

# Magnetic Susceptibilities and Electron Paramagnetic Resonance Spectra of Lithium-Rich Lanthanide Oxides $\text{Li}_8\text{PrO}_6$ and $\text{Li}_8\text{TbO}_6$

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Lithium-rich lanthanide oxides  $\text{Li}_8\text{PrO}_6$  and  $\text{Li}_8\text{TbO}_6$  were prepared and their magnetic properties were studied. The effective magnetic moments for the praseodymium and terbium ions and the observation of their electron paramagnetic resonance (EPR) spectra show that the lanthanide ions are in the tetravalent oxidation state in these compounds. The low effective magnetic moment for the  $\text{Pr}^{4+}$  ion in the  $\text{Li}_8\text{PrO}_6$  corresponds to the low  $g$  value measured from the EPR measurement. The observation of the EPR spectrum at room temperature strongly shows that the terbium ion is in the  $S$  ground state, i.e., in the tetravalent state. © 1997 Academic Press

## INTRODUCTION

The most stable oxidation state of lanthanide ions is trivalent. In addition to this state, cerium, praseodymium, and terbium have the tetravalent state (1). We are interested in the preparation of compounds in which these ions at the tetravalent state are accommodated and their magnetic properties to elucidate the behavior of  $4f$  electrons in solids.

In an earlier work (2, 3, 4), we studied the perovskite-type oxides  $\text{ABO}_3$  where  $A$  is a divalent ion (e.g., Sr, Ba) and the tetravalent metal ions are located at the  $B$  sites of the crystals. The oxygen stoichiometric tetravalent praseodymium perovskite  $\text{BaPrO}_3$  and terbium perovskites  $\text{BaTbO}_3$  and  $\text{SrTbO}_3$  were prepared (2, 3). The observation of the electron paramagnetic resonance (EPR) spectra for these compounds (for the case of  $\text{BaPrO}_3$ , it needs magnetic dilution with diamagnetic  $\text{BaCeO}_3$ ) (4) strongly indicates that the oxidation states of praseodymium and terbium ions are not trivalent, but tetravalent, because the non-Kramers  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  ions usually show no EPR spectra (5). These complex oxides show magnetic ordering at low temperatures ( $T_N = 11.5, 32.7,$  and  $30.5$  K, respectively).

In the present study, we focus our attention on the lithium-rich lanthanide oxides  $\text{Li}_8\text{LnO}_6$  ( $\text{Ln} = \text{Pr}, \text{Tb}$ ). This type of compound is isostructural with  $\text{Li}_8\text{SnO}_6$  (space group  $R\bar{3}$ ) (6–8), the structure of which consists of isolated  $\text{SnO}_6$  octahedra and a slightly distorted hexagonal closed

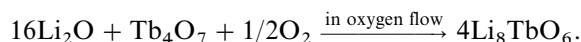
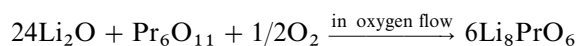
packing of oxygen atoms (9). That is, the praseodymium and terbium ions are octahedrally coordinated by six oxygen ions and we can easily analyze the results of the magnetic measurements.

## EXPERIMENTAL

### 1. Sample Preparation

Relatively little is known about the synthesis of ternary oxides of the lanthanides with alkali metals. This is due to the experimental reasons. The high melting points of the lanthanide oxides and the relatively high vapor pressures of the alkali metal oxides make it difficult to prepare the single phase of ternary oxides.

The synthesis of pure powder samples of the lithium-rich oxides  $\text{Li}_8\text{MO}_6$  is only possible when  $\text{Li}_2\text{O}$  or  $\text{Li}_2\text{O}_2$  is used as one starting material (10). In this study,  $\text{Li}_2\text{O}$  and  $\text{Pr}_6\text{O}_{11}$  ( $\text{Tb}_4\text{O}_7$ ) were used as the starting materials. The purity of these starting materials was 99.99%.  $\text{Li}_8\text{PrO}_6$  and  $\text{Li}_8\text{TbO}_6$  were prepared by the following reactions:



Both the compounds were prepared by heating pellets of the ground mixtures of  $\text{Pr}_6\text{O}_{11}$  ( $\text{Tb}_4\text{O}_7$ ) and 5 w/o excess  $\text{Li}_2\text{O}$  under flowing oxygen atmosphere at  $700^\circ\text{C}$ . After cooling to room temperature, the samples were crushed into powders in a dry box, pressed into pellets again, and reacted under the same conditions. The color of the  $\text{Li}_8\text{PrO}_6$  prepared in this study was pale yellow and that of  $\text{Li}_8\text{TbO}_6$  was bright yellow.

