

ANTIFERROMAGNETISM OF Cd, Dy, AND Er MONOSULFIDES

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The magnetic susceptibility of Gd, Dy, Er, and Ho monosulfides is investigated at temperatures between 4.2° and 300°K. Antiferromagnetic ordering is characteristic of the Gd, Dy, and Er compounds. The analysis of the experimental results is based on the theory of indirect exchange interaction via conductivity electrons.

**M**ONOCHALCOGENIDES of the rare earth elements (MeX, with Me = Ce → Tm and X = S, Se, Te) comprise a large class of magnetic materials that crystallize in a simple NaCl structure. These compounds of the rare earths, with the exception of Sm and Eu, possess metallic conductivity. They are characterized by uncompensated valency of the type [Me<sup>3+</sup>S<sup>2-</sup>]e<sup>-</sup>, when as many 4f electrons are localized on the ions of the 4f elements as on the triply-charged ions and the extra electron is a conduction electron. The concentration of these electrons can be as high as ~ 10<sup>22</sup> cm<sup>-3</sup>.<sup>[1]</sup> At low temperatures the rare-earth monochalcogenides become magnetically ordered. The ferromagnetic properties of semiconducting Eu compounds have been well studied.<sup>[2]</sup> For the monochalcogenides exhibiting metallic conductivity it is known only that antiferromagnetic ordering exists in the case of the lighter rare earths Ce, Nd,<sup>[3,4]</sup> and Gd.<sup>[14]</sup>

We here present the results obtained in our investigation of the static magnetic susceptibility of the Gd, Dy, Ho, and Er monosulfides at 4.2°–300°K in fields up to 10 kOe. Our polycrystalline alloy samples had been prepared using the technology described in<sup>[5]</sup>. X-ray analysis was performed with Debye cameras, of 57.3-mm diameter, employing Cr K<sub>α</sub> radiation. The lattice constants in the table are close to those given in<sup>[6]</sup>. The table also gives the electric resistivity at 300°K and the temperature coefficient of the resistivity for the 300–1300°K region. The magnetic susceptibility χ was measured at 77°–300°K with a magnetic balance,<sup>[7]</sup> and at 4.2°–77°K with a pendulum magnetometer similar to the one described in<sup>[8]</sup> but with photoelectric observation of pendulum displacements.<sup>1)</sup> The relative error of χ was 1% at 77°–300°K and about 3% at 4.2°–77°K. The largest temperature error, which occurred in the 30°–77°K region, was 2–3°; here an Allen-Bradley carbon thermometer with R<sub>comp</sub> = 100 ohm was used.

For all the investigated monochalcogenides the function χ<sup>-1</sup>(T) is represented by straight lines in the 80°–300°K region (Fig. 1a), and the parameters c<sub>g</sub> and Θ<sub>p</sub> of the χ = c<sub>g</sub>/(T – Θ<sub>p</sub>) law are given in the table. The values of μ<sub>eff</sub> for the rare-earth ions are close to the values calculated for the ground states of the free Me<sup>3+</sup> ions. For all the sulfides the Θ<sub>p</sub> constants are

<sup>1)</sup>The authors wish to thank Academician B. G. Lazarev for permitting low-temperature measurements in his laboratory.

	Compound			
	GdS	DyS	HoS	ErS
Lattice constant, Å	5.566	5.493	5.453	5.430
c <sub>g</sub> × 10 <sup>3</sup> , deg·cm <sup>3</sup> /g	4.12	6.71	6.33	5.14
μ <sub>eff</sub> , μ <sub>B</sub>	7.93	10.26	10.03	9.09
μ <sub>theor</sub> for Me <sup>3+</sup> , μ <sub>B</sub>	7.94	10.64	10.61	9.58
–Θ <sub>p</sub> , °K	98	56	15	12
T <sub>N</sub> , °K	45	32	220*	11
ρ(T = 300°K) × 10 <sup>5</sup> , ohm·cm	6.2	5.8	6.0	—
$\frac{1}{\rho_{300} \text{ } ^\circ\text{K}} \frac{d\rho}{dT} \cdot 10^3, \text{ deg}^{-1}$	1.50	1.32	1.22	—

\*We calculated T<sub>N</sub> = 38°, 20°, and 2°K for TbS, HoS, and TmS, respectively.

