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Crystal Structures and Magnetic Properties of Ordered Perovskites Ba_2LnNbO_6 (Ln = Lanthanide Elements)

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A series of double-perovskite oxides Ba_2LnNbO_6 (Ln = lanthanide elements) were synthesized. Their powder X-ray diffraction measurements and Rietveld analysis show that they are monoclinic with space group $P2_1/n$ and that Ln^{3+} and Nb^{5+} ions are structurally ordered. Although the average Ln–O bond length increases with the ionic radius of Ln^{3+}, the average Nb–O bond length is nearly constant for all the Ba_2LnNbO_6. Magnetic susceptibility measurements show that they are paramagnetic down to 2 K. The ^{151}Eu Mössbauer spectrum for Ba_2EuNbO_6 indicates that the Eu ion is in the trivalent state and a quadrupole interaction exists in this compound. Both the magnetic susceptibility and the electron paramagnetic resonance (EPR) spectrum measurements show that the Gd^{3+} ion is in the $^8S_{7/2}$ state. In addition, the anisotropic EPR spectrum indicates that the six oxygen coordination around the Gd^{3+} ion has no longer a perfect octahedral symmetry.

INTRODUCTION

It is well known that complex oxides with perovskite-type structure often show functional properties (1, 2). Among them, we have paid attention to the Ba_2LnNbO_6 (Ln = lanthanide elements) compounds. They were first synthesized by Brixner (1) and were determined to have a cubic perovskite-type structure with the exception of Ln = La which is a tetragonally distorted structure, and some of them have ferroelectric properties. Later, Filip'ev *et al.* (3) reported that the structure of Ln = La had a rhombohedrally distorted structure. Anderson *et al.* (4), however, point out that the crystal system of $A_2BB'O_6$ double perovskites is cubic, orthorhombic, or monoclinic, because the $B(B')$-cation arrangement is limited to be a random type, a rock salt type, or a layered type. When the $B(B')$-cation arrangement is a rock salt type, the crystal system should be either a cubic one ($Fm\bar{3}m$) or a monoclinic one ($P2_1/n$).

In order to clarify these discrepancies among them, we have prepared Ba_2LnNbO_6 (Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), carried out their X-ray diffraction measurements, and analyzed their crystal structures. In addition, magnetic susceptibility, electron paramagnetic resonance (EPR), and Mössbauer spectrum measurements have been performed for these compounds in the temperature range between 2 and 400 K to elucidate their electronic structures.

EXPERIMENTAL

1. Sample Preparation

Polycrystalline samples of Ba_2LnNbO_6 were prepared by a standard ceramic technique. As starting materials, barium carbonate $BaCO_3$, lanthanide sesquioxide Ln_2O_3 (Ln = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, and Lu), and diniobium pentaoxide Nb_2O_5 were used. For the case of Ce, Pr, and Tb, CeO_2, Pr_6O_{11}, and Tb_4O_5 were used. These reagents were weighed in appropriate metal ratios and ground intimately in an agate mortar. The mixtures were pressed into pellets and then heated in air at 1300°C for 24 h. The pellets were reground, repressed, and heated in air at 1400°C for 24 h. These procedures were repeated several times.

2. X-Ray Diffraction and Magnetic Measurements

Powder X-ray diffraction (XRD) patterns were measured with Cu$K\alpha$ radiation on a RINT2000 (Rigaku) diffractometer. XRD data were collected by step scanning over the range $10° \le 2\theta \le 120°$ in increments of 0.04° (2θ).

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The structure refinement was carried out by Rietveld analysis for the XRD data with the RIETAN-97ß program (5).

Magnetic susceptibilities were measured in a magnetic field of 0.1 T over the temperature range between 2 and 400 K with a SQUID magnetometer (Quantum Design, MPMS5S). The measurements were carried out under both zero-field-cooled condition (ZFC) and field-cooled condition (FC). The former was measured on heating the sample to 400 K after zero-field cooling to 2 K. The latter was measured on cooling the sample from 400 to 2 K at 0.1 T.

EPR measurements were made at room temperature using a JEOL-RE2X spectrometer operating at X-band frequency ($\sim$9.1 GHz). The magnetic field was swept up to 1.0 T.

The ^{151}Eu Mössbauer spectrum was measured with a conventional transmissional Mössbauer spectrometer VT-6000 (Laboratory Equipment Co.) in the constant acceleration mode at room temperature. A source of up to 100 mCi of $^{151}SmF_3$ was used and the spectrometer was calibrated using EuF_3 at room temperature.

