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Solid Solutions in Bromine–Iodine Mixtures

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The lattice spacings of a series of solid solutions of iodine and bromine have been determined for a range of composition 0–38 mole % bromine. The change of lattice spacing with composition is found to be linear over this range. The solid solution is found to belong to the space group *Ccm*, suggesting that the crystals contain oriented IBr molecules.

A method is described for obtaining refined values of lattice parameters from X-ray powder photographs of substances which do not give high-angle reflexions.

Introduction

The elements bromine and iodine crystallize in the orthorhombic system, and were shown by Terwogt (1905) to form a continuous series of solid solutions. This worker gave data for their melting phenomena which indicated a close approach of the solidus and liquidus curves in the vicinity of the composition IBr and, although his data are not sufficiently precise to decide exactly how closely the curves do approach, they leave no doubt that a substantial proportion of IBr molecules is present in the solids approaching that composition. The crystals of both of the free halogens belong to the space group *Ccma* (Vonnegut & Warren, 1936; Harris, Mack & Blake, 1928) containing four molecules per unit cell, and the symmetry of this structure is dependent upon the end-to-end symmetry of the halogen molecule. It is of interest, therefore, to examine the structure of these solid solutions not only to determine the effect of replacement upon the lattice dimensions, but also to examine the way in which the loss of symmetry of the halogen molecule is accommodated in the lattice.

The present report covers the system at room temperature only, at which powder photographs were obtainable up to a mole fraction of about 0·38 of bromine; beyond this the melting-point is so low that the diffraction lines lose their sharpness and measurements are possible only at lower temperatures.

Preparation of specimens

Appropriate quantities of a few grams of finely powdered Analar iodine and Analar bromine (both previously dried for several weeks over P_2O_5) were weighed into a test-tube with the centre portion constricted. Three or four thin-walled glass capillaries, sealed at one end, were dropped in and the halogen mixture was chilled in CO_2–alcohol mixture. The tube was then evacuated on an oil pump and sealed off at the constricted portion; it was next placed in a water or oil bath so that the open ends of the capillaries lay upwards. The bath temperature was then raised until the material was completely melted, the mixture well shaken to ensure good mixing, and the tube inverted and replaced in the bath so that the open ends of the capillaries lay downwards. It was next rapidly removed, wiped and cut open, thereby admitting air and driving the liquid mixture up into the capillaries, which were at once picked out and sealed at their open ends with a pinhead flame. Usually crystallization was sufficiently rapid to give a fine-textured solid which produced reasonable powder diagrams from a rotated specimen. A few specimens had to be discarded on account of being too coarse.

Lattice-parameter measurements

X-ray powder photographs were taken with copper *K* radiation, using a standard 19 cm. camera. The glass capillaries containing the mixture were supported in plasticine and rotated during exposure.

No attempt was made to keep the specimen at constant temperature, since the accuracy with which measurements could be made, particularly on specimens of high bromine content, did not justify this precaution. From the expansion coefficients for the iodine lattice, evaluated by Straumanis (1943), it is found that a variation in temperature of 5° C. produces changes in the *a*, *b* and *c* spacings of 0·06, 0·05 and 0·02 % respectively. The temperature variation of the specimen was probably less than 5° C., and the accuracy of the measured spacings is considered to be not more than 0·05 %.

Measurements were made on the films using a steel scale; the positions of the lines could be read to within 0·1 mm. Owing to the low contrast between the background and the X-ray lines obtained with these materials, no advantage accrues from the use of a microphotometer for these measurements.

The melting-point of iodine is about 114° C., and it falls in roughly linear fashion down to about 40° C. for the equimolecular mixture. Thus the amplitude of thermal vibrations of the crystal lattice is considerable at room temperature, increasing as the bromine content rises, and as a result the X-ray spectra are not very sharp, while, for mixtures rich in bromine, high-angle reflexions do not occur at all. It was found to be impossible to deal with mixtures containing more than about 40 mole % bromine. Lines were obtained with a specimen containing 37·9 mole % bromine with Bragg angles up to 36°, and on this film 12 lines were measured and indexed. Existing data on the lattice parameters of iodine by Harris *et al.* (1928) and more recently by Straumanis enabled the reflexions to be indexed.

For an orthorhombic crystal, with the usual notation,

$$\sin^2\theta = Ah^2 + Bk^2 + Cl^2. \qquad (1$$

where $A = \lambda^2/4a^2$, etc. It is required to find the values of A, B and C which give the best fit between the observed values of $\sin^2\theta$ and the corresponding values of $Ah^2 + Bk^2 + Cl^2$. Cohen (1935) has given a method whereby systematic errors may be eliminated and the best values of A, B and C found. As described by its author, the method is based on the Bradley–Jay extrapolation formula and is applied to high-angle reflexions. It may readily be extended to deal with low-angle reflexions in the following way.

