

## X-ray powder diffraction of $\text{Ag}_2\text{Te}$ at temperatures up to 1123 K

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**Abstract.** X-ray powder diffraction was performed on  $\beta$ - $\text{Ag}_2\text{Te}$  at room temperature, on ion conducting  $\alpha$ - $\text{Ag}_2\text{Te}$  at 523 K, 723 K and 923 K respectively and on  $\gamma$ - $\text{Ag}_2\text{Te}$  at 1123 K.

Rietveld profile refinement of  $\beta$ - $\text{Ag}_2\text{Te}$  confirmed the space group  $P2_1/c$  and the positional parameters of the model of Frueh (Z. Kristallogr. **112** (1959) 44–52).

For the  $\alpha$ -modification in space group  $Fm\bar{3}m$ , best results were obtained for a model with a statistical distribution of Ag ions: about 60% of the available Ag ions were placed into  $32f(x\bar{x}\bar{x})$  positions around the tetrahedral  $8c(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  sites and the remainder on the  $48i(x\bar{x}\frac{1}{2})$  positions. The probability density function (PDF) calculated with these formal structure parameters suggests next neighbour jumps of Ag ions via the  $48i$  sites.

The first structure refinement of  $\gamma$ - $\text{Ag}_2\text{Te}$  showed it to crystallize in space group  $I\bar{m}\bar{3}m$  and to be iso-structural to  $\alpha$ -AgI. Third order anharmonic coefficients of the temperature factor of the Ag ions could be refined from our X-ray powder data. Corresponding PDF maps show Ag-densities bridging next nearest as well as second next nearest neighbours.

### Introduction

Fast silver ion conductors exhibiting the cubic body centered structure like  $\alpha$ -AgI and its structural derivatives,  $\alpha$ - $\text{Ag}_2\text{S}$  or  $\alpha$ - $\text{Ag}_2\text{Se}$ , have attracted much attention (Chandra, 1981). The cubic face centered compound  $\alpha$ - $\text{Ag}_2\text{Te}$  however, was investigated to a much lesser extent. According to

Kracek, Ksanda and Cabri (1966)  $\text{Ag}_2\text{Te}$  shows three polymorphs between ambient temperature and its melting point at 1233 K: The monoclinic, low temperature  $\beta$ -modification (hessite) transforms continuously into the cubic, face centered  $\alpha$ -modification at temperatures ranging from 406 K to 427 K (Mamedov, Gadzhiev and Nurieva, 1977). Depending on stoichiometry, transformation to the body centered cubic  $\gamma$ -modification (Frueh 1961) takes place between 962 K and 1075 K. After contradicting results of earlier authors (see Manolikas 1987) on the crystal symmetry of  $\beta\text{-Ag}_2\text{Te}$ , Frueh (1959) performed X-ray single crystal investigations resulting in the assignment of space group  $P2_1/c$ . Using Patterson methods and least squares refinement he obtained the positional and thermal parameters listed in Table 1. Further X-ray work (Ching-Liang, Imamov and Pinsker, 1961) and electron diffraction (Manolikas, 1987) confirmed Frueh's result. A cell in space group  $P2_1/n$  found by Terao and Berghezan (1975) can be transformed to Frueh's cell. To check the quality of our sample, we reinvestigated monoclinic  $\beta\text{-Ag}_2\text{Te}$  and extended the structure refinement to anisotropic temperature factors.

The first structure determination of  $\alpha\text{-Ag}_2\text{Te}$  was carried out by Rahlfs (1936) on the basis of X-ray powder diffraction films. He proposed space group  $F43m$  and the following structure model: four anions on  $4a(000)$  sites and four cations on tetrahedral  $4d(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  sites form the zincblende structure. The remaining four cations are statistically distributed on the octahedral  $4b(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  sites, on the tetrahedral  $4c(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  sites and on  $16e(x\bar{x}x)$  sites. X-ray powder diffraction data at 523 K led Sakuma and Saitoh (1985) to the assignment of space group  $Fm\bar{3}m$  with Te at  $4a(000)$  sites, 5.2 Ag ions at tetrahedral  $8c(\frac{1}{4}\frac{1}{4}\frac{1}{4})$  sites and 2.8 Ag ions at  $32f(x\bar{x}x)$  sites ( $x = 0.422$ ), respectively. Refinement of a third order thermal parameter at  $8c$  sites was not significant. Okazaki (1977) measured ionic conduction and tracer diffusion of  $\alpha\text{-Ag}_2\text{Te}$ . He successfully explained the resulting Haven ratio by a correlated jump mechanism of cations between tetrahedral and octahedral sites. Tachibana, Kobayaschi and Okazaki (1988) performed molecular dynamics studies of the Ag ion motion. They predicted a decreasing occupation probability of tetrahedral sites with rising temperature, which concurrently flattens out towards the octahedral sites. In order to investigate the temperature dependence of probability density functions (PDF) of  $\alpha\text{-Ag}_2\text{Te}$ , we performed X-ray powder diffraction experiments at 523 K, 723 K, 923 K respectively.