RESULTS AND DISCUSSION

Crystal Structure

The results of the X-ray diffraction measurements show that all the samples in this study except for Ba_2CeNbO_6 were formed in a single phase. The XRD data were indexed with a monoclinic unit cell. The diffraction profiles of all the compounds showed the existence of the super lattice reflection at $2\theta \approx 18°$. Figure 1 shows the X-ray diffraction profile for Ba_2TmNbO_6, as an example. It is concluded that these compounds are ordered perovskites and their lattice parameters are double those of the single perovskite. We have performed the Rietveld analysis for the XRD data. Table 1 lists the lattice parameters and the reliability factors for Ba_2LnNbO_6 prepared in this study. The atomic parameters for Ba_2PrNbO_6 after refinement are listed in Table 2. Since the atomic parameters for other compounds Ba_2LnNbO_6 are comparable with those for Ba_2PrNbO_6, we will not list them.

The structures were refined by applying the space group $P2_1/n$. This space group allows two crystallographically distinct octahedral sites in the perovskite structure, thus permitting 1 : 1 positional ordering between the *B* site ions, Ln^{3+}, and Nb^{5+} ions. These ions are arranging alternately and they have a rock salt sublattice. Figure 2 shows the crystal structure of Ba_2LnNbO_6.

Figure 3 shows the variation of lattice parameters for the Ba_2LnNbO_6 with the ionic radius of Ln^{3+}. As the atomic number of lanthanide ions increases (which means the decrease of ionic radius of Ln^{3+}), the lattice parameters, *a*, *b*, *c*′, and the volume decrease. The parameter *c*′ is $c/\sqrt{2}$. The parameter β increases with ionic radius of Ln^{3+}, indicating that from $Ln = Lu$ to La the crystal structures of Ba_2LnNbO_6 are more distorted from the cubic symmetry, due to the larger difference in ionic radius between *B* site ions, Ln^{3+}, and Nb^{5+}.

Figure 4 shows the variation of the average *Ln*–O and Nb–O bond lengths with the ionic radius of Ln^{3+}. The average *Ln*–O bond length increases with the ionic radius of Ln^{3+}. On the other hand, the average Nb–O bond length is nearly constant ($\sim$1.94 Å). This value is shorter than the Nb–O bond length calculated from using Shannon's ionic radii, 2.04 Å (6). This result indicates the existence of the covalency in the Nb–O bond in these Ba_2LnNbO_6 compounds.

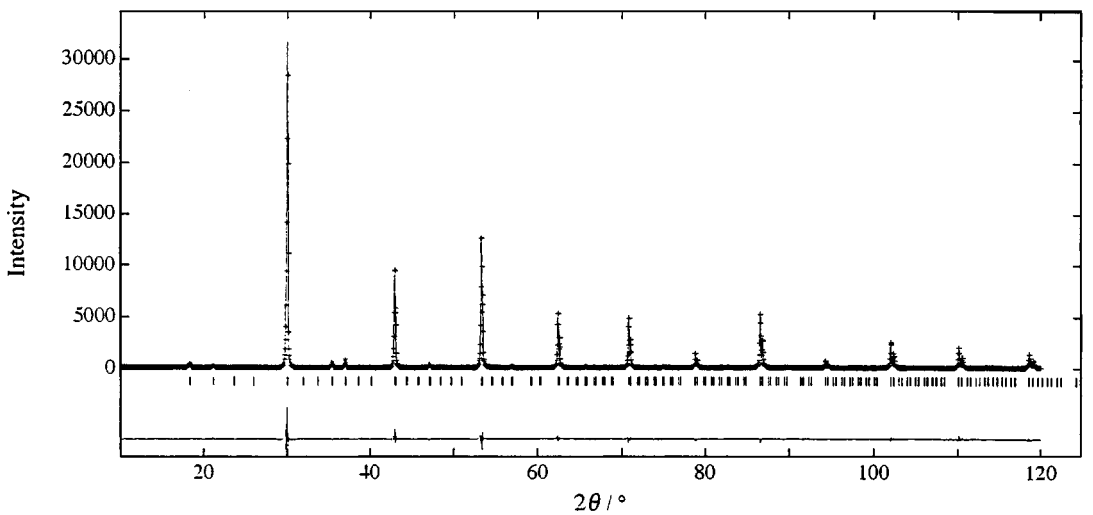

FIG. 1. Observed and calculated X-ray powder diffraction profiles for Ba_2TmNbO_6. The observed data are indicated by crosses and the calculated profile is the solid line. The short vertical lines below the profiles mark the positions of all possible Bragg reflections. The bottom continuous line is the difference between the observed and the calculated intensity.

