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Magnetic Susceptibility and Electron Paramagnetic Resonance Spectrum of Tetravalent Praseodymium Ions in $BaPrO_3$

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Tetravalent praseodymium perovskite, $BaPrO_3$, was prepared, and its magnetic susceptibility was measured in the temperature range between 4.2 K and room temperature. Magnetic ordering was found at 11.5 K. A very sharp decline of the susceptibility was observed when the temperature was increased through this transition temperature. Magnetic susceptibilities of $BaPr_{1-y}Ce_yO_3$ solid solutions were also measured. Electron paramagnetic resonance (EPR) spectra could be measured only at 4.2 K for the sample of praseodymium ion doped in diamagnetic $BaCeO_3$. The spectra were complicated. The results of magnetic measurements show that the praseodymium ion is in the tetravalent state. © 1993 Academic Press, Inc.

Introduction

The most stable oxidation state of praseodymium is trivalent. In addition to this state, it has the tetravalent state (*1*). As a result this element forms a series of oxide phases between sesquioxide (Pr_2O_3) and dioxide (PrO_2) (*2*). Although Pr_2O_3 is easily prepared by hydrogen reduction of praseodymium oxide, the preparation condition of PrO_2 is very severe (*3*); i.e., it seems very difficult to stabilize the tetravalent praseodymium ions in binary oxides. However, the situation is different in the ternary oxide system.

Perovskite-type oxides ABO_3, where A is a divalent ion (e.g. Sr, Ba), are known to accommodate a variety of tetravalent metal ions at the B sites of the crystals (*4*). The barium praseodymium oxide $BaPrO_3$ has been found to be orthorhombically distorted (*5*), although it was indexed previously as simple cubic (*6*). Several experimental results are available on the magnetic properties of this $BaPrO_3$. Kemmler-Sack and Hofelish measured its magnetic susceptibility in the temperature range between 77 and 473 K and reported that trivalent praseodymium ions were also contained in $BaPrO_3$ (*7*). Tofield *et al.* extended its temperature range down to 2.0 K and reported that there existed no magnetic interaction between praseodymium ions (*8*). Recently, Bickel *et al.* remeasured its magnetic susceptibility in the temperature range 4.2–300 K and reported the occurrence of magnetic ordering at 11.6 K (*9*). We suspect that this discrepancy may be due to oxygen nonstoichiometry in the samples.

In this study, we cautiously prepared oxygen-stoichiometric $BaPrO_3$ and measured its susceptibility to clarify the abovementioned inconsistent experimental results. Electron paramagnetic resonance (EPR) spectra were also measured to elucidate the electronic state of praseodymium ions in solids. Further, to clarify the nature

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of the magnetic interactions between praseodymium ions, solid solutions of $BaPrO_3$ diluted with diamagnetic $BaCeO_3$ were prepared and their magnetic susceptibilities and EPR spectra were measured.

Experimental

1. Preparation

$BaPrO_3$. As the starting materials, $BaCO_3$ and Pr_6O_{11} were used. The Pr_6O_{11} was reduced to the stoichiometric Pr_2O_3 by heating in a flowing hydrogen atmosphere at 1000°C for 8 hr. The $BaPrO_3$ was prepared by intimately grinding the $BaCO_3$ and Pr_2O_3 in the correct stoichiometric metal ratio and heating them in a flowing oxygen atmosphere at 1200°C in an SiC resistance furnace for 1 day. After cooling to room temperature, the sample was crushed into powder, reground, re-pressed into pellets, and heated under the same conditions to make the reaction complete. Since the $BaPrO_3$ loses a few oxygen atoms at high temperatures and is reoxidized to the stoichiometric composition during cooling (*10*), the sample was kept at 1000°C for 48 hr and cooled to room temperature in the furnace.

