Electron Diffraction Study of Phase Formation in Nano Layers of Cu$_2$Te−In$_2$Te$_3$, Cu−In−Te Systems and Short-Range Atomic Order in Amorphous CuIn$_5$Te$_8$ Films

© *G.E. Dashdamirova* [1], *E.B. Asgerov* [2,3,¶], *D.I. Ismailov* [1]

[1] Institute of Physics, National Academy of Sciences of Azerbaijan,
AZ1143 Baku, Azerbaijan
[2] Joint Institute for Nuclear Research,
141980 Dubna, Russia
[3] National Center for Nuclear Research,
370143 Baku, Azerbaijan

[¶] E-mail: elmar.asgerov@gmail.com

It is shown that with the simultaneous and sequential deposition of films of the Cu$_2$Te−In$_2$Te$_3$ system, as well as copper, indium, and tellurium of the highest purity used as starting materials, $\sim$ 99.999%, taken in the ratio Cu : In : Te = 1 : 5 : 8, regardless of the deposition order ternary compounds of the compositions CuInTe$_2$, CuIn$_3$Te$_5$, and CuIn$_5$Te$_8$ in the crystalline state are distinguished. During vacuum condensation of films on single-crystal substrates NaCl, KCl and amorphous celluloid cooled by liquid nitrogen to 203 K, the resulting films obtained both by co-evaporation of binary compounds of the Cu$_2$Te−In$_2$Te$_3$ system and by the synthesis of thin layers applied by Cu, In, Te are amorphous. For the first time in nanosized amorphous films of the composition CuIn$_5$Te$_8$, crystallizing in the tetragonal system with the periods of unit cells $a = 6.162$ Å, $c = 12.291$ Å, obtained both under normal conditions and under the influence of an external electric field with a strength of 500 V · cm^{-1}, the structure of the short-range atomic order is established — the number of nearest neighbors — coordination numbers and radius of coordination spheres. It was revealed that in amorphous CuIn$_5$Te$_8$ films obtained under the influence of an external electric field, in which the matrices consist of tetrahedral and octahedral environments of atoms, in opposite to films that are formed outside the field, the number of nearest neighbors remains unchanged, the radius of coordination spheres and interatomic distances are somewhat are shortened.

Keywords: phase formation, elektronogram, radial distribution function of atoms (RDFA), coherent electron scattering.

1. Introduction

Highly-dispersive and diamond-like complex semiconductor materials in thin-film design, measured in tens and units of nanometers in optoelectronics, semiconductor and quantum electronics, are created in the processes of synthesis of homogeneous phases based on elementary semiconductors, two- and three-component compounds. Physicochemical properties of stable phases (which in 3D-samples can be thermodynamically unstable, and if they can, then only at high temperatures), and, as a rule, the parameters of the photo-converting structures created on their basis depend on the size and orientation of the crystals in the formed thin films, the kinetic parameters of phase transformations, the preservation or destruction of the short-range atomic order in the structure and are determined by the conditions for their preparation (the nature and structure of the surface of the substrate itself, its purity and the orientation of the small crystals).

Since the preservation or destruction of the short-range order in the arrangement of atoms, which are necessary and fundamental links in the „composition–structure–property" relationship, is determined by the retention or loss of semiconductor properties, electron diffraction studies of amorphous films occupy a special place among the problems solved by this method. The electrophysical, optical, and other properties of semiconductor layers do not depend on the long-range order, but only on the structure of the short-range atomic order in amorphous and crystalline substances. Therefore, at the design stage of optoelectronic elements, for the corresponding calculations, knowledge is needed about the structure of amorphous substances and the degree of influence on their structures of various external conditions, i.e. temperature conditions, electric and magnetic fields on the coordination of atoms in amorphous films.

Therefore, such studies (determination of the phase composition, the boundaries of phase homogeneity, growth mechanisms and the degree of structure perfection) make it possible to conduct the targeted search for new materials in film version with unique, specified and reproducible properties that are unattainable in bulky crystals. As a

consequence of this and a number of other reasons not mentioned here, studies of the above processes in nano-thickness thin-film samples, which differ from bulky samples by easier separation of both thermodynamically stable phases and metastable ones — with intermediate transition structures that arise at various stages of chemical reactions along the route to equilibrium, are of general scientific importance, the results of which can be used to increase the application possibilities of multilayer heterostructures.