TABLE 1
Unit Cell Parameters and *R* Factors for Ba_2LnNbO_6

Compound	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	R_{wp}	R_I
Ba_2LaNbO_6	6.1407(1)	6.0899(1)	8.6031(2)	90.320(2)	12.30	2.65
Ba_2PrNbO_6	6.0913(1)	6.0539(1)	8.5509(2)	90.161(1)	12.25	3.74
Ba_2NdNbO_6	6.0764(1)	6.0437(1)	8.5365(2)	90.133(2)	12.48	2.54
Ba_2SmNbO_6	6.0187(4)	6.0156(4)	8.5355(3)	90.200(4)	11.94	2.92
Ba_2EuNbO_6	6.0035(4)	6.0043(3)	8.5242(3)	90.108(4)	12.53	2.37
Ba_2GdNbO_6	5.9962(5)	5.9961(4)	8.5119(2)	90.050(3)	12.31	3.32
Ba_2TbNbO_6	5.9845(4)	5.9838(3)	8.4820(2)	90.063(3)	12.20	2.37
Ba_2DyNbO_6	5.9752(7)	5.9751(7)	8.4610(2)	90.033(6)	13.40	2.80
Ba_2HoNbO_6	5.9653(5)	5.9644(4)	8.4396(4)	90.042(5)	12.79	3.37
Ba_2YNbO_6	5.9647(3)	5.9617(4)	8.4362(5)	90.017(7)	14.29	3.43
Ba_2ErNbO_6	5.9555(6)	5.9538(8)	8.4234(8)	90.020(8)	13.37	2.46
Ba_2TmNbO_6	5.9435(6)	5.9423(2)	8.4053(5)	90.041(7)	11.67	2.92
Ba_2YbNbO_6	5.9311(7)	5.9303(6)	8.3897(4)	90.026(8)	13.94	3.09
Ba_2LuNbO_6	5.9248(3)	5.9214(2)	8.3735(4)	90.015(9)	14.60	3.34

Note. $R_{WP} = \left[\sum_k w_k [I_k(\text{obs}) - I_k(\text{calc})]^2 \Big/ \sum_k w_k I_k(\text{obs})^2 \right]^{1/2}$,

$R_I = \sum_k |I_k(\text{obs}) - I_k(\text{calc})| \Big/ \sum_k I_k(\text{obs})$.

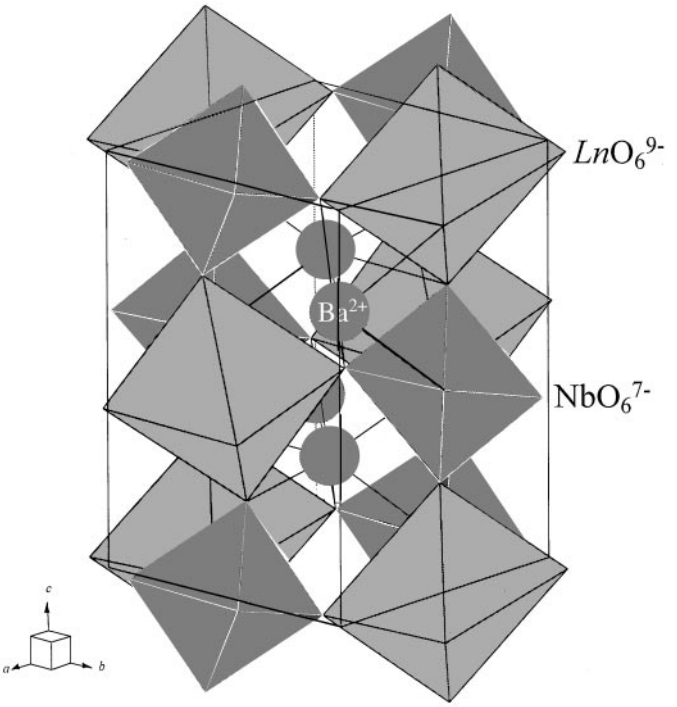

FIG. 2. Crystal structure of Ba_2LnNbO_6.

Magnetic Properties

The results of the magnetic susceptibility measurements for Ba_2LnNbO_6 show that they are paramagnetic down to 2 K. The electronic configuration of Nb^{5+} is $[Kr]4d^0$ ([Kr], krypton core); i.e., this ion is diamagnetic. Therefore, the paramagnetic ion in the Ba_2LnNbO_6 is a Ln^{3+} ion. Their magnetic susceptibilities except for Ba_2SmNbO_6 and Ba_2EuNbO_6 followed the Curie law except at very low temperatures. Table 3 shows the effective magnetic moments of these compounds, μ_{exp}, and the calculated moments for the free Ln^{3+} ion, μ_{calc}. The effective magnetic moments obtained experimentally (μ_{exp}) in the temperature range of 250–400 K are in good agreement with the calculated values (μ_{calc}). This result indicates that the Ln^{3+} ions in the Ba_2LnNbO_6 are not affected by the crystal field.