The  $\gamma$ -phase of  $\text{Ag}_2\text{Te}$  at 1098 K was first described by Frueh (1961) with a body centered cubic cell of dimension  $a = 5.29 \text{ \AA}$ . As there were only three reflections visible on a strong background, Frueh proposed a random arrangement of Ag ions based in a framework of Te atoms. However, no detailed structure model existed up to now. X-ray powder diagrams of this modification were thus measured at 1123 K in order to solve the structure and to perform a temperature factor analysis of Ag ions.

**Table 1.** Refined structure parameters of  $\beta$ -Ag<sub>2</sub>Te, (hessite) and agreement values in space group  $P2_1/c$ 

Refinement I: with isotropic temperature factors

Refinement II: with anisotropic temperature factors.

The anisotropic temperature factor coefficients are defined by  $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

Parameter	Frueh (1959)	Refinement I	Refinement II
$a$	[Å]	8.09	8.16172(7)
$b$	[Å]	4.48	4.46650(4)
$c$	[Å]	8.96	8.97348(8)
$\beta$	[°]	123.33	124.1530(4)
Ag(1)	$x$	0.018	0.0196(4)
	$y$	0.152	0.1499(5)
	$z$	0.371	0.3720(4)
	$B[\text{\AA}^2]$	2.02	1.56(5)
	$\beta_{11}$		0.0111(7)
	$\beta_{22}$		0.020(1)
	$\beta_{33}$		0.0054(6)
	$\beta_{12}$		-0.001(1)
	$\beta_{13}$		0.0048(5)
	$\beta_{23}$		0.000(1)
Ag(2)	$x$	0.332	0.3321(3)
	$y$	0.837	0.8398(7)
	$z$	0.995	0.9963(3)
	$B[\text{\AA}^2]$	2.75	2.46(6)
	$\beta_{11}$		0.0097(7)
	$\beta_{22}$		0.041(2)
	$\beta_{33}$		0.0073(6)
	$\beta_{12}$		0.005(1)
	$\beta_{13}$		0.0018(5)
	$\beta_{23}$		-0.0052(9)
Te	$x$	0.272	0.2715(2)
	$y$	0.159	0.1598(5)
	$z$	0.243	0.2428(2)
	$B[\text{\AA}^2]$	1.07	0.74(4)
	$\beta_{11}$		0.0046(5)
	$\beta_{22}$		0.007(1)
	$\beta_{33}$		0.0039(5)
	$\beta_{12}$		-0.0008(8)
	$\beta_{13}$		0.0021(4)
	$\beta_{23}$		0.0000(8)
$R_{wp}$	—	0.040	0.036
$S = R_{wp}/R_{\text{exp}}$	—	1.01	0.92
$R_{\text{Bragg}}$	0.157	0.055	0.043

## Experimental

Sample preparation started from lumps of commercially available (Ventron GmbH) 99.55% purity material. Crushing of the lumps and subsequent powdering was done in a steel mortar immersed in liquid nitrogen to overcome the extreme malleability of the material at room temperature. Abraded material from the steel mortar was separated by a magnet. The powder was then annealed at 130°C for 13 days in an evacuated quartz tube. Measurements were performed on a computer controlled STOE-STADIP focusing powder diffractometer (Wölfel, 1981) equipped with a curved Ge(111) monochromator, where the utilized  $\text{Mo}_{K\alpha 1}$ -line could well be separated ( $\lambda = 0.7093 \text{ \AA}$ ). To shorten measuring time, a STOE linear position sensitive detector (see Wölfel, 1983) filled with 4.4 bar Krypton gas was used. The resulting minimum halfwidth (FWHM) was 0.10 degrees and a step width of  $\Delta 2\theta = 0.02^\circ$  was selected. The 436 Bragg peaks contained in the measurement of  $\beta\text{-Ag}_2\text{Te}$  up to a cut off value of  $2\theta = 47.5^\circ$  ( $\sin\theta/\lambda = 0.57$ ) were considered to yield sufficient information to confirm Frueh's (1959) model. For the measurements at elevated temperatures a cut off value of  $2\theta = 37.5^\circ$  ( $\sin\theta/\lambda = 0.45$ ) was sufficient to measure all possible Bragg peaks which were detectable above the background. The computer controlled STOE stove 0.65.1 was used for measurements at elevated temperatures. The heating element of this stove consists of a current heated graphite tube oriented vertically within the horizontal scattering plane. The sample powder was contained in quartz capillaries of 0.2 mm diameter which were inserted into the graphite tube. This tube is kept in a nitrogen atmosphere to prevent chemical reactions of the graphite with air or moisture. Bores at right angle to the tube axis permit unobstructed pathways for the primary beam as well as for the radiation scattered by the sample. Sample temperatures in the rotating capillary were calibrated by an external standard of gold. The measured density of 3.74 g/cm<sup>3</sup> (packing factor 0.44) yielded a  $\mu \cdot R = 1.0(1)$ . As the sample volume inside the capillary can well be approximated by a cylinder, the corresponding tables of Weber (1967) were used to correct for absorption.