According to the data of the work [1] in the Cu−Te and In−Te systems, which are double sections of the Cu−In−Te ternary system, there are several modifications — low-temperature (α) and high-temperature (β) phases of various compositions Cu_2Te, Cu_3Te_2, Cu_4Te_3, $CuTe$, Cu_3Te_5 and $InTe$, In_4Te_3, In_2Te_3, In_2Te_5, $InTe_3$ respectively. According to the data of the work [2], in the Cu−In−Te system, along with the double telluride of the ternary compound $CuInTe_2$, there are also phases of compositions $CuIn_3Te_5$, $CuIn_5Te_8$.

In the works [2,3], the conditions for obtaining single crystals of the composition $CuIn_5Te_8$ were established by the technique of directional crystallization and the possibility of creating solar radiation photoconverters based on them was shown. Issues of phase formation, the structure of amorphous films, and phase transformations in ternary compounds included in the general group of chemical compounds $A^{I}B^{III}_{2n+1}C^{VI}_{3n+2}$, where the composition indices in this formula belong to the series of natural numbers $n = 0, 1, 2 \ldots$, in the film state, except for works [4,5], are not investigated.

The purpose of this work is to study the processes of phase formation — to establish the phase composition in the systems $Cu_2Te−In_2Te_3$ and Cu−In−Te in the ratios $Cu:In:Te = 1:5:8$ obtained under normal conditions and under exposure conditions of external electric field with a strength of $500 \, V \cdot cm^{-1}$ in amorphous $CuIn_5Te_8$ films, and determining the structure of short-range atomic order, since said studies are of particular importance in the technology of creating thin-film structures, serve as the basis for development and make it possible to intensify the production of new generation of modern solid-state electronics. There is no information in the literature about glass-formation based on glasses of the $Cu_2Te−In_2Te_3$ system and the Cu−In−Te ternary system.

2. Experimental methods

The theory and experimental methods that are used in the study of phase formation due to the interaction of thin layers are determined both by the specific features of each chemical element of the systems under study and by the method for the film production. In the development of optoelectronic technology, a significant role was played by the search for new and improvement of existing methods of film applying.

The study of triple films of copper, indium and tellurium is in connection with a number of experimental difficulties

associated, on the one hand, with the oxidation of copper upon contact with air, and on the other hand, with the volatilization of indium and tellurium during long-term storage in vacuum, especially at elevated temperatures.

To identify the optimal conditions for the process of phase formation in the systems $Cu_2Te−In_2Te_3$ and Cu−In−Te in the ratios $Cu:In:Te = 1:5:8$ and establishing the short-range atomic order in amorphous $CuIn_5Te_8$ we used the film encapsulation technique used in the works [6–8]. The films under study were coated on both sides with a protective layer of amorphous carbon. To do this, a carbon film was deposited on the surface of substrates consisting of NaCl and KCl single crystals by vacuum deposition, then the objects under study were deposited, and again carbon was deposited on top. The total thickness of the amorphous carbon films did not exceed 100 Å. The presence of protective layers only insignificantly increased the background of diffraction patterns. It should be noted that due to the numerous varied physical and technical parameters in the preparation of films, the conditions for the formation of thin layers for each class of substance turn out to be specific and are determined experimentally; determinations of the mechanism of formation and the influence of the conditions for obtaining films have not yet led to a integrated result. For each specific case, a technology for preparing thin layers is developed and the relationship with the structural and other features of vacuum condensates is studied.

To obtain films of the $Cu_2Te−In_2Te_3$ system from two sources located at the distance of 120 mm from each other, synthesized compounds Cu_2Te and In_2Te_3 were evaporated. For the evaporation of substances, we used heaters in the form of cone-shaped spiral baskets made of tungsten wire with diameter of 0.15 mm. The amount of evaporated Cu_2Te and In_2Te_3 was 11.2 and 8.8 mg, respectively. The calculated film thickness was 250 Å, the deposition rate was $\sim 15−20$ Å/s. As a result of the electron diffraction analysis of the products formed over the entire condensation plane, it was found that both during the simultaneous and sequential sublimation of the components, regardless of the sequence of their evaporation, thin layers formed on KCl substrates are formed in the crystalline state (Fig. 1).

