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Influence of spin arrangement on thermopower in $Zn_xCu_yCr_zSe_4$ spinels

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ABSTRACT

The thermopower analysis carried out on $Zn_xCu_yCr_zSe_4$ spinel single crystals show that the ferrimagnetic spin arrangement in the range $0.49 \le y \le 0.72$ makes easier the carrier diffusion from one side and hinders both the spin wave propagation and the transfer of the phonon momentum to the electron gas from the other. The opposite behaviour for the ferromagnetic spin arrangement in the range $0.81 \le y \le 0.95$ was observed. In particular, the maxima contributions to the total thermopower give a magnon component (9 μV/K) of ferromagnetic samples in the temperature range 25–100 K, a phonon component (20 μV/K) of ferromagnetic samples in the temperature range 150–200 K and a diffusion component (47 μV/K) of ferrimagnetic samples in the temperature range 250–400 K. The impurity component of thermopower does not significantly depend on a kind of spin coupling and it increases with increasing non-stoichiometry of a sample ($x+y+z \neq 3$). Its maximum value does not exceed 2.5 μV/K at 400 K.

1. Introduction

Recent investigations of the electronic transport forced by the temperature gradient are driven by the search for more efficient materials with a large thermopower, high electrical conductivity and low thermal conductivity. They are used in industrial, e.g., in thermopower generators as the solid-state devices with no moving parts and in space applications working in the wide temperature ranges from one side and an environment friendly from the other. The superexchange and double exchange interactions are the most important magnetic interactions in the spinels under study. The latter is usually connected with metallic conductivity [1]. For that the thermopower analysis was done in the temperature range 5–400 K based on the magnetic and thermopower experimental data (see Table 1 and Fig. 1) of ferri- and ferromagnetically ordered $Zn_xCu_yCr_zSe_4$ single crystals [1–3], using the high-temperature expansion of the magnetic susceptibility for the exchange integral calculations and the semiempirical formula [4] including magnon contribution for the thermopower component calculations. In the compositional range $0.49 \le y \le 0.72$ the ferrimagnetic coupling is demonstrated on the curves of the inverse susceptibility vs. temperature which deviate downward of their linear parts while in the compositional range $0.81 \le y \le 0.95$ the ferromagnetic coupling is demonstrated on the curves of the inverse susceptibility vs. temperature which deviate upward of their linear parts [3]. The magnetization data M_s presented in Table 1 were used for estimation of the Cr^{3+} and Cr^{4+} ion concentrations in the high-spin configurations $3d^3$ $t_{2g}^3 e_g^0$ and $3d^2$ $t_{2g}^2 e_g^0$, respectively, allowing to determine the effective exchange integral.

The experimental curve shape of thermopower $S(T)$ of the spinel single crystals under study is fitted according to the modified Matoba, Anzai and Fujimori semiempirical formula [4] including the magnetic contribution as follows:

$$S(T) = DT + ET^3 + \frac{F(T/\Theta_D)^3}{G + (T/\Theta_D)^4} + HT^{1/2} + \frac{I(T/J_{eff}^{aa})^{3/2}}{K + (T/J_{eff}^{aa})^{5/2}} \qquad (1)$$

where first and second terms of Eq. (1) correspond to the diffusion component, S_{diff}, where the small correction E is the temperature dependence of D [5], third term of Eq. (1) is the phonon drag component, S_{ph}, fourth term of Eq. (1) is the impurity component, S_{imp}, last term of Eq. (1) is the magnon drag component, S_{mag}, and D, E, F, G, H, I and K in Eq. (1) are the curve-fitting parameters (Table 2), θ_D is the Debye temperature estimated from the Debye theory [6], and J_{eff}^{aa}

