

MAGNETIC INTERACTION OF "EXCESS" CATIONS Cu^{+2} AND Fe^{+2} IN THE 2D-PLANE IN A SINGLE CRYSTAL $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$

A.I. JABBAROV

*Institute of Physics of NAS,
131, H. Javid ave. Baku, AZ 1143
E-mail: ayd.jabb @ list.ru*

This paper presents the results of measurements of the temperature dependence of the magnetic susceptibility and magnetization (in a magnetic field up to $H=50\text{kOe}$) of single crystals of the non-stoichiometric chalcopyrite type $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ ($\sim\text{Cu}_{1.13}\text{Fe}_{1.22}\text{Te}_2$) in the temperature range $2\leq T\leq 400\text{K}$. The measurement results indicate the presence of "clusters" ($\text{Cu}-\text{Te}-\text{Fe}=\text{Te}$) of an antiferromagnetic nature of the interaction, as well as "excess" of Cu^{+2} and Fe^{+2} cations in the 2D plane behaving like nanoparticles. The effective magnetic moment of iron atoms $M_{\text{eff}}>1.3\mu\text{B}$ at $H\leq 1000\text{Oe}$ and at $1.0\leq H\leq 50\text{kOe}$ $M_{\text{eff}}>2.0\mu\text{B}$.

In the isotherms of magnetization (hysteresis) $M(H)$ at temperatures of 2, 4, 100 and 300K, residual magnetizations are observed, which are associated with frustration of magnetic interactions during the formation of a disordered magnetic structure of iron and copper. Antiferromagnetically located "clusters" at $T_N=65\text{K}$ transform into a paramagnetic state, which coincides with the spin-glass state at $T_g=65\text{K}$ (T_g is the freezing temperature). These results are in good agreement with the Mossbauer spectra of CuFeTe_2 .

Keywords: magnetic susceptibility, frustration, spin-glass state, magnetization isotherm.

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1. INTRODUCTION

The strong temperature dependence of the isomeric shift of excess iron [1, 2], which appears as an intermediate hyperfine field, is an indicator that the electron density between Fe-Te (*CFT*, Fe_{1+x}Te) layers evolves significantly with increasing temperature of the two-dimensional nature of the material at low temperatures.

The embedded iron has a relatively large localized magnetic moment, at least for the region with the highest hyperfine field. These moments are almost randomly distributed over the interstitial sites of the sub lattice. Therefore, they strongly interact with electrons capable of forming Cooper pairs and preventing the onset of superconductivity. To obtain a superconducting material, it is necessary to remove this iron from the interstitial regions [1, 2].

Like the *HTSC* families of cuprites and ferropnictides, the terminal compound *CFT* and Fe_{1+y}Te is magnetically ordered and undergoes structural distortion, which lowers the high-temperature tetragonal symmetry of the lattice. The physics of these low-temperature phases and their relationship with superconductivity is of great interest and has been the subject of intense research [1, 2-7]. Two general trends in phase diagrams were established:

(1) if there is no first-order magneto structural transition, then the lattice distortion usually occurs at higher temperatures (T_S -structural transition) than magnetic ordering (T_N), T_S , or T_N and

(2) both T_S and T_N decrease with chemical substitution, so that both kinds tend to disappear as the superconducting state develops.

While this observation suggests an inextricable relationship between magnetic ordering, lattice distortion and superconductivity [1, 2]. Further studies of Fe-containing chalcogenide compounds are of interest. In this work, we present the results of magnetic

studies carried out to determine the magnetic state of a compound of nonstoichiometric chalcopyrite of the $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ (*CFT*) type and "excess" of Cu^{+2} and Fe^{+2} cations in the 2D plane.

Note that a lot of works [2-14, 16, 18] are devoted to growing single crystals, studying the crystal structure, and measuring magnetic, electrical and other physical characteristics of nonstoichiometric chalcopyrite type CuFeTe_2 .