The crystalline phase formed on NaCl substrates at room temperature gives the diffraction pattern typical of textured objects, but with blurry reflections of the diffraction field. Further recrystallization annealing at 343 K leads to texture perfection (Fig. 2). All diffraction reflections on the electron diffraction patterns from the polycrystal and textured films are indicated on the basis of the tetragonal lattice of the ternary compound $CuIn_5Te_8$ with unit crystal lattice spacings $a = 6.162$ Å and $c = 12.291$ Å [9].

The work [9] shows that the unit cell of tetragonal $CuIn_5Te_8$ obeys the space group of symmetry (SGS) $I\bar{4}$. However, according to the law of extinction of reflections observed in electron diffraction patterns obtained from polycrystalline and textured films, we found that $CuIn_5Te_8$ has a body-centered lattice and is described with the
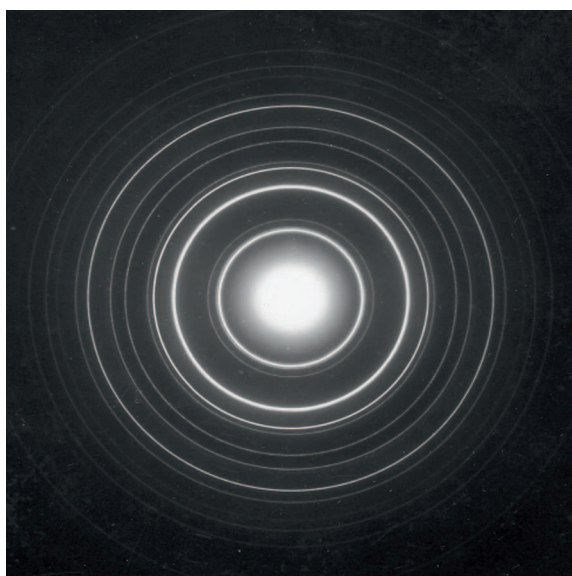
Figure 1. Electron diffraction pattern from polycrystalline $CuIn_5Te_8$ with the tetragonal lattice.
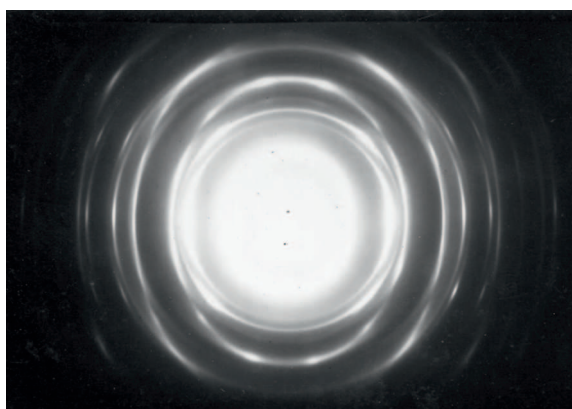

Figure 2. Electron diffraction pattern from the texture of tetragonal $CuIn_5Te_8$. Shooting angle is $45°$.
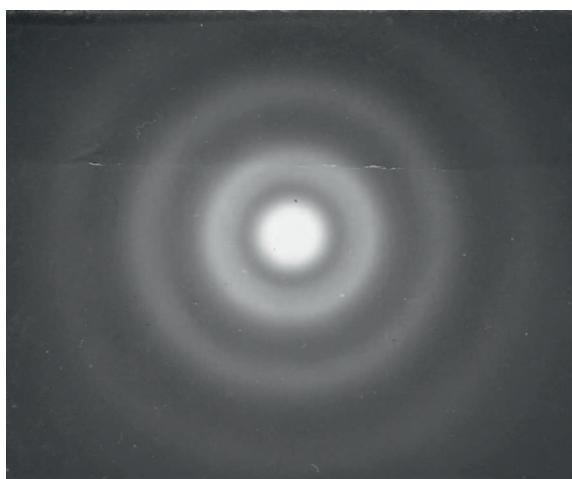

Figure 3. Electron diffraction pattern from amorphous $CuIn_5Te_8$ $T_n = -50°C$.

