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The Crystal Structure of Hexagonal Silver Iodide

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On the basis of oscillation data a structure has been assigned to hexagonal silver iodide at room temperature in which the silver atoms are distributed at random among four positions tetrahedrally surrounding the ideal position in the wurtzite structure. Previous work is discussed and evidence supporting the preference of this structure is presented. At liquid-air temperatures the structure is found to approximate closely that of wurtzite with the ideal parameter value of $1/8$. Physical characteristics of silver iodide are discussed in relation to the proposed structure.

INTRODUCTION

THE anomalous physical properties of crystalline silver iodide which in the main are still unexplained have led us to undertake a re-determination of the crystal structure of this substance in spite of the seemingly satisfactory state of our present knowledge of it.¹ Since the beginning of this work a structure has been found for the high temperature (above 146°C) form which can be correlated nicely with its physical character.² Also a reinvestigation of the low temperature hexagonal form by the powder method has been reported to show that it has essentially the wurtzite structure with a parameter slightly larger than the ideal value, one-eighth.³ The agreement between calculated and experimental intensities is certainly not good, the differences being attributed by the authors to preferred orientations in the sample. In addition, high orders where such a small difference in the parameter would become effective were not or could not be used in the powder analysis. The unusually high temperature factor introduces another complication. In view of these facts it seems doubtful that any great weight can be attached to the apparent (but very slight) deviation from the ideal structure.

In this investigation powder, Laue, and oscillation methods were used and the oscillation diffraction pictures found to be the most conclusive and satisfactory. Photographs were taken over a 300-degree temperature range. The low tempera-

ture data indicate that at -180°C the structure is essentially that of wurtzite with the ideal parameter value. On the basis of the room temperature pictures a structure has been assigned in which the silver atoms are distributed at random among four positions tetrahedrally surrounding the ideal position. A gradual transition (with rising temperature) is postulated between these two arrangements. The attempt has been made to explain some of the peculiarities of silver iodide on the basis of these structures.

PROCEDURE

Single crystals of silver iodide were prepared by a slight modification of the method of Zepharovich.⁴ Concentrated hydrogen iodide solution was saturated with silver iodide and a thin layer of absolute alcohol spread over the heavy liquid. The hydrogen iodide diffusing into the upper layer and reacting with the alcohol removed iodide ions slowly enough to permit good crystals of the salt to form. It was also found that placing silver in the saturated solution was effective in making crystals and somewhat simpler, the reaction of hydrogen iodide with metallic silver being sufficiently slow to allow the formation of small crystals. By the first method hexagonal plates of silver iodide with edges 5 mm in length were obtained. Hexagonal crystals, usually hexagonal pyramids, were formed exclusively by these procedures. No trace of a cubic modification was found in any case.

Laue photographs were taken along the hexagonal axis perpendicular to the thin plates. The

* National Research Fellow.

¹ R. B. Wilsey, *Phil. Mag.* **46**, 487 (1923).

² Lester Strock, *Zeits. f. physik. Chemie* **B25**, 441 (1934).

³ N. W. Kolkmeijer and J. W. A. van Hengel, *Zeits. f. Krist.* **88**, 317 (1934).

⁴ V. von Zepharovich, *Zeits. f. Krist.* **4**, 119 (1880).

pictures checked those of Aminoff,⁵ allowing for the difference in wave-length range used, and the data were found to be consistent with the space group C_{6h}^4 and with a structure approximating that of wurtzite. For the determination of the parameter value, however, the data were too meager. The Laue pictures were so poor in first order reflections that the best that could be done was to limit the range of the parameter between 0.625 and 0.700. Unsymmetrical pictures taken in an effort to increase the amount of data indicated that for no value of the parameter could the intensities be fitted, but the absorption in the case of these pictures was so large as to invalidate the results or at least to make them questionable. With a ten-day exposure no reflections requiring a larger unit were observed.

