Advanced Physical Research
Vol.5, No.1, 2023, pp.19-25

CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF THE COMPOUND $Cu_3Fe_{0.5}Se_2$

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Abstract. The crystal structure of the compound $Cu_3Fe_{0.5}Se_2$ was studied by XRD and the formation of a new phase crystallizing in an orthorhombic lattice was found. The crystallographic parameters were determined from the analysis of the diffraction spectrum: a = 7.982 Å, b = 7.823 Å, c = 13.331 Å, V = 831.08 Å^3, ρ = 6.17 g/cm^3, Z = 4. The magnetic susceptibility of the samples was studied in the range temperatures 80 K ≤ T ≤ 400 K and in a magnetic field H = 2 T. It has been established that at low temperatures the $Cu_3Fe_{0.5}Se_2$ compound has quasi-one-dimensional antiferromagnetic properties. The magnetic phase transition occurred at the Neel temperature T_N = 350 K.

Keywords: *Crystal structure, R-ray diffraction, $Cu_3Fe_{0.5}Se_2$, phase transition, Neel temperature, magnetic susceptibility.*

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***Received:** 18 January 2023; **Accepted:** 14 February 2023; **Published:** 3 April 2023.*

1. Introduction

There is a great demand for advanced materials containing 3***d*** and 4***f*** elements for modern electronic technology. The vast majority of compounds of this type have semiconductor properties and, depending on the order in which the 3***d*** and 4***f*** levels are filled, also have magnetic and ferroelectric properties (Bayramova *et al.*, 2022; Aliyev *et al.*, 2019; Kozlenko *et al.*, 2014; Agayev *et al.*, 2020; Alimirzayeva, 2022; Zulfigarov *et al.*, 2019). It is known that, depending on the electronic and crystal structure, various physical properties can form in crystals. Therefore, compounds with new functions are synthesized by cation-cation, anion-anion substitutions (Ordin, 2018; Asadov *et al.*, 2017). Recently, interest has increased in magnetic semiconductor compounds based on chemical and structural analogues of chalcopyrite with Se and Te. In the course of research carried out in this direction, the production technology, crystal structure and magnetic properties of $CuFeSe_2$ were studied in detail (Lamazares *et al.*, 1992). In the $CuFeS_2$ and $Cu(Ga,In)_{1-}$

How to cite (APA): Agamirzayeva, G.M., Huseynov, G.G., Aliyev, Y.I., Abdullayeva, T.T., & Novruzov, R.F. (2023). Crystal structure and magnetic properties of the compound $Cu_3Fe_{0.5}Se_2$. *Advanced Physical Research, 5*(1), 19-25.

$_x$Fe$_x$Se$_2$ systems, the process of phase formation was studied by X-ray diffraction analysis, its crystal structure was studied, and the magnetic susceptibility was studied. It has been established that the $CuFeSe_2$ crystal has a weak magnetic property, its crystal structure differs from chalcopyrite, but the electrical conductivity mechanism corresponds to a metallic character. It is shown that Cu and Fe atoms are distributed in states (0 0 0), (0 1/2 0) in the coordinate system of the space group (lattice constants: a = 5.53 Å, c = 11.05 Å), as a result, metal-metal bond in the structure (Lamazares *et al.*, 1992). As a result of structural studies, it was found that metal atoms in the crystal structure of $CuFeSe_2$ can be located in two different configurations (Table 1).

Table 1. Coordinates of metal atoms in the crystal structure of $CuFeSe_2$

I option	Cu (1)	2(*a*)	0, 0, 1/4
	Cu (2)	2(*e*)	0, 0, 0
	Fe	4(*m*)	0, 1/2, 0
II option	Fe (1)	2(*a*)	0, 0, 1/4
	Fe (2)	2(*e*)	0, 0, 0
	Cu	4(*m*)	0, 1/2, 0

Both structures correspond to the P-4c2 tetragonal symmetry corresponding to the same space group and therefore do not differ much from each other. For the completeness of the results obtained in the study of the crystal structure of the samples, it is important to analyze the chemical composition. Therefore, chemical elemental analysis of polycrystalline $CuFeSe_2$ samples obtained from the gas phase was also carried out (Najafov *et al.*, 2003).

