High Spin–Low Spin Transitions in $Cu_{0.2}Co_{0.76}Cr_{1.83}Se_4$ Semiconductor*

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Magnetization, ac and dc magnetic susceptibility measured in the zero-field-cooled mode were used to study the high spin–low spin transitions in polycrystalline $Cu_{0.2}Co_{0.76}Cr_{1.83}Se_4$ semiconductor. The real part component of fundamental susceptibility $\chi_1'(T)$ and its second (χ_2) and third (χ_3) harmonics revealed two spectacular peaks at 128 K and at 147 K, confirming the appearance of the spin-crossover phenomenon.

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1. Introduction

Electrical and magnetic studies carried out on single-crystalline $Cu_xCo_yCr_zSe_4$ spinels showed ferromagnetic ordering and p-type metallic conductivity for $y = 0.06$, 0.1 and 0.11 as well as a ferrimagnetic behaviour and n-type electrical semiconductivity for $y = 0.23$ [1]. Later, structural and electrical investigations carried out on polycrystalline $Cu_{1-x}Co_xCr_2Se_4$ spinels in the compositional range $0.0 \le x \le 1.0$ revealed a transformation from cubic to monoclinic structure above $x = 0.4$ as well as thermally activated conductance with activation energy 90–220 meV above room temperature for $x \le 0.5$ and metallic-type conductivity within intermediate temperature range $200 \le T \le 400$ K for $x \ge 0.6$ [2]. Recently, X-ray diffraction studies on the single phase $Cu_{1-x}Co_xCr_2Se_4$ samples ($x = 0$, 0.2, 0.8, 1) proved the existence of the cubic spinel-type structure for $x \le 0.2$ and the monoclinic Cr_3S_4-type one for $x \ge 0.8$ [3]. Magnetization and magnetic susceptibility of the $Cu_xCo_yCr_zSe_4$ polycrystals measured in the zero-field-cooled mode showed a transition from ferromagnetic order via ferrimagnetic one to antiferromagnetic-like behaviour with increasing Co content. This transition was accompanied with a lowering symmetry from cubic to monoclinic and for the latter the spin-crossover phenomenon occurred [4].

It is well known that compounds containing transition metals with d^4, d^5, d^6, and d^7 electron configurations are usually capable of forming either spin-free (HS) or spin-paired (LS) grounds states. When difference between the strength of the cubic ligand field and the mean spin-pairing energy is comparable to the thermal energy, both HS and LS spin states may be populated and cross over in thermal equilibrium [5]. This phenomenon is commonly known as spin crossover for that the Curie–Weiss law is not valid. So, the easiest way of following the spin conversion as a function of temperature is the measurement of the magnetic susceptibility [5].

2. Experimental details

A powder sample of $Cu_{0.2}Co_{0.76}Cr_{1.83}Se_4$ was obtained as ceramics using a preparation method which is described in detail elsewhere [2]. Chemical composition was determined by energy-dispersive X-ray fluorescence spectrometry (EDXRF) [6]. The sample was excited by the Rh target X-ray tube (XTF 5011/75, Oxford Instruments, USA). The X-ray spectrum was collected by thermoelectrically cooled Si-PIN detector (XR-100CR Amptek, Bedford, MA, USA) of 145 eV resolution at 5.9 keV. The quantitative EDXRF analysis was performed by fundamental parameters method based on the Sherman equation. The sample with nominal composition $Cu_{0.2}Co_{0.8}Cr_2Se_4$ [2] studied in this paper is the same sample. X-ray analysis using a Siemens D5000 diffractometer with filtered Cu K_α radiation showed the monoclinic phase, type-Cr_3S_4 with the following structural parameters: $a = 6.2787$ Å, $b = 3.6253$ Å, $c = 11.3730$ Å, $\beta = 91.008°$, and $V = 256.296$ Å^3 [2].

Magnetization, dc and ac magnetic susceptibility of $Cu_{0.2}Co_{0.76}Cr_{1.83}Se_4$ were measured in the zero-field-cooled mode using a vibrating sample magnetometer with a step motor [7] at 4.2 K and in applied external magnetic fields up to 150 kOe, a Faraday type Cahn RG automatic electrobalance in the temperature range 4.2–370 K and at 800 Oe, and a Lake Shore 7225 ac susceptometer, respectively. The in-phase $\chi_1'(T)$ and out-of-

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-phase $\chi_1''(T)$ components of the ac fundamental susceptibility were recorded in the temperature range 4.2–170 K simultaneously as a function of temperature in an oscillating field $H_{ac} = 1$ Oe with frequency of 120 Hz. The signals of the second (χ_2) and third (χ_3) harmonics associated with nonlinear susceptibilities were detected as a function of temperature using an oscillating field of 5 Oe with frequency of 120 Hz without the applied external magnetic field.