Powder pictures were taken of samples prepared according to the directions of Bloch and Muller⁶—the photographs obtained matched those of Kolkmeijer and van Hengel. No attempt was made to determine the structure from these pictures.

Oscillation pictures were taken with $\text{Mo } K\alpha$ radiation on two different spectrographs. Most of them were taken from the $(00\cdot1)$ cleavage face of the crystal. Three types of crystals were tried in an attempt to find the most satisfactory. First, a very small thin plate was used, with which it was hoped completely to avoid absorption effects, but a plate of the smallest practical dimensions, $0.2 \times 0.2 \times 0.05$ mm, was found to give too much absorption to permit the use of this technique. A small thick crystal totally included in the beam was used next. In this case the calculated intensities were multiplied by a factor $\sin \theta$ to take into account the fraction of the beam striking the prepared face of the crystal. The large absorbing crystal intercepting the entire beam was found most satisfactory because of the greater reflected intensity and the fact that the factor $\sin \theta$ was not necessary. Also absorption could be more easily taken into account for this case. The last two types of crystals gave concordant results. The cleavage faces were ground and no differences observed in the reflected

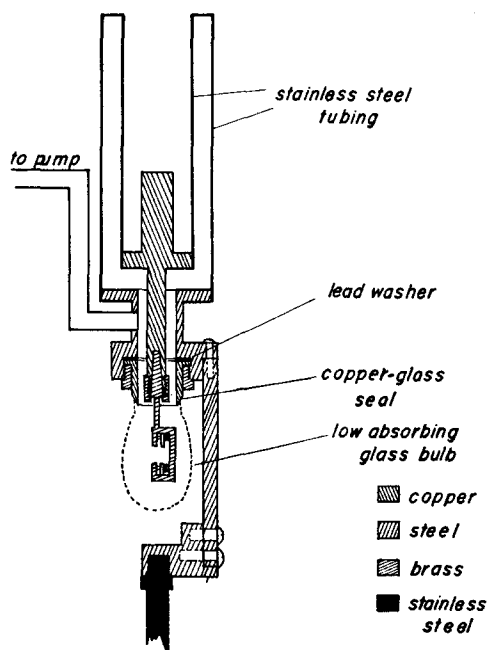


FIG. 1.

intensities from ground and freshly cleaved faces.

The large temperature factor, as will be seen later, plays an important role in an attempt to fit the experimental intensities. To obtain a value for this factor and to obtain more data an apparatus was constructed for taking oscillation pictures at temperatures down to that of liquid air. It was also desired later to investigate the anomalous contraction of silver iodide with rising temperature. This apparatus consists of a metal Dewar supported on a stand and open at the bottom, with the crystal support attached to the inside of the Dewar and extending out through the opening (Fig. 1). The Dewar is closed by means of a thin glass bulb which surrounds the crystal which is cooled by conduction down the supporting rod. It was assumed that with a good vacuum the temperature of the crystal was the same as that of the support after a period of one hour. The whole apparatus was oscillated in the x-ray beam, the connection to a diffusion pump being through rubber tubing. The agreement between experimental intensities and those

⁵ G. Aminoff, *Geol. Foren. Stockholm Forh.* **44**, 444 (1922).

⁶ R. Bloch and H. Muller, *Zeits. f. physik. Chemie* **A152**, 245 (1931).

calculated for different temperatures with the factor $e^{-2\theta(\sin \theta/\lambda)^2}$ indicates that within the errors of the intensity measurements the temperature of the liquid in the Dewar and the crystal were the same.

With the unit cell and the space group already known the intensities were of greatest interest for this work. For room temperature estimates, comparison pictures were taken. Three sets of five exposures differing in length by convenient multiples were obtained. Comparison of lines of equal intensity on photographs of different exposures gave fairly reliable estimates of relative intensity. Because of the difficulty of taking the low temperature pictures, this procedure was not possible and the relative intensities were measured by means of a calibrated scale. These two methods were checked one against the other for the room temperature case and the agreement was within the error of the comparison method. The estimates of intensity are probably reliable to 20 percent.