The presence of a number of unique properties observed in chalcopyrite ($CuFeS_2$) has led to increased attention to chalcopyrite analogues. Various physical properties of the $CuFeSe_2$ compound were also studied. The process of synthesis of the $CuFeSe_2$ crystal by various methods, the preparation of single crystals, electrophysical properties, valence states of Fe atoms by the Mössbauer and neutron diffraction methods, magnetic properties, issues of spin wave density have been studied (Woolley *et al.*, 1996; Viswanatha & Chitra Chetty, 1996; Gonzales-Jimenes *et al.*, 1999; Lu *et al.*, 2000; Mamedov *et al.*, 2021). However, during these studies, a number of inconsistencies were found. Thus, the Fe atoms in the $CuFeSe_2$ crystal turned out to be trivalent. But the value of the magnetic moment μ = 1.75 μB was determined, which does not correspond to the trivalent state of iron atoms.

Apparently, many issues have not been resolved according to the study of the structure and magnetic properties in the Cu-Fe-Se system. In this work, $Cu_3Fe_{0.5}Se_2$ single crystals were synthesized by partially replacing Cu atoms with Fe atoms, and their structural properties and magnetic susceptibility were studied.

2. Experimental part

The synthesis of the $CuFeSe_2$ compound was carried out according to the standard procedure for obtaining chalcogenide semiconductors (Jabarov *et al.*, 2022; Tagiyev *et al.*, 2015). A single crystal was grown from the obtained polycrystals by the Bridgman method. However, the process is not completed. Because the synthesis of chalcogenides must be carried out under vacuum. During the experiments, the ampoule was broken at a

temperature of $T \sim 870$ K during cooling. To overcome this difficulty, a double ampoule system was used. At the end of the process, the ampoule was removed from the oven. It was found that part of the 5-gram mass spilled out of the cracked first ampoule and overflowed into the second ampoule. But it was obtained in the form of a single crystal. The image of the obtained single crystals is shown in Fig. 1.

Fig. 1. General view of $Cu_3Fe_{0.5}Se_2$ single crystals (×4)

From the general approach to the crystallization process, it is known that decomposition occurs at a temperature of about $T = 870$ K during crystallization from an alloy, as well as during gas-phase crystallization. As a result, part of the taken mass is sublimated in the form of gas and accumulates in the empty part of the ampoule, as a result of which the ampoule cracks, and the gaseous sublimation splits the ampoule and exits the system.

The crystal structure of the $CuFeSe_2$ compound was studied by X-ray diffraction. The studies were performed on a D8 Advance diffractometer (Bruker, CuKα radiation, Ni filter). The obtained spectra were analyzed and the crystallographic parameters were determined.

The magnetic susceptibility of $Cu_3Fe_{0.5}Se_2$ single crystals was studied on a SQUID magnetometer at low temperatures ($T = 80$-400 K) in a magnetic field $H = 2$ T. The sample for the study was taken $m = 15.3$ mg.

3. Results and discussion

3.1. Study of the structure of the $CuFeSe_2$ compound

From the type of $CuFeSe_2$ compound shown in Fig. 1, it can be seen that the samples were synthesized in a single crystal form. To determine the crystal structure of the sample, it was crushed and examined on a D8 Advance diffractometer. The spectrum obtained in the range $10° \leq 2\theta \leq 85°$ under normal and room conditions is shown in Fig. 2. From the spectrum shown in Fig. 2, it can be seen that 20 diffraction maxima were observed in this range of diffraction angles. The parameters of these maxima: Miller indices, diffraction angle, d-interatomic distances, and relative intensity are given in Table 2. As a result of the spectrum analysis, the crystallographic parameters of the $Cu_3Fe_{0.5}Se_2$ compound were determined based on the values given in Table 2.

