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Electron Paramagnetic Resonance Spectra of Pr^{4+} Ions Doped in Sr_2SnO_4 and Ba_2SnO_4

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The isotropic electron paramagnetic resonance (EPR) spectra of powders with Pr^{4+} doped in M_2SnO_4 ($M = Sr$, Ba) with K_2NiF_4-type structure were measured at 4.2 K. A very large hyperfine interaction with the ^{141}Pr nucleus was observed. The results were analyzed based on the weak field approximation, and g values and hyperfine coupling constants A were obtained. The measured g values are much smaller than $|-10/7|$, showing that the crystal field effect on the behavior of a 4f electron is large. The value of $|g|$ decreases from 0.646 (Pr^{4+}/Ba_2SnO_4) to 0.615 (Pr^{4+}/Sr_2SnO_4), which is caused by the increase of the crystal field due to the shrinking of the lattice. In contrast, the hyperfine coupling constants are almost constant: $A = 0.0605\ cm^{-1}$. © 1997 Academic Press

INTRODUCTION

The electronic configuration of 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 when 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.

Although the trivalent oxidation state of praseodymium is the most stable, the tetravalent state is accessible. In an earlier study (1), 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. From the analysis of the spectrum, it was found that although this is a 4f-electron system, the crystal field influences the magnetic properties of a 4f electron.

To obtain more information on the behavior of a 4f electron in solids, we have prepared samples in which Pr^{4+} ions are doped in cubic layered perovskites Sr_2SnO_4 and Ba_2SnO_4 with the K_2NiF_4-type structure and measured their EPR spectra. The effect of the crystal field on the behavior of a 4f electron is discussed.

EXPERIMENTAL

1. *Sample Preparation*

$BaCO_3$ (or $SrCO_3$), Pr_6O_{11}, and SnO_2 were used as the starting materials. Before use, the Pr_6O_{11} was reduced to the stoichiometric Pr_2O_3 by heating in a flow of hydrogen gas at 1000°C for 8 hr, and the SnO_2 was heated in air at 850°C to remove any moisture and oxidized to the stoichiometric composition. They were weighed in the correct metal ratios $Sr(Ba)_2Pr_{0.02}Sn_{0.98}O_4$, intimately mixed, and heated in a flowing oxygen atmosphere at 1300°C in an SiC resistance furnace for one day. After cooling to room temperature, the samples were crushed into powder, reground, repressed into pellets, and heated again under the same conditions to make the reaction complete.

2. *Analysis*

An X-ray diffraction analysis was performed with Cu$K\alpha$ radiation on a Philips PW 1390 diffractometer equipped with a curved graphite monochromator. The samples prepared in this study were formed in a single phase with the K_2NiF_4-type structure.

3. *Electron Paramagnetic Resonance Measurement*

The EPR spectra at X band (9.053 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.

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RESULTS AND DISCUSSION

The EPR spectra could be measured at 4.2 K in both of the host materials. 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 (2).

The crystal structures for Sr_2SnO_4 and Ba_2SnO_4 are K_2NiF_4-type. They are shown in Fig. 1. In this layered perovskite structure, each Sn atom has around it an octahedron of oxygen atoms. In the samples prepared in this study, Pr^{4+} ions substitute Sn^{4+} ions.

Figure 2 shows the EPR spectra for Pr^{4+} doped in Sr_2SnO_4 and Ba_2SnO_4 measured at 4.2 K. Five absorption lines have been observed. They are due to the hyperfine interaction with nuclear spin for ^{141}Pr ($I = 5/2$) (natural abundance 100%). The EPR spectrum for Pr^{4+} doped in Sr_2SnO_4 is not sharp, which shows the small crystal field distortion from an octahedral field symmetry due to the mismatch in size of the Pr^{4+} ion into the Sn^{4+} site. In the spectrum for Pr^{4+}/Ba_2SnO_4, several very weak absorption lines are observed along with its main EPR absorption lines. The positions and magnitudes of their EPR absorption lines vary with Pr concentration (y value) in $Ba_2Pr_ySn_{1-y}O_4$; they are considered to be attributable to other phases of the PrO_2–Ba_2SnO_4 system.

