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# Ternary Semiconducting Compounds with Sodium Chloride-Like Structure: $AgSbSe_2$, $AgSbTe_2$, $AgBiS_2$, $AgBiSe_2$

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The high temperature modification of $AgSbSe_2$, $AgSbTe_2$, $AgBiS_2$, and $AgBiSe_2$ has a face-centered cubic statistically NaCl-type structure with Ag and Bi (or Sb) atoms distributed indistinguishably and on the average in one set of positions $(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \circlearrowright)$ and the Group VI atoms distributed on the average in the other set of positions $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; 0, 0, \frac{1}{2}; \circlearrowright)$. Because it is extremely unlikely that the Ag, Bi and Sb atoms all have the same effective sizes in these compounds, *at least one* group of atoms ($4(a)$ or $4(b)$) must not be centered exactly at the space group sites.

For $AgSbSe_2$ and $AgSbTe_2$, the cubic structure persists at room temperature. However, in the cases of $AgBiS_2$ and $AgBiSe_2$ an ordering of the Ag and Bi atoms takes place at temperatures well above room temperature. In the case of $AgBiSe_2$ (on which most of the detailed work has been done), above 287 °C., the disordered NaCl-type exists; between 287 °C. and about 120 °C., a rhombohedral phase exists which belongs to space group $D_{3d}(5)$–$R\bar{3}m$ with Ag in $1(a)$: $(0, 0, 0)$, Bi in $1(b)$: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and Se in $2(c)$: $\pm(x, x, x)$ with $x \cong 0{\cdot}26$. The lattice constants of this phase at 240 °C. are $a = 7{\cdot}022$ Å, $\alpha = 34° 40'$. Between 120 °C. and 25 °C. (and probably lower), there is another phase. The most probable space group of this modification is $D_{3d}(3)$–$P\bar{3}ml$ with three formula units per unit cell of dimensions $a = 4{\cdot}18 \pm 0{\cdot}02$, $c = 19{\cdot}67 \pm 0{\cdot}05$ Å. This cell is the original triply primitive hexagonal cell on which the rhombohedral modification may be indexed but with slight additional displacements of the atoms. In particular, pairs of Ag and of Bi atoms are no longer in the most highly specialized positions, and the three pairs of Se atoms are no longer equivalent.

The structure of the room temperature modification has been solved with the use of single crystal and powder X-ray diffraction data. Displacements of the atoms from the ideal positions are not large. Good agreement of calculated with observed intensities is obtained when parameters are adjusted such that the average Ag–Se and Bi–Se distances in $AgBiSe_2$ are 2·83 and 3·01 Å, respectively.

The room temperature form of $AgBiS_2$ is isostructural ($a = 4{\cdot}07 \pm 0{\cdot}02$, $c = 19{\cdot}06 \pm 0{\cdot}05$ Å) with that of $AgBiSe_2$ and presumably has an intermediate form analogous to that of $AgBiSe_2$.

## Introduction

There is now voluminous literature on semiconductors, elements and compounds, with diamond or related structure (e.g. zinc blende and chalcopyrite types). Much less attention has been given compounds with structures related to that of sodium chloride.* Included in two recent communications on new semiconductors (Wernick & Benson, 1957; Wernick *et al.*, 1958*a*) are preliminary results on some ternary compounds with sodium chloride-like structures. These compounds are not ionic; more likely, the bonding is largely covalent—an apparently important characteristic of high mobility semiconductors. Other than the preliminary work reported by us, there do not appear to be any reports in the literature of electrical measurements on ternary compounds with structures related to that of NaCl. Those that have been studied in some detail are the binaries: PbS, PbSe and PbTe.

This report will cover the structural investigations of the high (disordered, statistically NaCl-type), intermediate and low temperature forms of $AgBiSe_2$† and $AgBiS_2$; the room temperature modification of $AgSbSe_2$† and of $AgSbTe_2$† has the disordered (cubic) structure. For the sake of completeness, some results on $AgBiTe_2$† (Wernick *et al.*, 1958*b*) will also be included.

Some work on $AgBiS_2$ has already been done by others. Ramdohr (1938) investigated the mineral matildite, which is essentially $AgBiS_2$, and reported that it had orthorhombic symmetry with cell constants $a = 8{\cdot}14$, $b = 7{\cdot}87$, $c = 5{\cdot}69$ kX. Ramdohr (1938) also found a transition to the disordered structure at about 210 °C., and a lattice constant of 5·73 kX. at 239 °C., which is somewhat high compared with our value (Table 2). These results were obtained from X-ray powder photographs. Graham (1951) synthesized the two forms of $AgBiS_2$ and reported the room temperature form as body-centered orthorhombic with one formula unit per unit cell and with essentially *a*- and *b*-axes half those and *c*-axis equal to that

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* Recently, Euler *et al.* (1957) discussed a number of minerals with structures related to that of NaCl.

† As far as can be ascertained, the compounds $AgSbSe_2$, $AgSbTe_2$, $AgBiSe_2$ and $AgBiTe_2$ are new.

reported by Ramdohr (1938). The results of our studies of the low temperature modification of $AgBiS_2$ (and of isostructural $AgBiSe_2$) are not in agreement with those of either Ramdohr (1938) or Graham (1951).

## Preparation of the compounds

Except for $AgSbS_2$, the compounds were prepared by melting stoichiometric amounts of the component elements in sealed quartz tubes containing a nitrogen pressure of approximately two-thirds atmosphere. The compound $AgSbS_2$ was prepared by reaction of $Ag_2S$ with $Sb_2S_3$.

Single crystals of $AgSbTe_2$ were obtained from an as-cast ingot. The single crystal of the room temperature form of $AgBiSe_2$ used in this study was obtained from a zone-refined ingot. The room temperature form of $AgBiSe_2$ may be obtained simply on furnace cooling, the high temperature form by quenching from above the transition temperature, 287 °C., as found by differential thermal analysis (Wernick *et al.*, 1958*b*). The transformation, at approximately 175 °C., from the high to the intermediate temperature form of $AgBiS_2$, appears to be sluggish; consequently, the room temperature form of $AgBiS_2$ was obtained by annealing a zone-refined sample at 152 °C. for 15 days. No new phases were obtained by annealing samples of the cubic $AgSbSe_2$ and $AgSbTe_2$ compounds for four weeks at 85 °C. and 152 °C. and for 12 days at 180° C.

## Determination of the structures

### *High temperature modification*

Powder photographs of all samples were taken with Cu $K$ radiation using Straumanis type Norelco cameras of 114·6 mm. diameter. Accurate integrated intensity measurements were made on a sample of $AgSbSe_2$ with the Norelco diffractometer (Cu $K\alpha$ radiation).

Examination of the photographs of the high temperature phases indicated that they have the cubic NaCl-type structure with Ag and Sb (or Bi) atoms indistinguishable in the positions: $(0, 0, 0;\ 0, \frac{1}{2}, \frac{1}{2};\ \circlearrowright)$ and the Se (or Te or S) atoms in the positions: $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, 0;\ \circlearrowright)$ (see, however, later discussion). Under this assumption relative intensities were calculated for the compounds $AgSbSe_2$ and $AgSbTe_2$ using the relationship:

$$I_c = p|F_{hkl}|^2 \frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta} \times 10^{-5},$$

where $p$ is the multiplicity and $F_{hkl}$ the structure amplitude. The values of the atomic scattering factors were obtained from the *Internationale Tabellen* (1935). Corrections were made for dispersion (Dauben & Templeton, 1955). Corrections for absorption were not made. (These are not necessary for the diffractometer data.) An isotropic temperature factor determination was made only for $AgSbSe_2$. A surprisingly large value of $B$, 2·35 Å², was obtained; this is probably a consequence of the disordered nature of the structure.