## Results and discussion

### a) $\beta$ -modification, hessite, space group $P2_1/c$

The structure model of Frueh (1959) for the  $\beta$ -modification, space group  $P2_1/c$ , refined readily to the values listed in Table 1. The observed powder pattern diagram together with calculated and difference curves as well as peak position markers is shown in Figure 1a. The Rietveld refinement program WYRIET (Schneider, 1989) was used for refinement of structure parameters of the powder diagrams. This program implements the well

known DBW3.2S code (Sakthivel and Young, 1989) on personal computers. The agreement indices shown in Table 1 to Table 4 are defined in the following way:

weighted pattern <i>R</i> -factor	$R_{wp} = \sqrt{\frac{(\sum_i w_i(y_{oi} - y_{ci})^2)}{\sum_i w_i y_{oi}^2}}$
expected pattern <i>R</i> -factor	$R_{exp} = \sqrt{\frac{(N - P + C)}{\sum_i w_i y_{oi}^2}}$
goodness of fit	$S = R_{wp}/R_{exp}$
Bragg <i>R</i> -factor	$R_{Bragg} = \sum_j  I_{oj} - I_{cj}  / \sum_j I_{oj}$

where  $y_{oi}$  is the observed count at  $2\theta_i$ ,  $y_{ci}$  the calculated count at  $2\theta_i$  and  $w_i = 1/y_{oi}$  is the weight. N, P, C are the number of data points, the number of refined parameters and the number of constraints, respectively.  $I_{oj}$  are the "observed" and  $I_{cj}$  are the calculated integrated intensities of reflection  $j$ . All atoms in  $\beta$ -Ag<sub>2</sub>Te occupy general positions. Therefore the refined structural parameters were: 9 atomic coordinates, 3 isotropic or 18 anisotropic temperature factor coefficients and 4 cell parameters. Furthermore, scale factor,  $2\theta$  zero point as well as the halfwidth parameters  $U$ ,  $V$ ,  $W$ , asymmetry and 2 mixing parameters were refined for the Pearson-VII profile functions selected. A graphically modelled background was used. Refinement of a total of 39 parameters, 1980 data points and 436 Bragg peaks took 142 seconds per refinement cycle on a HP-Vectra (80386/80387 CPU, 20 MHz). Agreement of the refined positional parameters with those of Frueh within 4 estimated standard deviations (e.s.d.'s) is observed. This may be considered as a confirmation of his model although Rietveld e.s.d.'s were shown to depend on step widths and counting times (Hill and Madsen, 1986). Since the cell parameters of Frueh were obtained from Buerger precession photographs, we believe that ours are more accurate. As there are no e.s.d.'s given with Frueh's parameters a more detailed comparison of the results cannot be made. A further lowering of the  $R_{Bragg}$ -value to 0.043 was obtained by refinement of the coefficients of anisotropic temperature factors as shown in Table 1.

### b) $\alpha$ -modification, space group *Fm* $\bar{3}m$

Measurements of the cubic  $\alpha$ -modification were performed at 523 K, 723 K and 923 K, respectively. The diffraction pattern at 723 K is shown in Figure 1 b together with calculated and difference values of model 5 (see below) and peak markers. The modulated diffuse background was interpolated graphically and kept constant during refinement. Due to the high symmetry only 13 distinct Bragg peak positions were available for refinement. Starting with the simple antifluorite structure as model 1, the five structure models listed in Table 2 were tried for Rietveld refinement with the 723 K data set. The modified zincblende model of Rahlfs (1936) partly yielded negative temperature factors and was thus discarded. Model 2 assumes an additional Ag position at the  $4b(\frac{1}{2}\frac{1}{2}\frac{1}{2})$  site. The sum of the

