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Electrical Conductivity of Th_3P_4-Type $EuLn_2S_4$

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Electrical conductivity measurements of Th_3P_4-type $EuLn_2S_4$ (Ln = La–Gd) compounds have been made as functions of temperature and sulfur vapor pressure. These compounds are all p-type semiconductors, and their conductivities at room temperature have almost the same values for the specimens from $EuLa_2S_4$ to $EuNd_2S_4$ but increase on going from $EuNd_2S_4$ to $EuGd_2S_4$. In addition, the conductivity of $EuGd_2S_4$ is sensitive to sulfur vapor pressure and obeys the relationship $\sigma \propto P_{S_2}^{1/6}$. The mechanism of electrical transport in these compounds is discussed.

Introduction

Recently compounds of rare earth sulfides have been the object of many scientific investigations because of their interesting physical properties (*1–5*). Among the rare earth sulfides there is a group of Ln_3S_4–Ln_2S_3 solid solutions with Th_3P_4-type crystal structure. These solid solutions may be described by the formula $(Ln^{3+})_{3-x}V_x \cdot (S^{2-})_3(e^-)_{1+3x}$, where the vacancies designated by V are on the rare earth sites, and if $x = \frac{1}{3}$ and $x = 0$, stoichiometric compounds Ln_2S_3 and Ln_3S_4, respectively, are formed (*6*). The number of conduction electrons and the average magnetic moments in these compounds can be varied continuously over wide ranges by substitution of metal ions with different valences or by variation of the metal/sulfur ratio (*7*). The vacancies present in Ln_2S_3 can be accommodated by a large number of additional metal ions without changing the crystal structure. This fact leads to many interesting changes in the electrical and magnetic properties of these compounds.

Tien *et al.* (*8*) have reported that $LnLn'_2S_4$ (Ln = Sm, Eu, and Yb and Ln' = La–Gd) prepared by the solid state reaction between LnS and Ln'_2S_3 had a Th_3P_4-type crystal structure. Also, Lugscheider *et al.* (*9*) have recently reported that $EuLn_2S_4$ was antiferromagnetic at low temperature.

However, few studies on their electrical properties have been carried out. In this paper we investigate the dependence of temperature and sulfur vapor pressure on the electrical conductivity of $EuLn_2S_4$.

Experimental

Preparation. In this study, $EuLn_2S_4$ samples were prepared by the solid state reaction between EuS and Ln_2S_3 (Ln = La–Gd). First, EuS and Ln_2S_3 were each obtained by sulfurizing the corresponding rare earth chlorides in a dried H_2S stream (100 ml/min) at 900 to 1100°C for 5 hr. For the preparation of $EuLn_2S_4$, starting mixtures with the appropriate molecular ratio of

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EuS and Ln_2S_3 were ground together in an agate mortar and pressed into pellets at 200 kg/cm^2. The pellets were put in a graphite crucible in a quartz tube and were sintered in a dried H_2S stream (100 ml/min) at 1000°C for 3 hr.

X-ray diffraction technique. The phase purity and structure type of the resulting materials were characterized by X-ray powder data from a Rigaku Denki Rota-flex diffractometer with a scintillation detecter and CuK_α radiation ($\lambda = 1.5418$ Å). The lattice parameters were refined by a least-squares method for unambiguously indexed reflections.

Magnetic susceptibility measurements. The magnetic susceptibility data of the resulting materials were obtained with a Shimazu MB-11 magnetic balance in the temperature range 77 to 300°K.

Electrical conductivity measurements. The electrical conductivity measurements were carried out by applying a dc two-probe method with a polycrystalline sintered pellet in an atmosphere of He (at about 1 atm) or sulfur vapor under various pressures. For measurements in He, the electrical conductivities of the samples were measured as a function of temperature. A very thin layer of Au was deposited on the pellet end faces, which were in contact with the Ag electrodes. For the measurements in sulfur vapor, the dependence of sulfur pressure on conductivity was investigated. In these measurements, a thin layer of Au was also deposited on the pellet end faces and the pellet was held between two Pt plate electrodes supported by Pyrex glass plates.

Results and Discussion

X-ray diffraction measurements of the sintered EuLn_2S_4 (Ln = La–Gd) showed only the pattern expected for a Th_3P_4 structure (space group T_d^6–$I\bar{4}3d$). Magnetic susceptibility measurements were performed in the temperature range 77 to 300°K. These compounds were paramagnetic in the measured temperature range, and the magnetic susceptibility obeyed the Curie–Weiss law. The lattice parameters obtained from X-ray diffraction powder data and the effective magnetic moments are listed in Table I. Values of μ_{cal} for EuLn_2S_4 were calculated as

$$\mu_{\mathrm{cal}} = (\mu^2_{\mathrm{Eu}^{2+}} + z\mu^2_{Ln^{3+}})^{1/2}, \qquad (1)$$

where $\mu_{\mathrm{Eu}^{2+}}$ and $\mu_{Ln^{3+}}$ expressed the effective magnetic moments of free Eu^{2+} and Ln^{3+} ions, respectively. Since calculated values of the magnetic moment for EuLn_2S_4 were in good agreement with the observed values, the Eu ion in these compounds was confirmed as divalent and the Ln ion as trivalent.