$BaPr_{1-y}Ce_yO_3$. As the starting materials, $BaCO_3$, Pr_2O_3, and CeO_2 were used. Before use, CeO_2 was heated in air at 850°C to remove any moisture and was oxidized to the stoichiometric composition. The $BaCO_3$, Pr_2O_3, and CeO_2 were weighed in the correct metal ratios ($y = 0.05, 0.10, 0.15, 0.20, 0.90, 0.95$, and 0.98) and well mixed. The heating procedures were the same as in the case of $BaPrO_3$ except for the heating temperature. It was raised to 1300°C to make the formation of solid solutions 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 lattice parameters of the samples were determined by a least-squares method. The oxygen concentrations of the samples were checked by the weight change from before to after heating.

3. Magnetic Susceptibility Measurement

The magnetic susceptibility was measured with a Faraday-type torsion balance in the 4.2–300 K temperature range. The temperature of the sample was measured by an Ag vs Au–0.07 at.%Fe thermocouple (4.2 K ~ 40 K) (*11*) and an Au–Co vs Cu thermocouple (10 K ~ room temperature). Details of the experimental procedure have been described elsewhere (*12*).

4. Electron Paramagnetic Resonance Measurement

The EPR measurements were carried out with a JEOL RE-2X spectrometer operating

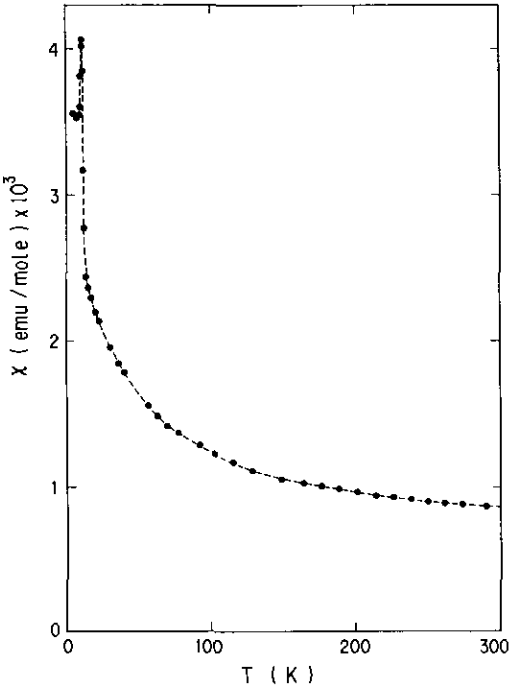

FIG. 1. Temperature dependence of magnetic susceptibility for $BaPrO_3$.

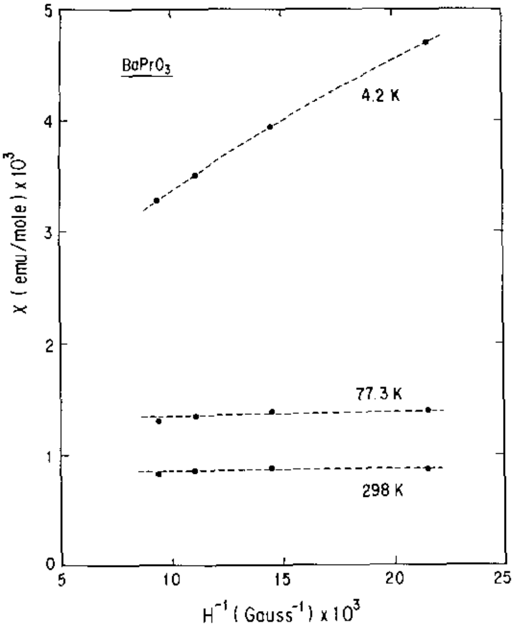

FIG. 2. Field dependence of magnetic susceptibility for $BaPrO_3$.

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 13,000 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 the sample tube. The magnetic field was monitored with a proton NMR gauss meter, and the microwave frequency was measured with a frequency counter.

Results and Discussion

X-ray powder diffraction analysis indicates that the $BaPrO_3$ prepared in this study was not cubic, but orthorhombic. The lattice parameters refined by a least-squares method were a = 6.188(1), b = 6.205(1), and c = 8.738(1) Å. The orthorhombic solid solutions of $BaPrO_3$ and $BaCeO_3$ were formed in a single phase. From oxygen analysis, the specimens prepared in this study are considered to have the ideal perovskite stoichiometry.