RESULTS

The size of the unit and the space group were found to be the same as previously reported in the literature: hexagonal unit with two molecules in the cell, $a = 4.59\text{\AA}$, $c = 7.52\text{\AA}$ ($c/a = 1.64$), and the space group C'_{6v} . The atomic positions for the wurtzite structure:

$$\text{Ag } 00u, \frac{1}{3}, \frac{2}{3}, u + \frac{1}{2}; \text{ I } 000, \frac{1}{3}, \frac{2}{3}, \frac{1}{2}.$$

The parameter is taken here in accordance with the first work of Aminoff and is equal to $1 - u'$, where u' is the value given by Kolkmeijer and van Hengel.

At liquid-air temperatures the size of the unit was found to be $a = 4.57\text{\AA}$, $c = 7.48\text{\AA}$ with $c/a = 1.63$. The data are given in Table I. These measurements cannot be considered as very accurate since the two crystals used at low temperatures gave broad diffuse lines, good for intensity estimates, but difficult to measure accurately, and layer line measurements are in themselves not very accurate.

The interest of the investigation lay in placing the silver atoms by plotting calculated intensities against the parameter u , and finding a value of u for which the calculated intensities match the

TABLE I.

REFLECTING PLANE	LINE	SIN θ	$d_{(00,1)}$
(00·4)	Mo $K\alpha$	0.1896	7.48A
(00·6)		.2854	7.46
(00·8)		.3798	7.47
(00·10)		.4735	7.48
(00·12)		.5664	7.49
(00·14)		.6621	7.49
(00·16)		.7580	7.48
			Average: 7.48
<hr/>			
FROM THE LAYER LINE MEASUREMENTS, LAYER LINE		SIN θ	$d_{(10,0)}$
1		0.1568	4.57A
2		.3080	4.60
3		.4658	4.57
			Average: 4.58

experimental. The intensities were calculated according to the formula:

$$I = C \frac{1 + \cos^2 \theta}{2 \sin 2\theta} |S|^2 e^{-\theta(\sin \theta/\lambda)^2} A,$$

where $|S|^2$ is the familiar absolute value of the structure factor squared. The values for f_1 and f_{Ag} , the atomic scattering factors, were taken from the tables of Pauling and Sherman⁷ and plotted against $\sin \theta$. For convenience these values were multiplied by $e^{-\theta(\sin \theta/\lambda)^2} ((1 + \cos^2 \theta) / 2 \sin 2\theta)^{1/2}$. Account was taken of the fact that in using Mo $K\alpha$ radiation the K electrons of silver and iodine do not contribute to the diffraction. The f values were decreased by two units over the range of $\sin \theta$ used here. Correction was also made for absorption by means of a formula easily derived if one neglects secondary extinction. The ratio A gives the factor by which the calculated intensity must be multiplied in order to take account of absorption:

$$A = 2 / \left(1 + \frac{\sin \alpha}{\sin (\varphi - \alpha)} \frac{1}{\cos \chi} \right),$$

where φ is the azimuthal angle of the reflection, α is the angle through which the crystal has been turned when reflection takes place (this can be easily found from the reciprocal lattice), and χ

⁷ Linus Pauling and J. Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

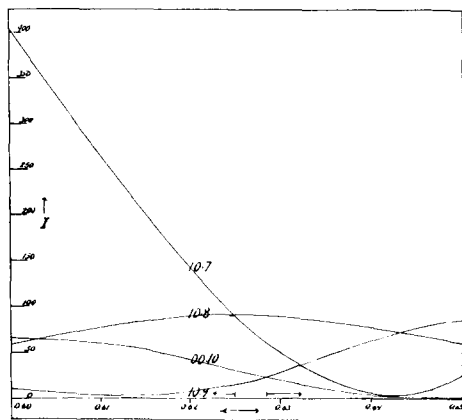


FIG. 2.

is the layer line angle. This relation could be checked semiquantitatively in cases where lines of the same form reflected at different α . The agreement was good enough so that it was though well worth while to use this correction factor. Naturally it holds only for the case of the large absorbing crystal where the limits for the calculation are well defined. A factor was also included in the calculations to take care of the relative time of exposure of the different lines. This factor, multiplying the calculated intensity, is $1/(1 - (h \lambda/d \sin 2\theta)^2)^{1/2}$, where h is the index of the layer line, and d the identity distance in the vertical direction.