Nelson & Riley (1945) have shown that the errors in a derived lattice spacing vary in a linear manner with the function $\left(\frac{\cos^2\theta}{\theta} + \frac{\cos^2\theta}{\sin\theta}\right)$ over the range of Bragg angles 13–90°. It may therefore be used in the elimination of systematic errors from readings in the range $13° < \theta < 36°$. We have

$$\frac{\delta d}{d} \propto \frac{\cos^2\theta}{\theta} + \frac{\cos^2\theta}{\sin\theta}, \qquad (2)$$

and, from the Bragg relation,

$$\frac{2\delta d}{d} = -\frac{\delta(\sin^2\theta)}{\sin^2\theta}, \qquad (3)$$

so that the error in the observed value of $\sin^2\theta$ is given by

$$\delta(\sin^2\theta) \propto \sin^2\theta\left\{\frac{\cos^2\theta}{\theta} + \frac{\cos^2\theta}{\sin\theta}\right\}$$

$$= D\sin^2 2\theta\left\{\frac{1}{\theta} + \frac{1}{\sin\theta}\right\} = Df(\theta).$$

Equation (1) therefore becomes

$$Ah^2 + Bk^2 + Cl^2 + Df(\theta) = \sin^2\theta_{\text{obs.}}.$$

Since the value of $Df(\theta)$ is small, $f(\theta)$ need be evaluated only to two significant figures. A table of values of $f(\theta)$ for 1° intervals of θ is given at the end of the paper (Table 3).

The method of least squares may be applied to the determination of the quantities A, B, C and D in the manner suggested by Cohen. This method has the disadvantage of treating all the $\sin^2\theta$ values as of equal weight, which is clearly unsound. Suitable weights may, however, be assigned to the $\sin^2\theta$ values on the basis that the accuracy of measurement of θ, and hence of $\sin^2\theta$, depends on the value of θ. The fractional error in $\sin^2\theta$ due to an uncertainty $d\theta$ (which is constant for all lines) is given by

$$\frac{d(\sin^2\theta)}{\sin^2\theta} = \cot\theta d\theta.$$

We therefore assign weights to the $\sin^2\theta$ values inversely proportional to the square of this, i.e. to $1/\cot^2\theta = \tan^2\theta$, in forming the normal equations for calculating the values A, B and C.

The value of D obtained serves to indicate the magnitude of any systematic errors in the measurements. The largest value obtained for D was 0·0003, which corresponds to an error in measuring the position of the line of 0·09 mm. As this is less than the limit of reproducibility of the measurements on these photographs, it may be assumed that no significant systematic errors were present.

As an indication of the reliability of measurements made using Bragg angles up to 36°, two sets of calculations were made on the measurements of one of the films taken with a pure iodine specimen. For one set, twelve lines were used, with Bragg angles ranging up to 36°. In this range the α-doublets are not resolved and the weighted mean of the α_1 and α_2 wave-lengths was used in calculating the lattice spacings. For the second set, sixteen lines were used with Bragg angles up to 84°. Measurements were made on the α_1 lines of well-resolved doublets. The following results were obtained for the lattice parameter of iodine:

I. Using well-resolved α-doublets up to $\theta = 84°$ ($\lambda\alpha_1 = 1{\cdot}5374$ kX.):

$$a = 4{\cdot}774 \pm 0{\cdot}001, \quad b = 7{\cdot}250 \pm 0{\cdot}001,$$
$$c = 9{\cdot}772 \pm 0{\cdot}002 \text{ kX.}$$

II. Using reflexions with Bragg angles up to $\theta = 36°$ ($\lambda_{\text{mean}} = 1{\cdot}5387$ kX.):

$$a = 4{\cdot}770 \pm 0{\cdot}003, \quad b = 7{\cdot}252 \pm 0{\cdot}004,$$
$$c = 9{\cdot}769 \pm 0{\cdot}005 \text{ kX.}$$

The values quoted by Straumanis for a temperature of 16° are

$$a = 4{\cdot}7748, \quad b = 7{\cdot}2487, \quad c = 9{\cdot}7704.$$

The units are given by Straumanis as Ångström units, although from the agreement between the two sets of values it would seem probable that Straumanis's figures are, in fact, in kX. units.

Lattice parameters of solid solutions

The values obtained for the unit-cell dimensions of the solid solutions are shown in Table 1.

Table 1. *Cell dimensions*

Mole % bromine	a (kX.)	b (kX.)	c (kX.)
0	4·774	7·250	9·772
6·3	4·753	7·204	9·689
14·9	4·732	7·163	$9{\cdot}61_0$
24·9	4·715	7·096	$9{\cdot}48_5$
34·0	$4{\cdot}68_7$	$7{\cdot}05_4$	$9{\cdot}39_0$
37·9	$4{\cdot}67_7$	$7{\cdot}02_2$	$9{\cdot}33_9$

The lattice parameters change linearly with composition as is shown in Fig. 1. The values obtained for *a*, *b* and *c* on extrapolating to 100 % bromine are less than those obtained for bromine at −150° C. by Vonnegut & Warren, so it is evident that the linear change of spacings with composition does not hold over the whole range of composition. The point of departure from the linear law can be determined only by observations at lower temperatures.

