The distribution of the electron density and spin density in the interplanar areas CuFeS$_2$ by NMR ^{63,65}Cu in a local field

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Abstract. Chalcopyrite CuFeS$_2$ is a known semiconductor mineral with a wide range of unique physical and chemical properties. These materials can be used as elements of solar batteries, coherent and incoherent sources of polarized radiation, in photovoltaic, thermoelectric and spintronic devices. Despite the relatively large number of studies on CuFeS$_2$, many questions about its magnetic and electronic properties, are still outstanding. In this paper we were carried out studies of the distribution of the electron density and spin density in the nuclei of iron and copper in the semiconductor mineral CuFeS$_2$. Special attention was devoted to interrelation of electronic and spin subsystems of the compound. The results of studies of the compound obtained in NMR ^{63,65}Cu local field at low temperatures were used to perform the corresponding analysis. The cluster approach was used. The biggest cluster had Cu$_9$Fe$_{10}$S$_{28}^{-4}$ formula. Calculations were carried out in the framework of restricted self-consistent Hartree - Fock with open shells (SCF-LCAO-ROHF), MINI basis. The calculations were made with the "foundation" on the quadrupole parameters (quadrupole ν_Q frequency and the asymmetry parameter of the electric field gradient tensor η), obtained from the experiment. Study of electron density maps were performed for the regions containing chains of Fe-S-Cu and S-Fe-S for the different layers of metals and sulfur atoms. It is shown that the nature of the connection of iron atoms belonging to neighboring layers with sulfur atoms of the intermediate layer is different, which is reflected on the electron density distribution.

1 Introduction

Chalcopyrite CuFeS$_2$ belongs to the class of magnetic semiconductors that allow, by varying their chemical composition and structure, to obtain materials with a wide range of physical characteristics, such as band gap, type of conductivity, specific electrical conductivity, etc. These materials can be used as solar cells, coherent and incoherent sources of polarized radiation, in photovoltaic, thermoelectric and spintronic devices [1-7]. Thin films [8], nanowires and spherical particles [9, 10], and nanocrystals [11-13] were synthesized. The crystal structure of CuFeS$_2$ is tetragonal with parameters **a** = 5.29 Å and **c** = 10.41 Å [14-17], space group I42d [18]. The metal atoms Cu and Fe are arranged in tetrahedra with four adjacent sulfur ions. Layers of cations consisting of alternating Fe and Cu atoms are separated by layers of S atoms. In each metal layer, with the successive alternation of copper and iron atoms, the spins of iron atoms are located parallel along the c axis, and in neighboring layers — antiparallel, which leads to an antiferromagnetic ordering of the CuFeS2 crystal lattice with a Neel temperature of 823 K[14, 15]. At low temperatures, the magnetic properties of chalcopyrite exhibit an anomalous character. In particular, the magnetic moment takes on a hysteresis form and depends on the magnetic history of the sample [19]. This compound has a wide band gap distribution from 3.5 to

0.6 eV [20] and depends on the particle size [11]. It is assumed that at least two ionic compounds are possible in chalcopyrite. When studying the electrical properties of CuFeS2 samples, it was found that all of them can have both electronic and hole-type conductivity, and the concentration of charge carriers can vary widely [7,15]. Thus, despite the relatively large number of papers devoted to the study of CuFeS2, many questions concerning its magnetic and electronic properties still remain unclear. The aim of this work is to study the CuFeS$_2$ semiconductor mineral by the ^{63,65}Cu NMR method in a local field at low temperatures to obtain information about the features of the interaction of the electron and spin subsystems of this compound.

2 Experiment

The resonance spectra on ^{63,65}Cu nuclei in chalcopyrite samples were previously studied in the temperature range of 77-300 K [23,24]. Their complex structure was revealed due to the existence of an internal magnetic field caused by the presence of a magnetic iron Fe atom in their composition. Finally, it was found that the observed spectrum is the NMR spectrum in the internal magnetic field. In this case, the complete nuclear spin Hamiltonian with a quadrupole moment can be represented as:

$$\hat{H} = \hat{H}_m + \hat{H}_q, \qquad (1)$$

where $\hat{H}_m$ is the magnetic interaction Hamiltonian, $\hat{H}_q$ is the quadrupole interaction Hamiltonian. If $\hat{H}_m >> \hat{H}_q$, then already in the first approximation of the perturbation theory, the NMR spectrum is a triplet with a central line, the frequency of which is determined by the Larmor precession in the magnetic field, and two (for spin J=3/2) equally spaced satellites, which is observed in the experimental spectra (figure 1). The obtained quadrupole parameters (quadrupole frequency $v_Q \sim 1.29$ MHz and the asymmetry parameter $\eta \sim 0.34$) were used by us to analyze the distribution of electron and spin densities in the region of the quadrupole core of copper. The cluster approach was used. A series of ab initio calculations for finding the cluster charge was performed using the self-consistent restricted Hartree-Fock method with open shells (SCF-LCAO-ROHF, FIREFLY program[25]). The frequency values were obtained taking into account the value of the nuclear quadrupole moment of copper $Q(^{63}Cu) = -0.211$ b [26,27]. Good agreement with the experiment was observed for the $Cu_9Fe_{10}S_{28}^n$ cluster at n= -4: $v_Q \sim 1.40$ MHz and $\eta \sim 0.50$, so the analysis of the electron distribution features was carried out within the framework of R. Bader's theory [28] for the $Cu_9Fe_{10}S_{28}^{-4}$ system (Figure 2).

