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Magnetic properties and crystal field effects in $TlLnX_2$ compounds ($X = S, Se, Te$)

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Abstract

Ternary thallium lanthanide chalcogenides $TlLnX_2$ ($X = S$, Se or Te) crystallize in the α-$NaFeO_2$ type of structure ($R\bar{3}m$). Each kind of the metal ions, surrounded by the distorted chalcogenide octahedra, forms separate layers. The TlX_6 octahedra are strongly elongated and the LnX_6 octahedra slightly shrunk along the threefold axis. The deformations of the coordination polyhedra and the cell volumes change regularly with the lanthanide ionic radii. The difference between the experimental and the calculated M–X distances increases on going from sulphides to tellurides, as a result of the growing covalent character of the bonds. The crystal field parameters were estimated from the high field magnetization (0–14 T) assuming trigonal distortion of the octahedral symmetry of LnX_6 polyhedra. The second-order crystal field parameters were found to correlate with the deformation of the lanthanide ions' environments. No magnetic transition was observed down to 4.2 K. © 1997 Elsevier Science S.A.

Keywords: Ternary lanthanide chalcogenides; Crystal field; Lattice deformation

1. Introduction

The continually growing group of ternary lanthanide compounds represents a broad variety of physical properties. Chalcogenides are a large and insufficiently explored group of these compounds.

The $TlLnX_2$ type compounds ($X = S$, Se or Te; Ln = lanthanide, except Ce and Pr) crystallize in the α-$NaFeO_2$ structure type [1]. This structure stabilizes the low coordination number (six) for the lanthanides. Symmetry of the first coordination sphere of the metal ions is almost octahedral. The crystal lattice of $TlLnX_2$ compounds consists of the layers of Ln^{3+} ions separated by three layers of the non-magnetic ions (–Ln–X–Tl–X–Ln–).

Our previous investigations on $TlLnX_2$ compounds involved magnetic and structural properties of the sulphides [2,3] and the selenides [4]. The layered structure of these compounds was confirmed and the regular change of the deformation of LnX_6 octahedra was found. All sulphides and selenides remain paramagnetic down to the liquid helium temperature. Their crystal field parameters were deduced from the high field magnetization. We have found that the second-order crystal field parameter changes similarly to the deformation of the coordination sphere of a lanthanide ion.

We now present results for thallium lanthanide ditellurides of heavy lanthanides (Gd–Tm).

2. Experimental details

Compounds were synthesized in polycrystalline form from the lanthanide sesquitellurides and Tl_2Te by solid-state reactions. Stoichiometric amounts of Ln_2Te_3 and Tl_2Te were mixed, pressed into pellets and heated in sealed quartz ampoules. Each sample was slowly heated to 670 K and held at this temperature for several days; then the temperature was raised

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to 820 K for 1 day and raised again to 1050 K for 12 h. In order to complete the reaction the crude material was crushed in a dry box, pressed into pellets and then, the heating procedure was repeated. Finally, samples were annealed at 670 K for 1–2 weeks. The ampoules were filled with inert gas (250–350 mmHg of argon) to prevent the sublimation of Tl_2Te. An increase of temperature above 1050 K usually led to the decomposition of compounds.

We have not tried to synthesize $TlYbTe_2$. Kabre et al. [1] could not obtain this compound since telluride anions stabilize divalent ytterbium (e.g. Yb_2Te_3 does not exist).

X-ray data were collected with a X'Pert powder diffractometer PW 1830 using Cu K_α radiation. The structural parameters were calculated according to our own computer program assuming the $R\bar{3}m$ space group. The preferred orientation of crystallites in a sample was taken into account by introducing the texture factor $[1+(\tau^2-1)\cos^2\varphi]^{-1/2}$, where τ was fitted together with the other structure parameters, and φ is the angle between the texture axis ([001] in the $TlLnX_2$ compounds) and a (hkl) plane [5]. Calculations were carried out for the angles $2\theta < 75°$ (Table 1).

Magnetic measurements were made within the temperature range 4.2–30 K in fields up to 14 T in the International Laboratory for Strong Magnetic Fields and Low Temperatures in Wrocław (Fig. 1). To avoid possible orientation of powders during the measurements, the sintered pellets were fixed in the sample holder.

The magnetic susceptibility was determined in the low-temperature region in order to find magnetic transitions. None of the studied compounds ordered magnetically down to the liquid helium temperature.

