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Crystal structure of synthesized $CuGaTe_2$ determined by X-ray powder diffraction using the Rietveld method

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A full profile X-ray powder diffraction structure refinement has been carried out on a sample of synthesized $CuGaTe_2$ using graphite monocromatized CuK_α step-scan data and a profile shape of the Pearson VII type. The most satisfactory convergence was achieved at $R_p = 0.0666$, $R_{wp} = 0.0884$, $R_B = 0.0106$ and $R_F = 0.0102$. The derived structural parameters at 26.5 °C are: $a = 0.602\,348(7)$, $c = 1.193\,979(2)$ nm and $x(\text{Te}) = 0.256(6)$. The ratio between lattice parameters, $\eta = c/2a = 0.9911\ (0)$, differs from 1.0, indicating a tetragonal distortion, and non-ideal anion displacements, $x(\text{Te}) \neq 1/4$, is manifested by the existence of bond alternation of Cu–Te and Ga–Te with interatomic distances of 0.262(5) and 0.2578(5) nm, respectively. These results show a light tetrahedral deformation produced by four-fold tetrahedra of the copper cation in the $CuGaTe_2$ chalcopyrite-type structure.

1. Introduction

The ternary ABC_2 chalcopyrites (A = Cu and Ag, B = Al, Ga and In, and C = S, Se and Te) form a group of semiconducting materials with diverse optical, electrical and structural properties [1]. These materials show some interesting structural anomalies [1–4] relative to their binary analogue zinc-blende lattices. First, rather than a single cation, the ternary chalcopyrites have two cations. Second, these often show a tetragonal distortion where the ratio between the lattice parameters, $\eta = c/2a$ (tetragonal deformation), differs from 1 by as much as 12%. Third, the anions are displaced from zinc-blende sites. So, in binary AC zinc-blende compounds, each cation A has four anions C as nearest neighbours (and vice-versa), whereas in a ternary chalcopyrite ABC_2, each cation A and B has four anions C as nearest neighbours, and each anion has two A and two B cations as nearest neighbours. As a result, the anion C usually adopts an equilibrium position closer to one pair of cations than to the other, that is, unequal bond lengths $R_{AC} \neq R_{BC}$ (bond alternation).

The crystal structure of the ternary chalcopyrites belongs to the non-symmorphic space group D_{2d}^{12} $I\bar{4}2d$ with the A cation site 4a at (0 0 0), the B cation in site 4b at $(0\,0\,\frac{1}{2})$, and the C anion in site 8d at $(x\ \frac{1}{4}\ \frac{1}{8})$ when the origin is at 4a [3]. The structure then requires only three parameters (excluding thermal vibration coefficients) to describe its atomic arrangement completely: the unit cell parameters a and c, and the anion positional coordinate x, called $x(\text{Te})$ in this paper. When $x = 1/4$, the chalcopyrite-type has the ideal structure, with no tetrahedral distortions.

Jaffe and Zunger [3] studied the changes in the electronic band gaps induced by structural variation. They found a simple empirical adjustment that corrected the band gaps with structural parameters (anion displacements, x, tetragonal distortion, $\eta = c/2a$, and unit cell parameter, a), obtaining a good agreement with experimental values. The accurate determination of these parameters is of great interest in the study of electronic band structure.

Consequently, the present study of synthesized $CuGaTe_2$ was carried out (1) in order to accurately characterize the crystal structure of this important material, and (2) as part of a broader investigation into the application of full-profile Rietveld-type powder diffraction structure refinement methods in the case of two-wavelength X-ray data obtained from a conventional automatized step-scan diffractometer. In a further work we will try to relate the structural parameters with the changes in the electronic band gap.

2. Experimental procedure

The difficulties of obtaining $CuGaTe_2$ single crystals [1, 5] led us to attempt the growth of homogeneous polycrystalline samples. Synthesis was carried out in an evacuated silica glass ampoule using elements of 99.999% purity. The heating and cooling cycle is described in Fig. 1. The quartz tube was heated up to 1130 °C avoiding over pressures. The cooling rate was especially low, 5–10 °C h^{-1}, across the phase transitions.

