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The crystal structure of γ Ag_8GeTe_6, a potential mixed electronic-ionic conductor*

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Abstract. γ Ag_8GeTe_6 belongs to space group $F\bar{4}3m$ with $Z = 4$ and $a = 11.58 \pm 0.02$ Å. The arrangement of the tellurium atoms is almost precisely that of both the magnesium and copper atoms in the Friauf-Laves cubic phase of $MgCu_2$. This arrangement produces 136 tetrahedra per unit cell, of which four are occupied by the Ge atoms. The remainder are divided among two 48-fold, two 16-fold and one 4-fold sets of positions. One of the 16-fold sets of tetrahedra which shares faces with the $GeTe_4$ tetrahedra is empty. The Ag atoms are distributed over the remaining sets with 29 of the 32 in the unit cell being in the two 48-fold sets and 25 in just one of these.

There are many routes whereby the Ag atoms may move through the crystal; in particular the two 48-fold sets themselves form such routes. Not all the Ag atoms are constrained to lie at the near-centers of the tetrahedra; some are closer to particular shared faces. There are substantial differences between the structure reported here and that reported earlier by Rysanek, Laruelle and Katty.

Introduction

Several papers have been published on the subject of one or more of the compounds Ag_8MX_6 where M is Si, Ge or Sn and X is S, Se or Te.

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In memoriam to Prof. Dr. Dr. h.c. Fritz Laves

(These compounds are not formed with all combinations of these elements.) The first preparation of these compounds with $X = S$ and Se was reported by Hahn, Schulze, and Sechser [1]. There followed a series of papers by Gorochov, Fichet, and Flahaut [2], Gorochov and Flahaut [3], and Gorochov [4, 5] which, in general, were investigations of phase diagrams with some minor structural observations. Pistorius and Gorochov [6] carried out high-pressure experiments on the compounds of composition Ag_8MX_6, with special interest in the effect of pressure on the phase transitions [5]. Petrov et al. [7] have reported thermal and electrical conductivities of some of the compounds with $M = Sn$, $X = S$ and Se, and $M = Ge$, $X = S$. At 280° K, the conductivities of the sulfides are $10^{-3}\,\Omega^{-1}\,cm^{-1}$; they are much higher for the selenides, $50-70\,\Omega^{-1}\,cm^{-1}$. Of course these compounds are semiconductors and the conductivities at this temperature will be sensitive to impurity content and/or (what is usually called) "self-doping" or non-stoichiometry. Bendorius et al. [8] have measured the energy gaps of several of the compounds optically. The materials appear to be direct gap semiconductors at 293° K. For the materials these authors investigated, the gaps were between 0.47 eV for Ag_8GeTe_6 and 1.37 eV for Ag_8GeS_6.

The main interest we have in these compounds is their electrical properties, especially because they have the structural features [9] of a solid electrolyte as first pointed out by Rysanek, Laruelle, and Katty [10], who reported a crystal structure for γ Ag_8GeTe_6. As has been pointed out in several papers [9], the electrolytic-conductivity phenomenon in solid electrolytes is so obviously tied to their crystal structures that structural information is absolutely necessary for a clear understanding of a particular solid electrolyte.

The attempt by Rysanek et al. [10] does fall short of the goal, however; their structure itself is surely incorrect in detail. Apects of the structure they report are illogical and this conclusion is supported by the comparison of their calculated with observed structure amplitudes. The authors reported an R value of 7.4% for 119 reflections. However, the list of calculated and observed amplitudes kindly sent to me on request by the Executive Secretary of the International Union of Crystallography contains 118 reflections for which the R value is 10.2%. But even this might be acceptable were it not for the presence of several very large discrepancies for structure amplitudes of moderate magnitude; six of these have discrepancies ≥ 57:

h k l	F_o	F_c	ΔF
10 6 0	180	123	57
8 4 2	153	63	90
17 5 5	98	19	79
7 7 9	289	148	141
9 7 9	167	56	111
11 11 9	170	75	95

These results alone are sufficient to cast doubt on the correctness of the reported structure. The reader will find that the authors' data obtained from film are only qualitatively similar to ours which are counter data, as will be briefly described subsequently.

Relative to the structures of the double-salt halogenide solid electrolytes [9, 11 – 13] on which all our solid electrolyte work has been done to date, the structure of γ Ag_8GeTe_6 has an unusual character. The silver ions are not constrained to the near-centers of the tetrahedra. This and its consequences will be discussed in detail later.

