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Specific Heat and Magnetic Properties of Single-Crystalline $(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ Semiconductor

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An antiferromagnetic order with a Néel temperature $T_N = 17.5$ K, a strong ferromagnetic exchange evidenced by a positive Curie–Weiss temperature $\theta_{CW} = 77.3$ K, the fuzzy peaks in the real component of susceptibility $\chi'(T)$ and the disappearance of the second critical field were established. The curvature of specific heat $C(T)$ and $C(T)/T$ in surrounding of T_N indicated a broad peak, characteristic for the system with inhomogeneous magnetic state (spin-glass-like phase). The calculated magnetic entropy showed the value of $S(T) \approx 1$ J/(mol K) which is extremely small; i.e., much lower than the magnetic contribution $R\ln(2S+1) = 11.52$ J/(mol K) calculated for the spin 3/2.

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1. Introduction

It is well known in literature that the p-type semiconducting [1] antiferromagnet [2] $ZnCr_2Se_4$ diluted by the nonmagnetic ions shows the effects of the site disorder, lattice frustration and random distribution of spin interactions [3–6], which create novel potential applications in the spin-based electronic technology. Recently, we have presented the specific heat data for the series of $ZnCr_2Se_4$ substituted by Al, Ga, In, or Ce [5, 6]. As the main conclusion we observed the following behaviours: the antiferromagnetic transition at T_N with a sharp peak of λ-type in the specific heat was strongly shifted to much lower temperatures in the applied magnetic fields, and the magnetic entropy at T_N is only about 10% of the full magnetic entropy expected for the complete alignment of the Cr magnetic moments. The first observation indicates on the second order phase transition, while the strong reducing of the entropy was explained as result of the spin fluctuations generated much above T_N. Spectacular lowering of the saturation magnetic moment to $M_s = 1.04\ \mu_B$/f.u. at 4.2 K and at 136 kOe for $(Zn_{0.84}In_{0.1})[Cr_{1.78}In_{0.14}]Se_4$ was most unexpected [5, 6].

The present contribution reports magnetic and specific heat measurements for almost stoichiometric $(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ to compare with those ones for non-stoichiometric $(Zn_{0.84}In_{0.1})[Cr_{1.78}In_{0.14}]Se_4$ [6], having similar composition.

2. Experimental details

The $(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ single crystal was obtained by a chemical vapour transport reaction using anhydrous chromium chloride $CrCl_3$ (purity 95%) as a transporting agent. Chemical composition of the single crystal was determined nondestructively by energy-dispersive X-ray fluorescence spectrometry (EDXRF). A single-crystal X-ray data collection was performed with Kuma KM4CCD diffractometer equipped with CCD detector and using Mo K_α radiation. Magnetization as well as dc and ac magnetic susceptibility with real (χ') and imaginary (χ'') components were measured in the zero-field-cooled mode using a vibrating sample magnetometer with a step motor at 4.2 K and in applied magnetic fields up to 150 kOe and a Lake Shore 7225 ac susceptometer up to 60 kOe in the temperature range 4.2–100 K, respectively. Specific heat was measured with a Quantum Design Physical Properties Measurement System (QD-PPMS) with heat capacity option in temperature range 1.8–24 K and at magnetic field up to 50 kOe.

3. Results and discussion

$(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ crystallizes in the cubic spinel structure with the space group symmetry $Fd\bar{3}m$ (No. 227). The In^{3+} substitution for Zn^{2+} revealed the appearance of the cation vacancies with the total cation deficiency of 2.9% as well as the large bond frustration resulting from the random distribution of

Cr/Zn–Se and Zn/In–Se bonds both in the tetra- (A) and octahedral (B) sites, although this spinel is almost stoichiometric. The cubic lattice parameter a equals to 10.5138(5) Å and it is larger in the comparison to the matrix $ZnCr_2Se_4$ with $a = 10.497(1)$ Å [6]. It may be attributed to the presence of In^{3+} in B site. The most stable and convergent refinements were obtained for the atom positions and SOFs presented in Table.

