ELSEVIER

Journal of Alloys and Compounds 323–324 (2001) 513–515

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Magnetic properties of $AgLnSe_2$ compounds (Ln=Ho, Er, Tm and Yb)

Marek Duczmal[a,]*, Stefan Pokrzywnicki[b]

[a]Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

[b]Institute of Mathematics, Physics and Chemistry, Technical University of Opole, ul. Luboszycka 7, 45-036 Opole, Poland

Abstract

The heavy lanthanide selenides $AgLnSe_2$ (Ln=Ho–Yb) crystallize in the orthorhombic $AgErSe_2$ type structure ($P2_12_12_1$). The lanthanide ions are placed in the centres of slightly distorted octahedra, whereas each of the silver ions is surrounded by four selenide ions forming a strongly distorted tetrahedron. The high field magnetization (up to 14 T) and the magnetic susceptibility were measured on the polycrystalline samples. The crystal field parameters were estimated from the field dependences of the magnetizations, assuming a rhombic distortion of $LnSe_6$ octahedra. The magnetic susceptibilities were also calculated using the same set of the crystal field parameters. None of the compounds described here undergoes a magnetic transition above 4.2 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ternary lanthanide chalcogenides; Crystal field; Magnetic measurements

1. Introduction

The silver lanthanide dichalcogenides clearly differ from the other Me^ILnX_2 type compounds (Me^I=Na, K, Rb, Cs, Tl or Ag; Ln=lanthanide; X=S, Se or Te). Most of them crystallize in rhombohedral structure of the α-$NaFeO_2$ type [1,2], whereas silver compounds possess various structures and, usually, two to three polymorphous modifications [3]. The crystal structures of sulphides were determined for $AgGdS_2$, $AgHoS_2$ and $AgYbS_2$. The low temperature modifications of the first two compounds crystallize in a monoclinic (pseudotetragonal) system and $AgYbS_2$ is cubic (metastable phase, tetragonal after annealing at 1000 K) [4]. Only the structure of $AgErSe_2$ is known for the selenides (orthorhombic, $P2_12_12_1$ space group) [5]. The analogous selenides with Ln=Dy to Lu were proved to be isostructural with $AgErSe_2$ [3].

In spite of very low point symmetry of Ln^{3+} ions in the $AgErSe_2$ structure, six selenide ions in the first coordination sphere form only a little distorted octahedron: the Er–Se distances are contained in the narrow interval 2.84–2.86 Å and the greatest deviation of Se–Er–Se angles from their ideal (octahedral) values is less then 4.2°. These facts prompted us to investigate magnetic properties of $AgLnSe_2$ compounds with heavy lanthanides and to attempt to interpret them on the ground of crystal field (CF) theory.

The magnetic properties of silver and the lanthanide dichalcogenides were not studied, except the magnetic susceptibility of $AgGdS_2$: the effective magnetic moment and the Weiss constant were equal to 7.38 μ_B and −32 K, respectively. The strong deviation of the inverse magnetic susceptibility from the Curie–Weiss law below 35 K suggests an antiferromagnetic ordering (T_N may be estimated from the $\chi^{-1}(T)$ plot as equal roughly to 17 K) [4].

The silver ions are known to be mobile. Analysis of electric conductivity of $AgErSe_2$ in the 300–770 K temperature interval suggests a mixed electronic and ionic conductivity [5].

2. Experimental details

2.1. Syntheses and X-ray investigation

The $AgLnSe_2$ compounds were obtained from Ag_2Se and the corresponding lanthanide sesquiselenides. The starting materials (1:1 molar ratio) were sealed in a quartz ampoule, slowly heated to 1250 K and held at this temperature for 3 days. The crude material was crushed under dry argon, pressed into pellets and heated once more to 1250 K. Then the temperature was raised to 1370 K (6 h). Finally the samples were annealed at 770 K for 2 weeks in order to obtain the low temperature modifications. After the synthesis the compounds seem to be resistant to air.

---

*Corresponding author.

0925-8388/01/$ – see front matter
PII: S0925-8388(01)01162-8

Powder X-ray data were obtained with an X'Pert Philips PW 1830 diffractometer using Cu Kα radiation. The lattice constants were found to be in a good agreement with the literature data [3]. On the $AgErSe_2$ and $AgTmSe_2$ diffractograms two weak lines were observed at 2θ equal approximately to 30.5 and 33.5°, which would not be indexed in the orthorhombic system; they probably came from Ag_2Se.

2.2. Magnetic measurements

Magnetic susceptibilities (at 0.428 T, Faraday method) and magnetization (extracting sample magnetometer, 0–14 T) were measured in the International Laboratory for Strong Magnetic Fields and Low Temperatures in Wrocław. To avoid possible orientation of powder particles during the high field measurements, the sintered pellets were fixed in a sample container.