Experimental

G. F. Ruse (of this laboratory) prepared the compound by mixing stoichiometric proportions of the elements (all 5 N or better), and sealing the mixture in a fused silica tube, with inside surface coated with pyrolytic graphite, at approximately 10^{-3} torr. The tube was placed in a furnace and heated from room temperature to 1000° C over a period of 4 h, held at 1000° C for 1 h, then placed in a furnace at 600° C which was then shut off; that is, the specimen was furnace-cooled from 600° C to room temperature.

Small pieces of the material were placed into a sphere grinder [14] similar to that described by Schuyff and Hulscher [15]. (Both are modifications of the original Bond sphere grinder [16].) Two different spherical crystals were aligned along a major axis which was designated the c axis. Buerger precession photographs taken with Ag$K\alpha$ radiation showed that the crystals of γ Ag_8GeTe_6 have diffraction symmetry $m3m$ and are face-centered because reflections hkl are present only when h, k, and l are all odd or all even. The lattice constant obtained is 11.58 ± 0.02 Å, not significantly different from the reported [10] 11.566(2) Å. The volume of the unit cell is 1553 Å^3; the formula weight is 1701.15; the calculated X-ray density is 7.28 g cm^{-3}. The reported [10] measured density is 7.20 g cm^{-3}.

The intensity data were collected with a Buerger-Supper diffractometer automated by a NOVA 1200 computer. Data were collected with both Ag$K\alpha$ and Mo$K\alpha$ radiation; there was good agreement among three sets. The set of data used for the structure refinement was obtained with Mo$K\alpha$ radiation from a crystal of 0.11 mm diameter with balanced Zr and Mo filters. The data collected were those of independent reflections within the range $10^\circ \leq 2\theta \leq 65^\circ$ and $l \leq 8$. Each reciprocal-lattice point was scanned at the rate of 1°/min over the range $(1.5 + 0.5\,Lp)$, where Lp is the Lorentz-polarization-Tunell factor. Background counts were taken at the beginning and at the end of the scan interval at one-quarter the scan time of each scan. Within the range $10^\circ \leq 2\theta \leq 65^\circ$, and $l \leq 8$, a total of 174 independent reflections were measured. Intensities of reflections above this range and for the crystal irradiated, were not significant. Of the 174 reflections 28 were below the 100-count threshold. That is to say, a total of 146 observed amplitudes were used in the refinement.

The linear absorption coefficient, μ, of γ Ag_8GeTe_6 for Mo$K\alpha$ radiation is $21.30\,\mathrm{mm}^{-1}$, from which for $R = 0.11$ mm, $\mu R = 2.34$. The linear absorption coefficient for Ag$K\alpha$ radiation is $10.96\,\mathrm{mm}^{-1}$. (Values of μ/ϱ for these calculations were obtained from Ref. 17.)

Space-group considerations

The probable space groups, based on the diffraction symmetry are $Fm3m$ (O_h^5), $F\bar{4}3m$ (T_d^2), and $F432$ (O^3). A positive piezoelectric effect was reported [10], thus ruling out $Fm3m$ because it is centrosymmetric, and $F432$ which belongs to the only noncentrosymmetric point group, all of whose piezoelectric moduli are identically zero. This leaves $F\bar{4}3m$ as most probable. It should be said, however, that even though such measurement is confirming, it can be recognized almost immediately that any arrangement of the 24 Te atoms possible in $Fm3m$ and $F432$ (the possibilities are identical) would not give a plausible structure. It should also be mentioned, in view of the rather unorthodox results [10], and especially with respect to the atoms designated Te(2), that twinning could not immediately be ruled out as a possibility, for example in the subgroup $F23$ (T^2) of $F\bar{4}3m$.

Determination and refinement of the structure

The 24 Te atoms must be in one 16-fold set, 16*e*, and two 4-fold sets of positions. Having found a large thermal vibration for their Te(2) in 4*d*, Rysanek et al. decided to put them in 24*g*, thus considering them to be disordered. This approach was supported by citing the appearance of a Fourier synthesis. However, the 4*a* positions in which they put their Te(1) atoms are structurally very similar to the 4*d* positions (see later discussion). Also, this change still produced a high β_{11} of 0.019 for Te(2). (It is possible that this is a typographical error in the paper [10].)

The arrangement of the 24 Te atoms distributed over 16*e*, 4*a* and 4*d* produce 136 tetrahedra in the unit cell divided into six crystallographically nonequivalent sets: two 48-fold, two 16-fold, and two 4-fold, one of which is occupied by the four Ge atoms. The remaining sets are left for the Ag atoms. There is no way in which the Ag atoms can be ordered in this structure.