TABLE

Anion parameter (u), site occupation factors (SOF) and equivalent isotropic displacement parameters (U_{iso}) at 295 K.

Atom	Wyckoff position	SOF	U_{iso} [$\times 10^2$ Å^2]
Zn/In	8*a* (1/8, 1/8, 1/8)	0.926(2)/0.054(2)	1.19(2)
Cr/In	16*d* (1/2, 1/2, 1/2)	0.918(3)/0.076(2)	1.27(2)
Se	32*e* (u, u, u) $u = 0.25951(2)$	1.0	1.03(1)

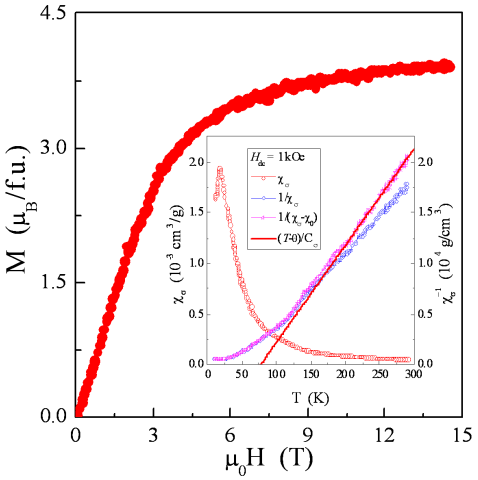

Fig. 1. Magnetization M vs. magnetic field $\mu_0 H$ at 4.2 K. Inset: magnetic susceptibilities vs. temperature $\chi_\sigma(T)$, $\chi_\sigma^{-1}(T)$, and $1/(\chi_\sigma - \chi_0)$ at $H_{dc} = 1$ kOe. The solid (red) line $(T-\theta)/C_\sigma$ indicates a Curie–Weiss behaviour.

Magnetization and magnetic susceptibility measurements are presented in Figs. 1–3. The saturation magnetic moment $M_s = 3.91$ μ_B/f.u. at 4.2 K. An antiferromagnetic order with a Néel temperature $T_N = 17.5$ K and a strong ferromagnetic exchange evidenced by a positive Curie–Weiss temperature $\theta_{CW} = 77.3$ K was established. The temperature independent component of susceptibility $\chi_0 = 7.509 \times 10^{-6}$ cm^3/g obtained from the fitting procedure [7] of the Curie–Weiss law suggests the temperature-independent contributions of orbital and Landau diamagnetism, Pauli and Van Vleck paramagnetism, as they cannot be separated. Because the $ZnCr_{2-x}In_xSe_4$ spinels are semiconductors [8], the Landau and Pauli contributions can be neglected. Thus, the positive value of χ_0 can come from the Van Vleck contribution, which usually arises from that part of the

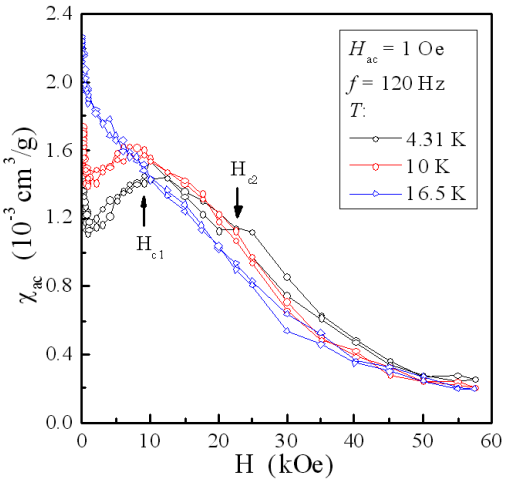

Fig. 2. Ac magnetic susceptibility, χ_{ac}, vs. static magnetic field H recorded at internal oscillating magnetic field $H_{ac} = 1$ Oe with internal frequency $f = 120$ Hz taken at different temperatures. The critical fields H_{c1} and H_{c2} are indicated by arrows.

