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Effect of double exchange on thermoelectric power of $Cu_xCo_yCr_zSe_4$

T. Groń [a,*], S. Mazur [a], H. Duda [a], J. Krok-Kowalski [a], E. Maciążek [b]

[a] *University of Silesia, Institute of Physics, ul. Uniwersytecka 4, 40-007 Katowice, Poland*
[b] *University of Silesia, Institute of Chemistry, ul. Szkolna 9, 40-006 Katowice, Poland*

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Abstract

A correlation between the thermoelectric power and the double exchange and superexchange magnetic interactions in the ferromagnetically ordered $Cu_xCo_yCr_zSe_4$ p-type spinel conductors (with low Co content y up to 0.11) and in the antiferromagnetically ordered n-type semiconductor (with Co content $y = 0.23$) in the temperature range from 5 to 400 K is considered, respectively. The magnetic and thermopower investigations showed that a bandwidth of the 3d t_{2g} band due to Cr^{3+} and Cr^{4+} ions narrows with increasing cobalt content. For p-type conductors (with Co content y up to 0.11) all thermopower components are positive while for n-type semiconductor ($y = 0.23$) the phonon drag component is positive and the diffusion and impurity components are negative. In the latter case the linear dependence between thermopower (S) and the normalized electrical resistivity ($\ln \rho/\rho_0$) suggests a polaron conduction at high temperatures. The carrier diffusion dominates in single crystals with high cobalt content and the impurity component increases with increasing non-stoichiometry of a sample. For samples with low cobalt content y up to 0.11 the strong ferromagnetic coupling connected mainly with double-exchange mechanism makes easier the magnon excitations. Their intensities increase with increasing sample stoichiometry (*i.e.* when $x + y + z \rightarrow 3$).

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1. Introduction

The spinel system $Cu_{1-x}Co_xCr_2Se_4$ has limited solubility [1]. The single-phase polycrystals with the spinel structure were obtained for cobalt content x up to 0.2 [1]. The $CuCr_2Se_4$ end member is a normal spinel showing strong ferromagnetic and p-type conducting properties [2]. The second end member, *i.e.* $CoCr_2Se_4$ compound forms a defect NiAs structure and exhibits n-type semiconducting properties in the temperature range of 270–650 K [3] and antiferromagnetic behavior with a sharp peak of the magnetic susceptibility at 199 K [4]. The related spinel solid solutions $Cu_{0.3}Co_{0.7}Cr_2S_{4-x}Se_x$ (where $x = 0.0, 0.1, 0.15, 0.2, 0.25$ and 0.5) and $Cu_{0.45}Co_{0.55}Cr_2S_{4-x}Se_x$ (where $x = 0.0$, 0.5, 0.8, 1.0, 1.2, 1.3, 1.4 and 1.5) are ferrimagnets and p-type semiconductors [5–7]. Electrical and magnetic studies carried out on the $Cu_xCo_yCr_zSe_4$ single crystals revealed the ferromagnetic ordering with a Curie temperature of 340 K, a Curie–Weiss paramagnetic temperature of 350 K and a p-type metallic conductivity for samples with low Co content y (up to 0.11) and the antiferromagnetic ordering and the n-type semiconducting properties for a sample with the highest Co content ($y = 0.23$) [8]. The physical properties above mentioned in the $Cu_xCo_yCr_zSe_4$ spinel system were interpreted in terms of the magnetic double exchange and the Kramers–Anderson super-exchange interactions and low spin state configurations of cations including non-stoichiometry [8].

The main purpose of this work is an attempt to study an influence of the magnetic double-exchange interaction on the electronic transport induced by the temperature gradient in the non-stoichiometric single crystals of the $Cu_xCo_yCr_zSe_4$ spinel system. For that the high-temperature expansion of the magnetic susceptibility and the thermopower analysis were used.

2. Experimental and results

Single crystals of $Cu_xCo_yCr_zSe_4$ spinel system have been prepared using a chemical vapour transport method [9,10]. The single crystals under study were

* Corresponding author.
E-mail address: gron@us.edu.pl (T. Groń).

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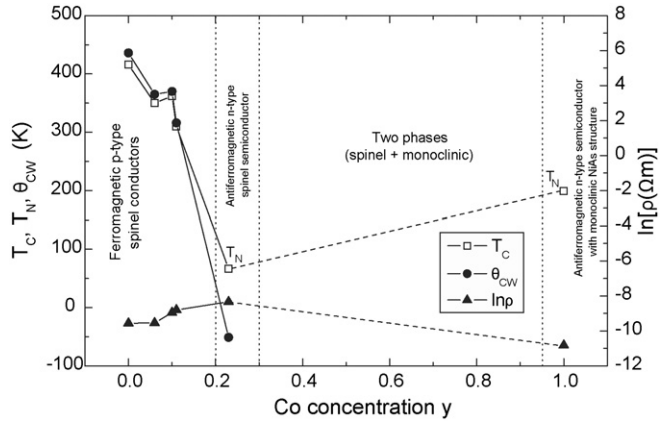

Fig. 1. The dependence of the Curie (T_C), Curie–Weiss (θ_{CW}), Néel (T_N) temperatures and the electrical resistivity at room temperature ($\ln \rho$) on cobalt concentration y in the $Cu_xCo_yCr_zSe_4$ system.

selected with the aid of a stereoscopic microscope and the Laue method for X-ray measurements. Precise lattice parameter measurements at room temperature were performed on a KM4 4-circle diffractometer with a graphite monochromator using Mo Kα radiation. The basis of 40 high-angle reflections was used [8]. The single crystals were chemically analysed with an X-ray electron probe microanalyzer JCXA 733 JOEL type. The thermoelectric power and the electrical resistivity measurements were done using the differential and the four-point methods, respectively [11]. DC measurements of the magnetic susceptibility and the magnetization were performed with an electronic balance by the Faraday method in the temperature range 77–600 K in a helium atmosphere with a magnetic field of 2100 Oe and with an induction method in magnetic field up to 7500 Oe at temperature of 77 K, respectively [12]. The preparation technique, the determination of composition and the measurement methods are described in details elsewhere [9–12].