Rysanek et al. placed the Ge atoms in 4*c*, which they say was indicated by the Patterson function. The Ag atoms were placed in six 48*h* sets, two of these said to be near faces of tetrahedra. One may ask why all the higher symmetry sets were generalized to the 48*h* sets and why not the 48-fold to 96-fold sets. An Ag(2,1)—Te(1) distance reported to be 2.4(1) Å is really 1.9 Å and an Ag(2,1)—Te(3) distance given as 2.8(2) Å can be 3.6, 2.9 or 2.1 Å. (See reference 10 for an explanation of the notation Ag(2,1).) The 1.9 Å Ag—Te distance is impossible; the 2.1 Å distance also seems short.

The above criticisms are written mainly to point out why the reported structure did not appear to be correct in detail.

My first approach was to put the Te atoms in 4*a*, 4*d* and 16*e* and the Ge atoms in 4*c* and try to distribute the Ag atoms only over the five sets of sites mentioned earlier. The thought was that our data were better and perhaps this would make the difference. Several least-squares cycles indicated that there was more involved than data accuracy. There was an indication of higher thermal vibration for the 4*d* than for the 4*a* atoms, but not always (see below). I decided to shift the origin by $\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$ and interchange the Ge positions with the other available 4-fold set.

After a number of least-squares cycles, with only selected parameters allowed to vary because of large interactions, the *R* value was reduced to 9.7% for 146 reflections, and it did not seem that any further reduction could be attained with this model. For later reference, it is worthwhile to display the resulting parameters in Table 1. Although no constraint was imposed on the total number of Ag atoms in the unit cell, the calculated total was exactly correct. It will also be noticed in Table 1, that the values of the thermal

Table 1. Final parameter values on constraining the Ag atoms to be distributed only over tetrahedral equilibrium sites ($R = 9.7\%$)

Atom	Position	Multiplier	x	y	z
Te(1)	16*e*	2/3	0.6240(4)	$= x$	$= x$
Te(2)	4*a*	1/6	0	0	0
Te(3)	4*c*	1/6	1/4	1/4	1/4
Ge	4*d*	1/6	3/4	3/4	3/4
Ag(1)	48*h*	0.919(49)	0.920(1)	$= x$	0.243(2)
Ag(2)	48*h*	0.222(26)	0.285(3)	$= x$	0.034(3)
Ag(3)	16*e*	0.115(29)	0.383(5)	$= x$	$= x$
Ag(5)	4*b*	0.078(14)	1/2	1/2	1/2

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	0.0047(1)	$= \beta_{11}$	$= \beta_{11}$	−0.0007(1)	$= \beta_{12}$	$= \beta_{12}$
Te(2)	0.0124(10)	$= \beta_{11}$	$= \beta_{11}$	0	0	0
Te(3)	0.0104(8)	$= \beta_{11}$	$= \beta_{11}$	0	0	0
Ge	0.0033(4)	$= \beta_{11}$	$= \beta_{11}$	0	0	0
Ag(1)	0.0136	$= \beta_{11}$	0.0209	−0.0009	−0.0068	$= \beta_{13}$
Ag(2)	0.0105	$= \beta_{11}$	0.0030	0.0055	−0.0009	$= \beta_{13}$
Ag(3)	0.0114	$= \beta_{11}$	$= \beta_{11}$	−0.0002	$= \beta_{12}$	$= \beta_{12}$
Ag(5)	0.0173	$= \beta_{11}$	$= \beta_{11}$	0	0	0

Note: $\text{Multiplier} = \dfrac{\text{number of atoms per set of sites}}{24}$

parameters of the Te atoms in the two crystallographically nonequivalent sets of 4-fold sites are close, their difference not being really statistically significant.

Actually, the agreement for the larger number of data already looked significantly better than that of the reported data [10]. Nevertheless, there were some large discrepancies, the largest being 64 for the 555 reflection with structure amplitude 302. There were other discrepancies for individual reflections that made it clear that a satisfactory solution had not been found.