Electrical conductivity measurements were carried out in the temperature range 77 to 770°K. The dependence of the electrical conductivities of EuLn_2S_4 on the reciprocal of the temperature is shown in Fig. 1. All of the EuLn_2S_4 obtained behaved as semiconductors with Ω-cm values of the order of 10^4 to 10^5 at room temperature. From the qualitative estimation of themoelectric power, the charge carrier for electrical conduction in all of these Th_3P_4-type EuLn_2S_4 was found to be positive. This finding represents relatively unusual behavior among Th_3P_4-type compounds, most of which are metallic or

TABLE I

LATTICE CONSTANTS AND μ_{eff} FOR SAMPLES OBTAINED

Samples obtained	Lattice constant a (Å)	μ_{eff} (μ_B) Observed	μ_{eff} (μ_B) Calculated
$EuLa_2S_4$	8.761	7.29	7.94
$EuCe_2S_4$	8.701	8.23	8.71
$EuPr_2S_4$	8.658	8.97	8.45
$EuNd_2S_4$	8.599	9.20	9.49
$EuSm_2S_4$	8.545	8.47	8.28
$EuGd_2S_4$	8.512	14.15	13.75

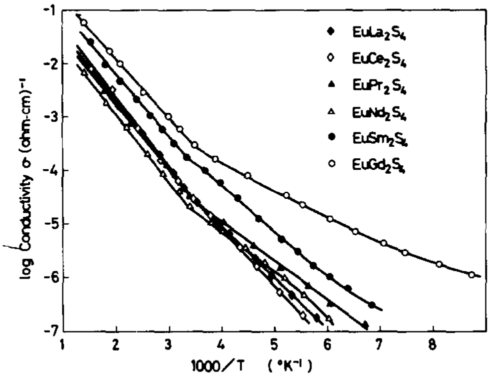

FIG. 1. Dependence of temperature on the electrical conductivity of $\mathrm{Eu}Ln_2\mathrm{S}_4$ in an atmosphere of He (at about 1 atm).

TABLE II

SOME OF THE ELECTRICAL CONDUCTIVITIES FOR THE SAMPLES OBTAINED[a]

Samples obtained	Conductivity at 300°K, $\sigma \times 10^5$ $(\Omega\text{-cm})^{-1}$	Activation energy ε (eV) At 300–700°K	Activation energy ε (eV) At 130–300°K
$EuLa_2S_4$	3.05	0.25	0.12
$EuCe_2S_4$	3.39	0.26	0.16
$EuPr_2S_4$	3.16	0.24	0.10
$EuNd_2S_4$	2.70	0.25	0.15
$EuSm_2S_4$	15.5	0.23	0.16
$EuGd_2S_4$	36.3	0.22	0.10

[a] All samples obtained were p-type semiconductors.

n-type semiconducting materials. Although the precise band structure is unknown for these Th_3P_4-type compounds, it is presumed that the valence band is mainly associated with the $3p$ states of sulfur and that the conduction band is made up of the $5d$ states of rare earths, analogous to the band model of Eu monochalcogenide proposed by Wachter (*10*). It is reasonable to assume that the $4f$ levels of rare earths are localized in a forbidden energy gap. Accordingly, positive holes may be created by ionizing the neutral electron acceptor of a metal vacancy level above the top of the valence band.

As shown in Fig. 1, breaks in the log σ vs $1/T$ plots can be seen at approximately 300°K for all compounds. Since no corresponding crystallographic or magnetic transitions were observed around this temperature, this electrical transport transition may represent the change from extrinsic to intrinsic semiconduction.

Other electrical property data are summarized in Table II. The activation energy ε was calculated by the equation, $\sigma = \sigma_0 \exp(-\varepsilon/kT)$. The values of the electrical conductivity at room temperature are almost constant on going from $EuLa_2S_4$ to $EuNd_2S_4$, but increase abruptly from $EuNd_2S_4$ to $EuGd_2S_4$. To understand the electrical property of the Th_3P_4-type $\mathrm{Eu}Ln_2\mathrm{S}_4$ series, it is helpful to take into account the nature of chemical bonding in $\mathrm{Eu}Ln_2\mathrm{S}_4$. The bond property can be appreciated by comparing the ionic and covalent radii of the corresponding elements in these compounds with the observed internuclear spacings. Miller *et al.* (*11*) proposed the concept of percentage covalency as the covalent contribution to the bonding in the Th_3P_4 structure, using the equation,

$$\%\ \text{covalency} = \frac{r_{\mathrm{S\,ion}} - r_{\mathrm{S\,obs}}}{r_{\mathrm{S\,ion}} - r_{\mathrm{S\,cov}}} \times 100, \qquad (2)$$

where $r_{\mathrm{S\,ion}}$, $r_{\mathrm{S\,cov}}$, and $r_{\mathrm{S\,obs}}$ are the ion, covalent, and observed radii of sulfur, respectively. Figure 2 shows the plots of the fraction of covalent bond character and the electrical conductivity at room temperature against atomic number. In $\mathrm{Eu}Ln_2\mathrm{S}_4$ with a Th_3P_4 structure, it appears that going from $EuLa_2S_4$ to $EuGd_2S_4$ makes the Ln–S bond less ionic. Ionic crystals are generally poor electrical conducting materials compared with covalent ones because of the former's small carrier mobility, resulting from their narrow bandwidths. This principle holds for the specimens obtained, except for $EuLa_2S_4$, $EuCe_2S_4$, and $EuPr_2S_4$. On the basis of crystallographic considerations, for example, lattice energy, ionization energy, and strength of crystal field, it is understandable