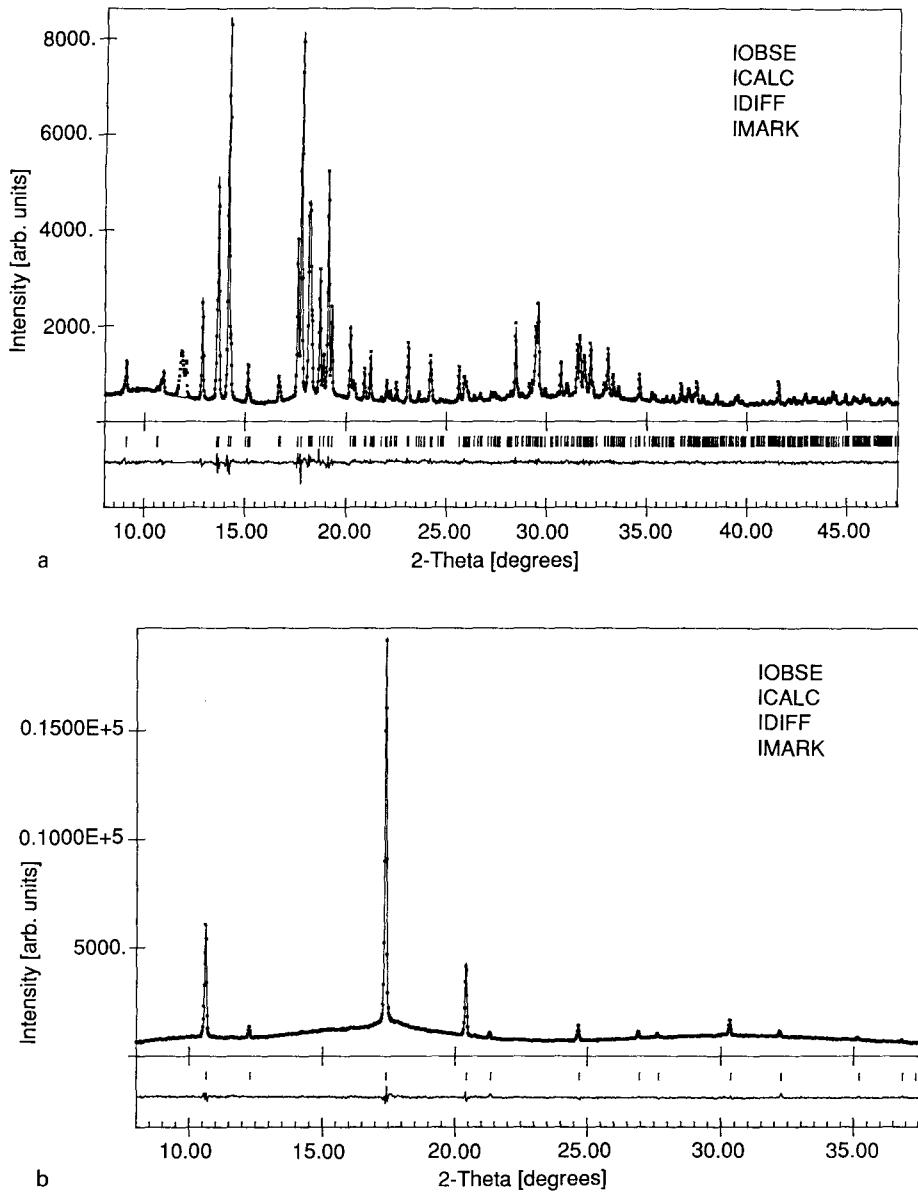
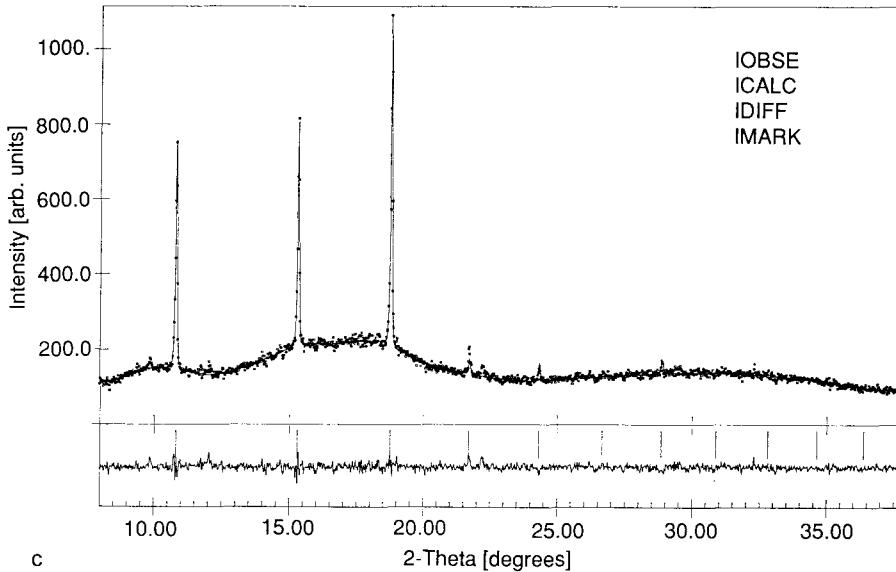


Fig. 1.

occupation of the two Ag sites was constrained to the stoichiometric value, yet individual isotropic temperature factors could be refined. A drastic reduction of  $R_{\text{Bragg}}$  to 0.073 as compared to 0.288 for model 1 resulted.



**Fig. 1.** Observed X-ray powder patterns of  $\text{Ag}_2\text{Te}$  together with refined and difference curves and Bragg peak position markers: a)  $\beta$ - $\text{Ag}_2\text{Te}$  (hessite) at room temperature. (The broad peak at  $2\theta = 12^\circ$  stemming from stray radiation was excluded from refinement.) b)  $\alpha$ - $\text{Ag}_2\text{Te}$  at 723 K as refined by model 5 of Table 2. c)  $\gamma$ - $\text{Ag}_2\text{Te}$  at 1123 K as refined by model 2 of Table 4.

