Spin Glasses in Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$-Based Solid Solutions

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Abstract—The discovery of the phenomenon of colossal magnetoresistance in spinel Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ as one of the effects contributing to the progress in magnetoelectronics stimulated the appearance of a cycle of works on studying physical properties of this and affine materials. This survey generalizes our investigations on synthesizing and studying magnetic and crystallochemical parameters of solid solutions based on this spinel in the context of searching for novel promising magnetic semiconductor phases.

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INTRODUCTION

The development of magneto- and nanoelectronics stimulates directed search for new materials possessing a complex of promising physical, chemical, and other properties [1–10]. Chalcogenide chromites with a structure of the CuCr$_2$X$_4$ spinel type (X = S, Se) are attractive in this aspect not only owing to the high temperature of ferromagnetic ordering $T_C = 367$ (S) and 437 K (Se) but also owing to the ability to form extended regions of solid solutions both between each other and upon introducing elements of groups III–V, which provides a large variety of magnetic, electric, optical, and other characteristics [11–16].

A significant disadvantage of the aforesaid materials which restricts the possibility of practical use is their high quasi-metallic conductivity. Attempts to obtain a high-temperature magnetic semiconductor by synthesizing solid solutions MCr$_2$X$_4$–CuCr$_2$X$_4$ (M = Cd, Hg, Fe, Zn, Co; X = S, Se, Te), where one of the initial compositions is a magnetic semiconductor with Curie temperature $T_C < 200$ K and the other initial composition is a quasi-metal ferromagnet with $T_C = 367–437$ K, were not successful because most of the aforesaid solutions, even at a small concentration of copper spinel, had quasi-metal $p$-type conductivity typical of CuCr$_2$X$_4$ without a significant increase in $T_C$.

At the same time (approximately from 1967), there is known sulfide spinel Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ which is unambiguously a high-temperature ferrimagnetic $n$-type semiconductor with Curie temperature $T_C = 343$ K at the stoichiometric composition. In spite of numerous publications, it has been inadequately studied to date to a considerable extent owing to the absence of scientifically justified ways of synthesizing and to features in the structure of this compound (the presence of a considerable number of defects, ambiguity in the distribution of cations, changes in their valence upon different substitutions, structural ordering, etc.).

The situation, however, began to change radically in the last decade after discovery in Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$, as in materials of the (La,Ca)MnO$_3$ type, of the phenomenon of colossal magnetoresistance as one of the effects contributing to progress in magnetoelectronics [17–29]. The magnetoresistance effect is a relative change in electrical resistance upon switching on a magnetic field caused by different scattering for two groups of electrons differing in spin orientation with respect to the magnetization direction of the magnetic structure scattering the electrons. At present, it is supposed that novel magnetoresistive material with colossal magnetoresistance will make it possible to implement a new breakthrough in magnetoelectronics and information science by providing information counting processes in magnetic media with colossal density of magnetic recording.

This work generalizes our investigations on synthesizing and studying magnetic, crystallochemical, and other parameters of solid solutions based on Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ spinel. The investigations were dictated by the needs for novel technology in functional magnetic semiconductor materials with sufficiently high Curie points and magnetoresistive effects. Chalcogenide spinels as magnetic semiconductors possess not only a sum of useful magnetic and semiconductor properties but also the interaction of the magnetic and electron subsystems responsible for these properties. This interaction is of exchange nature and manifests itself in different cross effects providing the possibility...
of controlling the electrical and optical properties of the material by the action of the magnetic field or temperature; as for magnetization, it is controlled by the action of carriers injected by illumination or an electric field.

The aim of investigations presented in this work was to develop a scientific basis for obtaining and studying magnetic properties of chalcocromite systems of the ferrimagnet—antiferromagnet type in a wide interval of fields and temperatures, to create efficient ways of synthesizing novel high-temperature Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$-based ferrimagnetic semiconductors by controlled substitution of Zn$_{2+}$ in the A sublattice (double replacement of copper and iron simultaneously) and of In$_{3+}$ and Ga$_{3+}$ ions (ordinary replacement of Fe$_{3+}$), and to find and establish fundamental relationships of the composition—structure—electron band—property type for new magnetoeactive phases [30–47].

