63Cu-NMR study on High-$T_c$ Superconductor La$_{2-x}$Ba$_x$CuO$_4$

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Abstract. In order to investigate the local structure in the CuO$_2$ plane of the La-based high-$T_c$ cuprate La$_{2-x}$Ba$_x$CuO$_4$, we have carried out measurements of 63Cu-NMR on single crystals with $x=0.08$ and 0.10 at low temperatures down to 4 K. In both samples, the local structure deduced from observed NMR spectra agreed with the averaged structure. In high-temperature region around 300K, detailed investigation of NMR line width has shown the existence of the local structure different from the averaged structure; that is, CuO$_6$ octahedra tilt from the $c$-axis toward the random direction by approximately 1.4 deg.

1. Introduction

Physical properties of metals are dominated by its crystal structure through two different ways. One is the modification of the band structure by the Bragg scattering of electronic wave in the structure with translational symmetry. The other is the pinning effect, that is, the crystal structure with the specific spatial pattern stabilizes the electronic state with the spatial pattern identical to the crystal structure, which is well known, for example, as the intrinsic pinning effect of superconducting magnetic flux in high $T_c$ cuprates [1]. In La-based high-$T_c$ cuprates, there is another intriguing pinning effect by the crystal structure, the stabilization of the stripe order. The stripe order in high-$T_c$ cuprates is a one dimensional segregation of holes and spins, and strongly suppresses the superconductivity [2]. So far, the stripe order in La-based high-$T_c$ cuprates has been intensively studied by many experimental techniques [2,3,4] and the existence of the strong stabilization effect on the stripe order by the structure of so-called low-temperature tetragonal phase (LTT) has been confirmed [5,6]. Furthermore, it has been reported that the local structure of LTT, which does not have a spatial coherence and hence cannot be detected by scattering techniques, appear in some conditions of temperatures or dopant concentration [7-11]. This incoherent local structure also shows a slight pinning effect on the stripe order if weaker than the LTT structure with the spatial coherence [8].

Though the important role of the LTT phase both coherent and incoherent in the stabilization of the stripe order is thus recognized, one is still far from the full understanding of the appearance mechanism of the LTT phase itself. Actually, the LTT phase appears in either case when hetero ions with radius larger than La$^{3+}$ such as Ba$^{2+}$ or smaller such as Nd$^{3+}$ are substituted, and its appearance mechanism cannot be simply explained in terms of the epitaxial distortion between the CuO$_2$ plane and the block layer consisting of the layered structure of La-based high-$T_c$ cuprates [12,13]. As for the local structure of the LTT phase, its existence itself is still in controversy [7-11,14]. The purpose of this paper is devoted to the microscopic detection of the local structure of LTT phase in La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) and to find out the appearance condition of the phase.

Before describing the NMR-detection of local structures, we briefly summarize the electronic phase diagram of La-based high-$T_c$ cuprates. First, the parent material La$_2$CuO$_4$ is a typical Mott insulator and becomes conductive when provided holes by substitution of La$^{3+}$ with Ba$^{2+}$ or Sr$^{2+}$. These divalent atoms are much larger than La$^{3+}$ ion and are expected to bring a structural instability into the system [5,12,15]. Particularly, LBCO shows a successive structural phase transition as lowering temperatures; the structure
changes from the high-temperature tetragonal phase (HTT, space group $I4/mmm$) to the low-temperature orthorhombic phase (LTO, $Cmca$) at $T_d1$ and then, within a limited region of $0.09<x<0.25$, successively to the LTT ($P4_2/ncm$) at $T_d2$ [5,16,17].

These three crystal structures are characterized by buckling patterns of the CuO$_2$ plane. In HTT phase, the plane is flat and CuO$_6$ octahedra stand upright. In low-temperature phases, the CuO$_2$ plane buckles along the line of (110)$_T$ in LTO phase, and along (100)$_T$ in LTT phase, respectively in the tetragonal notation. Especially, in the latter, the buckling direction coincides with that of the stripe order and stabilizes it as stated above[2,15,18]. The principle of detecting the LTT structure by Cu-NMR is based on this buckling structure in CuO$_2$ planes. Since the principal axis of the electric field gradient (EFG) tensor at the Cu site is approximately perpendicular to the basal plane of CuO$_6$ octahedra, one can obtain the buckling angle directly from the NMR shift, which delicately depends on the angle between the applied field and the principal axis of EFG. NMR is a local probe, and hence is capable of detecting the LTT structure both with and without the spatial coherence. We have previously applied this technique onto La$_{2-x}$Sr$_x$CuO$_4$ and related systems to reveal successfully an existence of the incoherent LTT phase at low temperatures [8]. In this article, we report results of NMR measurements on single crystals of LBCO at various temperatures.

