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Influence of nonstoichiometry on the lattice excitations in the $Zn_xCu_yCr_zSe_4$ p-type spinel ferromagnetic conductors

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Abstract

The thermoelectric power analysis was used to study an influence of nonstoichiometry on the lattice excitations in the ferromagnetically ordered $Zn_xCu_yCr_zSe_4$ p-type spinel conductors in the temperature range from 5 to 400 K between $y = 0.81$ and 0.97. The above investigations showed that the thermoelectric power can be well explained considering the diffusion, phonon drag, magnon drag and impurity components. With increasing stoichiometry of a single crystal (i.e., with $x+y+z \to 3$): diffusion and impurity components decrease, phonon drag and magnon drag components increase and the phonon and magnon drag peaks shift into higher temperatures and their intensity increase. Additionally, the thermoelectric power considerations showed that the strong ferromagnetic coupling connected mainly with double-exchange and RKKY mechanisms in the spinels under study make easier the spin wave excitations on one side and the nonstoichiometry hinders the spin wave excitations on the other. These effects are interpreted within a framework of the Mott, Debye and the Bloch theories.

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1. Introduction

The investigations of the system $Zn_{1-x}Cu_xCr_2Se_4$ ($0.0 \leqslant x \leqslant 1.0$), obtained both in polycrystalline and monocrystal forms showed a variety of the physical properties [1–8]. The magnetic measurements revealed a complex magnetic structure [1–3]. One observes a simple spiral for $0.0 \leqslant x \leqslant 0.025$, a conical spin structure for both $0.05 \leqslant x \leqslant 0.1$ (with dominating the antiferromagnetic component) and $0.2 \leqslant x < 0.49$ (with dominating the ferromagnetic component), spin glass for x somewhere between 0.1 and 0.2, the ferrimagnetic ordering for $0.49 \leqslant x < 0.8$ and the ferromagnetic ordering for $x \geqslant 0.8$. The electrical measurements revealed that near $x = 0.3$ a change of the electrical conductivity character from the semiconductive into the metallic one took place [4].

The strong ferromagnetic coupling in the spinel system of $Zn_{1-x}Cu_xCr_2Se_4$ for $x \geqslant 0.8$ has not been univocal explained up to now. There are many opposing models describing the magnetic state mentioned above. For example, in the Lotgering model [9] Cu ions are monovalent and Cr^{3+}–Cr^{4+} configurations form a mixed valence band in which the double-exchange mechanism takes place. Next, in the Goodenough model [10] the divalent Cu ions and the holes coming from the 3d configuration of Cu^{2+} are coupled antiparallel to the remaining Cr^{3+} ions which fill the lowest Mott–Hubbard subband of 3d t_{2g} band. It introduces an RKKY-type interaction between the Cr^{3+} ions which should be ferromagnetic. The latter model well correlates both with the X-ray absorption spectroscopy and the magnetic circular dichroism spectra and with the relativistic linear-muffin-tin-orbital band-structure calculations which revealed in the $CuCr_2Se_4$ spinel an induced magnetic moment on the Cu site showing antiparallel alignment of the

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magnetic moments between the Cu^{2+} 3d and Cr^{3+} 3d states [11].

The thermopower investigations carried out on single crystals of the nonstoichiometric $Zn_xCu_yCr_zSe_4$ spinel system showed that the height of the magnon peak is higher for the ferromagnetic single crystals than for the ferrimagnetic ones [5]. The positron annihilation studies [6–8] of the system $Zn_{1-x}Cu_xCr_2Se_4$ revealed that the largest average positron lifetime was observed for single crystals, suggesting that for the spinel structure single crystals contain more vacancies than polycrystals of the same composition. In particular, the vacancy model calculations [12] showed that the positron lifetime is related to the vacancy parameter, which is a measure of the vacancy concentration [12]. Moreover, the oxidation and adsorption processes strongly influence the electrical transport and the positron trapping in the polycrystalline samples leading to the shortening of the bulk lifetime in the semiconducting state and to the lengthening of the bulk lifetime in the conducting state [6–8].