Powder diffractometer data were collected with an automatic step-scanning Siemens D-500 powder diffraction system. CuK_α ($\lambda = 0.154\,184$ nm) radiation was utilized. The divergence slits located in the incident beam were selected to ensure complete illumination of the specimen surface at 12°(2θ). The powder

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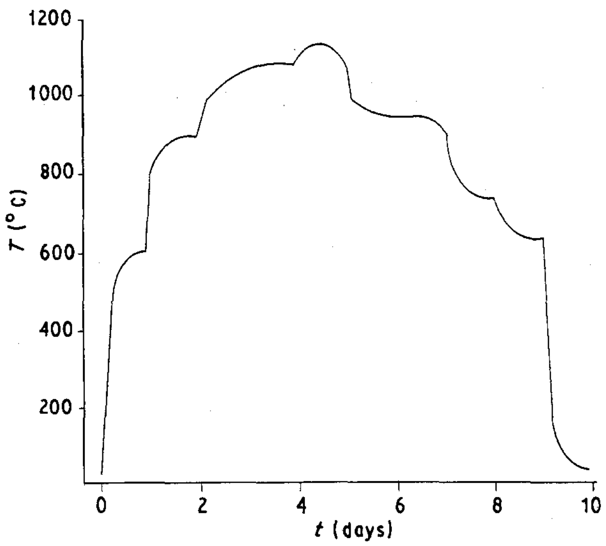

Figure 1 Diagram of the thermal cycle used to synthesize the $CuGaTe_2$ sample.

diffraction pattern was scanned in steps of 0.02°(2θ), and fixed-time counting (4 s) was employed. At the end of the data collection, the stability of the intensity of the incident beam was checked by recording the first lines of the pattern. All experiments were carried out at constant temperature of 26.5 °C. These conditions allowed the collection of profile data for a total of 118 Bragg reflections with background counts in the range 70–200 and a maximum peak intensity of 5800 counts. Data-collection parameters for the sample are listed in Table I.

To minimize preferred orientation effects due to the layer morphology of the crystallites, the $CuGaTe_2$ was ground in an agate mortar 1/4 h, and a sideloading method was used to prepare the sample for the diffractometer. Finally, the sample was repacked and rerun three times at a 0.04°(2θ) step-scan and counting time per step of 1 s to check for evidence of preferred orientation. Some changes in the intensity of the 0 2 4 peak were noticed between the three data sets, suggesting that preferred orientation effects can be relatively high according to this h k l vector direction.

TABLE I Data-collection parameters

Radiation	CuK_α ($\lambda = 0.154\,184$ nm)
Wavelengths	$\lambda_1 = 0.154\,060$ nm, $\lambda_2 = 0.154\,443$ nm
Detector	Scintillation
Monocromator	Graphite (diffracted beam)
Slits	
Primary	1°
Receiving	0.15°
Soller	Incident, diffracted
Scan	
Range (deg 2θ)	20–90
Step size (deg 2θ)	0.02
Time/step (s)	4
Temperature (°C)	26.5

3. Structure refinement

The least-squares structure refinements were undertaken with the full-profile, Rietveld-type, program DBW3.2S version 8804 [6, 7] locally modified for Schneider [8] for IBM-AT compatible microcomputers.

The observed X-ray powder profile for the $CuGaTe_2$ sample is plotted in Fig. 2. It is obvious that most of the peaks in the pattern appear relatively sharp (FWHM < 0.2° in all diagrams). A Pearson VII