Several trials were made by assuming that the crystal was twinned in $F23$. This really only generalized the parameters of the Ag atoms originally in the 48*h* sets of $F\bar{4}3m$, but this approach did not indicate further improvement. There was a strong indication that the remain-

Table 2. Final parameter values of the proposed structure

Atom	Position	Multiplier	x	y	z
Te(1)	16*e*	2/3	0.6233(3)	$=x$	$=x$
Te(2)	4*a*	1/6	0	0	0
Te(3)	4*c*	1/6	1/4	1/4	1/4
Ge	4*d*	1/6	3/4	3/4	3/4
Ag(1)	48*h*	0.719(82)	0.929(2)	$=x$	0.238(3)
Ag(2)	48*h*	0.137(26)	0.287(4)	$=x$	0.037(6)
Ag(3)	16*e*	0.043(17)	0.379(4)	$=x$	$=x$
Ag(5)	4*b*	0.037(9)	1/2	1/2	1/2
Ag(1−2)	96*i*	0.240(57)	0.104(4)	0.220(4)	0.067(4)
Ag(1−1)	24*f*	0.104(17)	0	0	0.213(5)
Ag(1−3)	48*h*	0.043(27)	0.105(10)	$=x$	0.300(4)

Atom	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Te(1)	0.0047(1)	$=\beta_{11}$	$=\beta_{11}$	−0.0007(1)	$=\beta_{12}$	$=\beta_{12}$
Te(2)	0.0130(10)	$=\beta_{11}$	$=\beta_{11}$	0	0	0
Te(3)	0.0105(8)	$=\beta_{11}$	$=\beta_{11}$	0	0	0
Ge	0.0034(4)	$=\beta_{11}$	$=\beta_{11}$	0	0	0
Ag(1)	0.0165(20)	$=\beta_{11}$	0.0171(36)	0.0067(25)	−0.0081(22)	$=\beta_{13}$
Ag(2)	4(1)					
Ag(3)	2(1)					
Ag(5)	6(2)					
Ag(1−2)	3.0(7)					
Ag(1−1)	4.0(8)					
Ag(1−3)	3(3)					

ing discrepancies must, in part, result from failure to obtain the correct distribution of Ag atoms.

It appeared that there must be only one remaining approach as indicated, to some extent, by Rysanek et al. The idea is that in this compound, the mobilities of the Ag ions at room temperature are such that they are not constrained to lie only near the centers of tetrahedra. The most likely places for their motions to be inhibited are near the faces of shared tetrahedra. Positions, Ag(*m*–*n*), initially tried were those half-way between adjacent equilibrium tetrahedral positions. The least-squares calculations rejected all but those shown in Table 2, the list of final parameters. They also indicated that the set of the 16-

Table 3. Observed and calculated structure amplitudes

H	K	FO	FC
***** L = 0 *****			
4	0	48	57
4	2	68	62
4	4	840	884
6	0	443	474
6	2	296	287
6	4	30	32
6	6	401	371
8	0	541	546
8	4	263	232
8	6	59	44
8	8	317	328
10	2	161	125
10	4	56	59
10	6	138	115
10	10	42	36
12	0	161	141
12	2	45	58
12	4	254	259
12	6	49	38
12	8	86	89
12	12	142	123
14	0	40	24
14	2	45	63
14	10	39	38
16	0	126	124
16	4	76	68
***** L = 1 *****			
3	1	341	327
3	3	230	261
5	1	526	564
5	3	234	267
5	5	99	90
7	1	227	235
7	3	212	193
7	5	197	206
7	7	85	88
9	1	169	149
9	3	225	222
9	5	127	132
9	7	154	149
9	9	87	96
11	1	105	107
11	3	126	123
11	5	101	107
11	7	80	96
11	9	75	75
11	11	73	54
13	1	84	102
13	3	99	89
13	5	77	82
13	7	57	58
13	9	60	47
13	11	42	54
15	1	76	74
15	3	45	46
15	5	58	56
15	7	64	52
***** L = 2 *****			
2	2	736	777
4	2	430	433
4	4	181	166
6	2	402	356
6	4	122	135
6	6	406	421
8	2	211	233
8	4	114	121
8	6	122	91
8	8	77	80
10	2	283	287
10	4	140	138
10	6	189	198
10	8	55	61
10	10	155	125
12	2	56	55
12	6	48	57
12	8	32	47
14	2	132	135
14	4	56	44
14	6	131	110
14	10	77	81
***** L = 3 *****			
3	3	738	745
5	3	261	271
5	5	256	231
7	3	134	154
7	5	208	208
7	7	113	109
9	3	103	111
9	5	114	122
9	7	100	108
9	9	118	120
11	3	38	72
11	5	81	92
11	7	94	85
11	9	86	93
13	3	67	80
13	5	83	72
13	7	85	79
13	9	44	61
13	11	50	38
15	3	83	61
15	5	47	56
***** L = 4 *****			
4	4	143	149
6	6	187	190
8	4	464	479
8	6	41	36
8	8	134	119
10	4	28	29
10	6	62	62
10	8	49	55
10	10	61	63
12	4	143	136
12	6	56	50
12	8	146	163
12	12	66	56
14	4	50	46
14	6	59	49
16	4	93	105