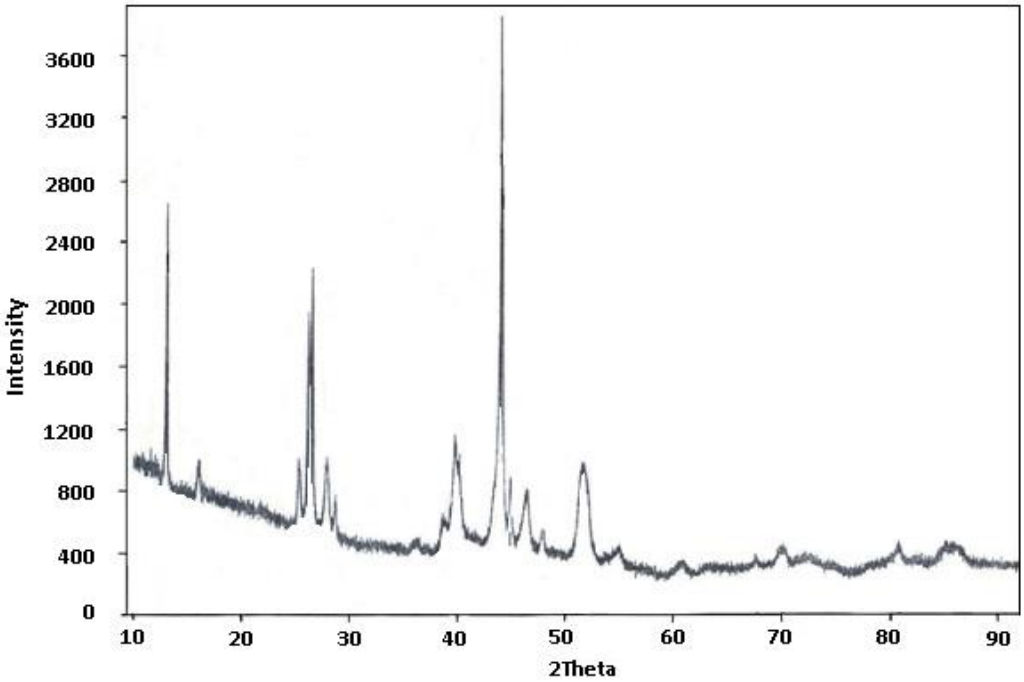

Fig. 2. X-ray diffraction spectrum of a $Cu_3Fe_{0.5}Se_2$ crystal at room temperature

Table 2. Parameters of the X-ray spectrum of the $Cu_3Fe_{0.5}Se_2$ crystal

2θ	I/I_0	d	hkl
13.24º	70	6.6671	0 0 2
16.08º	6	5.4960	1 1 0
25.48º	14	3.48517	1 1 3
26.20º	51	3.4262	0 2 2
26.60º	58	3.419	2 0 2
27.90º	16	3.1868	1 0 4
28.80º	6	3.0997	0 1 4
36.30º	5	2.4948	1 2 4
38.36º	6	2.3438	2 2 3
39.32º	21	2.3240	0 3 3
44.07º	100	2.0779	0 3 4
45.00º	14	2.0143	4 0 0
46.48º	14	1.9491	0 4 0
47.90º	6	1.8955	0 4 2
51.88º	26	1.7584	2 4 1
54.85º	4	1.6696	0 0 8, 4 0 4
60.80^0	4	1.5235	2 0 8
68.15^0	3	1.3665	2 1 9
70.30º	4	1.3334	0 0 10, 0 6 0
81.07º	4	1.1845	0 3 10, 1 3 10

It was found that the crystal structure of this compound corresponds to the orthorhombic syngony with the space group Pnma. The crystallographic parameters are: a = 7.982 Å, b = 7.823 Å, c = 13.331 Å, V = 831.08 Å^3, ρ = 6.17 g/cm^3, Z = 4. As can be

seen, Fe atoms can replace Cu atoms in elementary lattice. Therefore, the $Cu_3Fe_{0.5}Se_2$ compound can crystallize in a single-phase state. Otherwise, a two-phase solid solution consisting of Cu_2Se and FeSe compounds would be obtained.

