^{139}La NQR Study in La_2CuO_4 over Temperatures up to 800 K

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We have measured ^{139}La 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-T_c superconductor, La_2CuO_4, in a wide temperature range up to 800 K. From the abrupt increase of the quadrupole frequency ν_Q just below the tetra-ortho structural transition temperature T_{OT} which comes from the staggered tilt of the CuO_6 octahedra, the critical exponent β 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 CuO_2 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 $\alpha \sim 1.19$ toward T_{OT}.

Key words: La_2CuO_4; NQR; Structural Transition.

1. Introduction

Since the discovery of high-Tc superconductor, La_2CuO_4 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 CuO_2 plane. In this paper, we present the La NQR results in a wide range of temperature up to about 800 K. Many ^{139}La NQR/NMR in La_2CuO_4 performed so far are mainly concerned with the magnetic properties in the CuO_2 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 ^{139}La ($I = 7/2$) 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 ^{139}La, 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 CuO_6 octahedra around the [110] tetragonal axis [2], this abrupt increase of the NQR frequency is primarily attributed to the tilt of the CuO_6 octahedron as discussed later.

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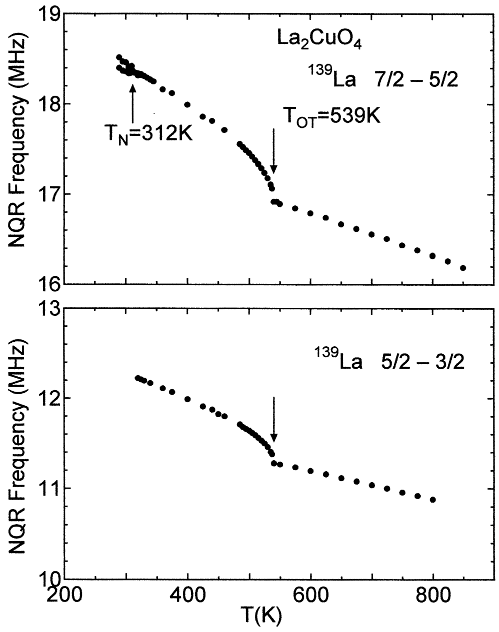

Fig. 1. The temperature dependence of the NQR frequencies for the H ($\pm 7/2 \leftrightarrow \pm 5/2$) and M ($\pm 5/2 \leftrightarrow \pm 3/2$) NQR lines.

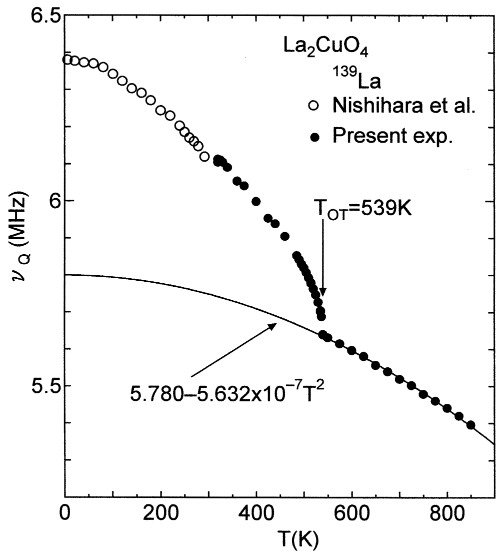

Fig. 2. The temperature dependence of the quadrupole frequency ν_Q. The solid line represent the least mean square fit for the T phase.