2. Experimental

Single crystals of LBCO $x=0.08$, $T_c=24$ K and $x=0.10$, $T_c=28$ K were prepared by the conventional floating zone method [19]. The superconducting critical temperature $T_c$ is defined as the mid point of the resistivity drop. In the sample of $x=0.08$, the spatially-coherent LTT phase is absent [17]. In $x=0.10$, the thermodynamic phase transition temperature to LTT phase $T_d2$ $\approx$ 39.2 K was determined from the small but finite step in the temperature dependence of the magnetic susceptibility [20].

NMR spectra were obtained by plotting the spin echo amplitude against the applied magnetic field. The NMR resonance peak position $H_{res}$ of the central transition $I_z = -1/2 \leftrightarrow +1/2$ is expressed by the angle $\phi$ formed by the principal axis of the electric field gradient tensor (EFG) and the magnetic field direction as

$$H_{res} = \frac{\nu}{\gamma(1+K)} - \frac{3v_Q^2}{16\nu\gamma(1+K)(1-9\cos^2\theta)(1-\cos^2\theta)}$$

where $K \approx 0$ is the Knight shift, and $\nu$, $\gamma$, and $v_Q$ are the injected radio frequency, the gyromagnetic ratio, and the quadrupole frequency of $^{63}$Cu nucleus, respectively. $v_Q$ was determined to be 32.2 and 32.8 MHz for $x=0.08$ and 0.10 respectively from the $\theta$-dependence of $H_{res}$[8,9]. As shown schematically in Fig. 1 (a), the neighboring two Cu nuclei become inequivalent, and spectrum splits into multiple peaks when the buckling

![Figure 1](image1.png)

**Figure 1.** (a) The principle of the NMR detection of the buckling of the CuO$_2$ plane. (b) Schematic drawings of CuO$_2$ plane showing the direction of principal axes of EFG tensor from top view.

![Figure 2](image2.png)

**Figure 2.** The temperature dependence of the profile of spectra in LBCO (a) $x=0.08$ and (b) $x=0.10$. Dashed and solid curves show the calculated spectra by assuming the local structure to be LTO or LTT phase with $\phi$ of 3.3 and 4 deg respectively. The convoluted Gaussian width was adjusted so that they reproduce the observed spectra.
angle of the CuO₂ plane $\phi$ is finite and the applied field is tilted from the $c$-axis. The splitting profile depends delicately on the spatial pattern of the buckling shown in Fig. 1 (b). When the field is tilted toward (110)$_T$ direction, the spectrum is expected to split into three peaks in LTO, and two in LTT. This allows one to discriminate the LTO from the LTT irrespective of their spatial coherence. Note that the discrimination still works well even if there exists a twinned structure in the LTO phase[8].

3. Results and discussion

Figure 2 (a) shows $^{63}$Cu-NMR spectra in LBCO ($x=0.08$) measured at various temperatures. We also show for comparison the calculated spectra, which are obtained from the convolution of resonance line positions by Gaussian width. The resonance line positions were calculated by eq. (1) with an assumption of the CuO₆ tilting angle $\phi$ to be 3.3 deg and 4 deg for LTO and LTT phases, respectively. The width was determined so that the calculation reproduces observed spectra. In the entire temperature region of our measurements, the observed NMR spectra composing a large peak at the center and small peaks at both sides match well with the simulated spectra based on the LTO structure. We insist that the calculated spectrum for the LTT phase consists of two peaks with the same amplitude and never coincides with the observation. The averaged crystal structure of this sample retains to be LTO down to 4.2K [8], so that the present NMR result indicates that there does not exists an incoherent local structure with a buckling pattern different from LTO. In LBCO ($x=0.10$) with the finite $T_{d2} \approx 39.2K$, on the contrary, observed NMR spectra changed their profile distinctly from the three-peaked shape (LTO) to the two-peaked shape (LTT) at around its $T_{d2}$ as shown Fig. 2 (b). From these two observations, we can conclude that the local structure is always in accordance with the averaged structure in LBCO. This makes a clear contrast to LSCO, where the existence of the local structure of LTT is reported in samples possessing the averaged structure of LTO [8,9]. In the present case of LBCO, a great disparity between the ionic radii of Ba$^{2+}$ and La$^{3+}$ may stabilize the spatially-coherent LTT structure to make the phase boundary between LTT and LTO distinct.