However, geometrical consideration of the octahedral void indicates that the exact  $4b$  site is energetically unfavourable, which is also reflected by its huge temperature factor in model 2. Thus model 3, assuming a cage of 12 atom positions on  $48i(x \times \frac{1}{2})$  sites around the octahedral  $4b$  site was tried. A significant lowering of cation thermal parameters and of  $R_{\text{Bragg}}$  to 0.041 was obtained as seen on Table 2. In model 4 the  $48i$  sites inside the octahedral voids were exchanged for  $32f(x \times x)$  sites. This model closely resembles the model of Sakuma and Saitoh (1985). Due to its lower  $R_{\text{Bragg}}$ -factor model 3 will be preferred however. In model 5 the tetrahedral  $8c$  site was replaced by  $32f(x \times x)$  sites which simulate the anharmonic vibration term of the model of Sakuma and Saitoh (1985). The equivalence of these  $32f$  split atom sites with a third order anharmonic term of the  $8c$  site was already verified in fcc CuI by Yude, Boysen and Schulz (1990). Model 5 may thus be considered as a generalization of model 3. Table 3 lists the parameters of model 5 at the three temperatures indicated. The temperature increase is accompanied by a linear increase of the cell parameter, by a linear increase of the isotropic temperature factor of the Te ions and by a linear increase of  $\beta_{11}$  of the Ag(1) ions. A decrease of Ag ion occupation

**Table 2.** Refinement results for various structure models of  $\alpha$ -Ag<sub>2</sub>Te (space group  $Fm\bar{3}m$ ,  $Z = 4$ ) at 723 K. The sum of the occupation numbers N of Ag(1) and Ag(2) atoms is constrained to the stoichiometric value of 8 per unit cell. In model 4 and model 5 anisotropic temperature factors were refined at the 32f sites.

Model	Atom	Site	<i>x</i>	<i>B</i> [Å <sup>2</sup> ]	N	<i>S</i>	<i>R</i> <sub>Bragg</sub>
1	Te	<i>4a</i> (000)		4.5(2)	4		
	Ag	<i>8c</i> (½ ¼ ¼)		9.7(3)	8	2.69	0.288
2	Te	<i>4a</i> (000)		8.9(1)	4		
	Ag(1)	<i>8c</i> (½ ¼ ¼)		15.0(3)	5.24(5)		
	Ag(2)	<i>4b</i> (½ ½ ½)		36(1)	2.76(5)	1.14	0.073
3	Te	<i>4a</i> (000)		15.5(2)	4		
	Ag(1)	<i>8c</i> (½ ¼ ¼)		9.2(1)	4.08(3)		
	Ag(2)	<i>48i</i> ( <i>xx</i> ½)	0.3777(5)	14.4(4)	3.92(3)	0.92	0.041
4	Te	<i>4a</i> (000)		11.1(1)	4		
	Ag(1)	<i>8c</i> (½ ¼ ¼)		8.6(1)	5.90(5)		
	Ag(2)	<i>32f</i> ( <i>xxx</i> )	0.4015(8)	—	2.10(5)	1.07	0.066
$\beta_{11} = 0.019(2)$ $\beta_{12} = -0.002(1)$							
5	Te	<i>4a</i> (000)	0	15.0(2)	4		
	Ag(1)	<i>32f</i> ( <i>xxx</i> )	0.261(2)	—	4.27(4)		
$\beta_{11} = 0.060(2)$ $\beta_{12} = 0.035(3)$							
	Ag(2)	<i>48i</i> ( <i>xx</i> ½)	0.3813(8)	16.4(6)	3.73(4)	0.89	0.034

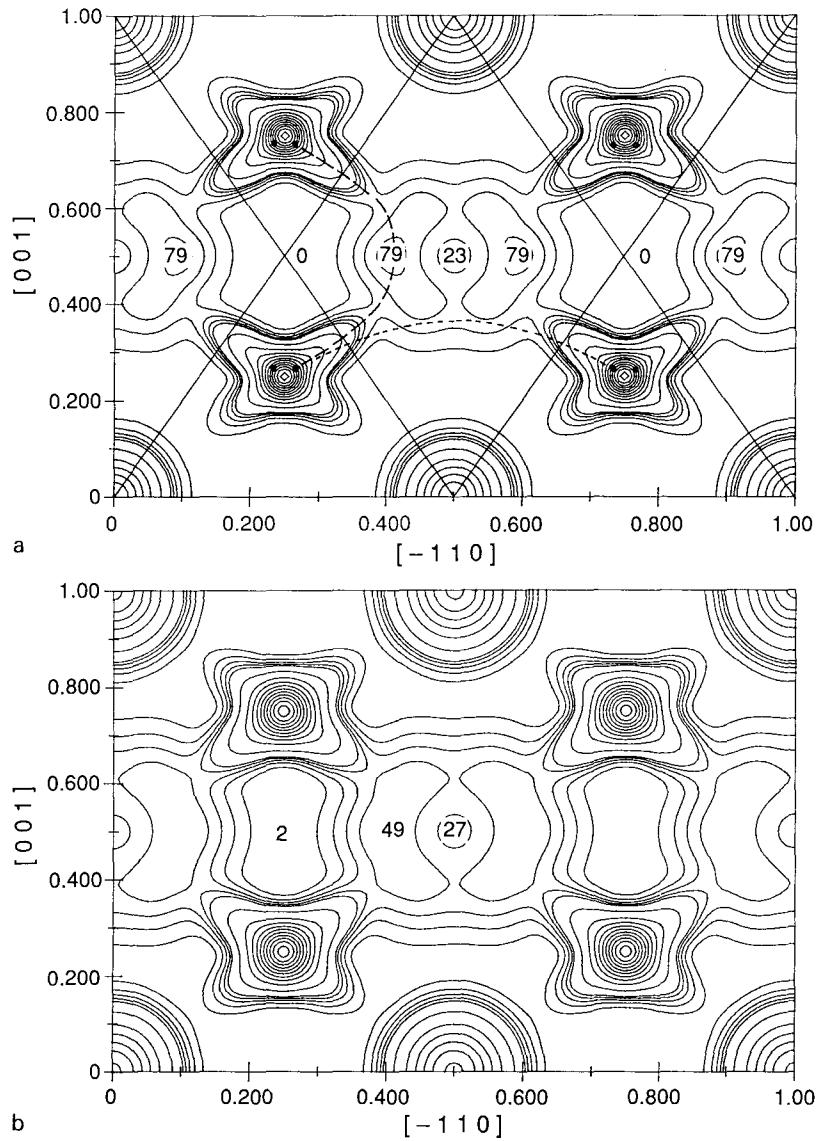
**Table 3.** Temperature dependence of the structure parameters of  $\alpha$ -Ag<sub>2</sub>Te as refined for model 5 (space group  $Fm\bar{3}m$ ,  $Z = 4$ ).

