1. INTRODUCTION

The magnetic semiconductor CuFeS$_2$ belongs to the group of ternary compounds of the I–III(VIII)–VI$_2$ type, which are isoelectronic analogs of II–VI$_2$-type compounds. Compounds I–III–VI$_2$ (I = Cu, Ag; III = In, Al, Ge; VI = S, Se, Te) are semiconductors with a band gap $E_g = 0.8–3.5$ eV. The replacement of atoms of Group III by a trivalent magnetic Fe atom (Group VIII) retains the crystal lattice symmetry but changes radically the band structure with the formation of an additional $d$-type conduction band in the band gap. As a result, the band structure of the magnetic semiconductor CuFeS$_2$ has a zero-gap character [1, 2]. The crystal structure of the tetragonal CuFeS$_2$ phase (α-CuFeS$_2$ phase, chalcopyrite structure) can be represented in the form of alternating metal layers separated by sulfur layers. In each metal layer with the sequential alternation of copper and iron atoms, spins of iron atoms are aligned in parallel along the $c$ axis, and these spins are arranged in an antiparallel manner in the neighboring layers, which leads to antiferromagnetic ordering of the CuFeS$_2$ crystal lattice with the Néel temperature equal to 823 K. Mössbauer investigations indicated that iron ions are in a trivalent state [3]. However, the experimental magnetic moment is $\mu_{Fe} = 3.85\mu_B$ [4], which is substantially lower than the magnetic moment $\mu_{Fe} = 5\mu_B$ that is characteristic of an isolated trivalent iron atom Fe$^{3+}(d^5)$. The decrease in the magnetic moment has been attributed to the delocalization of the Fe $d$ orbitals due to their hybridization with the S $sp$ orbitals.

At low temperatures, the magnetic properties of CuFeS$_2$ acquire an anomalous character. The magnetic susceptibility $\chi$ of polycrystalline antiferromagnetic chalcopyrite CuFeS$_2$ depends slightly on the temperature below room temperature; however, the quantity $\chi(T)$ begins to increase as the temperature decreases below $T \sim 100$ K [5]. The increase in the magnetic susceptibility at low temperatures has been attributed to the presence of magnetic inclusions; in this case, their character and content depend on the purity of the material (natural chalcopyrite) or on the conditions of its synthesis. Neutron diffraction investigations of CuFeS$_2$ revealed the magnetic phase transition at $T \sim 50$ K, which was explained by the antiferromagnetic ordering of magnetic moments of copper ($\mu_{Cu} = 0.05\mu_B$) [6]. It was found that, in the temperature range of the manifestation of magnetic anomalies, the behavior of the kinetic effects is also characterized by specific features: the power dependence of the electrical resistivity on the temperature for the most perfect samples exhibits a kink at ~50 K [1], and the magnetoresistance with a further decrease in the temperature acquires a hysteresis character [7]. Therefore, the study of the magnetic properties of the CuFeS$_2$ compound with a varying imperfection at low temperatures can provide interesting information on the nature of defects and specific features of the interaction between the electronic and magnetic subsystems.
In this work, we studied the magnetic susceptibility of polycrystalline chalcopyrite CuFeS₂, in which the anomalies of the kinetic effects were in [6]. We also measured the thermal conductivity, whose magnitude and temperature dependence at low temperatures are substantially affected by the defect crystal structure. The CuFeS₂ sample under investigation was synthesized using directional crystallization according to the technique described in [8] and had a chalcopyrite structure according to X-ray diffraction data. As was revealed in our earlier work [1], the electrical properties of this material depend not only on the high-temperature annealing that ends the synthesis process but also on the low-temperature annealing, namely, long-term storage of the material at room temperature. In the present work, we studied the as-prepared samples that were not subjected to low-temperature annealing.

The magnetic properties were measured by the vibration method. The thermal conductivity was measured by the steady-state heat flow method.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of the magnetic moment $M$ of the sample. The magnetic moment was measured by two regimes. In the first regime (curve 1 in Fig. 1), the residual magnetization was measured after a preliminary action of a magnetic field $H = 5.25$ kOe on the sample in the temperature range points measured during gradual cooling of the sample. In the second regime (curve 2 in Fig. 1), the $M(T)$ dependence was measured under the single action of the magnetic field $H = 22.5$ kOe on the sample at $T = 4.2$ K with subsequent measurement of $M$ during heating of the sample. As is seen below $T = 130$ K, the magnetic moment increases and begins to show a tendency to saturation only at the least temperatures. The $M(T)$ curve shapes, their dependences on the magnetic prehistory, and also the hysteresis dependence of the magnetization on magnetic field observed at $T < 30$ K in the sample under study are characteristic of a system of ferromagnetic clusters whose formation is likely due to a phase inhomogeneity of the crystal chalcopyrite.

The study of the structural properties of the chalcopyrite shows that its structure is dependent on the technology of preparing the material [8]. The crystal structure of CuFeS₂ has three modifications: the cubic $\beta$ phase ($a_0 = 5.328$ Å) having the sphalerite structure and two tetragonal phases with different sizes of the tetragonal cells, i.e., the basic $\alpha$ phase (or “chalcopyrite structure”) ($a_0 = 5.292$ Å, $c_0 = 10.407$ Å) characteristic of stoichiometric compositions and the $\gamma$ phase ($a_0 = 10.598$ Å, $c_0 = 5.380$ Å). The $\alpha$ phase is characterized by an ordered alternating of Fe and Cu atoms in the metal cation sublattice and a small tetragonal contraction, while in the cubic $\beta$ phase identical in composition to the $\alpha$ phase, Fe and Cu atoms are randomly arranged in sites of the metal sublattice. As the temperature increases above 830 K, the $\alpha$ phase decomposes into $\beta$ phase and pyrite FeS₂. As sulfur is scarce, vacancies do not form in its sublattice. Metal ions in excess with respect to sulfur are arranged in interstitial sites. Moreover, in such compositions, the cubic $\beta$ phase is stabilized at room temperature and, as the temperature increases above 230°C, the $\beta$ phase is transformed to the tetragonal $\gamma$ phase. Various growth defects and impurities in the real crystals can initiate formation of additional phases even in perfect compositions. The study of the neutron diffraction spectra of stoichiometric CuFeS₂ shows the presence, along with the basic $\alpha$ phase, of small contents of additional phases, namely, the face-centered cubic phase ($a_0 = 5.415$ Å) that corresponds to the pyrite parameters and an unknown cubic phase ($a_0 = 7.99$ Å) whose diffraction peaks are well marked only at low temperatures ($T < 45$ K) [6]. The as-prepared chalcopyrite sample studied in this work contains likely an impurity of the $\beta$ phase with the sphalerite structure which is characterized by disordered arrangement of atoms in the metal sublattice. One iron atom, intersecting the position with a neighboring copper atom, leads to formation of a cluster of five neighboring iron atoms in the ferromagnetic metal layer. As the disorder increases, the iron clusters can increase. The existence of other phases and also interstitial Fe atoms can favor the formation of iron clusters in which ferromagnetic ordering can be manifested. Inclusions of paramagnetic pyrite (FeS₂) must not markedly influence the