

# Magnetic Properties of Layered Perovskites $\text{NaLnTiO}_4$ ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ )

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The magnetic properties of the layered perovskite compounds  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ ) are reported. Their dc susceptibilities were measured from 4.5 to 320 K. The Mössbauer spectrum of  $^{151}\text{Eu}$  and the electron paramagnetic resonance (EPR) spectrum of  $\text{Gd}^{3+}$  were also measured at room temperature.  $\text{NaEuTiO}_4$  shows Van Vleck paramagnetism which corresponds to the singlet ground state  ${}^7F_0$  of  $\text{Eu}^{3+}$  ions, with a spin-orbit coupling constant  $\lambda = 323 \text{ cm}^{-1}$ .  $\text{NaSmTiO}_4$  also behaves as a Van Vleck paramagnet. The magnetic susceptibility of  $\text{NaGdTiO}_4$  follows the Curie law. The Mössbauer spectrum of  $\text{NaEuTiO}_4$  clearly shows that Eu is in the trivalent state, and a quadrupole interaction is found to exist in this compound. From the EPR measurement the  $g$  value of  $\text{Gd}^{3+}$  in  $\text{NaGdTiO}_4$  is determined to be 1.99. Both the magnetic susceptibility results and the EPR measurements show that  $\text{Gd}^{3+}$  ion in this compound is scarcely affected by the crystal field. © 1998 Academic Press

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## INTRODUCTION

It is known that the series of lanthanide elements forms layered perovskite compounds  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{lanthanide elements}$ ) with sodium and titanium. These compounds were first synthesized by Blasse *et al.* and were determined to have the tetragonal structure (1). Toda *et al.* (2) recently refined the structure of the layered perovskite compounds  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ ) and pointed out that they have the orthorhombic structure with space group *Pbcm* (No. 57). A feature of these layered  $A_2\text{BO}_4$  (Ruddlesden-Popper type) perovskite compounds is that monovalent  $\text{Na}^+$  and trivalent  $\text{Ln}^{3+}$  in *A*-cation sites are ordered. Because the  $\text{Ln}$  ion is the only magnetic ion in these compounds, it is convenient to examine the magnetic behavior of  $\text{Ln}^{3+}$  ions in solids. In this study, we synthesized layered perovskite compounds  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ )

and measured their magnetic susceptibilities, Mössbauer spectra, and EPR spectra.

## EXPERIMENTAL

### 1. Sample Preparation

Samples of  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ ) were prepared by standard solid state reaction (2). The starting materials were  $\text{Ln}_2\text{O}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{TiO}_2$ . They were weighed and ground in an agate mortar. The mixtures were pressed into a pellet and heated in air at  $950^\circ\text{C}$  for 30 min. An excess of  $\text{Na}_2\text{CO}_3$  (30 mol%) was added to compensate for the loss due to sodium evaporation during heating. After the reaction, the excess  $\text{Na}_2\text{CO}_3$  was removed by filtration with methanol.

### 2. X-Ray Diffraction and Magnetic Measurements

Powder X-ray diffraction patterns were measured with an RINT2000 (Rigaku) with  $\text{CuK}\alpha$  radiation. The X-ray data were refined using Rietveld analysis with Rietan (3).

Dc magnetic susceptibilities were measured with a SQUID magnetometer (Quantum Design, Model MPMS) in the temperature range 4.5 K to room temperature.

EPR measurements were made at room temperature using a JEOL 2XG spectrometer operating at X-band frequency ( $\sim 9.1 \text{ GHz}$ ). The magnetic field was swept up to 13,500 G.

The  $^{151}\text{Eu}$  Mössbauer spectrum was measured with a VT-6000 spectrometer (Laboratory Equipment Co., Japan) at room temperature.