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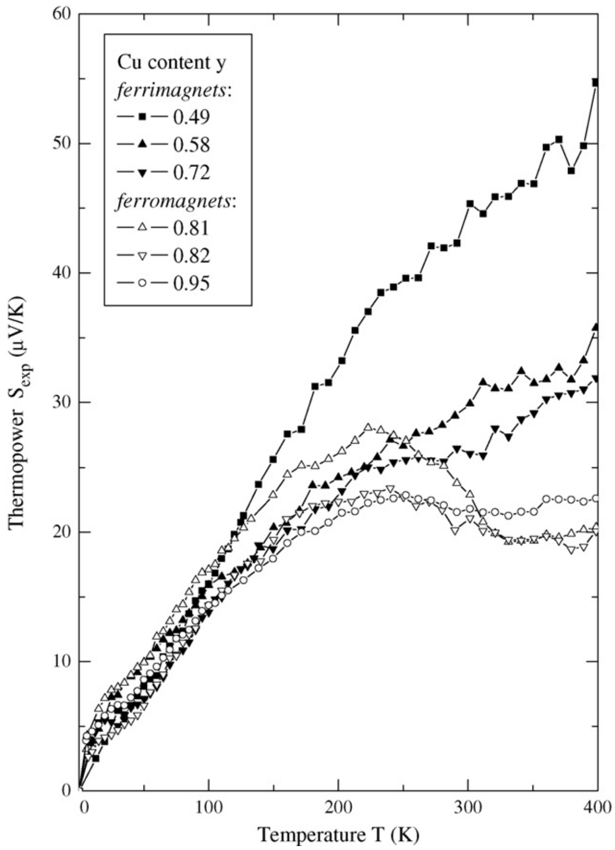

Fig. 1. Experimental thermopower S_{exp} vs. temperature T for single crystals with $y = 0.49$, 0.58, 0.72, 0.81, 0.82 and 0.95 of the $Zn_xCu_yCr_zSe_4$ spinel system. Data are taken from Ref. [1].

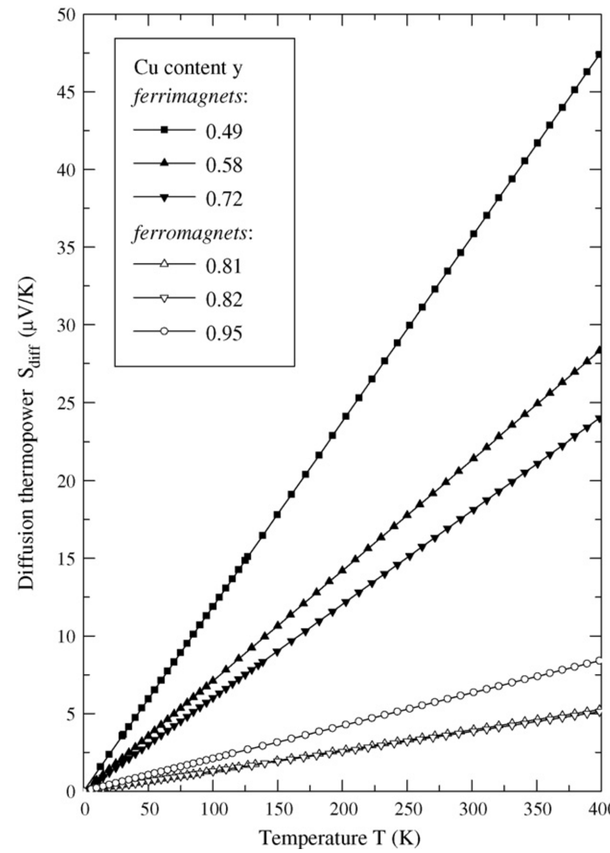

Fig. 2. The diffusion component of thermopower S_{diff} vs. temperature T for single crystals with $y = 0.49$, 0.58, 0.72, 0.81, 0.82 and 0.95 of the $Zn_xCu_yCr_zSe_4$ spinel system.

Table 1
The magnetic [1–3] and calculation parameters of $Zn_xCu_yCr_zSe_4$ spinel single crystals. T_C is Curie temperature, θ_{CW} is Curie–Weiss temperature, M_s is the saturation magnetization at 4.2 K and at 140 kOe, J_{eff}^{aa} is the effective exchange integral for the first coordination sphere and θ_D is the Debye temperature.

x	y	z	$x+y+z$	Experiment			Calculations	
				T_C (K)	θ_{CW} (K)	M_s (μ_B)	J_{eff}^{aa} (K)	θ_D (K)
Ferrimagnets								
0.42	0.49	2.12	3.03	405	221	4.6	387.34	474
0.33	0.58	2.08	2.99	395	299	4.4	393.47	476
0.31	0.72	2.37	3.4	388	264	5.33	375.98	474
Ferromagnets								
0.17	0.81	2.16	3.14	373	392	5.15	381.83	476
0.19	0.82	2.2	3.21	396	409	4.69	409.97	476
0.07	0.95	2.19	3.21	402	423	5.13	412.67	476

is the effective exchange integral for the first coordination sphere calculated with the aid of the exchange Hamiltonian consisting the components of superexchange and double exchange interactions. The agreement index R between the experimental (S_{exp}) and the theoretical (S_{theor}) thermopowers is high and exceeds 99% for ferrimagnetic samples and 94% for ferromagnetic ones (Table 2). The values of θ_D and J_{eff}^{aa} are collected in Table 1.