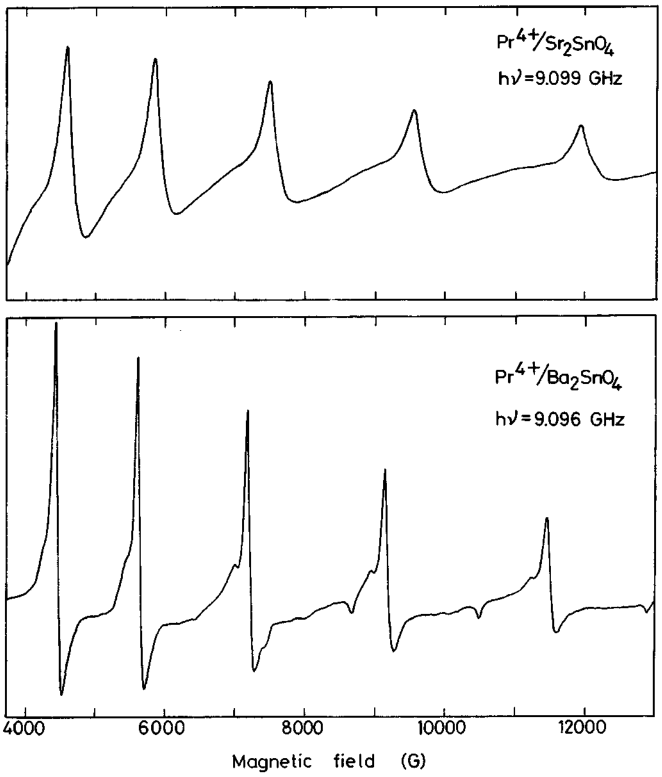

FIG. 2. EPR spectra for Pr^{4+} doped in Sr_2SnO_4 and Ba_2SnO_4 measured at 4.2 K.

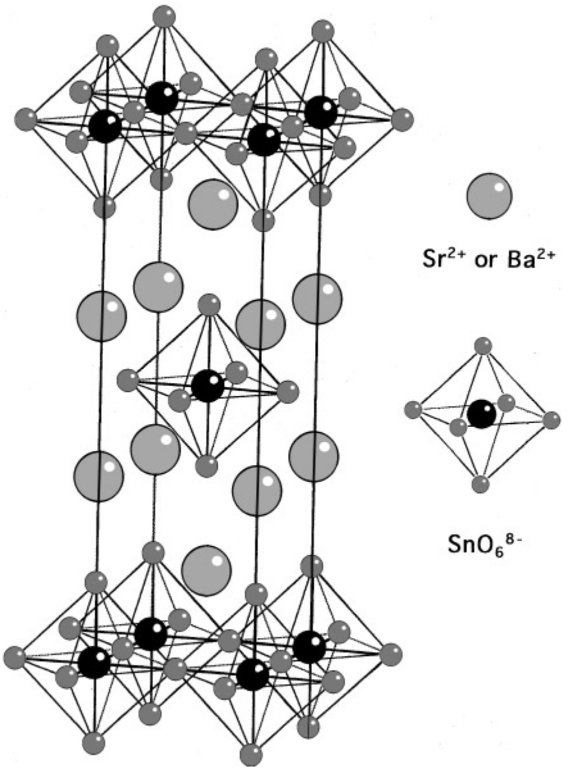

FIG. 1. Crystal structure of Sr_2SnO_4 and Ba_2SnO_4.