The crystal field parameters were estimated by fitting the calculated M(H) curves to the experimental

Table 1
Crystallographic data and calculated [6] structural parameters of $TlLnTe_2$ compounds (z and τ were obtained assuming the isotropic thermal parameter equal to 0.5 Å^2)

	a (pm)	c (pm)	V (nm^3)	z	τ	c^*/a^{*a}		$d^{calc}-d^{exp}$ (pm)	
						TlX_6	LnX_6	Tl–X	Ln–X
$TlGdTe_2$	442.4	2425	0.4110	0.265	0.82	1.079	0.748	21.5	10.4
$TlTbTe_2$	441.6	2427	0.4100	0.264	0.40	1.073	0.759	22.9	8.2
$TlDyTe_2$	440.0	2425	0.4066	0.265	0.40	1.085	0.752	22.4	9.0
$TlHoTe_2$	440.1	2430	0.4075	0.266	0.36	1.095	0.745	20.8	8.7
$TlErTe_2$	437.6	2423	0.4018	0.264	0.19	1.083	0.763	24.7	7.2
TlTmTe2	435.3	2425	0.3980	0.265	0.54	1.100	0.758	24.0	8.4
Mean value for selenides [4]						1.114	0.739	14.7	4.9
Mean value for sulphides [2,3]						1.151	0.714	7.4	3.3

[a] 0.8165 in an ideal octahedron.

Table 2
The crystal field and exchange parameters of $TlLnSe_2$ compounds (x, W, B_2 are crystal field parameters, λ is the molecular field coefficient)

	x	W (K)	B_2 (K)	λ (T/μ_B)	$A_2\cdot d^3_{Ln-X}$ (arb. units)	$A_4\cdot d^5_{Ln-X}$ (arb. units)	Ground term splitting (K)	Reference
$TlNdSe_2$	0.79	−6.0	−0.20	−1.8	698	19280	339	[4]
$TlTbS_2$	−0.97	−2.0	−0.73	−0.24	1776	23970	488	[3]
$TlTbSe_2$	−0.93	−1.2	−0.21	−0.28	575	16830	269	[4]
$TlTbTe_2$	−0.82	−1.2	−0.062	−0.16	212	21880	255	This work
$TlDyS_2$	−0.66	1.0	−0.53	−0.18	2139	18420	426	[2]
$TlDySe_2$	−0.70	0.92	−0.16	−0.18	754	22430	388	[4]
$TlDyTe_2$	−0.76	0.75	−0.039	−0.20	217	27610	335	This work
$TlHoS_2$	0.47	−0.55	−0.26	−0.26	3200	14530	316	[3]
$TlErS_2$	0.62	0.84	0.091	−0.0034	985	21970	317	[2]
$TlErSe_2$	0.40	0.33	0.025	−0.017	314	6860	136	[4]
$TlErTe_2$	0.50	0.40	0.022	+0.023 (?)	344	14930	154	This work
$TlTmTe_2$	−0.86	−1.3	0.061	−0.0009	198	23990	281	This work
$TlYbS_2$	−0.95	19.8	0.58	−5.8	539	22950	613	[2]
$TlYbSe_2$	−0.89	18.1	0.055	−5.8	58	24530	531	[4]

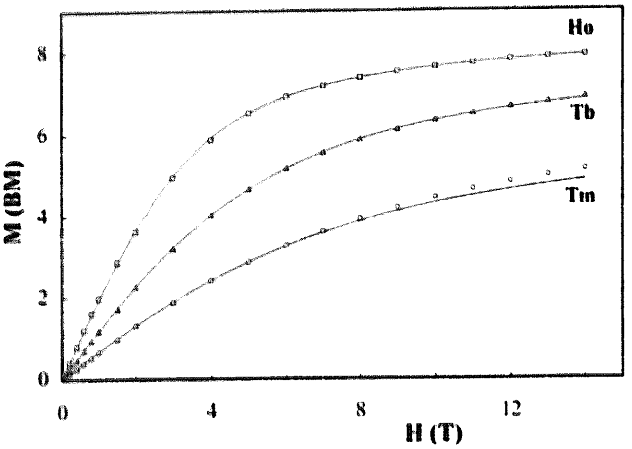

Fig. 1. Magnetization of $TlTbTe_2$ (△), $TlHoTe_2$ (□) and $TlTmTe_2$ (○) vs. magnetic field at 4.2 K. The lines were calculated using the parameters given in Table 2.

results at 4.2 K assuming the distorted octahedral symmetry and isotropic exchange in the molecular field approximation. The trigonal distortion of the crystal field was taken into consideration by adding the axial term $B_2O_2^0$ (B_2 = crystal field parameter, O_2^0 = Stevens' operator equivalent) to the octahedral crystal field Hamiltonian with the main axis along the [111] direction [7].

