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Magnetic Properties of RPd_3S_4 (R = Ce, Gd)

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Magnetic properties of palladium sulfide bronzes RPd_3S_4 (R = Ce, Gd) are reported. They crystallize in a cubic platinum bronze type structure. Their magnetic susceptibilities were measured from 2 to 350 K. The initial magnetization and magnetic hysteresis loop were measured at 2 K by changing the applied magnetic field between −5 and 5 T. The electron paramagnetic resonance (EPR) spectrum of Gd^{3+} was also measured at room temperature. $GdPd_3S_4$ shows an antiferromagnetic behavior below 5.8 K. Above 10 K the magnetic susceptibility follows the Curie law, and the effective magnetic moment is determined to be 7.36 μ_B. The magnetic moment is not saturated up to 5 T and no magnetic hysteresis has been found. From the EPR measurement the g value of Gd^{3+} in $GdPd_3S_4$ is determined to be 2.00. $CePd_3S_4$ shows ferromagnetism below 5.8 K. The residual magnetization is only 0.39 μ_B and the magnetic moment at 5 T is 0.83 μ_B at 2 K. This result shows that the ground state Γ_8 of Ce^{3+} is split into two Kramer's doublets by the crystal field. From the magnetic transition temperature of both $GdPd_3S_4$ and $CePd_3S_4$, the superexchange interaction is considered to be dominant in the magnetic interaction of these compounds. © 1999 Academic Press

INTRODUCTION

It is known that a series of lanthanide elements form sulfide bronzes with palladium, RPd_3S_4 (R = rare earths). Keszler and Ibers first synthesized $LaPd_3S_4$, $TbPd_3S_4$, and $SmPd_3S_4$ and found that they have an ideal $NaPt_3O_4$-type structure (1). They also reported that the temperature dependences of magnetic susceptibilities of $TbPd_3S_4$ and $SmPd_3S_4$ were derived from a Curie–Weiss paramagnetism for the free Tb^{3+} ion and from a van Vleck paramagnetism for the Sm^{3+} ion, respectively (1).

In their succeeding paper, Keszler *et al.* measured the magnetic susceptibilities of RPd_3S_4 (R = Pr, Sm, Tb, Ho) and found that they were paramagnetic from liquid He temperature to room temperature (2). Moreover, the electrical conductivity of $LaPd_3S_4$ was measured as a function of temperature between 100 and 300 K, and it was found to be metallic (2). This metallic conduction of RPd_3S_4 was supposed to fill partially the $d_{x^2-y^2}$ bands, which were substantially dispersive in all three directions of the lattice, and predicted to be genuine three-dimensional metals (3).

The electrical conductivity of RPd_3S_4 (R = La, Nd, Eu) was reported to be metallic at temperatures between 15 and 300 K (4). From the Hall coefficient measurements, the numbers and types of carriers are determined and the formulas are suggested to be $R^{3+}(Pd_3^{2+}e^-)S_4^{2-}$ for La and Nd compounds and $Eu_{0.5}^{2+}Eu_{0.5}^{3+}(Pd_3^{2+}e_{0.5}^-)S_4^{2-}$ for Eu compounds (4).

In this study, we synthesized palladium sulfide bronzes, RPd_3S_4 (R = Ce, Gd), of which the magnetic properties have not been reported yet, and measured their magnetic susceptibilities, magnetization, and electron paramagnetic resonance (EPR) spectra.

EXPERIMENTAL

To obtain rare-earth sulfides (Ce_2S_3 and Gd_2S_3), rare-earth oxides (CeO_2 and Gd_2O_3) with 99.9% purity were heated to 1273 K in a flow of the mixed gas of CS_2 and N_2 which was obtained by bubbling the N_2 gas through liquid CS_2. The calculated amounts of rare-earth sulfides, palladium powder with 99.9% purity, and sulfur with 99.999% purity were mixed in an agate mortar. The mixture was put into a quartz tube, evacuated, and sealed. Then, the ampule was heated at 1173 K for 3 days.

Powder X-ray diffraction measurements were performed on a Rigaku powder diffractometer (RINT2200) with Cu$K\alpha$ radiation monochromatized with curved pyrolytic graphite. The magnetic susceptibility and magnetization were measured by using a SQUID magnetometer (Quantum Design, Model MPMS). The temperature dependence of the magnetic susceptibilities was measured under both zero-field-cooled condition (ZFC) and field-cooled condition (FC). The former was measured on heating the samples to 350 K after zero-field cooling to 2 K. The applied magnetic field was 0.1 T. The latter was measured on cooling the sample from 350 to 2 K at 0.1 T. The field dependence of the magnetization was measured at 2 K by changing the applied

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magnetic field between − 5 and 5 T. For CePd$_3$S$_4$, it was also measured at 4.5 K by changing the field between − 0.3 and 0.3 T. The EPR spectra were obtained at room temperature with a JEOL 2XG spectrometer for the X band ($\nu = 9.1$ GHz). The magnetic field was monitored with a proton NMR gaussmeter.