Atom	Site	Parameter	523 K	723 K	923 K
Te Ag(1)	4a	$a[\text{\AA}]$	6.6016(1)	6.6433(1)	6.6808(1)
		$B[\text{\AA}^2]$	10.0(1)	15.0(2)	19.6(3)
	32f	$x$	0.266(1)	0.261(2)	0.255(2)
		$\beta_{11}$	0.051(2)	0.060(2)	0.070(2)
		$\beta_{12}$	0.036(3)	0.035(3)	0.033(4)
		N	5.13(4)	4.27(4)	3.74(4)
Ag(2)	48i	$x$	0.400(1)	0.3813(8)	0.3687(5)
		$B[\text{\AA}^2]$	11.2(7)	16.4(6)	15.2(5)
		N	2.87(4)	3.73(4)	4.26(4)
$R_{\text{wp}}$			0.028	0.029	0.024
$S = R_{\text{wp}}/R_{\text{exp}}$			0.77	0.89	0.77
$R_{\text{Bragg}}$			0.027	0.034	0.037

at the  $32f$  sites within the tetrahedral voids and an increasing Ag ion occupation at the  $48i$  sites can clearly be seen. This fact is in close agreement with predictions of Tachibana, Kobayashi and Okazaki (1988) from molecular dynamics calculations. However, the structure parameters are not to be considered as independent parameters, but they make only sense as they describe best the observed density. In the following they are used to calculate a joint probability density function (PDF, see Zucker and Schulz, 1982). Only this PDF will be discussed. PDF maps obtained by transferring the  $F$ -observed data of model 5 to the PROMETHEUS program system (Zucker, Perenthaler, Kuhs, Bachmann, Schulz, 1983) are shown in Figures 2a, 2b, and 2c. PDF lobes of Ag(1) atoms at  $32f(x \bar{x} \bar{x})$  sites point in  $\langle 111 \rangle$  directions and clearly penetrate the faces of the tetrahedral voids. Local PDF maxima at the center of "V"-shaped ridges are produced by Ag(2) atoms at  $48i(\bar{x} \bar{x} \frac{1}{2})$  sites. This result indicates that Ag(1) atoms perform anharmonic motion around the  $8c(\frac{1}{4} \frac{1}{4} \frac{1}{4})$  sites resulting in jumps to next nearest neighbours via the  $48i(x \bar{x} \frac{1}{2})$  positions. An Ag atom diffusion path anticipated by this structure model is shown in Figure 2a. Starting at the center of the Te tetrahedron it extends in  $\langle 111 \rangle$  directions towards a neighbouring octahedral void. However, after penetration of

**Table 4.** Refinement results for various structure models of  $\gamma\text{-Ag}_2\text{Te}$ , space group  $Im\bar{3}m$ , at 1123 K. The occupation number of Ag atoms is constrained to the stoichiometric value of 4 per unit cell.

Model	Atom	Site	$a, B, U_{ii}$	S	$R_{\text{Bragg}}$
I. Rietveld refinement					
1	Te	$2a(000)$	$B = 12.1(3) \text{ \AA}^2$	0.67	0.093
	Ag	$12d(\frac{1}{4}0\frac{1}{2})$	$B = 24.9(3) \text{ \AA}^2$ $a = 5.3287(3) \text{ \AA}$		
2	Te	$2a(000)$	$B = 13.3(4) \text{ \AA}^2$	0.64	0.063
	Ag	$12d(\frac{1}{4}0\frac{1}{2})$	$u_{11} = 0.32(3) \text{ \AA}$ $u_{22} = 0.36(3) \text{ \AA}$ $u_{33} = u_{22}$ $a = 5.3288(3) \text{ \AA}$		
II. PROMETHEUS refinement					
3	Te	$2a(000)$	$B = 14.9(9) \text{ \AA}^2$	0.018	
	Ag	$12d(\frac{1}{4}0\frac{1}{2})$	$u_{11} = 0.51(6) \text{ \AA}$ $u_{22} = 0.52(5) \text{ \AA}$ $u_{33} = u_{22}$ $C_{133} = 1.5(5) \times 10^{-3}$ $C_{122} = -C_{133}$		



**Fig. 2.**  $(xxz)$ -section of joint probability density function as derived from refinement of  $\alpha\text{-Ag}_2\text{Te}$ : model 5, Table 3. a) 523 K (niveau lines range from 10 to 100 in steps of 20 and from 200 to 2200 in steps of 200). The straight lines indicate traces of the tetrahedral and octahedral faces in the  $(110)$  plane and black dots show the refined  $32f(XXX)$  positions. The dashed line indicates the suggested diffusion pathway to next neighbours and the dotted line a possible diffusion pathway to second next neighbours. b) 723 K (niveau lines range from 10 to 50 in steps of 10 and from 100 to 1000 in steps of 100). c) 923 K (niveau lines range from 10 to 50 in steps of 10 and from 100 to 500 in steps of 100).