Table 3. (continued)

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
*****	L = 5		*****	15	5	81	67	*****	L = 7		*****
5	5	302	303	15	7	31	33	7	7	122	121
7	5	101	116					9	7	115	108
7	7	149	126					9	9	49	67
9	5	97	91	*****	L = 6		*****	11	9	29	49
9	7	106	110	6	6	305	272	11	11	36	41
9	9	85	85	8	6	42	67	13	7	59	44
11	5	93	95	8	8	38	48	13	9	45	39
11	7	67	80	10	6	175	190				
11	9	85	83	10	8	46	57				
11	11	47	45	10	10	93	104	*****	L = 8		*****
13	5	41	52	12	6	63	63	8	8	216	218
13	7	57	59	14	6	84	91	12	8	81	75

Table 4. Threshold and calculated structure amplitudes of unobserved reflections

H	K	FO	FC	H	K	FO	FC	H	K	FO	FC
*****	L = 0		*****	12	10	32	26	14	8	33	6
8	2	26	9	12	12	34	24	*****	L = 5		*****
10	0	29	19	14	8	33	33	13	9	30	37
10	8	33	0	16	2	33	26	*****	L = 6		*****
12	10	37	39	16	4	33	21	12	8	30	22
14	4	36	3	16	6	34	25	12	10	31	21
14	6	36	17	*****	L = 3		*****	14	8	31	13
14	8	38	30	11	11	35	18	*****	L = 7		*****
*****	L = 1		*****	15	7	36	24	11	7	34	28
17	1	33	49								
17	3	33	36	*****	L = 4		*****	*****	L = 8		*****
*****	L = 2		*****	6	4	22	26	10	8	30	27
12	4	29	32	12	10	33	5	10	10	35	17

fold positions sharing faces with the $GeTe_4$ tetrahedra did not contain Ag atoms. (This does not necessarily mean that no Ag atoms pass through them, but it is unlikely that they do at room temperature.) The approach worked well, reducing the R value to 8.0% for 146 observed reflections. The individual agreement improved greatly. For example, for the 555 reflection previously mentioned, ΔF is only 1. Table 3 compares the calculated with observed structure amplitudes. Table 4 gives the threshold values of the unobserved structure amplitudes and the calculated values for these. Seven of the 28 have slightly higher calculated values; if the sum of these differences is added to the numerator of the R ratio, R is increased to 8.2%. For the observed reflections, the standard deviation of a structure amplitude with unit weight is 1.33. The observed data were weighted according to:

$\sigma = 0.07\,(100.0 - F) + 7.0 \quad F < 100.0,$
$\sigma = 0.07\,F \quad F \geq 100.0,$
and $w = 1/\sigma^2$.

In the antepenultimate cycle, only the multipliers and positional parameters of the Ag atoms were allowed to vary because of very large interactions between the thermal parameters and multipliers of these atoms. In this cycle, the largest change in a multiplier was that of Ag(1 − 2), namely 0.16 of the standard error. The remainder of the multipliers changed between 0.03 and 0.14 of a standard error. The standard errors of the multipliers listed in Table 2 are from the antepenultimate cycle. In the last two cycles, the thermal and positional parameters of all atoms were varied. For all Ag atoms but Ag(1), the thermal parameters were taken as isotropic. For Ag(5), they are actually isotropic. In the final cycle, the changes in the parameters of the Te and Ge atoms were between 0.01 and 0.21 of a standard error, the largest being for the thermal parameters of Te(2) and Te(3), 0.14 and 0.21 of a standard error respectively, the correlation coefficient between the two being −0.65. For the Ag atoms, the changes were between 0.03 and 0.45 of a standard error. As can be seen in Table 2, the standard errors for most of the Ag parameters are large.

The least-squares calculations (with space group $F\bar{4}3m$) were performed with the NUCLS5 program [18]. The atomic scattering factors were taken from the paper by Cromer and Mann [19]. Correction for the real parts of anomalous dispersion were taken from reference [17].

