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Influence of cation substitution on electrical conductivity of the n-type $Cu_xIn_yCr_zSe_4$ spinels

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ABSTRACT

The single-crystal X-ray diffraction studies have shown that indium ions admixed with $CuCr_2Se_4$ may locate both in tetra- and octahedral sites of the spinel structure. This property has strong impact on electrical conductivity of the compounds under study. It appeared that octahedral coordination of In^{3+} ions leads to metallic conduction, while tetrahedral coordination of In causes semiconducting properties. The thermopower measurement revealed that all samples show n-type conduction in the temperature range 290–480 K. In $Cu[Cr_{1.38}In_{0.62}]Se_4$ a collective electron behaviour in the unfilled of the lowest Cr^{3+} Mott-Hubbard sub-band of $3d^3$ t_{2g} band is observed, while in $(Cu_{0.46}In_{0.54})Cr_{2.08}Se_4$ a hopping process involving a transfer of electrons from Cr^{2+} to Cr^{3+} takes place.

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1. Introduction and experimental

A complex order–disorder–order transition connected with a change of magnetic coupling from ferromagnetism (for $y < 0.48$) *via* spin glass (for $y = 0.48$) to antiferromagnetism (for $y > 0.48$) has been found in the single crystals of the $Cu_xIn_yCr_zSe_4$ spinels (where $y = 0.074$, 0.1, 0.12, 0.15, 0.16, 0.48 and 0.54) with tetrahedral coordination of In ions [1,2]. A sample with $y = 0.62$ has an octahedral coordination of the In ions and shows a ferromagnetic ordering of magnetic moments with the Curie temperature of 290 K [1]. The $Cu_xIn_yCr_zSe_4$ spinel has a limited solubility. The parent $CuCr_2Se_4$ exhibits a strong p-type metallic conduction ($\sigma = 2.63 \times 10^5\ \Omega^{-1}\ m^{-1}$; $S = 20.5\ \mu V/K$ at 300 K) with the chromium spins coupled ferromagnetically *via* exchange interactions involving conduction electrons [3,4]. The second end member of the system, *i.e.*, $InCr_2Se_4$ is not known, yet [5]. Previous electrical and magnetic investigations of the $Cu_{1/2}In_{1/2}Cr_2S_4$ and $Cu_{1/2}In_{1/2}Cr_2Se_4$ spinels revealed an insulating behaviour in both cases and a collinear antiferromagnetic spin structure below the Néel temperature $T_N \approx 40\ K$ evidenced by a large negative Curie–Weiss temperature $\theta_{CW} = -77\ K$ [6] and a spin-glass-like behaviour below the freezing temperature $T_f \approx 14\ K$ [7] accompanied with a large positive Curie–Weiss temperature $\theta_{CW} = 100\ K$ [6], respectively.

The $Cu_xIn_yCr_zSe_4$ single crystals were obtained by the chemical vapour transport method [1]. The chemical composition of the compounds was determined by the scanning electron microscope (Hitachi 3400N) equipped with the X-ray energy dispersive spectrometer (Thermo Noran Si(Li)) with ultrathin window. The sample crystals standardless quantification has been performed for several selected points at the crystal surface followed by the area analysis which was assumed to be representative for the volume chemical composition. The accelerating voltage of 25 kV has been applied and the counting time of X-ray inten-

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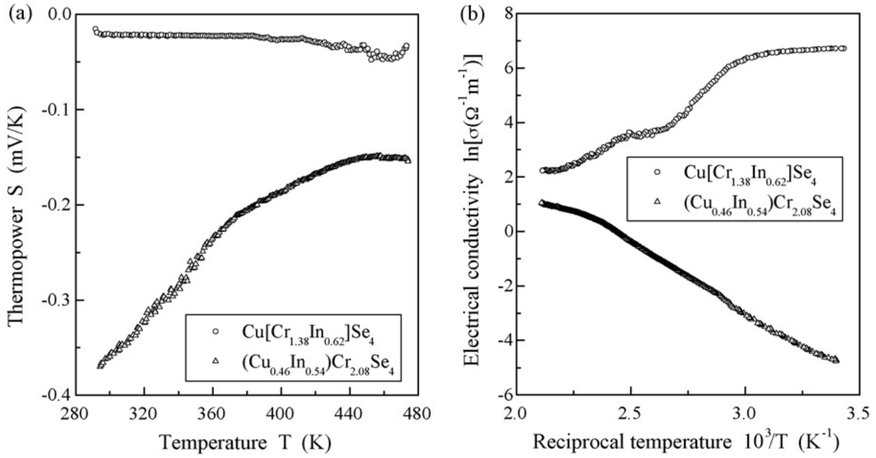

Fig. 1. Temperature dependences of thermopower S (a) and electrical conductivity $\ln\sigma$ (b) for crystals with tetra- and octahedral coordination of In ions.

sities was established for 100 s. A standard deviation did not exceed 3 at.% for Cu, Cr and Se and 10 at.% for In. The detailed composition and the cation distribution have been determined by a single-crystal X-ray analysis. The electrical conductivity $\sigma(T)$ and thermopower $S(T)$ were measured in the temperature range 290–480 K with the aid of the 4-point dc method using a semi-automatic bridge [8] containing the CA3160 integral circuit with the input impedance of 1.5 TΩ and the HP 34401A digital multimeters controlled by the computer and LabView® commands, and a differential method [9] with the temperature gradient ($T \approx 5$ K, respectively. The maximal error $\delta\sigma/\sigma$ was less than ±1%. The accuracy of the value of thermopower was estimated to be better than 3 μV/K.

