The orbital degree of freedom has become an important topic in the physics of strongly correlated electron systems \([1,2]\). One of the recent topics is a quantum effect in the orbital ordering dominated by electron correlations. Especially, Mott insulators with \(t_{2g}\) degenerated orbitals are prospective in this viewpoint, since the Jahn-Teller (JT) coupling for \(t_{2g}\) orbitals is weaker than \(e_g\) states and the large degeneracy enhances the quantum effect. The RTiO\(_3\) (R: rare earths) system is fascinating from the above viewpoint \([2,3,4,5,6]\). RTiO\(_3\) has an orthorhombically distorted perovskite structure (space group: \(Pbnm\)), in which the electronic configuration of a Ti\(^{3+}\) ion is \(t_{2g}\) \(^1\). While several studies have reported that YTiO\(_3\) takes an orbital ordering state from both experimental and theoretical aspects \([2,3,4,6,10,11]\), the orbital state in LaTiO\(_3\) is now under controversy \([2,3]\). LaTiO\(_3\) undergoes \(G\)-type antiferromagnetic ordering below \(T_N \sim 150\) K with the reduced ordered moment of 0.46 \(\mu_B\) \([10]\). The question is what interaction lifts the degeneracy of threefold \(t_{2g}\) orbitals in the ground state. The octahedra of TiO\(_6\) in LaTiO\(_3\) exhibit small distortions. One would expect, at first sight, quadruply degenerated single-ion ground states represented by fictitious angular momentum \(j = 3/2\) due to spin-orbit (SO) interaction, which have unquenched orbital moment. This scenario is consistent with the observed reduced magnetic moment. However, Keimer et al. suggested that the SO interaction is not dominantly working in this system from the isotropic spin wave dispersion \([2]\). Under these circumstances, a picture of strongly fluctuating orbital states was proposed \([2,3]\), followed by a refined calculation on the orbital excitations \([2]\). On the other hand, Mochizuki and Imada have successfully explained the physical properties of LaTiO\(_3\) by an orbital state expressed approximately as \(1/\sqrt{3}(d_{xy} + d_{yz} + d_{zx})\) \([12]\). Subsequently, corresponding distortions of the TiO\(_6\) octahedra have been reported from detailed structural data \([13,14]\).

In this paper, we report the results of analyses on NMR measurements for LaTiO\(_3\). The NMR spectra show that the quadrupole moment of a 3\(d\) electron in LaTiO\(_3\) is rather large and unfavorable for the orbital liquid model, while the spectra are well explained by the \(1/\sqrt{3}(d_{xy} + d_{yz} + d_{zx})\)-like orbital ordering state with appropriate parameters.

Experimental procedures are mentioned in Ref.10. It is known that the magnetic properties are particularly sensitive to the oxygen content \(\delta\) in LaTiO\(_3+\delta\) \([15]\). We used powdered samples with the Néel temperature \(T_N \sim 147\) K (\(\delta \sim 0.0\)) for NMR measurements. Frequency-swept NMR spectra of LaTiO\(_3\) were taken point by point of frequency by using a super-heterodyne coherent pulsed spectrometer at 1.5 K in the antiferromagnetically ordered state under zero external field. As for the properties of \(^{47}\)Ti and \(^{49}\)Ti nuclei, the nuclear spin \(^{47}I = \frac{3}{2}\) and \(^{49}I = \frac{7}{2}\), the quadrupole moment \(^{47}Q = 0.29\times10^{-24}\) and \(^{49}Q = 0.24\times10^{-24}\) cm\(^2\), and the gyromagnetic ratio \(^{47}\gamma_N/2\pi = 2.4000\) and \(^{49}\gamma_N/2\pi = 2.4005\) MHz/T are used in this paper \([16]\).