Figure 1 shows the temperature dependence of magnetic susceptibility for $BaPrO_3$. An antiferromagnetic transition has been found at 11.5 K. Similar magnetic behavior was reported by Bickel *et al.* (9) and their transition temperature is very close to ours. A very sharp decline of the susceptibility is observed when the temperature is increased through this transition temperature. This susceptibility decrease is much more remarkable than that reported by Bickel *et al.* Figure 2 shows the dependence of magnetic susceptibility on field strength at 4.2, 77.3, and 298 K. The susceptibility at 4.2 K depends on the magnetic field, but this is not true at 77.3 or 298 K. This result is

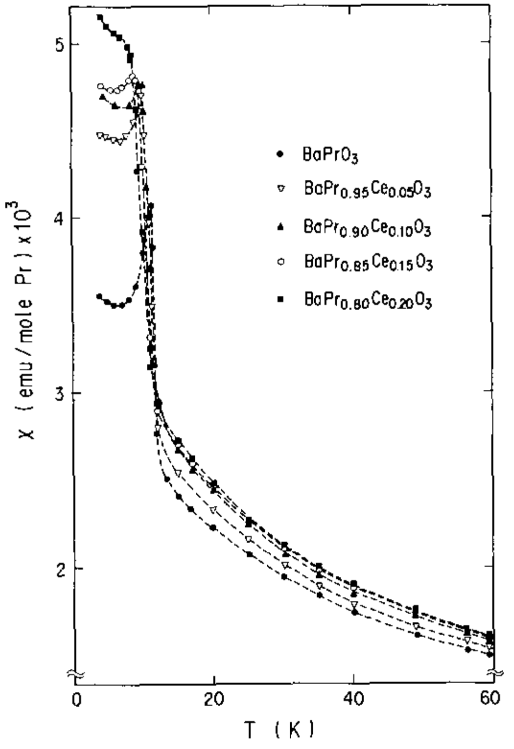

FIG. 3. Magnetic susceptibilities of $BaPr_{1-y}Ce_yO_3$ solid solutions (y = 0 ~ 0.20) at low temperatures.

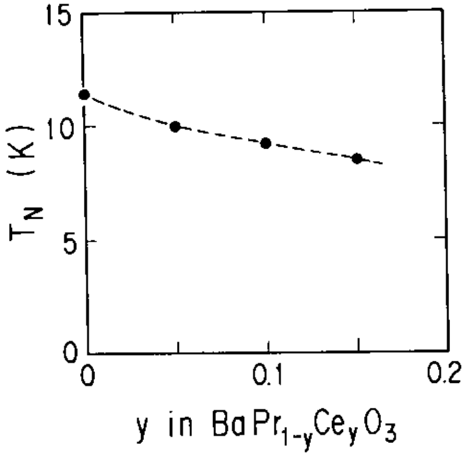

FIG. 4. Variation of T_N for $BaPr_{1-y}Ce_yO_3$ solid solutions with cerium concentration, y.

consistent with magnetic ordering below 11.5 K. These magnetic properties have been confirmed for all three samples which were prepared independently.

To clarify the nature of magnetic interactions between praseodymium ions, some diamagnetic cerium ions were substituted for praseodymium ions. Figure 3 shows the temperature dependence of magnetic susceptibilities for the $BaPr_{1-y}Ce_yO_3$ solid solutions at low temperatures. As expected, magnetic interactions between praseodymium ions are weakened with cerium substitution for praseodymium. The susceptibilities of praseodymium ions in $BaPr_{1-y}Ce_yO_3$ solid solutions are found to increase with cerium concentration (y). This small increase of susceptibility is due to the magnetic dilution by tetravalent cerium ions. Similar magnetic behavior has been found in the susceptibilities of $U_{1-y}Th_yO_2$ and $U_{1-y}Zr_yO_2$ solid solutions (*12*, *13*). Figure 4 shows the variation of transition temperatures (Néel temperatures, T_N) with cerium concentration, y. We cannot determine the critical concentration at which the antiferromagnetic transition disappears. For the $BaPr_{0.80}Ce_{0.20}O_3$ solid solution, the antiferromagnetic transition is no longer found in its susceptibility vs temperature curve (Fig. 3). However, at 4.2 K this solid solution showed a field dependence of magnetic susceptibility, which is shown in Fig. 5. We consider that magnetic interactions between praseodymium ions still operate in this solid solution.