It was soon found in trying to fit the intensities that, with reasonable values of β , the agreement was fairly good for the wurtzite structure with $u = 0.63$ (compare with 0.629 of Kolkmeijer and van Hengel) except for two qualitative comparisons which ruled the structure out altogether as shown in Fig. 2. (10·7) is observed stronger than (10·8) forcing the parameter to lie below 0.625, and (10·9) is observed stronger than (00·10) giving 0.629 as the lowest possible value by this comparison. This is indicated by the two arrows at the bottom of the plot. The use of larger values of u solves the (10·9) \geq (00·10) difficulty and aggravates the (10·7) \geq (10·8) discrepancy. The region in which no value of u is permitted is narrowed down considerably by increasing β but with $\beta = 6$ the dilemma is still unresolved and the quantitative relationships of other lines are thrown out by a factor of two or more. There is the additional objection to increasing β that at a

value of five the qualitative agreement in the prism reflections, which are independent of u , is upset, (10·0) becoming stronger than (30·0) while actually the reverse is observed. From specific heat data one obtains a value of 3.0 for β assuming that the crystal behaves as a simple cubic lattice and that it is still in the temperature range where these formulae are valid. It was assumed from these considerations that no solution was to be reached by using β as an additional parameter.

Believing that wurtzite had been ruled out, we investigated numerous combinations of structures or alternating structures with fractional atoms at positions consistent with the space group. Combinations of the special positions for wurtzite with those of niccolite or sphalerite were tried but gave no agreement at all, so that, although it is probable that all combinations were not tried, we feel confident that nothing of this nature would represent the state of the crystal. As an example of this sort of procedure: the atom positions were taken Ag/2: $\frac{1}{3}, \frac{2}{3}, p + \frac{1}{2}$; $\frac{2}{3}, \frac{1}{3}, p + \frac{1}{2}$; 2 at 0, 0, p . I: $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}$; 2 at 0, 0, 0. This variation is one of the simplest and gave no possibility of fitting the layer line intensities. However it shows the sort of attempts that were made. The failure of this procedure led us to believe that whatever the structure was it could not be very different from wurtzite itself.

Next we attempted to place the silver atoms at random among four positions at points extended tetrahedrally from the ideal wurtzite position ($u = 0.625$) toward the faces of the tetrahedra formed by the surrounding iodine atoms. This treatment uses two wurtzite positions and six more equivalent positions belonging to C_6^4 . The atomic positions for the structure are:

$$\text{I: } 0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$$

$$\text{Ag: } \frac{1}{4}, \frac{2}{3}, \frac{1}{8}, \frac{3p}{4}; \frac{1}{3} + \frac{p}{\sqrt{6}}, \frac{2}{3} - \frac{p}{\sqrt{6}}, \frac{1}{8} + \frac{p}{4};$$

$$\frac{1}{3} - \frac{2p}{\sqrt{6}}, \frac{2}{3} - \frac{p}{\sqrt{6}}, \frac{1}{8} + \frac{p}{4}; \frac{1}{3} + \frac{p}{\sqrt{6}}, \frac{2}{3} - \frac{2p}{\sqrt{6}},$$

$$\frac{1}{8} + \frac{p}{4}; 0, 0, \frac{5}{8} - \frac{3p}{4}; -\frac{p}{\sqrt{6}} + \frac{p}{\sqrt{6}}, \frac{5}{8} + \frac{p}{4};$$