The first part of the survey presents results obtained in the study of conditions for synthesizing solid solutions (Cu$_{0.5}$Fe$_{0.5}$)$_{1-x}$Zn$_x$Cr$_2$S$_4$, as well as data from studying their magnetic properties, characterization, and determination of homogeneity regions. The limiting compositions here are semiconductor spinels—ferrimagnetic Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ and antiferromagnetic ZnCr$_2$S$_4$; the magnetic phase diagram of the obtained solid solution is presented. The next part of the survey presents data from studying the synthesis conditions and magnetic properties of solid solutions by tiospinels—ferrimagnetic Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ and antiferromagnetic Cu$_{0.5}$In$_{0.5}$Cr$_2$S$_4$; the magnetic phase diagram of the obtained solid solution is presented. The next part of the survey presents data from studying the synthesis conditions and magnetic properties of solid solutions by tiospinels—ferrimagnetic Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ and antiferromagnetic Cu$_{0.5}$Ga$_{0.5}$Cr$_2$S$_4$ ($T_N = 30$ K).

All the compounds (with exception of ZnCr$_2$S$_4$) and most of the solid solutions studied in this work relate to a wide class of spinel compounds of the A$_{x}$Zn$_{1-x}$Cr$_2$X$_4$ type (X = S, Se) with tetrahedral A sites occupied by equal numbers of univalent and trivalent cations. These sites form two equivalent face-centered Bravais sublattices, where each site of one sublattice is surrounded by four sites of a similar sublattice. This causes the possibility of structural ordering of such spinel by the 1:1 type.

In the studied solid solutions, the statistical replacement of paramagnetic Fe$^{3+}$ ions positioned in tetrahedral A sites of Cu$_{0.5}$Fe$_{0.5}$Cr$_2$S$_4$ spinel by diamagnetic ions of a structurally ordered diluent compound prevails. This manifests itself in the form of ferrimagnet—antiferromagnet concentration magnetic transitions observed in the experiment. The aforementioned transitions, as a rule, occur in terms of an intermediate state of spin glass. This state, according to investigators, is a good model for solving some problems in allied branches of science, e.g., optimization theory and organization of parallel computations in computer networks. In addition, spin glasses are interesting in connection with the neural network action model introduced on their basis in organizing nonlocal memory resistant to structural defects and possessing accuracy and rapidness of information processing.

**METHODS**

The synthesis was performed using powdered ZnS (extrapure grade) and S (extrapure grade), carbonyl Fe (99.99%), reduced Cu (99.99%), In (99.999%), Ga (99.999%), and Cr (99.8%) (Koch Light) as initial elements weighed in given proportions. The sample weights were poured into quartz ampoules and sealed under a vacuum of $10^{-2}$ Pa. The samples were fired in a muffle furnace. To avoid an explosion of the ampoule due to a sharp increase in sulfur vapor pressure, the temperature was first slowly (two or three days) raised to 600°C and held for a day to bind sulfur vapors in sulfides; then it was raised to the annealing temperature of 900°C and held for a week to complete the solid phase reaction. The ampoules were cooled to 600°C for two or three days and then quenched to a room temperature and opened. The completeness of the solid phase reaction was determined by X-ray phase analysis: mixed-phase samples were ground, sealed in evacuated ampoules, and annealed again by the same annealing scheme. To obtain single-phase samples, two annealing series were required.

The X-ray patterns were taken on a Rigaku/D/MAX 2500 diffractometer (Japan) with a rotatable anode and maximum X-ray tube power of 18 kW. The device parameters were as follows: Cu anode, output beam cross section 5 × 10 mm, vertical scanning from 0.7 to 145 degrees (by 2θ), plane graphite monochromator, scintillation detector, accelerating voltage of the generator of 50 kV, and tube current of 250 mA. The imaging was performed at 2θ = 20–70. The obtained spectra were compared with those from the PDF2 base. The XRPD spectra were processed using the WinXpow (STOE) program. In some cases, the diffraction patterns were taken on a DRON-1, Cu Kα radiation, Ni filter, 20 = 10–90 degrees. The accuracy in the measurements of the lattice parameter depending on the device type was 0.0006–0.005 Å.

The microscopic study was performed on a LEO SUPRA 50VP (Carl Zeiss, Germany) microscope with field emission in combination with an INCA x-sight (Oxford Inst., Great Britain) energy-dispersive X-ray microanalyzer using SE2 and InLense detectors of secondary electrons. The microphotographs were taken at an accelerating voltage of 10 kV; electron probe microanalysis (EPMA) was performed at an electron energy of 20 kV with a diaphragm of 60 μm. The spectra were taken at a spectrometer resolution of 10 eV per channel and counting rate from 2000 to 20000 pulses per second (at a constant counting rate of 6, 5, and 4). The energy resolution of the spectrometer over the $K_{\alpha}$Mn line was 129 eV at a constant counting...