System accuracy: calibration constants (both ac and dc) are accurate within ±1.0%. The ac susceptibility sensitivity to 2×10^{-8} emu in terms of equivalent magnetic moment and dc moment sensitivity: 9×10^{-8} emu. All the ac measurements were made in the same regime.

3. Results and discussion

The magnetization isotherm, $\sigma(H)$, in Fig. 1 shows linear magnetic field dependence with hysteresis without remanence and coercivity as well as a pronounced small value of magnetic moment at 140 kOe, not exceeding

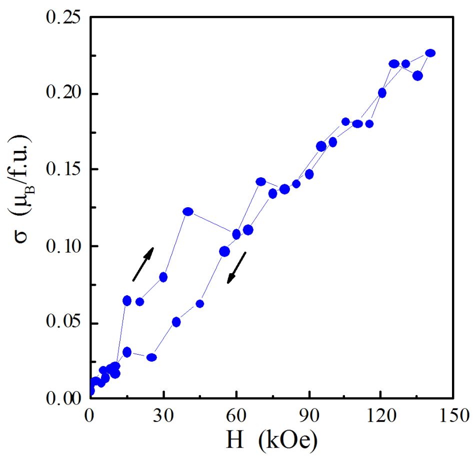

Fig. 1. Magnetization σ vs. magnetic field H at 4.2 K.

0.22 μ_B/f.u. at 4.2 K. It may suggest the LS state of the Co^{2+} ions in the t_2 orbital, because the Cr^{3+} ions are usually in the HS state. Eventually, an antiferromagnetic coupling between the Co^{2+} and Cr^{3+} magnetic moments induced by the uniaxial anisotropy may occur, too.

Figure 2 reveals the low values of magnetic susceptibility, $\chi_\sigma = 10^{-5}$ cm^3/g and a weak temperature dependence of the magnetic susceptibility without a Curie–Weiss region. The effective magnetic moment, given by the expression $\mu_{eff}(T) = 2.83\sqrt{\chi_{mol}T}$, shows anomalous temperature dependence (inset of Fig. 2), characteristic for the HS–LS transitions. The fitting procedure of the Curie–Weiss law [8] shows that the experimental (green) curve of $\chi_\sigma^{-1}(T)$ in Fig. 2 deviates downward from its linear part (red curve). It indicates the paramagnetic temperature independent contribution to the magnetic susceptibility with the value of $\chi_0 = 4.663 \times 10^{-6}$ cm^3/g, for which the Pearson correlation coefficient R is over 99%. Usually χ_0 contains

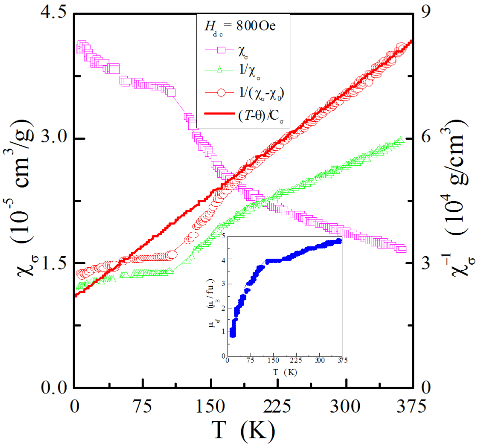

Fig. 2. Dc magnetic susceptibility χ_σ and inverse susceptibility $1/\chi_\sigma$ (experiment) and $1/(\chi_\sigma - \chi_0)$ (fit) vs. temperature T. Inset: effective magnetic moment μ_{eff} vs. temperature T.