## RESULTS AND DISCUSSION

X-ray data showed that all the samples in this study were formed in a single phase. They were indexed with an

orthorhombic unit cell, space group  $Pbcm$  (No. 57). The reliability factors  $R_{\text{wp}}$

$$R_{\text{wp}} = \left\{ \frac{\sum_i w_i [y_i - f_i(x)]^2}{\sum_i w_i y_i^2} \right\} \quad [1]$$

were as low as 0.10, where  $y_i$  and  $f_i(x)$  are the observed and calculated intensities, respectively, and  $w_i$  is the weight for each intensity. These results are in agreement with previous structural data (2). The structure of these compounds is shown in Fig. 1. In these compounds, the lanthanide ions are nine-coordinated by oxygen ions, and the average  $\text{Ln}-\text{O}$  distances are 2.556, 2.551, and 2.546 Å for  $\text{NaSmTiO}_4$ ,  $\text{NaEuTiO}_4$ , and  $\text{NaGdTiO}_4$ , respectively. This trend of the  $\text{Ln}-\text{O}$  distance is easily understandable by considering the ionic radius of  $\text{Ln}^{3+}$  in  $\text{NaLnTiO}_4$ .

### $\text{NaEuTiO}_4$

The temperature dependence of the dc magnetic susceptibility of  $\text{NaEuTiO}_4$  is shown in Fig. 2. The shape of this susceptibility vs temperature curve is characteristic of a Van Vleck paramagnet, with a constant susceptibility for the lower temperature range and a decreasing susceptibility with increasing temperature for temperatures  $\geq 100$  K.

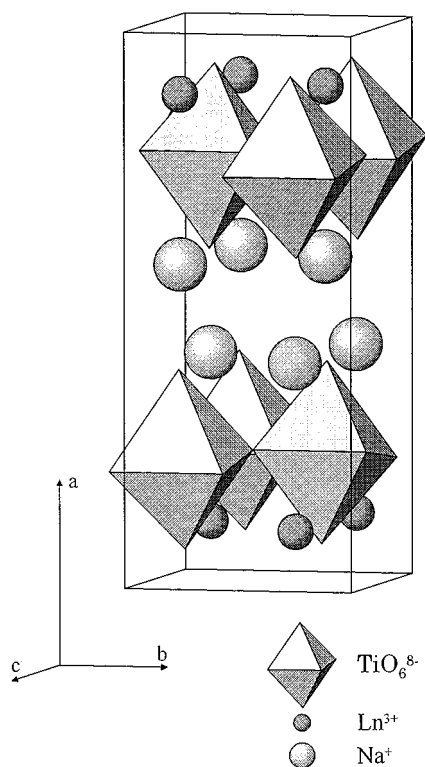


FIG. 1. Crystal structure of  $\text{NaLnTiO}_4$  ( $\text{Ln} = \text{Sm}, \text{Eu}, \text{and Gd}$ ).

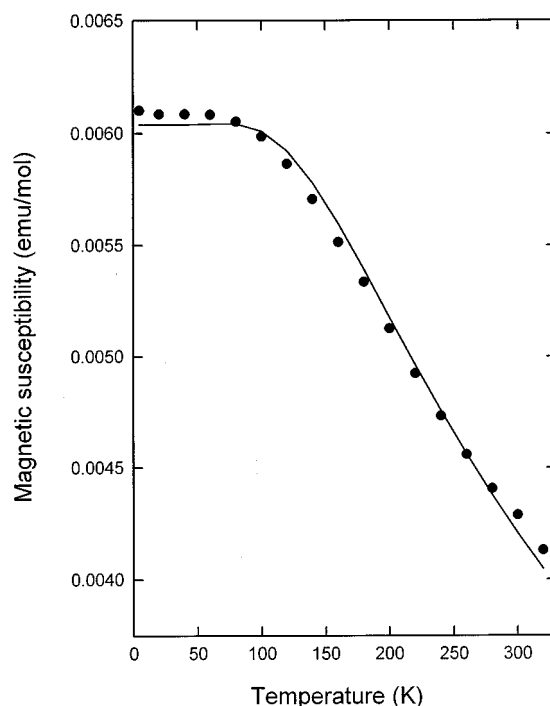


FIG. 2. Magnetic susceptibility vs temperature for  $\text{NaEuTiO}_4$ . The best fit to  $\chi(T)$  (solid line), using Eq. [2], was achieved for  $\lambda = 323 \text{ cm}^{-1}$  (see text).