The present contribution reports the single-crystal X-ray diffraction data, thermopower and electrical conductivity properties for two representative compositions of the crystal series with anti- and ferromagnetic ordering. It was thus natural to expect the low conductivity (typical of dielectrics) from one side and the high electrical conductivity (typical of metals) from the other.

2. Results and discussion

In Table 1 are shown selected crystal data, experimental details and structure refinement results for two compounds differing in concentration and location of the indium admixture. The sample composition is given on the basis of the refined site occupation factors for the cations involved. The tetrahedral location of the In ions results in lower cubic symmetry $F\bar{4}3m$ with ordered positions of the cations at two distinct sites. The octahedral indium location does not break the $Fd\bar{3}m$ spinel symmetry. Electrical measurements depicted in Fig. 1 revealed the n-type conduction for both crystals, semiconducting character for $(Cu_{0.46}In_{0.54})Cr_{2.08}Se_4$ and metallic one for $Cu[Cr_{1.38}In_{0.62}]Se_4$. Ferromagnetism correlates well with the metallic conductivity in $Cu[Cr_{1.38}In_{0.62}]Se_4$ spinel. The In ions (spin defects) located in the octahedral sites of the spinel structure cause the lowering of the Fermi level in the lowest Cr^{3+} Mott-Hubbard sub-band of $3d^3$ t_{2g} partly filled band allowing a collective electron behaviour. The n-type conduction in this case may originate from the Se-deficiency, too. Similar mechanism of conductivity

Table 1
Crystal data, experimental details and structure refinement results for the crystals with tetrahedral (A) and octahedral [B] coordination of In ions.

Spinel	$(Cu_{0.46}In_{0.54})Cr_{2.08}Se_4$	$Cu[Cr_{1.38}In_{0.62}]Se_4$
Crystal system, space group	Cubic, $F\bar{4}3m$	Cubic, $Fd\bar{3}m$
Lattice parameter (Å)	10.550(1)	10.373(1)
$2\theta_{max}$ for data collection	94.47	84.66
Reflections collected	6667	2781
Reflections > $2\sigma(I)$	459	220
Final R indices: $[I > 2\sigma(I)]$ R_1	0.039	0.031
wR_2	0.098	0.041
Atom, site and isotropic displacement parameter U_{iso} ($\times 10^3$ Å^2)	Cu, 4*a* (0, 0, 0) 0.81(3) In, 4*d* (3/4,3/4,3/4) 1.18(2) Cr, 16*e* (x, x, x) 1.05(2) Se(1) 16*e* (x_1, x_1, x_1) 1.03(2) Se(2) 16*e* (x_2, x_2, x_2) 1.02(2) $x = 0.3708$; $x_1 = 0.6115$; $x_2 = 0.1329$	Cu, 8*a* (1/8, 1/8, 1/8) 10.4(1) Cr/In, 16*d* (1/2, 1/2, 1/2) 14.8(3) Se 32*e* (x, x, x) 11.1(2) $x = 0.25763(4)$
Interatomic distances (Å) and angles (deg)	Cu–Se(2): 2.4332(8) 4× In–Se(1): 2.5071(9) 4× Cr–Se(1): 2.5524(10) 3× Cr–Se(2): 2.5193(10) 3× Se(2)–Cu/In–Se(2): 109.47(0) 4× Se(2)–Cr–Se(2): 87.58(6) 3× Se(1)–Cr–Se(2): 94.91(1) 3× Se(2)–Cr–Se(1): 176.54(8) 3× Se(1)–Cr–Se(1): 82.49(6) 3×	Cu–Se: 2.3866(6) 4× Cr/In–Se: 2.5146(4) 6× Se–Cu–Se: 109.47(0) 6× Se–Cr/In–Se: 93.76(2) 6× Se–Cr/In–Se: 86.24(2) 6× Se–Cr/In–Se: 180.0(0) 3×

has been considered in the n-type $CdCr_2Se_4$ (In-doped) spinel [10]. In the crystal of $(Cu_{0.46}In_{0.54})Cr_{2.08}Se_4$, the In^{3+} ions located in the tetrahedral sites induce the Cr^{2+} ions, with their moments aligned antiparallel to the Cr^{3+} moments at the octahedral sites. This leads to the antiferromagnetic ordering below $T_N = 21$ K [1] and low conductivity being characteristic of dielectrics. The n-type conduction in this spinel indicates a hopping process involving a transfer of electrons from Cr^{2+} to Cr^{3+} [10,11].

In conclusion, a change of magnetic ordering from anti- to parallel coupling of magnetic moments accompanied with increasing crystal symmetry induces a change from hopping to collective electron transport in the spinels under study.

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