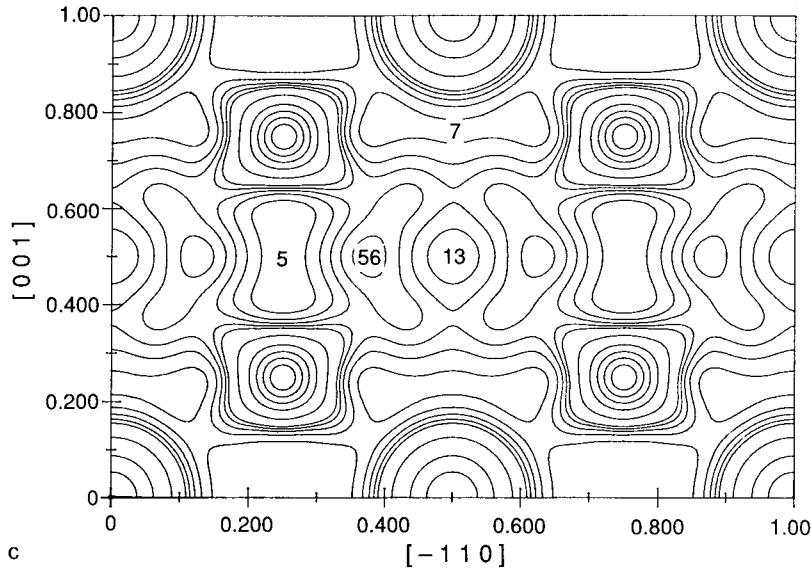
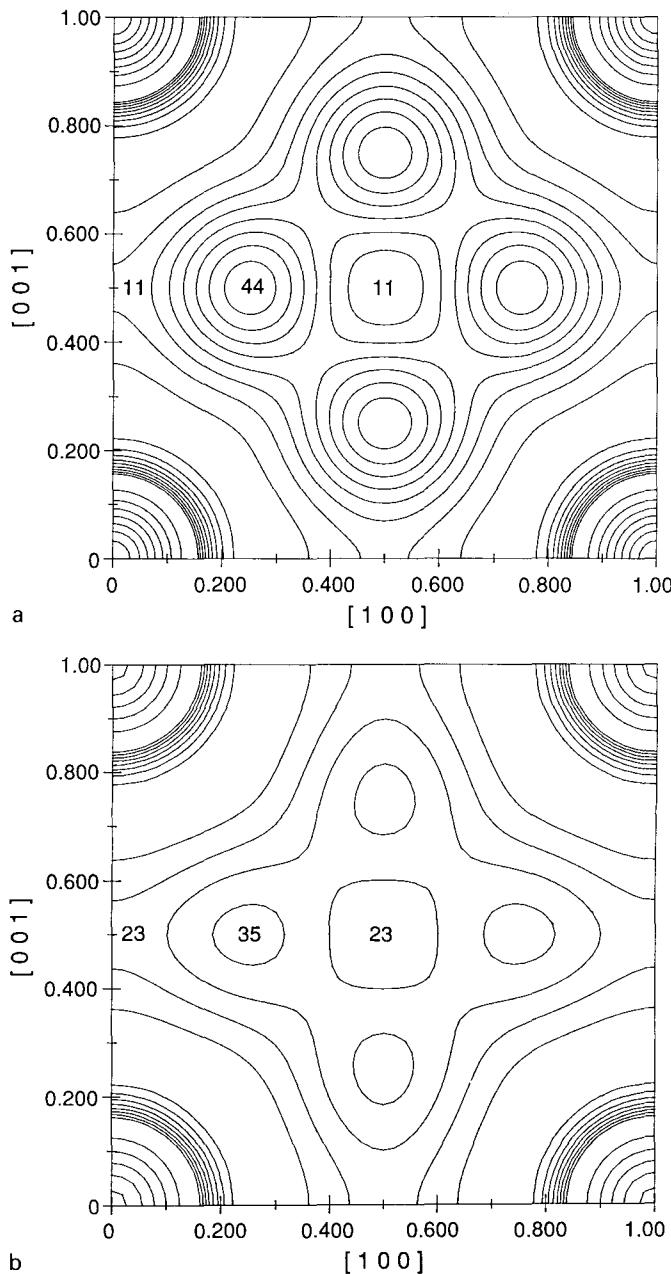


Fig. 2.

the tetrahedron/octahedron face the Ag ions move to a next neighbour tetrahedral position as indicated (dashed line) in Figure 2a. Jumps in  $\langle 001 \rangle$  – direction across tetrahedral edges at  $(\frac{1}{4}\frac{1}{4}\frac{1}{2})$  cannot be seen, however. Figure 2a shows a further diffusion path (dotted line) between second nearest neighbours. This is in contrast to anion conducting fluorite structures like  $\text{PbF}_2$  (Bachmann, 1984) and Ca stabilized Zirconia (Lorenz, Frey, Schulz and Boysen, 1988). Whereas this general behaviour is maintained at the three temperatures measured, inspection of Figures 2a, 2b and 2c clearly reveals a general smearing out of PDF's with rising temperature reflecting an increase of Ag disorder and entropy.

