STRUCTURAL TRANSITIONS IN $Cu_{2-x}M_yS$ CRYSTALS (x=0.30, 0.25, 0.20, 0.15; y=0.05; M=In, Fe)

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It was carried out high-temperature x-ray diffraction investigations of structural transitions in $Cu_{2-x}M_yS$ crystals. At room temperature the above crystals consist of an orthorhombic phase (anilite) a monoclinic phase (djurleite) and their metastable high-temperature face-centered cubic phases $(FCC)_1$ and $(FCC)_2$, respectively. A crystallographic relation has been found between the lattices of the orthorhombic, monoclinic and $(FCC)_1$ phase. The effect of partial replacement of copper by indium and iron on the regularities of structural transitions in $Cu_{2-x}S$ non-stoichiometric compounds have been considered.

A clearly defined polymorphism and a statistical distribution of copper atoms among individual positions of high-temperature FCC structure is typical for the $Cu_{2-x}S$ ($0.25>x>0$) system along with larger numbers of crystal phases [1-3]. At room temperature non-stoichio-metric compounds $Cu_{2-x}S$ are two-phase, i.e. they consist of djurleite ($Cu_{1.96}S$) and anilite ($Cu_{1.75}S$) [2] and the difference of the investigated copper chalcogenides in the main leads to the change of quantitative ratio of these phases.

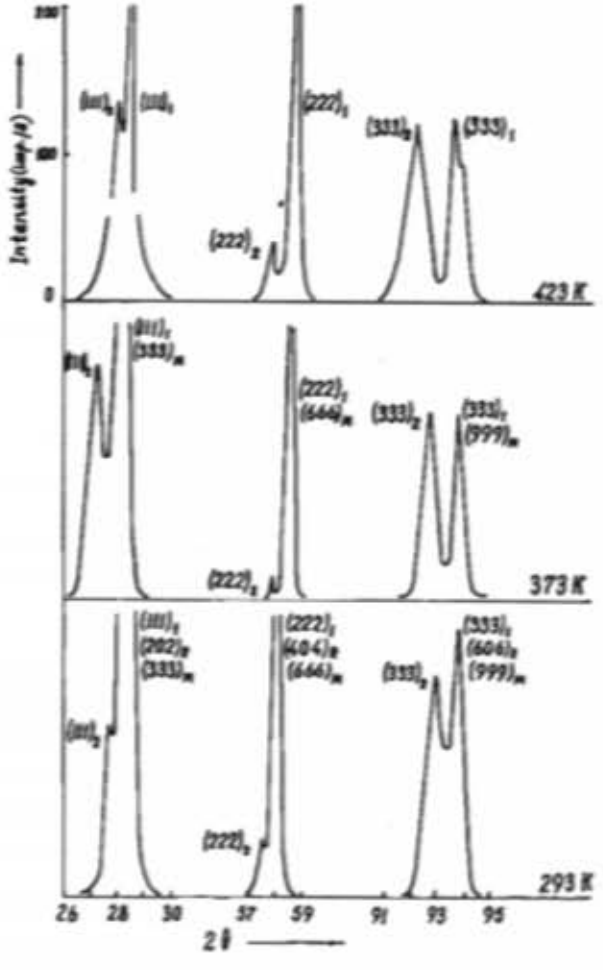

Fig. 1. Fragments of diffraction patterns of $Cu_{2-x}M_yS$ crystals.

In this work the results of investigation of the influence of partial replacement of copper atoms by indium or iron ones on the regularities of structural transitions in $Cu_{2-x}S$ are generalized.

$Cu_{2-x}M_yS$ crystals are obtained by combination of Bridgmen and slow cooling methods with following prolonged annealing at 573 K. The x-ray investigation was carried out with a "DRON-1.5"-type diffractometer with a "URVT-2000"-type high-temperature attachment and with CuK_α-radiation.

All registrated from $Cu_{2-x}In_yS$ and $Cu_{2-x}Fe_yS$ specimens reflections at room temperature were indexed on the basis both an orthorhombic lattice ($Cu_{1.75}S$) and a monoclinic one($Cu_{1.96}S$), i.e. each reflection is the superimpose reflections from different planes of these two crystal lattices. More over superimposed (202), (404) and (606) orthorhombic and (333), (666) and (999) monoclinic reflections also put on (111), (222) and (333) reflections from FCC lattices with a_1=5.54 and a_2=5.56 Å. Therefore these reflections are most intense. As seen from Figure 1, for $Cu_{2-x}In_yS$ it is revealed reflections from (111), (222) and (333) planes of FCC lattice with a= 5.58 Å from side smaller angles.