### 2. Analysis

An X-ray diffraction analysis was performed with  $\text{CuK}\alpha$  radiation on a Phillips PW 1390 diffractometer equipped with a curved graphite monochromator. The lattice parameters of the samples were determined by a least-squares method.

### 3. Magnetic Susceptibility Measurements

The temperature dependence of the magnetic susceptibilities was measured both with a Faraday-type torsion balance and with a commercial SQUID magnetometer (Quantum Design, MPMS model).

The temperature range of the magnetic susceptibility measurements with the magnetic balance was between 4.2 K and room temperature. The apparatus was calibrated with  $\text{CoHg}(\text{SCN})_4$  as a standard (11). The temperature of the sample was measured by a "normal" Ag vs Au-0.07 at% Fe thermocouple (4.2–40 K) (12) and an Au-Co vs Cu thermocouple (10 K – room temperature).

The magnetic susceptibility measurements with the SQUID magnetometer were carried out at 1000 G in the temperature range between 4.5 and 300 K.

The magnetic susceptibility measurements with the magnetic torsion balance and with the SQUID magnetometer gave the same results.

### 4. Electron Paramagnetic Resonance Measurements

The EPR measurements were carried out with a JEOL RE-2X spectrometer operating at X-band frequency (9.1 GHz) with 100-kHz field modulation. Measurements were made both at room temperature and at 4.2 K. The magnetic field was swept from 100 to 13,500 G. Before the specimen was measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or sample tube. The magnetic field was monitored with a proton NMR gaussmeter, and the microwave frequency was measured with a frequency counter.

## RESULTS AND DISCUSSION

The X-ray diffraction analysis shows that the compounds prepared in this study,  $\text{Li}_8\text{PrO}_6$  and  $\text{Li}_8\text{TbO}_6$ , are both hexagonal and that their lattice parameters are  $a = 5.609$ ,  $c = 15.982 \text{ \AA}$  and  $a = 5.550$ ,  $c = 15.710 \text{ \AA}$ , respectively. These compounds were also prepared by heating the mixtures of starting materials in an evacuated quartz tube at the same temperature, 700°C. However, the compounds prepared under a flowing oxygen atmosphere were more crystalline than those prepared in a quartz tube. We also tried to prepare these lithium-rich oxides from  $\text{Li}_2\text{CO}_3$  as one starting material. However, the desired compounds were not prepared, as Hoppe *et al.* had pointed out (10).

Figure 1 shows the reciprocal magnetic susceptibility vs temperature curve for  $\text{Li}_8\text{PrO}_6$ . This figure clearly indicates that there exists no magnetic cooperative phenomenon between praseodymium ions. No magnetic field dependence of the susceptibility was found at 4.2 K, 77.3 K, and room temperature. This result is easily understood from its crystal structure (see Fig. 2). The praseodymium ions are octahed-