In the following, we will discuss each of the magnetic behaviors of Ln^{3+} ions in these compounds.

TABLE 2
Atomic Positions and Isotropic Thermal Parameters for Ba_2PrNbO_6

Atoms	Sites	*x*	*y*	*z*	*B* (Å)
Ba	4*e*	0.0007(0.0014)	0.0019(0.0023)	0.2478(0.0008)	0.32
Pr	2*d*	0.5000	0.0000	0.0000	0.30
Nb	2*c*	0.5000	0.0000	0.5000	0.38
O(1)	4*e*	0.2062(0.0101)	0.2695(0.0124)	0.0035(0.0060)	0.80
O(2)	4*e*	0.2366(0.0122)	−0.2947(0.0108)	0.0013(0.0086)	0.71
O(3)	4*e*	−0.0467(0.0071)	0.5161(0.0193)	0.2278(0.0052)	0.73

(a) *Ba_2PrNbO_6*. The temperature dependence of magnetic susceptibility for Ba_2PrNbO_6 is shown in Fig. 5. It increases with decreasing temperature, but this increase does not become prominent in some temperature range. In this compound, the Pr^{3+} ion ($4f^2$) is coordinated by six oxygen ions with nearly octahedral symmetry. In the presence of an octahedral crystal field, the $^3H_4$ state of the Pr^{3+} ion (a nine-fold degenerate state) is split into a singlet (Γ_1), a doublet (Γ_3), and two triplets (Γ_4 and Γ_5) (7). Since the ground state of the Pr^{3+} ion is a singlet Γ_1 in this environment, the magnetic susceptibility of the Pr^{3+} ion should exhibit a temperature-independent behavior in a lower temperature region. We consider that an almost temperature-independent paramagnetic susceptibility found in the temperature region between 70 and 120 K (see Fig. 5) corresponds to this theoretical consideration. A sharp increase of magnetic susceptibility with decreasing temperature is observed at very low temperatures. This may be attributable to the paramagnetic behavior of Nb^{4+} ions (the electronic configuration is $[Kr]4d^1$) formed by the oxygen deficiency of this compound. It is known that some oxygen atoms are apt to be lacking in the perovskite oxides ABO_3.

(b) *Ba_2EuNbO_6*. The molar magnetic susceptibility of Ba_2EuNbO_6 as a function of temperature is shown in Fig. 6. Except at very low temperatures, the shape of this

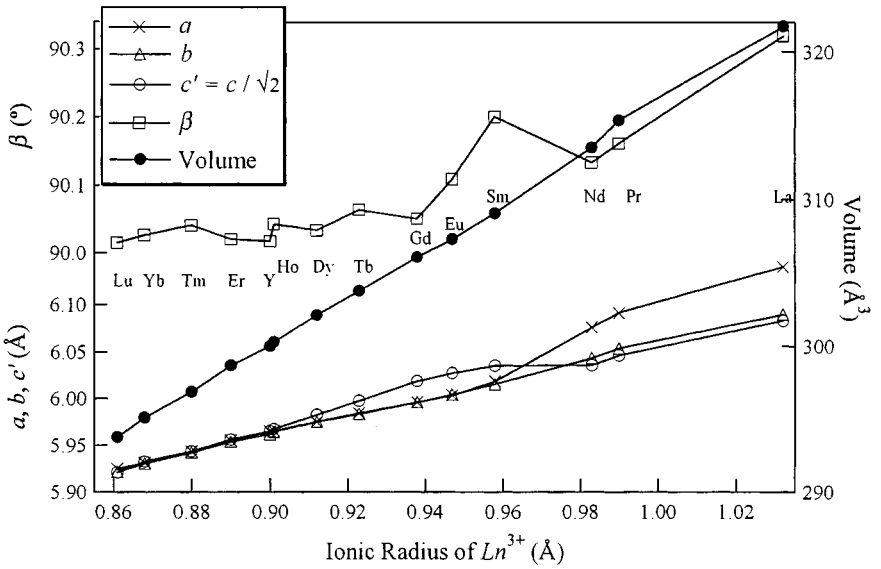

FIG. 3. Variation of lattice parameters for Ba_2LnNbO_6 with the ionic Ln^{3+} radius.

susceptibility vs the temperature curve is characteristic of a Van Vleck paramagnetism, with a constant susceptibility for the lower temperature range and a decreasing susceptibility with increasing temperature for $T \geq 100$ K.

