Journal of Alloys and Compounds 478 (2009) 14–18

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Antimony valence and the magnetization processes in the spinels (Cu)[CrSb]Se_4

J. Krok-Kowalski[a], J. Warczewski[a,*], P. Gusin[a], T. Śliwińska, G. Urban[a], E. Malicka[b], A. Pacyna[c], T. Mydlarz[d], P. Rduch[a], G. Władarz[a]

[a] University of Silesia, Institute of Physics, ul. Uniwersytecka 4, 40007 Katowice, Poland
[b] University of Silesia, Institute of Chemistry, ul. Szkolna 9, 40006 Katowice, Poland
[c] Institute of Nuclear Physics, ul. Radzikowskiego 152, 31342 Kraków, Poland
[d] International Laboratory of High Magnetic Fields and Low Temperatures, ul. Gajowicka 95, 53529 Wrocław, Poland

ARTICLE INFO

Article history:
Received 23 September 2008
Received in revised form 5 November 2008
Accepted 6 November 2008
Available online 14 November 2008

Keywords:
Magnetically ordered materials
Semiconductors
Spin glasses
Magnetic measurements
Exchange and superexchange

ABSTRACT

The spinel stoichiometric compounds of the $CuCr_{2-x}Sb_xSe_4$ family were obtained for the first time and prepared with the assumption of the valence of Sb ions equal to 3. The magnetization isotherms at 4.2 K and at the magnetic stationary fields up to 14 T as well as the temperature dependencies of magnetic susceptibility were studied in the temperature range of 4.2 ÷ 400 K. These results were compared with analogous measurements performed earlier by the authors for the nonstoichiometric spinel family built of the same elements and obtained under the assumption of the valence of Sb ions equal to 5. From this comparison it follows that these two spinel series reveal significant differences: (1) The interval of possible concentrations of Sb ions in the obtained stoichiometric spinel samples under study is up to 1.0, whereas for the nonstoichiometric spinels is (0.30 ÷ 0.48). (2) The corresponding intervals for the appearance of the spin glass states are: (0.2 ÷ 1.0) and (0.30 ÷ 0.48), whereas the freezing temperatures do not differ significantly. (3) The magnetization processes in the stoichiometric samples depend strongly on the Sb concentration, whereas in the nonstoichiometric samples they run very hardly.

1. Introduction

As it follows from the numerous papers the magnetic spinel compounds attract still many physicists because of their interesting features, e.g. coexistence of ferromagnetism and ferroelectricity [1,2], complex spin order and spin dimerization [3–5], spin-orbital liquid [6], orbital glass [7], heavy-fermion properties [8], large magnetostriction and negative thermal expansion [9], giant magnetoresistance [10–17], spin glass state [16–28] and thermoelectric effect [29]. One has to admit that the giant magnetoresistance effect and spin glass state effect can be useful in the switching facilities and spintronics. The thermoelectric effect can be used both in the thermopower generators and in the electronic refrigerators.

Many papers on the magnetic and electrical properties of spinel compounds (Cu)[CrSb]X_4 (X = S, Se) were published, also by the authors (e.g. [17,23]). It turned out that the dilution of the magnetic chromium subarray by the nonmagnetic antimony ions leads to the stoichiometric compounds in the case of S anions or to the nonstoichiometric compounds in the case of Se anions [e.g. [17,23]]. The spinels with sulphur magnetize very hardly revealing spin-flop phase transitions. The magnetization isotherms taken both at the zero field cooling (ZFC) and field cooling (FC) of the samples differ significantly between each other and, moreover, both curves show the spontaneous magnetic moments [16,30]. On the other hand the nonstoichiometric spinels with selenium magnetize also very hardly showing the jump-like behavior of the magnetization isotherms and both spin-flop and spin-flip phase transitions [17]. The nonstoichiometry of the selenium spinels comes –as it seems– from the ascribing the valence 5 to the antimony ions in the process of preparation of the samples. However, as it follows from the XANES and EXAFS studies of the stoichiometric spinels with the sulphur anions performed by some of us, the valence of the antimony ions should be equal to 3 [31].

The aim of this work is to prepare the spinel compounds of the $CuCr_{2-x}Sb_xSe_4$ family according to our results mentioned above concerning the valence of the antimony ions equal to three as well as to study the magnetic properties of these compounds.