If the praseodymium ion were in the tetravalent state, the EPR spectrum should be measured because the Pr^{4+} ion is Kramers ion ($[Xe]4f^1$ configuration). However, no EPR spectra were measured even at 4.2 K for $BaPrO_3$ or $BaPr_{1-y}Ce_yO_3$ ($y = 0.05 \sim 0.20$) solid solutions. This is due to the strong spin–spin interactions which are found experimentally in the magnetic susceptibility measurements. So, we prepared three samples in which Pr^{4+} ions were diluted with much more Ce^{4+}; i.e., y values of $BaPr_{1-y}Ce_yO_3$ were 0.90, 0.95, and 0.98.

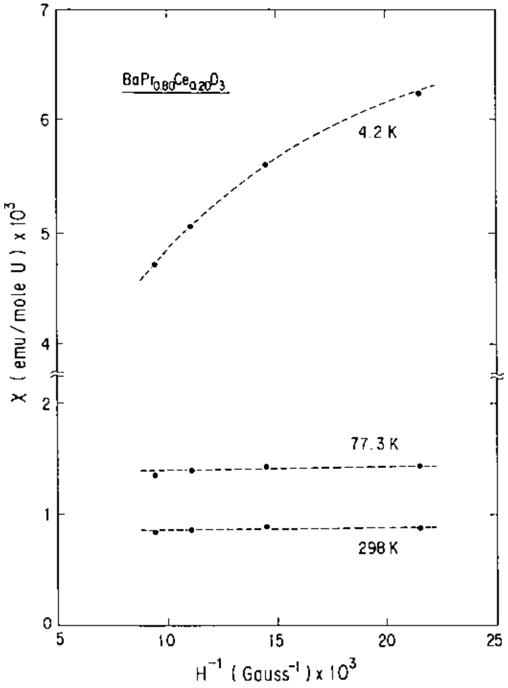

FIG. 5. Field dependence of magnetic susceptibility for $BaPr_{0.80}Ce_{0.20}O_3$.

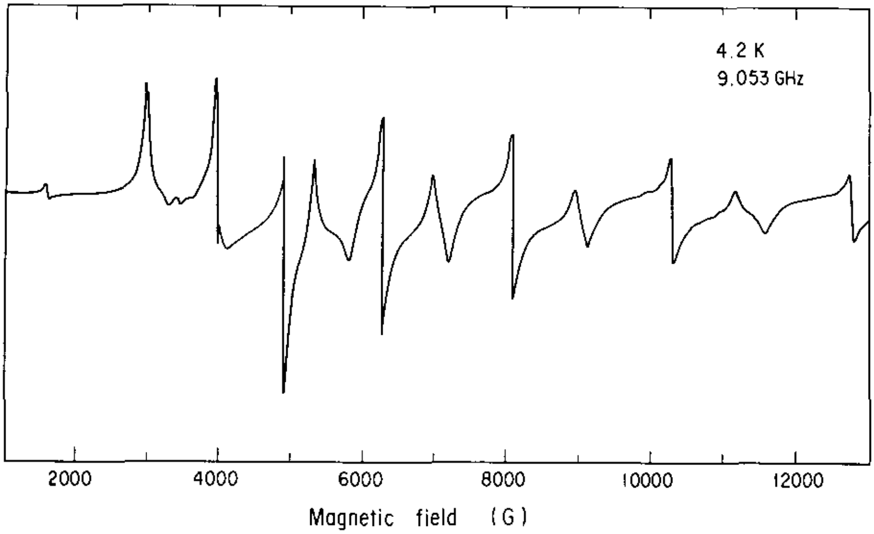

FIG. 6. EPR spectrum of $BaPr_{0.02}Ce_{0.98}O_3$ at 4.2 K.