$$\frac{2p}{\sqrt{6}}, \frac{p}{\sqrt{6}}, \frac{5}{8} + \frac{p}{4}; \frac{p}{\sqrt{6}}, -\frac{2p}{\sqrt{6}}, \frac{5}{8} + \frac{p}{4}$$

where p , the parameter here is the altitude of the tetrahedron at the corners of which the silver atoms are located. Reasons for choosing this structure will be discussed later; certainly it was the only one found that would resolve the difficulties enumerated above. That this is not just a subterfuge to decrease the f value of the silver atom is shown by the fact that if the silver atoms are spread out toward the corners of the iodine tetrahedron (rather than the faces), the agreement is considerably worse than for wurtzite itself. The intensity comparisons are found in Table II, the third column giving calculated intensities from the tetrahedral silver structure and the fourth those from wurtzite. The amount of data is not imposing but it may be mentioned that the intensity relationships in the fourth layer line follow very closely those in the second as is borne out by the calculations. With the axis 11·0 vertical the odd layer lines are greatly influenced by absorption and have not been considered in the room temperature pictures. (2 $\bar{1}$ ·6) and (2 $\bar{1}$ ·8) were observed on pictures taken with the

TABLE II.

(<i>hk</i> · <i>l</i>)	<i>I</i> _{obs}	<i>I</i> _{calc} TETRAHEDRAL Ag $\beta = 3.5$	<i>I</i> _{calc} WURTZITE $\beta = 4.0$
(00·2)	whole beam not intercepted		
(00·4)	1.2	1.2	1.0
(00·6)	10.0	8.0	10.0
(00·8)	3.6	3.0	3.2
(00·10)	0.25	0.20	0.15
<i>Second layer line</i>			
(10·5)	16.0	14.5	17.5
(10·6)	1.6	1.7	1.9
(10·7)	0.70	0.62	0.38
(10·8)	.60	.53	.68
(10·9)	.30	.25	.19
(10·10)	.00	.05	.05
(10·11)	.15	.13	.13
<i>Third layer line</i>			
(2 $\bar{1}$ ·6)	4.1	3.8	4.6
(2 $\bar{1}$ ·8)	1.6	1.4	2.0
<i>Fourth layer line</i>			
(20·7)	0.60	0.60	0.26
(20·8)	.30	.26	.55
<i>Prism reflections†</i>			
(10·0)	60.0	56.0	
(20·0)	23.0	23.0	
(30·0)	28.0	29.5	
(40·0)	2.8	2.2	
(50·0)	0.70	0.65	
(60·0)	0.0	0.50	

† The calculated and observed intensities for the prism planes bear no relation to the preceding values.

TABLE III.

(<i>hk</i> · <i>l</i>)	<i>I</i> _{obs}	<i>I</i> _{calc}	(<i>hk</i> · <i>l</i>)	<i>I</i> _{obs}	<i>I</i> _{calc}
(00·4)	0.60	0.65	(01·8)	6.5	7.1
(00·6)	20.0	19.7	(01·9)	2.7	1.9
(00·8)	15.0	15.0	(01·10)	1.4	1.5
(00·10)	3.5	3.1	(01·11)	4.5	4.1
(00·12)	0.10	0.01	(01·12)	0.0	0.00
(00·14)	.60	1.0	(01·13)	1.75	1.85
(00·16)	.30	.50			
(03·16)	.20	.20	(2 $\bar{1}$ ·6)	12.0	9.0
			(2 $\bar{1}$ ·8)	10.0	7.0
(01·6)	1.9	1.75	(2 $\bar{1}$ ·10)	1.7	2.0
(01·7)	1.5	1.3			

axis 10·0 vertical. The (20·7) \cong (20·8) difficulty in the fourth layer line is more acute than the corresponding case in the second layer line since the f values for these reflections are more nearly equal. Also the difference in intensity is more marked.