Description of the structure

The interatomic distances, calculated with the use of the computer program ORFFEC [20] are listed in Table 5. A projection down the c axis is shown in Figure 1 and a stereoscopic view (almost) down the c axis (out of the paper) is shown in Figure 2. Only the Te and Ge atoms

Table 5. Interatomic distances in γ Ag_8TeGe_6

Te(1) – Te(1) (3)	4.040(12) Å	Te(2) – Te(1) (12)	4.807(4) Å	Te(3) – Te(1) (12)	4.795(4) Å
– Te(1) (3)	4.149(12)	– Te(3) (4)	5.014(4)	– Te(2) (4)	5.014(4)
– Te(2) (3)	4.807(4)				
– Te(3) (3)	4.795(4)				
Ag(1) tetrahedron		Ag(2) tetrahedron		Ag(3) tetrahedron	
Ag(1) – Te(1) (2)	2.83(2) Å	Ag(2) – Te(1) (2)	2.85(5) Å	Ag(3) – Te(1) (3)	2.83(4) Å
– Te(2)	2.98(3)	– Te(2)	3.52(7)	– Te(3)	2.60(8)
– Te(3)	2.94(3)	– Te(3)	2.53(6)	Average	2.77(5)
Average	2.90(3)	Average	2.94(6)	Te(1) – Te(1) (3)	4.040(12)
Te(1) – Te(1)	4.040(12)	Te(1) – Te(1)	4.149(12)	– Te(3) (3)	4.795(4)
Te(1) – Te(2) (2)	4.807(4)	Te(1) – Te(2) (2)	4.807(4)	Average	4.418(8)
Te(1) – Te(3) (2)	4.795(4)	Te(1) – Te(3) (2)	4.795(4)	Ag(3) – Ag(1) (3)	1.83(3)
Te(2) – Te(3)	5.014(4)	Te(2) – Te(3)	5.014(4)	– Ag(5)	2.42(1)
Average	4.710(6)	Average	4.728(6)		
Ag(1) – Ag(1)	2.31(6)	Ag(2) – Ag(1) (2)	1.72(5)		
– Ag(2) (2)	1.72(5)	– Ag(2)	1.20(13)		
– Ag(3)	1.83(3)	– Ag(4)	?		
Ag(4) tetrahedron		Ag(5) tetrahedron		Ge tetrahedron	
Ag(4) – Ag(2) (3)	?	Ag(5) – Te(1) (4)	2.474(7)	Ge – Te(1) (4)	2.540(7)
– Ge (1)	?	Te(1) – Te(1) (6)	4.040(12)	Te(1) – Te(1) (6)	4.149(12)
Te(1) – Te(1) (3)	4.149(12)				
– Te(2) (3)	4.807(4)				
Average	4.478(6)				

Note: The number of equivalent distances is in parentheses at the left of the distance. The standard error is in parentheses at the right

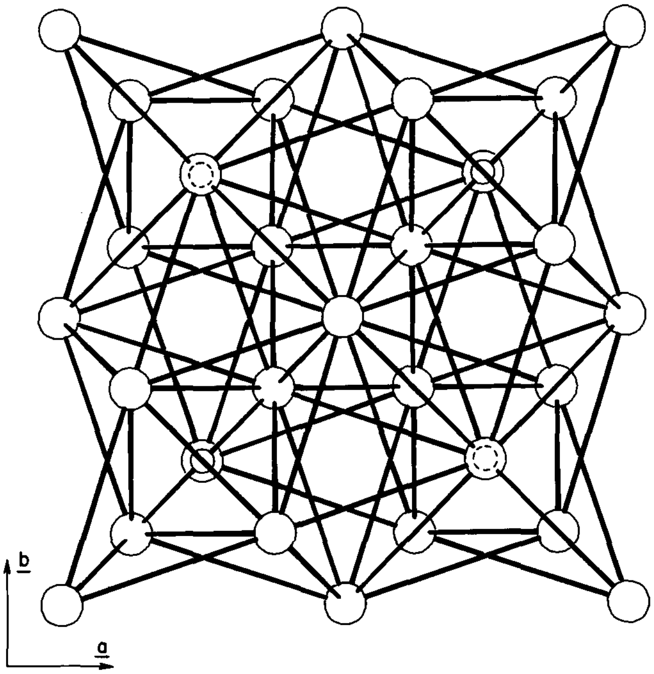

Fig. 1. Projection of the framework of tellurium atoms down the *c* axis. The germanium atoms (smaller circles) are also shown