At room temperature, no EPR spectra were measured. At 4.2 K, the EPR spectra could be measured for two samples, $BaPr_{0.02}Ce_{0.98}O_3$ and $BaPr_{0.05}Ce_{0.95}O_3$. Figure 6 shows the spectra for $BaPr_{0.02}Ce_{0.98}O_3$. Compared to the spectra for $BaPr_{0.02}Ce_{0.98}O_3$, the spectra for $BaPr_{0.05}Ce_{0.95}O_3$ were much weaker in intensity. The observation of EPR spectra strongly indicates that the oxidation state of praseodymium is tetravalent, because the Pr^{3+} ion (non-Kramers ion) shows no EPR spectra (*14*). The spectra are complicated and composed of many adsorption lines. If these lines were just due to the hyperfine interactions with ^{141}Pr (natural abundance 100%), the number of hyperfine lines should be 6 because the nuclear spin of ^{141}Pr is $\frac{5}{2}$ and the lines should be equally spaced. We consider that ^{141}Pr ions in different electronic states contribute to these spectra; i.e., the complicated spectra might be due to both small crystal field splittings of the ground state $^2F_{5/2}$ and hyperfine interactions with the nuclear magnetic moment of ^{141}Pr. The average magnetic field of the absorption lines is ~7500 G, which means the g-value is ~0.86. In this case, the Pr^{4+} ion is in a slightly distorted octahedral field. For an f^1 electron perturbed by octahedral crystal field, the g-value should be in the range of $-1.43 \leq g \leq 2.00$ (which is determined by the relative strengths of the crystal field and the spin–orbit interactions) (*15*); i.e., the g-value obtained in this EPR measurement is an acceptable one.

Next, we will discuss the effective magnetic moment of praseodymium obtained from the magnetic susceptibility measurements. From the extrapolation of the measured magnetic susceptibility (χ_{exp}) of $BaPrO_3$ to $1/T \rightarrow 0$, the temperature independent susceptibility (χ_{TIP}) was determined to be 6.8×10^{-4} emu/mole. The resulting temperature-dependent susceptibility ($\chi(T) = \chi_{exp} - \chi_{TIP}$) follows the equation $\chi(T) = 0.058/(T + 10.3)$. If we calculate the effective magnetic moment of praseodymium from this temperature-dependent part of the susceptibility, it is 0.68 μ_B. This moment is much smaller than that expected for a free f^1 ion (2.54 μ_B), which indicates that the effect of the crystal field on the magnetic properties is significant. When an octahedral crystal field operates on the Pr^{4+}, the ground state $^2F_{5/2}$ splits into a Γ_7 ground state and a Γ_8 excited state. This is the same situation as for the actinide ion with $[Rn]5f^1$ configuration ([Rn]; Rn core) in an octahedral crystal field, and a comparable small magnetic moment has been reported for Th^{3+}, Pa^{4+}, and U^{5+} compounds (*16, 17*). Since the g-value measured in this EPR study is 0.86, the effective magnetic moment is calculated to be 0.74 μ_B from the relation $\mu_{\text{eff}} = g\sqrt{S(S+1)}$ (S, spin quantum number). The moment of Pr^{4+} obtained from the susceptibility measurement for $BaPrO_3$ (0.68 μ_B) is still smaller than that from the EPR measurement for $BaPr_{0.02}Ce_{0.98}O_3$. This is due to the magnetic interactions between praseodymium ions, which are found experimentally in the susceptibility of $BaPrO_3$. As shown in Fig. 3, the susceptibility of the praseodymium ion in $BaPr_{1-y}Ce_yO_3$ increases with y value (cerium concentration), which results in the increase of the effective moment μ_{eff}.

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