139La NQR Study in La2CuO4 over Temperatures up to 800 K

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We have measured 139La NQR spectra and the nuclear spin-lattice relaxation rate for the highest (7/2 → 5/2) and the middle (5/2 → 3/2) NQR lines in the parent compound of high-Tc superconductor, La2CuO4, in a wide temperature range up to 800 K. From the abrupt increase of the quadrupole frequency $Q$ just below the tetra-ortho structural transition temperature $T_{OT}$ which comes from the staggered tilt of the CuO6 octahedra, the critical exponent $\alpha$ is evaluated to be 0.4 which is close to 0.5 expected in the standard mean field approximation for second order phase transition. In higher temperature than $T_{OT}$, the nuclear spin-lattice relaxation at La site is dominated by the quadrupole relaxation, not reflecting the critical spin dynamics in the CuO2 plane. We successfully discriminate the two types of quadrupole relaxation rate, $W_{Q1}$ and $W_{Q2}$. The relaxation rate $W_{Q2}$ is one order of magnitude larger than $W_{Q1}$ and increases with the critical exponent $\alpha \approx 1.19$ toward $T_{OT}$.

Key words: La2CuO4; NQR; Structural Transition.

1. Introduction

Since the discovery of high-Tc superconductor, La2CuO4 has attracted special interest in its basic electronic structure as a typical parent compound for high-Tc superconductors as well as in its magnetic properties as an ideal two-dimensional spin 1/2 quantum Heisenberg antiferromagnet (2D-QHAF) in the CuO2 plane. In this paper, we present the La NQR results in a wide range of temperature up to about 800 K. Many 139La NQR/NMR in La2CuO4 performed so far are mainly concerned with the magnetic properties in the CuO2 plane below the Neel temperature $T_N$, namely, the ordered spin structure, spin dynamics and the T-dependence of the sublattice magnetization. We report the results above $T_N$ focusing especially on the orthogonal-tetragonal (OT) structural phase transition. We also remark a little on the critical spin dynamics in 2D-QHAF at $T > T_N$, but we found, unfortunately, that it cannot be probed by NQR at La site.

2. Experimental Results and Discussions

The measurements were performed on the same powdered polycrystalline sample as that used in the previous Cu-NQR [1], where the sample preparation was described in detail. The phase coherent spin echo method was used for the 139La (I = 7/2) NQR. The NQR probe coil with the sample shielded in a quartz tube was placed directly in the electric oven where the temperature was controlled within ±0.2 K.

The measurements were carried out on the highest (±7/2 → ±5/2) and the middle (±5/2 → ±3/2) NQR lines for 139La, which we call hereafter H and M lines, respectively. The linewidth is small (50 KHz) enough to determine the resonance frequency by the ‘zero beat’ of the echo signal. Figure 1 shows the temperature dependence of the respective NQR frequencies. The hyperfine field splitting is seen below $T_N = 312$ K for the H line. The NQR frequency decreases monotonously with decreasing temperature in the tetragonal (T) phase. This decrease in the T phase is probably ascribed to the volume expansion of the crystal. The NQR frequency shows abrupt increase at the structural transition temperature $T_{OT} = 539$ K. Since the OT transition accompanies the staggered tilt of the CuO6 octahedra around the [110] tetragonal axis [2], this abrupt increase of the NQR frequency is primarily attributed to the tilt of the CuO6 octahedron as discussed later.

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Fig. 1. The temperature dependence of the NQR frequencies for the H ($\pm 7/2 \rightarrow \pm 5/2$) and M ($\pm 5/2 \rightarrow \pm 3/2$) NQR lines.

Fig. 2. The temperature dependence of the quadrupole frequency $\nu_Q$. The solid line represents the least mean square fit for the T phase.