The above compounds are characterized by the presence of different positions of magnetic ions, which introduces disorder into their magnetic subsystem and, as a consequence, leads to frustration of magnetic interactions during the formation of a disordered magnetic structure. And the excess of Cu^{+2} and Fe^{+2} atoms are located in the $2c$ 'position with coordinates (0, 0, 0.715) and (0, 0.5, 0.715), respectively [4]. The valence of cations at this position significantly affects the type of phase transitions (magnetic, spin-glass, and structural).

Polycrystals $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ were synthesized by alloying initial high-purity elements (Cu, Fe, Te) in quartz ampoules evacuated to 10^{-3}Pa , and their single crystals were grown by the Bridgman-Stockbarger method [4, 5, 14, 16]. The studied *CFT* single crystals crystallize in a tetragonal system with cell periods: $a=3.97$; $c=6.11\text{\AA}$, $v=96.2991\text{\AA}^3$, $\rho_{\text{prent}}=6.63\text{g/cm}^3$, etc. $P4/nmm$, $z=1$, which is in full agreement with the data [7].

2. EXPERIMENT

We have studied the crystal structure and magnetic properties of $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ (*CFT*) single crystals grown by the modified Bridgman method. Single crystals grown from a melt are structural with Rikkardit - $\text{Cu}_{4-x}\text{Te}_2$ [15], with the only difference that in the sub tetragonal structure $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ (*CFT*) both Cu and Fe metal atoms are

statically distributed in double crystallographic positions. Copper atoms are coordinated with $4\text{Fe}+4\text{Te}$, forming a tetragonal prism. $4\text{Cu}+\text{Fe}+\text{Te}$ form a polyhedron in the form of empty octahedral (fig. 1).

Taking into account that the minerals Cuprostitbit $-\text{Cu}_2(\text{Sb}, \text{Te})$ and Rikkardit $-\text{Cu}_{2-x}\text{Te}$ [15] have similar unit cell parameters and such symmetries, it can be assumed that the crystallization of CuFeTe_2 changes the valence of metals due to the lack of a part tellurium atoms (Te) and a composition with an excess of metal atoms is formed. This compound is converted to a tetragonal structure by CFT compounds. It was found that the Cu and Fe ions occupy a double position $2a: (0, 0, 0)$, and two Te atoms are located in the $2c$ position with coordinates $(0, 0.5, 0.28)$. And the excess of Cu and Fe atoms are located in the $2c'$ position with coordinates $(0, 0, 0.715)$ and $(0, 0.5, 0.715)$, respectively [2, 6]. It was shown in [4, 18] that copper atoms are surrounded by eight ($4\text{Te}+4\text{Fe}$) atoms in the form of a tetragonal prism. Each such prismatic layer is located at a distance of $\sim 3.0\text{\AA}$ from the next analogous layers, which gives the structure a layered character and perfect cleavage. In other words, prismatic copper layers alternate parallel to the (001) plane of the crystal with empty prismatic layers. The chemical bond is found according to the scheme $\text{Cu}^+-\text{Te}^{2-}-\text{Fe}^{3+}=\text{Te}^{2-}$ as a "cluster", and the excess of 15% of Cu and Fe ions are randomly located in the voids of the lattice (Fig.1). It is known that a magnetic cluster exhibits fractal properties with increasing temperature. The presence of nonmagnetic tellurium atoms in the system leads to loosening of the structure of the magnetic cluster (see fig.1).