A precise atomic content determination of each crystal with the aid of the X-ray microprobe showed that the single crystals of the $Cu_xCo_yCr_zSe_4$ spinel system are non-stoichiometric and all of them have an excess of the cation concentration, *i.e.* $x+y+z>3$ [11,12]. Correlation between the concentrations of copper x, cobalt y, chromium z and the cation concentration $x+y+z$ for the single crystals of the $Cu_xCo_yCr_zSe_4$ spinel system is given below:

x	0.87	0.78	1.1	1.28
y	0.06	0.1	0.11	0.23
z	2.3	2.2	2.0	2.09
$x+y+z$	3.23	3.08	3.21	3.5

Generally, the non-stoichiometry of a single crystal increases with increasing cobalt content y. The sample with $y=0.1$ is the most stoichiometric because the cation concentration $x+y+z$ is close to 3.

A brief summary of the experimental results at room temperature as a function of the cobalt concentration y is given in Fig. 1. We plotted there the Curie temperature T_C, the Curie–Weiss temperature θ_{CW}, the Néel temperature T_N [4,8] and the electrical resistivity ($\ln \rho$) [3,8] indicating also the kind of the magnetic ordering and the type of the electrical conductivity. The temperature dependences of the above mentioned quantities were published in Refs. [3,4,8]. The high values both of the Curie temperature T_C and the Curie–Weiss temperature θ_{CW} for single crystals of the $Cu_xCo_yCr_zSe_4$ spinel system with y up to 0.2 (see Fig. 1) suggest that both the long-range and strong short-range ferromagnetic coupling may be present. It is well known from the literature that for pure $CuCr_2Se_4$ p-type spinel conductor the double-exchange interaction between Cr^{3+} and Cr^{4+} is responsible for the strong ferromagnetic coupling and the hole metallic conductivity [2,13]. With increasing cobalt content y in a sample of the $Cu_xCo_yCr_zSe_4$ spinel system the electrical resistivity increases, a change from metallic p-type into semiconductive n-type conduction is observed, a dilution of the octahedral magnetic sub-lattice by the diamagnetic cobalt ions leads to a change from ferromagnetic to antiferromagnetic coupling and the saturation magnetic moment M_s remains almost constant (see Fig. 2) [8]. It suggests the appearance of the Co^{3+} ions both in a low-spin configuration of the t_{2g} orbital and in the octahedral sites from one side and a compensation of their orbital magnetic moments from the other.

3. Discussion

3.1. Magnetic interactions

The superexchange and double-exchange interactions are the most important magnetic interactions in spinels. The latter is usually connected with the metallic conductivity. To study an effect of double exchange on thermoelectric power the exchange integral calculations and the thermoelectric power analysis were done. From magnetization depicted in Fig. 2 it follows that the cobalt ions do not contribute to the magnetic moment, so we assumed that they are in the low spin configurations (diamagnetic state), while the Cr^{3+} and Cr^{4+} ions are in the high spin configurations. Thus, to determine the exchange constants of the superexchange and double-exchange interactions an estimation of the Cr^{3+} and Cr^{4+} portions is necessary. Portions z_3 and z_4 of the chromium ions: Cr^{3+} and Cr^{4+}, respectively, were calculated from the saturation magnetization M_s:

$$M_s = 2(g_3 S_3 z_3 + g_4 S_4 z_4) \quad (1)$$

taking into account the following normalization condition: $z_3 + z_4 = 1$, where M_s is the experimental value of the saturation magnetization taken from Ref. [8], $S_3 = 3/2$ is the spin of Cr^{3+} ion, $S_4 = 1$ is the spin of Cr^{4+} ion and $g_3 = 2.0$ and $g_4 = 1.86$ are the Landé factors for Cr^{3+} and Cr^{4+} ions, respectively.

Results of the above calculations are depicted in Fig. 2. With increasing cobalt content y: (1) concentration of Cr^{3+} ions

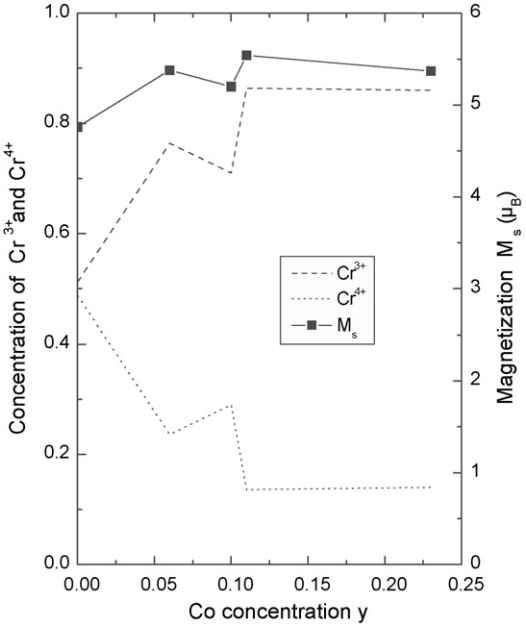

Fig. 2. Magnetization M_s and concentrations of the chromium ions: Cr^{3+} and Cr^{4+} vs. cobalt concentration y for single crystals with $y=0.06$, 0.1, 0.11 and 0.23 of the $Cu_xCo_yCr_zSe_4$ spinel system.