

THE QUESTION OF DISORDER IN THE TETRAGONAL PHASE $\text{Cu}_{4-x}\text{Te}_2$

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The γ^{I} and γ^{II} modifications of the tetragonal phase $\text{Cu}_{4-x}\text{Te}_2$ have been studied by the electron diffraction method. Both compounds crystallize in one structure type with space group D_{4h}^7-P4/nmm , with $a = 3.98 \text{ \AA}$ and $c = 6.12 \text{ \AA}$ for the γ^{I} phase and $a = 3.98 \text{ \AA}$ and $c = 6.55 \text{ \AA}$ for the γ^{II} phase. The tetragonal modification belongs to a phase of variable composition. Both the Cu II and the Cu I atoms occupy their positions in a disordered manner.

The tetragonal phase $\text{Cu}_{4-x}\text{Te}_2$ corresponds to natural copper telluride, the mineral rickardite, to which the composition Cu_3Te_2 has been assigned. Data on the phase $\text{Cu}_{4-x}\text{Te}_2$ are quite contradictory, particularly in regard to the composition of this phase. An x-ray structure study of both the mineral rickardite from Colorado and a synthetic compound of composition Cu_4Te_3 was carried out in [1]. It was found that both phases crystallize in the tetragonal system with $a = 3.98 \text{ \AA}$ and $c = 6.12 \text{ \AA}$, of the structure type Cu_2Sb . The space group is D_{4h}^7-P4/nmm , with 2 Cu in (a), $(2-x)\text{Cu}$ in (c), with $z_{\text{Cu}} = 0.27 \pm 0.01$, and 2 Te in (c) with $z_{\text{Te}} = 0.715 \pm 0.005$. The structure is strongly defective. The authors concluded that the empirical composition Cu_4Te_3 should be replaced by $\text{Cu}_{4-x}\text{Te}_2$ where $x \approx 1-1.2$, or by Cu_3Te_2 , since $x \approx 1$. In [2], the composition Cu_7Te_5 is indicated for this same phase at 41.7 at. % Te. An analogous phase ($a = 3.98 \text{ \AA}$, $c = 6.12 \text{ \AA}$) with additional reflections indexed on the basis of a superstructure with $a' = 5a$ and $c' = 2c$, which the authors are continuing to study, was observed in [3].

In this work, films of 10^{-5} - 10^{-6} cm thickness were prepared by separate evaporation of Cu and Te (in excess) in vacuum with subsequent condensation of the vapors on a substrate of single-crystal NaCl. The specimens prepared in this manner were subjected to anneals of different lengths at

varying temperatures. The γ^{I} phase was indexed on the basis of a cell with periods $a = 3.98 \text{ \AA}$ and $c = 6.12 \text{ \AA}$. Reflections from the $5a, 2c$ superstructure were observed on all electron diffraction patterns of this type. The intensities of these reflections as compared with the primary reflections were different on the different patterns. In all, 53 reflections with $\sin \vartheta/\lambda = 0.773 \text{ \AA}^{-1}$ were measured. The intensities of the $hk0$ reflections were determined photometrically, and the rest by visual comparison with the $hk0$ reflections. Scattering was calculated by the kinematic method.

The periods of the γ^{I} phase coincided with those given in [1], and this allowed us to assume that the z coordinates of the atoms likewise should not differ from the literature values. It appeared of interest to confirm the composition of this phase. According to [1], the disorder of the structure was determined to be about 46% filling of the positions of the Cu II atoms. In the first stage the method of minimization of the R_{hkl} factor was used, the literature values of the z parameters being retained and only the content of Cu II atoms being varied. In this case the minimum value of the R_{hkl} factor was obtained at 60% Cu II content.

It was assumed that subsequent refinement of the composition was accomplished by analysis of the heights of potential peaks on the $\varphi(x0z)$ Fourier synthesis. However, this synthesis could prove to