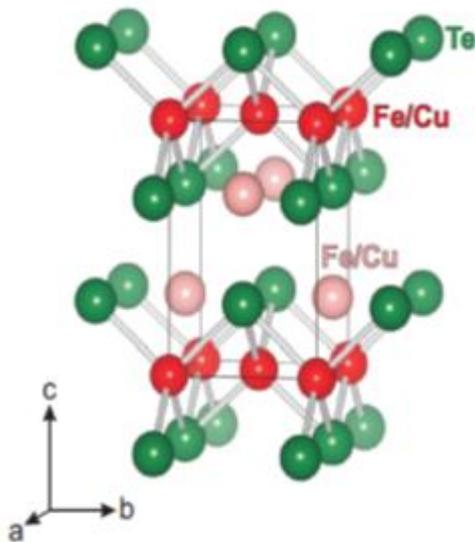


Fig. 1. Crystal structure CuFeTe_2

3. MAGNETIC SENSITIVITY. METHODS FOR MEASURING MAGNETIC PROPERTIES

The magnetic properties of the samples were studied using an MPMS-XL-5 SQUID magnetometer

(MPMS-Magnetic Property Measurement System) from Quantum Design, the absolute sensitivity of which is $\pm 1 \cdot 10^{-11} \text{G} \cdot \text{cm}^3$ at $0 \text{ Ge} \leq H \leq 10 \text{ kOe}$ and $\pm 5 \cdot 10^{-11} \text{G} \cdot \text{cm}^3$ at $10 \text{ kOe} < H \leq 50 \text{ kOe}$.

When studying magnets in a metastable state, methods of measuring the susceptibility are usually used when cooling without an external magnetic field (ZFC-zero field cooling) and during cooling in an external magnetic field (FC - field cooling) [16].

The magnetic susceptibility was measured in the temperature range $2-400\text{K}$ and the range of magnetic fields H up to 50kOe . To study the temperature dependence of the magnetic susceptibility, the samples were cooled in zero magnetic field (ZFC) to 2K . Then a magnetic field (FC) with a strength of 1000 Oe was turned on; this magnetic field was kept constant. Magnetic susceptibility was measured during temperature rise (ZFC). At the next stage, the samples were cooled again, but already at the value of the magnetic field set at the previous stage, while taking readings (FC). These measurements were repeated at magnetic field strengths of 10 and 20kOe . The field dependences of magnetization (hysteresis) were measured at temperatures of $2, 4, 100$ and 400K in magnetic fields up to 50kOe .

4. EXPERIMENTAL RESULTS

The temperature dependences of the magnetic susceptibility (χ) (1) and its inverse value ($1/\chi$) (2) in a magnetic field $H=1.0\text{kOe}$ for single crystals parallel to the plane (001) $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ in the temperature range $2-400\text{K}$ are shown in fig.2.

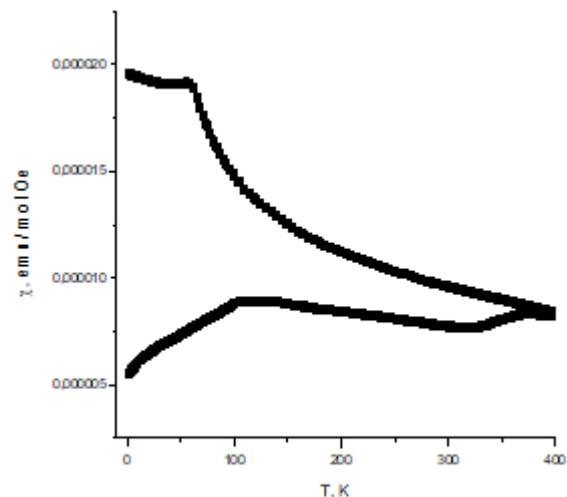


Fig. 2. Magnetic susceptibility of a CFT single crystal in χ ZFC and χ FC modes. The magnetic field $H=1000 \text{ Oe}$ is applied parallel to the plane (001) .

