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Magnetic properties of layered oxysulfide (LnO)CuS:Ln = La, Pr, Nd

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Abstract

We have prepared rare earth oxysulfides (PrO)CuS and (NdO)CuS in order to introduce magnetic moments into the non-magnetic p-type semiconductor (LaO)CuS. Both compounds are semiconductors with high electrical resistivity, and show the paramagnetic behavior. The temperature dependence of the magnetic susceptibility is well explained by the trivalent rare earth ion. However, it deviates from simple Curie Wiess law below 100 K due to the crystal field effect on rare earth ions. We have succeeded to reproduce their magnetic properties by the calculation taking the crystal field effect into account using the operator equivalent method.

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Keywords: Layered rare earth oxysulflde; Crystal field; Magnetic semiconductor

1. Introduction

Lanthanum copper oxysulfide (LaO)CuS is a nonmagnetic p-type semiconductor. It belongs to the tetragonal *P*4/*nmm* group [1,2]. O and Cu ions are surrounded tetrahedrally by La and S ions, respectively. The physical properties of (LaO)CuS have been previously investigated by our research group [3–7]. Ueda et al. reported (LaO)CuS is transparent at visible wavelengths region and that (LnO)CuS (Ln: Ce, Pr, Nd) were paramagnetic and the effective magnetic moments μ_{eff} were estimated to be $2.1\mu_{\mathrm{B}}$, $3.1\mu_{\mathrm{B}}$ and $3.3\mu_{\mathrm{B}}$ for (CeO)CuS, (PrO)CuS and (NdO)CuS, respectively [8,9]. However, details of magnetic properties have not been clear yet. In the present study, we have synthesized (LaO)CuS, (PrO)CuS and (NdO)CuS, measured the electrical resistivity and the magnetization of (LnO)CuS (Ln: La, Pr, Nd), and explained the magnetic properties of latter two compounds by the calculation taking account of the crystal field effect using the operator equivalent method.

2. Experimental

(LnO)CuS (Ln: La, Pr, Nd) were obtained by the solid-state reaction. The starting materials were Ln_2O_3, Ln_2S_3, Cu, and S for (LaO)CuS and (NdO)CuS. For (PrO)CuS, we used Pr, Pr_2S_3, and CuO as the starting materials instead of using air sensitive Pr_2O_3. Those starting materials were mixed and pressed into bars. They were sealed in a evacuated silica tube ($\sim 1.5 \times 10^{-5}$ Torr) and heated at 1173 K ((LaO)CuS, (PrO)CuS) or 1323 K ((NdO)CuS). In the case of (PrO)CuS, the bars were reheated at the same temperature and hours with intermediate grinding. The powder X-ray diffraction measurement was performed at room temperature with Cu Kα radiation. The temperature dependences of the electrical resistivity were measured from 160 to 300 K by a standard four-probe method. Magnetic measurements were carried out using a SQUID in a temperature range $4 < T < 300$ K with a magnetic field of 1 T. All samples were found to be almost of single phase. Lattice parameters refined by Rietveld analysis [10] were $a = 3.9930$ nm, $c = 8.5158$ nm for (LaO)CuS, $a = 3.9409$ nm, $c = 8.4390$ nm for (PrO)CuS and $a = 3.9220$ nm, $c = 8.4345$ nm for (NdO)CuS.

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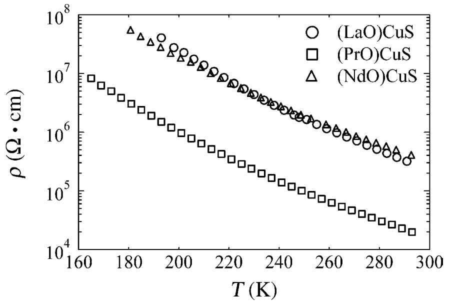

Fig. 1. The temperature dependence of the electrical resistivity of (LnO)CuS.

3. Results and discussion

3.1. Electrical properties

Fig. 1 shows the temperature dependence of the electrical resistivity of (LnO)CuS. They are semiconductive. The absolute values of the electrical resistivity at room temperature are $2.9 \times 10^5\ \Omega$ cm for (LaO)CuS, $3.8 \times 10^4\ \Omega$ cm for (PrO)CuS, and $2.0 \times 10^5\ \Omega$ cm for (NdO)CuS, respectively.