The ground state $^7F_0$ of Eu^{3+} is nonmagnetic and the excited states ^7F_J are close enough to give energy differences comparable to k_BT (k_B, Boltzmann constant) at room temperature. Therefore, the magnetic susceptibility becomes independent of temperature in a lower temperature range. The molar magnetic susceptibility of the Eu^{3+} ion is expressed by the following equation (8),

$$\chi_M(Eu^{3+}) = \frac{0.12506}{\gamma T}\cdot \frac{24 + (13.5\gamma - 1.5)e^{-\gamma} + (67.5\gamma - 2.5)e^{-3\gamma} + (189\gamma - 3.5)e^{-6\gamma}}{1 + 3e^{-\gamma} + 5e^{-3\gamma} + 7e^{-6\gamma}}, \quad [1]$$

where $\gamma = \lambda/(k_BT)$ is the ratio of the multiplet width (the spin–orbital coupling constant, λ) and the thermal energy (k_BT). From the fitting of Eq. [1] to the experimental data, we have obtained $\lambda = 339$ cm^{-1}. This value is reasonable as

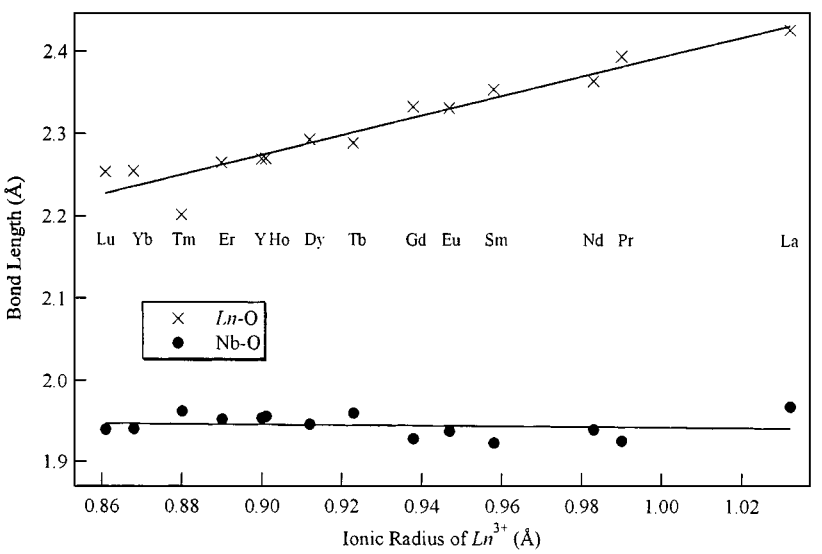

FIG. 4. Variation of *Ln*–O and Nb–O bond lengths with the ionic Ln^{3+} radius.

TABLE 3
The Experimental Magnetic Moments for Ln^{3+} (μ_{exp}) and the Calculated Magnetic Moments (μ_{calc}) for Ba_2LnNbO_6

Ln^{3+}	μ_{exp}/μ_B	μ_{calc}/μ_B
Pr^{3+}	3.45	3.58
Nd^{3+}	3.31	3.62
Gd^{3+}	7.96	7.94
Tb^{3+}	9.51	9.72
Dy^{3+}	9.93	10.63
Ho^{3+}	10.71	10.60
Er^{3+}	9.04	9.59
Tm^{3+}	7.22	7.57
Yb^{3+}	4.47	4.54

the spin–orbit coupling constant for Eu^{3+} ions in solids and it is comparable with $364\,cm^{-1}$ for Ba_2EuIrO_6 (9) and $340\,cm^{-1}$ for Sr_2EuIrO_6 (10). A paramagnetic behavior found in this compound at very low temperatures may be also attributable to the Nb^{4+} ions formed due to the oxygen deficiency.