Antiferromagnetically located "clusters" at $T_N=65\text{K}$ are transformed into a paramagnetic state. In the temperature dependence of the magnetic susceptibility $\chi(T)$ below $T_g=65\text{K}$, splitting is observed for the ZFC and FC regimes as in the spin-glass state. In spin glasses below a certain temperature T_g , the spin-glass state (freezing point), a thermodynamic nonequilibrium metastable magnetic state arises,

characterized by a "frozen" spatial random distribution of the orientation of the spin magnetic moments. As can be seen from fig. 2, the course of the temperature dependences of the susceptibility in a weak magnetic field ($H=1.0\text{kOe}$) reveals a divergence of the ZFC-FC curves in the temperature range of 65-350K. These discrepancies in the temperature dependences $\chi(T)$ and $1/\chi(T)$ for ZFC and FC($H=1.0\text{kOe}$) and determination of the irreversibility temperature T_B for CFT single crystals $T_B=360\text{K}$ into the blocked state are characteristic of super paramagnets. The different behavior of the $\chi(T)$ ZFC and $\chi(T)$ FC dependences upon cooling below the blocking temperature ($T \leq T_B$) is one of the main signs that testify in favor of such a transition. To determine the magnetic characteristics of CFT single crystals in the temperature range above T_B , the temperature dependences of the inverse paramagnetic susceptibility $1/\chi(T)$ were plotted in strong fields (up to $H=20\text{kOe}$). As seen from fig. 3, the $\chi(T)$ curves have a maximum at $T_N=T_g=65\text{K}$. Spin-glass state, which is very sensitive to the magnitude of the magnetic field (the highest magnitude of the susceptibility is observed in the smallest magnetic field of the used fields, $H=1.0\text{kOe}$, and it decreases at $H=20\text{kOe}$).

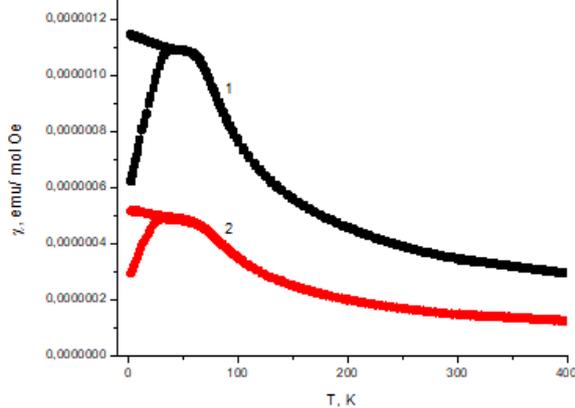


Fig. 3. The magnetic susceptibility of the CFT single crystal in the χ ZFC and χ FC modes, the magnetic field is applied parallel to the (001) plane: 1-10 and 2-20 kOe.

This behavior of the susceptibility χ is typical for spin glasses and was observed by neutron diffraction in $\text{Fe}_{1+\delta-x}\text{Cu}_x\text{Te}$ compounds [3]. The spin-glassy state is also supported by the fact that the low-temperature magnetization of the sample splits in the field or without it. In the intermediate region ($T \approx 65\text{-}360\text{K}$), the contribution of the paramagnetic susceptibility decreases under the influence of superparamagnetic clusters of the ferrimagnetic type and charge carriers. In the temperature range above $T_B > 360\text{K}$, the behavior of the susceptibility is mainly determined by free carriers and paramagnetic centers. The effective magnetic moments of paramagnetic clusters were calculated by linear approximation of the inverse susceptibility dependence for the paramagnetic temperature range. The estimation of the effective magnetic moment of iron ions in CFT from the results of studying the temperature dependences of the magnetic susceptibility $10^{-2}/\chi=f(T)$ was carried out using the expression [15]:

$$M_{\text{eff}} = 2.83 (CM)^{1/2} \mu_B,$$

where, M_{eff} is the effective magnetic moment, C is the Curie constant, M is the molar mass, μ_B is the value in the Bohr magneton.

As can be seen from table 1, the paramagnetic susceptibility obeys the Curie-Weiss law, while the asymptotic Curie temperatures θ_p have a negative sign due to the predominance of antiferromagnetic interaction in clusters, which is consistent with $\text{Cu}_{1.13}\text{Fe}_{1.22}\text{Te}_2$ [16]. This is also evidenced by the form of the temperature dependence of the inverse susceptibility, with the convexity facing upward. 1-1.0, 2-10, and 3-20kOe for the CFT single crystal (fig. 3) in the temperature range 2-400K.