Table 1. *Calculated and observed intensities for* $AgSbSe_2$ *and* $AgSbTe_2$ (Cu *K radiation*)

| | $AgSbSe_2$ | | | | | $AgSbTe_2$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $d$ (Å) | | | | | $d$ (Å) | | | |
| *hkl* | Obs. | Calc. | $I_o$ Visual* | $I_o$ Diffractometer | $I_c$ | Obs. | Calc. | $I_o$ Visual* | $I_c$ |
| 111 | 3·336 | 3·341 | *w–m* | 7·8 | 7·7 | 3·480 | 3·509 | *vvw* | 0·4 |
| 200 | 2·883 | 2·893 | *vs* | 74·7 | 90·0 | 3·033 | 3·039 | *vs* | 190·0 |
| 220 | 2·039 | 2·046 | *s* | 56·0 | 57·1 | 2·144 | 2·149 | *s–vs* | 141·0 |
| 311 | 1·741 | 1·745 | *w* | 3·4 | 2·9 | 1·830 | 1·833 | *vvvw* | 0·2 |
| 222 | 1·668 | 1·670 | *m* | 15·8 | 16·5 | 1·751 | 1·755 | *ms* | 49·6 |
| 400 | 1·446 | 1·447 | *w–m* | 6·8 | 6·5 | 1·518 | 1·520 | *m* | 22·7 |
| 331 | 1·326 | 1·327 | *vvw* | 0·8 | 0·9 | 1·394 | 1·394 | *vvvw* | 0·1 |
| 420 | 1·293 | 1·294 | *m* | 14·5 | 15·0 | 1·357 | 1·359 | *s* | 60·8 |
| 422 | 1·181 | 1·181 | *w–m* | 9·5 | 9·9 | 1·240 | 1·241 | *m–s* | 45·4 |
| 333, 511 | 1·114 | 1·114 | *vvvw* | 0·8 | 0·6 | — | 1·170 | abs. | 0·1 |
| 440† | 1·023 | 1·023 | *w* | 3·6 | 2·7 | 1·075 | 1·074 | *w* | 15·4 |
| 531 | — | 0·9780 | abs. | < 0·8 | 0·5 | — | 1·027 | abs. | 0·1 |
| 600, 442 | 0·9639 | 0·9643 | *w–m* | 4·9 | 5·6 | 1·013 | 1·013 | *m–s* | 35·5 |
| 620 | 0·9145 | 0·9148 | *w* | 3·3 | 3·9 | 0·9607 | 0·9610 | *m* | 27·5 |
| 533 | — | 0·8824 | abs. | 0·0 | 0·2 | — | 0·9269 | abs. | 0·1 |
| 622 | 0·8722 | 0·8723 | *w* | 3·9 | 3·8 | 0·9163 | 0·9163 | *m* | 28·5 |
| 444 | 0·8351 | 0·8351 | *vw* | 1·2 | 1·3 | 0·8772 | 0·8773 | *w* | 10·3 |
| 551, 711 | 0·8105 | 0·8102 | *vvvw* | < 0·8 | 0·5 | — | 0·8511 | abs. | 0·1 |
| 640 | 0·8024 | 0·8024 | *w–m* | 4·4 | 4·7 | 0·8429 | 0·8429 | *m–s* | 36·4 |
| 642 | 0·7733 | 0·7732 | *m–s* | ‡ | 33·2 | 0·8123 | 0·8122 | *m–s* | 47·0 |

* *s* = strong, *m* = medium, *w* = weak, *v* = very.

† Beginning here, the *d*-values for the $\alpha_1$ and $\alpha_2$ reflections were averaged. The visual intensities of the $\alpha_1$ and $\alpha_2$ reflections were added.

‡ Angle too high for observation.

The agreement between calculated and observed intensities (Table 1) is very good for the antimony compounds. Intensities were not calculated for the high temperature bismuth compounds, but the data indicate that these are definitely isostructural with the antimony compounds.

A single crystal chip of $AgSbTe_2$ was photographed with a Buerger precession camera thereby establishing that no superstructure reflections, too weak to appear in the powder patterns, have been missed (see for example, Geller & Bala, 1956) and corroborating the cubic symmetry.

The crystallographic data on the high temperature forms are collected in Table 2. Because the $AgBiSe_2$ pattern was not sharp, particularly in the high angle region, its lattice constant has been deduced in another way. Solid solutions of $AgSbSe_2$ and $AgBiSe_2$ have been made (Wernick *et al.*, 1958*b*); quenched cubic phase samples give sharp patterns at high Bi content. The lattice constant of pure $AgBiSe_2$ was therefore obtained by extrapolation. Both this value and that obtained from the $AgBiSe_2$ data are listed. The $AgBiTe_2$ value was obtained similarly from $AgSbTe_2$–$AgBiTe_2$ solid solution data. (Wernick *et al.*, 1958*b*).

Table 2. *Crystallographic data on the high temperature phases**

| Compound | Lattice constant | Density (g.cm.$^{-3}$) Measured† | X-ray |
|---|---|---|---|
| $AgSbS_2$ | 5·647 ± 0·003 Å | — | 5·42 |
| $AgSbSe_2$ | 5·786 ± 0·003 | 6·69 | 6·60 |
| $AgSbTe_2$ | 6·078 ± 0·003 | 7·12 | 7·12 |
| $AgBiS_2$ | 5·648 ± 0·003 | 7·04 | 7·02 |
| $AgBiS_2$ (200° C.) | 5·682 ± 0·003 | — | 6·90 |
| $AgBiS_2$ (243° C.) | 5·693 ± 0·003 | — | 6·86 |
| $AgBiSe_2$ | 5·82 ± 0·02‡ | — | 8·00 |
| $AgBiSe_2$ | 5·832 ± 0·003§ | — | 7·95 |
| $AgBiSe_2$ (300 °C.) | 5·887 ± 0·003 | — | 7·72 |
| $AgBiTe_2$ | 6·155 ± 0·003§ | — | 8·14 |

* Taken at 25 °C. unless otherwise indicated.

† By liquid displacement method.

‡ From pure $AgBiSe_2$—broad high angle powder pattern lines.

§ From solid solution extrapolation.

It is extremely unlikely that the Ag, Bi and Sb atoms all have the same effective sizes in these compounds. It follows, therefore, that the disordered structures cannot be as simple as indicated earlier. It is highly probable that *at least one* group of atoms must not be centered at their space group sites but are distributed statistically about these sites such that they appear (from the coherent X-ray scattering data) to be *at* these sites. From the data thus far collected, there is no way of ascertaining the *exact* nature of the disorder.