The ground state  ${}^7F_0$  of  $\text{Eu}^{3+}$  is nonmagnetic and the excited states  ${}^7F_J$  are close enough to give energy differences comparable to  $k_B T$  at room temperature. The susceptibility per mole of  $\text{Eu}^{3+}$  is given by

$$\chi(\text{Eu}^{3+}) = \frac{\left(\frac{C}{T}\right) (24/\gamma) + (13.5 - (3/2\gamma))e^{-\gamma} + (67.5 - (5/2\gamma))e^{-3\gamma} + \dots}{1 + 3e^{-\gamma} + 5e^{-3\gamma} + \dots} \quad [2]$$

with  $C = [N_A \mu_B^2 / (3k_B)]$ , where  $N_A$  and  $\mu_B$  are Avogadro's number and the Bohr magneton, respectively (4). The parameter  $\gamma = \lambda / (k_B T)$  is the ratio of the multiplet width (the spin-orbit coupling constant,  $\lambda$ ) and the thermal energy ( $k_B T$ ). Subsequent terms not shown in Eq. [2] give negligible contributions to the magnetic susceptibility of  $\text{Eu}^{3+}$  in this temperature range.

The best fit of Eq. [2] to the experimental data is shown in Fig. 2 with a solid line, which gives  $\lambda = 323 \text{ cm}^{-1}$ . This value is reasonable for the spin-orbit coupling constant for  $\text{Eu}^{3+}$  in solids. In the case of  $\text{Eu}^{3+}$  compounds, the energy difference between the ground state  ${}^7F_0$  and the first excited state  ${}^7F_1$  is just equal to the value of the spin-orbit coupling constant. The energy difference determined here from the magnetic susceptibility measurements is comparable to those found in other  $\text{Eu}^{3+}$  compounds, for example,

365  $\text{cm}^{-1}$  ( $\text{Eu}_2\text{BaZnO}_5$ ) (5) and 370  $\text{cm}^{-1}$  ( $\text{EuAlO}_3$ ) (6). The value for  $\text{NaEuTiO}_4$  is slightly smaller than those for  $\text{Eu}_2\text{BaZnO}_5$  and  $\text{EuAlO}_3$ , which may be due to the larger screening effect in  $\text{NaEuTiO}_4$  compared with those in  $\text{Eu}_2\text{BaZnO}_5$  and  $\text{EuAlO}_3$ .

Figure 3 is the  $^{151}\text{Eu}$  Mössbauer spectrum of  $\text{NaEuTiO}_4$  measured at room temperature. The Eu site in  $\text{NaEuTiO}_4$  ( $Pbcm$ ) has the point symmetry  $m$ . This point symmetry indicates that an electric field gradient (EFG) tensor (7) exists. Therefore nonzero quadrupole interaction is expected at the Eu site. The quadrupole interaction is given by

$$H_Q = \frac{e^2qQ}{4I(2I-1)} [3I_z^2 - I(I+1) + \eta(I_x^2 - I_y^2)], \quad [3]$$

where  $I$  is the nuclear spin,  $Q$  is the quadrupole moment,  $eq = V_{zz}$ , and  $\eta = (V_{xx} - V_{yy})/V_{zz}$  ( $V_{ii}$  is the electric field gradient tensor) (8). Actually, the spectrum exhibited a slightly asymmetric line. It is impossible to fit such a spectrum with a single Lorentzian line because of the distortion due to the quadrupole interaction. The point symmetry  $m$  is not axially symmetric, and the asymmetry parameter  $\eta \neq 0$  in Eq. [3].