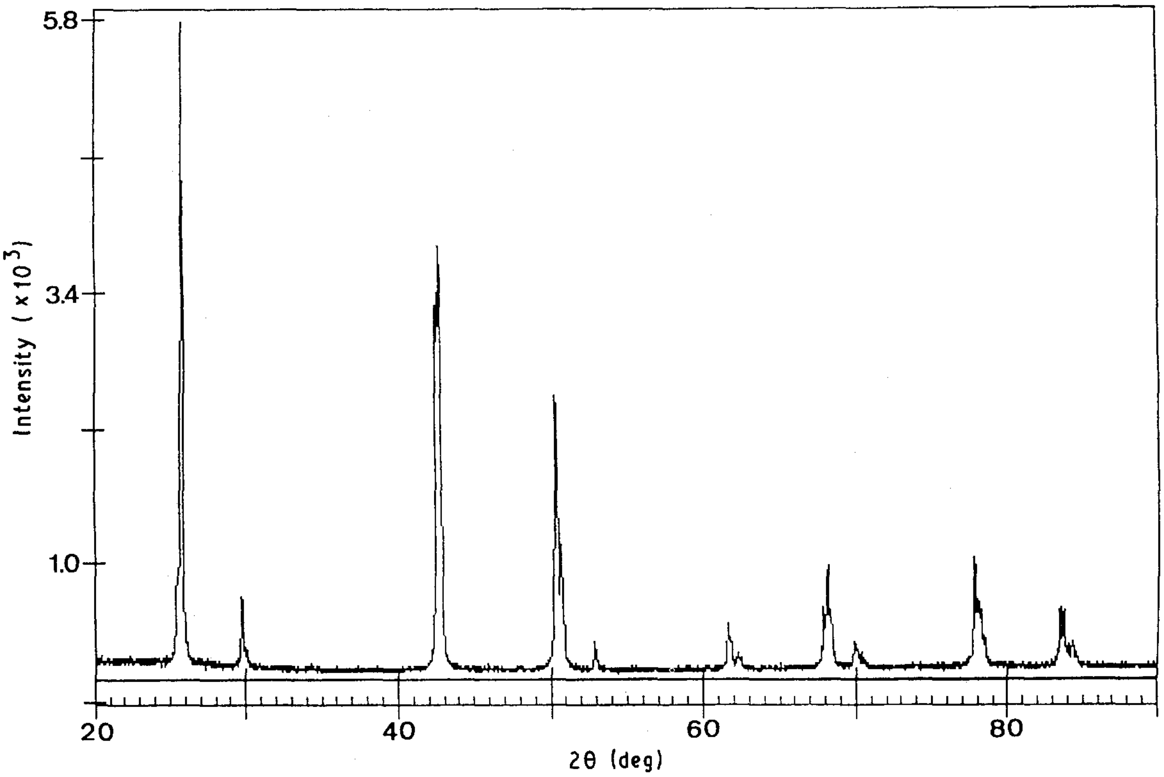

Figure 2 Observed X-ray diffraction pattern for $CuGaTe_2$.