### *Low temperature modification*

As pointed out earlier, the room temperature form of $AgBiSe_2$ formed readily on furnace cooling an ingot. Nevertheless, there was great difficulty in obtaining an untwinned single crystal suitable for X-ray examination. As will be seen, an attack on the structure problem with the use only of powder data could have little chance of success. After several attempts to obtain a single crystal, a large zone-refined sample was made. Fortunately a small crystal with rectangular cross section of 0·15×0·30 mm. was found which was accurately aligned along a rational direction by means of the Hendershot (1937) method. Weissenberg (Cu $K\alpha$ radiation) and Buerger precession (Mo $K\alpha$ radiation) photographs were taken. When Mo $K\alpha$ radiation was used, very long exposures were needed to record the superstructure reflections which are all very weak. The large linear absorption coefficients for both Cu $K\alpha$ and Mo $K\alpha$ radiations (1516 and 754 cm.$^{-1}$ respectively) as well as the unsatisfactory shape of the crystal precluded the use of the single crystal data for highly accurate determination of the atomic positions. Attempts to obtain spherical crystals of 0·1 mm. or less yielded highly disordered specimens which also could not be used for accurate intensity measurements.

Because of the high absorption and unsatisfactory shape of the crystal, difficulty was encountered in determining the diffraction symmetry. This was particularly true of the Weissenberg photographs taken with Cu $K\alpha$ radiation. From these it might appear that the diffraction symmetry could be no higher than $2/m$ and the probable space groups would be $C_{2h}(3)$–$A2/m$, $C_2(3)$–$A2$ and $Cs(3)$–$Am$. (These are subgroups of $D_{3d}(3)$–$P\bar{3}ml$). The rotation axis of the crystal appeared to be a twofold axis.

When both the $AgBiSe_2$ and $AgBiS_2$ lattice constants were determined on the monoclinic basis and the powder patterns indexed, these crystals fell quite accurately into an orthohexagonal description ($c_m = b_m\sqrt{3}$, $\beta = 90°$)* of a hexagonal cell. It will be shown later that one might expect the transition from the disordered NaCl-type structure to be to a trigonal phase.

The precession camera photography indicated somewhat more reliably that the room temperature modification has diffraction symmetry $D_{3d}$–$\bar{3}m$ with symmetry planes perpendicular to the direct cell axes. However, this cannot be said to be unequivocally established. On a 70-hour exposure zero-layer precession photograph on which $(hh{\cdot}l)$ reflections were recorded (precession axis: $[21{\cdot}0]$ direction), no reflections $(00{\cdot}l)$ for $l \neq 3n$ were observed.† Several reflections of the types $(11{\cdot}l)$ and $(22{\cdot}l)$ with $l \neq 3n$ did appear. The $(22{\cdot}l)$ reflections with $l \neq 3n$ and with the higher values of $l$ for $l = 3n$ yielded $|F|^2$ values slightly higher than the analogous $(11{\cdot}l)$ reflections. With primitive unit-cell dimensions $a = 4{\cdot}18 \pm 0{\cdot}02$, $c = 19{\cdot}67 \pm 0{\cdot}05$ Å, the cell contains three formula

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* In accordance with the convention $c < a$, the 19·67 Å axis was designated $a$.

† The (00·1) and (00·2) reflections could not appear on the film.

units. In such a case the apparently systematic absences of $(00{\cdot}l)$, $l \neq 3n$ would imply that the structure belongs to one of the space groups $D_3(4)$–$P3_121$ or $D_3(6)$–$P3_221$. This is almost without doubt impossible; either of these space groups would not permit a description of a structure which is in the first approximation an ordering of the Ag and Bi atoms in the ideal positions of the ideal NaCl-type structure. If the $(hh{\cdot}l)$ structure amplitudes as obtained from the photograph described above were *undoubtedly* the correct ones, the structure could not belong to any other trigonal space group (see the discussion below); the symmetry could be no higher than monoclinic. However, there is reason to believe that the large absorption effects, largely different atomic thermal vibrations and imperfect ordering could be among the more important causes of the observations.

In the high temperature disordered $AgBiSe_2$ phase, the (111) planes (statistically) contain alternately Se atoms and Ag and Bi atoms in disordered array. This is true for any set of planes in the form $\{111\}$. The simplest ordering that can take place is one in which one set of (111) planes has alternately Ag atoms, then Se, then Bi, then Se atoms and so on. Any other set of (111) planes now has alternately planes of Se atoms and planes containing both Ag and Bi atoms (Fig. 1). The highest possible symmetry of the new structure is that of a uniaxial space group and if no further change took place the symmetry would be rhombohedral, space group $R\bar{3}m$, with one formula unit per cell; the atoms would be arranged as follows: Ag in (0, 0, 0), Bi in $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Se in $\pm(x, x, x)$ with $x \cong \frac{1}{4}$. The rhombohedral axes are derived by connecting the origin of the cubic cell to the three far face centers (Fig. 1).

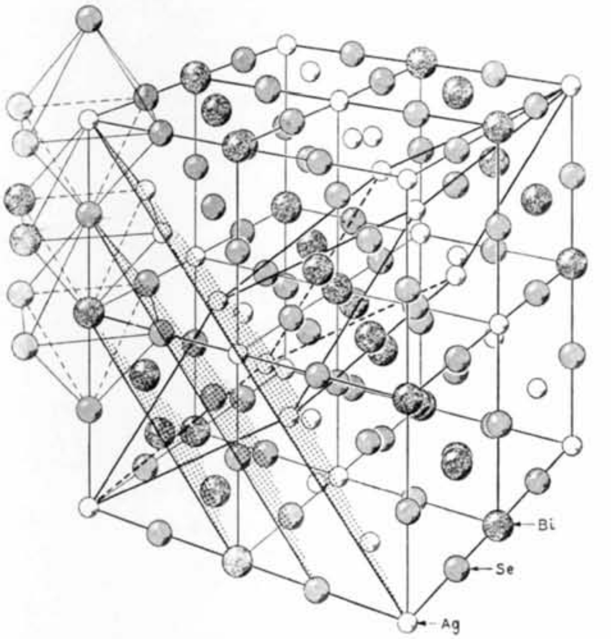

Fig. 1. Relation between the ordered $AgBiSe_2$ rhombohedral structure (idealized) and cubic lattice of the disordered structure.

With such an ordering, one would expect at the very least some changes in dimension: these do occur. For example, if one takes the lattice constant, 5·832 Å, of the disordered form of $AgBiSe_2$ (Table 2), and transforms to the hexagonal cell, one finds the lattice constants $a = 4{\cdot}12$, $c = 20{\cdot}20$ Å. Thus, in the actual cell (see above or Table 4), there has been a contraction along the now unique threefold axis and an expansion perpendicular to it.

Secondly, following or concurrently with such ordering one might expect further displacements of the atoms depending on such factors as their sizes and metallic nature. Further displacements do occur in various ways, thereby leading to different structures. One of these is the room temperature form of $AgBiSe_2$ and $AgBiS_2$ which is a deviation from the ideal ordered rhombohedral form.