The ^{151}Eu Mössbauer spectrum of Ba_2EuNbO_6 compound was measured at room temperature (Fig. 7). The Eu site in this Ba_2EuNbO_6 (space group, $P2_1/n$) has the point symmetry $\bar{1}$. It is known that an electric field gradient tensor exists in this point symmetry (11). Therefore, a nonzero quadrupole interaction is expected at the Eu site. The quadrupole interaction is given by

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

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) (12). Since the point symmetry $\bar{1}$ is not axially symmetric, the asymmetry parameter $\eta \neq 0$ in Eq. [2]. The observed spectrum exhibits a slightly asymmetric line (see Fig. 7). It is impossible to fit such a spectrum with a single Lorentzian line, because of the distortion due to a quadrupole interaction. As shown in Fig. 8, 12 possible transitions due to the quadrupole interaction should be considered in analyzing this Mössbauer spectrum. The spectrum is, therefore, fitted with 12 Lorentzian lines (13). The ^{151}Eu Mössbauer parameters, the isomer shift δ, the quadrupole coupling constant $eV_{zz}Q_g$, and the asymmetry parameter η were determined (Table 4). The following numerical values were adopted in this study: $R_Q = 1.312$ (the ratio of the excited and ground state quadrupole moments, Q_e/Q_g) and $Q_g = 1.14$ (14). It is noted that the Eu ions are in the trivalent state from the value of the isomer shift δ (1.50 mm/sec) (15). Since the quadrupole coupling constant ($eV_{zz}Q_g$) and the asymmetry parameter (η) were determined to be 4.96 mm/sec and 0.35, respectively, the quadrupole coupling interaction exists in this Ba_2EuNbO_6 compound. It is, therefore, confirmed that the electric field gradient at the Eu nuclei exists. The quadrupole coupling constant is positive in this case. This is the same result as those for Ba_2EuIrO_6 (4.92 mm/sec) and Sr_2EuIrO_6 (3.39 mm/sec) (9).

(c) *Ba_2GdNbO_6*. The magnetic susceptibility of Ba_2GdNbO_6 follows the Curie law, i.e., its reciprocal susceptibility vs temperature curve is fitted well with a straight

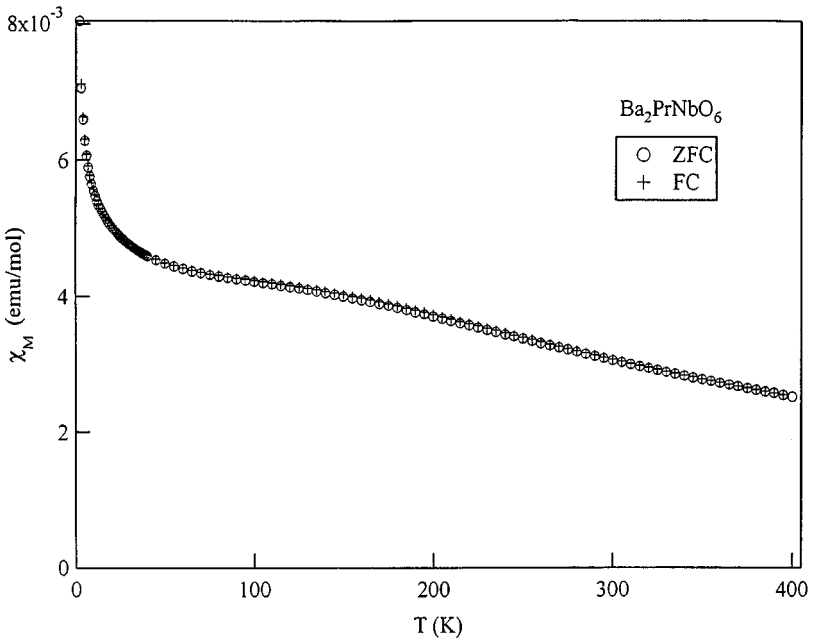

FIG. 5. Magnetic susceptibility vs temperature for Ba_2PrNbO_6.

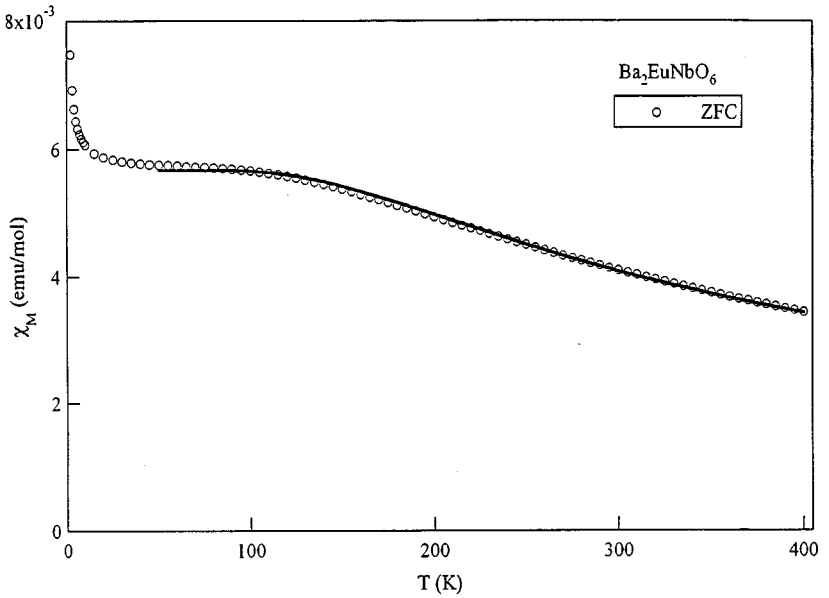

FIG. 6. Magnetic susceptibility vs temperature for Ba_2EuNbO_6. The solid line is calculated with Eq. [1] in the temperature range of 50–400 K.