Figure 1 shows the frequency-swept \(^{47,49}\)Ti NMR spectra in the antiferromagnetically ordered state of LaTiO\(_3\), which were previously reported in Ref.10. These spectra are consistent with the data in Ref.17. Each peak...
of the spectra is assigned for $^{47}$Ti and $^{49}$Ti nuclei as shown by the arrows in Fig. 1. The attribution of the peaks to the $^{47}$Ti and $^{49}$Ti nuclei is the same as previous reports,[16, 17], although the parameters such as the quadrupole frequency $\nu_Q$ and the asymmetry parameter of the electric field gradient (EFG) $\eta$ are not unique to reproduce the spectra.

The NMR spectrum of Ti nuclei is determined by the hyperfine interaction. The hyperfine interaction $\mathcal{H}$ in the 3$d^1$ transition metal ion is expressed as

\[ \mathcal{H} = \mathcal{H}_{\text{mag}} + \mathcal{H}_{\text{el}} = -\gamma_N \hbar \mathbb{H}^{\text{eff}} \cdot \mathbf{I} + \frac{e \mathbf{Q} \cdot \mathbb{V}^{\text{eff}} \cdot \mathbf{I}}{2I(2I-1)} + \mathcal{H}_{\text{mag}} = 2\mu_B\gamma_N \hbar \langle r^{-3} \rangle_{\text{mag}}[-\kappa \mathbf{S} \cdot \mathbf{I} + \mathbf{L} \cdot \mathbf{I} + \frac{2}{21}] \times \{L(L+1)\mathbf{S} \cdot \mathbf{I} - \frac{3}{2}(\mathbf{L} \cdot \mathbf{I})(\mathbf{L} \cdot \mathbf{S}) - \frac{3}{2}L(S)(L \cdot I)\} = 2\mu_B\gamma_N \hbar \langle r^{-3} \rangle_{\text{mag}}[-\kappa \mathbf{S} \cdot \mathbf{I} + \mathbf{L} \cdot \mathbf{I} - \frac{2}{21}] \mathbf{S} \cdot \mathbf{q} \cdot \mathbf{I} \right] (2) \] \[ \mathcal{H}_{\text{el}} = \mathcal{H}_{\text{el}}^\text{on} + \mathcal{H}_{\text{el}}^\text{out}, \] \[ \mathcal{H}_{\text{el}}^\text{on} = \frac{e^2 Q}{2I(2I-1)} (r^{-3})_{\text{on}} \left\{ 3(L \cdot I)^2 + \frac{3}{2}(L \cdot I) \right\} - L(L+1)(I(I+1)) = \frac{e^2 Q}{2I(2I-1)} (r^{-3})_{\text{on}} \left\{ I \cdot \mathbf{q} \cdot \mathbf{I} \right\}, \] \[ \mathcal{H}_{\text{el}}^\text{out} = \frac{(1 - \gamma\infty)eQ}{6I(2I-1)} \sum_{\alpha\beta} V_{\alpha\beta}^\text{out} \left\{ \frac{3}{2} \mathbf{I} \alpha \beta \right\} - \delta_{\alpha\beta} L^2 \right\} = (1 - \gamma\infty) \frac{eQ}{2I(2I-1)} [ I \cdot \mathbf{V}^{\text{out}} \cdot \mathbf{I} ], \] where $\mathcal{H}_{\text{mag}}$ represents the magnetic hyperfine interaction, $\mathcal{H}_{\text{el}}$ the electric hyperfine interaction, $\mathcal{H}_{\text{el}}^\text{on}$ the electric hyperfine interaction with on-site $d$ electrons, $\mathcal{H}_{\text{el}}^\text{out}$ the effective internal magnetic field, $\mathbb{V}^{\text{eff}}$ the effective electric field gradient (EFG) tensor, $\hbar$ the Planck's constant, $\mu_B$ the Bohr magneton, $\langle r^{-3} \rangle_{\text{mag}}$ and $\langle r^{-3} \rangle_{\text{el}}$ the expectation values of $r^{-3}$ for the Ti 3$d$ electron, $\kappa$ a parameter for the Fermi contact interaction due to a core-polarization effect, $\gamma\infty$ the Sternheimer antishielding factor, $\mathbf{S}$ the spin, $\mathbf{L}$ the orbital momentum, $\mathbf{I}$ the nuclear spin operator, $\mathbf{q}$ the electron quadrupole moment tensor of which the components are defined as $q_{\alpha\beta} \equiv 2(L_\alpha L_\beta + L_\beta L_\alpha) - \delta_{\alpha\beta} L^2 \left( \alpha, \beta = x, y, \text{and } z \right)$, $\mathbf{V}^{\text{out}}$ the EFG tensor by the outside ions, and $V_{\alpha\beta}^\text{out}$ the components of the EFG tensor, respectively.