RESULTS AND DISCUSSION

Samples were obtained as powder products. By the powder X-ray diffraction measurements, both of the rare-earth palladium sulfides were found to be formed in a cubic platinum bronze type structure and their lattice parameters were determined to be 6.7099(1) and 6.6518(1) Å for CePd$_3$S$_4$ and GdPd$_3$S$_4$, respectively, which are in agreement with the previous structural data (2, 5).

Figure 1 shows the temperature dependence of the reciprocal susceptibility (χ^{-1}) of GdPd$_3$S$_4$. This compound shows typical antiferromagnetic behavior below 5.8 K. The difference in the magnetic susceptibility between the FC and ZFC is not observed. Above 10 K, a linear relationship is found in the χ^{-1} vs T curve. In this compound, the palladium ions have four square-planar-coordinated sulfur ions and their oxidation state is + 1.67(4). One itinerant electron exists in the $d_{x^2-y^2}$ bands, which consist of the palladium d orbitals, per chemical formula (RPd$_3$S$_4$). The other bands, except for the $d_{x^2-y^2}$ bands, are completely filled and the magnetism of the palladium ions is expected to show a Pauli paramagnetism in a low-spin configuration. So the temperature dependence of susceptibilities is derived from that of the gadolinium ions. The ground state of the Gd^{3+} ion is $^8S_{7/2}$ and hence the orbital angular momentum vanishes, so the crystal field does not affect the susceptibility of the Gd compound. The effective magnetic moment is calculated to be 7.36 μ_B from the slope of the χ^{-1} vs T curve. This value is slightly smaller than the theoretical magnetic moment ($\mu_{eff} = 7.94$ μ_B) of a free Gd^{3+} ion.

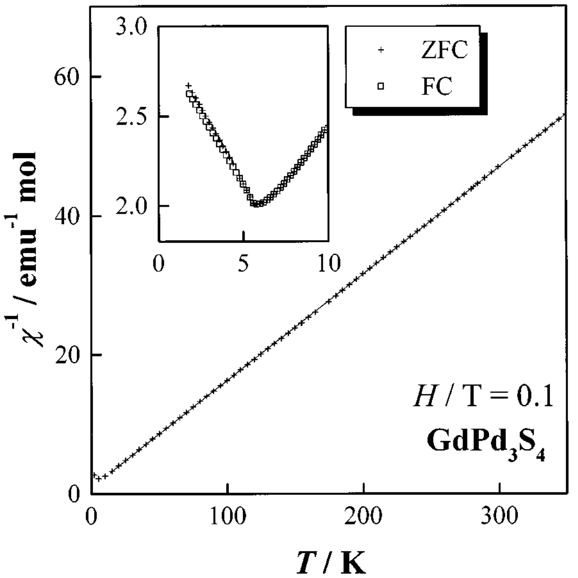

FIG. 1. Temperature dependence of the reciprocal susceptibility (χ^{-1}) of GdPd$_3$S$_4$. The inset shows χ^{-1} near the transition temperature.

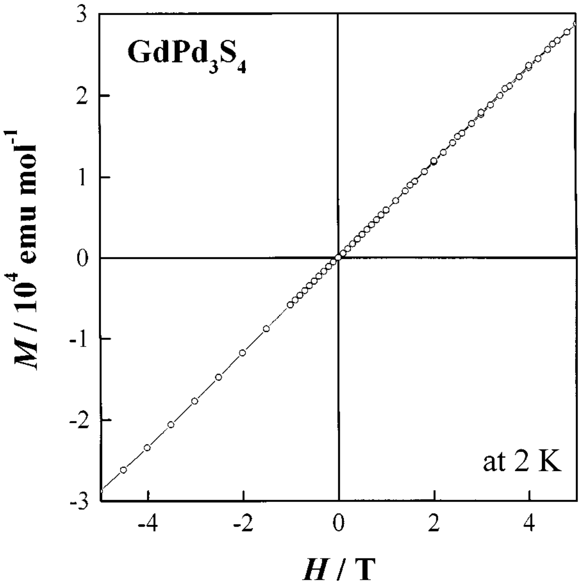

FIG. 2. Magnetization vs magnetic field curve at 2 K for GdPd$_3$S$_4$.

Figure 2 shows the variation of the magnetization in the field range between − 5 and 5 T measured at 2 K for GdPd$_3$S$_4$. No magnetic hysteresis has been found.