be ineffective in view of the strong nonuniform cutoff and the absence of a significant number of reflections, which lie in the cone of inaccessibility. In this regard, during the calculation of the $\varphi(x0z)$ synthesis all the reflections from the sphere of 0.773 \AA^{-1} radius were used, including 53 experimentally independent reflections and 75 which were calculated from our data on composition and literature values of the parameters of hkl reflections. In this case we settled on the correctness of the preliminary structure model and on the position that 15% of the strongest reflections of the total number contained about 70% of the information about the structure. In the composition, the 75 additional reflections included about 10 $00l$ reflections of average intensity and an additional number of weak ones. From the height of the maxima on the cross section, it was determined that the Cu I atoms fill their positions to about 82%, the Cu II atoms fill their positions to about 53%, and the Te atoms fill their positions to $\sim 100\%$. The values calculated according to [4] and the experimental values of potentials at the centers of the atoms are given in Table 1. The z coordinates are practically unchanged: $z_{\text{Te}} = 0.714 \pm 0.005$, and $z_{\text{Cu II}} = 0.269 \pm 0.020$. Upon taking account of total value of mean square errors and cutoff of approximately 36 V, the composition of the γ^{I} phase can be represented as $\text{Cu}_{2-y} \cdot \text{Cu}_{2-z}\text{Te}_2$, where $y = 0.36 \pm 0.11$ and $z = 0.92 \pm 0.11$, or $\text{Cu}_{4-x}\text{Te}_2$ for $x = 1.28 \pm 0.11$. The R_{hkl} factor, on the basis of 53 experimental amplitudes, is 0.276 for $(\text{Cu I})_{1.64}(\text{Cu II})_{1.10}\text{Te}_2$ with $z_{\text{Te}} = 0.714$ and $z_{\text{Cu II}} = 0.269$. The high value of R_{hkl} evidently is explained by the presence of superstructure. For these familiar tolerances, we basically confirmed existing data [1, 3] about the γ^{I} phase, since the composition based on the empirical formula agrees well with literature data. In view of insufficiency of experimental material, a structure study of the superstructure with periods $5a, 2c$ was not carried out.

The electron diffraction pattern of the γ^{II} modification was indexed on the basis of a tetragonal cell

with $a = 3.98 \text{ \AA}$ and $c = 6.55 \text{ \AA}$. The superstructure reflections from $5a, 2c$ were not observed, but reflections were present on the zero layer line (and on several others) almost exactly in the place of $hk0$ reflections of the forbidden space group with $h + k = 2n + 1$, which at first were assumed to be superstructure reflections from a cell with $2a, 2c$ but later found another explanation.

The c period differs from the literature value of 6.12 \AA by 0.43 \AA . This circumstance indicates possible deviation of the composition or atomic coordinates from those given in the literature.

The intensities of 125 reflections with $\sin \vartheta/\lambda \leq 0.910 \text{ \AA}^{-1}$ were measured in the usual manner. Since the difference in the c period as compared with literature values and values for the γ^{I} phase is rather large, the $P(xy)$ and $P(xz)$ Patterson projections were constructed on the basis of the $(hk0)$ and $(h0l)$ reflections. The $P(xy)$ projection was consistent with the literature model of [1], but superfluous peaks were present on the $P(xz)$ projection which perhaps are explained by the nonuniform cutoff and "dead zone."

The composition $(\text{Cu I})_2(\text{Cu II})_{1.2-1.3}\text{Te}_2$, i.e., $\text{Cu}_{4-x}\text{Te}_2$ where $x = 0.7-0.8$, was determined by minimization of the R_{hk0} factor on the basis of 15 $hk0$ reflections. The coordinates $z_{\text{Te}} = 0.706$ and $z_{\text{Cu II}} = 0.220$ were obtained for these compositions by minimization of the R_{h0l} factor as calculated from 33 reflections.

The $\varphi(x0z)$ Fourier cross sections for the composition $(\text{Cu I})_2(\text{Cu II})_{1.3}\text{Te}_2$ with $z_{\text{Te}} = 0.706$ and $z_{\text{Cu II}} = 0.220$, both with nonuniform cutoff present and after its removal, are given in Figs. 1A and 1B. From analysis of the cross section we see that the height of the heavy Te atom is not changed significantly: 3090 (in relative units) with nonuniform cutoff (A) and 2500 after removal of the nonuniform cutoff (B). In an analogous manner, for an ordered Cu I atom we get 1900 (A) and 1500 (B); and, rather significantly, the change in height of the disordered Cu II atom (defectivity approximately 40%) is from 400 (A) to 1100 (B). In this case, it should be noted

TABLE 1. Calculated and Experimental Potential Peak Heights, in V, and Percent Filling of Their Positions by Cu and Te Atoms in the Structure of the Tetragonal γ Modification

Atoms	γ^{I} modification			γ^{II} modification		
	calculated, for $B = 1.0 \text{ \AA}^2$ and 100% filling	experimental peak heights	% filling	calculated, for $B = 1.0 \text{ \AA}^2$ and 100% filling	experimental peak heights	% filling
$\varphi(0)_{\text{CuI}}$	746	613	82 ± 6	925	830	90 ± 4
$\varphi(0)_{\text{CuII}}$	746	394	53 ± 6	925	638	69 ± 4
$\varphi(0)_{\text{Te}}$	1177	1255	~ 100	1460	1477	100