SGS of crystals $I4/mcm$-D_{4h}^{18}. The coordination of atoms in the $CuIn_5Te_8$ structure, which has not yet been fully deciphered, is possibly more complex than in $CuIn_5S_8(Se_8)$, and has its own structure type.

In subsequent experiments, three sources of evaporation — conical wound tungsten spirals were installed along the condensation plane so that the outer ones, which evaporated Cu and In, were located at a distance of 150 mm from each other and at a height of 60 mm over freshly cleaved NaCl single crystals, and the third source with Te was located at a height of 70 mm from the plane of the substrates, exactly between the Cu and In sources. The thickness of the obtained films of the $Cu-In-Te$ system in the ratio $1:5:8$, formed by smooth change in the percentage of components during their simultaneous and layer-by-layer condensation on NaCl and KCl (which are at room temperature without taking into account the thickness of the carbon capsule in which these films were placed, as in the works [6–8]), was amounted to ~ 200 Å. The encapsulation technique requires special accuracy to minimize the effects associated with the absorption of moisture from atmospheric air by the samples and during the heat treatment of the samples. The electron diffraction analysis of the studied films of the $Cu-In-Te$ system showed that, along with the binary compounds of the $Cu-Te$, $In-Te$ systems (which are double sections of the $Cu-In-Te$ ternary system), in result of the interaction between the films, in a fairly wide area of the condensation plane enriched with tellurium (directly under the Te source), the ternary compound of the $CuInTe_2$ composition is formed with the periods of the tetragonal unit cell (UC) $a = 6.197$ Å, $c = 12.453$ Å, SGS $I\bar{4}2d$-D_{2d}^{12}, consistent with the data of the work [2]. Composition compounds $CuIn_3Te_5$ ($Cu_5In_{15}Te_{25}$) with constants $a = 6.173$ Å, $c = 12.334$ Å and $CuIn_5Te_8$ ($Cu_3In_{15}Te_{24}$) with the structural characteristics given in the works [2,9] are formed in very narrow range of compositions.

The amorphous phases $CuIn_5Te_8$ and $CuIn_3Te_5$ are formed at substrate temperature of 223 K. However, in this case, despite the geometric factor exclusion (the geometry of the experiments remains unchanged), depending on the sequence of deposition of the components, some change occurs in the proportion of boundaries formed on the collector of amorphous phases of ternary compounds of the $Cu-In-Te$ system. The electron diffraction pattern of amorphous films of $CuIn_5Te_8$ (Fig. 3) contains diffuse lines with values $S = 4\pi \sin\theta/\lambda$ equal to 1.66, 3.20 and 4.91 Å^{-1}.

3. Results and discussion

The most rational method for studying the short-range atomic order in thin amorphous layers is the method of electron diffraction structural analysis (EDSA). Massive glassy substances and thin amorphous layers, having the less ordered internal structure, are characterized at the same temperatures and pressures by correspondingly larger

volume, higher internal energy and entropy than substances in the crystalline state.

For various reasons, information about the atomic structure of glassy substances of various compositions of Cu−Te, In−Te, Cu−In−Te systems and thin amorphous films is very limited and overwhelmingly uncertain. Obtaining stable states in amorphous substances, i.e. corresponding to the minimum of the thermodynamic potential at given pressures and temperatures, is associated with the establishment of both certain distances between the particles and certain configurations of their mutual arrangement. The structure of the short-range order in amorphous substances is described by the radial distribution function of the atomic density.

The experimental curves of the electron scattering intensity (Fig. 4) for the amorphous phase $CuIn_5Te_8$ were obtained on EMR-102 serial electron diffractometer, equipped with a system that allows filtering out the signal associated with inelastic electron scattering. The system for measuring the intensity of electronic diffraction patterns, using electrometric registration by scanning the diffraction field in front of a high-sensitivity fixed sensor, can significantly improve the accuracy of structural studies.

