# Magnetic and electrical properties of $CuCr_2Se_4$ nanoparticles

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Magnetic spinels with general formula $CuCr_2X_4$ (where X = S, Se and Te) are ferromagnetic [1] and metallic conductor at room temperature [2]. For this reason, these spinels have been extensively studied in terms of their potential applications in thermoelectric devices [3]. $CuCr_2Se_4$ obtained by solid phase synthesis has a normal cubic type structure with the symmetry of the $Fd\bar{3}m$ space group and the zero magnetic moment of the Cu ion in the tetrahedral site, whereas the three Bohr magnetons, corresponding with $Cr^{3+}$ ions in the octahedral site [4]. Pure $CuCr_2Se_4$, both in mono and polycrystalline form has strong ferromagnetic long-range interactions below the Curie temperature of $T_C$ = 460 K with strong ferromagnetic short-range interactions evidenced by a large positive Curie-Weiss temperature of $\theta$ = 465 K [1] as well as the electrical resistivity of $3.8 \cdot 10^{-6}$ $\Omega$m and the positive Seebeck coefficient of 20.5 $\mu$V/K at room temperature [2] .

Spinel nanocrystallites of $CuCr_2Se_4$ with a size of 32 nm were obtained as a result of five-hour grinding of single crystals of this compound (in order to avoid phase impurities) by high-energy ball milling. The static magnetic susceptibility was recorded both in zero-field-cooled and field-cooled mode. Dynamic magnetic susceptibility was measured at an internal oscillating magnetic field $H_{ac}$ = 3.9 Oe with an internal frequency $f$ = 1 kHz in the temperature range of 5–300 K. Magnetization isotherms were measured at 5, 20, 40, 60, and 300 K using a SQUID magnetometer in applied external fields up to 70 kOe. Electrical conductivity $\sigma(T)$ and thermoelectric power S(T) of the nanoparticles under study were measured by the DC method using a KEITHLEY 6517B Electrometer/High Resistance Meter and a Seebeck Effect Measurement System, respectively, within the temperature range of 77–400 K.

Magnetic and electrical studies have shown that the reduction of $CuCr_2Se_4$ single crystals to the size of nanoparticles leads to: 1) weakening of the long-range ferromagnetic interactions visible in the decrease of the Curie temperature from 460 to 196 K, 2) weakening of the short-range ferromagnetic interactions visible in the decrease of the paramagnetic Curie-Weiss temperature from 465 to 231 K, 3) lack of saturation of magnetization at 5 K and 70 kOe, 4) change of electrical conductivity from metallic to semiconductor, and 5) reducing the thermoelectric power factor $\sigma S^2$ by three orders of magnitude at 400 K. The above results were considered in terms of magnetic interactions and their exchange integrals, derived from the high-temperature expansion of magnetic susceptibility. Calculations of the exchange integrals and the band width of the mixed valency of chromium ions [$Cr^{3+}$, $Cr^{4+}$] showed that the decrease in the size of the crystallites causes a significant weakening of the mechanism of the double exchange magnetic interactions, without changing the strength of the superexchange magnetic ones, and the reduction of the band width [$Cr^{3+}$, $Cr^{4+}$] from 0.76 to 0.19 eV. Similar behavior was found for $CuCr_2S_4$ nanoparticles [5].

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