MAGNETIC PROPERTIES OF LAYER-TYPE COMPOUNDS TlGdS$_2$ AND TlGdSe$_2$

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Ternary thallium lanthanide dichalcogenides TlLnX$_2$ (X = S, Se, or Te; Ln = lanthanide, except Ce and Pr) crystallize in the rhombohedral structure of α-NaFeO$_2$ type ($R\bar{3}m$). Their crystal lattice consists of the layers of Ln^{3+} ions separated by three layers of the non-magnetic ions (-Ln-X-Tl-X-Ln-). The magnetization was measured in the field range 0–14 T. The molecular field constants λ_m were estimated by fitting the Brillouin function to the experimental magnetization plots. The difference between the λ_m values for the thallium gadolinium sulphide and the selenide corresponds to the different character of Gd–S and Gd–Se bonds and gives rise to the different J_1 and J_2 exchange integrals.

PACS numbers: 75.50.Ee, 75.30.Cr

1. Introduction

The thallium lanthanide chalcogenides of the TlLnX$_2$ type (Ln = Nd to Lu, X = S, Se or Te) crystallize in the rhombohedral structure of the α-NaFeO$_2$ type ($R\bar{3}m$) [1]. It belongs to the class of layered structures, where the layers of magnetic Me^{3+} ions are separated by three layers of non-magnetic ions (-X^{2-}-Tl^{+}-X^{2-}-).

The better known group of isomorphous compounds is formed by the ternary chromium(III) sulphides and selenides with alkali metals and silver. They possess rather unusual magnetic properties. For example KCrS$_2$ and NaCrS$_2$ are antiferromagnets with large positive paramagnetic Curie constants θ_p (+30 and +112 K respectively) and large deviations from the Curie–Weiss law up to $T \approx 5T_N$ [2, 3].

The occurrence of the large group of isomorphous TlLnX$_2$ compounds of fairly high symmetry gives a possibility of studying the crystal-field interactions across the lanthanide-chalcogenide series [4]. This work is also connected to magnetic and EPR studies on gadolinium chalcogenides with the Th$_3$P$_4$-type structure [5]. In this paper the magnetic properties of the thallium gadolinium disulphide and diselenide are presented.

2. Experiments

The samples were obtained in polycrystalline form from the corresponding gadolinium chalcogenides Gd_2X_3 and Tl_2X by solid state reactions at 800–900 K. The ampoules were filled with inert gas (300 mm Hg of argon) to prevent the sublimation of Tl_2X.

Powder X-ray data were collected with the Philips PW 1830 diffractometer using Cu K_α radiation. The lattice constants (Table I) are in good agreement with the literature data [1].

TABLE I

Crystallographic data and the shortest $Gd^{3+}-Gd^{3+}$ distances: n.n. — nearest neighbors, n.n.n. — next nearest neighbors, 3rd n.n. — 3rd coordination sphere (nearest neighbors in adjacent layers).

	a (pm)	c (pm)	n.n. (6) (pm)	n.n.n. (6) (pm)	3rd n.n. (2×3) (pm)
$TlGdS_2$	404.8	2240	405	701	782
$TlGdSe_2$	418.3	2308	418	742	808

Magnetic measurements were performed in the International Laboratory of High Magnetic Field and Low Temperatures in Wrocław. Magnetization was measured with magnetic flux density up to 14 T employing the extraction sample magnetometer. The magnetic susceptibility of $TlGdSe_2$ was determined by the Faraday method with the flux density equal to 0.428 T. The results are shown in Figs. 1–3 and in Table II.
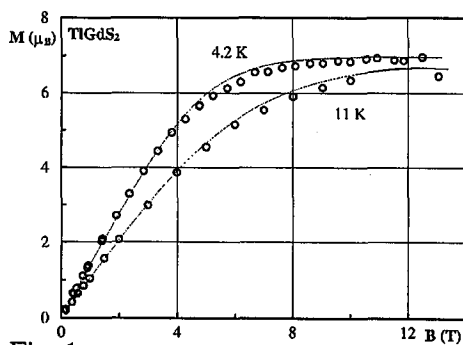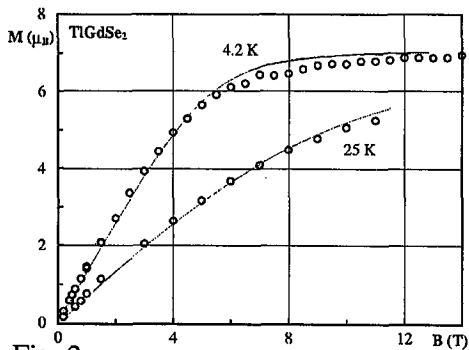

