Synthesis and magnetic properties of $CuCr_{1.65}Se_4$ nanoparticles

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The chromium-based spinel chalcogenides, ACr_2X_4 (A = Cu, Cd, Hg, Fe, Co; X = S, Se, Te) [1] which are ferro/ferrimagnetic insulators, semiconductors, or even metals display unique properties in the bulk [2,3]. Powders of copper, chromium and selenium (99,99% purity) were mixed to give the desired composition and next they were milled in the Fritsch Pulverisette 6 planetary ball mill equipped with hardened steel vial and balls with diameter of 15 mm. The mechanical alloying process [4] was performed in a protective atmosphere of argon. The ball-to-powder weight ratio and rotational speed were 10:1 and 500 rpm, respectively. Milling times of 30 minutes were alternated with equal periods of rest to avoid temperature increase. After selected time intervals the samples of milled powder were examined by the X-ray diffraction method.

The XRD measurements were performed on the Philips X'Pert PW 3040/60 diffractometer using $Cu_{K\alpha}$ radiation (λ = 1.54056 Å). X'Pert HighScore Plus software and ICDD (PDF-2, 2009) files were used for phase identification. Surface morphology of compacted $CuCr_{1.65}Se_4$ powders was studied by using a scanning microscope (Jeol JSM-6480). Magnetization and magnetic susceptibility were measured with a Quantum Design Physical Properties Measurement System (QD-PPMS) in the temperature range 1.8–360 K and at magnetic field up to 70 kOe.

The temperature dependence of magnetic susceptibility, χ(T), and its reverse, $1/\chi$(T), indicate a lack of the Curie-Weiss behaviour. The magnetization isotherms, *M*(H), show a hysteresis with coercivity of 5.6 kOe and remanence of 0.03 μ_B/f.u. at 5 K as well as a linear dependence *M vs. H* at 350 K. The hysteresis is far from saturation because M = 0.23 μ_B/f.u. at 70 kOe. The theoretical value of the effective magnetic moment of $CuCr_{1.65}Se_4$ is $\mu_{eff} \sim$ 4.97 μ_B/f.u. for a high-spin Cr^{3+} (S = 3/2, g = 2). Whereas the temperature dependence of the effective magnetic moment estimated from equation: $\mu_{eff} = 2.83\sqrt{\chi \cdot T}$ strongly depends on temperature. It shows both a broad maximum around the temperature of 170 K and a broad minimum close to room temperature. At the maximum μ_{eff} is close to the spin-only value. Upon lowering the temperature μ_{eff} gradually decreases from 4.77 μ_B/f.u. at 170 K to 1.21 μ_B/f.u. at 5 K. It can mean, that the ferrimagnetic order dominates from one side and the strong spin-orbit coupling exists in the sample from the other. A superparamagnetism wasn't stated in the $CuCr_{1.65}Se_4$ nanoparticles since the magnetization curves were deviated from the universal function of magnetization *vs.* magnetic field divided by temperature [5].

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