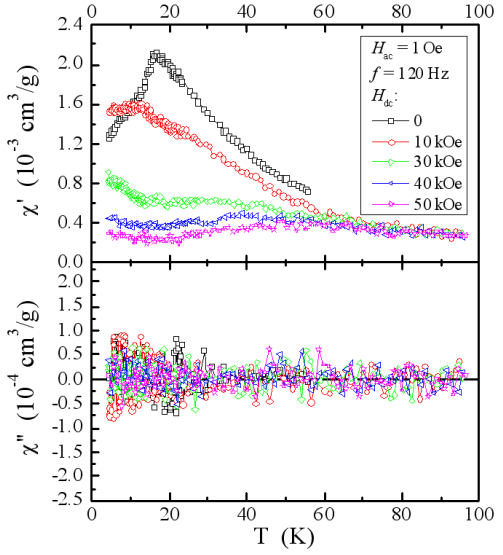

Fig. 3. Real χ' and imaginary χ'' components of ac magnetic susceptibility vs. temperature T recorded at $H_{ac} = 1$ Oe with $f = 120$ Hz taken at different external magnetic fields H_{dc}.

orbital moment which has been admixed back into the ground state by the orbital Zeeman effect [9]. $\chi_{ac}(H)$ in Fig. 2 shows a slight shift of the first critical field H_{c1} and the disappearance of the second critical field H_{c2} with the temperature. The fuzzy peak at $T_m = 40$ K in $\chi'(T)$ and the $\chi''(T)$ signal oscillating around zero depicted in Fig. 3 indicate the weak ferromagnetic order persisting in the paramagnetic region.

$(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ exhibits similar field dependence of T_N and strong lowering of entropy $S(T)$ in comparison with $(Zn_{0.84}In_{0.1})[Cr_{1.78}In_{0.14}]Se_4$ [6], how-

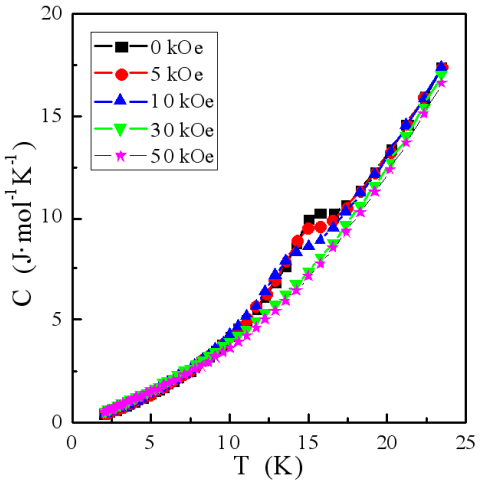

Fig. 4. Specific heat, C, vs. temperature T taken at different external magnetic fields.

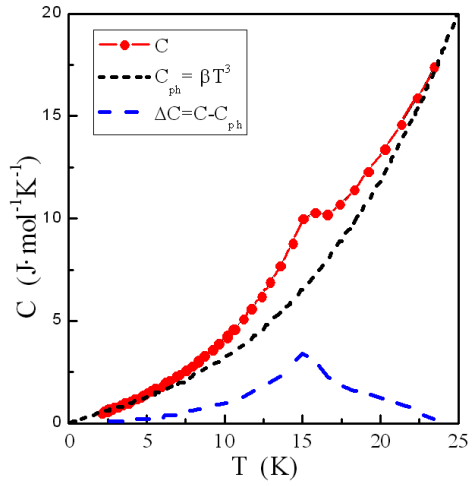

Fig. 5. Specific heat, C, vs. temperature T taken in zero magnetic field. $C_{\rm ph}$ is the Debye fit and $\Delta C = C - C_{\rm ph}$.

ever, it has quite different curvature of $C(T)$ and $C(T)/T$ in surrounding of $T_{\rm N}$. Namely, instead of the sharp λ-type anomaly we observed a broad peak, characteristic of the system with inhomogeneous magnetic state (spin-glass-like phase). From this point of view, this compound seems to be interesting. In Fig. 4 we present the specific heat vs. temperature at different magnetic fields. The maximum in the $C(T)/T$ data (not shown in this paper) is at 15.1 K for the magnetic field $\mu_0 H = 0$, and linearly decreases with increasing field; e.g., for $\mu_0 H = 5$ T, $T_{\rm max} \approx 2.6$ K. In Fig. 5 we present the $C(T)$ data obtained at $\mu_0 H = 0$, and the magnetic contribution ΔC when $C(T)$ are subtracted by the calculated phonon contribution $C_{\rm ph} = \beta T^3$.