For the case of $Pr^{4+}/BaCeO_3$, we have measured and analyzed the EPR spectrum of the Pr^{4+} ion in which six absorption lines due to allowed transitions are observed along with five weaker absorption lines due to forbidden transitions (1). In the present case, no EPR absorption lines due to forbidden transitions are observed. The sixth absorption line due to the hyperfine interaction with nuclear spin for ^{141}Pr has not been observed in this experiment.

The spin Hamiltonian for the isotropic EPR spectrum of Pr^{4+} 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 $I = 5/2$. In the Pr^{4+}/Sr_2SnO_4 and Pr^{4+}/Ba_2SnO_4 spectra, the spacings between EPR absorption lines are large and become wider with resonance magnetic field, which indicates that the electron spin quantum number (m_S) and the nuclear spin quantum number (m_I) are not good (pure) quantum numbers. We must solve the Hamiltonian [1] exactly. The solution has been given by Ramsey (3) and others (4).

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 ($\Delta F = \pm 1$; $\Delta m_F = \pm 1$) are observable (see Fig. 3). By fitting the observed EPR spectra to the parameters of the spin Hamiltonian [1], the best fit parameters are obtained with $|g| = 0.615$ and $A = 0.0605\ \text{cm}^{-1}$ for Pr^{4+}/Sr_2SnO_4, and $|g| = 0.646$ and $A = 0.0605\ \text{cm}^{-1}$ for Pr^{4+}/Ba_2SnO_4, with g'_N set equal to 0.0.

The results of fitting the experimental and calculated EPR absorption line positions for both Pr^{4+}/Sr_2SnO_4 and Pr^{4+}/Ba_2SnO_4 are shown in Tables 1 and 2, respectively. The resonance fields for the sixth allowed transition (the highest resonance field) are 15,364 and 14,623 G, respectively, which are beyond our maximum magnetic field obtainable (13,500 G). Figure 3 shows the Zeeman energy levels calculated for Pr^{4+} in Ba_2SnO_4. Arrows show the observable EPR transitions.

TABLE 1
Experimental and Calculated EPR Absorption Line Positions for $Sr_2Pr_{0.02}Sn_{0.98}O_4$[a]

Experimental	Calculated[b]	Difference
—	15,364	—
12,276	12,286	−10
9,696	9,643	53
7,578	7,513	65
5,904	5,896	8
4,650	4,715	−65

[a] All values are given in Gauss.

[b] Spin-Hamiltonian parameters: $|g| = 0.615$, $A = 0.0605\ \text{cm}^{-1}$, g_N set equal to 0.0.

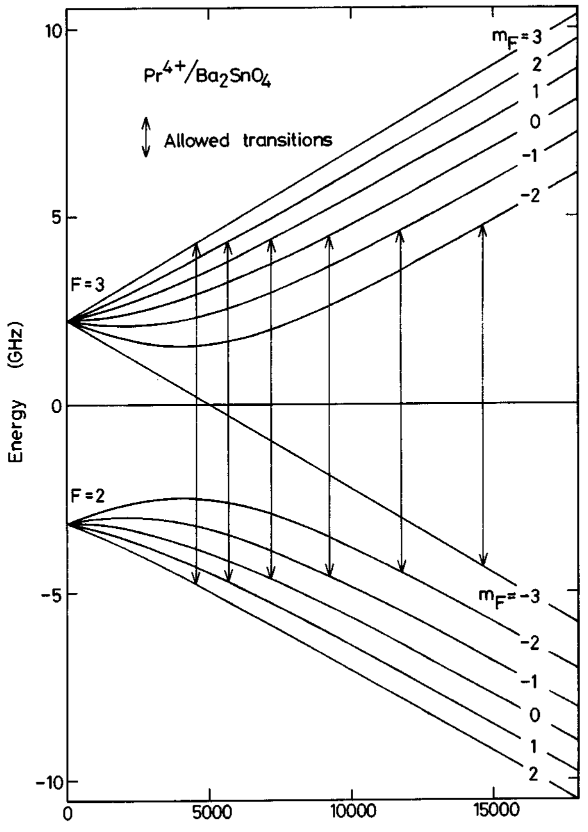

FIG. 3. Zeeman energy levels for Pr^{4+} in Ba_2SnO_4, Arrows show the observable EPR transitions at 4.2 K.