From the two NQR frequencies ν_H and ν_M of H and M lines, we can deduce the quadrupole frequency $\nu_Q(\equiv \frac{3e^2qQ}{2I(2I-1)})$ and the asymmetry parameter η of the field gradient tensor at the La site. When η is small, ν_Q and η are evaluated as $\nu_Q = \frac{\nu_H}{3(1-\eta^2/10}$ and $\eta = \left\{\frac{10(2r-3)}{11r-3}\right\}^{1/2}$, where $r \equiv \frac{\nu_H}{\nu_M}$. The estimated values of η 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 ν_Q are shown in Fig. 2 together with the results by Nishihara et al. below 300 K [3]. The abrupt increase of ν_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 ϕ is small, which is about 5° according to the neutron scattering experiment [2], the increment of ν_Q below T_{OT}, $\Delta\nu_Q$, is proportional to ϕ, at least in the vicinity of T_{OT}. Thus we can evaluate the critical exponent β in the relation $\phi \propto \varepsilon^\beta$ associated with the OT transition, where $\varepsilon \equiv 1 - T/T_{OT}$. Figure 3 shows the log-log plot for $\Delta\nu_Q/\Delta\nu_Q(0)$ vs. ε. 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): $\Delta\nu_Q(T) = \nu_Q(T) - \nu_Q^v(T)$, where an effect of volume expansion is assumed to be the extrapolation from the T phase, $\nu_Q^v(T)$, as drawn by the solid line in Figure 2. The critical exponent β is 0.425 and 0.389 for the case (1) and case (2), respectively. The value of β, being

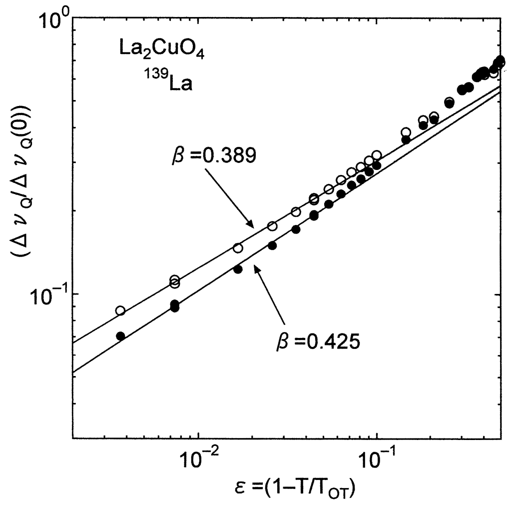

Fig. 3. The log-log plot for $\Delta\nu_Q(T)/\Delta\nu_Q(0)$ vs. ε. The critical exponent β on the OT transition is evaluated for the case (1) (•) and case (2) (○), (see text).

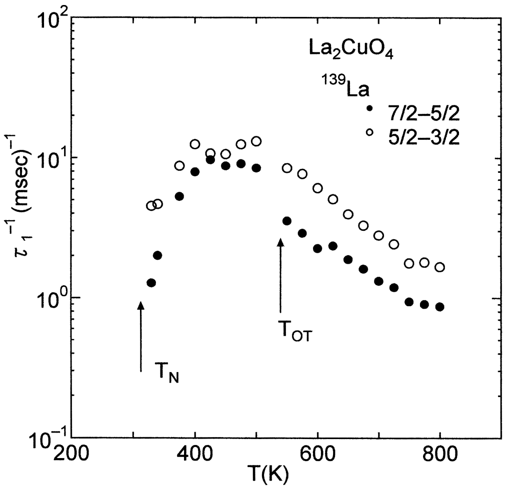

Fig. 4. The temperature dependence of the effective nuclear spin-lattice relaxation rate for the H and M lines.