In deriving the transformations between the cubic and hexagonal cells, the unique threefold hexagonal axis is taken collinear with the [111] direction of the cubic cell. The hexagonal $a$- and $b$-axes are taken collinear with the $[1\bar{1}0]$ and $[01\bar{1}]$ directions respectively (Fig. 2). The transformation matrices are as follows: from cubic to hexagonal indices:

$$\tfrac{1}{2}, \bar{\tfrac{1}{2}}, 0/0, \tfrac{1}{2}, \bar{\tfrac{1}{2}}/2, 2, 2$$

and from hexagonal to cubic indices:

$$\tfrac{1}{6}(8, 4, 1/\bar{4}, 4, 1/\bar{4}, \bar{8}, 1)\,.$$

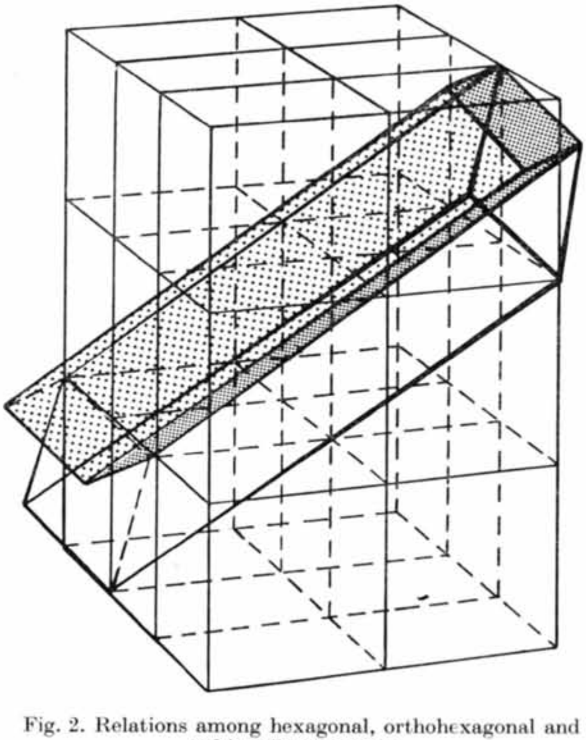

Fig. 2. Relations among hexagonal, orthohexagonal and cubic cells of $AgBiSe_2$.

One sees that if the structure is the disordered NaCl-type, only reflections with hexagonal indices, $(-h+k+l) = 3n$ and $l$ even will occur. These are the conditions for the very special primitive rhombohedral cell ($\alpha = 60°$) contained in the face-centered cubic cell. Now if ordering of the Ag and Bi atoms occurs on the $4(a)$ sites (Fig. 1), the condition that $l$ must be even is removed; the rhombohedron of the first ordered structure has twice the body diagonal and about half the rhombohedral angle (33° 33′)[*] of the disordered rhombohedron. The new reflections would result strictly from the destructive interference of the Ag and Bi atoms. Ideally this structure belongs to $R\bar{3}m$ and Se displacements along the threefold axes would probably also occur.

If further, a pair each of Ag and Bi atoms and three pairs of Se atoms were displaced independently along the threefold axes (Fig. 1), the triply-primitive hexagonal cell would become primitive; thus all reflections would be allowed. This most likely describes the room temperature form of $AgBiSe_2$ and of $AgBiS_2$. The reflections for which $(-h+k+l) \neq 3n$ are extremely weak indicating that displacements from the ideal positions are small indeed. Thus, space groups $D_3(4)$–$P3_121$ and $D_3(6)$–$P3_221$ are ruled out. The probable space groups are $D_{3d}(3)$–$P\bar{3}m1$, $C_{3v}(1)$–$P3m1$ and $D_3(2)$–$P321$. It is somewhat less likely that the crystal would belong to $P3m1$ than to one of the other two: in this space group, only the onefold positions would satisfy the condition of only small deviation of atoms from ideal positions. The positions which the atoms would occupy are common to both $P\bar{3}m1$ and $P321$; it is customary then to assign the crystal to the space group of higher symmetry.

The positions in which the atoms lie may be derived by transforming from the ideal cubic coordinates to the hexagonal,[†] leading to: Ag in $1(a)$: $(0, 0, 0)$; Bi in $1(b)$: $(0, 0, \frac{1}{2})$; Ag in $2(d)$: $\pm(\frac{1}{3}, \frac{2}{3}, z)$ with $z = -\frac{1}{3}$, Bi in $2(d)$ with $z = \frac{1}{6}$; Se in $2(c)$: $\pm(0, 0, z)$ with $z = \frac{1}{4}$, 2 pairs of Se in $2(d)$ with $z = -\frac{1}{12}$ and $\frac{5}{12}$. With the parameters exactly those shown, the simplest cell would be the primitive rhombohedral one (space group $R\bar{3}m$) referred to earlier. In this space group the Se atoms would have one degree of freedom; that is, they would actually lie in $(0,0,0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}) \pm (0,0,z)$, $z \simeq 0{\cdot}26$ putting them closer to Ag than to Bi atoms. However, the displacements from the ideal positions make the triply primitive hexagonal cell primitive. To obtain some idea of the values of the parameters, the intensities of the $(hh{\cdot}l)$ reflections on precession photographs (precession axis: orthohexagonal $a$-axis) were estimated. (As mentioned earlier, these could not be very accurate.) With atoms in the positions given above, the intensities of the $(hh{\cdot}l)$ reflections depend only on the $z$-parameters. It was a simple matter to determine the signs of $(hh{\cdot}l)$ structure amplitudes with $l = 3n$. For those with $l \neq 3n$, the signs were determined by trial, after which the $F$'s were summed for constant $l$ and a Fourier projection on the $c$-axis calculated. This led to the following values of the parameters: for the $\mathrm{Se_I}$ in $2(c)$, $z = 0{\cdot}248$, and for the $\mathrm{Ag_{II}}$, $\mathrm{Bi_{II}}$, $\mathrm{Se_{II}}$, $\mathrm{Se_{III}}$ in $2(d)$, $z = -0{\cdot}327$, $0{\cdot}163$, $-0{\cdot}078$, $0{\cdot}413$ respectively. Because the accuracy of the single crystal data was in question, after further adjustment of the parameters to bring the average Ag–Se and Bi–Se distances into better accord with expected distances (as deduced from the high temperature phases), the powder diffraction data (Cu $K\alpha$ radiation) were used to test the validity of the structure (Table 5). The final parameters are: for $\mathrm{Se_I}$ in $2(c)$, $z = 0{\cdot}253$, for Ag, Bi, $\mathrm{Se_{II}}$ and $\mathrm{Se_{III}}$ in $2(d)$: $z = -0{\cdot}328$, $0{\cdot}163$, $-0{\cdot}074$ and $0{\cdot}406$ respectively.

The measurements given in Table 3 are those taken with a Norelco diffractometer (Cu $K\alpha$ radiation) on a powder from a zone-refined sample of $AgBiSe_2$. The comparison of calculated with observed intensities establishes that the structure determination is essentially correct.

In the calculation of intensities the formula used is that given earlier in this paper. The scattering factors for Ag and Se were taken from the recent paper of Thomas & Umeda (1957), for Bi from the *Internationale Tabellen* (Vol. II), and for S from the paper of Viervoll & Ögrim (1949). Corrections were made for dispersion (Dauben & Templeton, 1955). An isotropic temperature correction with $B = 0{\cdot}5$ Å$^2$ was applied to the calculated intensities. Calculations were carried out by Miss D. P. Booth of these Laboratories. The programs used were described elsewhere (Booth, 1957).

Because the powder pattern of $AgBiSe_2$ was not sharp, only intensities up to $2\theta = 80{\cdot}3°$ inclusive were measured. It is seen that there is only one observed intensity in this range which results from reflections with indices not satisfying the relationship $(-h+k+l) = 3n$: this is the $(\{10{\cdot}3\}, \{01{\cdot}3\})$ intensity (see following section).