2. Results and discussion

The results of thermopower analysis of the $Zn_xCu_yCr_zSe_4$ single crystals with $y = 0.49$, 0.58, 0.72, 0.81, 0.82 and 0.95 are presented in Figs. 2–5. With increasing copper content y in a sample: (1) the diffusion component S_{diff} decreases, (2) the phonon drag component S_{ph} increases in ferrimagnetic phase and decreases in ferromagnetic one, (3) the magnon drag component S_{mag} oscillates both in ferri- and ferromagnets, although the S_{mag} intensity of the latter is higher,

Table 2
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. R is the agreement index.

y	D (µV/K^2)	E (µV/K^4)	F (µV/K)	G (10^{-3})	H (µV/K$^{1.5}$)	I (µV/K)	K (10^{-3})	R (%)
Ferrimagnets								
0.49	0.1189	1.0×10^{-19}	4.205	12.25	0.05898	0.20234	1.09	99.55
0.58	0.07103	1.0×10^{-19}	3.907	8.33	0.04104	1.05733	2.38	99.51
0.72	0.06018	1.7×10^{-11}	4.133	5.33	0.1212	0.31203	0.38	99.61
Ferromagnets								
0.81	0.01316	1.0×10^{-19}	11.331	11.15	0.07677	1.84	3.65	94.53
0.82	0.01283	1.5×10^{-14}	8.9468	11.46	0.09825	1.48055	6.9	98.94
0.95	0.02109	1.3×10^{-11}	7.93476	18.63	0.10025	2.02608	6.65	97.74

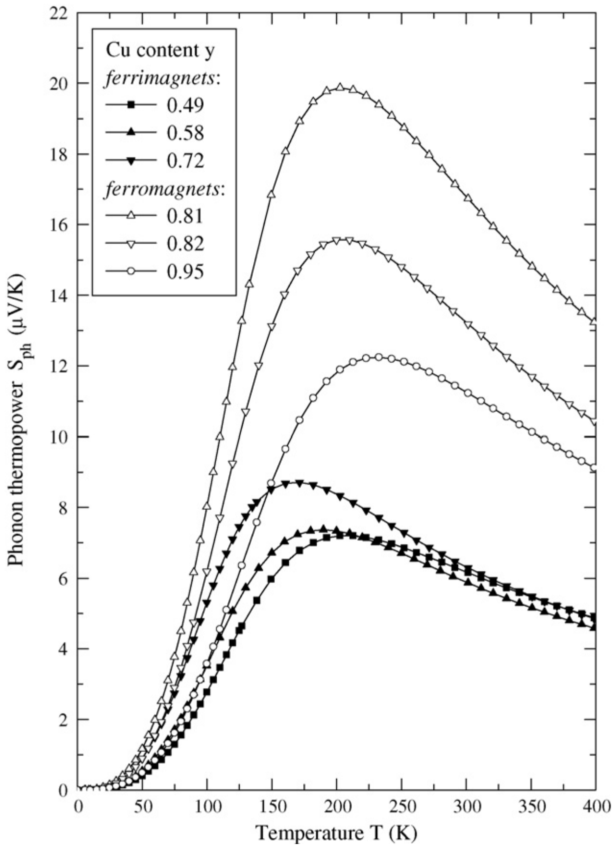

Fig. 3. The phonon drag component of thermopower S_{ph} vs. temperature T for single crystals with y = 0.49, 0.58, 0.72, 0.81, 0.82 and 0.95 of the $Zn_xCu_yCr_zSe_4$ spinel system.