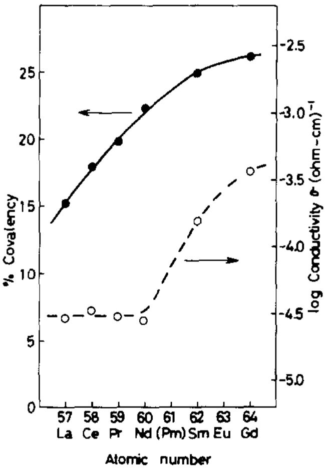

FIG. 2. Plots of the percentage covalency and the electrical conductivity of $\mathrm{Eu}Ln_2\mathrm{S}_4$ at room temperature against the atomic number of Ln components.

that metal vacancies are introduced more easily in ionic crystals than in covalent ones. Because in ionic crystals such as $EuLa_2S_4$, $EuCe_2S_4$, and $EuPr_2S_4$ the concentration of the positive hole increases with increases of these metal vacancies, these compounds seem to have higher electrical conductivities than are expected from their percentage covalency.

The behavior of the conductivity in sulfur vapor for $EuGd_2S_4$ is shown in Figs. 3 and 4. The time dependence on the electrical conductivity in various sulfur pressures is illustrated in Fig. 3. The higher the sulfur pressure was, the more time was required to reach the equilibrium of the conductivity. This fact suggests that a thin layer exists in grain boundaries of the sintered sample and that the sulfur passage through such a layer to the bulk is the rate-determining stage for the diffusion of sulfur into $EuGd_2S_4$. Figure 4 shows the plots of logarithmic conductivity σ vs logarithmic sulfur pressure P_{S_2}. The conductivity values increased as the sulfur pressure increased, and the slope of log σ vs log P_{S_2} was 1/5.9 at all temperatures. This positive variation is usually observed in p-type metal oxide or sulfide semiconductors, such as NiO or PbS. For the increase of electrical conductivity under high sulfur pressure, the following two processes may be taken into account by Eq. (3) or Eq. (4)

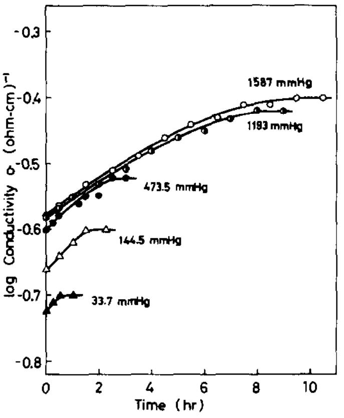

FIG. 3. Time dependence on the electrical conductivity of $EuGd_2S_4$ in various sulfur pressures at 500°C.

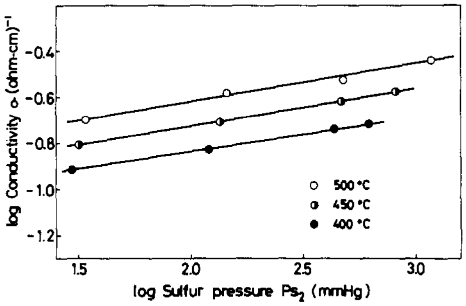

FIG. 4. Dependence of sulfur pressure on the electrical conductivity of $EuGd_2S_4$ at various temperatures.

$$\tfrac{1}{2}S_2 \rightleftarrows S_S + V_{Eu}^{-} + h^{+}, \qquad (3)$$

$$\tfrac{1}{2}S_2 \rightleftarrows S_S + V_{Eu}^{2-} + 2h^{+}, \qquad (4)$$

where S_S represents a S atom on a normal lattice site, V_{Eu}^{-} a singly and V_{Eu}^{2-} a doubly ionized Eu vacancy, and h^+ a positive hole. The generation of Eu vacancy is accelerated by the transition of Eu^{2+} to Eu^{3+}. The following relationships can be obtained by adapting the mass action law to Eqs. (3) and (4):

$$\sigma \propto [h^{+}] \propto P_{S_2}^{1/4}, \qquad (5)$$

$$\sigma \propto [h^{+}] \propto P_{S_2}^{1/6}. \qquad (6)$$

Equation (6) is inconsistent with the results in Fig. 4, where the values of the slopes of the log σ vs log P_{S_2} plots were 1/5.9. The dependence of the electrical conductivity on the inverse of the sixth power of logarithmic sulfur pressure, illustrated in Fig. 4, clearly indicates that reaction (4) takes place at constant temperature over the range 400 to 500°C and thermodynamic equilibrium with the sulfur vapor.

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