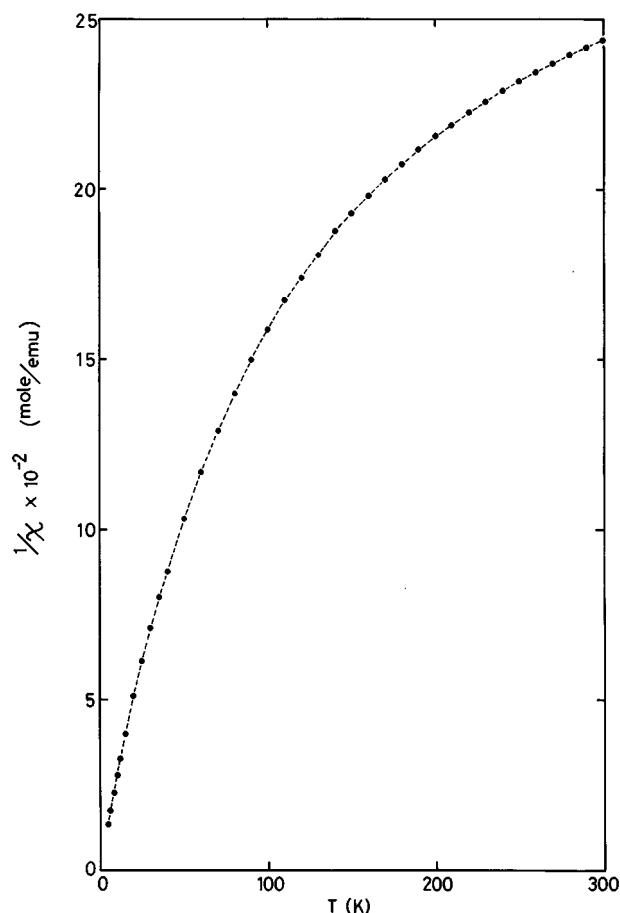
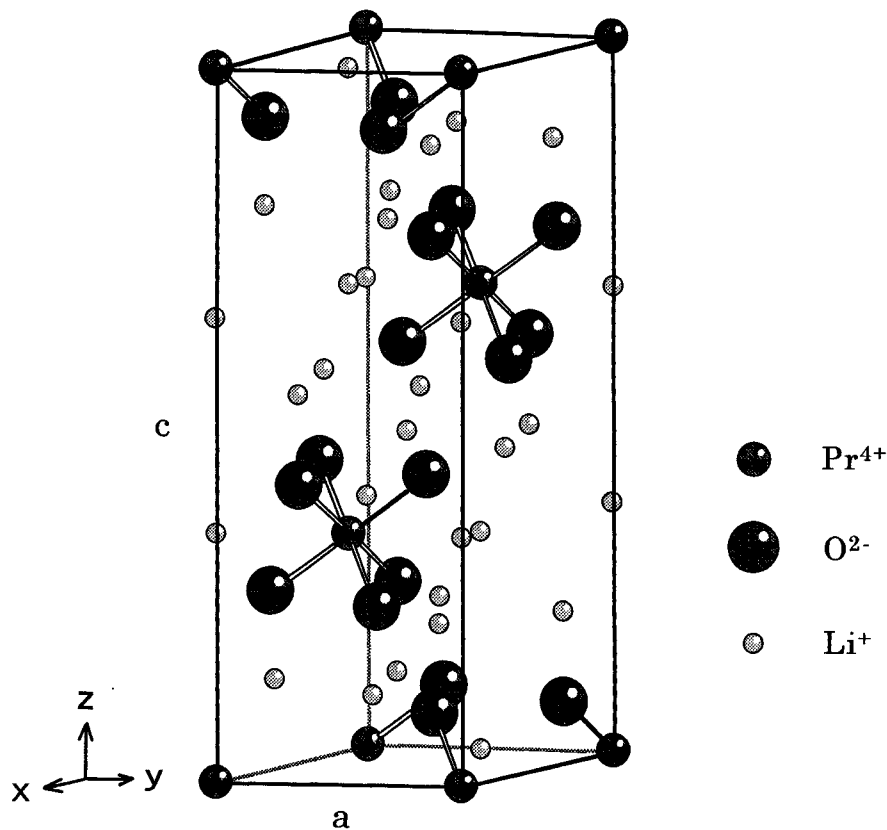


FIG. 1. Temperature dependence of reciprocal magnetic susceptibility for  $\text{Li}_8\text{PrO}_6$ .

rally coordinated by six oxygen ions and their octahedra are located separately, which indicates that the possibility of magnetic interaction between neighboring praseodymium ions is quite low.