For a single *f* electron in an octahedral field, the sevenfold orbitally degenerate energy state is split into a singlet state Γ_2 and two triplet states Γ_4 and Γ_5 (see Fig. 4) (5). The energy difference between Γ_2 and Γ_5 is labeled as Δ, and the energy difference between Γ_4 and Γ_5 is labeled as Θ. When spin–orbit coupling is taken into account (with ζ the spin–orbit coupling constant), the Γ_2 orbital state is transformed into a doublet Γ_7, and the Γ_5 and Γ_4 states are split into Γ'_7 and Γ_8, and Γ_6 and Γ'_8, respectively. The ground state Kramers doublet is a Γ_7 state and is coupled to the excited Γ'_7 state, arising from the Γ_5 orbital state, by the spin–orbit coupling.

The g value for the ground state Γ_7 doublet is calculated to be

$$\begin{aligned} g &= 2\langle\Gamma_7|L + 2S|\Gamma_7\rangle \\ &= 2\cos^2\theta - 4/\sqrt{3}\sin 2\theta, \end{aligned} \qquad [2]$$

TABLE 2
Experimental and Calculated EPR Absorption Line Positions for $Ba_2Pr_{0.02}Sn_{0.98}O_4$[a]

Experimental	Calculated[b]	Difference
—	14,623	—
11,677	11,693	−16
9,219	9,176	43
7,205	7,148	57
5,617	5,610	7
4,414	4,486	−72

[a] All values are given in Gauss.

[b] Spin-Hamiltonian parameters: $|g| = 0.646$, $A = 0.0605\ \text{cm}^{-1}$, g_N set equal to 0.0.

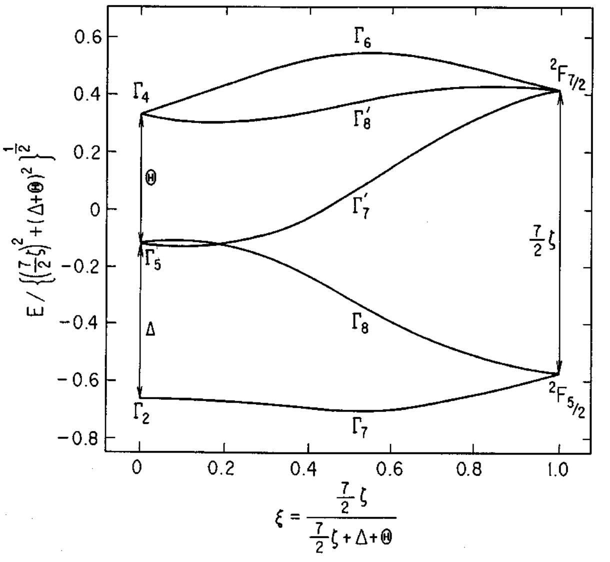

FIG. 4. Relative energy splittings of an f^1 electron as the relative magnitudes of the crystal field (with octahedral symmetry) and spin–orbit coupling interactions change.

where θ is the parameter describing the admixture of the Γ_7 levels in the ground state, determined by the relation

$$\tan 2\theta = 2\sqrt{3}/(\Delta - 1/2\,\zeta). \qquad [3]$$

Equation [2] indicates that the g value for an f electron perturbed by the octahedral crystal field should be between $-10/7$ (for the Γ_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 (6, 7).