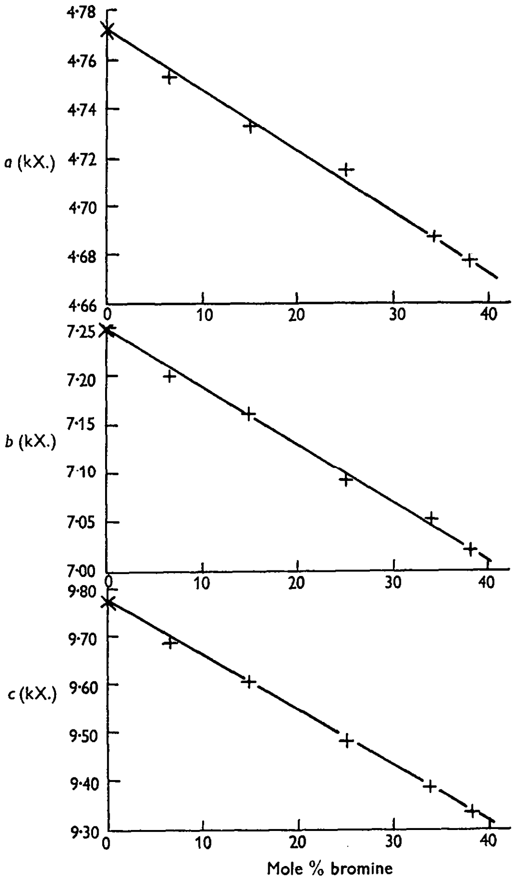

Fig. 1. Variation with composition of lattice parameters of bromine–iodine solid solutions.

Structure of the solid solutions

The work of McMorris & Yost (1931) and of Blair & Yost (1933) proves conclusively that IBr molecules are extensively present in gaseous mixtures, and the form of the solidus and liquidus curves points to extensive formation of mixed molecules in the solid solution.

The arrangement of IBr molecules in the lattice may take one of two forms. If the orientations of the unsymmetrical IBr molecules throughout the lattice are random, then the symmetry of the system will be the same as that for pure iodine or bromine, the space group being *Ccma*, and the relative intensities of the X-ray spectra will be the same as those for pure iodine. If, however, the IBr molecules are arranged in a regular fashion on the lattice the effect is to reduce the symmetry to that of space group *Ccm*. The positions of the atoms in the iodine lattice are given by Harris *et al.* (1928) as $x = 0{\cdot}150$, $z = 0{\cdot}117$ (fractions of the unit-cell edge). The corresponding positions for bromine, found by Vonnegut & Warren (1936), are $x = 0{\cdot}135$, $z = 0{\cdot}110$. It is almost certain that in the IBr structure the coordinates will lie between these values and, with this assumption, the intensities of reflexions may be calculated for the IBr structure. An examination of the relative intensities of the lines on the 37·9 % bromine film then enables a choice to be made between the possible configurations.

It was found impossible to obtain reliable intensity measurements with a microphotometer owing to the poor contrast between the X-ray lines and background. The intensities were therefore estimated visually, using the categories very weak, weak, medium, strong and very strong. Since the diffuse background on the films decreases considerably as the Bragg angle increases, there is a tendency to over-estimate the intensities of the higher angle lines. However, this affects both the iodine and the iodine–bromine films equally, and will not influence observations on the change of relative intensity of a line of given indices.

The results of observations on ten lines are given in Table 2.

Table 2. *Data from powder photographs*

hkl (1)	Calculated intensity for I_2 in *Ccma* structure (2)	Calculated intensity for IBr in *Ccm* structure (3)	Observed intensities I_2 specimens (4)	Observed intensities 37 % Br specimens (5)
112	37	27	*vs*	*s*
004	7·9	5·2	*m*	*w*
201	6·0	5·4	*m*	*w*
131	4·4	9·2	*w*	*m*
024	10·2	8·2	*m*	*m*
132	12·8	9·5	*m*	*vs*
203	5·5	5·2	*m*	*w*
115	3·8	5·3	*m*	*s*
311	5·5	4·9	*s*	*m*
116	6·3	5·0	*s*	*m*

Comparison of the change in calculated intensities (Table 2, columns (2) and (3)) with the observed changes (columns (4) and (5)) consequent upon replacement of iodine atoms in the lattice by bromine strongly suggests that the solid solution has the ordered structure with space group *Ccm*. Of the ten lines examined, the behaviour of all except the (132) reflexion is consistent with this conclusion. It is difficult to ascribe a cause to this abnormality, but it is worth noting that Harris *et al.* found an unduly high intensity with this reflexion on oscillation photographs of pure iodine.