The magnetic susceptibility of this compound follows the modified Curie-Weiss law. From the extrapolation of the measured magnetic susceptibility ( $\chi_{\text{exp}}$ ) to  $1/T \rightarrow 0$ , the temperature-independent paramagnetism ( $\chi_{\text{TIP}}$ ) was obtained ( $267 \times 10^{-6}$  emu/mole). The resulting temperature-dependent susceptibility ( $\chi(T) = \chi_{\text{exp}} - \chi_{\text{TIP}}$ ) followed the Curie law ( $\chi = 0.0316/T$  (emu/mole)). The effective magnetic moments of praseodymium can be calculated from this temperature-dependent part of the susceptibility; it is  $0.503 \mu_B$ . This small effective magnetic moment of  $\text{Pr}^{4+}$  in  $\text{Li}_8\text{PrO}_6$  is in accordance with the results from the EPR spectrum measurement, which will be described later. The obtained moment is much smaller than that expected for a free  $f^1$  ion ( $2.54 \mu_B$ ), which indicates that the crystal field with octahedral symmetry has a significant effect on the magnetic properties of the  $\text{Pr}^{4+}$  ion. A comparably small magnetic moment

FIG. 2. Crystal structure of  $\text{Li}_8\text{PrO}_6$ .

has been found in the  $\text{Pr}^{4+}$  ion for  $\text{BaPrO}_3$  and in the actinide ion with  $[\text{Rn}]5f^1$  configuration ( $[\text{Rn}]$ : Rn core) in the same octahedral crystal field environment (13–15).

For the praseodymium ion in the tetravalent state, an EPR spectrum should be observed because the  $\text{Pr}^{4+}$  ion is a Kramers ion ( $[\text{Xe}]4f^1$  configuration). However, no EPR spectra were observed even at 4.2 K for pure  $\text{Li}_8\text{PrO}_6$ . Our previous study (3, 4) shows that the EPR spectra of the  $\text{Pr}^{4+}$  ion can be observed by diluting it in a diamagnetic substance. So, in this study, we have prepared the samples for the EPR measurements in which the  $\text{Pr}^{4+}$  ion is doped in a diamagnetic  $\text{Li}_8\text{CeO}_6$ . The preparation procedure is the same as that for  $\text{Li}_8\text{PrO}_6$ ; the intimate mixtures of  $\text{Li}_2\text{O}$ ,  $\text{Pr}_6\text{O}_{11}$ , and  $\text{CeO}_2$  were heated under a flowing oxygen atmosphere at  $700^\circ\text{C}$  (the ratio of which is  $\text{Li}_2\text{O}/2:\text{Pr}_6\text{O}_{11}/6:\text{CeO}_2 = 8:0.02:0.98$ ). No EPR spectra were measured at room temperature. At 4.2 K, the EPR spectrum could be measured. The EPR spectrum for  $\text{Pr}^{4+}/\text{Li}_8\text{CeO}_6$  is shown in Fig. 3 (bottom). The observation of the EPR spectrum means that the praseodymium ion is not in the trivalent state, but in the tetravalent state (5). A very large hyperfine interaction with the  $^{141}\text{Pr}$  nucleus was observed. Since the nuclear spin for the  $^{141}\text{Pr}$  nucleus (natural abundance 100%) is  $I = 5/2$ , the number of the resonance peaks

should be six. In the range of magnetic field swept here, however, the number of peaks observed is four.

The tetravalent praseodymium  $\text{Pr}^{4+}$  is a Kramers' ion with one unpaired  $4f$  electron and in a magnetic field one isotropic EPR spectrum may be observable. The isotope  $^{141}\text{Pr}$  has a nuclear spin of  $I = 5/2$  and a nuclear magnetic moment of  $+4.3$  nuclear magnetons. The spin Hamiltonian for the EPR spectrum of  $\text{Pr}^{4+}/\text{Li}_8\text{CeO}_6$  is

$$\mathcal{H} = g\beta H \cdot S' + AI \cdot S' - g'_N \beta H \cdot I, \quad [1]$$

where  $g$  is the  $g$  value for  $\text{Pr}^{4+}$  with an effective spin  $S' = 1/2$ ,  $A$  is the hyperfine coupling constant,  $g'_N$  is the effective nuclear  $g$  value (in units of Bohr magnetons),  $\beta$  is the Bohr magneton, and  $H$  is the applied magnetic field. Usually the assumption can be made that the electronic Zeeman term (the first term on the right-hand side of Eq. [1]) is much larger than the hyperfine term (the second term on the right-hand side), which would result in a six-line spectrum for an isotropic resonance with  $I = 5/2$ . Experimental results show that the observed hyperfine spacings between the absorption lines are quite large and they increase with magnetic field (see Fig. 3). In this case, hyperfine interaction with the  $^{141}\text{Pr}$  nucleus is so large that the above