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 τ_1^{-1} as an effective relaxation rate, where τ_1 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 τ_1^{-1} for respective NQR lines. The T-dependence of τ_1^{-1} shows the same trend as T_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_1^{-1} at La site is expected as, $(T_1^{-1})_{\mathrm{La}} \approx (T_1^{-1})_{\mathrm{Cu}} \cdot \left[\frac{\gamma_{\mathrm{La}} h_{\mathrm{hf}}^{\mathrm{La}}}{\gamma_{\mathrm{Cu}} h_{\mathrm{hf}}^{\mathrm{Cu}}}\right]^2$, here γ_{La} and γ_{Cu} are the gyromagnetic ratios for respective nuclei, $h_{\mathrm{hf}}^{\mathrm{La}}$ and $h_{\mathrm{hf}}^{\mathrm{Cu}}$ are the amplitude of the fluctuating hyperfine fields at respective sites. Since $h_{\mathrm{hf}}^{\mathrm{La}} \sim 1$ kG [3] and $h_{\mathrm{hf}}^{\mathrm{Cu}} \sim 78$ kG [5, 6], $(T_1^{-1})_{\mathrm{La}}$ should be three orders of magnitude smaller than $(T_1^{-1})_{\mathrm{Cu}}$. However, the experimental value of τ_1^{-1} is of the same order as $(T_1^{-1})_{\mathrm{Cu}}$. Even if we consider the rough estimate $(T_1^{-1})_{\mathrm{La}} \sim \frac{1}{10}\tau_1^{-1}$ in the case of magnetic relaxation, $(T_1^{-1})_{\mathrm{La}}$ is at least two orders of magnitude too

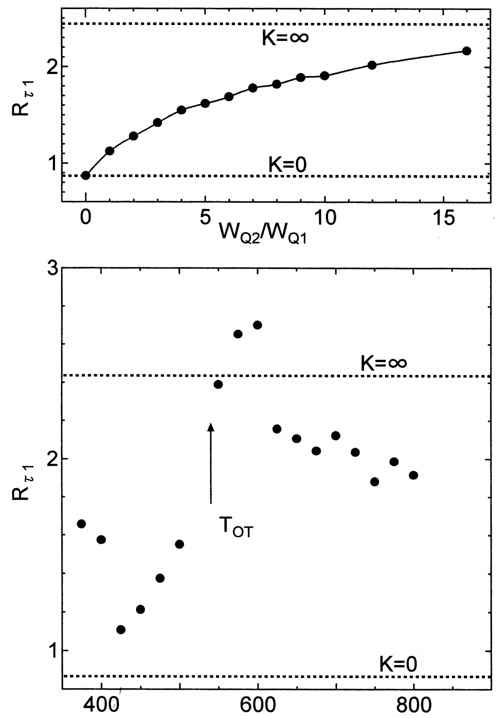

Fig. 5. The upper figure shows $R_{\tau 1}$ calculated numerically for respective $K = W_{Q2}/W_{Q1}$ values. The lower figure shows the T-dependence of $R_{\tau 1}$ obtained experimentally.

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,

$$W_{m,n}^{Q1} = \frac{W_{Q1}}{2I(2I-1)^2} \cdot \left\{ \left|\langle m|I_z I_+ + I_+ I_z|n\rangle\right|^2 + \left|\langle m|I_z I_- + I_- I_z|n\rangle\right|^2 \right\}$$

and

$$W_{m,n}^{Q2} = \frac{W_{Q2}}{2I(2I-1)^2} \left\{ \left|\langle m|I_+^2|n\rangle\right|^2 + \left|\langle m|I_-^2|n\rangle\right|^2 \right\},$$

the master equation for the relaxation is formulated as $\mathrm{d}\,\boldsymbol{u}/\mathrm{d}\,t = -\mathbf{A}\boldsymbol{u}$, where $\boldsymbol{u}$ is the nuclear polarization vector consisting of the polarization of the respective NQR lines. $\mathbf{A}$ is the relaxation matrix whose element

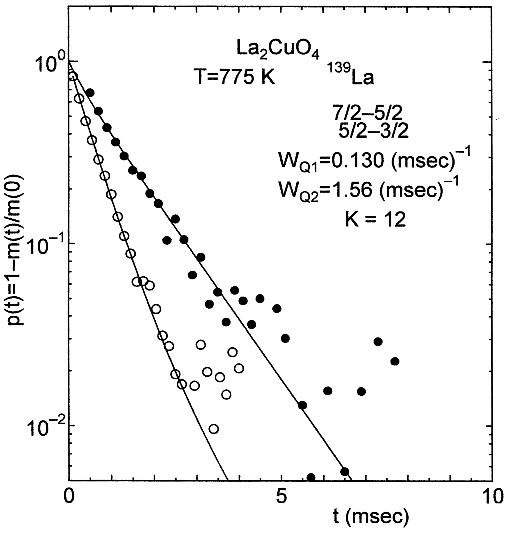

Fig. 6. Representative magnetization recovery for the H and M lines at 775 K. The solid lines represent the calculated recovery by using K obtained from Figure 5.