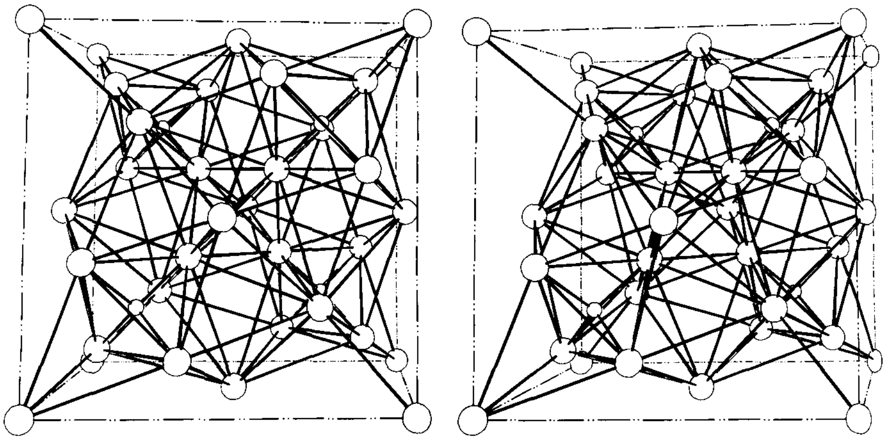

Fig. 2. Stereoscopic drawing of the framework of tellurium atoms looking approximately along the *c* axis (pointing out of the paper). The germanium atoms (smaller circles) are also shown

are shown. These figures were drawn with the use of the computer program ORTEP [21].

One of the most interesting aspects of this structure is that the arrangement of the Te atoms is very nearly the same as the arrangement of both the Mg and Cu atoms in the cubic Friauf-Laves phase [22] of $MgCu_2$. $MgCu_2$ belongs to the space group $Fd3m$. The Mg atoms are in the positions $8a$: $0, 0, 0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}$. The Cu atoms are in $16d$: $\frac{5}{8}, \frac{5}{8}, \frac{5}{8}; \frac{5}{8}, \frac{7}{8}, \frac{7}{8}; \frac{7}{8}, \frac{5}{8}, \frac{7}{8}; \frac{7}{8}, \frac{7}{8}, \frac{5}{8}$ (both sets, of course, are plus face-centering.) If the x parameter of Te(1) were exactly 0.625, the arrangement of the Te atoms in the γ Ag_8GeTe_6 unit cell would be exactly the same as that of the Cu atoms in $MgCu_2$. The Te(2) and Te(3) atoms are in exactly the same positions as the Mg atoms. Thus, the coordination of the Te atoms in γ Ag_8GeTe_6 is the same as the coordination of the Mg and Cu atoms in $MgCu_2$.

In $MgCu_2$ a Mg atom is coordinated to 12 Cu and 4 Mg atoms at distances $a\sqrt{11}/8$ and $a\sqrt{3}/4$ respectively, where a is the lattice constant. For γ Ag_8GeTe_6, with the Te atoms in precisely the $MgCu_2$ arrangement, these distances are 4.801 and 5.014 Å respectively. The first is precisely the average of the Te(2) – Te(1) and Te(3) – Te(1) distances (see Table 5). The second is obviously the precise value for Te(2) – Te(3) (equivalent to Mg – Mg). The Cu – Cu distance in $MgCu_2$ is given by $a\sqrt{2}/4$. For the idealized Te(1) arrangement, one obtains 4.094 Å, which is again the average of the two different Te(1)–Te(1) distances in the actual structure (Table 5).

There are many crystals having structural frameworks that are related to metal structures. The cations of the spinel structure have exactly the same arrangement as the atoms in $MgCu_2$ (first pointed out to me over 20 years ago by Hellner). The cations in the garnet structure have exactly the same arrangement [23] as in, say, Nb_3Sn with the β tungsten structure. The arrangement of the iodides in $RbAg_4I_5$ [24] is close to that of the Mn atoms in β Mn, but the relation is not as close as in the two mentioned immediately above and in γAg_8GeTe_6.

In γ Ag_8GeTe_6, the shifting of the origin by $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ from the arrangement originally given [10], however, brings the relation into focus. It appears that the difficulty with the thermal parameters of Te(2) and Te(3) (Te(2) and Te(1) respectively in reference 10) could have been an artifact of the calculation. In the results reported here, the values are essentially the same, despite a substantial correlation between them.

In Table 2, it will be noticed that the thermal vibrations of Te(2) and Te(3) are much higher than that of Te(1), but this is relatively easily explained. The coordination of the Ge atoms with low thermal vibration is only to Te(1) atoms, and the Te(1) atoms are much more tightly bound to each other than to the Te(2) and Te(3) atoms.

As indicated in Table 5, the Te(1) atoms have 12 coordination to Te atoms which form an icosahedron; the average Te(1) – Te distance is 4.45 ± 0.02 Å. The Te(2) and Te(3) atoms have 16 coordination with Te(2) – Te and Te(3) – Te distances 4.86 ± 0.03 Å and 4.85 ± 0.03 Å respectively. These coordination polyhedra have 28 triangular faces and are sometimes called Friauf polyhedra.

The Ge – Te distance is 2.54 ± 0.02 Å. Pauling's tetrahedral radii [25] for Ge and Te are 1.22 and 1.32 Å respectively, the sum being exactly equal to the observed value.