Figure 4 shows 12 possible transitions due to a quadrupole interaction. The spectrum was, therefore, fitted with 12 Lorentzian lines as shown in Fig. 3 (9). The positions of the lines depend on the isomer shift  $\delta$ , the quadrupole coupling constant  $eV_{zz}Q_g$ , the ratio  $R_Q = Q_e/Q_g$  of the excited and ground state quadrupole moments, and the asymmetry parameter  $\eta$ . The following numerical values were adopted in this study:  $R_Q = 1.312$  and  $Q_g = 1.14$  (10). Table 1 shows the  $^{151}\text{Eu}$  Mössbauer parameters determined for the  $\text{Eu}^{3+}$  in  $\text{NaEuTiO}_4$ . The value of the isomer shift  $\delta$  (0.59 mm/s) confirms that the Eu ions are in the trivalent state (11). The quadrupole coupling constant ( $eV_{zz}Q_g$ ) and the asymmetry

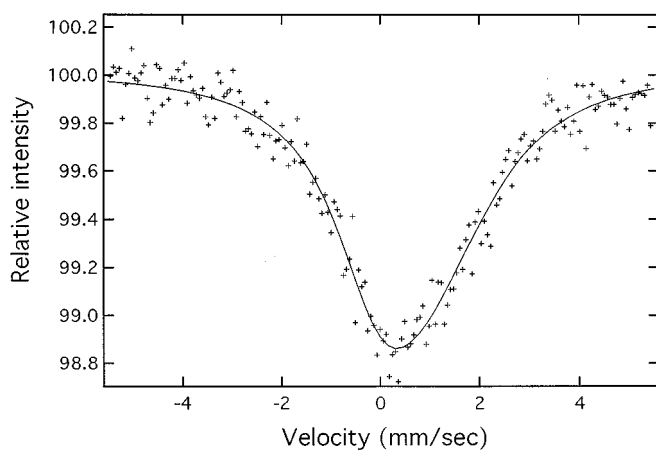


FIG. 3.  $^{151}\text{Eu}$  Mössbauer spectrum of  $\text{NaEuTiO}_4$  at room temperature. The solid line is a computer fit with 12 Lorentzians.

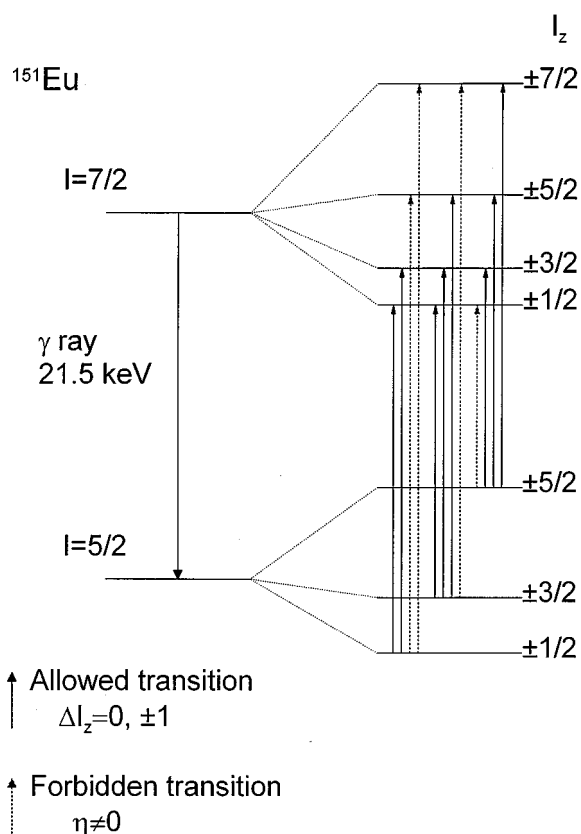


FIG. 4. Twelve transitions due to quadrupole interaction of  $^{151}\text{Eu}$ .

parameter are determined to be  $-7.04$  mm/s and 0.17, indicating the existence of the quadrupole interaction in  $\text{NaEuTiO}_4$ , i.e., the electric field gradient at the Eu nuclei. The quadrupole coupling constant is negative in this case.