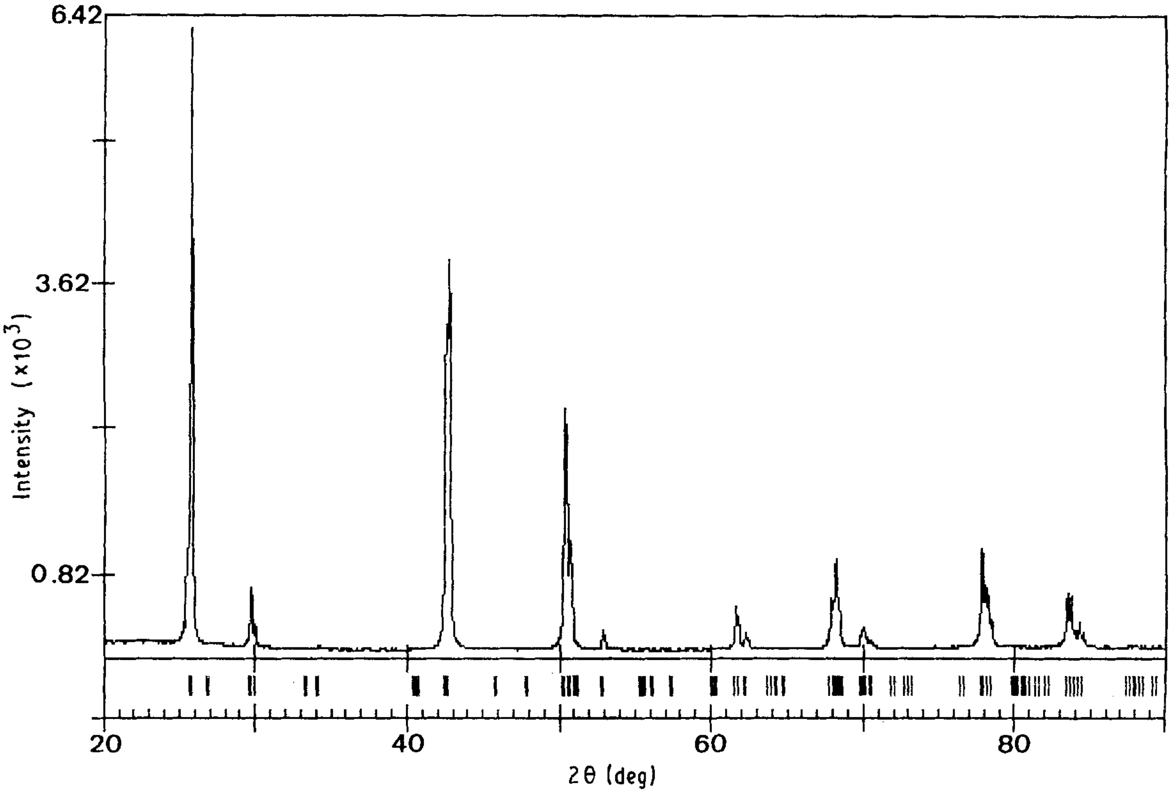

Figure 3 Calculated X-ray diffraction pattern, for $CuGaTe_2$ from the final Rietveld refinement. The vertical markers show positions calculated for the Bragg reflections.

function [9] was used for representation of the profile; in this powerful function, the parameter m can be refined as a function of 2θ as

$$m = NA + NB/2\theta + NC/(2\theta)^2 \qquad (1)$$

where the refinable variables are NA, NB and NC.

On the other hand, this program can accept X-ray data obtained from a conventional diffractometer, because it allows the simultaneous refinement of two wavelengths (i.e. α_2 and α_1) if their intensity ratio is known (0.5 in the present case). The weight assigned to the intensity observed at each step i in the pattern is $W_i = 1/Y_{io}$ and the function minimized in the least-squares procedures is $W_i(Y_{io} - Y_{ic})^2$, where Y_{io} and Y_{ic} are the observed and calculated intensities at point i in the pattern included the background intensity points, respectively.

The refined quantities were a C-scale factor, a 2θ zero shift parameter, and the Pearson VII profile shape parameters NA, NB and NC; these two last parameters were refined in the final cycles. A peak full width at half maximum (FWHM) function described by the usual quadratic form in tan(θ)

$$\mathrm{FWHM}^2 = U\tan^2(\theta) + V\tan(\theta) + W \qquad (2)$$

where U, V and W are parameters whose values were refined. This function was calculated for 3.5 half-widths on either side of the peak position. A peak asymmetry parameter P, the unit cell constants a and c, and x coordinate of the tellurium atom, x(Te), and isotropic thermal parameters, B, for all three atoms were also refined. The background intensity was evaluated in regions without contribution from Bragg reflections, and linear interpolation of these values led to the background correction. The last variable to be refined was the preferred-orientation factor G_1.

The refinements were initiated using $a = 0.600\,00$ nm, $c = 1.190\,00$ nm, $x = 0.2500$, $NA = 0.4$, $NB = NC = 0.0$, $B(\mathrm{Cu}) = B(\mathrm{Ga}) = 1.2 \times 10^{-2}$ nm^2, $B(\mathrm{Te}) = 1.3 \times 10^{-2}$ nm^2 and a scale factor and a half-width parameters ($U = V = 0$ and $W = 0.04$), estimated by inspection of the observed diffraction pattern. The complete set of results for the best-fit model are given in Table II. Fig. 3 shows the calculated X-ray powder profile for the $CuGaTe_2$ for the final Rietveld refinement. A plot of the observed, calculated and difference profiles for the final refinement is given in Fig. 4. A list of observed and calculated integrated peak intensities, together with their d-spacings is given in Table III.

4. Discussion

4.1. Discrepancy indices

The quantities used to estimate the agreement between the observations and the model during the course of the Rietveld refinement can be written as:

The profile $R_p = \Sigma|Y_{io} - (1/C)Y_{ic}|/\Sigma|Y_{io}|$,

The weighted profile

$R_{wp} = |\Sigma W_i[Y_{io} - (1/C)Y_{ic}]^2/\Sigma W_i[Y_{io}]^2|^{1/2}$

The Bragg $R_B = R_I = \Sigma|I_o - I_c|/\Sigma I_o$

The structure factor

$R_F = \Sigma|I_o^{1/2} - I_c^{1/2}|\Sigma I_o^{1/2}$

The expected $R_{exp} = R_E = |(N - P)/\Sigma W_i[Y_{io}]^{1/2}|^{1/2}$

The goodness of fit $\mathrm{GF} = |R_{wp}/R_{exp}|^2$.