line. This property is characteristic of the ground state of $^8S_{7/2}$. The effective magnetic moment of the Gd^{3+} ion is determined to be 7.96 μ_B from this susceptibility measurement.

Figure 9 shows the X-band EPR spectrum for Gd^{3+} ion ($4f^7$) in Ba_2GdNbO_6 measured at room temperature. A single broad line centered at the magnetic field 3278 G was observed. The effective magnetic moment of the Gd^{3+} ion is calculated to be 7.87 μ_B from EPR data ($g = 1.98$). Both the effective magnetic moments of the Gd^{3+} ion determined from the magnetic susceptibility and the EPR measurements are in good agreement with the calculated magnetic moment (7.94 μ_B), which means that the ground state of the Gd^{3+} ion in Ba_2GdNbO_6 is a pure $^8S_{7/2}$ state. The anisotropic spectrum indicates that the six oxygen coordination around the Gd^{3+} ion has no longer a perfect octahedral symmetry.

(d) *Ba_2YbNbO_6*. Figure 10 shows the temperature dependence of magnetic susceptibility measured for

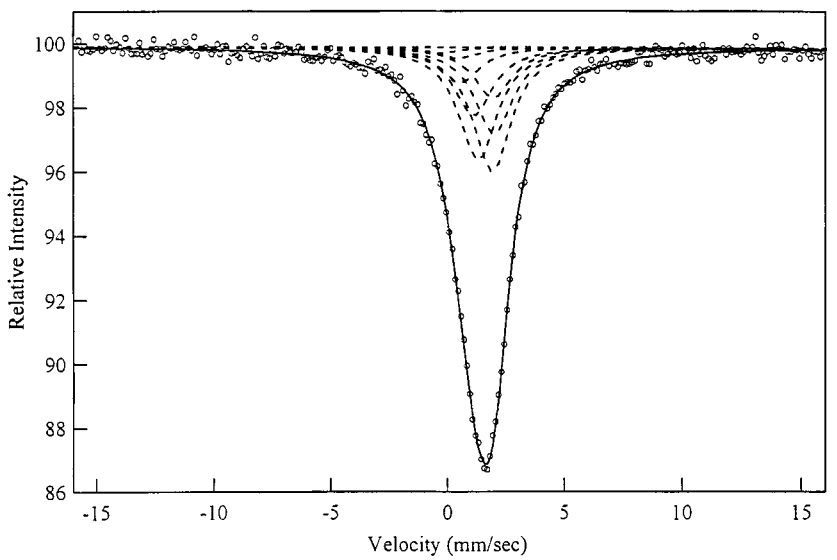

FIG. 7. ^{151}Eu Mössbauer spectrum of Ba_2EuNbO_6 at room temperature. The solid line is a calculated line with 12 Lorentzians.

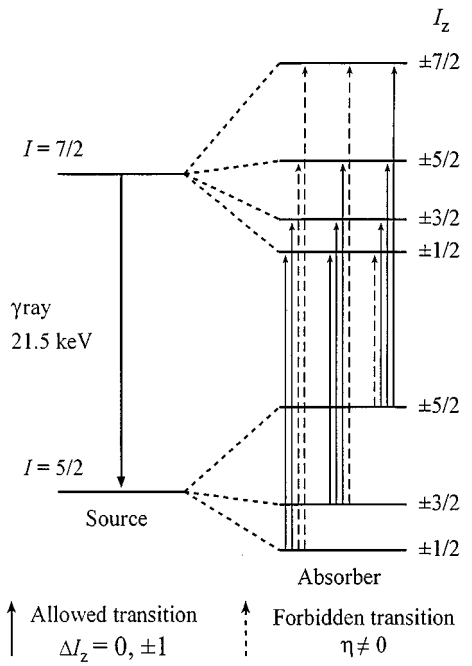

FIG. 8. Twelve possible transitions by a quadrupole interaction of ^{151}Eu nucleus.