In Tables 1, 2 and 5, Ag(4) is missing; this is my designation of the 16*e* set which shares faces with the Ge tetrahedra. The approximate value of *x* for Ag(4) is 0.83. However, both models indicated that these sites are empty.

In the Ag(1)-type tetrahedra (which are most highly occupied), the range of Ag – Te distances is lowest. It is not clear, however, that this is directly related to the high occupancy of these sites. The shortest Ag – Te distances are found in Ag(5) tetrahedra but, although the thermal parameter for these sites is large, the calculations did not reject occupancy of these sites. Pauling's tetrahedral radii [25] give 2.84 Å for the Ag – Te distance, to be compared with the averages shown in Table 5. The range of Ag(2) – Te distances is very wide, but the average is very close to that of the Ag(1) – Te distances.

The Ag-Ag distances given in Table 5 are those passing through shared faces and therefore show which tetrahedra share faces with others and the routes that Ag atoms moving through the crystal might take. It is possible for such motion to occur through the Ag(1) and Ag(2) tetrahedra alone. At least at room temperature, most of the Ag ions are at these sites or near the shared faces of their tetrahedra (see later discussion). The total occupancy of the Ag(1) and Ag(2) tetrahedra, obtained by adding the multipliers of Ag(1), Ag(2), Ag(1 – 2) and Ag(1 – 1) is 29 (out of 32) atoms with a standard error of about 3 atoms. Actually most of the atoms are in the Ag(1) tetrahedra: The Ag(1 – 1) atoms and Ag(1 – 2) atoms are much closer to Ag(1) than to Ag(2). The sum of the multipliers is 1.06 for a total of 25.5 atoms in the Ag(1) tetrahedra, with a standard error of 1.7 atoms. Presumably there will be significant changes in the distribution at higher temperatures.

None of Ag(1 − 2), Ag(1 − 1) and Ag(1 − 3) is closer than 2.45(17) Å to any Te atom. The list of distances involving these is long and will not be given here. All the results appear to be plausible. Further discussion of these will be given in the next section.

Further discussion of the results

If we compare the results of Table 1 for the case in which the Ag atoms were constrained to lie at equilibrium tetrahedral sites with those in Table 2 for the case in which atoms were arbitrarily introduced at halfway points between adjacent equilibrium sites, we find consistency. In both cases, the unconstrained sum of Ag atoms came out exactly right in the calculation, even though with substantial standard error. The total occupancy of the Ag(1) sites from Table 1 is 22.0 ($\sigma = 1.2$) atoms compared with 25.5 ($\sigma = 1.7$) from Table 2, a not statistically significant difference. For the total in Ag(1) and Ag(2) sites, from Table 1 we get 27.4 ($\sigma = 1.1$) atoms compared with 29 ($\sigma = 3$) from Table 2. Some differences exist in positional and thermal parameters, but they are not statistically significant either.

It is not the purpose here to emphasize the difference in *R* value alone as indicating that the results of Table 2 are closer to the mark. In fact, the high standard errors of some of the Ag atom parameters in the proposed structure should be disturbing. It is rather the improvement of agreement of calculated with certain observed structure amplitudes that could not be gotten through other arduous approaches that should be emphasized.

The really important conclusion is that the X-ray data in this case "see" a distribution of the Ag atoms more spread-out than in the cases of the many double-salt halogenide, solid-electrolyte structures determined by the author and coworkers. It cannot be only anharmonic motion of the atoms that causes this. It is probable that because of the difference in bonding in chalcogenides and halides, the cation mobilities would be different even if the structures were the same. The mobility of the Ag cations in γ Ag_8GeTe_6 must be less than in all the AgI-based solid electrolytes at room temperature for which structures have been determined to date.

In the calculations, the "atoms" Ag(1 – 2), Ag(1 – 1) and Ag(1 – 3) moved from the positions at which they were introduced. The standard errors of all their parameters are high. It is not the thesis of this work that these are accurately determined positions of maximum electron density. The important points are those made above.

From the results obtained here, it is possible to suggest that if the electrical ionic conductivity of the material increases substantially with temperature, the ionic mobility must increase (assuming the number of mobile cations to be constant or nearly so) and if so the X-rays will not see a spreading out of the distribution over other than the equilibrium sites. This may seem contradictory but it is the resolution time of the X-ray diffraction technique that one must consider here. Of course at the higher temperatures both harmonic and anharmonic contributions to the carrier motions will increase and this could cause considerable difficulty. Nevertheless, we hope to carry out such experiments.

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