Magnetic properties of semiconducting $ZnCr_2Se_4$:Re single crystals

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Seleno-spinels are promising compounds in the commercial use of thermoelectric devices [1] due to a fairly large cubic cell unit (~10 Å) and a strong covalent bond. Pure $ZnCr_2Se_4$, both in mono and polycrystalline form combines *p*-type semiconductor conductivity and helical antiferromagnetic (AFM) order below the Néel temperature T_N = 20 K with a strong ferromagnetic (FM) short-range interaction, as evidenced by the high positive Curie-Weiss temperature θ = 115 K [2,3]. The magnetic order at T_N is accompanied by structural transformation from cubic $Fd\bar{3}m$ to tetragonal $I4_1/amd$ symmetry with a small contraction along the *c* axis [4]. Rhenium is a conductor and paramagnetic, it has hexagonal symmetry and crystallizes in $P6_3mmc$ space group. The unit cell parameters of rhenium crystal are as follows: *a* = 276.0 and *c* = 445.8 pm [5].

$ZnCr_2Se_4$ single crystals doped with rhenium ions with the content of 0.06, 0.07, 0.08, 0.09. 0.10 and 0.11 located in the tetrahedral sites of the spinel structure were grown from binary selenide ZnSe, elemental rhenium and selenium by chemical vapor transport with anhydrous $CrCl_3$ as transport agent. Dynamic AC magnetic susceptibility, χ_{ac}, was measured in the temperature range 2-300 K and at an internal oscillating magnetic field H_{ac} = 1 Oe with an internal frequency *f* = 120 Hz taken at external static DC magnetic fields H_{dc} = 0, 10, 20, 30, 40 and 50 kOe. Magnetization isotherms, M(H), were measured at 2, 4, 10, 20, 40, 60, and 300 K and in the static DC magnetic field up to 70 kOe. Specific heat measurements were made in the temperature range of 2-300 K. For these purposes a Quantum Design MPMS-XL-7AC SQUID magnetometer was used. The electrical conductivity σ(T) was measured by the DC method using KEITHLEY 6517B Electrometer/High Resistance Meter in the temperature range of 77–400 K.

Magnetic (AC), specific heat, and electrical (DC) measurements showed semiconductor behavior, coupling of the phonon system and electron gas by a spin lattice determined by the Debye temperature of 295 K, two singularities on magnetization isotherms in critical fields of 12 and 60 kOe, AFM long-range order with the Néel temperature of T_N = 21.7 K, and a strong FM short-range interaction, as evidenced by an increase in the positive Curie–Weiss temperature, θ, from 75 to 83 K with increasing Re content in the sample. With the increase of the external DC magnetic field, a shift of T_N towards lower temperatures and θ towards higher ones was observed, as well as the appearance of broad peaks in the paramagnetic region at H_{dc} = 40 and 50 kOe, characteristic of spin fluctuations. Similar behavior was found in $ZnCr_2Se_4$:Ta single crystals [6].

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