From the two NQR frequencies $\nu_H$ and $\nu_M$ of H and M lines, we can deduce the quadrupole frequency $\nu_Q(\equiv \frac{3\nu_H\nu_M}{\nu_H^2 - \nu_M^2})$ and the asymmetry parameter $\eta$ of the field gradient tensor at the La site. When $\eta$ is small, $\nu_Q$ and $\eta$ are evaluated as $\nu_Q = \frac{\nu_H + \nu_M}{2}$ and $\eta = \frac{\nu_H - \nu_M}{\nu_H + \nu_M}$, where $r \equiv \frac{\nu_H}{\nu_M}$. The estimated values of $\eta$ are $\eta = 0 \pm 0.006$ and $\eta = 0.02 \pm 0.02$ in the T and the orthorhombic (O) phase, respectively. These are independent of temperature within the experimental accuracy. The T-dependence of $\nu_Q$ is shown in Fig. 2 together with the results by Nishihara et al. below 300 K [3]. The abrupt increase of $\nu_Q$ below $T_{OT}$ is due to the tilt of the CuO$_6$ octahedron as mentioned before, where the tilt angle is regarded as an order parameter for the structural transition [4]. When the tilt angle $\phi$ is small, which is about 5° according to the neutron scattering experiment [2], the increment of $\nu_Q$ below $T_{OT}$, $\Delta \nu_Q$, is proportional to $\phi$, at least in the vicinity of $T_{OT}$. Thus we can evaluate the critical exponent $\beta$ in the relation $\phi \propto \xi^{\beta}$ associated with the OT transition, where $\xi \equiv 1 - T/T_{OT}$. Figure 3 shows the log-log plot for $\Delta \nu_Q/\Delta \nu_Q(0)$ vs. $\xi$. There is an ambiguity to estimate $\Delta \nu_Q$ since it may contain a contribution from the volume expansion. Then we consider the following two cases: Case (1): $\Delta \nu_Q(T) = \nu_Q(T) - \nu_Q(T_{OT})$, where an effect of volume expansion is neglected, Case (2): $\Delta \nu_Q(T) = \nu_Q(T) - \nu_Q(T_{OT})$, where an effect of volume expansion is assumed to be the extrapolation from the T phase, $\nu_Q(T)$, as drawn by the solid line in Figure 2. The critical exponent $\beta$ is 0.425 and 0.389 for the case (1) and case (2), respectively. The value of $\beta$, being...
slightly small but close to 0.5, suggests the OT transition to be three-dimensional second order where the mean field approximation works for the driving force causing the tilt of the octahedrons.

Next, we present the results of the nuclear spin-lattice relaxation at La site. The magnetization recovery curve becomes multi-exponential inevitably for both the magnetic relaxation and quadrupole relaxation. Then we adopt here $\tau_{\text{OT}}^{-1}$ as an effective relaxation rate, where $\tau_{\text{OT}}$ is the time that the nuclear magnetization recovers to $e^{-1}$ value of the thermal equilibrium one. Figure 4 shows the $T$-dependence of the relaxation rate $\tau^{-1}$ for respective NQR lines. The $T$-dependence of $\tau_{\text{OT}}^{-1}$ shows the same trend as $T_{\text{1}}^{-1}$ at the Cu site. However the relaxation at the La site does not reflect the low frequency spin dynamics in the CuO$_2$ plane for the following reason. If the relaxation for both La and Cu sites occurs through the same mechanism of the spin dynamics in the CuO$_2$ plane, $T_{\text{1}}^{-1}$ at La site is expected as, 

$\langle T_{\text{1}}^{-1} \rangle_{\text{La}} \approx \langle T_{\text{1}}^{-1} \rangle_{\text{Cu}} \cdot \left[ \frac{\gamma_{\text{La}} h_{\text{La}}^q}{\gamma_{\text{Cu}} h_{\text{Cu}}^q} \right]^2$, 

here $\gamma_{\text{La}}$ and $\gamma_{\text{Cu}}$ are the gyromagnetic ratios for respective nuclei, $h_{\text{La}}^q$ and $h_{\text{Cu}}^q$ are the amplitude of the fluctuating hyperfine fields at respective sites. Since $h_{\text{La}}^q \sim 1$ kG [3] and $h_{\text{Cu}}^q \sim 78$ kG [5, 6], $\langle T_{\text{1}}^{-1} \rangle_{\text{La}}$ should be three orders of magnitude smaller than $\langle T_{\text{1}}^{-1} \rangle_{\text{Cu}}$.

However, the experimental value of $\tau_{\text{OT}}^{-1}$ is of the same order as $\langle T_{\text{1}}^{-1} \rangle_{\text{Cu}}$. Even if we consider the rough estimate $\langle T_{\text{1}}^{-1} \rangle_{\text{La}} \sim \frac{1}{10} \langle T_{\text{1}}^{-1} \rangle_{\text{Cu}}$ in the case of magnetic relaxation, $\langle T_{\text{1}}^{-1} \rangle_{\text{La}}$ is at least two orders of magnitude too large to ascribe it to magnetic relaxation originating in the spin dynamics in the CuO$_2$ plane. Therefore we conclude that the quadrupole relaxation is dominant at La site in this high temperature range.