Single crystals of the room temperature modification of $AgBiS_2$ were not obtained during this investigation. The powder photograph of $AgBiS_2$ leaves no doubt that this compound is isostructural (lattice constants: $a = 4{\cdot}07 \pm 0{\cdot}02$, $c = 19{\cdot}06 \pm 0{\cdot}05$ Å) with the room temperature modification of $AgBiSe_2$. However, some $Ag_2S$ and Bi seemed always to be present. A powder pattern of one of the $AgBiS_2$ samples was recorded with the Norelco diffractometer (Cu $K\alpha$ radiation) and integrated intensities measured. Intensities were calculated with the same parameters found for $AgBiSe_2$ (see above). The agreement between calculated and observed intensities is significantly poorer than for $AgBiSe_2$. However, the worst discrepancies in the $AgBiS_2$ case (Table 3) are those for which there

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[*] If no changes in dimensions took place, which is not actually the case, the cell edge $a_r$ of this rhombohedron is related to that, $a_c$, of the cubic cell by $a_r = a_c\sqrt{(\frac{3}{2})}$ and $\alpha = \cos^{-1}\frac{5}{6}$.

[†] The transformation matrices may be readily derived from those given earlier for indices.

Table 3. *Calculated and observed spacings and intensities of* $AgBiSe_2$ *and* $AgBiS_2$ (Cu $K\alpha$ *radiation*)