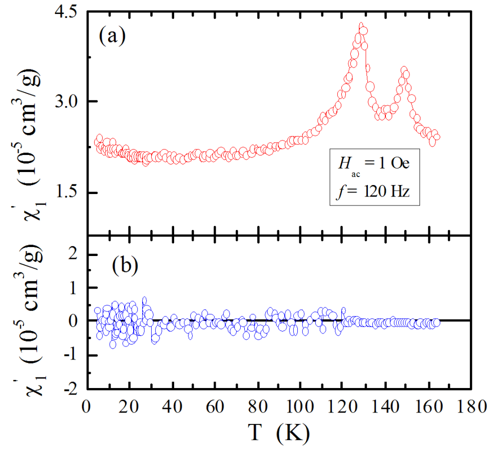

Fig. 3. In phase χ_1' (a) and out of phase χ_1'' (b) components of ac magnetic susceptibility vs. temperature T recorded at internal oscillating magnetic field H_{ac} = 1 Oe with internal frequency $f = 120$ Hz.

the orbital and Landau diamagnetism, Pauli and Van Vleck paramagnetism as well as others, as they cannot be separated. Because $Cu_{0.2}Co_{0.76}Cr_{1.83}Se_4$ is the semiconductor [2], the Landau and Pauli contributions can be neglected.

Two spectacular peaks were observed on the in-phase $\chi_1'(T)$ curve at $T_1 = 128$ K and at $T_2 = 147$ K, while the out-of-phase $\chi_1''(T)$ curve exhibits the values close to zero (Fig. 3), indicating a lack of the energy dissipation. It means that these peaks are not connected, for example, with magnetic coupling, magnetic-domain-wall-motion or with rotation of magnetization within domain [9]. Small values of the magnetic moments in Fig. 1 well correlate with these observations.

The second (χ_2) and third (χ_3) harmonics of the ac magnetic susceptibility presented in Figs. 4 and 5 also reveal two peaks at the same T_1 and T_2 temperatures.

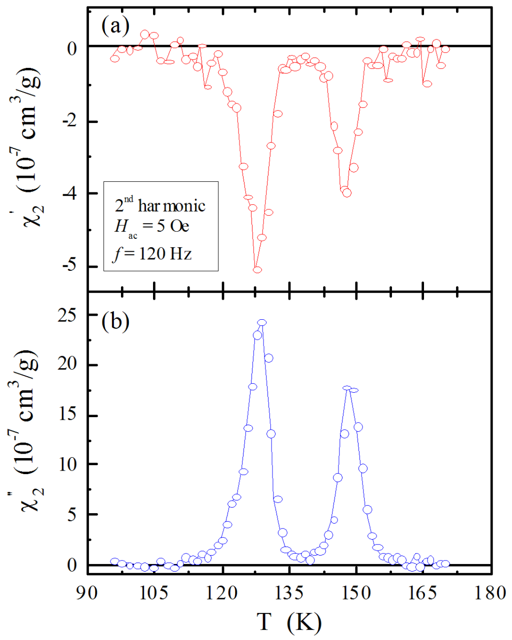

Fig. 4. In phase χ_2' (a) and out of phase χ_2'' (b) second harmonics of ac magnetic susceptibility vs. temperature T recorded at internal oscillating magnetic field H_{ac} = 5 Oe with internal frequency f = 120 Hz.

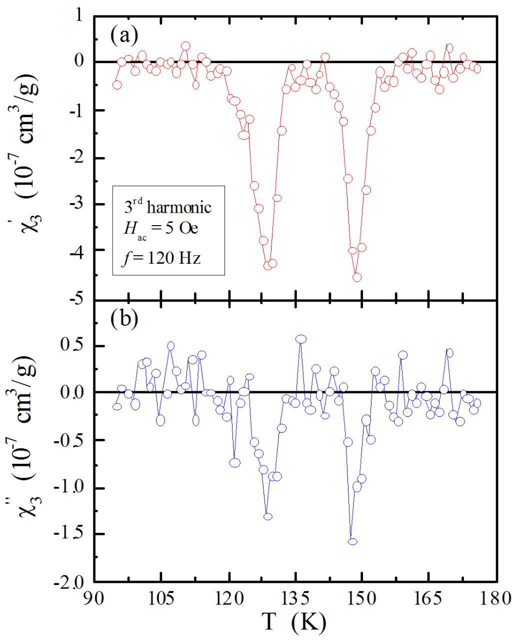

Fig. 5. In phase χ_3' (a) and out of phase χ_3'' (b) third harmonics of ac magnetic susceptibility vs. temperature T recorded at internal oscillating magnetic field H_{ac} = 5 Oe with internal frequency f = 120 Hz.

However, according to the molecular field theory the second harmonic should vanish at the temperature of magnetic ordering [10]. It means that there is no any region with magnetic coupling in this case. Moreover, the signs of the $\chi_2'(T)$, $\chi_2''(T)$, $\chi_3'(T)$ and $\chi_3''(T)$ components in Figs. 4 and 5 are characteristic for a spin frustration of the re-entrant type [11].

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