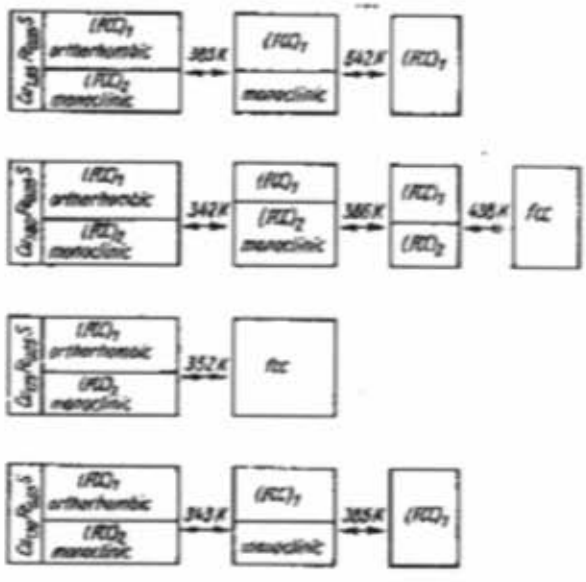

Diagram 1. Diagram of structural transformations in $Cu_{2-x}Fe_{0.05}S$ composition.

The results of high-temperature x-ray investigations of structural transitions in $Cu_{2-x}M_yS$ crystals are summarized in Diagram 1 and 2.

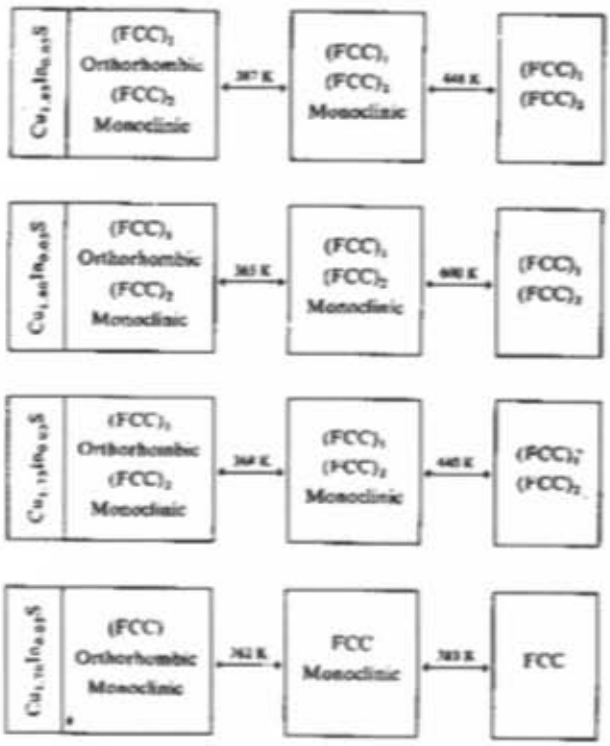

Diagram 2. Diagram of the structural transitions in $Cu_{2-x}In_{0.05}S$ crystals.

At room temperature $Cu_{2-x}Fe_yS$ crystals, as seen from Diagram 1 consist from the orthorhombic and monoclinic phases, as $Cu_{2-x}S$. But $Cu_{2-x}Fe_yS$ crystals differ from $Cu_{2-x}S$ at room temperature contain a metastable high-temperature FCC modifications in addition to the orthorhombic and monoclinic phases. These high-temperature modification marked as $(FCC)_1$ and $(FCC)_2$ differ themselves lattice parameters and concentrations of metal atoms. The lattice parameters of low- and high-temperature modifications of $Cu_{2-x}Fe_yS$ crystals calculated at room temperature are given in Table 1.

If one judges by the numbers and intensities of diffraction reflections belonging to the $(FCC)_2$ modification, the relative amount of the $(FCC)_2$ modification is minimum and unstable in $Cu_{2-x}Fe_yS$ crystals. As seen from Diagram 1 the $(FCC)_2$ phase merges gradually with the $(FCC)_1$ one as the temperature is increased.

In $Cu_{2-x}In_yS$ crystals consisting at high-temperature from $(FCC)_1$ and $(FCC)_2$ phases (Diagram 2), with decreasing temperature at first $(FCC)_2$ and then $(FCC)_1$ phase is transformed to a monoclinic and an orthorhombic phases, respectively. At room temperature the crystals of the indicated compositions consist of an orthorhombic, a monoclinic and their metastable high-temperature modifications at any value of x, except $Cu_{1.70}In_{0.05}S$.