### c) $\gamma$ -modification, space group $Im\bar{3}m$

The X-ray diffraction pattern measured at 1123 K is shown in Figure 1c. The three dominant reflections could be indexed as the (110), (200) and (122) planes of a body centered cubic cell of dimension  $a = 5.3287(3)$  Å. This is in close agreement with  $a = 5.29$  Å obtained by Frueh (1961) from single crystal data at 1098 K. Placing 2Te ions at  $2a(000)$  sites and 4 Ag ions at the tetrahedral  $12d(\frac{1}{4}\frac{1}{4}\frac{1}{2})$  sites (occupancy = 0.33) of space group  $Im\bar{3}m$  the Rietveld refinement converged rapidly to the values of the isotropic model given in Table 4. A remarkable lowering of  $R_{\text{Bragg}}$  from 0.093



**Fig. 3.** ( $x0z$ ) sections of joint probability density function of  $\gamma\text{-Ag}_2\text{Te}$  at 1123 K: a) As derived from refinement of the harmonic, anisotropic model 2 of Table 4. (Niveau lines range from 5 to 50 in steps of 5 and from 100 to 400 in steps of 50). b) As derived from refinement of the anharmonic model 3 of Table 4. (Niveau lines range from 5 to 50 in steps of 10 and from 100 to 300 in steps of 50).

to 0.063 could be achieved by allowing for anisotropic thermal parameters of Ag ions. The resulting r.m.s. displacements of  $u_{11} = 0.32(3)$  Å and of  $u_{22} = u_{33} = 0.36(3)$  Å are comparable to those of Ag ions in  $\alpha\text{-AgI}$  (Cava, Reidinger, Wuensch, 1977), although that investigation was carried out at about 600 K. At this stage the  $F$ -observed data obtained from the Rietveld refinement were transferred to the PROMETHEUS program system. A joint PDF map of the ( $x0z$ ) plane corresponding to the anisotropic model is shown in Figure 3a. In addition to Te atoms at the corners and Ag atoms at their  $12d(\frac{1}{4}0\frac{1}{2})$  sites, density bridges between next nearest Ag neighbours in  $\langle 101 \rangle$  direction as well as bridges between second next nearest neighbours in  $\langle 100 \rangle$  direction can be seen. This suggests ion conduction pathways by respective Ag ion jumps. A shallow minimum of probability is displayed at the octahedral  $6b(\frac{1}{2}0\frac{1}{2})$  site. Subsequent refinement of  $C_{133}$  (Gram-Charlier expansion), the single third order thermal parameter of the Ag positions allowed by their site symmetry, was significant. It removed the anisotropy from the second order parameters  $u_{ii}$  and lowered the  $R_w$ -factor from 0.051 to 0.018. The corresponding joint PDF map is shown in Figure 3b. Reproducing the gross features of the harmonic case (Fig. 3a), it reveals a much more delocalized probability density and hence shallower potentials of Ag ions. The remarkable similarity of Figures 3a, 3b with the corresponding section of partial Fourier syntheses obtained by Cava, Reidinger, Wuensch (1977) from single crystal neutron scattering data of  $\alpha\text{-AgI}$  and by Oliveria, McMullan, Wuensch (1988) from single crystal neutron scattering data of  $\alpha\text{-Ag}_2\text{Se}$  should be emphasized. Some features in the diffraction pattern of the  $\gamma$ -modification, which may be considered as very weak additional reflections, were not taken into account. They may point to a very weak superstructure of the  $\gamma$ -modification. The determination of the average structure by the clearly visible reflections is not affected in such a case. These features may point to a beginning decomposition, which again cannot have an influence on our structure investigation.

## Conclusion

It has been shown that X-ray powder diffraction in combination with careful profile refinement methods can be used to locate itinerant scattering density at so called interstitial positions. Probability density function maps derived from harmonic X-ray Rietveld refinement results were able to indicate possible ion conduction pathways. Subsequent "single crystal" refinement yielded a significant contribution of anharmonic, third order thermal parameters of Ag ions in the first structure refinement of  $\gamma\text{-Ag}_2\text{Te}$ . However, it has to be taken into account, that only the PDF calculated by combination of structure parameters give physically meaningful results.

The single structure parameter itself may be highly correlated to other ones. In any case the structure refinement has to search for the best combination of structure parameters which allow the best description of the observed density.<sup>1</sup>

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<sup>1</sup> Additional material to this paper can be ordered referring to the no. CSD 54308, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

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