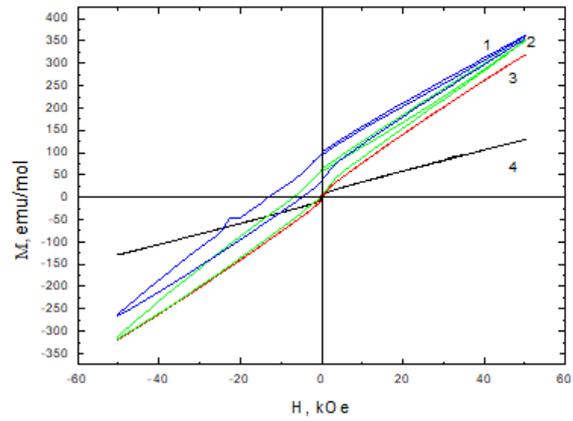


Fig. 4 a. Magnetic hysteresis of a CFT single crystal in the (001) plane at temperatures: 1 - 2, 2 - 4, 3 - 100 and 4 - 300K.

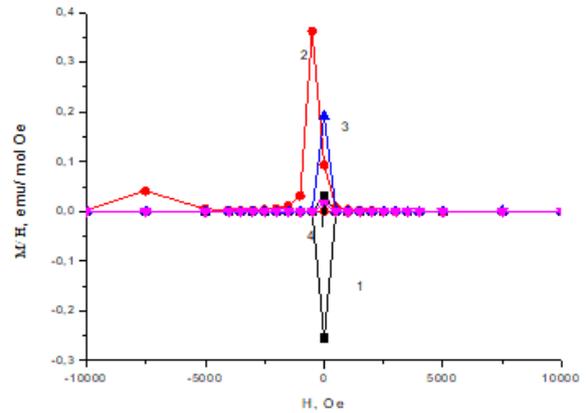


Fig. 4b. Residual magnetization (M/H) in a CFT single crystal in the (001) plane at temperatures: 1-2, 2-4, 3-100 and 4-300K.

Figures 4a and 4b show the isotherms (hysteresis) of magnetization (M) and the ratio of the isotherm of magnetization to the magnetic field M/H (remnant magnetization) of the CFT single crystal in the (001) plane at temperatures of 2, 4, 100, and 300K.

In [18], the temperature dependence $C_p(T)$ of $\text{Cu}_{1.04}\text{Fe}_{1.12}\text{Te}_{1.84}$ was investigated in the temperature range 2-306K. As shown, the total heat capacity CFT is the sum of various contributions, which are complexly dependent on temperature. In the lower part of the

investigated temperature range, the heat capacity can be represented as: $C_p(T) = \Delta C_p + C_D$. Here, the first term is the contribution of various components $\Delta C_p(T)$ to the heat capacity, the second is the lattice (Debye) component of the heat capacity.

5. CONCLUSION

In the *CFT* crystal structure ($P/4nmm$), the chemical bond along the "c" axis as a "cluster" $Cu^+ - Te^{2-} - Fe^{3+} = Te^{2-}$ and eight such molecules create an antiferromagnetik interaction (see fig.5) [17].

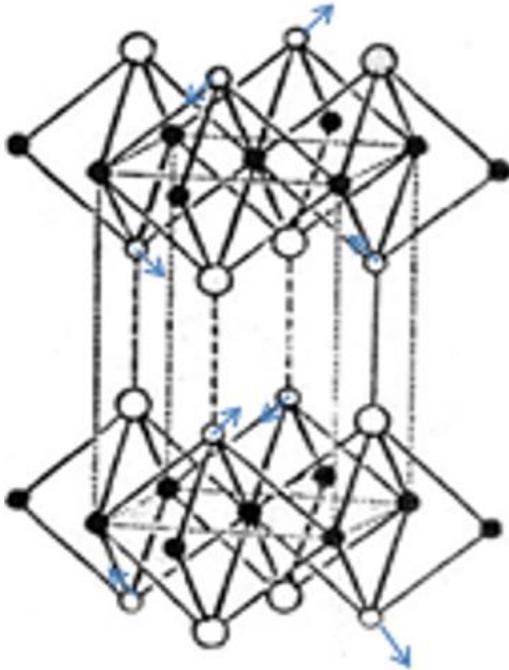


Fig. 5. The direction of the magnetic moments in the CFT structure.