3.2. Study of the magnetic properties of $CuFeSe_2$

When studying the crystal structure of the $Cu_3Fe_{0.5}Se_2$ compound, it was found that this compound crystallizes into one phase in the orthorhombic system. It is known that the high symmetry of the crystal structure leads to the formation of a long-range magnetic order. Therefore, it is important to study the magnetic properties of the $Cu_3Fe_{0.5}Se_2$ compound. For this purpose, the magnetic susceptibility of $Cu_3Fe_{0.5}Se_2$ single crystals was studied. It is known that magnetic properties are mainly observed at low temperatures. Therefore, studies were carried out on a SQUID magnetometer in a magnetic field H = 2 T in the temperature range T = 80-400 K. The temperature dependence of the magnetic susceptibility of the crystal is shown in Fig. 3.

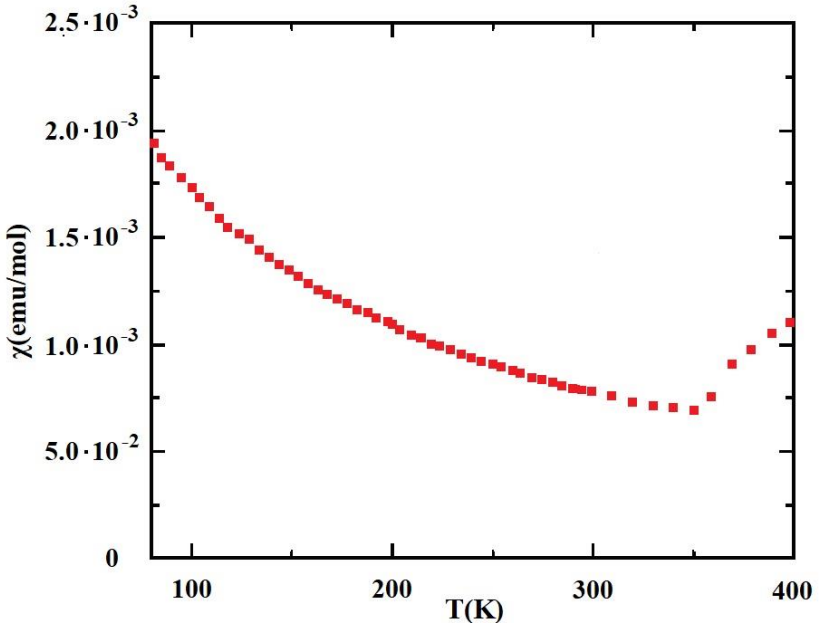

Fig. 3. Temperature dependence of the magnetic susceptibility of a $Cu_3Fe_{0.5}Se_2$ single crystal at low temperatures

When studying the magnetic properties, it was found that the temperature dependence of the magnetic susceptibility of Cu3Fe0.5Se2 single crystals practically corresponds to the characteristic characteristic of quasi-one-dimensional antiferromagnets. As can be seen from the temperature dependence of the magnetic susceptibility, the antiferromagnetic-paramagnetic phase transition occurs at the Neel temperature TN = 350 K. It is known that with increasing temperature, the amplitude of the lattice vibrations of atoms that form the crystal structure increases, and therefore the long-range magnetic regularity is violated. For this reason, antiferromagnetic properties were not observed in the Cu3Fe0.5Se2 single crystal at high temperatures.

4. Conclusions

The compound $Cu_3Fe_{0.5}Se_2$ was synthesized by partial cation-cation substitution of Cu atoms by Fe atoms, and a single crystal was grown by the Bridgman method. The structure of the resulting crystal was studied and its crystallographic parameters were determined. The crystal structure of this compound was found to have orthorhombic symmetry (space group: Pnma). The magnetic susceptibility of the samples was studied in the temperature range 80 K $\leq T \leq$ 400 K and in magnetic fields H = 2 T. It has been established that the $Cu_3Fe_{0.5}Se_2$ compound has antiferromagnetic properties at low temperatures. The antiferromagnetic-paramagnetic phase transition occurred at the Neel temperature T_N = 350 K. This process is explained by the violation of magnetic regularity in the far zone due to thermal fluctuations at high temperatures.

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