The calculated magnetic entropy per formula unit shown in Fig. 6, $S(T) = \int_0^T \frac{\Delta C(T)}{T} {\rm d}T$ is at $T_{\rm N}$ only ≈ 2 J/(mol K). The value of $S \approx 1$ J/(mol K) calculated per Cr ion is extremely small; i.e., much lower than the magnetic contribution $R\ln(2S+1) = 11.52$ J/(mol K) calculated for the spin 3/2. So much strongly reduced magnetic entropy $S(T)$ can in part result from the spin fluctuations observed above $T_{\rm N}$, however this is not the only one reason. In the similar compounds (cf. Ref. [4] and [6]) the entropy is also strongly reduced, however, the value of $S(T)$ per one Cr atom was measured about 4 times larger. The reason of the strong $S(T)$ anomaly for $(Zn_{0.925}In_{0.054})[Cr_{1.84}In_{0.152}]Se_4$ single crystalline sample seems well not to be understood, although the sample stoichiometry and the structural defects play an essential role in this case.

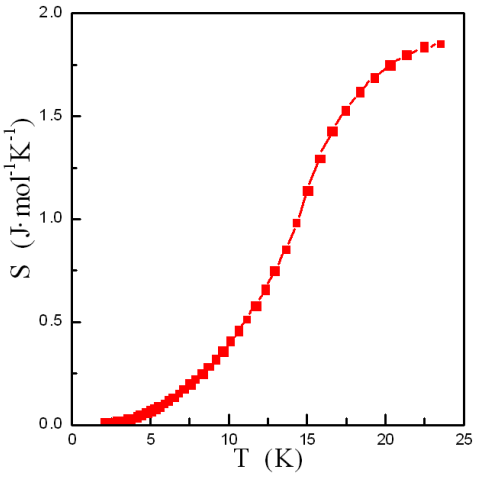

Fig. 6. Entropy S per formula unit vs. temperature T in zero magnetic field.

References

[1] F.K. Lotgering, in: *Proc. Int. Conf. on Magnetism, Nottingham*, ed. L.F. Bates, Institute of Physics, London 1965, p. 533.

[2] R. Plumier, *J. Phys. (Paris)* **27**, 213 (1966).

[3] E. Malicka, T. Groń, H. Duda, A.W. Pacyna, J. Krok-Kowalski, *Acta Phys. Pol. A* **116**, 964 (2009).

[4] E. Malicka, T. Groń, A. Ślebarski, A.W. Pacyna, J. Goraus, M. Fijałkowski, J. Heimann, *J. Phys. Chem. Solids* **72**, 974 (2011).

[5] E. Malicka, T. Groń, A.W. Pacyna, A. Gągor, T. Mydlarz, *J. Phys. Conf. Series* **303**, 012077 (2011).

[6] E. Malicka, T. Groń, A. Ślebarski, A. Gągor, A.W. Pacyna, R. Sitko, J. Goraus, T. Mydlarz, J. Heimann, *Mater. Phys. Chem.* **131**, 142 (2011).

[7] T. Groń, A.W. Pacyna, E. Malicka, *Solid State Phenom.* **170**, 213 (2011).

[8] T. Groń, J. Kopyczok, I. Okońska-Kozłowska, J. Warczewski, *J. Magn. Magn. Mater.* **111**, 53 (1992).

[9] R.M. White, *Quantum Theory of Magnetism*, McGraw-Hill, Inc., New York 1970.