In quadrupole relaxation, there are two kind of relaxation processes in which the nucleus changes its quantum number $m$ by $\Delta m = \pm 1$ or $\Delta m = \pm 2$. When respective transition probabilities are written as,

\[
W_{m,m+1}^{Q_1} = \frac{W_{Q_1}}{2(2I-1)^2} \cdot \left\{ |\langle m| I_x I_y + I_y I_x |n \rangle |^2 + |\langle m| I_z I_x + I_x I_z |n \rangle |^2 \right\}
\]

and

\[
W_{m,m+2}^{Q_2} = \frac{W_{Q_2}}{2(2I-1)^2} \cdot \left\{ |\langle m| I^2 |n \rangle |^2 + |\langle m| I_z^2 |n \rangle |^2 \right\},
\]

the master equation for the relaxation is formulated as $d\mathbf{P}/dt = -A\mathbf{P}$, where $\mathbf{P}$ is the nuclear polarization vector consisting of the polarization of the respective NQR lines, $A$ is the relaxation matrix whose element
is a function of $W_{Q1}$ and $W_{Q2}$. We can calculate numerically the magnetization recovery for the respective NQR lines by considering a transformation matrix $P$ to make the matrix $A$ diagonal [7]. In usual, it is difficult to discriminate the two relaxation processes experimentally because both the magnetization recoveries become multi-exponential. However we noticed that the ratio $R_{r+1} \equiv \tau_{1M}^{-1}/\tau_{1H}^{-1}$ is a good measure to discriminate the relaxation process. The upper part of Fig. 5 shows the numerical calculation of $R_{r+1}$ for the respective ratio $K = W_{Q2}/W_{Q1}$. The monotonous increase of $R_{r+1}$ ensures to determine $K$ experimentally. The lower part of Fig. 5 shows the experimental $T$-dependence of $R_{+1}$. From these figures, we can estimate the value of $K$ for each temperature. Then we can analyze the magnetization with $W_{Q1}$ as the only fitting parameter. For example, the magnetization recovery for H and M lines at 775 K are shown in Fig. 6, where the solid lines are calculated recovery curves with $K = 12$, $W_{Q1} = 0.130$ (msec)$^{-1}$, so that $W_{Q2} = 1.56$ (msec)$^{-1}$. The agreement between the experiment and the calculation is satisfactory.

Figure 7 shows the $T$-dependence of the respective quadrupole relaxation rates above $T_{OT}$. The relaxation process with $W_{Q2}$ is dominant in this temperature range. When the temperature approaches to $T_{OT}$ from above, $W_{Q2}$ increases progressively. This behavior suggests that some collective modes of CuO$_6$ octahedra associated with the structure of the O phase become slow down with lowering temperature. The critical exponent as shown in Fig. 8 is $\alpha = 1.19$, except for the extreme vicinity of $T_{OT}$ if we define $W_{Q2} \propto (\varepsilon)^\alpha$.

In the intermediate temperature range, $T_{N} \leq T \leq T_{OT}$, the very long component appears in the nuclear magnetization recovery in addition to the short quadrupole components. The long component is probably attributed to the magnetic contribution to the re-
laxation process discarded above $T_{OT}$, which make
the magnetization recovery too complex to analyze
the relaxation process in this temperature range.

3. Conclusion

We have measured NQR frequencies and the nu-
clear spin-lattice relaxation times for the H and M
NQR lines at La site over the wide temperature range
up to 800 K. The abrupt increase of the quadrupole
frequency just below $T_{OT}$ allows us to determine the
critical exponent $\beta$ at the OT transition. The obtained
value $\beta \sim 0.4$ is close to 0.5 expected in the stan-
dard mean field approximation for second order phase
transition. The nuclear spin-lattice relaxation is dom-
inated by quadrupole relaxation, at least above $T_{OT}$,
not reflecting the critical spin dynamics in the CuO$_2$
plane. The relaxation rate $W_{Q}\text{2}$ is one order of mag-
nitude larger than $W_{Q}\text{1}$ and increases with the critical
exponent $\alpha \sim 1.19$ toward $T_{OT}$.

[1] M. Matsumura, H. Yasuoka, Y. Ueda, H. Yamagata,
Hunter, J. L. Wagner, B. Dabrowski, K. G. Vandervoort,
B49, 4163 (1994).
T. Imai, S. Sasaki, S. Kanbe, K. Kishio, K. Kitazawa,
Owence, C. P. Poole, Jr., and H. A. Farach, Academic
Press 1979, p.79.
[7] D. E. MacLaughlin, J. D. Williamson, and J. Butter-