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BRIEF COMMUNICATION

Electron Paramagnetic Resonance Spectra of Pr^{4+} Ions Doped in Pyrochlore-Type Compounds $La_2Sn_2O_7$ and $La_2Zr_2O_7$

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The electron paramagnetic resonance spectra of powders with the Pr^{4+} ions doped in the B sites of the pyrochlore-type compounds $A_2B_2O_7$ (A = La; B = Sn or Zr) were successfully measured at 4.2 K. A very large hyperfine interaction with the ^{141}Pr nucleus was observed. The spectra were isotropic, which indicates that the symmetry of the oxygen coordination around Pr^{4+} ions is almost octahedral. The results were analyzed based on the weak field approximation, and the g values and hyperfine coupling constants A were obtained. The measured g values are smaller than $|-10/7|$ (which is calculated for the Γ_7 ground doublet in the $^2F_{5/2}$ multiplet), showing that the crystal field is effective to some extent on the behavior of a 4f electron in solids. The value of $|g|$ decreases from 1.270 ($Pr^{4+}/La_2Zr_2O_7$) to 1.262 ($Pr^{4+}/La_2Sn_2O_7$), which is caused by the increase of the crystal field due to shrinking of the lattice. On the other hand, the hyperfine coupling constants are the same: $A = 0.076\ (1)\ cm^{-1}$.

INTRODUCTION

Although the trivalent oxidation state of praseodymium is most stable, the tetravalent state is also accessible. The electronic configuration of this tetravalent praseodymium ion is [Xe]$4f^1$ ([Xe], xenon electronic core). For electronic structure analysis, this f^1 configuration is straightforward, as only the crystal field and spin-orbit coupling interaction are important. Especially, in the case that this ion is located in an octahedral crystal field environment, such a compound is suitable to study the behavior of a 4f electron in solids because it is easy to compare the experimental results with the theoretical calculation.

Perovskite-type oxides, ABO_3, where A is a divalent ion (e.g., Sr, Ba) accommodate tetravalent metal ions at the B site of the crystal (1). In an earlier study (2), we successfully measured for the first time the EPR spectrum of Pr^{4+} ion in an octahedral crystal field by doping it in the perovskite $BaCeO_3$ (where the Pr^{4+} ion is substituted for the Ce^{4+} ion) and lowering the experimental temperature down to liquid helium temperature. In the EPR spectrum, a very large hyperfine interaction with the ^{141}Pr nucleus (nuclear spin $I = 5/2$) was measured. Although the crystal structure of $BaCeO_3$ is an orthorhombically distorted perovskite, the distortion from an ideal cubic perovskite structure is very small, and the EPR results could be analyzed based on the weak field approximation with an octahedral crystal field around Pr^{4+} (2).

In this study, we have paid attention to the pyrochlore-type oxides. For the ideal $A_2B_2O_7$ pyrochlore structure, all A cations are equivalent and all B cations are equivalent, but there are two types of oxygens. Thus, it is sometimes preferred to write the pyrochlore formula as $A_2B_2O_6O'$ (3). The space group of the ideal pyrochlore structure is $Fd3m$ and there are eight molecules per unit cell. The structure is composed of two types of cation coordination polyhedra (Fig. 1). The A cations (usually more than 1 Å ionic radius) are eight coordinated and are located within distorted cubes. The smaller B cations (0.6–0.8 Å ionic radius) are six coordinated and are located within trigonal antiprisms with all the six anions at equal distances from the central cations. However, in many cases, the six-fold and eight-fold coordination polyhedra in the pyrochlore structure are referred to as octahedral and cubic coordination polyhedra, respectively, as a first approximation.