Figure 3 shows the X-band EPR spectrum for GdPd$_3$S$_4$ measured at room temperature in the magnetic field swept from 0 to 800 mT. A single broad line, which is centered at 323.3 mT with a peak-to-peak linewidth of 74.9 mT, associates with the Gd^{3+} ions. This isotropic spectrum indicates that the Gd^{3+} ions are located in cubic symmetry. The g value is calculated to be 2.00, which is in good agreement with the theoretical g value ($g = 2.00$) of the free Gd^{3+} ion.

The temperature dependence of the reciprocal magnetic susceptibility (χ^{-1}) and the magnetic susceptibility (χ) of CePd$_3$S$_4$ is shown in Fig. 4 and its inset, respectively. This compound shows a ferromagnetic behavior below 5.8 K. The divergence in the magnetic susceptibility between the FC and ZFC is observed below 3.6 K. In this compound, the rare-earth ions are eight-fold coordinated by sulfur ions and its symmetry is cubic. The ground state ($^2F_{5/2}$) of the Ce^{3+} ion would split into a low-lying quartet (Γ_8) and an excited Kramer's doublet (Γ_7) under the crystal field of the cubic symmetry (6). Then, the temperature dependence of the magnetic susceptibility for the Ce^{3+} ion can be

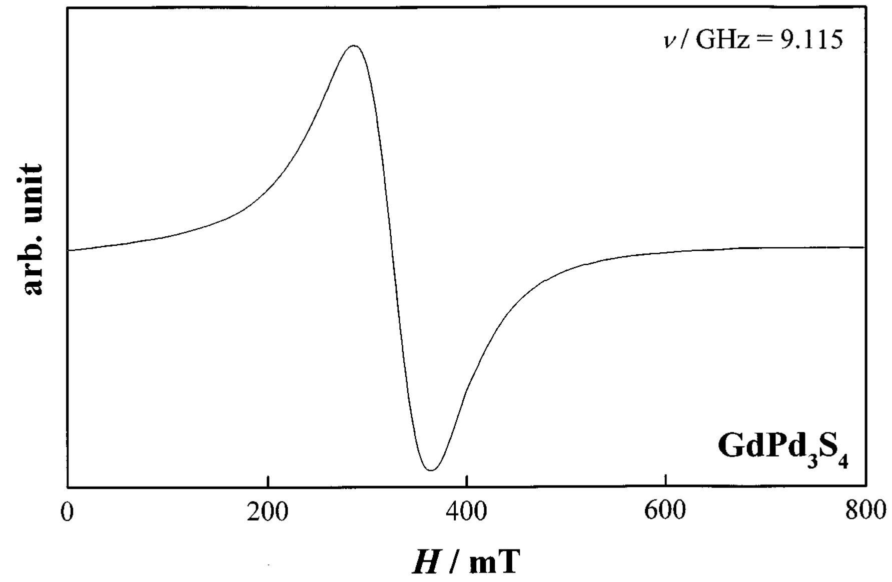

FIG. 3. EPR spectrum of Gd^{3+} in GdPd$_3$S$_4$ at room temperature.

calculated exactly to be

$$\chi(\mathrm{Ce}^{3+}) = \frac{N_A g_J^2 \mu_B^2 J(J+1)}{3k_BT} \times \frac{26 + 5e^{-\Delta_{87}/k_BT} + 32(k_BT/\Delta_{87})(1 - e^{-\Delta_{87}/k_BT})}{21(2 + e^{-\Delta_{87}/k_BT})} \qquad [1]$$

where N_A, g_J, μ_B, J, and Δ_{87} are Avogadro's number, the Landé g factor, the Bohr magneton, the total angular momentum, and the separation energy between Γ_8 and Γ_7, respectively. The measured susceptibilities were fitted in the range of 10–350 K by using Eq. [1] as shown in Fig. 4 (solid line). The fitted curve is in good agreement with the experimental data. The effective magnetic moment is calculated to be 2.14 μ_B, which is smaller than the theoretical magnetic moment ($\mu_{\mathrm{eff}} = 2.54\ \mu_B$) of the free Ce^{3+} ion. The separation energy, Δ_{87}, is 293 cm^{-1}, which is close to those of other compounds containing the Ce^{3+} ion, for example, 278 cm^{-1} (400 K) for CeMo$_6$S$_8$ (7) and 229 cm^{-1} (330 K) for CeMo$_6$Se$_8$ (8).