#### $\text{NaSmTiO}_4$

The molar magnetic susceptibility of  $\text{NaSmTiO}_4$  as a function of temperature is shown in Fig. 5. At low temperatures, only the magnetic  $^6H_{5/2}$  ground multiplet is populated. However, similarly to the  $\text{Eu}^{3+}$  case, the energy difference between the ground state  $^6H_{5/2}$  and the first excited state  $^6H_{7/2}$  for  $\text{Sm}^{3+}$  is not so large compared to  $k_B T$ ; we must take the population to the excited state into

TABLE 1  
 $^{151}\text{Eu}$  Mössbauer Parameters of  $\text{NaEuTiO}_4^a$

$\delta$ (mm/s)	$eV_{zz}Q_g$ (mm/s)	$\eta$
0.59	-7.04	0.17

<sup>a</sup>  $\delta$ ,  $eV_{zz}Q_g$ , and  $\eta$  are isomer shift, quadrupole coupling constant, and asymmetry parameter, respectively.

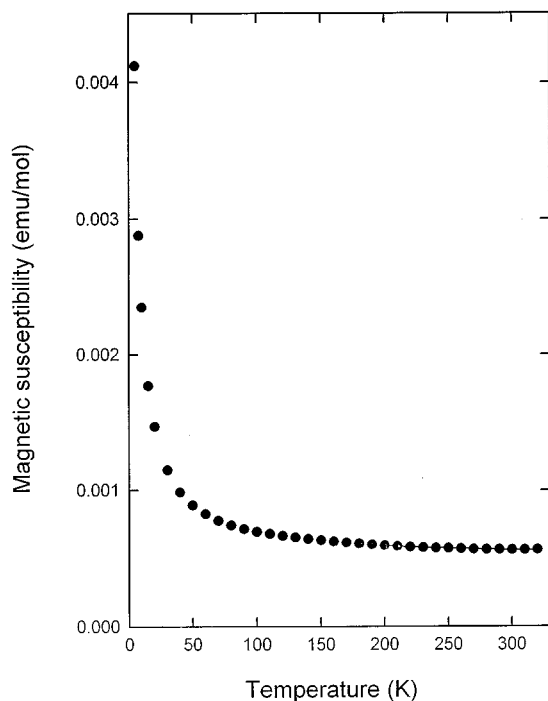


FIG. 5. Magnetic susceptibility vs temperature for  $\text{NaSmTiO}_4$ . The best fit to Eq. [4] in the high-temperature range is shown by a solid line.

consideration in the calculation of the magnetic susceptibility at high temperatures. The magnetic susceptibility for  $\text{NaSmTiO}_4$  in the temperature range 200–320 K is given by

$$\chi(\text{Sm}^{3+}) = \frac{C_1}{T} + \alpha_1 + \frac{C_2}{T} e^{-\Delta/T}, \quad [4]$$

where  $\Delta$  is the energy difference between the ground state and the first excited state, and  $C_i$  and  $\alpha_1$  are the Curie and Van Vleck constants, respectively.  $\Delta$  and  $\alpha_1$  have the relation  $\alpha_1 = 1.07/\Delta$ , when  $\Delta$  is given in kelvins.  $C_2$  is fixed at 1.34, which is calculated for the first excited state  ${}^6H_{7/2}$ . The fit to the experimental data (see Fig. 5) gives  $C_1 = 0.0195$  and  $\Delta = 1500 \text{ cm}^{-1}$ . The calculated effective magnetic moment at 300 K is calculated to be  $\mu_{\text{eff}} = 0.405 \mu_B$ . The magnetic moment determined in this study is smaller than the free moment for  $\text{Sm}^{3+}$ , which is probably due to the effect of the crystal field.