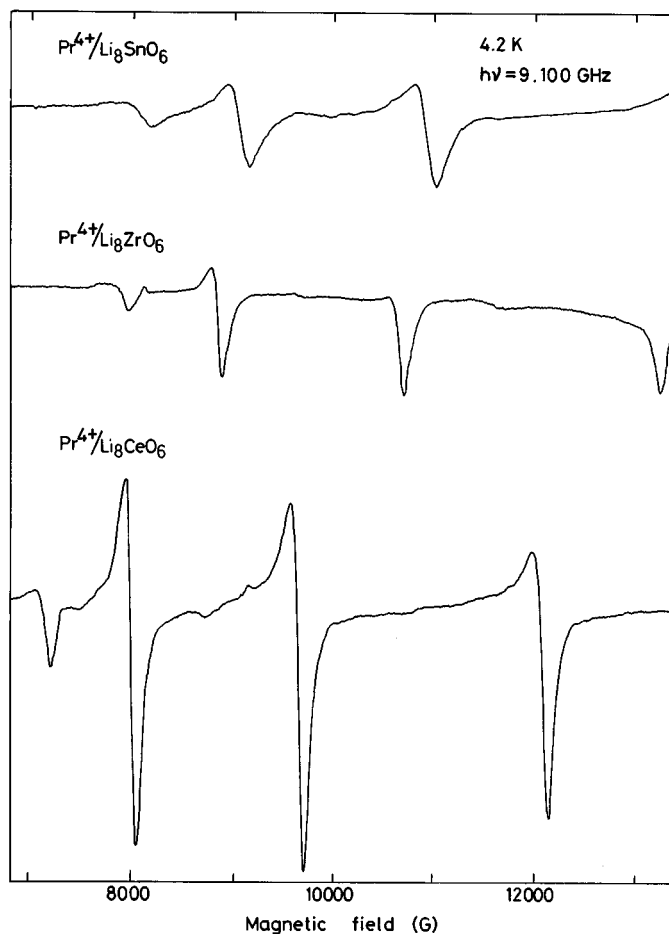


FIG. 3. EPR spectra for  $\text{Pr}^{4+}$  doped in  $\text{Li}_8\text{MO}_6$  ( $M = \text{Ce}, \text{Zr}, \text{Sn}$ ) measured at 4.2 K.

Hamiltonian must be solved exactly. The solution has been given by Ramsey (16) and others (17).

First,  $I$  and  $S$  are coupled together to form the resultant  $F$ , where  $F = I + S$ . For  $S = 1/2$  and  $I = 5/2$  in the absence of a magnetic field, there are two states  $F = 2$  and  $F = 3$  which are separated by  $3A$ . When the magnetic field is included, each of these two states splits into  $(2F + 1)|m_F\rangle$  Zeeman levels, and six allowed transitions ( $\Delta F = \pm 1$ ;  $\Delta m_F = \pm 1$ ) should be observable. We tried to fit the four observed resonance peaks to those calculated to obtain the  $g$  value and the hyperfine coupling constant  $A$ .

The  $g$  value for a  $4f^1$  electron perturbed by the octahedral crystal field should be between  $-10/7$  (no crystal field effect, for the  $\Gamma_7$  ground doublet in the  ${}^2F_{5/2}$  multiplet) and 2.00 (no spin-orbit interaction), and it increases from  $-10/7$  with increasing crystal field strength (18, 19). Although the sign of the  $g$  value is not obtained by this experiment, comparison with other  $f^1$  systems in octahedral symmetry, such as  $\text{NpF}_6/\text{UF}_6$  (20) and  $\text{Pa}^{4+}/\text{Cs}_2\text{ZrCl}_6$  (17), indicates that the  $g$  value for the  $\text{Pr}^{4+}/\text{Li}_8\text{CeO}_6$  should be

