Electron Paramagnetic Resonance Spectrum of Pr^{4+} in Sr_2CeO_4

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The electron paramagnetic resonance (EPR) spectra of Pr^{4+} diluted in Sr_2CeO_4 were measured at 4.2 K. A very large hyperfine interaction with the ^{141}Pr nucleus was observed. The spectra were anisotropic, due to the distortion of the octahedral oxygen coordination symmetry around the Pr^{4+} ion. The results were analyzed based on the weak field approximation, and the following g values and hyperfine coupling constants A were obtained: $|g_\parallel| = 1.169$, $|g_\perp| = 0.966$, $|A_\parallel| = 0.0703$ cm^{-1}, and $|A_\perp| = 0.0669$ cm^{-1}. The measured g values are smaller than $|-10/7|$, showing that the crystal field is effective to some extent on the behavior of a $4f$ electron in Sr_2CeO_4. © 1999 Academic Press

INTRODUCTION

The most stable oxidation state of lanthanide elements is trivalent. In addition to this state, cerium, praseodymium, and terbium have the tetravalent state (1). The Pr^{4+} ion is of special interest because its electron configuration is $[Xe]4f^1$ ([Xe], xenon electronic core), which makes its electronic analysis straightforward as only the crystal field and spin–orbit coupling interactions are important. For example, in an octahedral crystal field environment, a measurement of the g value of an f^1 ion gives information on the relative magnitude of the spin–orbit interaction to the crystal field interaction. Harris *et al.* reported the first electron paramagnetic resonance (EPR) measurement of the Pr^{4+} ion doped in the tetragonal zircon $ZrSiO_4$ (2). The spectrum showed weak anisotropy due to the tetragonal crystal field around the Pr^{4+} ion.

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 (3). In an earlier study (4), we successfully measured for the first time the EPR spectrum of the 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 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. In addition to the allowed hyperfine interactions, forbidden hyperfine transitions were observed. The EPR results could be analyzed based on an octahedral crystal field around the Pr^{4+} ion (4). The measured $|g|$ values are much smaller than $|-10/7|$, which shows that the crystal field effect on the behavior of a $4f$ electron is large.

To obtain further information on the behavior of Pr^{4+} in solids, we have synthesized the ternary oxide Sr_2CeO_4. Very recently, the crystal structure of this compound has been determined (5). The crystal system is not triclinic as previously reported (6), but orthorhombic with a *Pbam* space group. Figure 1 shows the crystal structure of Sr_2CeO_4. The structure consists of linear chains of trans edge-sharing CeO_6 octahedra, with four equatorial μ^2-O atoms and two terminal Ce–O bonds per octahedron, surrounded by interchain Sr^{2+} cations. Thus Sr_2CeO_4 possesses an unusual one-dimensional chain structure type. The terminal Ce–O bonds are shorter than the equatorial bonds by ~ 0.1 Å. We consider that the Ce^{4+} ion in Sr_2CeO_4 is octahedrally coordinated by six oxygen ions, and that this octahedral coordination is tetragonally distorted. In this study, we have prepared samples of Pr^{4+}/Sr_2CeO_4 in which the Pr^{4+} ions are substituted for the Ce^{4+} ions. Through analysis of the EPR spectra, the coordination environment around the Pr^{4+} ion in Sr_2CeO_4 and the crystal field effect on the behavior of the $4f$ electron of the Pr^{4+} ion will be discussed.

EXPERIMENTAL

1. Sample Preparation

Sr_2CO_3, Pr_6O_{11}, and CeO_2 were used as the starting materials. Before use, Pr_6O_{11} and CeO_2 were heated in air

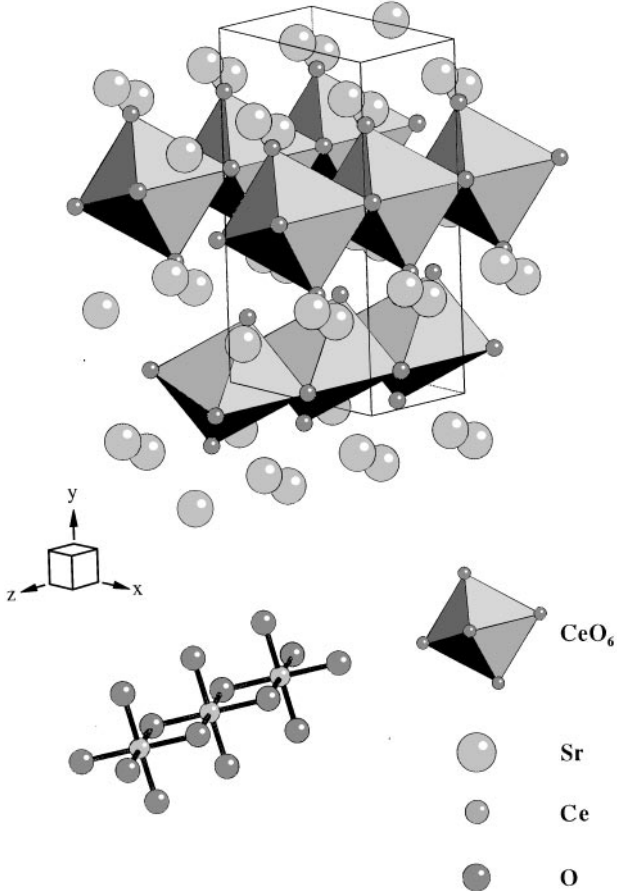[1] To whom correspondence should be addressed.