| | $AgBiSe_2$ | | | | | $AgBiS_2$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| hk·l | $d_{calc}$ | $d_{obs}$ | $F^2\times10^{-4}$ | $\Sigma I_c\times10^{-5}$ | $I_{obs}$ | $d_{calc}$ | $d_{obs}$ | $F^2\times10^{-4}$ | $\Sigma I_c\times10^{-5}$ | $I_{obs}$ |
| 00·1 | 19.67 | | 0.01 | 0.0 | < 1.5 | 19.06 | | 0.00 | 0.0 | < 1.5 |
| 00·2 | 9.84 | | 0.00 | 0.0 | < 1.5 | 9.53 | | 0.00 | 0.0 | < 1.5 |
| 00·3 | 6.56 | 6.56 | 0.39 | 10.9 | 12.3 | 6.35 | 6.38 | 0.59 | 15.7 | 14.5 |
| 00·4 | 4.92 | | 0.00 | 0.0 | < 1.5 | 4.77 | | 0.00 | 0.0 | < 1.5 |
| 00·5 | 3.93 | | 0.02 | 0.3 | < 1.5 | 3.81 | | 0.04 | 0.4 | < 1.5 |
| 10·0 | 3.62 | | 0.00 | 0.0 | < 1.5 | 3.52 | | 0.00 | 0.0 | < 1.5 |
| 10·1 | 3.560 | 3.56 | 0.87 | 21.0 | 18.2 | 3.466 | 3.464 | 0.78 | 17.9 | 14.0 |
| 01·1 | | | 0.00 | | | | | 0.00 | | |
| 10·2 | 3.397 | 3.397 | 0.00 | 53.6 | 54.0 | 3.306 | 3.310 | 0.00 | 129 | 120 |
| 01·2 | | | 2.53 | | | | | 6.50 | | |
| 00·6 | 3.278 | 3.278 | 2.65 | 17.1 | 16.3 | 3.177 | 3.170 | 6.36 | 39.7 | 36.0 |
| 10·3 | 3.169 | 3.16 | 0.05 | 1.2 | 3.1 | 3.082 | 3.082 | 0.03 | 0.7 | 3.5• |
| 01·3 | | | 0.01 | | | | | 0.01 | | |
| 10·4 | 2.915 | 2.915 | 22.12 | 331 | 265 | 2.834 | 2.831 | 14.16 | 205 | 194 • |
| 01·4 | | | 0.00 | | | | | 0.00 | | |
| 00·7 | 2.810 | | 0.03 | 0.1 | < 1.5 | 2.723 | | 0.07 | 0.3 | < 1.5 |
| 10·5 | 2.664 | 2.663 | 0.02 | 17.3 | 12.3 | 2.588 | 2.583 | 0.08 | 11.7 | 11.5 |
| 01·5 | | | 1.38 | | | | | 0.90 | | |
| 00·8 | 2.459 | | 0.02 | 0.0 | < 1.5 | 2.383 | | 0.01 | 0.0 | < 1.5 |
| 10·6 | 2.430 | | 0.00 | 0.0 | < 1.5 | 2.360 | | 0.00 | 0.0 | < 1.5 |
| 01·6 | | | 0.00 | | | | | 0.00 | | |
| 10·7 | 2.220 | 2.21 | 0.09 | 2.3 | 2.7 | 2.155 | 2.15 | 0.33 | 3.6 | 7.3• |
| 01·7 | | | 0.20 | | | | | 0.13 | | |
| 00·9 | 2.189 | 2.18 | 1.88 | 4.8 | 3.2 | 2.118 | 2.11 | 1.01 | 2.1 | 1.8 |
| 11·0 | 2.090 | 2.090 | 18.34 | 126 | 129 | 2.035 | 2.034 | 11.56 | 79.0 | 84.0 |
| 11·1 | 2.078 | | 0.00 | 0.0 | < 1.5 | 2.024 | | 0.00 | 0.0 | < 1.5 |
| 11·2 | 2.044 | | 0.00 | 0.0 | < 1.5 | 1.990 | | 0.00 | 0.0 | < 1.5 |
| 10·8 | 2.034 | 2.038 | 0.00 | 106 | 112 | 1.974 | 1.971 | 0.00 | 68.0 | 83.0• |
| 01·8 | | | 16.57 | | | | | 10.71 | | |
| 11·3 | 1.991 | 1.991 | 0.30 | 3.4 | 9.1 | 1.938 | 1.94 | 0.44 | 5.3 | 6.8 |
| 00·10 | 1.967 | | 0.00 | 0.0 | < 1.5 | 1.906 | | 0.00 | 0.0 | < 1.5 |
| 11·4 | 1.924 | | 0.00 | 0.0 | < 1.5 | 1.872 | | 0.00 | 0.0 | < 1.5 |
| 10·9 | 1.871 | | 0.05 | 1.9 | < 1.5 | 1.815 | | 0.10 | 1.5 | < 1.5 |
| 01·9 | | | 0.32 | | | | | 0.20 | | |
| 11·5 | 1.846 | | 0.01 | 0.2 | < 1.5 | 1.795 | | 0.03 | 0.3 | < 1.5 |
| 20·0 | 1.810 | | 0.00 | 0.0 | < 1.5 | 1.762 | | 0.00 | 0.0 | < 1.5 |
| 20·1 | 1.802 | 1.80 | 0.00 | 2.9 | 3.6 | 1.755 | 1.75 | 0.00 | 2.6 | 3.5 |
| 02·1 | | | 0.63 | | | | | 0.56 | | |
| 00·11 | 1.788 | | 0.38 | 0.6 | < 1.5 | 1.733 | 1.731 | 0.26 | 21.2 | 31.5 |
| 20·2 | 1.780 | 1.779 | 18.68 | 8.4 | 12.1 | 1.733 | | 45.29 | | |
| 02·2 | | | 0.00 | | | 1.733 | | .0.00 | | |
| 11·6 | 1.762 | | 19.55 | 17.4 | 19.6 | 1.714 | 1.712 | 44.99 | 40.4 | 58.8• |
| 20·3 | 1.745 | | 0.00 | 0.2 | < 1.5 | 1.698 | | 0.01 | 0.2 | < 1.5 |
| 02·3 | | | 0.03 | | | | | 0.02 | | |
| 10·10 | 1.728 | 1.726 | 21.26 | 9.0 | 8.2 | 1.677 | 1.673 | 44.35 | 18.8 | 25.2 |
| 01·10 | | | 0.00 | | | | | 0.00 | | |
| 20·4 | 1.699 | 1.699 | 0.00 | 61.5 | 55.8 | 1.653 | 1.652 | 0.00 | 39.9 | 37.5 |
| 02·4 | | | 15.25 | | | | | 9.69 | | |
| 11·7 | 1.677 | | 0.02 | 0.2 | < 1.5 | 1.630 | | 0.05 | 0.4 | < 1.5 |
| 20·5 | 1.644 | 1.639 | 1.01 | 19.7 | 20.1 | 1.600 | 1.60 | 0.67 | 3.1 | 4.0 |
| 02·5 | | | 0.09 | | | | | 0.06 | | |
| 00·12 | 1.639 | | 12.56 | | | 1.588 | 1.588 | 8.34 | 10.5 | 14.5• |
| 10·11 | 1.603 | | 0.05 | 0.3 | < 1.5 | 1.555 | 1.55 | 0.12 | 1.2 | 1.8 |
| 01·11 | | | 0.04 | | | | | 0.19 | | |
| 11·8 | 1.592 | | 0.01 | 0.1 | < 1.5 | 1.547 | | 0.00 | 0.0 | < 1.5 |
| 20·6 | 1.585 | | 0.00 | 0.0 | < 1.5 | 1.541 | | 0.00 | 0.0 | < 1.5 |
| 02·6 | | | 0.00 | | | | | 0.00 | | |
| 20·7 | 1.522 | 1.510 | 0.15 | 9.7 | 7.7 | 1.480 | 1.48 | 0.10 | 1.2 | 4.0•+ |
| 02·7 | | | 0.08 | | | | | 0.26 | | |
| 00·13 | 1.513 | | 0.53 | | | 1.466 | 1.465 | 0.34 | 5.1 | 3.8• |
| 11·9 | 1.511 | | 1.40 | | | 1.467 | | 0.76 | | |
| 10·12 | 1.493 | | 0.05 | 0.3 | < 1.5 | 1.448 | | 0.00 | 0.0 | < 1.5 |
| 01·12 | | | 0.01 | | | | | 0.00 | | |
| 20·8 | 1.458 | 1.458 | 12.39 | 32.2 | 31.8 | 1.417 | 1.410 | 8.03 | 22.4 | 21.0 |
| 02·8 | | | 0.00 | | | | | 0.00 | | |
| 11·10 | 1.432 | | 0.00 | 0.0 | < 1.5 | 1.391 | | 0.00 | 0.0 | < 1.5 |
| 00·14 | 1.405 | | 0.0 | 0.0 | < 1.5 | 1.361 | | 0.01 | 0.0 | < 1.5 |
| 10·13 | 1.396 | 1.39 | 1.74 | 5.1 | 3.0 | 1.354 | 1.35 | 0.84 | 3.0 | 2.5 |
| 01·13 | | | 0.09 | | | | | 0.16 | | |
| 20·9 | 1.394 | | 0.24 | | | 1.355 | | 0.16 | | |
| 02·9 | | | 0.04 | | | | | 0.07 | | |
| 21·0 | 1.368 | | 0.00 | 0.0 | < 1.5 | 1.332 | 1.33 | 0.00 | 2.0 | 2.5• |
| 21·1 | 1.365 | 1.36 | 0.48 | 9.8 | 10.0 | 1.329 | | 0.42 | | |
| 12·1 | | | 0.00 | | | | | 0.00 | | |
| 11·11 | 1.359 | | 0.30 | | | 1.319 | 1.319 | 0.20 | 16.6 | 20.9 |
| 21·2 | 1.355 | | 0.00 | | | 1.319 | | 0.00 | | |
| 12·2 | | | 1.49 | | | | | 3.45 | | |
| 21·3 | 1.339 | | 0.03 | 0.2 | < 1.5 | 1.304 | | 0.02 | 0.1 | < 1.5 |
| 12·3 | | | 0.00 | | | | | 0.01 | | |
| 20·10 | 1.332 | 1.33 | 0.00 | 3.6 | 5.5 | 1.294 | 1.292 | 0.00 | 7.8 | 6.2 |
| 02·10 | | | 1.69 | | | | | 3.40 | | |
| 21·4 | 1.318 | 1.318 | 11.79 | 51.0 | 47.2 | 1.283 | 1.28 | 7.54 | 33.6 | 22.5 |
| 12·4 | | | 0.00 | | | | | 0.00 | | |
| 00·15 | 1.311 | | 0.01 | | | 1.271 | 1.27 | 0.10 | 7.0 | 7.8 |
| 10·14 | 1.310 | | 0.01 | | | 1.270 | | 0.00 | | |
| 01·14 | | | 1.87 | | | | | 3.32 | | |
| 21·5 | 1.292 | 1.290 | 0.07 | 41.5 | 43.8 | 1.258 | 1.25 | 0.05 | 29.8 | 28.2 |
| 12·5 | | | 0.78 | | | | | 0.51 | | |
| 11·12 | 1.290 | | 9.78 | | | 1.252 | | 6.56 | | |
| 20·11 | 1.272 | 1.27 | 0.00 | 0.1 | < 1.5 | 1.236 | 1.23 | 0.14 | 0.4 | 3.6• |
| 02·11 | | | 0.04 | | | | | 0.09 | | |
| 21·6 | 1.263 | | 0.00 | 0.0 | < 1.5 | 1.229 | | 0.00 | | |
| 12·6 | | | 0.00 | | | | | 0.00 | | |
| 10·15 | 1.233 | 1.23 | 0.44 | 3.2 | 2.2 | 1.195 | 1.20 | 0.31 | 2.0 | 3.5 |
| 01·15 | | | 0.08 | | | | | 0.17 | | |
| 21·7 | 1.230 | | 0.06 | | | 1.197 | | 0.19 | | |
| 12·7 | | | 0.12 | | | | | 0.08 | | |
| 00·16 | 1.229 | | 0.02 | | | 1.191 | | 0.01 | 0.6 | < 1.5 |
| 11·13 | 1.226 | | 0.42 | | | 1.190 | | 0.15 | | |
| 20·12 | 1.215 | 1.21 | 0.01 | 18.1 | 13.8 | 1.180 | 1.18 | 0.00 | 0.0 | 2.5•+ |
| 02·12 | | | 0.00 | | | | | 0.00 | | |
| 30·0 | 1.207 | | 10.81 | | | 1.175 | 1.17 | 6.90 | 13.0 | 12.8 |
| 30·1 | 1.204 | | 0.00 | 0.0 | < 1.5 | 1.173 | | 0.00 | | |
| 03·1 | | | 0.00 | | | | | 0.00 | | |
| 30·2 | 1.198 | 1.196 | 0.00 | 32.4 | 28.2 | 1.166 | 1.16 | 0.00 | 23.8 | 26 •+ |
| 03·2 | | | 0.00 | | | | | 0.00 | | |
| 21·8 | 1.196 | | 0.00 | | | 1.163 | | 0.00 | | |
| 12·8 | | | 9.86 | | | | | 6.45 | | |

• $Ag_2S$ line    + Bi line

Notes: 1. The (11·3) reflection of $AgBiSe_2$ is badly overlapped by the preceding (10·8) reflection, the recorded value of $I_0$ is therefore in doubt.