The following Curie–Weiss parameters were obtained from the linear parts of $\chi^{-1}(T)$ plots (effective magnetic moment and Weiss constant, respectively): 10.50 μ_B (theoretically 10.61 μ_B) and -7 K for $AgHoSe_2$, 9.34 μ_B (theoretically 9.58 μ_B) and -5 K for $AgErSe_2$, 7.78 μ_B (theoretically 7.56 μ_B) and -5 K for $AgTmSe_2$, 4.63 μ_B (theoretically 4.54 μ_B) and -54 K for $AgYbSe_2$.

None of the compounds orders magnetically down to the liquid helium temperature.

2.3. Calculation of crystal field parameters

The CF parameters were estimated by fitting the calculated $M(H)$ curves to the experimental results at 4.2 K, assuming distorted octahedral symmetry of the crystal field and isotropic exchange in the molecular field approximation. In the case of $AgYbSe_2$ the temperature dependence of susceptibility, not magnetization, was used to calculate the CF parameters. For Yb^{3+} ion the only level populated at 4.2 K is the Kramers doublet Γ_6, isolated from the higher Γ_8 and Γ_7 levels. Magnetization resulting from such the level arrangement is weekly influenced by changes of crystal field. Temperature dependence of magnetic susceptibility seems to be more sensitive, bearing in mind strongly non-linear character of $\chi^{-1}(T)$ dependence for ytterbium(III) compounds.

Examining the shape of the first coordination sphere of Er^{3+} ion in the $AgErSe_2$ lattice [5], one can notice that the most pronounced deformation takes place along a 2-fold axis of the octahedron. It has been taken into account by adding the axial term $B_2O_2^0$ (B_2, CF parameter; O_2^0, Stevens' operator equivalent) to the octahedral CF Hamiltonian expressed with respect to the [110] direction [6]. The magnetization of polycrystalline samples was calculated as the weighed average [7] over the [001], [111] and [110] directions. The O_2^0 operator was transformed into [001] and [111] directions using the method given by Rudowicz [8]. Details of the calculations were described elsewhere [9].

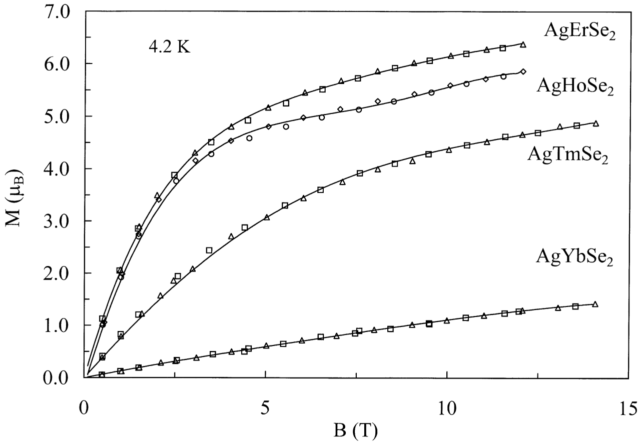

Fig. 1. Magnetizations of $AgLnSe_2$ compounds versus magnetic field at 4.2 K. (△,◇) Increasing field; (□,○) decreasing field. The lines were calculated using the parameters given in Table 1.

3. Results and discussion

The calculated results presented in Fig. 1 together with the experimental $M(H)$ curves show that the model of distorted octahedral crystal field is appropriate to interpretation of magnetic properties of the silver and lanthanide diselenides. Only the ground terms levels were taken into account in the calculations, but such an assumption is taken frequently in analysis of magnetic properties of heavy rare-earth compounds. The ground terms of the heavy lanthanide ions are almost pure $^{2S+1}L_J$ states as a consequence of high values of spin–orbit coupling constants.

The computed magnetic susceptibilities showed in Fig. 2 were obtained with the same set of CF parameters as the magnetizations. They fit the experimental points fairly

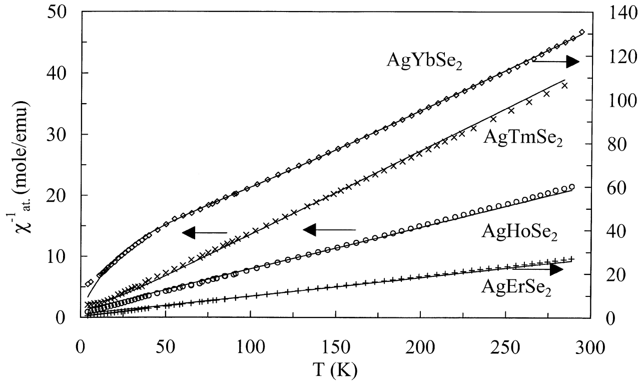

Fig. 2. Inverse magnetic susceptibility of $AgHoSe_2$ (○), $AgErSe_2$ (+), $AgTmSe_2$ (×) and $AgYbSe_2$ (◇). The lines were calculated using the crystal field parameters given in Table 1.

well. A source of the deviation of $AgYbSe_2$ susceptibility, calculated near the liquid helium temperature, from the experimental points is not clear. That may be an effect of a short-range ordering near a magnetic transition temperature. On the other hand from de Gennes rule one can deduce that the compounds containing Er and Ho should possess higher transition temperatures then $AgYbSe_2$.

