NMR study of orbital ordering in $RTiO_3$ (R = Y, Gd, and La)

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Abstract

Recently, the orbital degree of freedom has attracted renewed interest in strongly correlated electron systems. The $RTiO_3$ (R: rare earths) system is one of the attracting systems in the study of the orbital degree of freedom. While an orbital ordering state is observed in a ferromagnet $YTiO_3$, no orbital ordering has yet been observed in an antiferromagnet $LaTiO_3$. In this study, we have measured ^{47,49}Ti NMR spectra of $RTiO_3$ (R = Y, Gd, and La). We investigate the orbital state by analyzing the NMR spectra of $RTiO_3$.

Key words: $RTiO_3$; orbital ordering; NMR

In addition to the charge and spin degrees of freedom, the orbial degree of freedom plays an important role in the physical properties of the transition-metal oxides. In spite of the importance of the orbital degree of freedom, experimental techniques to observe the orbital states have been limited so far.

In this paper, we report the results of NMR measurment of $RTiO_3$ (R = Y, Gd, and La). The NMR technique is expected to be powerful to investigate the orbital states. We focus on ferromagnetic $YTiO_3$(Curie temperature T_C=30 K), $GdTiO_3$(T_C=34 K), and antiferromagnetic $LaTiO_3$(Néel temperature T_N = 150 K). $RTiO_3$ has an orthorhombically distorted perovskite structure (space group: P_{bnm}), in which the electronic configuration of Ti^{3+} ions is ${t_{2g}}^1$. Many experimental and theoretical studies suggested that the degeneracy of ${t_{2g}}^1$ configuration in $YTiO_3$ is lifted by the *d*-type Jahn-Teller distortion and the "antiferromagnetic" orbital ordering, and it causes the ferromagnetism in $YTiO_3$[1–5]. By contrast, no orbital ordering has yet been observed in $LaTiO_3$, which undergoes *G*-type antiferromagnetic ordering. The origin of *G*-type antiferromagnetic ordering and the orbital state at the ground state in $LaTiO_3$ have been unclear[6,7]. Substitution of La by smaller rare earth ions in $LaTiO_3$ brings about magnetic transition from antiferromagnetism to ferromagnetism. It is not well understood how the orbital states of this system are related with the magnetic transition. Thus, the relationship between the magentism and the orbital states is an attracting problem in this system[7]. So, in order to investigate the orbital states, we performed zero-field NMR measurements of $RTiO_3$ and the simulation of the NMR spectra assuming various orbital states.

Polycrystalline $RTiO_3$ (R=Y, Gd, and La) samples were prepared by arc melting of appropriate mixtures of R_2O_3 , TiO_2, and Ti in an argon atmosphere. All samples were confirmed to be almost a single phase by powder x-ray measurements. ^{47,49}Ti NMR measurements of $RTiO_3$ were performed in zero external field. Frequency-swept NMR spectra were taken point by point of frequency by using a coherent pulsed spectrometer.

Figure 1 shows the frequency-swept ^{47,49}Ti NMR spectra in magnetically ordered states of $RTiO_3$ (R = Y, Gd, and La). The solid curves represent the results of

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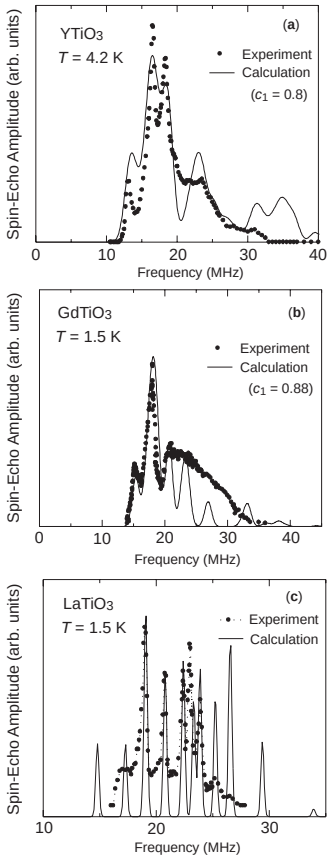

Fig. 1. ^{47,49}Ti NMR spectra in (a) $YTiO_3$, (b) $GdTiO_3$, and (c) $LaTiO_3$. Solid circles represent experimental data taken in zero external field. Solid curves show the calculated spectra based on the orbital ordering model(see the text).