While $\mathcal{H}_{\text{mag}}$ generates a single resonance peak for each of $^{47}$Ti and $^{49}$Ti, the EFG at Ti nuclei splits the spectrum to 2$I$ resonance peaks through $\mathcal{H}_{\text{el}}$ in the case of $\mathcal{H}_{\text{el}} \ll \mathcal{H}_{\text{mag}}$. As seen in Fig. 1, the NMR spectra of $^{49}$Ti are split to seven peaks with almost the same frequency interval of $\sim 1.6$ MHz, indicating $\mathcal{H}_{\text{el}} \ll \mathcal{H}_{\text{mag}}$. Since the EFG tensor $\mathbb{V}^{\text{eff}}$ is symmetric tensor, $\mathbb{V}^{\text{eff}}$ can be diagonalized by an appropriate rotation of the coordination system. Now we take the $x'y'z'$-coordination system to diagonalize $\mathbb{V}^{\text{eff}}$, and refer to the maximum value of the diagonal components as $V_{z'z'}^{\text{eff}}$. The quadrupole frequency $\nu_Q$ is defined using $V_{z'z'}^{\text{eff}}$ as

\[ \nu_Q \equiv \frac{3eQ V_{z'z'}^{\text{eff}}}{2H(2I-1)}. \] $\nu_Q$ increases with the deviation from cubic symmetry for EFG around the nuclei ($\nu_Q = V_{z'z'}^{\text{eff}} = V_{x'x'}^{\text{eff}} = V_{y'y'}^{\text{eff}} = 0$ in cubic symmetry because the trace of $\mathbb{V}^{\text{eff}}$ is 0). The splitting frequency $\Delta \nu$ is expressed by the first order perturbation theory of $\mathcal{H}_{\text{el}}$, for example, in the case of the axial symmetric EFG, as

\[ \Delta \nu = \frac{3 \cos^2 \theta - 1}{2} \nu_Q \leq |\nu_Q|, \] where $\theta$ represents the angle between the $z'$-axis and $\mathbb{H}^{\text{eff}}$. The inequality $\Delta \nu \leq |\nu_Q|$ is valid in general for $\mathcal{H}_{\text{el}} \ll \mathcal{H}_{\text{mag}}$. Therefore, since the present NMR spectra show $49\nu_Q$ is about 1.6 MHz,

\[ |49\nu_Q| \geq 1.6 \text{ MHz}. \] As mentioned above, $\nu_Q$ reflects the distortion of the EFG, i.e., the charge distribution. The EFG at Ti nuclei is contributed from the on-site 3$d$ electron and the outside $O^{2-}$, $La^{3+}$ and $Ti^{3+}$ ions. Generally, it is very difficult to estimate the contribution of outside ions to the EFG quantitatively, because the EFG from the outside ions is largely enhanced by core electrons (the Sternheimer antishielding factor $\gamma\infty$ corresponds to this effect). However, we could naively expect that the EFG originating from outside ions is small, since the distortion of $TiO_6$ octahedra is small in $LaTiO_3$.