The object of this study is to prepare specimens in which the Pr^{4+} ions are doped in the pyrochlore-type oxides and to investigate the electronic state of the ions in their oxides through their EPR measurements. Two kinds of specimens, $Pr^{4+}/La_2Sn_2O_7$ and $Pr^{4+}/La_2Zr_2O_7$, were successfully prepared (where the Pr^{4+} ions are substituted for the Sn^{4+} or Zr^{4+} ions) and their EPR spectra were, for the first time, measured by lowering the experimental temperature down

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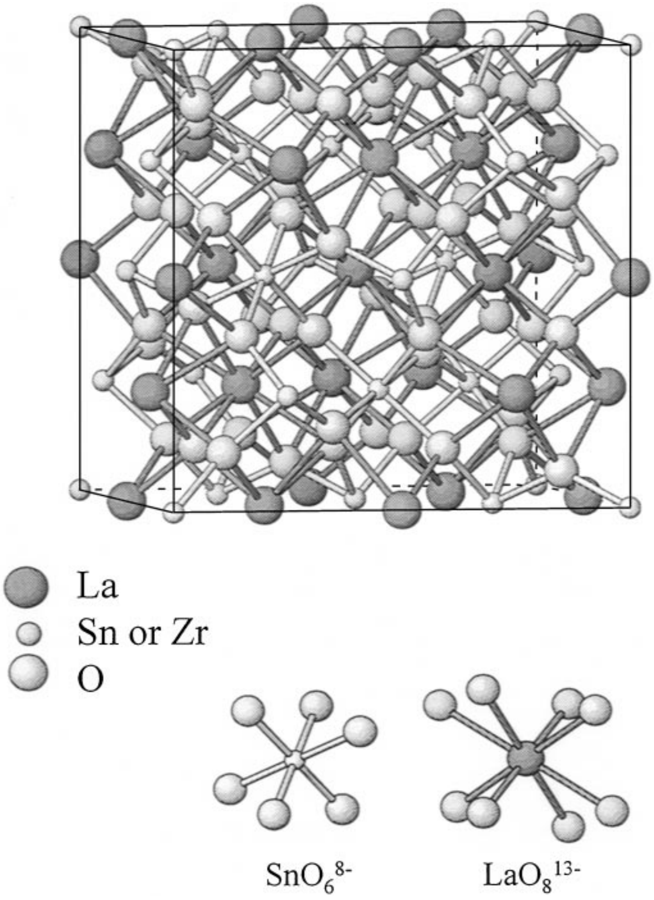

FIG. 1. Crystal structure of pyrochlore-type $A_2B_2O_7$.

to liquid helium temperatures. We will discuss these experimental results.

EXPERIMENTAL DETAILS

1. *Sample Preparation*

As starting materials, La_2O_3, Pr_6O_{11}, and SnO_2 (or ZrO_2) were used. Before use, these oxides were heated in air at 850°C to remove any moisture and oxidized to the stoichiometric compositions. They were weighed in the correct metal ratios $La_2Pr_xM_{2-x}O_7$ ($M =$ Sn, Zr; $x = 0.02$, 0.05, 0.10), intimately mixed, pressed into pellets, and heated in a flowing oxygen atmosphere at 1300°C in an SiC resistance furnace for 12 h. After cooling to room temperature, the samples were crushed into powder, reground, re-pressed into pellets, and heated under the same conditions to make the reaction complete. Since these oxides lose a few oxygens at high temperatures, the samples were kept at 1000°C for 10 h and cooled to room temperature in the furnace so as to prepare oxygen stoichiometric compounds.

2. *Analysis*

X-ray diffraction analysis was performed with Cu$K\alpha$ radiation on a RINT2000 diffractometer (Rigaku) equipped with a curved graphite monochromator.

3. *Electron Paramagnetic Resonance Measurement*

The EPR spectra at X band (9.091 GHz) were measured using a JEOL RE-2X spectrometer operating with an Air Products Helitran cooling system. The magnetic field was swept from 100 to 13,500 G, which was monitored with a proton NMR gaussmeter, and the microwave frequency was measured with a frequency counter. Before the samples were measured, a blank was recorded to eliminate the possibility of interference by the background resonance of the cavity and/or the sample tube.

RESULTS AND DISCUSSION

The EPR spectra could be measured at 4.2 K for both of the specimens $Pr^{4+}/La_2Sn_2O_7$ and $Pr^{4+}/La_2Zr_2O_7$. With increasing temperature, all the assigned absorption EPR lines become considerably weaker in intensity. This observation of the EPR spectra strongly indicates that the oxidation state of the praseodymium ion is not trivalent, but tetravalent, because the non-Kramers Pr^{3+} ion usually shows no EPR spectrum (4).