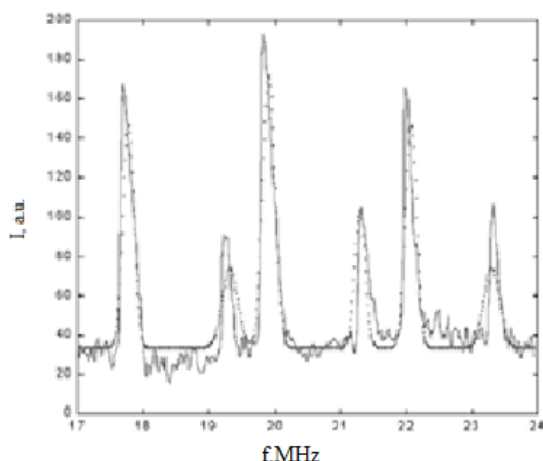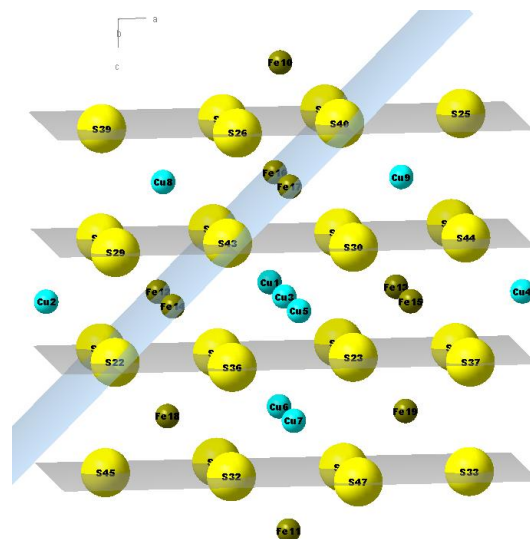**Fig. 1.** NMR $^{63,65}Cu$ in $CuFeS_2$ at 77K (solid line - experiment, dashed line - numerical modeling).

Fig. 2. A cluster of 47 atoms $Cu_9Fe_{10}S_{28}^n$ (chalcopyrite) within a radius of R ~ 5.9Å by Cu atom resonance.

3 Results and discussion

Figure 3 and Figure 4 show the electron density distribution maps for the Fe14-S43-Cu3 and Fe17-S43-Cu3 chains, respectively. Here are the lines connecting the atoms of the communication line, the blue dots on the lines of communication – a critical point of (3,-1), blue line passing through the points (3,-1) – base line (the line of zero flow gradient of the electron density), which separates the basins of the atoms. As can be seen from the above figures, the Fe-S bond in these chains is of a different nature. Thus, the Fe14-S43 bond is characterized by a closed behavior of electron density lines – it is localized in the region of its core, respectively, the nature of this bond is close to the ionic one. At the same time, the Fe17-S43 pair has a total electron density of 0.08 e/A^3, i.e. it is not localized and is close to the covalent bond type.
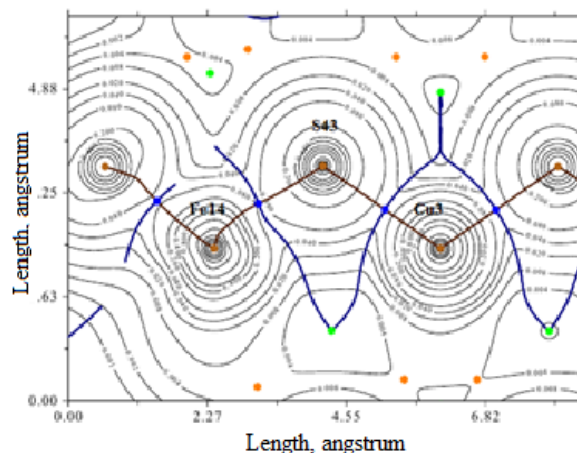

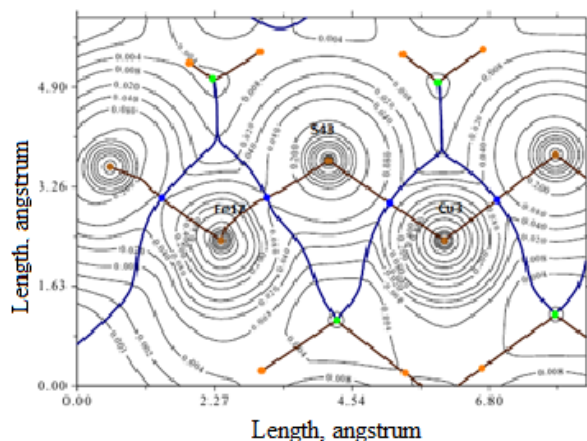**Fig. 3.** Electron density map for the area Fe14-S43-Cu3.