It might have been expected that a random structure would obtain at temperatures approaching the melting-point of these crystals (where thermal vibrations are considerable), possibly changing to an ordered structure on cooling. Evidently, however, the polar character of the IBr molecule is sufficiently strong to produce orientation in the lattice, even at room temperature.

Table 3. *Values of the function* $\sin^2 2\theta\left(\frac{1}{\theta}+\frac{1}{\sin\theta}\right)$

θ	$f(\theta)$	θ	$f(\theta)$	θ	$f(\theta)$
10	1·34	20	2·39	30	2·93
11	1·47	21	2·47	31	2·96
12	1·59	22	2·55	32	2·97
13	1·70	23	2·61	33	2·98
14	1·81	24	2·67	34	2·98
15	1·92	25	2·73	35	2·99
16	2·03	26	2·79	36	2·98
17	2·12	27	2·83	37	2·97
18	2·22	28	2·88	38	2·95
19	2·30	29	2·90	39	2·93

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Affine Gitterkonstanten

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The *affine lattice constants* are a set of six constants, five of them angular and one linear. The former characterize extensions and shears by which the general, i.e. triclinic, crystal cell may be deformed into a cubic cell, and the linear constant gives the absolute length of the edge of this cube. Two of the five angles used coincide with angles introduced by Fedorow. Two angular constants may be interpreted as the two extensions required to transform an orthogonal cell of volume equal to that of the crystal cell into a cube without changing the length of the edge; this length being the linear constant. The three other angular constants are the shear angles by which the triclinic cell may be made orthogonal without change of volume. Formulae are given for the various crystal systems for transforming the usual axial constants (three lengths, three angles) into the affine constants, and vice versa.

Zur Charakterisierung der triklinen Kristalle benutzt Fedorow in seinem Lebenswerk *Das Kristallreich* fünf Winkel, die graphisch mit Hilfe des stereographischen Netzes gefunden werden (Fedorow, 1920; Niggli, 1926, S. 663, 1928, S. 297; Padurow, 1931, 1932*a*).

In den affinen Gitterkonstanten haben wir eine weitere Entwicklung der Fedorow'schen Idee. In ihnen fallen zwei Winkel (Δ und Δ_β) mit denen von Fedorow zusammen. Grundsätzlich neu ist die Einführung des Gittermaßstabs a_0.

Mit Hilfe der affinen Gitterkonstanten können bedeutende Vereinfachungen bei der Auffindung der 'richtigen Aufstellung' der Kristalle (Niggli, 1928, S. 297; Padurow, 1931, 1932*a*) und bei verschiedenen strukturmorphologischen Forschungen erreicht werden.

Die Anwendung affiner Gitterkonstanten bei der Verwertung der Ergebnisse der goniometrischen Messung der Kristalle und bei dem Indizieren der Röntgenfilme führt auch zu bedeutenden Vereinfachungen.

Der Verfasser ist wiederholt auf die Ausarbeitung dieser Frage zurückgekommen (Delonay, Padurow & Alexandrow, 1934; Padurow, 1931, 1932*a*, *b*; Agafonow, 1934), aber eine zufriedenstellende Lösung ist erst Ende 1947 gefunden worden. Die Ausarbeitung der neuen Methode ist gegenwärtig so weit fortgeschritten, daß die Methode an einigen Objekten geprüft werden konnte. Als erstes Beispiel wurde Chrysotilasbest gewählt, dessen Strukturzelle ermittelt wurde.

Allgemeine Bemerkungen

Die Strukturzellen sind verschiedenartige Parallelepipede und können stets mit Hilfe von homogenen Deformationen (Dehnung und Schiebung) in einen Kubus mit einer Kante a_0 verwandelt werden. Die affinen Gitterkonstanten charakterisieren die Größe und die Richtung solcher Deformationen.

Im allgemeinen Fall, also bei einem triklinen Kristall, sind sechs affine Konstanten vorhanden. Fünf von ihnen charakterisieren die Winkelverhältnisse und können wie aus den Ergebnissen goniometrischer Kristallmessungen, so auch auf dem Wege der Röntgenanalyse errechnet werden.

Die affinen Winkelkonstanten werden entweder als Winkel $\Delta, \Delta_2, \Delta_\beta$, Δ_α und Δ_γ oder als Tangenten dieser Winkel, $t = \mathrm{tg}\Delta$, $t_2 = \mathrm{tg}\Delta_2$, etc., angegeben.

Die Winkelkonstanten t und t_2 charakterisieren die Dehnungen, die übrigen, t_β, t_α und t_γ, die Schiebungen.