In the $A_2B_2O_7$ pyrochlore structure, there are two kinds of cation sites, i.e., A sites and B sites. The Pr^{4+} ions are considered to be incorporated into the B sites, not the A sites, because in the present case, the valence state of B sites is tetravalent (Sn^{4+}, Zr^{4+}), which is the same as that of the praseodymium ion.

Figures 2a and 2b shows the EPR spectra for Pr^{4+} doped in $La_2Sn_2O_7$ and $La_2Zr_2O_7$ measured at 4.2 K, respectively. Six strong absorption lines are observed. By increasing the size of the host materials ($La_2Sn_2O_7 \rightarrow La_2Zr_2O_7$), all these absorption lines move to a lower magnetic field.

The isotope ^{141}Pr (natural abundance 100%) 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 Pr^{4+} ion is

$$\mathscr{H} = g\beta H \cdot S' + AS' \cdot I - g'_N \beta H \cdot I, \qquad [1]$$

where g is the g value for 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), β 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 $I = 5/2$.

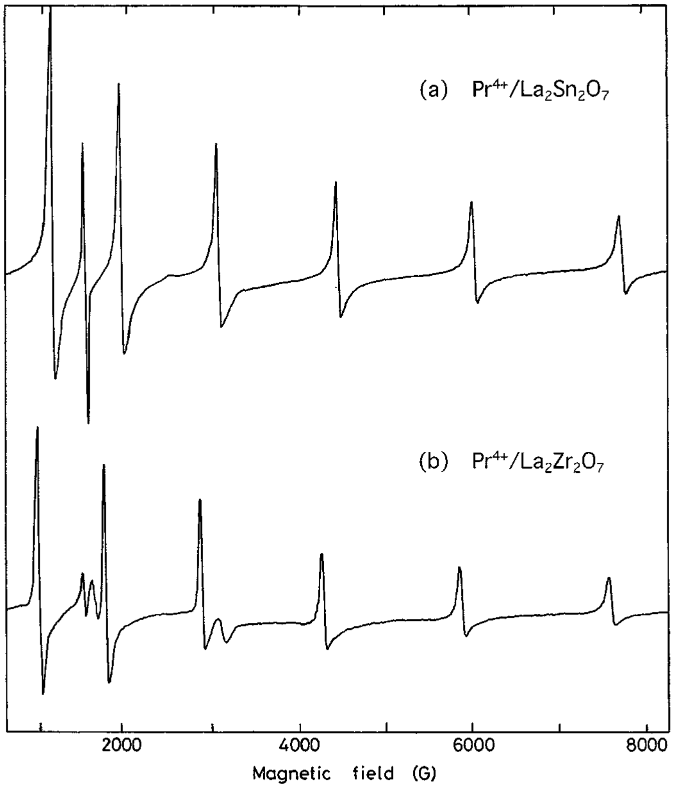

FIG. 2. EPR spectra for Pr^{4+} doped in $La_2Sn_2O_7$ (a) and $La_2Zr_2O_7$ (b) measured at 4.2 K ($h\nu = 9.091$ GHz).

In these $Pr^{4+}/La_2Sn_2O_7$ and $Pr^{4+}/La_2Zr_2O_7$, six EPR absorption lines have been measured. The spacings between them are large enough and they become wider with resonance magnetic field, which indicates that electron spin quantum number (m_s) and nuclear spin quantum number (m_I) are not good (pure) quantum numbers. We have to solve the Hamiltonian [1] exactly. The solution has been given by Ramsey (5) and others (6).

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 ($\Delta F = 0, \pm 1$; $\Delta m_F = \pm 1$) are observable as shown in Fig. 3. For $Pr^{4+}/BaCeO_3$, five forbidden transitions ($\Delta F = \pm 1$; $\Delta m_F = 0$) have been also observed (2). By fitting the observed EPR spectra to the parameters of the spin Hamiltonian [1], the best fit parameters g and A are obtained; $|g| = 1.262$, $|A| = 0.0752$ cm^{-1} for $Pr^{4+}/La_2Sn_2O_7$, and $|g| = 1.270$, $|A| = 0.0768$ cm^{-1} for $Pr^{4+}/La_2Zr_2O_7$. Figure 3 shows the Zeeman energy levels calculated for Pr^{4+} in $La_2Sn_2O_7$ using the parameters determined in this experiment (assuming $A > 0$). Arrows show the observable EPR transitions.