The variation of the g value for an f^1 configuration in octahedral symmetry against the $\Delta/(7/2\,\zeta)$ (ratio of the crystal field splitting to spin–orbit interaction) is shown in Fig. 5. In this figure, the g values for NpF_6/UF_6 ($g = -0.608$, strong crystal field) (8) and for Pa^{4+}/Cs_2ZrCl_6 ($g = -1.142$, weak crystal field) (4) are also plotted. 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 (8) and Pa^{4+}/Cs_2ZrCl_6 (4) indicates that the g values for these Pr^{4+}/Sr_2SnO_4 and Pr^{4+}/Ba_2SnO_4 should be negative. This figure indicates that the crystal field strength is large in these compounds.

The crystal field strength for Pr^{4+} in Sr_2SnO_4 should be larger than that in Ba_2SrO_4, because the lattice parameter for the $Sr_2Pr_{0.02}Sn_{0.98}O_4$ is smaller than that for $Ba_2Pr_{0.02}Sn_{0.98}O_4$. According to Fig. 5, the value of $|g|$ which is obtained from this EPR experiment decreases with increasing crystal field strength. The value of $|g|$ obtained for Pr^{4+}/Sr_2SnO_4 is 0.615, which is smaller than the value obtained for Pr^{4+}/Ba_2SnO_4 ($|g| = 0.648$). This result is in agreement with the above consideration that the value of $|g|$ should decrease with increasing the crystal field strength. In contrast, the value of A is almost constant.

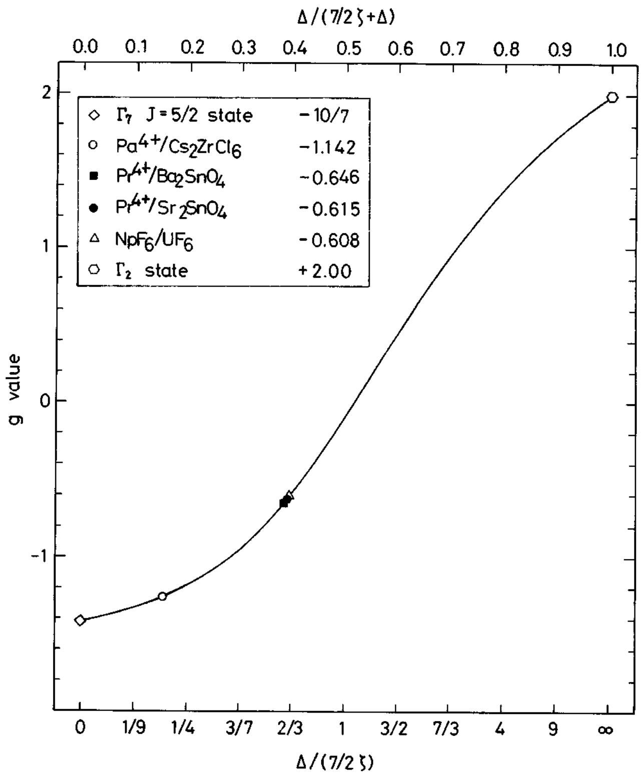

FIG. 5. g values vs the ratio $\Delta/(7/2\,\zeta)$ for f^1 configuration in octahedral symmetry.

ACKNOWLEDGMENT

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REFERENCES

1. Y. Hinatsu and N. Edelstein, *J. Solid State Chem.* **112,** 53 (1994).
2. A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Chap. 5. Oxford Univ. Press, London, 1970.
3. N. F. Ramsey, "Molecular Beams." Clarendon Press, Oxford, 1956.
4. J. D. Axe, H. J. Stapleton, and C. D. Jeffries, *Phys. Rev.* **121,** 1630 (1961).
5. B. R. Judd, "Operator Techniques in Atomic Spectroscopy." McGraw–Hill, New York, 1963.
6. Y. Hinatsu, T. Fujino, and N. Edelstein, *J. Solid State Chem.* **99,** 182 (1992).
7. Y. Hinatsu, *J. Alloys Compounds* **203,** 251 (1994).
8. C. A. Hutchison and B. Weinstock, *J. Phys. Chem.* **32,** 56 (1960).