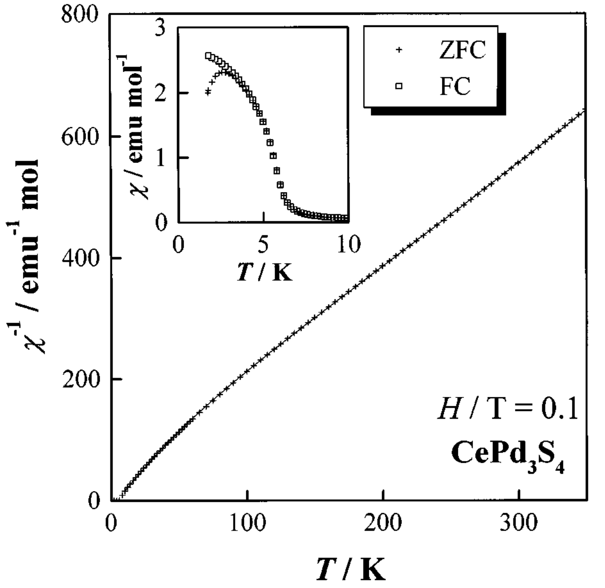

FIG. 4. Temperature dependence of the reciprocal susceptibility (χ^{-1}) of CePd$_3$S$_4$. The inset shows χ near the transition temperature.

Figure 5 shows the initial magnetization (after ZFC) and hysteresis curve of CePd$_3$S$_4$ at 2 K (open circles) and 4.5 K (closed circles) by changing the field between − 0.3 and 0.3 T. The inset of Fig. 5 shows the magnetic hysteresis curve measured at 2 K by changing the field between − 5 and 5 T. The area of hysteresis at 2 K is quite larger than that at 4.5 K. The residual magnetization is determined to be only 0.39 μ_B per formula unit at 2 K, which is larger than 0.18 μ_B at 4.5 K. This very small magnetization means that the ordered state cannot be accounted for as a simple ferromagnetic state. The hysteresis curve tends to flatten at higher fields, and the magnetic moment is calculated to be 0.83 μ_B at 5 T. This value means that the ground state of Ce^{3+} ions is a doublet and is not compatible with the Γ_8 quartet. Hence, we propose that the symmetry of the rare-earth site is slightly distorted from cubic symmetry and the ground state (Γ_8) is split into two Kramers' doublets by the crystal field. At high temperatures, the magnetic

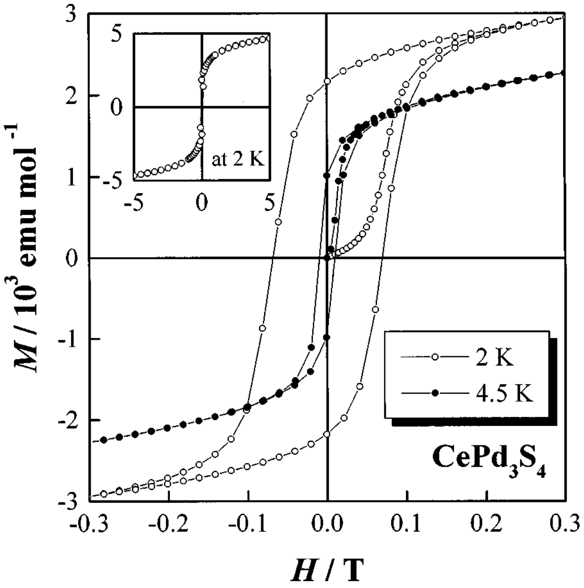

FIG. 5. Initial magnetization (after ZFC) and magnetic hysteresis curves at 2 and 4.5 K for $CePd_3S_4$.

susceptibility can be approximated by the model that the ground state is Γ_8 and that the it is split into two doublet states of which the separation energy is very small.

A series of RPd_3S_4 compounds have metallic conductivity. For such compounds, one of some possible mechanisms which play a role in the magnetic interaction is the RKKY interaction-type indirect interaction (8). This is mediated by conduction electrons which are associated with a PdS_4 columnar chain by analogy with the magnetic mechanism of the rare-earth Chevrel sulfides, RMo_6X_8 (R = rare earths, X = S and Se) (9, 10). However, the exchange energy for the RKKY interaction is proportional to the de Gennes factor $(g_J - 1)^2 J(J + 1)$ which is identical to the square of the J component of the total spin moment S (10). The present $CePd_3S_4$ and $GdPd_3S_4$ have the same magnetic transition temperatures ($T = 5.8$ K), although the spin momentum ($S = 1/2$) for the Ce^{3+} ion is smaller compared with that ($S = 7/2$) for the Gd^{3+} ion. The magnetic transition temperature for the Ce^{3+} compound should be quite smaller than that for the Gd^{3+} compound. So the RKKY interaction is not so strong. According to our X-ray structural refinement, the Gd^{3+} ion has six neighboring Gd^{3+} ions at a distance of 6.6518 Å and this distance is too far to consider the dipole–dipole-interaction-type direct interaction between rare-earth ions. Consequently, the linear R–S–R superexchange interaction is considered to be dominant in RPd_3S_4.

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