This value is in excellent agreement with the values of the density found experimentally for highly crystalline samples of PTFCE [7] and calculated for 100% crystallinity from the infrared spectrum [8].

The absence of equatorial reflections and the presence on the x-ray photograph of Fig. 2 of intense almost spot-like reflections on the first, second, and third layer lines shows that the first reflection should be indexed as (101) and not as (100) as had been done in all the previous studies.

Work is continuing on the refinement of the structure of PTFCE.

## LITERATURE CITED

- H. S. Kaufman, J. Amer. Chem. Soc., <u>75</u>, 1477 (1953).
- A. V. Ermolina, G. S. Markova, and V. A. Kargin, Kristallografiya, 2, 623 (1957) [Soviet Physics - Crystallography, Vol. 2, p. 615].

- H. G. Kilian and E. Jenckel, Z. Electrochem., 63, 308 (1959).
- S. Liang and S. Krimn, J. Chem. Phys., 25, 563 (1956).
- Yu. D. Kondrashev, Tr. Gos. In-Ta Prikl. Khimii, 46, 158 (1960).
- A. Ginye, X-Ray Study of Crystals [Russian translation] (Izd.-vo in.Lit., Moscow, 1961), p. 26.
- D. D. Chegodaev, Z. K. Naumova, and T. S. Dunaevskaya, Fluoropolymers [in Russian] (Goskhimizdat, Moscow, 1960).
- 8. H. Matsuo, J. Polymer Sci., 25, 234 (1957).

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

## STUDY OF THE COPPER-TELLURIUM SYSTEM

## IN THIN FILMS

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Attention is drawn to the incompleteness of xray data on the phase structure in the Cu – Te system. The structure of the compound CuTe was determined in [1] by the Debye powder pattern trial and error method. The lattice constants were a =  $3.15 \pm 0.02$ ; b =  $4.07 \pm 0.02$ ; c =  $6.92 \pm 0.02$  A; z = 2. The space group was  $D_{2h}^{13}$ ; Cu in 2 (b) with  $z_{Cu} = 0.46 \pm 0.02$  and Te in 2 (a) with  $z_{Te} = 0.22$  $\pm 0.01$ . Thus the position of atoms in the structure was determined very approximately to an accuracy of 0.1 A.

As far as other phases are concerned, reports are contradictory. Paper [2] gives the results of a determination of the hexagonal structure of  $Cu_2Te$ , which the author considers stable at room temperature. In a subsequent paper [3], however, this phase could not be found at all. The author observed phases of varying composition  $Cu_{2-x}$  for  $0 \le x \le 0.33$  and determined the periods of two hexagonal phases having complex structure:  $Cu_2Te - a = 12.54 \approx 3a_0$  and  $c = 21.71 \approx 3c_0$ ;  $Cu_3Te_5 - a = 12.45 \approx 3a_0$  and  $c = 21.56 A \approx 3c_0$ . Finally, in [4] the phase  $Cu_5Te_3$  was established within a specified range of homogeneity.

In the present work films of Cu – Te alloys were prepared by sublimation in vacuo of molecular beams of Cu and Te, condensing on the faces of rock salt crystals, previously annealed and held at room temperature. The films were subjected to annealing for various periods at various temperatures. Near the "tellurium edge" of the concentration diagram was observed a diffraction pattern corresponding to



Fig. 1. Electron diffraction photograph of the rhombic phase of CuTe.

laminar texture of crystallites of the rhombic phase with the c axis (Fig. 1).

A picture taken at an oblique angle to the beam gave the spacings: a = 3.10; b = 4.02; c = 6.86 A, differing slightly from the x-ray data indicated above. Similar samples were obtained by annealing films for ~1.5 h at 80°C and for 30 min at 200°C.