FIG. 1. Crystal structure of Sr_2CeO_4.

at 850°C to remove any moisture and to oxidize them to the stoichiometric compositions. They were weighed in the correct metal ratios $Sr_2Pr_xCe_{1-x}O_4$ ($x = 0.02, 0.05, 0.10$), 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, repressed into pellets, and heated under the same conditions to make the reaction complete. Since these oxides lose a few oxygen atoms 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

An X-ray diffraction analysis was performed with $CuK\alpha$ 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-2× 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. The spectra for $Sr_2Pr_{0.05}Ce_{0.95}O_4$ were stronger in intensity than the others.

RESULTS AND DISCUSSION

The EPR spectrum for Pr^{4+}/Sr_2CeO_4 was measured at 4.2 K as is shown in Fig. 2 (the upper spectrum). The spectrum is anisotropic and consists of 12 widely spaced hyperfine lines. With increasing temperature, all the absorption EPR lines become considerably weaker in intensity. These observations strongly indicate that the oxidation state of the praseodymium ion is not trivalent, but tetravalent, because the non-Kramers Pr^{3+} ion would either have no or a distinctly different EPR spectrum (7). Two very weak absorption lines at ca. 1100 and 1500 G (marked in Fig. 2) are not assigned to the Pr^{4+} ion, because they were observed even at room temperature.

The shape of this EPR spectrum is typical for the case of g tensor anisotropy (see below) with the relation $|g_\parallel| > |g_\perp|$ (axial symmetry). The 12 absorption lines are divided into two groups. Each consists of 6 absorption lines, which are due to the hyperfine interaction with the nuclear spin for ^{141}Pr ($I = 5/2$) in the orientations parallel and perpendicular to the fourfold symmetry axis. The anisotropic spectrum shows that we no longer have octahedral oxygen coordination symmetry around the Pr^{4+} ion.

The spin Hamiltonian appropriate for the distorted octahedral site of the Pr^{4+} ion in Sr_2CeO_4 is (8)

$$\mathcal{H} = \beta H \cdot g \cdot S' + S' \cdot A \cdot I + I \cdot Q \cdot I, \qquad [1]$$

where g, A, and Q are the g (or Zeeman), hyperfine, and quadrupole tensors, respectively. S' and I are the effective spin and nuclear spin quantum numbers, respectively. For the Pr^{4+} configuration, $S' = 1/2$ and the nuclear spin of ^{141}Pr is $I = 5/2$. EPR spectra of Pr^{4+} doped in cubic perovskites where the Pr^{4+} ion is at a site of octahedral symmetry showed that the hyperfine term cannot be regarded as a perturbation of the Zeeman term and the effective Hamiltonian has to be solved exactly (4, 9). The quadrupole tensor contribution is expected to be small compared to the Zeeman and hyperfine terms and in the preliminary analysis is set equal to zero. As discussed previously, the shape of the present EPR spectrum indicates that this is the case for axial symmetry $|g_\parallel| > |g_\perp|$ ($g_z = g_\parallel, g_x = g_y = g_\perp$; therefore $A_z = A_\parallel, A_x = A_y = A_\perp$); i.e., the parameters that have to be fitted are $g_\parallel, g_\perp, A_\parallel$, and $A_\perp$.