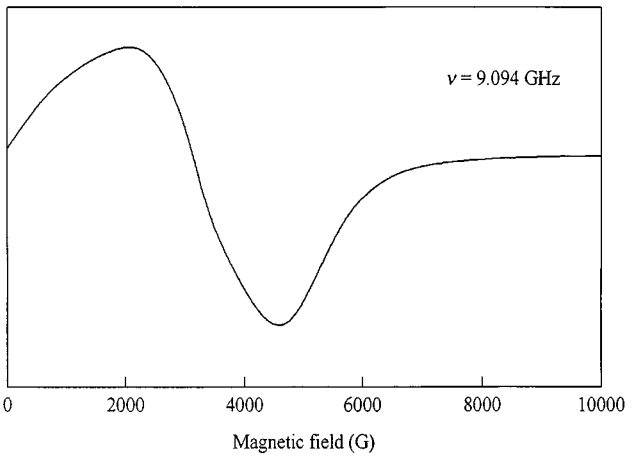

FIG. 9. EPR spectrum of Gd^{3+} in Ba_2GdNbO_6 at room temperature.

Ba_2YbNbO_6. When an Yb^{3+} ion ($4f^{13}$) exists in the octahedral crystal field, the ground state $^2F_{7/2}$ of the Yb^{3+} ion is split into two doublets (Γ_6 and Γ_7) and one quartet (Γ_8). The ground state is Γ_6 (7). The magnetic susceptibility is given by the following equation (16),

$$\chi_M(Yb^{3+}) = \frac{N_A g_J^2 \mu_B^2 J(J+1)}{3k_B T}.$$

$$\frac{98 + 260e^{-b} + 162e^{-a} + 432(e^{-b} - e^{-a})/(a-b) + 560(1 - e^{-b})/b}{378(1 + 2e^{-b} + e^{-a})}, \quad [3]$$

where $a = \Delta_{67}/(k_B T)$ and $b = \Delta_{68}/(k_B T)$; Δ is the energy difference between the Γ_6 ground state and the Γ_7 or Γ_8 excited state. By fitting Eq. [3] to the experimental susceptibility data, we have obtained $\Delta_{67} = 1058\ cm^{-1}$, $\Delta_{68} = 368\ cm^{-1}$, and $\mu_{exp} = 4.30\ \mu_B$. This effective magnetic moment of Yb^{3+} experimentally determined is a little smaller than the free ion value (4.54 μ_B), which means the Yb^{3+} ion in Ba_2YbNbO_6 is slightly affected by the crystal field.

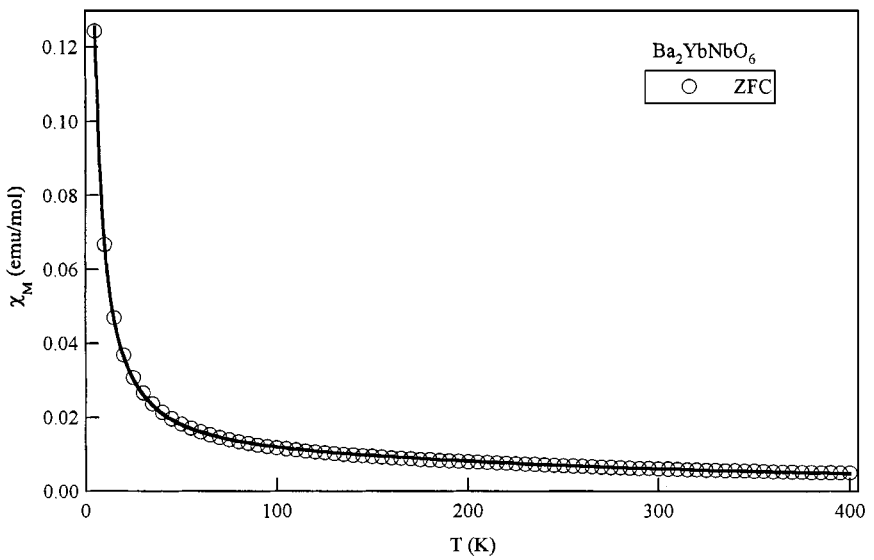

FIG. 10. Measured (○) and calculated (solid line) magnetic susceptibility for Ba_2YbNbO_6.

TABLE 4
^{151}Eu Mössbauer Parameters of Ba_2EuNbO_6

δ (mm/sec)	$eV_{zz}Q_g$ (mm/sec)	η
1.50	4.96	0.35

Note. δ, $eV_{zz}Q_g$, and η are isomer shift, quadrupole coupling constant, and asymmetry parameter, respectively.

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