The best agreement for the tetrahedral arrangement of silver atoms was obtained at $p = 0.0425$, giving the distance of the atoms from the center of the tetrahedron as 0.23A. For this value of p the bonded silver iodine distance is 2.74A and the "nonbonded" distance 3.05A.

The low temperature exposures gave much the same pictures with no indication of a radical change in structure or parameter value, but with greatly enhanced intensities and more orders. Whereas at room temperature (00·10) had been barely visible after long exposure, even the much more complicated reflection (03·16) was quite strong at liquid air temperatures. At this temperature the intensities are accounted for satisfactorily by assuming the ideal wurtzite structure ($p = 0$), with the exception of the line (00·12) which is too strong experimentally. This reflection appears on only one photograph and may be explained without too great difficulty. The data are given in Table III. The factor multiplying the calculated intensities to bring them to agreement with the arbitrary experimental standard is here the same as for the room temperature case so that the check indicates that the change of intensity with temperature is given fairly well by the factor $e^{-2\theta(\sin\theta/\lambda)^2}$.

The first thing that was noticed in the low temperature pictures is that (00·4) becomes decidedly weaker in absolute intensity at -180°C .

The intensity of this line depends essentially on $(f_I - f_{Ag})^2$, so that this behavior is contrary to what one would expect and can only be interpreted as meaning that the silver atom has lost mobility or has become less spread out in going from the higher to the lower temperatures as these are the only means by which f_{Ag} can be increased. This is, of course, true only in the absence of some structural change, but would be true if with decreasing temperature silver iodide changed from the postulated room-temperature structure to ideal wurtzite. As can be seen, this fits the x-ray data nicely.

This result opened up another line of attack on the room-temperature intensities. Rigorously one should use an individual β for each type of atom in the crystal, and it was thought possible that by giving the silver atoms a larger temperature factor than the iodine the anomalous behavior of (00·4) could be explained as well as the (10·7) \cong (10·8) and (10·9) \cong (00·10) difficulties. By using $\beta_I = 3.00$ and $\beta_{Ag} = 5.00$ this can be done in a measure, but then (00·4) becomes approximately three times too large in relative intensity. The value of u again lies close to 0.63. The attempt to fit intensities in this way was abandoned because of (00·4) and because so large a difference in the temperature factors appears unsound.

In another attempt to account for the data, the scattering matter of each silver atom was distributed over the surface of a sphere about the ideal position of the atom; the radius of this sphere being used as the parameter. This was done on the assumption that the greater mobility of the silver was causing the troublesome intensity relationships, or that the silver existed in the crystal with different coordination numbers, causing it to oscillate among several positions approximately on the surface of a sphere. The calculations were carried out by multiplying the f values by $\sin x/x$, and making a set of curves for each value of the parameter. x here = $4\pi r \sin \theta/\lambda$ θ and λ having the usual meaning, and r being the radius of the sphere. At $r = 0.25\text{\AA}$, the difficulties still persisted, and in reality this procedure amounts to little more than giving one atom a larger β value than the other at one particular temperature. To explain the behavior of (00·4) one would have to assume a gradually decreasing radius for the sphere with decreasing tempera-

ture. Also the distance of closest approach of the silver and iodine seemed rather small on this picture so the attempt was abandoned in favor of the structure with the tetrahedrally distributed silver atoms.

With the introduction of three new positions for each silver atom reflections of the type $(n0\cdot l)$ $n = 3 \bmod 3$ and l odd, absent in wurtzite, should appear. In no case were these lines observed but the calculated intensities show them to be vanishingly small due to the symmetrical distribution of silver atoms around the ideal position. The calculated intensities were always smaller than those of allowed lines not observed in the photographs.