2. Experimental and results

The preparation procedure of the compounds under study was similar to the procedure applied in our previous work concerning the nonstoichiometric spinels $Cu_{1+x}Cr_{1.5+y}Sb_{0.5+z}Se_{4+t}$ (where: $-0.02 \leq x \leq 0.01$, $0.03 \leq y \leq 0.35$, $-0.2 \leq z \leq -0.02$, $0.01 \leq t \leq 0.08$) in which the assumed Sb valence was 5 [17] with the exception, that this time the assumed Sb valence was 3. The powder samples, namely $CuCr_{2-x}Sb_xSe_4$ (where x = 0.1, 0.2, 0.3, 0.5, 0.8, 1.0), were this time obtained by the triple annealing of the stoichiometric mixtures of the constituent elements in the evacuated quartz ampules, namely two times at 800 K and once at 900 K, in every case for 170 h. The

* Corresponding author. Tel.: +48 323591782; fax: +48 322588431.
E-mail address: warcz@us.edu.pl (J. Warczewski).

0925-8388/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2008.11.021

Table 1
The most important characteristics of the samples under study (a, lattice parameter; $\mu_{4.2\,K,\,14\,T}$, magnetic moment at 4.2 K and 14 T; T_C, Curie temperature; θ_{C-W}, Curie-Weiss temperature; T_f, spin glass freezing temperature; T_N, Néel temperature; J_1/k, exchange integral for the first coordination sphere; J_2/k, exchange integral for the second coordination sphere).

Spinel compounds	a (Å)	$\mu_{4.2\,K,\,14\,T}$ (μ_B)	T_C (K)	θ_{C-W} (K)	T_f (K)	T_N (K)	J_1/k (K)	J_2/k (K)	θ_{C-W}/T_C, T_N
$CuCr_{1.9}Sb_{0.1}Se_4$	10.3755	5.71	357	375	–	–	59.8	−5.8	1.05
$CuCr_{1.8}Sb_{0.2}Se_4$	10.4162	4.52	240	261	50	–	40.3	−3.8	1.09
$CuCr_{1.7}Sb_{0.3}Se_4$	10.4502	2.59	–	125	35	54	−19.0	4.0	2.31
$CuCr_{1.5}Sb_{0.5}Se_4$	10.4598	2.38	220	300	40	–	−28.0	8.0	1.36
$CuCr_{1.2}Sb_{0.8}Se_4$	10.4823	1.76	260	360	50	–	−33.0	9.5	1.38
$CuCr_{1.0}Sb_{1.0}Se_4$	10.4906	1.36	250	330	50	–	−32.8	8.6	1.32

atomic emission spectrometry (inductionally coupled high frequency plasma–ICP-AES) was used for the determination of the chemical composition of the samples. The lattice parameters were determined with the use of X-ray powder diffraction (diffractometer SIEMENS D5000). The experimental data were analysed with the aid of the programs HX61 s and Checkcell. The magnetization was measured with the use of the induction magnetometer in the high stationary magnetic fields up to 14 T. The dc magnetic susceptibility was measured with the aid of the Faraday method using the magnetic Cahn balance. The most important structural and magnetic characteristics of all the six stoichiometric spinel samples under study are presented in Table 1.

Thus assuming the results of our XANES and EXAFS investigations [29] one obtains indeed the stoichiometric spinel samples.

Fig. 1 presents the magnetization isotherms at 4.2 K for all the six spinel samples under study. One can see in this figure that with the increase of the Sb concentration x the magnetization decreases very fast and the magnetization processes become more and more hard. Moreover, these isotherms exhibit the hysteresis phenomena which are the largest at $x = 0.3$ and 0.5. The analogous curves taken at room temperature for selected Sb concentrations x ($x = 0.1$, 0.2, 0.3) presents Fig. 2. Also here it is clear that the higher x the greater slope of the curves and the lower the values of the magnetization, which means that the magnetization processes become more and more hard. The evolution of the temperature dependence of the dc magnetic susceptibility for the three samples with the Sb concentrations $x = 0.1$, 0.2 and 0.3 is shown in Figs. 3–5, respectively. Note that for $x = 0.1$ (Fig. 3) the behavior of the curve is typical as for a ferromagnetic sample, in this case as for the matrix $CuCr_2Se_4$. Also the values of T_C and θ_{C-W} are relatively high, which means not much lower than the corresponding values for the matrix $CuCr_2Se_4$. The behavior of the susceptibility at $x = 0.2$ (Fig. 4) exhibits the significant new features, namely a broad maximum with the ZFC and FC hysteresis. The values of T_C and θ_{C-W} are lower of more than 100 K in comparison with the corresponding values for the $x = 0.1$ sample. Moreover one can see in Fig. 5 a diametrically different shape of the $x = 0.3$