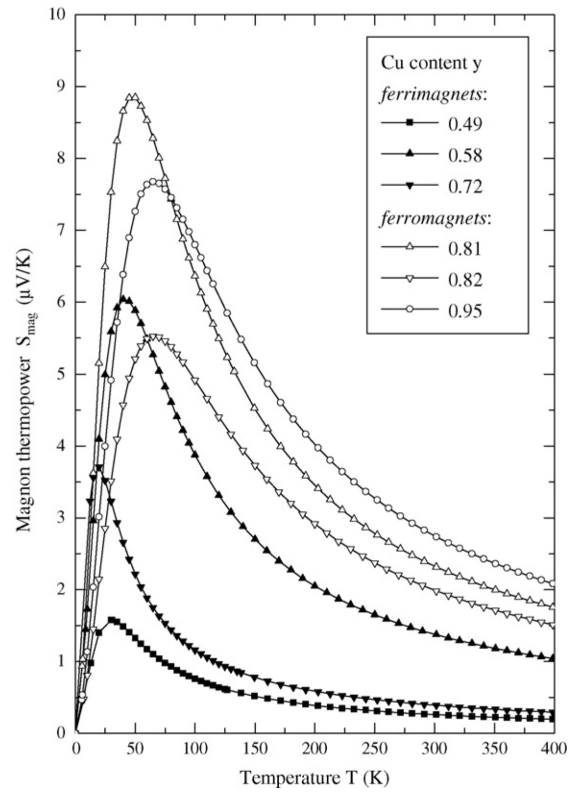

Fig. 4. The magnon drag component of thermopower S_{mag} vs. temperature T for single crystals with y = 0.49, 0.58, 0.72, 0.81, 0.82 and 0.95 of the $Zn_xCu_yCr_zSe_4$ spinel system.

and (4) the impurity component S_{imp} oscillates in ferrimagnetic phase and increases in ferromagnetic one. In general, the impurity component S_{imp} increases with increasing non-stoichiometry of a sample ($x+y+z \neq 3$). For practical applications are of importance the ferromagnetic spinel conductors whose a magnon component generates 9 μV/K in the temperature range 25–100 K, the ferromagnetic spinel conductors whose a phonon component generates 20 μV/K in the temperature range 150–200 K and the ferrimagnetic spinel conductors whose a diffusion component generates 47 μV/K in the temperature range 250–400 K. The impurity component of thermopower of spinel conductors generates maximum 2.5 μV/K in the temperature range 4.2–400 K.

One can conclude that the spin arrangement strongly influences on thermopower components of the $Zn_xCu_yCr_zSe_4$ single crystals. Especially, the ferromagnetic ordering of magnetic moments and double exchange interactions make easier the spin wave propagation at low temperatures and phonon excitations in the middle temperature range in comparison with the ferrimagnetic phase where the superexchange and RKKY interactions play a dominant role. The opposite behaviour takes place in the case of the diffusion contribution at higher temperatures. A larger contribution to the magnon drag thermopower coming from the double exchange interaction may be connected with coherent transfer of the magnon momentum to an electron jumping between Cr^{3+} and Cr^{4+} ions in the lowest Mott-Hubbard sub-band of $3d^3t_{2g}^3e_g^0 - 3d^2t_{2g}^2e_g^0$ band or eventually to the holes in the $3d^9$ $Cu^{2+}e_g^4t_{2g}^5$ orbital [7]. It seems thus natural to expect that thermopower analysis is a sensitive tool for studying materials for potential applications in the thermoelectric power generators.

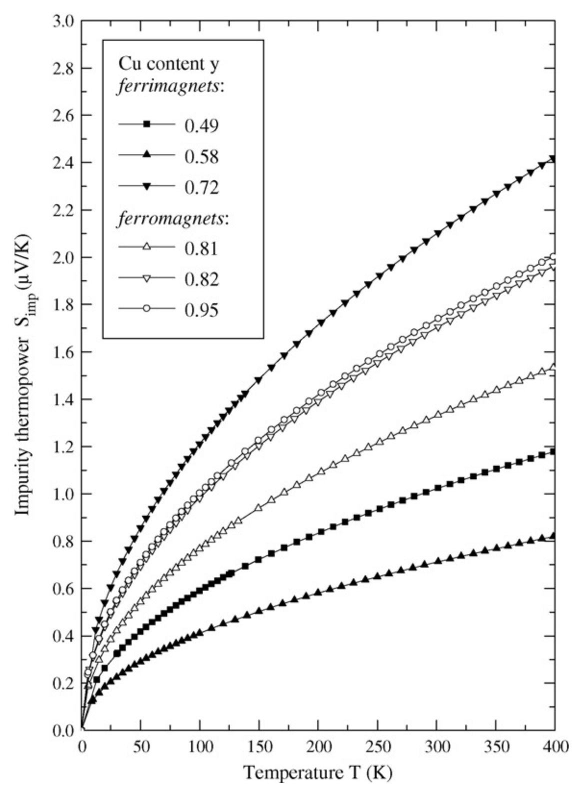

Fig. 5. The impurity component of thermopower S_{imp} vs. temperature T for single crystals with y = 0.49, 0.58, 0.72, 0.81, 0.82 and 0.95 of the $Zn_xCu_yCr_zSe_4$ spinel system.

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