negative. Therefore, the value of  $|g|$  which is obtained from this EPR experiment decreases with increasing crystal field strength. The  $|g|$  value obtained for  $\text{Pr}^{4+}/\text{Li}_8\text{CeO}_6$  is 0.55, which is quite lower than two and near the value for  $\text{Pr}^{4+}/\text{BaCeO}_3$  ( $|g| = 0.740$ ) (4). This result strongly indicates that the crystal field effect on the  $\text{Pr}^{4+}$  ion is strong. The effective magnetic moment of  $\text{Pr}^{4+}$  is calculated to be  $0.48 \mu_B$  from the relation  $\mu = g\sqrt{S'(S' + 1)}$ . This moment is close to the moment of  $\text{Li}_8\text{PrO}_6$  ( $0.503 \mu_B$ ) derived from the magnetic susceptibility measurement. The difference might indicate a very weak Pr-Pr interaction present in the crystal.

The crystal structures of  $\text{Li}_8\text{ZrO}_6$  and  $\text{Li}_8\text{SnO}_6$  are the same as that of  $\text{Li}_8\text{CeO}_6$  (6-8), and the lattice parameters decrease with  $\text{Li}_8\text{CeO}_6 \rightarrow \text{Li}_8\text{ZrO}_6 \rightarrow \text{Li}_8\text{SnO}_6$ . Then, the strength of the crystal field affecting the electronic state of the central  $\text{Pr}^{4+}$  ion doped in the  $\text{Li}_8\text{MO}_6$  ( $M = \text{Ce}, \text{Zr}, \text{Sn}$ ) increases with the host materials  $\text{Li}_8\text{CeO}_6$ ,  $\text{Li}_8\text{ZrO}_6$ , and  $\text{Li}_8\text{SnO}_6$ . In Fig. 3, the EPR spectra for  $\text{Pr}^{4+}$  ion doped in the  $\text{Li}_8\text{ZrO}_6$  and the  $\text{Li}_8\text{SnO}_6$  are also shown. With increasing crystal field strength ( $\text{Li}_8\text{CeO}_6 \rightarrow \text{Li}_8\text{ZrO}_6 \rightarrow \text{Li}_8\text{SnO}_6$ ), each of the hyperfine absorption peaks shifts toward higher magnetic field, which gives a lower  $|g|$  value. This result is in accordance with the theoretical consideration. On the other hand, hyperfine coupling constant  $A$  is obtained to be  $0.074 \text{ cm}^{-1}$ . This value is a little larger than that for  $\text{Pr}^{4+}/\text{BaCeO}_3$  ( $0.0610 \text{ cm}^{-1}$ ).

Figure 4 shows the temperature dependence of the reciprocal magnetic susceptibility for  $\text{Li}_8\text{TbO}_6$ . No magnetic transition is found down to 4.2 K. This result is qualitatively understandable from its crystal structure. The structure for  $\text{Li}_8\text{TbO}_6$  is the same as that for  $\text{Li}_8\text{SnO}_6$ ; the terbium ions are octahedrally coordinated by six oxygen ions and their octahedra are located separately. As shown in Fig. 4, the linearity between the reciprocal susceptibility and temperature is found down to 4.2 K, i.e., the temperature dependence of the susceptibility follows the Curie law. This result is in contrast to the magnetic susceptibility of  $\text{BaTbO}_3$  (3). The temperature dependence of the susceptibility for  $\text{BaTbO}_3$  follows the Curie-Weiss law above 60 K with the Weiss constant  $\theta = -54.8 \text{ K}$ . In that case, an antiferromagnetic ordering is found at 32.7 K and the terbium ion is in the tetravalent state. The magnetic properties of alkali metal lanthanide oxides  $M_2\text{TbO}_3$  ( $M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) have been reported (21). Their magnetic susceptibilities follow the Curie-Weiss law with relatively large Weiss constants and the measured values of the magnetic moment for  $\text{Tb}^{4+}$  are smaller than the calculated value  $7.94 \mu_B$ . The present magnetic susceptibility data on  $\text{Li}_8\text{TbO}_6$  are characteristic for the paramagnetic rare earth ion with the  $S$  ground state with no magnetic exchange interaction, which strongly suggests the exclusion of the existence of the trivalent terbium ion in this compound and the oxidation state of terbium should be tetravalent. From the slope of the reciprocal susceptibility