Films corresponding to a large copper content were also submitted to around two hours annealing at 100°C, and photographs showed the presence of three hexagonal phases  $\beta^{I}$ ,  $\beta^{II}$ , and  $\beta^{III}$ , beside CuTe. The spacings of these phases were approximately integral multiples of  $a_0 = 4.24$  and  $c_0 = 7.29$  A;  $\beta^{I} - 2a_0$  and  $c_0$ ;  $\beta^{II} - 2a_0$  and  $3c_0$ ;  $\beta^{III} - 2a_0$  and  $5c_0$ .



Fig. 2. Electron diffraction photograph of the  $\beta^{III}$  phase.



Fig. 3. Section of  $\Phi$ -series in the (100) plane for the rhombic phase CuTe.

More exact measurement of the spacings, using electron diffraction patterns of oblique textures from various film samples of phase  $\beta^{I}$  showed a certain scatter: sample I – a = 8.29; c = 7.22 A; sample II – a = 8.31; c = 7.20 A; sample III – a = 8.32; c = 7.25 A; sample IV – a = 8.33; c = 7.26 A.

In spite of the large number of experiments carried out, no phase with spacings  $a_0$  and  $c_0$  was observed; however, in the photograph of Fig. 2, taken with a  $\beta^{\text{III}}$ -phase sample, reflections corresponding to these spacings are outstanding in sharpness and intensity.

We proceeded to check the structure of the rhombic phase. Using microphotometer and visual methods and also density marks, we determined the intensities of almost 200 reflections on photographs of oblique textures. Construction of  $\Phi^2$ - and  $\Phi$ - series enabled us to confirm the structural model proposed in [1] and to obtain more accurate parameter values:  $z_{Te} = 0.223$ ;  $z_{Cu} = 0.449$  (Fig. 3).

One may try to interpret the picture (Fig. 2) of



Fig. 4. Section of  $\Phi^2$ -series along  $[1/3^2/3 z]$  for the "small" cell.

the  $\beta^{\text{III}}$ -phase mentioned above as diffraction from a superstructure formed of the phases described in [2]. The formation of the superstructure may be a result of the ordered replacement of part of the Te atoms by atoms of Cu. To check this proposition we calculated a one-dimensional section of the  $\Phi^2$ series in the direction  $[1/3^{2}/_{3}z]$  in the "small cell" with axes  $a_0$  and  $c_0$ . In this calculation we used values of  $\Phi^2$  (from experimental intensities) of around 40 reflections corresponding to the "small cell." A strong maximum would have been expected in this section for  $z \cong c/3$  (Cu - Cu vector). However no such maximum appeared (Fig. 4).

For the structure  $\beta^1$  we calculated, by means 2. of the experimental intensities of all (around 200) 3. the reflections (Fig. 2), the sections of the  $\Phi^2$ -series 4. in the directions  $[1/_6 5/_6 z]$ ,  $[1/_6 1/_3 z]$ ,  $[1/_3 1/_6 z]$ , and  $[1/_3 2/_3 z]$  (large cell: 2a<sub>0</sub>) (Fig. 5). Here also



Fig. 5. Sections of  $\Phi^2$  series in the direction  $[{}^{1}/_{6}{}^{5}/_{6} z], [{}^{1}/_{6}{}^{1}/_{3} z], [{}^{1}/_{3}{}^{1}/_{6} z], and [{}^{1}/_{3}{}^{2}/_{3} z].$ Notation ----, ---, ---- for the hexagonal  $\beta^{I}$  phase.

there was no maximum for z = c/3. Another important absence is that of a maximum at z = 0. Thus the structure described in [2] is not confirmed by our experiments.

Work on the structural study of phases in the system mentioned is continuing.

E. E. Malitskii participated in the work.

## LITERATURE CITED

- K. Anderko and K. Schubert, Z. Metallkunde, 45, 371-378 (1954).
- 2. H. Nowotny, Z. Metallkunde, 37, 40-42 (1946).
- 3. L. Patzak, Z. Metallkunde, 47, 418-420 (1956).
  - M. Khansen and K. Anderko, Structure of Binary Alloys [in Russian] (1962), Vol. 2, pp. 682-684.