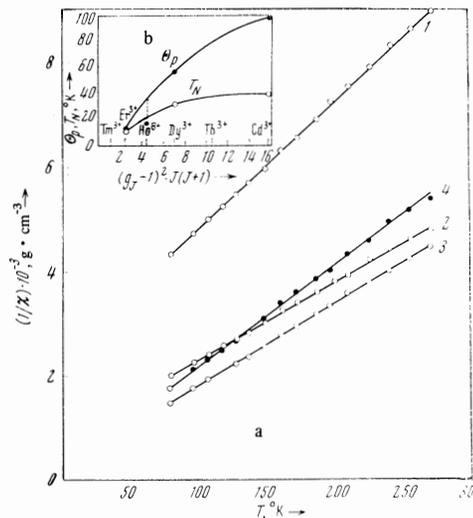


FIG. 1. (a)–Temperature dependence of the reciprocal magnetic susceptibility for (1) GdS, (2) DyS, (3) HoS, and (4) ErS; (b) variation of Θ<sub>p</sub> and T<sub>N</sub> in the Gd → Er series as functions of (g<sub>j</sub> – 1)<sup>2</sup>J(J + 1).

negative; these results differ considerably from the values given in<sup>[9]</sup>. Below 70°K the magnetic-field dependence of the magnetization is represented by linear functions m = χH, while the χ(T) curves exhibit peaks (Fig. 2), which can be regarded as indicating the antiferromagnetic transition points (see the table). The sharpest susceptibility peak is observed for DyS (χ<sub>T<sub>N</sub></sub>/χ<sub>4.2°K</sub> ≅ 2.50); the maxima are least prominent for GdS and ErS (χ<sub>T<sub>N</sub></sub>/χ<sub>4.2°K</sub> = 1.14).

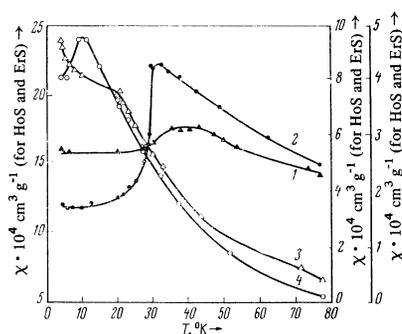


FIG. 2. Temperature dependence of magnetic susceptibility at 4.2°–77°K for (1) GdS, (2) DyS, (3) HoS, and (4) ErS.

Since the investigated compounds are metallic, we may as a first approximation assume that the principal mechanism of exchange interaction is indirect exchange via conduction electrons. We know that this kind of interaction, mediated by electrons that can be described by a Fermi distribution, is oscillatory: the regions of positive and negative exchange interactions are interchanged as the conduction band population is increased. Assuming that the  $t_{2g}$  states of the 5d band, which are triply degenerate with respect to the orbital angular momentum, are the conductive states, we find that the characteristic band population in the monochalcogenides is 0.33 electron states per magnetic atom. According to Mattis' calculations for a face-centered cubic lattice,<sup>[10]</sup> the given concentration is associated with a negative exchange interaction.

Another theoretical result that has been confirmed for the ferromagnetic state of rare earth metals is that the paramagnetic Curie temperature  $\Theta_p$  is proportional to  $(g_J - 1)^2 J(J + 1)$ , where  $g_J$  is the Landé factor and  $J$  is the quantum number representing the total mechanical moment of the 4f shell. We can assume a similar relation for the antiferromagnetic state of rare earth metals.<sup>[11]</sup> Figure 1b shows  $T_N$  and  $\Theta_p$  for the investigated monochalcogenides as functions of  $(g_J - 1)^2 J(J + 1) \equiv f(S, J)$ ; here they are not represented by the straight lines that are derived from the simplest type of theory. However, the smooth curves for  $\Theta_p$ ,  $T_N = f(S, J)$  enable us to predict  $T_N$  for TbS, HoS, and TmS. It should be noted that magnetic ordering is far from being an obvious possibility for these compounds, which are formed with ions having an even number of 4f electrons; we cannot exclude the possibility that their lowest states in an octahedral crystal field will be singlets.<sup>[12]</sup> In this case the possibility of ordering depends on the ratio of the effects produced by the crystal field and the exchange interaction.<sup>[13]</sup> However, if these compounds are ordered their Néel temperatures will probably be close to the values given in the table.

We also studied the case of HoS, which, unlike the other sulfides, exhibits no maximum of  $\chi(T)$  below 4.2°K (Fig. 2). Distinctive behavior of  $\chi(T)$  is observed around 20°K.  $\Theta_p$  for HoS is derived from the common curve in Fig. 1b, thus also providing evidence of magnetic behavior differing from that of the other monosulfides. We at present have insufficient data to confirm antiferromagnetism in HoS. The investigation of the magnetic properties of Gd–Tm monosulfides should obviously be extended to single crystals of these compounds.

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