2. The $AgBiSe_2$ reflection at $d$ = 1·318 Å is broad enough to include the (01·14) reflection. Two peaks are indicated but they cannot be properly resolved.

is interference from the $Ag_2S$ and Bi impurities. This is not to imply that it is necessarily the case that the atomic coordinates in $AgBiS_2$ are exactly the same as those in $AgBiSe_2$. In fact, this is not to be expected. However, examination of Table 3 corroborates the conclusion that the structure given in this paper for $AgBiS_2$ is essentially correct.

Lattice constant and density data on the low temperature forms of $AgBiS_2$ and $AgBiSe_2$ are given in Table 4. Interatomic distances in the two compounds are given in Table 5.

Table 4. *Crystallographic data on low temperature modifications*

| Compound | Lattice constants | | Density (g.cm.$^{-3}$) | |
|---|---|---|---|---|
| | $a$ (Å) | $c$ (Å) | Measured | X-ray |
| $AgBiS_2$ | 4·07±0·02 | 19·06±0·05 | — | 6·94 |
| $AgBiSe_2$ | 4·18±0·02 | 19·67±0·05 | 8·00 | 7·94 |
| $AgBiTe_2$* | 4·37±0·02 | 20·76±0·05 | — | 8·30 |

* This is a transitory phase; there is no thermodynamically stable phase of $AgBiTe_2$ at room temperature and atmospheric pressure (Wernick *et al.*, 1958*b*).

Table 5. *Interatomic distances in the room temperature modification of* $AgBiSe_2$ *and* $AgBiS_2$

| Atom | $AgBiSe_2$ | | $AgBiS_2$ | |
|---|---|---|---|---|
| Ag(I) | 6 Se(II) | 2·81 Å | 6 S(II) | 2·74 Å |
| Ag(II) | 3 Se(I)<br>3 Se(III) | 2·83<br>2·86 | 3 S(I)<br>3 S(III) | 2·75<br>2·78 |
| Bi(I) | 6 Se(III) | 3·04 | 6 S(III) | 2·95 |
| Bi(II) | 3 Se(I)<br>3 Se(II) | 2·99<br>2·98 | 3 S(I)<br>3 S(II) | 2·91<br>2·90 |
| Se or S(I) | 3 Ag(II)<br>3 Bi(II) | 2·83<br>2·99 | 3 Ag(II)<br>3 Bi(II) | 2·75<br>2·91 |
| Se or S(II) | 3 Ag(I)<br>3 Bi(II) | 2·81<br>2·98 | 3 Ag(I)<br>3 Bi(II) | 2·74<br>2·90 |
| Se or S(III) | 3 Ag(II)<br>3 Bi(I) | 2·86<br>3·04 | 3 Ag(II)<br>3 Bi(I) | 2·78<br>2·95 |

### *High temperature investigations.—Intermediate modification*

In the discussion of the structure determination of the room temperature modification, it was shown that the simplest transition from the disordered to an ordered phase should result in the formation of a one formula unit rhombohedral cell. It has also been shown that the room temperature modification is only a slight distortion from such a structure. Unfortunately, the powder photograph of the room temperature modification records only one of the superstructure intensities which distinguish the two forms. And because this is weak, it is not always easily seen. In this regard, the Norelco diffractometer has been a more sensitive tool. A powder sample of some zone-refined $AgBiSe_2$ was placed on a sample holder designed by Wood (1956) for work up to 600 °C. The reference line was the $\{10\cdot4\}$ $K\beta$ line (which is so strong that it is not completely filtered out by a 0·007 in. Ni filter) which is adjacent to the $\{10\cdot3\}$ $K\alpha$ line. As the temperature of the sample was increased, the height of the $\{10\cdot4\}$ $K\beta$ line stayed about the same but the $\{10\cdot3\}$ $K\alpha$ line gradually disappeared. At 110° C. it was barely discernible whereas at 150 °C. it was completely gone. When the temperature was dropped to 25 °C. again, the $\{10\cdot3\}$ $K\alpha$ line (which was about the same height as the filtered $\{10\cdot4\}$ $K\beta$) returned; that is the process is easily reversible.

One would predict that this transition (although $P\bar{3}m1$ is not a subgroup of $R\bar{3}m$) is of higher than first order. Differential thermal analysis of a sample of $AgBiSe_2$ (Wernick *et al.*, 1958*b*) does not find this transition: the only solid state transition observed is that between the disordered cubic form and the ordered rhombohedral form. The latter most likely belongs to space group $R\bar{3}m$ with 1 Ag in $1(a)$: $(0, 0, 0)$; Bi in $1(b)$: $(0, 0, \frac{1}{2})$; and Se in $2(c)$: $\pm(x, x, x)$ with $x \cong 0{\cdot}26$. Although the same experiment has not been carried out on $AgBiS_2$, there is little doubt that it behaves much the way $AgBiSe_2$ does.

Lines in the back reflection region of the room temperature powder patterns of the low temperature forms of $AgBiSe_2$ and $AgBiS_2$ and of the quenched disordered cubic form of $AgBiSe_2$ are always very broad. Powder photographs of $AgBiSe_2$ were taken at 150, 240 and 300 °C. using a camera designed and built by Bond (1958). At 150 °C., the structure is rhombohedral with the lines in the back-reflection region somewhat sharper than those of the room temperature modification. At 240 °C., the lines are sharp with observable resolution of the Cu $K\alpha_1$, $\alpha_2$ lines; the phase is still rhombohedral with lattice constants $a = 7{\cdot}022\pm0{\cdot}010$ Å, $\alpha = 34° 30'\pm20'$.* At 300 °C. the phase has the cubic disordered structure with $a = 5{\cdot}887\pm0{\cdot}003$ Å; in this case again, the lines are sharp. This sample when cooled to room temperature and photographed again, retained the cubic structure, but as expected, the lines in the back-reflection region were very broad. It should be noted that the sample was contained in a glass capillary open to the atmosphere. At 300 °C., oxidation occurred; the powder photograph showed $Bi_2O_3$ lines which, of course, were also recorded on the room temperature photograph taken directly after cooling from 300 °C. (This cooling may be considered to be a quench.)