3.2. Magnetic properties

Fig. 2 shows the temperature dependence of the magnetization. (LaO)CuS shows a diamagnetic behavior. On the other hand, (PrO)CuS and (NdO)CuS show paramagnetic behavior. The temperature dependence of the inverse magnetic susceptibility of them is shown in Fig. 3. These values decrease linearly above 100 K, following Curie Weiss law, and the effective magnetic moment μ_{eff} are estimated to be $3.5\mu_{\text{B}}$ and $3.7\mu_{\text{B}}$ for (PrO)CuS and (NdO)CuS, respectively. They are slightly larger than those previously reported [9] and almost agree with the trivalent free ion values. However, at lower temperature below 100 K, the temperature dependence deviates from Curie Weiss law. It is considered to be due to the crystal electric field effect. Then, we have tried to calculate their magnetization taking account of the crystal field effects.

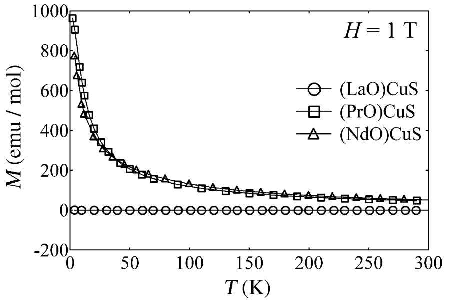

Fig. 2. Temperature dependence of the magnetization with a magnetic field of 1 T.

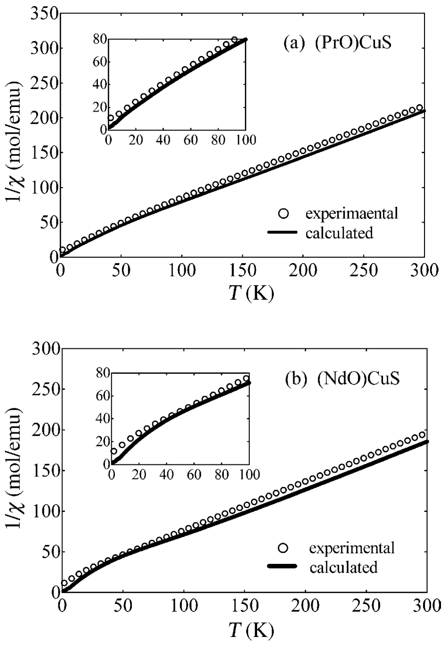

Fig. 3. The temperature dependence of the inverse magnetic susceptibility: (a) (PrO)CuS and (b) (NdO)CuS. Open circles are experimental values and solid lines are calculated ones.

3.3. Calculation of the magnetization using the operator equivalent method

The single ion Hamiltonian acting on the ground state multiplet of R^{3+} ion is expressed as the sum of the Zeeman term and the crystal field term

$$\tilde{H} = \tilde{H}_{\text{Zeeman}} + \tilde{H}_{\text{cry}}. \tag{1}$$

The Zeeman term is expressed as follows:

$$\tilde{H}_{\text{Zeeman}} = g\mu_B \sum_{i=x,y,z} \tilde{J}_i H_i, \tag{2}$$

where g and μ_{B} are Landé factor and Bohr magneton, respectively. The crystal field term is expressed

$$\tilde{H}_{\text{cry}} = \sum_{m,n} B_n^m \tilde{O}_n^m, \tag{3}$$

where B_n^m and $\tilde{O}_n^m$ are crystal field (CF) parameters and Stevens' operator equivalents, respectively [11]. The summation for m and n is performed over (n, m)=(2, 0), (4, 0), (4, 4), (6, 0), (6, 4), because the crystal structure of (LnO)CuS is tetragonal. Diagonalization of Hamiltonian, Eq. (1), gives the eigenvalues and eigenfunctions, and the magnetization is calculated using them.