The absorption line centered at ca. 1520 G for the spectrum of $Pr^{4+}/La_2Sn_2O_7$ is not assigned to the Pr^{4+} ion. The temperature dependence of this EPR line is quite different from that of the others. The assigned lines become considerably weaker in intensity with increasing temperature, but the intensity of the absorption line centered at 1520 G does not change with temperature. In addition, the corresponding absorption line has not been found in the spectrum of $Pr^{4+}/La_2Zr_2O_7$. For this reason, we consider that this EPR line is not due to the Pr^{4+} ion.

Although the sign of the g value is not obtained by this experiment, comparison with other f^1 systems in octahedral symmetry, such as NpF_6/UF_6 (7) and Pa^{4+}/Cs_2ZrCl_6 (6), where the sign of the g value has been measured, indicates that the g value for the Pr^{4+} ion doped in these pyrochlore-type compounds should be also negative.

We will discuss the g value determined in this experiment. The Pr^{4+} ion is substituted for the Sn^{4+} (Zr^{4+}) ion and it is octahedrally coordinated by six oxygen ions as a first approximation. For one f electron, the ^2F Russell-Saunders state breaks up into two J states, $J = 5/2$ and $J = 7/2$, when the effect of spin–orbit coupling is included. If we assume octahedral symmetry for the Pr^{4+} ion in the pyrochlore-type

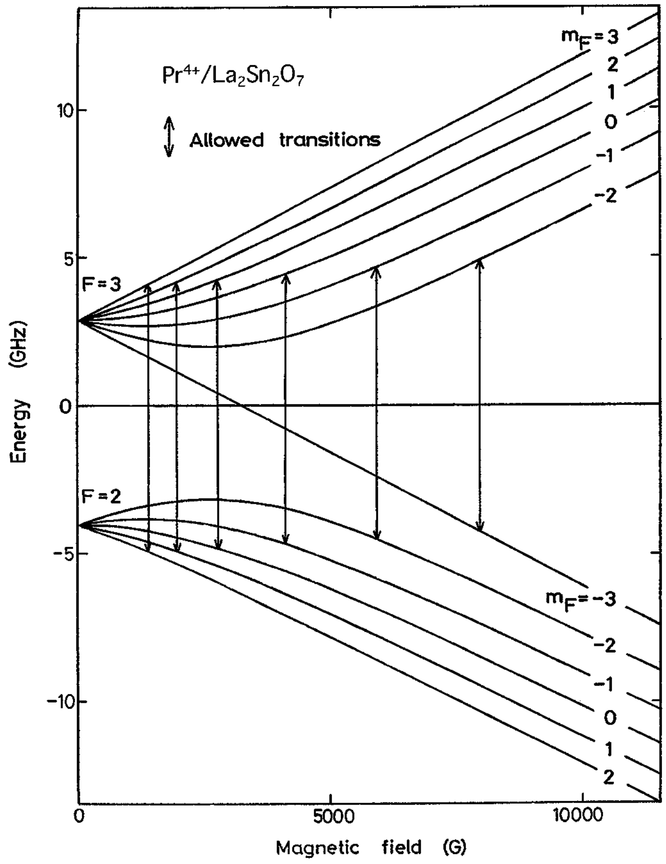

FIG. 3. Zeeman energy levels for Pr^{4+} in $La_2Sn_2O_7$ ($A > 0$). Arrows show the observable EPR transitions at 4.2 K.