Fig. 4. Electron density map for the area Fe17-S43-Cu3.

Spin density studies were also carried out for the considered regions (Fig. 5,6). For the Fe14-S43-Cu3 region, the spin density distribution is relatively local, especially in the region of the Fe14 atom. The spin density for the Fe17-S43-Cu3 region is noticeably delocalized in the Fe17 atom region. Moreover, we can talk about different spin density polarizations in the region of copper atoms for the Fe14-S43-Cu3 and Fe17-S43-Cu3 regions.
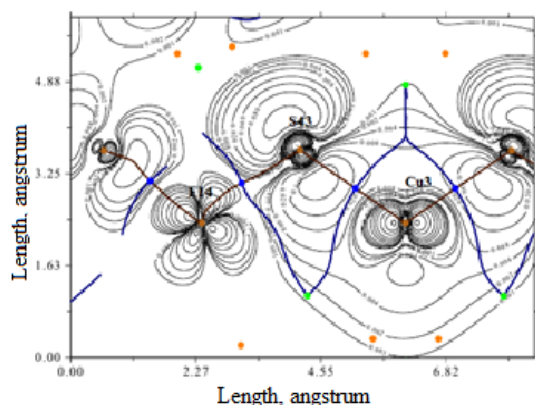

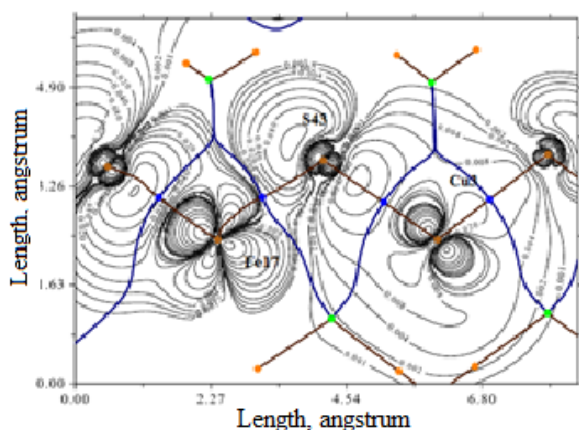**Fig. 5.** The distribution of spin density map for the area Fe14-S43-Cu3.

Fig. 6. The distribution of spin density map for the area Fe17-S43-Cu3.

Thus, based on the calculations carried out, it can be assumed that in neighboring metal layers (with the opposite direction of the magnetic moments), the nature of the Fe-S bond is different, which can lead, in particular, to a change in the valence states of the Fe and Cu atoms.

Electron density distribution maps were also studied in planes where each iron atom is associated with two sulfur atoms: S22-Fe14-S43 and S43-Fe17-S40. It was found that the nature of the connection, these chains are markedly different. In particular, for the Fe14-S43 pair, the electron density is concentrated mainly in the region of the pool of its atom and we can talk about a bond with a noticeable ionic component, while the S22-Fe14 bond has a noticeable covalent component – the total electron density isoline at 0.08 e/A3. For the S43-Fe17-S40 chain, the electron density isoline at 0.08 e / A3 is common to all three atoms of the chain, and it can be assumed that there is a three-center bond with an electron deficit.

4 Conclusion

1. Analysis of the obtained electron density distribution in the region of the quadrupole core of copper (Cu-S bond) suggests that this bond in chalcopyrite is not covalent, but is formed mainly by the type of interaction of closed shells. Despite the use of the cluster approach, the energy level diagram defines chalcopyrite quite well as a semiconductor with a very narrow LUMO-HOMO gap ($\Delta \sim 0.133$ eV)and quite admits the idea of chalcopyrite as a gapless semiconductor.

2. Even without taking into account any magnetic ordering, the nature of the bond of iron atoms belonging to neighboring layers with sulfur atoms from the intermediate layer is different, which is reflected in the distribution of the electron density.

3. The nature of the bond in the Fe-S-Cu planes, when the iron atoms belong to neighboring layers, also differs markedly. In this case, both the distribution of the electron density and the distribution of the spin density in the region of the atoms under consideration change markedly. In this case, certain prerequisites are created for the manifestation of various valence states of Fe and Cu.

4. Under certain assumptions, all the bonds considered in this paper belong to an intermediate type with an appropriate degree of covalence. The possibility of the formation of a three-center bond in S-Fe-S chains in chalcopyrite, which we discovered, is not considered in R. Bader's theory, and further research in this area is needed.

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