At present, the only method for obtaining the radial distribution function of atoms (RDFA) is the method of integral transformation of the scattering intensities of X-rays, electrons, or neutrons. The spherically symmetric RDFA makes it possible to calculate the parameters of interatomic interaction (sets the probability of finding atoms oriented in space in a certain way at a certain distance from each other) and to establish the arrangement of coordination groups, i.e. the number of atoms in the coordination spheres. Method specified, which determines the radial distribution curve of atoms (RDCA) of amorphous substances consisting of atoms of different types, is based on the formula presented in the work [10]:

$$4\pi r^2 \sum_m K_m U_m(r) = 4\pi r^2 U_0 \sum_m K_m$$
$$+ \frac{2r}{\pi} \int_0^\infty \sin(s)\sin(sr)ds. \quad (1)$$

Here, $\sum$ is summation over molecular composition, K_m represents the effective scattering power of an atom in the substance under study, which in electron diffractometry, according to [11], is defined as

$$K_m^{el} = (Z_m/Z_l)^{0.75}, \quad (2)$$

where Z_m is atomic number m in the Periodic system of elements, Z_l is atomic number of the lightest atom in the compound; $U_m(r)$ is atomic density distribution function; $4\pi r^2 U_m dr$ is average number of atoms in a spherical layer bounded by radii r and $r + dr$; U_0 is average density (at/Å^3) in a given volume, which is determined from the formula $U_0 = d/Mm_n$, where d is density of an amorphous substance, m_n is mass of a hydrogen atom, equal to
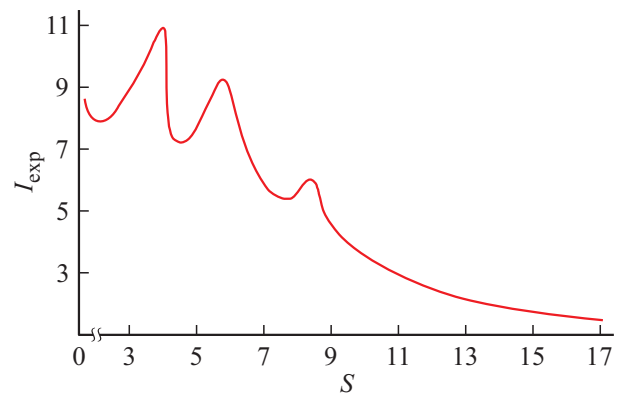

Figure 4. Experimental intensity curve $I_{exp}(S)$ of amorphous $CuIn_5Te_8$.

$1.65 \cdot 10^{-24}$ g; $S = 4\pi \sin\theta/\lambda_e$, where θ is scattering angle, λ_e is electron wavelength depending on applied accelerating voltage. Interference function is defined as

$$i(s) = \frac{I_H^k(s)}{f^2(s)} - 1. \quad (3)$$

Here, $I_H^k(s)$ is the normalized intensity of coherent scattering; $f(s)$ is atomic factor of applied radiation. The coherent scattering intensity $I_H^k(s)$ is found from the experimental intensity curve $I_e(s)$ by diminution the background intensity from it. Experimental data for the background during electron diffraction can be determined by the theoretical dependence

$$I^{back}(s) = k\left\{\frac{4ZS(s)}{a_0 S^4} + f^2(s)\left[1 - e^{-2M}\right]\right\}, \quad (4)$$

where Z is sequential number; a_0 is lattice spacing; $S(s)$ is Heisenberg–Bewilogua inelastic function; $f^2(s)$ is atomic factor; e^{-2M} is Debye temperature factor.

However, the most optimal method to take into account the background and determine the function $i(s)$, which allows you to determine the background intensity through the function $I_{av}(S)/f^2(s)$, where $I_{av}(S)$ — average intensity, presented in the work [10].

Since the interference function $i(s)$ is determined only by the coherent part of the intensity, it is calculated directly from the experimental intensity curve without preliminary determination and exclusion of the background. The experimental scattering intensity $I_{exp}(S)$ can be represented as the sum of the coherent scattering intensity $I^k(s)$ and the background intensity $I^{back}(s)$ measured in relative units

$$I_{exp}(S) = I^k(s) + I^{back}(s), \quad (5)$$

and the average scattering intensity

$$I_{av}(s) = I^{back}(s) + \frac{1}{\alpha}f^2(s). \quad (6)$$

Using the formula proposed in [10], the intensity of coherent scattering is normalized as

$$\alpha \int\limits_0^\infty I^k(s) i^2 ds = \int\limits_0^\infty f^2(s) s^2 ds, \qquad (7)$$

where α is a normalizing factor, and taking into account (5)

$$\int\limits_0^\infty I_e(S) S^2 ds = \int\limits_0^\infty I_{av}(S) S^2 ds. \qquad (8)$$