If to compare Diagram structural transitions $Cu_{2-x}S$ [2] with Diagram 1 and 2 it becomes obvious that a partial replacement of copper atoms by indium or iron leads to a radically changes of the number of the phases and structural phase transition temperatures in $Cu_{2-x}M_yS$ crystals.

Table 1.

The unit cell parameters of the phases in $Cu_{2-x}Fe_yS$ crystals (at T=295 K)

Compositions	Orthorhombic			Monoclinic (β=90.13°)			$(FCC)_1$	$(FCC)_2$
	a, Å	b, Å	c, Å	a, Å	b, Å	c, Å	a, Å	a, Å
$Cu_{1.70}Fe_{0.05}S$	7.87	7.83	11.12	26.89	15.75	13.57	5.55	5.65
$Cu_{1.75}Fe_{0.05}S$	7.87	7.84	11.07	26.89	15.74	13.57	5.56	5.65
$Cu_{1.80}Fe_{0.05}S$	7.88	7.95	11.13	26.89	15.75	13.57	5.56	5.65
$Cu_{1.85}Fe_{0.05}S$	7.88	7.84	11.12	26.89	15.75	13.57	5.57	5.65

It is known, that the crystallization temperatures of $Cu_{2-x}M_yS$ crystals higher than temperatures of structural transitions. In this condition always to grow crystals of the high-temperature FCC modification, permitting the dissolution more amount of the metal atoms. Redistribution of metal atoms on cooling leads to the formation of an orthorhombic (anilite), a monoclinic (djurleite) and a metastable FCC phases. In $Cu_{2-x}M_yS$ crystals exist the crystallographic bond between the orthorhombic, monoclinic and $(FCC)_1$ lattices, where the (111) plane of the cubic lattice is superimposed on the (202) plane of the orthorhombic lattice and the (333) plane of the monoclinic lattice (Table 2).

Table 2.

Interplanar spacings, which testify the crystallographic bond between lattices of the orthorhombic, monoclinic and $(FCC)_1$ phases.

№№	d_{exp}, Å	Orthorhombic		Monoclinic		$(FCC)_1$	
		d_{calc}, Å	hkl	d_{calc}, Å	hkl	d_{calc}, Å	hkl
1	3.202	3.207	202	3.198	333	3.202	111
2	1.601	1.603	404	1.605	666	1.601	222
3	1.067	1.067	606	1.066	999	1.067	333

Thus a partial replacement copper atoms by atoms from III and VIII groups in the cation sublattice of the copper chalcogenides leads to the formation of the metastable phases which stable in wide temperature intervals. Structural transitions in $Cu_{2-x}M_yS$ crystals occur by monocrystall-monocrystall-type and the interrelationship exists between the monoclinic, orthorhombic and $(FCC)_1$ lattices.

[1] *E.H.Roseboom.* Econ. Geol. 1966, v.61, p.641.
[2] *K.M.Jafarov.* Fizika (Baku). 1996, v.2, № 2, p.61.
[3] *Yu.G. Asadov, D.I. Ismailov, K.M. Jafarov.* IV All-Union Congress. Kishinev, 1985, p.120.

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$Cu_{2-x}M_yS$ (x=0.30, 0.25, 0.20, 0.15; y=0.05; M=Fe, In) KRİSTALLARINDA QURULUŞ KEÇİDLƏRİ

$Cu_{2-x}M_yS$ kristallarında quruluş faza keçidləri rentgenoqrafik metodla tədqiq olunmuşdur. Müəyyən olunmuşdur ki, $Cu_{2-x}S$ birləşmələrində mis atomlarının III və VIII qrup atomları ilə izomorf əvəz olunması geniş temperatur diapazonunda dayanıqlı olan metastabil fazaların yaranmasına gətirib çıxarır.

К.М. Джафаров

СТРУКТУРНЫЕ ПЕРЕХОДЫ В КРИСТАЛЛАХ $Cu_{2-x}M_yS$ (x=0.30, 0.25, 0.20, 0.15; y=0.05; M=In, Fe)

Проведено рентгенографическое изучение структурных переходов в монокристаллах сульфидов меди $Cu_{2-x}M_yS$. Рассмотрено влияние частичной замены атомов меди атомами индия и железа на закономерности структурных фазовых переходов в нестехиометрических соединениях $Cu_{2-x}S$.

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