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 $R_{\tau 1} \equiv \tau_{1M}^{-1}/\tau_{1H}^{-1}$ is a good measure to discriminate the relaxation process. The upper part of Fig. 5 shows the numerical calculation of $R_{\tau 1}$ for the respective ratio $K = W_{Q2}/W_{Q1}$. The monotonous increase of $R_{\tau 1}$ ensures to determine K experimentally. The lower part of Fig. 5 shows the experimental T-dependence of $R_{\tau 1}$. 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

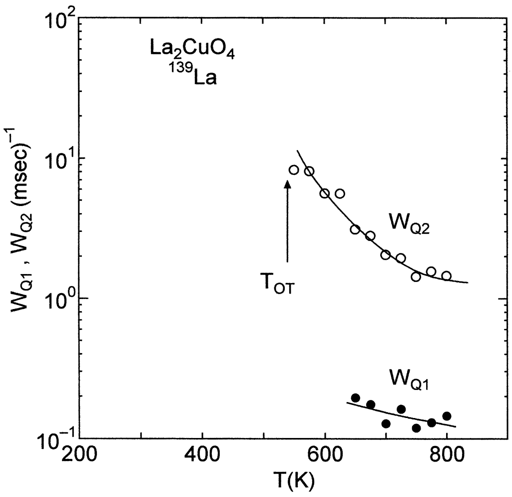

Fig. 7. The temperature dependence of W_{Q2} and W_{Q1} in the T phase.

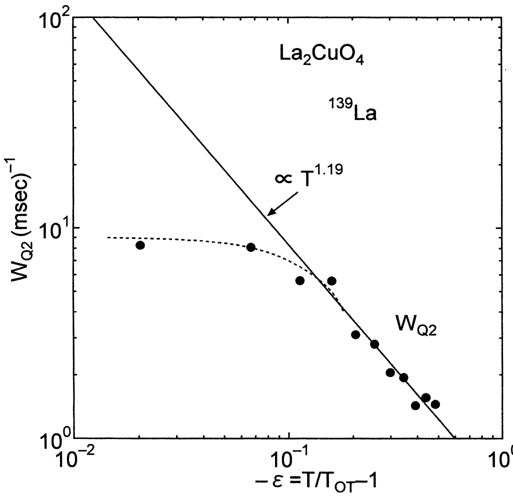

Fig. 8. The log-log plot for W_{Q2} vs. $(-\varepsilon)$. The critical exponent $\alpha \approx 1.19$ except for the extreme vicinity of T_{OT} in $W_{Q2} \propto (-\varepsilon)^{\alpha}$.

octahedra associated with the structure of the O phase become slow down with lowering temperature. The critical exponent as shown in Fig. 8 is α = 1.19, except for the extreme vicinity of T_{OT} if we define $W_{Q2} \propto (-\varepsilon)^{\alpha}$.

In the intermediate temperature range, $T_{\mathrm{N}} \leq T \leq T_{\mathrm{OT}}$, 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 relaxation 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 nuclear 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 β at the OT transition. The obtained value $\beta \sim 0.4$ is close to 0.5 expected in the standard mean field approximation for second order phase transition. The nuclear spin-lattice relaxation is dominated by quadrupole relaxation, at least above T_{OT}, not reflecting the critical spin dynamics in the CuO_2 plane. The relaxation rate W_{Q2} is one order of magnitude larger than W_{Q1} and increases with the critical exponent $\alpha \sim 1.19$ toward T_{OT}.

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