THE MAGNETIC AND STRUCTURAL PROPERTIES OF $Fe_{1-x}Cu_xCr_2S_4$ SINGLE CRYSTALS GROWN BY CHEMICAL TRANSPORT REACTIONS

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Abstract

Single crystals of the $Fe_{1-x}Cu_xCr_2S_4$ system with substitution of Cu for Fe x = 0.4, 0.5, and 0.6 have been succesfully grown using the chemical transport reaction method. Bromine was used as a transport agent. Wave-length dispersive spectroscopy analysis has shown that the real concentration of substitution for the grown samples deviates from the initial concentration. The Curie temperature of the single crystals prepared with bromine increases considerably in comparison with that for the samples grown with chlorine and approaches that of the stoichiometric polycrystalline samples.

1. Introduction

Magnetic AB_2X_4 compounds (A = Cu, Cd, Zn, Hg, Fe, Co; B = Sc, Cr, Ir; X = S, Se, Te) with spinel structure recently have attracted much attention because of exotic behaviour and unconventional ground states, e.g., spin-liquid, spin-orbital liquid, and spin-orbital glass stemming from strong frustration effects that influence both the spin and orbital degrees of freedom. A number of new physical phenomena, such as colossal magnetoresistance [1], colossal magnetocapacitance [2], and spin Jahn-Teller effect [1, 3], have been discovered; these phenomena are important from the theoretical point of view and are promising for application in novel spintronic and magneto-optical devices.

2. Experimental

The single crystals of $Fe_{1-x}Cu_xCr_2S_4$ were grown by the chemical transport reaction method from the preliminary synthesized polycrystals using a two-zone furnace in which a temperature gradient of 50K was created. Bromine was used as a transport agent. X-ray diffraction was performed utilizing a STADI-P (STOE&CIE) spectrometer. The composition of the samples was checked by the wave-length dispersive spectroscopy analysis (WDS) using Cameca SX 50. Magnetization was measured with a commercial SQUID magnetometer (MPMS-5, Quantum Design) in a temperature range of 2–400 K and in a magnetic field of up to 50 kOe.

3. Results and discussion

Using chemical transport reactions, the single crystals of the $Fe_{1-x}Cu_xCr_2S_4$ system with substitution concentration x = 0.4, 0.5, and 0.6 have been successfully grown. The samples grow in the form of an octahedron and plates with dimensions of up to 5 mm by edge. The XRD

studies of the crashed single crystals showed a pure cubic structure (space group Fd-3m) and the absence of foreign phases.

Recently, it has been shown experimentally [4] that an increase in the substitution concentration in this system in samples grown with Cl results in an increase in the magnetic moment and the Curie temperature (T_C) (dotted line with filled squares in Fig. 1) and in a decrease in the lattice parameter (dashed line with open squares in Fig. 2). It was observed that the sum of the concentration of Cl and S ions in the samples as determined by WDS is very close to stoichiometry, which suggests that the Cl ions (with ionic radius of 1.81 Å) replace the S ions (with very similar ionic radius of 1.84 Å) in the anionic positions. The penetration of Cl^- ions in the crystals with one electron more compared to S^{2-} ions leads to a significant change in internal crystal fields, which probably can explain the observed considerable lowering of T_C of the single-crystalline samples compared to polycrystalline ones.

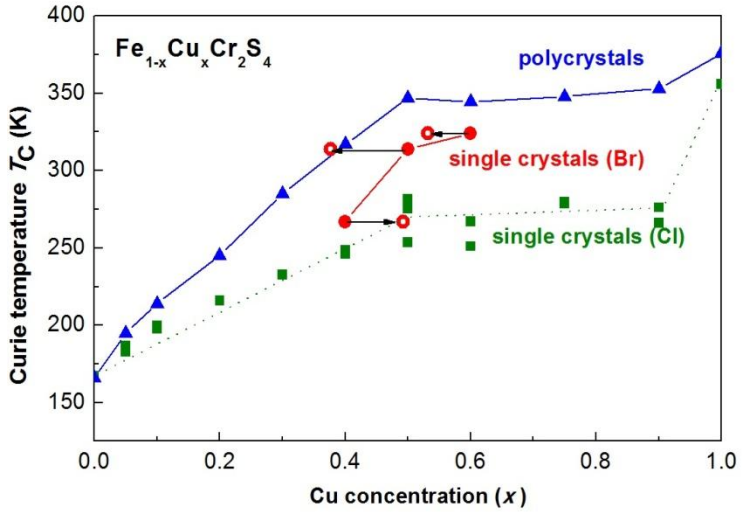

Fig. 1. Dependence of the Curie temperature on the substitution concentration of Cu for Fe for single crystals prepared with different transport agents and stoichiometric polycrystals.