Taking into account that $I_H^k(s) = \alpha I^k(s)$ using (6), (7) the interference function is defined as

$$i(s) = \frac{\alpha I^k(s) - f^2(s)}{f^2(s)}$$

$$= \alpha \left[\frac{I_e(S)}{f^2(s)} - \frac{I_{av}(S)}{f^2(s)} \right] = \alpha i(s). \qquad (9)$$

The dependence of the experimental intensity of coherent scattering of electrons (I_e) on S, as mentioned above, was recorded by us in the mode of direct recording of the electron current. The incoherent background was taken into account by the [10] methodology, and the RDFA was calculated by the formula (1). For the amorphous structure CuIn₅Te₈, curves of functions $I_e(S)/\sum_m f_m^2(S)$ and $I_{av}(S)/\sum_m f_m^2(S)$ were plotted. The interference function curve $i(S)$ constructed for amorphous CuIn₅Te₈ is shown in Fig. 5.

Average value of the normalizing factor $\alpha_{av} = 33$. To calculate U_0, the density of amorphous CuIn₅Te₈ is assumed to be $5.30 \, \text{g/cm}^3$, i.e. 10% less than the density of the crystalline compound. RDFA of amorphous CuIn₅Te₈ (Fig. 6) contains two pronounced maxima. The first maximum is identified at $r_1 = 2.70 \, \text{Å}$, the second one is found at $r_2 = 3.04 \, \text{Å}$.

The areas under the maxima corresponding to the distances r_1 and r_2 are equal to $\Delta_1 = 22.5$, $\Delta_2 = 40.5$. The
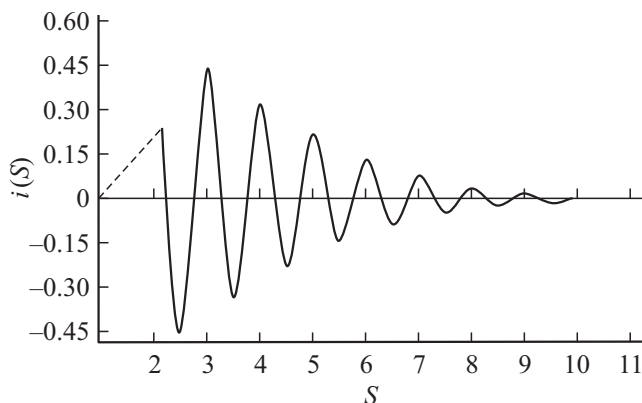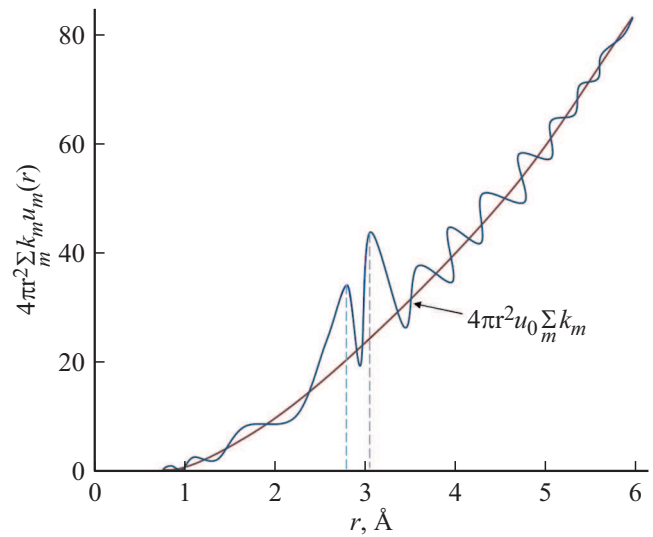
Figure 6. Radial distribution curve of atoms CuIn₅Te₈.