the simulation based on the orbital ordering model with the hyperfine hamiltonian $\mathcal{H}$. The hyperfine interaction $\mathcal{H}$ on $3d$ transition-metal ions of a shell less than half-filled is expressed as[4],

$$\mathcal{H} = \mathcal{H}_{\rm mag} + \mathcal{H}_{\rm el}^{(1)} + \mathcal{H}_{\rm el}^{(2)}, \quad (1)$$

$$\mathcal{H}_{\rm mag} = 2\mu_B\gamma_n\hbar\langle r^{-3}\rangle_{\rm mag}[-\kappa\mathbf{S}\cdot\mathbf{I} + \mathbf{L}\cdot\mathbf{I} + \xi\{L(L+1) - \frac{3}{2}(\mathbf{L}\cdot\mathbf{I})(\mathbf{L}\cdot\mathbf{S}) - \frac{3}{2}(\mathbf{L}\cdot\mathbf{S})(\mathbf{L}\cdot\mathbf{I})\}], \quad (2)$$

$$\mathcal{H}_{\rm el}^{(1)} = \frac{S\xi e^2Q}{I(2I-1)}\langle r^{-3}\rangle_{\rm el}\{3(\mathbf{L}\cdot\mathbf{I})^2 + \frac{3}{2}(\mathbf{L}\cdot\mathbf{I}) - L(L+1)I(I+1)\}, \quad (3)$$

$$\mathcal{H}_{\rm el}^{(2)} = (1-\gamma_\infty)\frac{eq}{6I(2I-1)} \times \sum_{\alpha\beta} V_{\alpha\beta}[\frac{3}{2}(I_{\alpha\beta} + I_{\beta\alpha}) - \delta_{\alpha\beta}I^2], \quad (4)$$

where μ_B represents the Bohr magneton, $\gamma_{\rm n}$ the nuclear gyromagnetic ratio ($^{47}\gamma_n = 2\pi\times2.400\times10^2$ Hz/Oe and $^{49}\gamma_n = 2\pi \times 2.405 \times 10^2$ Hz/Oe), $\hbar$ the Planck's constant, $\langle r^{-3}\rangle_{\rm mag}$ and $\langle r^{-3}\rangle_{\rm el}$ the expectation values of r^{-3} for the $3d$ orbital, κ the Fermi contact interaction parameter, Q the nuclear quadrapole moment ($^{47}Q = +0.29$ and $^{49}Q = +0.24$ barns) , γ_∞ the Sternheimer antishielding factor, $V_{\alpha\beta}$ (α,β=x,y,and z) a component of the electric field gradient (EFG) tensor, $\mathbf{S}$ the total spin, $\mathbf{L}$ the total orbital momentum, l the orbital momentum, and $\mathbf{I}$ the nuclear spin operator ($^{47}I = 5/2$ and $^{49}I = 7/2$).

The calculated curves reproduce well the experimental result in $YTiO_3$. The curves are obtained by using the parameters, κ=0.83, $\langle r^{-3}\rangle_{\rm mag} = 0.5\langle r^{-3}\rangle_{\rm HF}$, $\langle r^{-3}\rangle_{\rm el} = 0.6\langle r^{-3}\rangle_{\rm HF}$, and $\gamma_\infty = -4$ and $c_1 = 0.8$ where the $3d$ wave function of the Ti(1) site is expressed as $\psi_1 = c_1yz + c_2xy \quad (c_1^2 + c_2^2 = 1)$. The notation of the wave functions at Ti(1)-Ti(4) sites follows Ref. 4. $\langle r^{-3}\rangle_{\rm HF}$ represents the Hartree-Fock value of 2.522 atomic units. The value of c_1 is consistent with theoretical studies[1,2]. The spectrum of $GdTiO_3$ is also well reproduced with the parameters κ=1, $\langle r^{-3}\rangle_{\rm mag} = 0.53\langle r^{-3}\rangle_{\rm HF}$, $\langle r^{-3}\rangle_{\rm el} = 0.6\langle r^{-3}\rangle_{\rm HF}$, and $\gamma_\infty = -4$ and $c_1 = 0.87$, although a discrepancy is seen around 30 MHz. This result indicates that $GdTiO_3$ takes almost the same orbital ordering configuration as $YTiO_3$. As for $LaTiO_3$, an orbital ordering model accompanied with a D_{3d} distortion is proposed by Mochizuki and Imada[7]. Under the D_{3d} distortion, Ti $3d$ electron occupies the lower a_{1g} level such as $\frac{1}{\sqrt{3}}(xy+yz+zx)$. The solid curves in the Fig. 1(c) are obtained assuming this type of orbital ordering with the parameters κ=0.83, $\langle r^{-3}\rangle_{\rm mag} = 0.62\langle r^{-3}\rangle_{\rm HF}$, $\langle r^{-3}\rangle_{\rm el} = 0.6\langle r^{-3}\rangle_{\rm HF}$, and $\gamma_\infty = -4$. The experimental results show an agreement with the calculated one and it supports this type of orbital ordering model.

In summary, we made ^{47,49}Ti NMR measurements on $RTiO_3$ (R = Y, Gd, and La) and the simulation of the NMR spectra assuming various orbital ordering. The NMR spectra of $RTiO_3$ were understood by the proposed orbital ordering models.

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