The quantity, C, is the refinable scale factor. The values Y_{io} and Y_{ic} are the observed and calculated

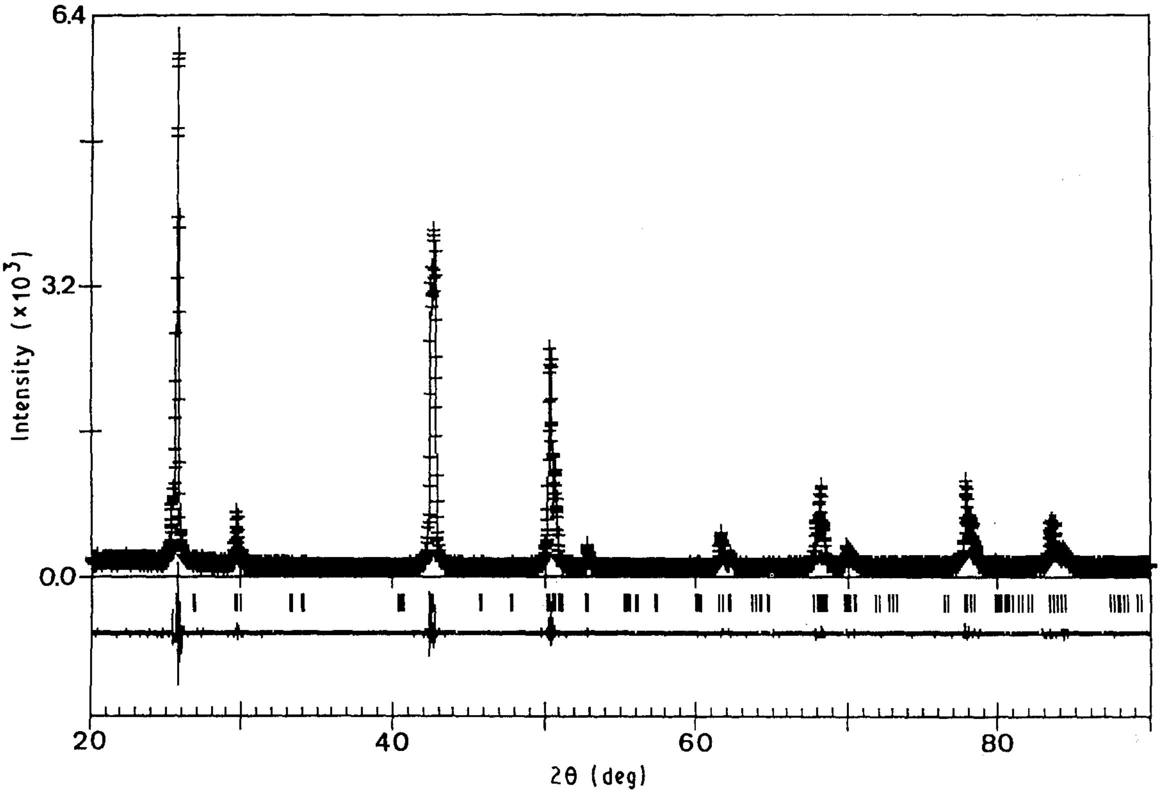

Figure 4 The final Rietveld refinement plot of $CuGaTe_2$ from the Siemens D-500 data. The upper trace shows the observed data by pluses, and the calculated pattern is shown as a solid line. The lower trace is a plot of the difference: observed minus calculated. The vertical markers show positions calculated for the Bragg reflections.

intensities at point i in the pattern included the background intensity points. In this case the number of intensity points is 3501. The observed and calculated integrated Bragg intensities are denoted I_o and I_c, where the observed intensities are calculated by partitioning the raw data in accordance with the calculated intensities of the component peaks. The number of step intensities and parameters refined are denoted N and P, respectively. N is normally the number of step intensities within the integration range of the Bragg reflections.