The geometrical CF factors $A_n d^{n+1}(Ln{-}Se)$ (for definition see, for example, Ref. [10]) should remain constant along the series of isostructural compounds. One can see in Table 1 that $A_4 d^5$ and $A_6 d^7$ terms do not change much but the second-order coefficient $A_2 d^3(Ln{-}Se)$ varies significantly. It is, in a first approximation, responsible for deformation of octahedral crystal field. The well-marked correlation between the second-order geometrical coordination factor and the crystallographic distortion was observed in the series of $TlLnX_2$ type compounds (X=S, Se or Te) [2]. Unfortunately, the lack of precise structural data for the remaining silver compounds, except $AgErSe_2$, makes difficult a detailed analysis of this effect.

The second-order CF parameters are weekly ‘localized’ — they are significantly influenced by distant coordination spheres. In the case of higher order (four or six) coefficients the situation is quite different: they are more ‘localized’ and, for the $AgErSe_2$ type structure, contributions from the second coordination sphere to A_4 and A_6 have the same signs as the contributions coming from the first sphere. It means that one should not expect the situation similar to that found, e.g. in the series of $LnTa_3O_9$-type compounds [10] with perovskite-related structure, where contributions from the second coordination sphere (having different signs for the four- and six-order parameters) are able to change the sign of A_4.

The splittings of the ground terms in $AgLnSe_2$ compounds are similar to those in $TlLnSe_2$ compounds [2], but the absolute values of the second-order CF parameter B_2 are much larger. In a consequence, the parent (pure cubic) levels Γ_8, Γ_3, Γ_4 and Γ_5 are split significantly (up to 40 K in $AgHoSe_2$ and 47 K in $AgYbSe_2$). After applying magnetic field these levels may cross, producing some irregularities on the magnetization curves (see, for example, the magnetization of $AgHoSe_2$).

References

[1] W. Bronger, W. Brüggemann, M. von der Ahe, D. Schmitz, J. Alloys Comp. 200 (1993) 205.
[2] M. Duczmal, L. Pawlak, J. Alloys Comp. 262–263 (1997) 316.
[3] M. Julien-Pouzol, M. Guittard, Ann. Chim. 8 (1973) 139.
[4] A. van der Lee, R. van de Belt, G.A. Wiegers, J. Alloys Comp. 178 (1992) 57.
[5] M. Julien-Pouzol, P. Laruelle, Acta Crystallogr. B33 (1977) 1510.
[6] M.T. Hutchings, in: F. Seitz, D. Turnbull (Eds.), Solid State Physics, Vol. 16, Academic Press, New York, 1969, p. 227.
[7] Y. Ayant, E. Belorizky, M. Guillot, J. Rosset, J. Phys. 26 (1965) 385.
[8] Cz. Rudowicz, J. Phys. C 18 (1985) 1415.
[9] M. Duczmal, S. Pokrzywnicki, L. Pawlak, Acta Phys. Polon. A 77 (1990) 687.
[10] S. Ebisu, H. Morita, S. Nagata, J. Phys. Chem. Solids 61 (2000) 45.

Table 1
The crystal field and exchange parameters of $AgLnSe_2$ compounds. x, W, B_2 are the crystal field parameters, λ is the molecular field coefficient and A_2, A_4, A_6 are the crystal field geometrical coordination factors

	Ground term	x	W (K)	B_2 (K)	λ (T/μ_B)	$A_2 d^3(Ln{-}Se)$ (arb. units)	$A_4 d^5(Ln{-}Se)$ (arb. units)	$A_6 d^7(Ln{-}Se)$ (arb. units)	Ground term splitting (K)
$AgHoSe_2$	$^5I_8$	0.65	−0.81	−0.41	−0.28	59	382	48	464
$AgErSe_2$	$^4I_{15/2}$	0.43	−0.79	−0.12	−0.11	−16	193	52	323
$AgTmSe_2$	$^3H_6$	−0.88	−1.76	−0.37	−0.054	−13	258	17	395
$AgYbSe_2$	$^2F_{7/2}$	−0.91	17.1	2.92	−5.25	33	258	31	520