Next, in order to investigate the local structure in the HTT phase where the averaged structure is the completely flat CuO₂ plane, we investigated the field-direction dependence of the center peak signal of $^{63}$Cu of LBCO ($x=0.10$). The spectral profile at each field direction at room temperature is shown in Fig. 3. Note that both the shift and the width are significantly dependent on the field direction. In order to show the change in width clearly, we compare the two typical spectra at different angles in the inset of Fig. 4. Now, while the $\theta$-dependence of the shift is simply described by eq. (1), the latter dependence is explained in terms of the local tilting of the principal axis of EFG tensor as follows. Generally the width of the eqq-perturbed NMR resonance line, $\Delta H_{\text{res}}$, is contributed both by the distribution in the tilting angle $\Delta \theta$ and in the quadrupole frequency $\Delta v_Q$ as,

$$\Delta H_{\text{res}} = \left| \frac{\partial H_{\text{res}}}{\partial \theta} \right| \Delta \theta + \left| \frac{\partial H_{\text{res}}}{\partial v_Q} \right| \Delta v_Q + \text{const.} \quad (2)$$

Figure 3. The profile of $^{63}$Cu-NMR spectra corresponding to the central transition line at various field direction in the HTT phase of the sample $x=0.10$.

Figure 4. The field-direction dependence of FWHM. The grey curve shows the calculation with $\Delta \theta=1.4(2)$ deg and $\Delta v_Q=0.0(1)$ MHz. The insets show typical spectra at different angles.
When there is a distribution in either $\theta$ or $\nu_Q$, it must contribute to the distribution of $\Delta H_{\text{res}}$. The $\theta$-dependence of the two terms in eq. (2), that is, $\partial H_{\text{res}} \partial \nu_Q$ and $\partial H_{\text{res}} \partial \nu_Q$ is quite different, which allows us to determine $\Delta \theta$ and $\Delta \nu_Q$ independently. In Fig. 4, the observed dependence of the width on $\theta$ is shown. We fitted eq. (2) to the observed dependence of $\Delta H_{\text{res}}$ on the field direction to obtain $\Delta \theta$ and $\Delta \nu_Q$ to be 1.4(2) deg and 0.0(2) MHz, respectively.

This result shows that CuO$_6$ octahedra tilt from the $c$-axis toward the random direction by approximately 1.4 deg even in the HTT phase, where the averaged structure is the completely flat CuO$_2$ plane. The existence of the local structure in the HTT phase is so far argued by the neutron scattering [7]. However, due to the extremely fast time scale of the neutron experiment one was not able to determine whether the local structure was static or dynamically fluctuating. The result of the present work, which is based on the quasi static probe of NMR spectra, assures that this local structure of the random tilting of octahedra in the HTT phase is static one. This type of static and random local structure has been argued to be one of the triggers for the appearance of LTT phase[13]. We expect that a further investigation on the Ba-concentration dependence of the tilting angle in HTT phase will reveal the critical condition of the appearance of LTT phase.

4. Summary

By NMR measurements on single crystals of LBCO, we have shown that the local structure of LBCO is always in accordance with the averaged structure in LTO and LTT phases, making a clear contrast with the LSCO, where the discrepancy of the two is reported. In HTT phase at room temperature, where the averaged structure of CuO$_2$ plane is flat, CuO$_6$ octahedra are found to tilt from the $c$-axis toward the random direction by approximately 1.4 deg.

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