#### $\text{NaGdTiO}_4$

The reciprocal magnetic susceptibility of  $\text{NaGdTiO}_4$  as a function of temperature is shown in Fig. 6. This  $1/\chi-T$  plot is fitted well with a straight line. This property is characteristic of the ground state of  ${}^8S_{7/2}$ . It obeys the Curie law. The effective magnetic moment of the  $\text{Gd}^{3+}$  ion is determined to be  $7.89 \mu_B$  from this gradient.

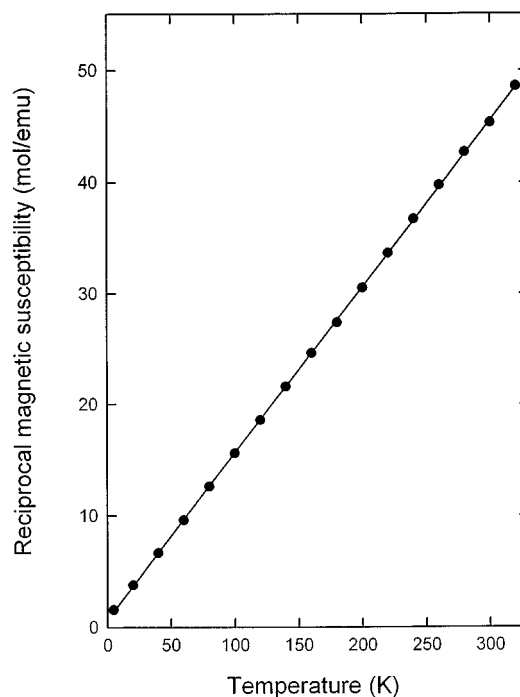


FIG. 6. Reciprocal magnetic susceptibility vs temperature for  $\text{NaGdTiO}_4$ . The best fit is shown by a solid line.

Figure 7 shows the X-band EPR spectrum for  $\text{Gd}^{3+}$  in  $\text{NaGdTiO}_4$  at room temperature. A single broad line centered at the magnetic field 3274 G (therefore  $g = 1.99$ ) was observed. The effective magnetic moment ( $\mu_{\text{eff}} = 7.90 \mu_B$ ) calculated from the EPR data is in good agreement with that from the magnetic susceptibility. The ground state of a trivalent gadolinium free ion is  ${}^8S_{7/2}$  and the theoretical magnetic moment is  $7.94 \mu_B$ . From this experiment, the  $\text{Gd}^{3+}$  ion in  $\text{NaGdTiO}_4$  is scarcely affected by the crystal field because the effective magnetic moment of the  $\text{Gd}^{3+}$  ion

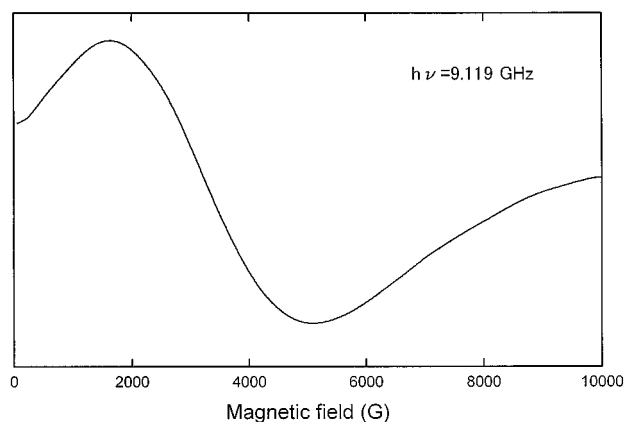


FIG. 7. EPR spectrum of  $\text{Gd}^{3+}$  in  $\text{NaGdTiO}_4$  at room temperature.

determined from both the magnetic susceptibility and EPR measurements agrees well with the theoretical moment for the free  $Gd^{3+}$  ion.

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