Magnetic characteristics of $CuCr_2S_4$ nanospinels obtained by mechanochemical synthesis of CuS-Cr_2S_3 (1:1) mixture

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$CuCr_2S_4$ belongs to the group of spinel chalcogenides with general formula $CuCr_2X_4$ where X = S, Se and Te that they are ferromagnetic at room temperature (with Curie temperatures of 377, 430, and 360 K for $CuCr_2S_4$, $CuCr_2Se_4$, and $CuCr_2Te_4$, respectively) and are also metallic [1]. This group of compounds are promising materials for commercial application as magnetic [2] or thermoelectric devices [3]. The spinel $CuCr_2S_4$ obtained with the aid of the solid-phase synthesis crystallizes in the cubic type structure (space group *Fd*3*m* [1]). It has a normal cation distribution with copper ions located at the tetrahedral sites and chromium ions in octahedral coordination. $CuCr_2S_4$ nanocrystals synthesized by mechanical alloying (MA) of the constituent elements at ambient temperature showed a spin glass with a spin freezing temperature of 30 K and insulating behavior with the spin-dependent variable-range hopping within the ranges T<50 K and T>100 K [4]. $CuCr_2S_4$ nanocubes and nanoclusters obtained by the colloidal synthesis using a facile solution-based method showed superparamagnetic behavior with the blocking temperature near room temperature as well as ferromagnetic one at lower temperatures [5].

Mechanochemical synthesis of $CuCr_2S_4$ spinel phase was carried out from CuS and Cr_2S_3 precursors mixed in 1:1 molar ratio, by high-energy ball milling. Sulphide precursors were also obtained by the same method under analogous conditions, from high purity elemental Cu, Cr and S powders mixed in a proper ratio. The milling process was performed in the Fritsch Pulverisette 7 planetary ball mill at a rotation velocity of 600 rpm, under the argon protective atmosphere. Hardened steel vial (20 cm^3) and balls (10 mm) were used. The ball-to-powder weight ratio was 10:1. To avoid excessive temperature increase, milling times of 20 min were alternated with equal rest periods.

The results of dc magnetic susceptibility and magnetization measurements of the $CuCr_2S_4$ nanospinels showed an antiferromagnetic order at the Néel temperature T_N = 40 K, a split of the ZFC–FC susceptibility, suggesting the superparamagnetic state with the blocking temperature T_b ~120 K. While ferromagnetic behavior is evident in the hysteresis having both low coercivity field of ~0.026 T and low remanence of ~0.09 μ_B/f.u at 10 K. Interestingly, neither loop saturates at a magnetic field of 1 T. Preliminary electrical studies shown that investigated nanospinels are semiconductors. This means that MA method changes both the order of magnetic moments from ferromagnetic to antiferromagnetic and the character of the electrical conductivity from metallic to semiconducting as well as introduces also the spin disorder.

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