Recently, a crossover from positive to negative magnetoresistance in the $Zn_{0.95}Cu_{0.05}Cr_2Se_4$ spinel was discovered at 25 K [13]. The change of sign of magnetoresistance might be an indication of double-exchange coupling [14]. In particular, at low temperatures negative magnetoresistance is connected with the variable-range hopping of carriers between double-exchange clusters. In contrast, at high temperatures positive magnetoresistance is connected with the thermal activation of carriers across a band gap which swamps any residual double-exchange conduction [13]. The above results are in good agreement with the Lotgering model [9].

The main purpose of this work is an attempt to study an influence of nonstoichiometry on the lattice excitations basing on the experimental thermoelectric power data [15] of ferromagnetically ordered $Zn_xCu_yCr_zSe_4$ single crystals. For thermoelectric power analysis, a semiempirical formula [16] including a magnon drag component [17] was used.

2. Thermopower theory

Thermopower is both one of the easiest experiments that can be performed on conductors and the most sensitive probes of the carriers in the system [18]. The interpretation is not difficult in some simple (ideal) situations with characteristic behaviours for metals, semiconductors, superconductors, etc., and a lot of information can be easily obtained from thermopower measurements. If the behaviour is not ideal, some intuition remains into what thermopower measures. In conventional metals, for example, theory [16,19] predicts that thermopower consists of a diffusion component, which according to the Mott formula [20] is proportional to temperature and a phonon drag component, which is more complex. The diffusion thermopower for an electron gas is due to carrier diffusion and it contains information about the Fermi edge [21].

The theory of the phonon drag thermopower is well established [20–22]. Generally, the phonon drag contribution results from a transfer of the phonon momentum to the electron gas. It drops both at low temperatures as the phonons freeze out and at high temperatures as the excess phonon momentum is limited by phonon–phonon (anharmonic) scattering. Thus the "phonon drag peak" rises as T^3 below $\Theta_D/10$ (where Θ_D is the Debye temperature) and falls as T^{-1} above approximately $\Theta_D/2$ [19]. It is known from conventional metals that the phonon drag thermopower is often diminished by impurities [19]. However, there are cases (even in metals) in which the introduction of electron scatters leads to no change or even a small increase in the phonon drag thermopower [19,20]. The so-called the impurity component of thermopower is described by the $T^{1/2}$ law [23]. The term $T^{1/2}$ comes from the variable range hopping between localized electronic states near Fermi level [16,23].

In the magnetic materials, additionally, the magnetic component of thermopower should be considered. It may result from a coupling of the phonon system to the electron gas via the spin lattice (magnon gas), which is known as the Kasuya model [24], or from the transfer of the magnon momentum to the electron gas (magnon drag) [19] under condition that the magnetic contribution coming from the spin waves takes place. This magnetic contribution is described by the Bloch law [25], i.e. the spontaneous magnetization decreases with temperature at $T^{3/2}$ when T is small [26]. Magnon drag thermopower S_{mag} should drop proportionally to $T^{3/2}$ both at low temperatures as the specific heat of a Heisenberg ferromagnet behaves in the

Table 1
The fitting parameters: D, E, F, G, H, I and K in Eq. (1) of the thermoelectric power analysis of the $Zn_xCu_yCr_zSe_4$ spinel system

y	D ($\mu V/K^2$)	E ($\mu V/K^4$)	F ($\mu V/K$)	G ($\mu V/K^{1.5}$)	H	I ($\mu V/K$)	K	R (%)
0.81	0.037	1.0×10^{-9}	0.8263	9.6×10^{-4}	0.83568	0.0141	0.0015	99.58
0.82	0.015	1.0×10^{-19}	9.0436	0.00852	1.0×10^{-9}	2.658	0.2940	95.93
0.86	0.036	1.0×10^{-10}	1.0509	0.00213	0.72151	0.21	0.02	98.99
0.90	0.23	1.0×10^{-19}	6.5993	0.00617	1.0×10^{-5}	1.915	0.2004	98.99
0.94	0.022	1.0×10^{-19}	8.014	0.008	1.0×10^{-8}	2.1098	0.2321	97.51
0.97	0.026	1.0×10^{-19}	7.2	0.0075	1.0×10^{-3}	1.0361	0.1269	98.86

R is the agreement index.