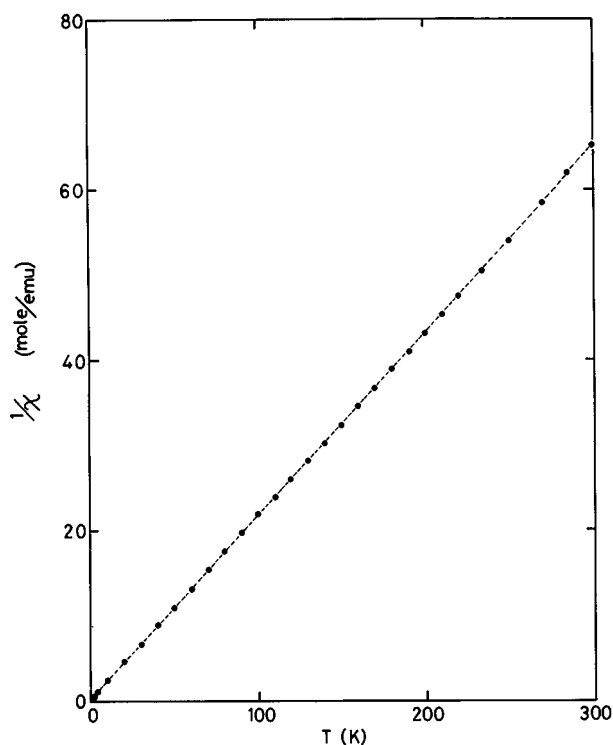


FIG. 4. Temperature dependence of reciprocal magnetic susceptibility for  $\text{Li}_8\text{TbO}_6$ .

vs temperature curve, the effective magnetic moment of terbium ion is obtained to be  $6.06 \mu_B$ , which is a little below the theoretical effective magnetic moment ( $7.94 \mu_B$ ) for the  $4f^7$  ion under the Russell-Saunders coupling scheme, and much smaller than the moment ( $9.72 \mu_B$ ) for the  $4f^8$  ion. The discrepancy between the moment obtained experimentally and the moment calculated is in the weight determination of the sample used for the magnetic susceptibility measurement. Because the  $\text{Li}_8\text{TbO}_6$  is hygroscopic, superficial water adsorption might occur, which resulted that the weight of the sample used for the magnetic susceptibility measurements might be larger than the true weight of  $\text{Li}_8\text{TbO}_6$  without superficial water adsorption. If this point is taken into consideration, the effective magnetic moment of  $\text{Li}_8\text{TbO}_6$  will become nearer to the theoretical value.

It is well known that the EPR spectra for rare earth ions can be measured only at very low temperatures because of the rapid spin-lattice relaxation. However, the situation is different for the rare earth ions with a half-filled  $f$  shell such as  $\text{Gd}^{3+}$ ,  $\text{Eu}^{2+}$ , or  $\text{Tb}^{4+}$  because the ground states of these are  $S$  states. So, if the oxidation state is tetravalent (the

electronic configuration is  $[\text{Xe}]4f^7$ ), the EPR spectrum should be observed at room temperature. We could measure the EPR spectrum for  $\text{Li}_8\text{TbO}_6$  even at room temperature, although it was very broad (the linewidth is over 3000 G). The observation of the spectrum also strongly indicates that the oxidation state of terbium is not trivalent but tetravalent, because it is usually impossible to observe an EPR spectrum for a non-Kramers ion such as  $\text{Tb}^{3+} (4f^{8+}) (5)$ . To analyze the EPR spectrum for  $\text{Li}_8\text{TbO}_6$ , we have diluted the  $\text{Tb}^{4+}$  ion in a diamagnetic  $\text{Li}_8\text{CeO}_6$  (which is isomorphous with  $\text{Li}_8\text{TbO}_6$ ) and measured its EPR spectrum with complicated structure due to the hyperfine interaction with a nuclear spin of  $^{159}\text{Tb} (I = 3/2)$ . We will report the EPR spectrum and its analysis elsewhere. Anyway, measurements of the EPR spectrum at room temperature strongly indicate that the terbium ion is in the tetravalent state in the  $\text{Li}_8\text{TbO}_6$ .

#### ACKNOWLEDGMENTS

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