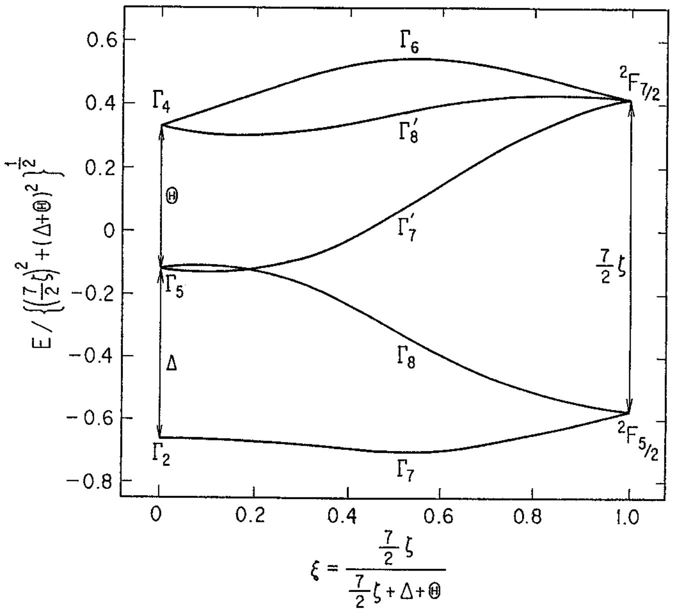

FIG. 4. Relative energy splittings of an *f* electron as the relative magnitudes of the crystal field (with octahedral symmetry) and spin–orbit coupling interactions change.

structure, the $J = 5/2$ state breaks up into a doubly degenerate Γ_7 state and a four-fold degenerate Γ_8 state. The higher-lying $J = 7/2$ state breaks up into two doubly degenerate states, Γ_6 and Γ'_7, and a four-fold degenerate Γ'_8 state (8). Figure 4 shows the relative energy level splittings of an f^1 electron in octahedral symmetry. The ground state in this symmetry is the $J = 5/2$, Γ_7 state. The g value for the Γ_7 ground doublet in a pure $J = 5/2$ manifold would be $-5/3$ times the Landé g factor. Since the Landé factor for the f^1 configuration is equal to 6/7, the g value is $-10/7$. When the crystal field interaction is not small as compared to the spin–orbit coupling interaction, the excited $J = 7/2$, Γ'_7 state is mixed into the ground $J = 5/2$, Γ_7 state via this interaction. The resulting expression for the ground state g value is given by

$$g = -2(5/7\cos^2\alpha - 8/21\sqrt{3}\cos\alpha\sin\alpha - 12/7\sin^2\alpha) \qquad [2]$$

with

$$|\Gamma_7\rangle = \cos\alpha|J = 5/2, \Gamma_7\rangle + \sin\alpha|J = 7/2, \Gamma'_7\rangle. \qquad [3]$$

With increasing admixture (i.e., increasing crystal field strength), the g value becomes larger, but can never exceed two (9, 10). From the measured g value, the admixture of $J = 7/2$, Γ'_7 state into the ground $J = 5/2$, Γ_7 state is at most 1%. The $|g|$ values obtained here are smaller than $|-10/7|$, which indicates that the crystal field is effective to some extent on the behavior of a 4*f* electron in this compound. Since the g value for an f electron in octahedral symmetry is negative, the value of $|g|$ which is obtained from this EPR experiment should decrease by increasing the crystal field strength. By decreasing the size of the lattice ($Pr^{4+}/La_2Zr_2O_7 \rightarrow Pr^{4+}/La_2Sn_2O_7$) which means the increase of the crystal field strength, the value of $|g|$ decreases. This is in agreement with the above discussion. Compared with the $|g|$ values for the Pr^{4+} ions doped in cubic perovskite-type structures $BaMO_3$ (M = Sn, Zr, Ce) (2, 11), it is found that the crystal field does not have much influence on the electronic state of the Pr^{4+} ions doped in these pyrochlore-type structures.

On the other hand, the hyperfine coupling constant A is given by the following equation (12),

$$A = -2g_N\beta\beta_N\langle r^{-3}\rangle(16/7\cos^2\alpha + 8/21\sqrt{3}\cos\alpha\sin\alpha - 16/7\sin^2\alpha), \qquad [4]$$

where g_N is the nuclear g value, β is the Bohr magneton, and β_N is the nuclear magneton. This equation indicates that that the sign of A should be also negative in this case.

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