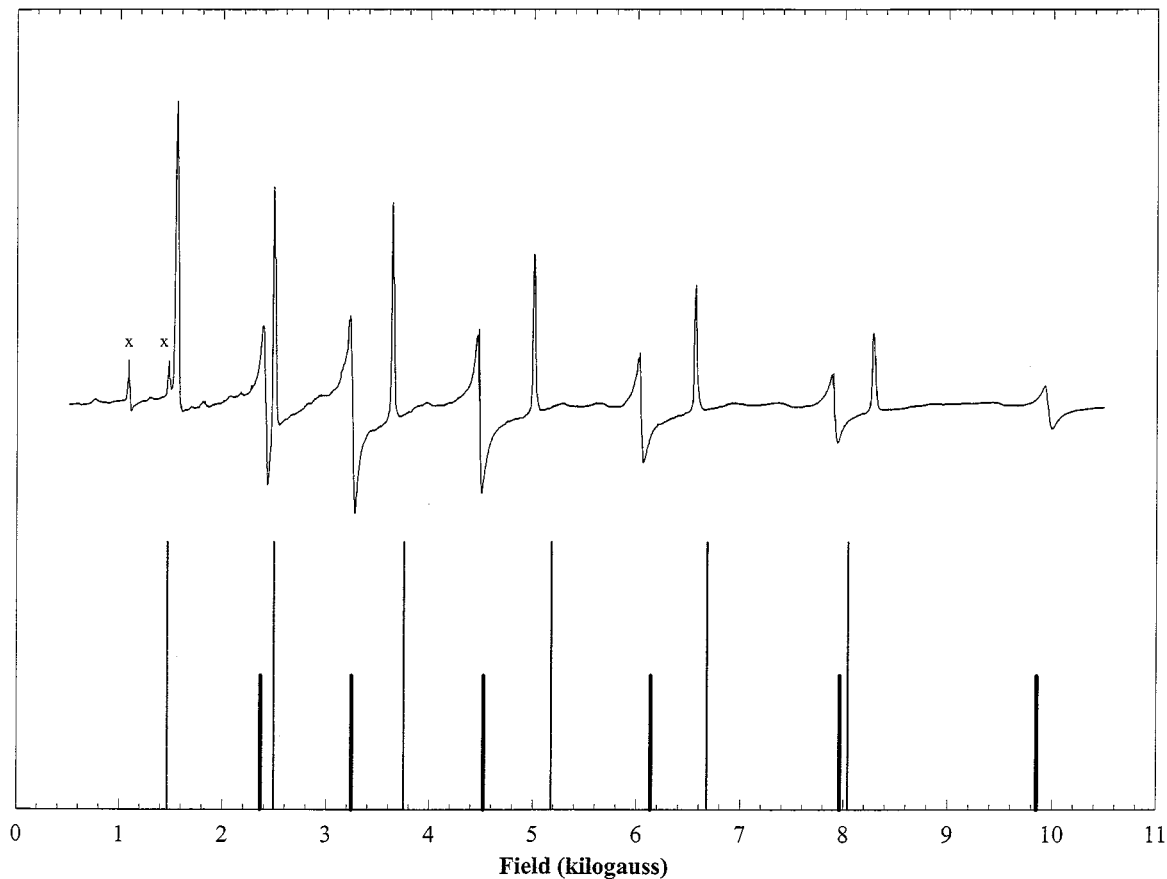**FIG. 2.** EPR spectra for Pr^{4+} doped in Sr_2CeO_4. (Top) Experimental spectrum; (bottom) calculated line positions.

The Hamiltonian [1] is usually solved with the approximation that the hyperfine term is much smaller than the Zeeman term and perturbation theory can be applied. For the Pr^{4+} ion, this approximation is not valid. In order to analyze the spectrum, we assume that the parallel spectrum is independent of the perpendicular spectrum and each can be treated separately. We use for each of these two spectra the Breit–Rabi formulation as described previously for the octahedral case, Pr^{4+} diluted in $BaCeO_3$. With these approximations we obtain $|g_{\parallel}| = 1.169$, $|g_{\perp}| = 0.966$, $|A_{\parallel}| = 0.0703 \, cm^{-1}$, and $|A_{\perp}| = 0.0669 \, cm^{-1}$. The calculated line positions are shown at the bottom of Fig. 2. The fits are reasonable considering the approximations and reproduce most of the features of the observed spectrum.

Although the sign of the g value is not obtained by this experiment, comparison with other f^1 system in octahedral symmetry, such as NpF_6/UF_6 (10) and Pa^{4+}/Cs_2ZrCl_6 (11), where the sign of the g value has been measured, indicates that the g values for the Pr^{4+} ion doped in this Sr_2CeO_4 should be negative.

Here, we will briefly discuss the g values obtained here. Although the anisotropy in the g value (i.e., $|g_{\parallel}| > |g_{\perp}|$)

means there is a distortion from octahedral symmetry at the Pr^{4+} site, we will consider the case of a single $4f$ electron in an octahedral crystal field as a first approximation, so as to discuss the g value quantitatively.