Fig. 1.   Magnetization of $TlGdS_2$ vs. magnetic flux density. The solid lines were calculated from Eq. (1).

Fig. 2.   Magnetization of $TlGdSe_2$ vs. magnetic flux density. The solid lines were calculated from Eq. (1).
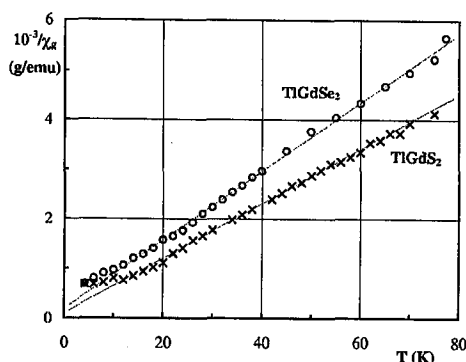
Fig. 3. Inverse magnetic susceptibility of TlGdS$_2$ ($B = 5$ T) and TlGdSe$_2$ ($B = 0.428$ T). The solid lines were obtained from fits to the Curie–Weiss law (Table II).

TABLE II

Magnetic data extracted from magnetization and susceptibility.

	μ_{eff} (μ_B)	θ_p (K)	λ_{m} (T/μ_B)
TlGdS$_2$	7.85	−1.8	−0.55
TlGdSe$_2$	7.75	−2.7	−0.61

3. Results and discussion

Magnetic properties of TlGdS$_2$ and TlGdSe$_2$ arise from the $^8S_{7/2}$ ground term of Gd^{3+} ions. Due to the spherical symmetry of the S-state the crystal field affects magnetic properties (i.e. magnetization and magnetic susceptibility) only very slightly. The high field magnetization of both chalcogenides are presented in Figs. 1 and 2. The calculated values were obtained using the Brillouin function B_S in the form

$$M(H,T) = Ng\mu_{\text{B}}SB_S(x), \qquad (1)$$

where $x = g\mu_{\text{B}}S(H + \lambda_{\text{m}}M(H,T))/k_{\text{B}}T$ and λ_{m} is the molecular field constant (the fitting parameter), k_{B} is the Boltzmann constant, μ_{B} is the Bohr magneton, N is the Avogadro number, $g = 2.00$ and $S = 7/2$ for Gd^{3+}.

The α-NaFeO$_2$ structure is related to the NaCl-type structure with the layers of mono- and trivalent metal ions arranged alternately between the close-packed anion layers along the c axis (the (111) direction in NaCl). Analogically to the NaCl-type compounds like europium monochalcogenides, we suppose the ferromagnetic exchange interactions between the nearest neighbors (only six Gd^{3+} ions instead of 12 in the NaCl structure) giving the J_1 exchange integral. The interactions with the next nearest neighbors (2×3 ions in the adjacent Gd^{3+} layers) have an antiferromagnetic character (J_2 exchange integral). It means that in TlGdX$_2$ compounds the hexagonal planes (001) are ferromagnetically coupled and the spins

in adjacent layers are antiparallel. The similar model was confirmed by neutron diffraction in $NaCrX_2$ compounds [3].

The values of the exchange integrals J_1 and J_2 were estimated from the paramagnetic Curie temperatures θ_p and the molecular field constants λ_m as $J_1 = 0.05$ K, $J_2 = -0.08$ K for $TlGdS_2$ and $J_1 = 0.05$ K, $J_2 = -0.10$ K for $TlGdSe_2$. The J_1 values are similar to the analogical value in EuTe [6] while the $|J_2|$ values are lower due to increase in distance between the neighboring Gd^{3+} layers.

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