The quantity minimized in a Rietveld refinement is the weighted profile R-value, R_{wp}, but its numerical value may be somewhat misleading. Thus it is not the value of the minimum reached in the weighted profile R-factor but the structure parameter set (R_B and R_F)

TABLE II Final Rietveld refinement parameters for $CuGaTe_2$

Cell dimensions	$a = 0.602\,348(7)$ nm $c = 1.193\,979(2)$ nm	
Volume	$0.433\,20(4)$ nm^3	
Tetrahedral distortion	$u(\text{exp}) = x(\text{Te}) = 0.256(6)$	
Isotropic temperature factors	(10^{-2} nm^2) $B(\text{Cu}) = 1.1(4)$ $B(\text{Ga}) = 1.3(4)$ $B(\text{Te}) = 1.2(6)$	
Pearson VII coefficients	$NA = -0.43(2)$ $NB = 156.(0)$ $NC = -3270.(0)$	
Asymmetry parameter	$P = 1.89(8)$	
Preferred orientation coefficient	$G_1 = 0.36(1)$	
FWHM function parameters	$U = -0.102(4)$ $V = 0.133(2)$ $W = -0.014(2)$	
Zero-shift	0.073(2)	
Scale factor	$0.16(2) \times 10^{-6}$	
Bragg reflections	118 (2 × 59)	
Parameters	18	
Agreement indices	R_p	0.0666
	R_{wp}	0.0884
	R-expected	0.0649
	R-Bragg	0.0106
	R-structure factors	0.0102
	Goodness of fit (GF)	1.8550

Values in parentheses are estimated standard deviations in the last place.

TABLE III Observed and calculated integrated peak intensities and d-spacings for $CuGaTe_2$ reflections with intensities greater than 1% of the maximum calculated value.

hkl	d (nm)	I_o	I_c
1 1 2	0.346 73	100.3	100.0
0 2 0	0.301 17	9.4	9.2
0 0 4	0.298 50	4.4	4.5
2 2 0	0.212 96	49.5	48.5
0 2 4	0.212 01	64.9	64.4
1 3 2	0.181 47	50.2	49.2
1 1 6	0.180 29	24.3	24.2
2 2 4	0.173 36	4.0	3.9
0 4 0	0.150 59	13.6	13.7
0 0 8	0.149 25	6.6	6.7
3 3 2	0.138 12	11.9	11.9
1 3 6	0.137 60	18.8	18.5
2 4 0	0.134 69	2.2	2.2
0 4 4	0.134 45	1.7	1.7
0 2 8	0.133 73	1.8	1.7
2 4 4	0.122 77	24.7	24.6
2 2 8	0.122 22	12.2	12.2
1 5 2	0.115 88	11.9	11.9
3 3 6	0.115 58	5.9	5.9
1 1 10	0.114 97	5.9	5.9

obtained from the minimum which is of importance. After Rietveld refinement, the obtained agreement indices $R_B = 0.0106$ and $R_F = 0.0102$ indicate the same degree of confidence as for a single-crystal refinement and thus that the $CuGaTe_2$ structure is correct. Obviously, other criteria must be used along with the agreement indices discussed to assess accurately the quality of the refined structure. Probably, the most important test of a structure refinement is whether occupancy factors and bond distances and angles make reasonable chemical sense [10].

4.2. Structural parameters

The refined positional parameter for tellurium, $x(\mathrm{Te}) = 0.256(6)$, is very close to the value calculated by Jaffe and Zunger [3] from the "CTB plus $n = n_{\mathrm{tet}}$ rule", using Pauling radii ($u_{\mathrm{calc}} = 0.263$). Refined unit-cell parameters (Table II) show the following values: $a = 0.602\,348(7)$ and $c = 1.193\,979(2)$ nm. For powder patterns having many overlapping reflections, as in the case of $CuGaTe_2$, Rietveld refinement is probably the method of choice for determining accurate unit-cell parameters. Moreover, the 2θ positions of Bragg reflections obtained after Rietveld refinement (Table III) were re-indexing with the program PIRUM for determination of accurate cell parameters from powder data by the method of least squares [11, 12]; the obtained figure of merit was surprisingly high, $M(20) = 1167(0.000\,0015)$ and $F(20) = 724(0.000\,220, 125)$. Note that the lattice parameters determined from the profile refinement, even allowing for the tetragonal symmetry and well-crystallized nature of the sample used, is unusually precise; these results seem to indicate the good fit of the Pearson VII function-type used in the Rietveld refinement.

