonuniform chemical pressure effect on T_c more than what would be expected

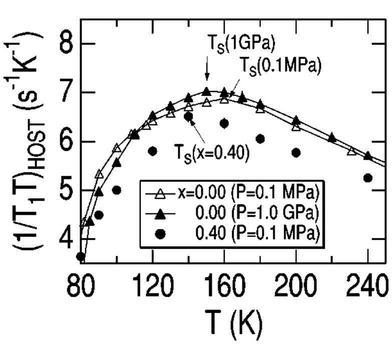

FIG. 5. The Sr-doping effect (from Fig. 4) and the hydrostatic pressure effect (reproduced from Ref. 8) on $(1/T_1T)_{HOST}$ around the pseudo spin-gap temperature T_s. The solid curves are guides for the eye.

from the thermal expansion.[13] The nonuniform compression between the plane and the chain causes the large difference in the shifts of the Cu NQR spectra between the plane and the chain. The cancellation among the competing anisotropic local pressure effects may reduce the enhancement effect on T_c. Here, we assume that the site disorder has essentially a weak effect on the Cu electron spin dynamics. However, it is hard to investigate the uniaxial external pressure effects of a few GPa in polycrystalline ceramics. A further discussion on the completely exclusive effects of the chemical pressure and site disorder is beyond the present study.

In conclusion, we found that the effect of the site disorder due to Sr substitution on the Cu(2) electronic states of Y124 is quite different from that due to the in-plane impurities such as Zn and Ni. The site disorder due to Sr does not induce local moments nor any significant inhomogeneous relaxation process, but causes chemical pressure shifts and broadening in the Cu NQR spectra. Further investigations, e.g., physical pressure and/or carrier doping dependence of the Sr doping effect, will have to be conducted to separate the roles of the chemical pressure and the site disorder.

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