The CF parameters B_n^m are given by

$$B_n^m = A_n^m \left\langle r^n \right\rangle \theta_n, \tag{4}$$

where $\langle r^n \rangle$ and θ_n are nth moment of the radial part of the wave functions and Stevens' parameters, respectively. A_n^m is geometrical factor, which is determined by the distribution of the electric charges surrounding one rare earth ion. Then, the

Table 1
Crystal field parameters B_n^m of (PrO)CuS and (NdO)CuS

	Pr (K)	Nd (K)
B_2^0	0.0	0.0
B_4^0	1.24×10^{-1}	-4.18×10^{-2}
B_4^4	-5.36×10^{-1}	1.81×10^{-1}
B_6^0	1.55×10^{-3}	1.22×10^{-3}
B_6^4	1.81×10^{-2}	1.42×10^{-2}

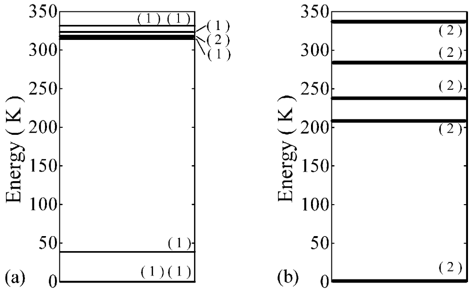

Fig. 4. Crystal field splittings of the ground state *J* multiplets of Pr and Nd ions using crystal field parameters which give best fit: (a) (PrO)CuS and (b) (NdO)CuS. Numbers in decimals indicates the degree of degeneracy.

values of the CF parameters were tentatively estimated by the point charge calculation at first. All ions within a radius of 250 nm are taken into account. Numerical calculation using the CF parameters obtained by the point charge calculation failed to reproduce the experimental values, because the obtained value of B_2^0 is too large. However, the ratios B_4^4/B_4^0 and B_6^4/B_6^0 are close to those of cubic symmetry. Then, CF parameters were treated as adjustable parameters and we varied them, keeping the above ratios constant and B_2^0 zero. The values of the CF parameters which give the best fit are shown in Table 1. The results of the calculation of the inverse magnetic susceptibility are also shown in Fig. 3. The crystal field splittings of the ground state *J* multiplets of (PrO)CuS and (NdO)CuS are shown in Fig. 4. For (PrO)CuS, the lowest energy level is singlet and the magnetic susceptibility at 0 K is finite. On the other hand, for (NdO)CuS, the inverse magnetic susceptibility approaches zero at 0 K as the Kramers doublet remains.

4. Conclusion

In (LnO)CuS (Ln: La, Pr, Nd), Ln ions are trivalent. The temperature dependence of the magnetic susceptibility of (PrO)CuS and (NdO)CuS were well explained by the crystal field effect calculated by using the operator equivalent method.

References

[1] M. Palazzi, C. Carcaly, J. Flahaut, J. Solid State Chem. 35 (1980) 150.
[2] K. Ishikawa, S. Kinoshita, Y. Suzuki, S. Matsuura, T. Nakanishi, M. Aizawa, Y. Suzuki, J. Electrochem. Soc. 138 (1991) 1166.
[3] Y. Takano, K. Yahagi, K. Sekizawa, Phys. B 206 (1995) 764.
[4] K. Sekizawa, Y. Takano, K. Mori, K. Yahagi, Czech. J. Phys. 46 (1996) 1943.
[5] Y. Takano, K. Mori, K. Koizumi, H. Ozaki, K. Sekizawa, J. Alloys Compd. 275 (1998) 447.
[6] Y. Furukawa, S. Ikeda, K. Kumagai, K. Mori, Y. Takano, K. Sekizawa, Phys. Rev. B 62 (2000) 15598.
[7] K. Takase, M. Koyano, T. Shimizu, K. Makihara, Y. Takahashi, Y. Takano, K. Sekizawa, Solid State Commun. 123 (2002) 531.
[8] K. Ueda, S. Inoue, S. Hirose, H. Kawazoe, H. Hosono, Appl. Phys. Lett. 77 (2000) 2701.
[9] K. Ueda, K. Takafuji, H. Hosono, J. Solid State Chem. 170 (2003) 182.
[10] F. Izumi, T. Ikeda, Mater. Sci. Forum 198 (2000) 321.
[11] M.T. Hutchings, Solid State Phys. 16 (1964) 227.