DISCUSSION

It will be seen from Table II that the agreement between experimental and calculated intensities is almost as good for wurtzite with $u = 0.63$ as for the postulated random distribution of silver atoms. The decision between the two structures rests on three main points. (1) The very small change from the ideal position seems improbable for two reasons. If, as this structure would indicate, the crystal is composed of silver iodide molecules one would think a larger difference should exist between the bonded and non-bonded Ag-I separations which are here 2.77Å and 2.835Å, respectively. Then, too, for this arrangement an axial ratio corresponding so closely to hexagonal close packing would hardly be anticipated. (2) If the crystal is of a homopolar nature with covalent bonds running throughout the structure, it seems hardly likely that the silver atoms can have a temperature factor enough larger than the iodine atoms to explain the results since the two types of atoms are so intimately connected. It is seen too in this connection that when the intensities in general are accounted for by the use of differing β values, (00·4) becomes much too strong. It is true that the intensity of this line is very sensitive to small errors in the f values, but even the allowance of a five percent error in each curve will not account for the discrepancy. (3) The impossibility of fitting the intensity relationships (10·7) \cong (10·8) and (10·9) \cong (00·10) seems to eliminate the wurtzite structure entirely. In thirty oscillation

pictures taken from (00·1) of ten different crystals these intensity relations are observed and in no case the opposite. The comparison (10·9) against (00·10) may not be as good as could be desired since the lines are somewhat diffuse but we feel that in making the intensities equal adequate allowance has been made for the uncertainties involved in qualitative comparison.

The anomalies of the physical behavior of AgI are well known. It was hoped at the outset to explain the pronounced basal cleavage by reference to the crystal structure. This cannot be done rigorously but suggestions can be made. Wurtzite (hexagonal ZnS) itself has good prismatic cleavage and poor basal cleavage. The explanation presumably lies in the fact that basal cleavage with the breaking of one bond per unit cell leaves the two halves oppositely charged while breaking the same number of bonds in cleaving along (10·0) leaves both halves neutral. In order to leave both cleaved basal planes neutral it would be necessary to break two bonds per unit cell. For the case of the structure here suggested for silver iodide, however, only an average of 1.25 bonds must be broken to produce the observed cleavage if we assume that the long Ag-I distance is nonbonded. At room temperature the mean thermal displacement of the atoms from the equilibrium positions is of the order of magnitude of the distance between the four equivalent silver positions indicating that there is probably continual movement of the silver atoms between these potential minima. This shifting of bonds would be such as further to weaken the basal plane binding relative to that of the prism planes. These considerations show how basal cleavage (poor in wurtzite) may become more pronounced in silver iodide, but they cannot be said to give a thoroughly reliable explanation of the cleavage.

The movement of the silver atoms from place to place in the lattice is familiar in the explanation of the electrolytic cation conductivity of the high temperature form.² Somewhat similar motion is shown here with the difference that in the low temperature structure it is impossible for the silver atoms to escape from their tetrahedra of surrounding iodine atoms so that they cannot contribute to the conductivity.

No exact explanation has been obtained about the volume contraction with rising temperature

found over a 150° range up to 146°C;⁸ however, it might be suggested that the increased movement of the silver atoms among the tetrahedral positions may be responsible for this effect. Pictures of sufficient accuracy to give a microscopic substantiation of this phenomenon have not yet been obtained.

The low temperature pictures indicate that the structure is that of ideal wurtzite. The data are probably not as good as for the room temperature case, since the intensity estimates are not good to more than 30 percent and the method of applying the absorption correction is not exact. Two discrepancies are observed: (00·12) is stronger than would be expected for the ideal structure and (10·9) is noticeably weaker. These two difficulties may be explained if one assumes that all of the silver atoms have not yet given up the tetrahedral positions. Calculation shows that if one-fifth of the atoms are placed in the tetrahedral positions, the intensities of these two lines are brought into agreement with observation and the other lines are practically unaffected.