If we assume that spin-orbit coupling is negligible, the seven f orbital split into three levels, a singlet Γ_2 level and two triply degenerate levels, Γ_4 and Γ_5, using group theory notation for the octahedral group (O_h). With the addition of spin-orbit coupling, the Γ_2 level becomes a doubly degenerate Γ_7 state, the Γ_5 level splits into a fourfold degenerate Γ_8 state and a doubly degenerate Γ'_7 state, and the Γ_4 level splits into a fourfold degenerate Γ'_8 state and a doubly degenerate Γ_6 state. The energy levels can be calculated in terms of three parameters, the spin-orbit coupling constant ζ, Δ, and Θ, where Δ is the splitting between the Γ_2 and Γ_5 levels, and Θ is the splitting between the Γ_4 and Γ_5 levels in the strong crystal field limit. This is a common formalism for f^1 compounds and is shown on the left-hand side of Fig. 3.

We may also use the weak crystal field formulation. If we only consider spin-orbit coupling, the ^2F Russell–Saunders state breaks up into two J states, $J = 5/2$ and $J = 7/2$, as
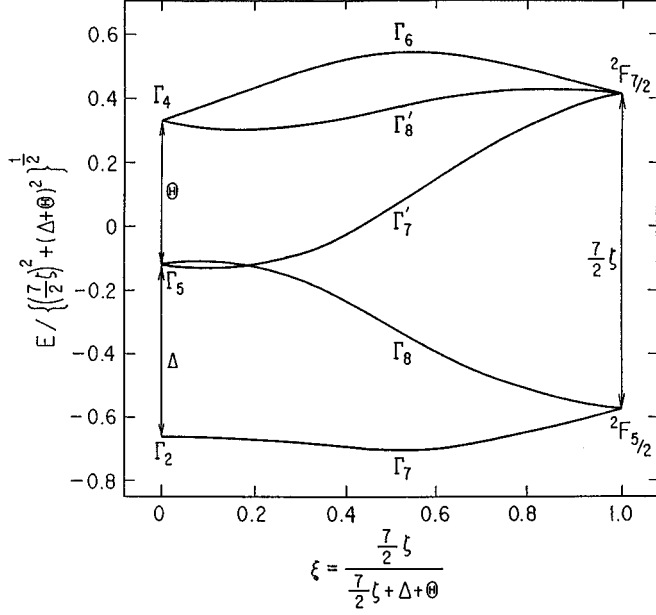
FIG. 3. Relative energy splittings of an f^1 electron as the relative magnitudes of the crystal field and spin-orbit coupling interactions change (octahedral symmetry).

shown on the right-hand side of Fig. 3. Including the octahedral crystal field interaction, the $J = 5/2$ state breaks up into a doubly degenerate Γ_7 state and a fourfold 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 fourfold degenerate Γ_8' state (12). Fig. 3 shows the relative energy level splittings of an f^1 electron in octahedral symmetry as the relative strengths of the spin-orbit coupling and the crystal field interaction change. The ground state in this symmetry is the $J = 5/2$, Γ_7 state. We have considered Pr^{4+} diluted in $BaCeO_3$ previously and from the measured g value, the Γ_7–Γ_8 splitting obtained from neutron scattering experiments for $BaPrO_3$ and the Pr^{4+} free ion coupling constant, we calculated the optical spectrum for this system (4). Our calculated levels were quite good agreement with the reported measurements (13).

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 $-10/7$. Indeed, the g value for Pa^{4+} in Cs_2ZrCl_6 is -1.142 (11). When the crystal field interaction is not small 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

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

with

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

With increasing admixture, the g value becomes larger, but can never exceed two. 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 2%. The $|g|$ values obtained here are smaller than $|-10/7|$ indicate that the crystal field is effective to some extent on the behavior of a $4f$ electron in this compound. Compared with the $|g|$ value for the Pr^{4+} ions doped in cubic perovskite-type structures $BaMO_3$ ($M =$ Sn, Zr, Ce) (4, 9), it is found that the crystal field does not much influence on the electronic state of the Pr^{4+} ions doped in this Sr_2CeO_4.

On the other hand, the hyperfine coupling constant A is given by (14)

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

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

The hyperfine coupling constants ($|A_\parallel| = 0.0703$ cm^{-1} and $|A_\perp| = 0.0669$ cm^{-1}), like the g values, show the existence of an anisotropy. There is a small difference between the ratios $A_\parallel/g_\parallel$ and $A_\perp/g_\perp$ which confirms the $^2F_{7/2}$ admixtures in the ground state.

The major conclusion determined from the EPR spectrum of the Pr^{4+} ion doped in Sr_2CeO_4 is the existence of the large tetragonal distortion from octahedral symmetry at the Pr^{4+} site. A g value anisotropy of greater than 20% is needed to qualitatively simulate the observed spectrum.

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