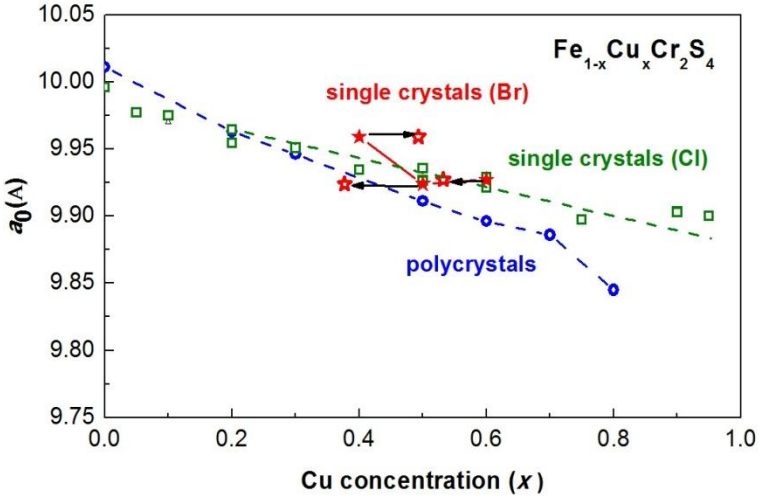

Fig. 2. Dependence of the lattice parameter on the substitution concentration of Cu for Fe for single crystals prepared with different transport agents and stoichiometric polycrystals.

The problem of doping with Cl can be resolved by changing the transport agent Cl with Br (with a much larger ionic radius of 1.96 Å) which has no free space in the lattice and therefore cannot be accomodated like Cl ions. It was found that the Curie temperature of the single crystals prepared with bromine increases considerably in comparison with those doped with Cl and approaches that of the stoichiometric polycrystalline samples (line with circles in Fig. 1).

The WDS analysis of the obtained crystals has shown that the real concentration of the substitution of Cu for Fe for the single crystalline samples grown by Br deviates from the initial concentration (table). For the samples with initial concentration x = 0.5, 0.6, the real concentration is lower, but for the sample with initial concentration x = 0.4, the real substitution concentration is higher. This difference however cannot be explained by simple geometric notions and needs further investigation.

Results of the WDS analysis of the composition of the grown single crystals

Substitution concentration Cu (x)	Fe (wt %)		Cu (wt %)	
	Initial concentration	Real concentration	Initial concentration	Real concentration
0.4	0.6	0.506	0.4	0.494
0.5	0.5	0.623	0.5	0.377
0.6	0.4	0.467	0.6	0.532

It was also found that, with a decrease in the temperature, the magnetization of the samples with concentration of substitution x = 0.4, 0.5 shows a peak at temperature T_m (~ 100 K for x = 0.4 and 175 K for x = 0.5) in zero field cooled (ZFC) susceptibility. However, in the field cooled (FC) curves for these samples and in the susceptibility curves of the sample with concentration of substitution x = 0.6, this anomaly was absent (Fig. 3).

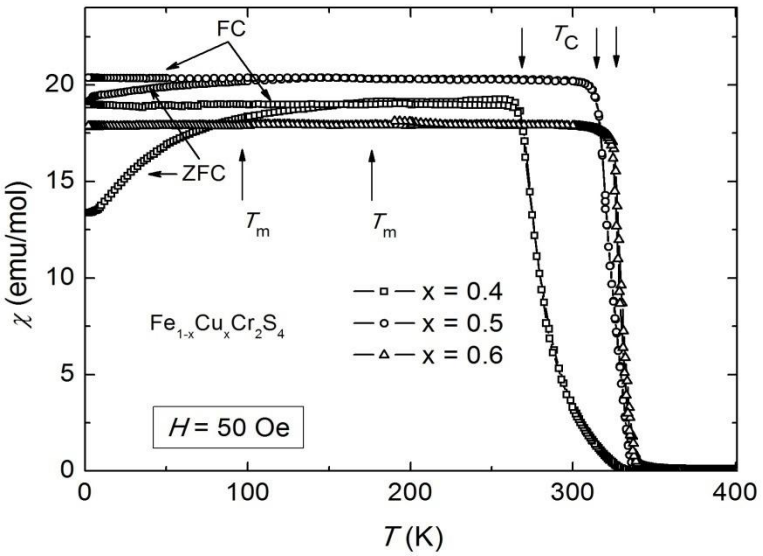

Fig. 3. Temperature dependence of the susceptibility for samples with different substitution concentration (x = 0.4, 0.5, 0.6).

This increase of temperature T_m for compounds with x = 0.4, 0.5 can be attributed to a reduction of the antiferromagnetic interaction between the iron and chromium ions which takes place with an increase in the concentration of substitution.

4. Conclusions

The substitution of Cl by Br as a transport agent in the process of growth of crystals of the $Fe_{1-x}Cu_xCr_2S_4$ system allowed obtaining single-crystalline samples with the Curie temperature close to that of stoichiometric polycrystals.

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