According to the author [17], if the elementary crystallographic cell contains one magnetic ion, then the antiferromagnetik structure in the crystal will have an elementary magnetic cell that is larger than the crystallographic one. If there is more than one magnetic ion in an elementary crystallographic cell, then an alternative is possible for a magnetic cell: preserving the cell or increasing it.

In this *AFM* magnetic structure, the direction of the magnetic moments is shown in fig. 5. In $Cu_{1.04}Fe_{1.12}Te_{1.84}$, the magnetic and spin-glass phase transitions at the temperature $T_N = T_g = 65K$ coincide. In the (001) plane, the excess (15%) of Cu^{+2} and Fe^{+2} ions are statistically located randomly in the voids of the lattice (fig. 1).

As shown in fig. 4b, these excess copper and iron interact ferrimagnetically and exhibit magnetism (ferron [3], antiferromagnetik [5, 9, 16], spin density waves (*SDW*) [1, 12, 14]) in copper-iron-telluride up to 300K ... The excess component of the heat capacity

$\Delta C_p(T)$, as it were, shows the magnetic contribution of excess cations to the heat capacity [20], repeating the temperature dependence $M/H(T)$.

It was determined that the paramagnetic state of the samples exists in the temperature range exceeding 65K. When approximating the temperature dependences of the magnetic susceptibility in the high-temperature region in accordance with the Curie-Weiss law, it was determined that the paramagnetic Curie temperatures of all studied compounds had a negative sign, which characterizes the possibility of antiferromagnetik interactions between "clusters" and ferrimagnetik orders between magneto active Cu^{+2} and Fe^{+2} (between layers). An analysis of the temperature dependences of the effective magnetic moments (M/H in fig. 4b) in the 65–350K range for the samples provided additional evidence of the manifestation of such an interaction in the form of an exchange enhancement of paramagnetic with decreasing temperature. The values of M_{eff} , decreasing with increasing temperature, asymptotically approach constant values at temperatures exceeding 65K.

As seen in fig. 2, (1 and 2), the behavior of the temperature dependences of the susceptibility in a weak magnetic field ($H = 1.0 kOe$) reveals a divergence of the ZFC - FC curves in the temperature range 65–360K, and at 10 (3 and 4) and 20 kOe (5 and 6) match.

Table 1.

H, kOe	1.0	10	20
M_{eff}, μ_B	1.3	2.12	2.22
Θ_P, K	-176	-204	-244

Despite the existence of a single crystallographic structure, sp.gr. $P4/nmm, z=1$ for an excess of iron and copper in $CuFeTe_2$ (*CFT*), at least three different types of these atoms are observed. This situation can arise due to the partial filling of the available intermediates in the structures of copper and iron and the possibility of some ordering of these atoms at the positions ($P4/nmm$). As shown in [1], with the highest magnetic hyperfine field, it probably contains almost isolated ions (Cu, Fe), that is, surrounded by vacancies at intermediate positions, which can be seen in fig. 4b. These results are in good agreement with the Mossbauer spectra of $CuFeTe_2$. Any kind of arrangement on interstitial areas has a short-range order, since it is invisible by diffraction methods.

The magnetism of excess iron, copper and spin density waves (*SPW*) are related. The excess of iron and copper indicates some contributions to the hyperfine field causing the *SSW*. While the irregularity of the *VSP* shape is due to the random distribution of interstitial iron. Both types of magnetism disappear at the same transition temperature ($T_N = T_g = 65K$). However, the available data cannot exclude some other exotic mechanisms of superconductivity.

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