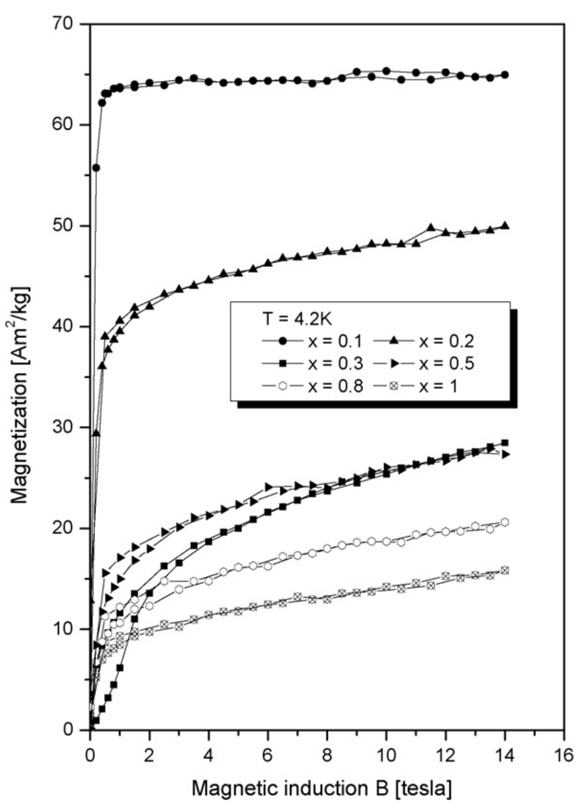

Fig. 1. The magnetization isotherms at 4.2 K of all the six spinel samples under study with the general formula $CuCr_{2-x}Sb_xSe_4$.

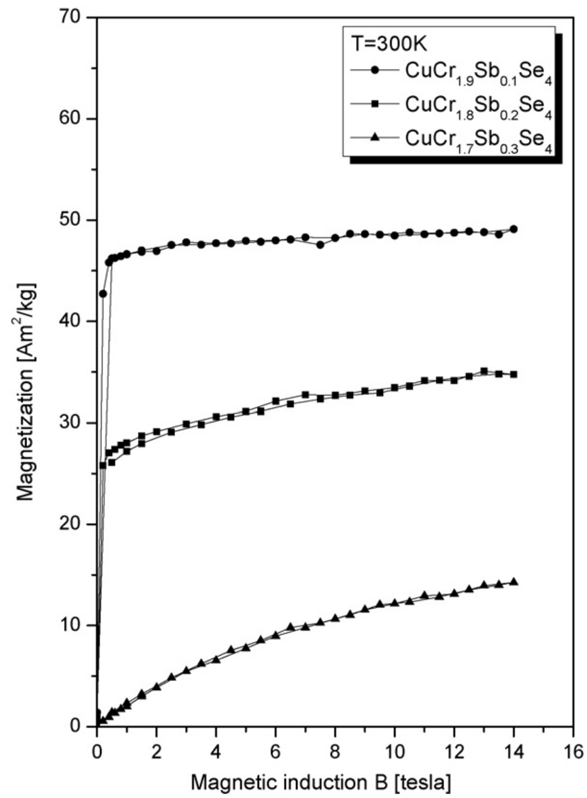

Fig. 2. The magnetization isotherms taken at room temperature for three selected spinel samples under study with the general formula $CuCr_{2-x}Sb_xSe_4$.

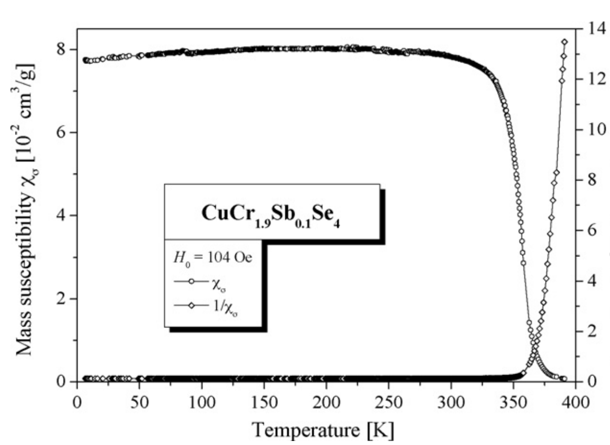

Fig. 3. The temperature dependence of the dc magnetic susceptibility for $CuCr_{1.9}Sb_{0.1}Se_4$.