The crystal field parameters B_4 and B_6 obtained from the fitting procedure were changed into the Lea, Leask and Wolf parameters x and W [8]. Table 2 summarizes the crystal field parameters, the exchange parameters and the ground term splittings, estimated for thallium lanthanide tellurides and for previously studied sulphides and selenides.

3. Results and discussion

The α-$NaFeO_2$ structure type which is characteristic of $TlLnX_2$ compounds, may be described as a layer-type structure. The layers containing thallium and the lanthanide ions are placed alternately between the anion layers (–X–Ln–X–Tl–X– sequence along the c-axis). The nearest neighbours of cations form distorted octahedra (D_{3d} point symmetry). TlX_6 octahedra are elongated and LnX_6 octahedra are shortened along the threefold axis.

In order to correlate crystallographic distortions with crystal field deformations one must determine the quantitative measure of that distortion. The reduced ratio c^*/a^* was chosen as a measure of distortion, where c^* denotes the height of an octahedron (equals to the distance between the neighboring anion layers) and a^* denotes the distance between the chalcogenide ions in an anion layer (equals to the lattice constant a). For an ideal octahedron the reduced ratio equals to 0.8165.

The c^*/a^* ratios for $LnTe_6$ and $TlTe_6$ polyhedra are given in Table 1, while Fig. 2 shows the deformation of the LnX_6 octahedra for sulphides, selenides and tellurides. On going from the light to the heavy lanthanides, the hexagonal cell constant a decreases whereas the c constant varies only a little for a given anion. Consequently, the c^*/a^* ratio for LnX_6 as well as for TlX_6 increases which means that deformation of the lanthanide coordination sphere decreases while the thallium one increases.

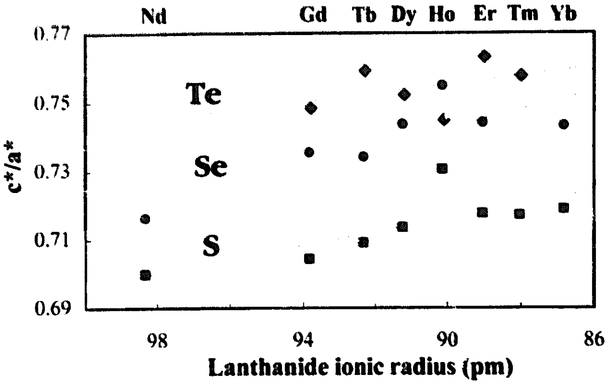

Fig. 2. Deformation of LnX_6 octahedra in sulphides (■) [2,3], selenides (●) [4] and tellurides (◆) vs. lanthanide ionic radii.

The crystal field parameters determined from high field magnetization of the thallium lanthanide chalcogenides are presented in Table 2. B_2, x and W were converted to the A_n parameters [8]. The geometrical coordination factors $A_n \cdot d_{Ln-X}^{n+1}$ should not be dependent on the metal ion. The term $A_4 \cdot d_{Ln-X}^5$ changes little whereas $A_2 \cdot d_{Ln-X}^3$ for the sulphides and selenides decreases from Nd to Yb and is very small for the tellurides. It reflects the deformation of the crystal field which affects a lanthanide ion. Fig. 3 demonstrates that a close relationship exists between the crystal-field deformation and the deformation of the lanthanide coordination sphere.

Replacing sulphide ions with selenide and telluride ones results in an increase of the covalent character of the Me–X bonds. Table 1 presents both the experi-

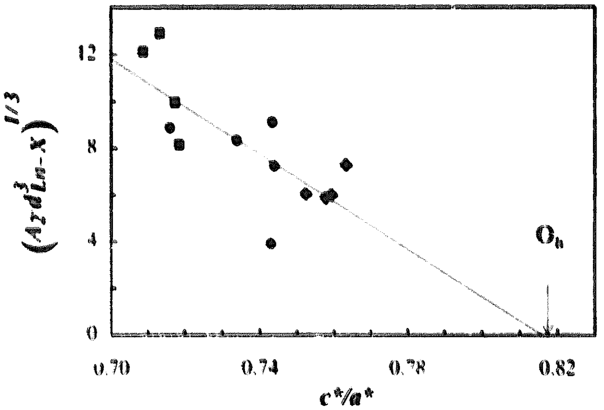

Fig. 3. Deformation of the octahedral crystal field vs. the c^*/a^* ratio in $TlLnX_2$ compounds. X = S (■), Se (●) and Te (◆).

mental Tl–X and Ln–X bond lengths and calculated values as sums of the appropriate ionic radii [6]. The differences between these lengths are small for sulphides and bigger for selenides and tellurides, in accordance with growing covalent character of bonds. This effect is particularly clear for Tl–X bonds.

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