first maximum at $r_1 = 2.70 \, \text{Å}$ corresponds to the Cu−Te interatomic distance. Value of the sum of the ionic radii of copper and indium is $In^{+3} + Te^{-2} = 0.94 + 2.1 = 3.04 \, \text{Å}$. The calculation of the corresponding coordination number (K_4) gives $n_1 = 4$, which indicates the tetrahedral environing of copper ions by indium atoms. The second maximum on the RDFA corresponds to the distances between the Cu and Te ions. Value of the sum of covalent radii $Cu-Te = 1.32 + 1.38 = 2.70 \, \text{Å}$ is close to r_2. K_4, equal to $n_2 = 6$, indicates the octahedral environing of copper ions by tellurium atoms. In amorphous films of CuIn₅Te₈ obtained under the influence of an electric field of $500 \, \text{V} \cdot \text{cm}^{-1}$, the interatomic distances Cu−Te, In−Te are somewhat shortened and amount to 2.70 and 3.04 Å respectively, which may be due to the molecule dipole-elastic polarization of amorphous CuIn₅Te₈. Wherein, in both cases, the number of nearest neighbors of atoms does not change and tetrahedral and octahedral environments of atoms are observed [9].

4. Conclusion

It is shown for the first time that in the binary field of components during simultaneous and successive deposition of Cu₂Te−In₂Te₃, as well as during evaporation of films of the Cu−In−Te system in the ratio 1:5:8, due to a smooth change in the percentage of components at room temperature, films of ternary compounds CuInTe₂, CuIn₃Te₅ and CuIn₅Te₈ in the crystalline state are formed. At temperature of single-crystal substrates 223 K, amorphous phases CuIn₃Te₅ and CuIn₅Te₈ are realized. Based on an integral analysis of the scattering intensities of high-energy electrons, the curve of the radial distribution of atomic density in amorphous CuIn₅Te films was plotted; the function is established that, in a static framework, determines the probability of meeting an atom of one

Figure 5. Interference function of electron scattering in amorphous CuIn₅Te₈.

sort or another, located at the distance r from this atom. The parameters of short-range atomic order in amorphous $CuIn_5Te_8$ are calculated and determined. In particular: interatomic distances, radii of coordination spheres, and the number of nearest neighbors of atoms. It has been established that the matrices of amorphous $CuIn_5Te_8$ layers consist of tetrahedral and octahedral atomic environings.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M. Hansen, K. Anderko. *Struktura dvoinykh splavov* (M., Metallurgizdat, 1962) (in Russian).

[2] C. Rinson, S.M. Wasim, G. Marin, E. Hernández, J.M. Delgado, J. Galibert. J. Appl. Phys., **88**, 3439 (2000).

[3] I.V. Bodnar', V.Yu. Rud', E.I. Terukov, A.M. Kovalchuk. FTP, **45** (5), 617 (2011) (in Russian).

[4] A.M. Abo, T.A. Hendia, L.I. Soliman, H.A. Zayed, M.A. Kenawy. J. Mater. Sci., **28**, 1182 (1993).

[5] A.Ch. Mamedova, N.K. Kerimova, D.I. Ismailov, S.M. Bagirova, A.M. Nurieva. Poverkhnost. Rentgenovskie, sinkhrotronnye i nejtronnye issledovaniya, **2**, 62 (2016) (in Russian).

[6] E.B. Asgerov, A.I. Madadzada, D.I. Ismailov, R.N. Mekhtieva. FTP, **48** (11), 1484 (2014) (in Russian).

[7] E.B. Asgerov, A.I. Madadzada, D.I. Ismailov, R.N. Mekhtieva. FTP, **48** (9), 1265 (2014) (in Russian).

[8] G.E. Dashdamirova, E.B. Asgerov, D.I. Ismailov. FTP, **56** (3), 297 (2022) (in Russian).

[9] I.D. Olekseyuk, O.Ye. Zhbankov. J. Alloys Compd., **436**, 247 (2007).

[10] I.D. Nabitovich, Ya.I. Spetsiv, Ya.V. Volushchuk. Kristallografiya, **12** (4), 584 (1967) (in Russian).

[11] B.K. Weinstein. Kristallografiya **2** (1), 29 (1957) (in Russian).