The fact that silver does not form four strong tetrahedral bonds is indicated by the softness of the crystal and its loose structure. It is one of the few crystals for which the molecular volume is as much as ten percent larger than the sum of the atomic volumes of the components. The three coordinated randomly distributed silver atoms in the proposed structure fit in nicely with the structure found by Strock for the high temperature form, indicating that at 146°C the already randomly arranged silver atoms with large temperature motion can "melt" inside the iodine lattice, allowing the sodium atoms to rearrange and give rise to the high temperature modification.

A possible explanation for the rearrangement of the silver atoms between liquid air and room temperatures is that there are in reality five potential minima within the iodine tetrahedra of nearly the same energy, and that the ideal wurtzite position is of slightly lower energy. Then at low temperatures the crystal would assume essentially the wurtzite structure and at 25°C the distribution would be random among the five positions. With four-fifths of the atoms in the

⁸ Rodwell, *Proc. Roy. Soc.* **25**, 280 (1876); *Trans. Roy. Soc.* **173**, 1125 (1882).

tetrahedral positions the intensity calculations would be but little different from those given in this paper, although it would probably mean a small increase in the parameter value. The intensity data, however, do not warrant this calculation.

Evidence for three coordinated silver atoms has been found by Dr. Harker of this laboratory in a preliminary investigation of proustite and

pyrargyrite where he also finds silver in a flattened pyramidal arrangement with a silver radius of approximately 1.45Å. The silver radii from this investigation are: tetrahedral —1.53Å, three coordinated —1.46Å. The radius of the nonbonded silver is 1.77Å.

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A Study of the Molecular Structure of Diiodoethane

Iodine Bond Resonance and the Molecular Structure of Diiodoethylene. Molecular Packing in Their Crystal Lattices

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Using data from an x-ray study of the crystal structure of *sym*-diiodoethane and *sym*-diiodoethylene (*trans* form) the positions of the iodine atoms in the crystal cells were located. Iodine bond resonance is discussed and a factor of 0.92 of the length of the longer bond proposed for evaluating the interatomic distance for any resonating bond. On the basis of the concepts of tetrahedral carbon bonds, bond resonance, Pauling's normal covalent bond radii, etc., reasonable molecular models for the above substances were predicted. Comparison of these with the x-ray data showed the iodine-iodine distances to be in excellent agree-

ment with certain iodine-iodine distances within the crystal cells, thus locating the molecules within the cells. These models together with Mack's concept of the atomic domain radius of atoms in crystals permitted a consideration of the packing of the molecules in the crystal lattice, thus locating the atomic coordinates of the carbon and hydrogen atoms in the cell. The domain radii found were; iodine = 1.97Å, and hydrogen = 1.23Å. The resulting molecular packing is seen to explain and be in excellent agreement with observed physical properties of the two crystals.

INTRODUCTION

AT present our most important methods for investigating molecular structure are based on comparison of experimental data with the results to be expected from a model which we have visualized from our best theoretical and experimental knowledge.

The results of x-ray diffraction studies on crystals give important data for consideration of the structure of the crystal molecule, especially in the case of organic substances. It is often possible to determine important interatomic distances in the molecule from these studies, thus permitting a study of the structure of the molecule, constancy of bond radii, bond angles, bond resonance, etc., by comparison with reasonable molecular models.

In a recent x-ray study¹ of the crystal structures of *sym*-diiodoethane and *sym*-diiodoethylene it was found possible to locate the iodine atoms in the unit cells with considerable accuracy. Using data from this investigation we have made a study of the molecular structures and molecular packing in the crystals of these compounds.

CRYSTAL STRUCTURE DATA

s-diiodoethane was found to possess a two-molecule monoclinic cell with the following dimensions:

$$\begin{aligned} a'_0 &= 4.768\text{Å}, & b'_0 &= 12.897\text{Å}, \\ c'_0 &= 4.784\text{Å}, & \beta' &= 105^\circ 5'. \end{aligned}$$

Its space group is C_{2h}^5 . The four-molecule pseudo-

¹ The detailed results of this study are reported in *Zeits. f. Krist.* **90**, 495 (1935).