The interatomic distances and angles resulting from the determined a, c and $x(\mathrm{Te})$ values are summarized in Table IV. The ideal distances of the bond lengths Te–Cu and Te–Ga are, in both cases, $\pm 0.260(5)$ nm calculated from $x(\mathrm{Te}) = \frac{1}{4}$. Note that the differences between these bond lengths and the real ones obtained are 0.023(5) nm in both cases, too. On the other hand, in the ideal structure, the bond angles are 109.48°, whereas in the $CuGaTe_2$ structure studied the Te–Ga–Te angles are 109.59(2)° and 109.20(8)°. These values are very close to the ideal chalcopyrite-type structure. On the contrary, the obtained values for the Te–Cu–Te bond angles 110.61(4)° and 108.84(9)° show a slight deviation from the ideal value. A plot representative of the determined structure is given in Fig. 5.

These results indicate that the structural deformation is essentially due to the four-fold copper in the $CuGaTe_2$ chalcopyrite-type structure.

TABLE IV Bond distances (nm) and angles (deg) for $CuGaTe_2$

[Ga Te_4] tetrahedron		
Ga–Te	[x4]	0.2578(5) nm
Te–Ga–Te	[x3]	109.59(2)°
Te–Te	[x3]	0.4213(5) nm
Te–Ga–Te	[x3]	109.20(8)°
Te–Te	[x3]	0.4233(5) nm
[Cu Te_4] tetrahedron		
Cu–Te	[x4]	0.2624(5) nm
Te–Cu–Te	[x2]	110.61(4)°
Te–Te	[x2]	0.4315(5) nm
Te–Cu–Te	[x4]	108.84(9)°
Te–Te	[x4]	0.4268(5) nm

Shortest distance between cations: Cu–Cu = Cu–Ga = Ga–Ga = 0.4240(5) nm

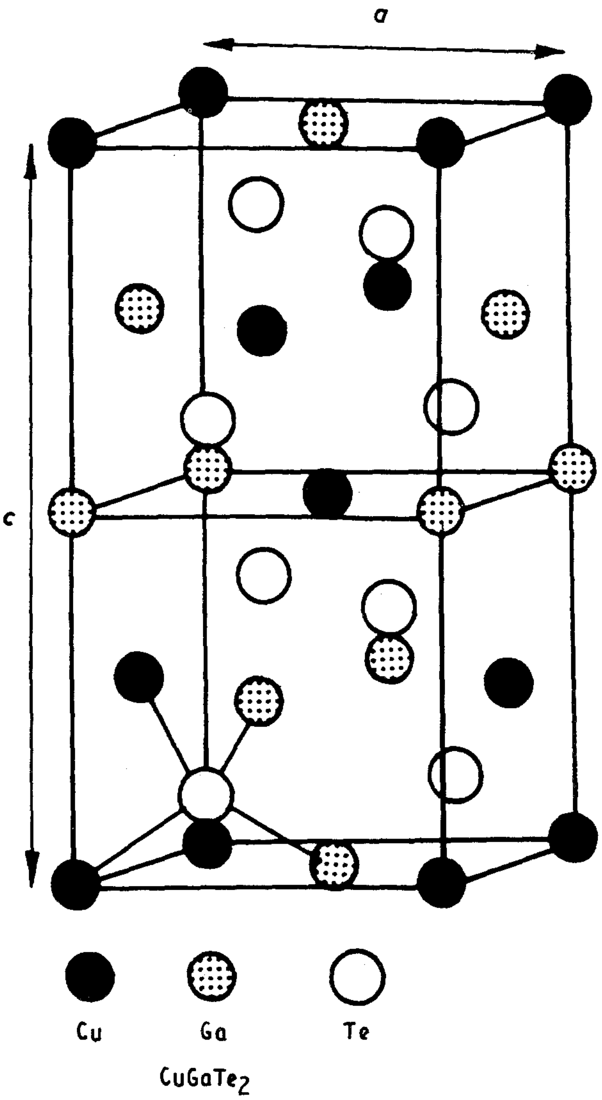

Figure 5 Crystal structure of $CuGaTe_2$, showing the linkage of the $TeCu_2Ga_2$ tetrahedron. The tetrahedron is indicated by the single lines.

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