## Discussion

Much of the discussion pertaining to the relationships among the three structures has already been given. It is worth emphasizing that the average interatomic distances (e.g. Ag–Se, Bi–Se, Ag–S, Bi–S etc.) in the disordered structures are probably equal (or nearly so) to the corresponding average distances in the ordered

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* The lattice constants of the triply primitive hexagonal cell are $a = 4{\cdot}184\pm0{\cdot}005$, $c = 19{\cdot}78\pm0{\cdot}02$ Å.

structures. This is established mainly by the almost negligible difference in density between the disordered and ordered phases, and by the good agreement between calculated and observed intensities for the room temperature modification. The latter is probably of lesser significance because the limits of error on the distances may be larger than ±0·05 Å. The contraction along the unique axis and expansion perpendicular to it are logical consequences of the ordering. In the ordered form, only like atoms lie in any *one* of the hexagonal (00·1) planes, whereas in the cubic form, all $\{111\}$ planes of metal atoms contain mixed atoms. Also in the disordered cubic phases, the metal as well as the Se atoms (in $AgBiSe_2$, for example) need only *on the average* lie in the $\{111\}$ planes; in fact, at least one group of atoms (metal or Group VI) *must not* be centered exactly in the planes. In the trigonal forms, all other than the (00·1) planes of metal atoms contain mixed atoms. It is then seen that an expansion (1·5%) in the direction perpendicular to the unique axis results mainly from the ordering of the Ag and Bi atoms; the contraction (2·6%) along the unique axis occurs from the allowed closer packing as a result of both the ordering of the metal atoms and *smoothing* of the planes.

It has been mentioned that there is a possibility that the true symmetry of the room temperature modification is monoclinic and belongs to one of the subgroups of $P\bar{3}m1$: $C_{2h}(3)$–$A2/m$, $C_2(3)$–$A2$, $C_s(3)$–$Am$. In such a case, the cell (Fig. 2) would have orthohexagonal dimensions: $b=4{\cdot}18$, $c=4{\cdot}18\sqrt{3}$, $a=19{\cdot}67$ Å, $\beta = 90°$ and contain six formula units. The space group *Am* would be ruled out leaving only *A*2/*m* and *A*2 as possibilities. If *A*2/*m* were the correct one, there would be Ag atoms in 2(*a*) and 4(*i*), Bi atoms in 2(*c*) and 4(*i*) and Se atoms in 4(*i*) (3 sets). Again deviations from the rhombohedral one formula unit structure could be only slight.

First order transitions do not have simple mechanisms and the transition from the cubic $AgBiSe_2$ to the rhombohedral is no exception. A triangle of Se atoms stands in the way of the motion of any Ag or Bi atom. If this triangle remained rigid, a Ag or Bi atom moving through it would at some time have its center only 2·4 Å from the center of a Se atom. Thus it appears that Se atoms must also move in the ordering process.

The sharpening of the $AgBiSe_2$ reflections with increasing temperature indicates that the line broadening at lower temperatures is caused by some type of disorder. This is to be expected from the types of structures discussed here. For example, at room temperature, all of the atom centers may still not be exactly in the appropriate planes. Long annealing of the room temperature modification of $AgBiSe_2$ has tended to narrow the reflections somewhat.

The comparisons of cell sizes of the high temperature modification of the Sb and Bi compounds and of the Sb and Bi radii are of special interest. The lattice constants (Table 2) of $AgSbS_2$ and $AgBiS_2$ do not differ at all; those of the Se and Te compounds by 0·046 and 0·075 Å, respectively. The indication is that the $AgSbS_2$ cell size is too large.* Also the difference in effective sizes of Sb and Bi appears to be small.

In the isostructural elements, As, Sb, Bi the difference between nearest-neighbor and next-nearest-neighbor distances decreases as the elements become more metallic. Also Te is more metallic than Se, which in turn is more metallic than S. In $AgSbS_2$, one would expect a greater difference between shortest and longest Sb–S distances in a given $[SbS_6]$ octahedron, than that between the corresponding Bi–S distances in $AgBiS_2$. The analogous situation would be expected to exist in the pairs: $AgSbSe_2$–$AgBiSe_2$ and $AgSbTe_2$–$AgBiTe_2$. However, as the Group VI element becomes more metallic, one would expect the distances to neighbors in a given octahedron to become more nearly equal. The greater distortion of octahedra in $AgSbS_2$ than in $AgBiS_2$ would account for the greater than expected volume of $AgSbS_2$. The significant lattice constant difference between the Se compounds and the increase in this difference between the Te compounds gives further substance to this conclusion.

Although it is not clear as to what the bond type is in these compounds, there is little doubt that the bonding is mainly covalent in nature. Ionic semiconductors have very low mobilities whereas measurements on the Pb compounds (see e.g. Winkler, 1955) as well as on $AgSbSe_2$ (Wernick *et al.*, 1958*a*) indicate high mobilities for these compounds.†

Mooser & Pearson (1956) have proposed that there is a simple rule governing the number $n_e$ of valence electrons per molecule in a semiconductor, namely:

$$\frac{n_e}{n_a}+b = 8\ ,$$

where $n_a$ is the number of Group IV to VII atoms molecule and $b$ is the number of bonds formed by *one* of these atoms with other atoms in Groups IV to VII. This rule appears to apply to Pb compounds only because Mooser & Pearson (1956) have arbitrarily made Pb a Group II element. The rule does not apply to the ternary compounds discussed in this report. For any one of these compounds, $n_e = 18$, $n_a = 3$ and $b$ is equal to 6 if we choose to look at an Sb or Bi atom or 3 if we choose to look at a Group VI atom.

Further work is contemplated on other compounds related to the NaCl structure.

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† Further measurements of mobilities are being made at present; results will be published elsewhere.

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# The Crystal Structures of Some Anthracene Derivatives. III. 9:10-Dichloroanthracene

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Crystals of 9:10-dichloroanthracene are monoclinic with four molecules in the unit cell, and the structure has been determined by Patterson and Fourier projections along the *a* and *c* crystal axes. Values of the bond lengths and valency angles in the molecule and intermolecular distances have been obtained.

## Introduction

Continuing the investigation of the crystal structures of anthracene derivatives with substituents in the 9 and 10 positions (Trotter, 1958*a*, *b*), the structure of 9:10-dichloroanthracene has been determined. Since the crystals are not isomorphous with those of the dibromo analogue, the structure analysis has of course been carried out completely independently.

## Experimental

Crystals of 9:10-dichloroanthracene, which were obtained by crystallization from petroleum ether, are greenish-yellow in colour, and consist of plates elongated along the *a*-axis with (010) developed, and smaller (001) faces. The density was determined by flotation in aqueous potassium iodide solution. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal rotating about the *a*-axis, *hkl* Weissenberg films with $h = 0, 1, 2, 3$, and *h*0*l*, *h*1*l*, *hk*0 and *hk*1 precession films.

## Crystal data

9:10-Dichloroanthracene, $C_{14}H_8Cl_2$; $M = 247{\cdot}1$; m.p. 209–210 °C.

Monoclinic,

$a = 7{\cdot}04 \pm 0{\cdot}02$, $b = 17{\cdot}93 \pm 0{\cdot}04$, $c = 8{\cdot}63 \pm 0{\cdot}02$ Å, $\beta = 102° \, 56' \pm 10'$.

Volume of the unit cell = 1062·3 Å³. Density, calculated (with four molecules per unit cell) = 1·535 g.cm.$^{-3}$, measured = 1·525 g.cm.$^{-3}$. Absorption coefficient for X-rays, $\lambda = 1{\cdot}542$ Å, $\mu = 51{\cdot}3$ cm.$^{-1}$; $\lambda = 0{\cdot}7107$ Å, $\mu = 5{\cdot}85$ cm.$^{-1}$.

Total number of electrons per unit cell = $F(000) = 504$.

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