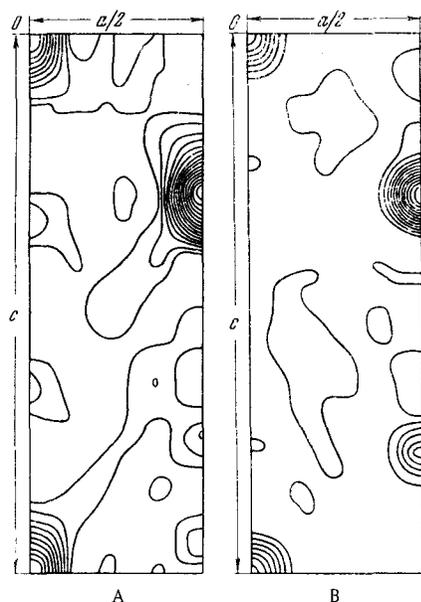


Fig. 1. Three-dimensional $\varphi(x0z)$ potential synthesis of the structure of the γ^{II} phase, calculated for the composition $(\text{Cu I})_2 \cdot (\text{Cu II})_{1.3}\text{Te}_2$ with $z_{\text{Cu II}} = 0.220$ and $z_{\text{Te}} = 0.706$. A) Nonuniform cutoff present; B) nonuniform cutoff removed.

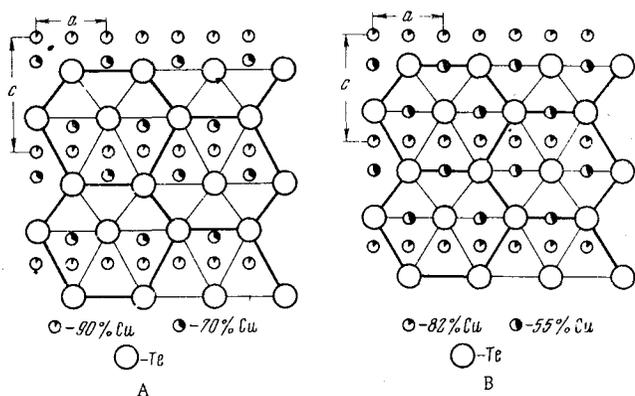


Fig. 2. Projections of the structures on the (yz) plane. A) γ^{II} phase, $\text{Cu}_{3.2}\text{Te}_2$, $a = 3.98 \text{ \AA}$, $c = 6.55 \text{ \AA}$; B) γ^{I} phase, $\text{Cu}_{2.74}\text{Te}_2$, $a = 3.98 \text{ \AA}$, $c = 6.12 \text{ \AA}$.

that the difference between the coordinates $z_{\text{Cu II}}$ and z_{Te} was found to be within the limits of the errors in determination of the coordinates (they were calculated in accordance with [4, 5]): namely, $\Delta z_{\text{Cu II}} = \pm 0.02$, and $\Delta z_{\text{Te}} = \pm 0.005$. In addition, parasitic peaks, one of which is comparable in magnitude with the height of the Cu II atom, were observed on the cross section in Fig. 1A. The values $z_{\text{Te}} = 0.708$ and $z_{\text{Cu II}} = 0.220$ were determined from

the cross section in Fig. 2B. The potential of the Cu I atom was calculated to be 830 V, for Cu II 638 V, and for Te 1477 V (see Table 1). Giving attention to the fact that $\varphi_{\text{Cu}}(0) = 925 \text{ V}$ and $\varphi_{\text{Te}}(0) = 1460 \text{ V}$ for this nonuniform cutoff, and that $B = 1.0 \text{ \AA}^2$, along with the total of errors in determination of the potential (about 40 V), it can be concluded that the Cu I atoms fill their positions with a probability of 85 and 94%, the Cu II atoms with a probability of 65 to 73%, and the Te atoms with a probability of 100%. Consequently, the compositions should be described as $\text{Cu}_{2-y}\text{Cu}_{2-z}\text{Te}_2$, where $y = 0.20 \pm 0.09$ and $z = 0.62 \pm 0.09$, or as $\text{Cu}_{4-x}\text{Te}_2$, where $x = 0.82 \pm 0.09$. R_{hkl} is 0.25 for the composition $(\text{Cu I})_2(\text{Cu II})_{1.3}\text{Te}_2$ and 0.24 for $(\text{Cu I})_{1.8}(\text{Cu II})_{1.4}\text{Te}_2$ with $x_{\text{Cu II}} = 0.220$ and $z_{\text{Te}} = 0.708$. The (yz) projections of the γ^{II} (A) and γ^{I} (B) structures are depicted in Figs. 2A and 2B.