The above value of $|49\nu_Q|$ is much larger than those of $ATiO_3$ compounds with $Ti^{4+}(3p^0)$, in which the EFG is determined only by the contribution of the outside ions[16, 19]. It is reported that the value of $49\nu_Q$ is 1.1 MHz for $MgTiO_3$, in which both of the crystalline and $TiO_6$ distortions are much larger than those in $LaTiO_3$[19]. Padro et al. systematically and quantitatively investigated the relationship between the EFG and the structural parameters for $ATiO_3$ compounds[19]. They found that the shear strain of $TiO_6$ octahedra well correlates with the EFG magnitude. In accordance with their argument, we derived the shear strain $|\Psi|$ of $LaTiO_3$ as 0.27 using the structural data at 8 K in Ref.13. From this value of $|\Psi|$ we estimate the value of $49\nu_Q$ contributed by the outside ions as $\sim 0.15$ MHz at 8 K. Even if we consider the difference of the valence of ions between $La^{3+}$+$Ti^{3+}$O$_3$ and $A^{2+}$+$Ti^{4+}$O$_3$, it is difficult to ascribe the origin of the large $\nu_Q$ value in $LaTiO_3$ to the outside ions. Therefore, the main contribution to the EFG at Ti nuclei should come from the on-site 3$d$ electron. So, we treat only $\mathcal{H}_{\text{el}}^\text{on}$ as the electric hyperfine interaction hereafter.

The conclusion mentioned above means that the shape of 3$d$ orbital is deformed from cubic symmetry. The
quadrupole frequency $\nu_Q$ is associated with the electron quadrupole moment $\mathbf{q}$. We define $q_{z'z'}$ as the maximum value of the principal-axes components for $\mathbf{q}$. We also introduce $r_{el}$ defined as $r_{el} = \langle r^{-3}\rangle_{el}/\langle r^{-3}\rangle_{F1}$, in which $\langle r^{-3}\rangle_{F1}$ represents the $r^{-3}$ expectation value of the 3d electron calculated for a free Ti$^{3+}$ ion, 2.552 a.u. [15]. We could expect $r_{el} < 1$ due to the hybridization with oxygen 2p states. Using Eqs. (4), (6), and (8), the following inequality is obtained for $q_{z'z'}$:

$$4^{9}\nu_Q = \frac{e^2 Q}{\hbar I(2I-1)} r_{el} \langle r^{-3}\rangle_{F1} q_{z'z'}, \quad (9)$$

$$|q_{z'z'}| \equiv |3L_2^2 - L^2| \geq 1.62/r_{el}. \quad (10)$$

The value of $|q_{z'z'}|$ takes 6 at the maximum for 3d$^1$ states, which is the case with the $d_{xy}$-type ($q_{z'z'} = 6$) and $d_{z^2}$-type ($q_{z'z'} = -6$) orbitals. The mixing among those orbitals reduces $|q_{z'z'}|$. Eq. (10) shows that the magnitude of the electron quadrupole moment $|q_{z'z'}|$ in LaTiO$_3$ is at least $1.62/6 \sim 27\%$ of those for $d_{xy}$-type or $d_{z^2}$-type orbitals. This result seems to be inconsistent with the proposed orbital liquid models [3, 4], since it is supposed to give a cubically symmetric charge distribution for 3d electrons and very small $q_{z'z'}$. Thus, another orbital ordered state is expected to be realized in LaTiO$_3$.

The neutron scattering measurements have shown that the ordered magnetic moment is 0.46 $\mu_B$ in the stoichiometric LaTiO$_3$ [21]. Since the spin-wave approximation for a three dimensional $S=1/2$ model gives shrunken ordered spin moments of 0.84 $\mu_B$, the observed moment is about 0.4 $\mu_B$ smaller. The origin of this shrinkage is unclear. The present NMR spectra show that the internal magnetic field $|\mathbf{H}^{eff}|$ at Ti nuclei is 92 kOe. $|\mathbf{H}^{eff}|$ is expressed as

$$|\mathbf{H}^{eff}| = 2\mu_H r_{mag} \langle r^{-3}\rangle_{F1}|(-\kappa \mathbf{S} - \frac{2}{21} S \cdot q + L)| = 92 \text{ kOe}, \quad (11)$$