As has already been noted, additional reflections which seem to be single-crystal reflections from the primary phase, arising as the result of partial azimuthal orientation of the specimen, are present on the electron diffraction patterns of the γ^{II} phase along with the predominant reflections from the primary cell. This assumption is confirmed by the fact that the reflections were found only in those regions which could be tested by the primary reflections.

Finally, it is interesting to compare the data obtained for the γ^{I} and γ^{II} modifications with the literature data for the tetragonal rickardite $\text{Cu}_{4-x}\text{Te}_2$, where $x \approx 1-1.2$. For the γ^{I} phase, $z_{\text{Te}} = 0.714 \pm 0.005$, $z_{\text{Cu II}} = 0.269 \pm 0.20$; for the γ^{II} phase, $z_{\text{Te}} = 0.708 \pm 0.003$, $z_{\text{Cu II}} = 0.220 \pm 0.010$; for rickardite, $z_{\text{Te}} = 0.715 \pm 0.005$, $z_{\text{Cu II}} = 0.27 \pm 0.01$. Errors in determination of the coordinates were calculated in accordance with the equations from [4, 5].

In the literature, the phase $\text{Cu}_{4-x}\text{Te}_2$ is assigned to a layer structure with tetrahedral coordination and with equal valence states of the Cu atoms. Actually, however, the coordination number 4 with distorted tetrahedral coordination is characteristic only for $\text{Cu}^{+1}-\text{Cu}^{+2}$ and $\text{Cu}-\text{Te}$ bonds, whereas atoms of more than one kind enter into the nearest surroundings of each atom. The interatomic distances are given in Table 2.

The tetragonal modifications belong to a phase of variable composition. In the γ^{II} phase, the percentage content of Cu atoms is increased as compared with the γ^{I} phase, which may have led to increase of the c period by 0.43 \AA . This substantial difference from literature data lies in the fact that

TABLE 2. Comparison of Interatomic Distances Calculated from Electron Diffraction Structural Data for the γ^{I} and γ^{II} Phases with Literature Data for Tetragonal Rickardite

Bonds	Distance, Å			Bonds	Distance, Å		
	γ^{I} phase	γ^{II} phase	Rickardite		γ^{I} phase	γ^{II} phase	Rickardite
CuI — CuI	2.82	2.82	2.82	CuI — Te	2.65	2.76	2.72
CuI — CuII	2.58	2.46	2.59	CuII — Te	2.72	2.86	2.65— 2.82
CuII — CuII	3.98	4.03	—	Te — Te	3.84	3.92	—

not only do the Cu II atoms occupy their positions in disordered fashion, but the Cu I atoms as well, though with a lesser degree of disorder. According to the classification of [6], this structure type is intermediate between the substitution and interstitial phases, forming compounds of variable composition. The semiconductor properties of the copper tellurides [3] also indicate that they belong to a phase of variable composition.

The phases examined can be considered as disordered structures of the first kind [7]. Concentration disorder occurs here.

If a function of the type [7]

$$s_i = \exp(1 - 1/p_i) \begin{cases} = 1, & \text{if } p = 1 \\ = 0, & \text{if } p = 0 \end{cases}$$

is selected as a "partial" long-range order parameter, then $s_{\text{Cu I}} = e^{-0.22} = 0.80$ and $e^{-0.11} = 0.90$, and $s_{\text{Cu II}} = e^{-0.85} = 0.43$ and $e^{-0.45} = 0.64$ for the γ^{I} and γ^{II} phases, respectively.

It can be assumed that the tetragonal modifications prepared and studied in this work represent a continuous series of compounds of variable composition with a rather wide range of existence. The percentage content of Cu atoms varies within the limits 57.6 ± 1 and $61.4 \pm 0.7\%$. From our data a continuous region of homogeneity, joining the lines with 38.6 ± 0.7 at. % and 42.4 ± 1 at. % Te, apparently exists on the phase diagram of the Cu—Te system for the $\text{Cu}_{4-x}\text{Te}_2$ phase. A different degree of disorder of the Cu atoms in two phases of nearly the same composition is observed in this region, while the structure type and nature of the interatomic forces is maintained during change of composition.

It should be noted that only the γ^{I} (always with superstructure reflections from the $2a, 5c$ phase) and γ^{II} modifications were obtained under conditions of multiply reproducible experiment. No other intermediate modifications belonging to the region of existence of the $\text{Cu}_{4-x}\text{Te}_2$ phase was found. This phenomenon remains incomprehensible, but may be explained by some peculiarities characteristic of the experimental process. The electron diffraction patterns of the films of the γ^{II} phase were obtained for more prolonged and higher-temperature anneals.

The calculations for analysis of the structures of the γ^{I} and γ^{II} compounds were carried out mainly on the "Ural-2" computer in the Institute of Crystallography of the Academy of Sciences of the USSR.

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