where $r_{mag}$ represents $\langle r^{-3}\rangle_{mag}/\langle r^{-3}\rangle_{F1}$. The first term of Eq. (11) represents the Fermi contact field, the second the dipole field due to the electron spin moment, and the third the orbital field coming from the electron orbital moment. $r_{mag} \times \kappa$ is supposed to be 0.63 $\sim$ 0.75, since the isotropic hyperfine coupling constant $A_{iso} = -159.7 \times r_{mag} \kappa$ [kOe/$\mu_B$] by the Fermi contact interaction is generally given as $-100 \sim -120$ kOe/$\mu_B$ [12]. On the other hand, the ordered magnetic moment of 0.46 $\mu_B$ should correspond to

$$|\langle 2\mathbf{S} + \mathbf{L}\rangle| = 0.46. \quad (13)$$

So, Eqs. (12) and (13) must be satisfied at the same time. This restriction is so hard that it makes a good test for the models of the electronic states in LaTiO$_3$. As a rough estimation, if we assume that $\mathbf{S}$ and $\mathbf{L}$ are antiparallel, the orbital moment $|\mathbf{L}|$ cannot exceed 0.29/$r_{mag}$, since $|\kappa |\mathbf{S}|$ is larger than $2/21|\mathbf{S} \cdot q|$ in the present $d^1$ case.

As noted above, the NMR spectra of LaTiO$_3$ show that a certain amount of the Ti 3d electronic quadrupole moment is present. Mochizuki and Imada as well as Cwik et al. proposed that 3d electrons in LaTiO$_3$ occupy $1/\sqrt{3}(d_{xy}+d_{yz}+d_{zx})$-like orbitals and explained the physical properties of LaTiO$_3$ successfully [12, 13]. This model is consistent with the present NMR results. So we simulated the NMR spectra assuming this type of orbital state. We assumed that the magnetic moment is parallel to the $a$-axis [13, 21]. Furthermore, we set $A_{iso}$ as $-100$ kOe/$\mu_B$ with the assumption that $\mathbf{S}$ and $\mathbf{L}$ are antiparallel. The resonance intensity was derived from the transition probability between the nuclear spin eigenstates. The result is shown in Fig. 2. The simulated spectra well explain the experimental data. Especially, the resonance frequency is completely reproduced, while the deviation of the intensity is seen for outside peaks. The used parameters are listed in Table I. The 3d orbital states of Ti(1) - Ti(4) sites in LaTiO$_3$ are represented as $ad_{xy} - bd_{yz} - cd_{zx} = ad_{xy} - cd_{yz} - bd_{zx}$, $ad_{xy} + bd_{yz} + cd_{zx}$ and $ad_{xy} + cd_{yz} + bd_{zx}$, respectively, where $a^2 + b^2 + c^2 = 1$. The four Ti sites give same spectra in the case of $\mathbf{H}^{eff}$ parallel to the $a$-axis. The orbital parameters are determined as $a = 0.565$, $b = 0.452$ and $c = 0.690$, which are close to the results in Refs. 12 and 13. Figure 3 shows the orbital states in LaTiO$_3$ expected from these pa-
pointed out by Cwik et al.\textsuperscript{[13]}, and that some part of the reduced magnetic moment should be ascribed to other reasons. Mochizuki and Imada have accounted for the reduction by the itinerancy of the $t_{2g}$ electrons, i.e., the double occupation of up and down spin electrons in the $t_{2g}$ state\textsuperscript{[12]}. It seems to support this account that the increase of oxygen content gradually decreases the ordered moment and finally leads to a Pauli paramagnetic state.

In summary, we analyzed the $^{47,49}$Ti NMR spectra of LaTiO$_3$. The NMR technique can evaluate the electron quadrupole moment $q_{\text{el}}$, i.e., the order parameter of orbital ordering, quantitatively. The NMR spectra show that the electron quadrupole moment is rather large. It is supposed that LaTiO$_3$ takes an orbital ordering state represented approximately as $1/\sqrt{3}(d_{xy} + d_{yz} + d_{zx})$.

This work was supported by the Yamada Science Foundation and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.