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The Crystal Structure of The Room-Temperature Modification of Indium Chloride, InCl

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The yellow crystals of the room-temperature modification of indium chloride, InCl, are cubic with $a = 12{\cdot}368 \pm 0{\cdot}001$ Å.

The space group is $P2_13$ and the unit cell contains 32 molecules of InCl. The positions of the In atoms were determined by a Patterson synthesis and those of the Cl atoms by two Fourier syntheses, using three-dimensional data. InCl has a deformed NaCl structure; the deformation is such that of the twelve In^+ ions surrounding a given In^+ ion three are much nearer to it than the other nine, these distances being about 3·65 and 4·70 Å, respectively. This structure can be explained only by postulating cation bonding.

Introduction

An investigation of the crystal structure of InCl has been carried out to verify our hypothesis that a special bonding between the In^+ ions would lead to mutually short distances (van den Berg, 1964). Such short distances between cations with an outer s^2 shell have been observed in InBr (Stephenson & Mellor, 1950) and InI (Jones & Templeton, 1955) and in a number of compounds of the type A_mB_n with $A = Tl^+$, Ge^{2+}, Sn^{2+} and Pb^{2+}. A survey of the experimental evidence of bonding between cations in general was given by van Arkel (1961).

Preparation

A weighed quantity of indium trichloride, $InCl_3$, was introduced into a small Pyrex tube, a slight excess of indium shavings added and the tube sealed, shaken and heated with a burner. The contents rapidly formed a dark red, almost black liquid, which was kept in the molten state for several minutes. On cooling it solidified to an orange-yellow solid. Guinier photographs could not at first be indexed unambiguously. Slower cooling and more tempering, however, resulted in better photographs, which could be indexed in terms of a cubic lattice. The colour of the improved sample was yellow. To obtain single crystals the sample was placed in an electric furnace at 200°C, and slowly cooled to 150°C. Then the sample was tempered at this temperature for some days, cooled to 100°C, and tempered again for a week. Very slow cooling to room temperature produced bright yellow crystals.

Modifications of indium chloride

Two modifications of InCl have been reported (Klemm, 1926). We studied the transition under the microscope, and our observations agree with those of Klemm. The compound is bright yellow below about 120°C and red above this temperature. The following experiment shows that the change of colour coincides with a transition to another modification.

Powder diagrams of a tempered, originally yellow sample were made at room temperature and at 110°, 130° and 150°C. Before each exposure at the various temperatures the colour of the sample was checked. At 110°C it was still yellow but at 130°C it had changed to red. The pattern of the diagram made at 130°C had also changed. On slow cooling the powder remained red; diagrams made at 130°, 110°C and room temperature all showed the pattern of the red modification. A diagram of the same sample, made at room temperature the next day, contained lines of both modifications. Apparently on cooling the red modification changes only very slowly into the yellow one.

The structure which will be discussed here is that of the yellow, room temperature modification.

Crystallographic investigation

Cell constants and space group

A Guinier powder photograph of the yellow sample, calibrated with potassium chloride powder lines, was indexed on a cubic lattice with $a = 12{\cdot}368 \pm 0{\cdot}001$ Å. It was impossible to index a number of weak reflexions, which proved to be due to the red modification. Klemm gives a value of 4·1925 g.cm^{-3} for the density of yellow InCl. A rough check, based on 32 molecules of InCl in the unit cell, gave a density of 4·218 g.cm^{-3} for our specimen.

In view of the intensities of the Guinier photograph the specimen was assumed to have a deformed rock-salt structure with the length of its cell axis doubled. This is also in agreement with the number of molecules in the unit cell of InCl. In the range of small θ, the *hkl* reflexions whose indices divided by two are all even or all odd – for instance, 222, 400 and 440 – are considerably stronger than the rest. This is in agreement with the sodium chloride structure, for which reflexions 111, 200 and 220 are consistent with the face-centring.

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The space group could not be determined unambiguously. Besides, with such a large number of molecules in the cell, it was expected that the structure would be too complicated to be solved with the aid of a powder diagram. Attempts to obtain single crystals were finally successful. A crystal of very irregular form could be isolated from the melt.

Weissenberg photographs were made, with unfiltered Cu *K* radiation, about the [100] and the [110] directions, for layer lines 0, 1 and 2. The intensities were estimated visually, corrected for Lp factor and scaled to each other. As the irregular form of the crystal could not be properly defined, it was impossible to correct the intensities for absorption. This made it difficult to scale the intensities of the various reciprocal planes. But because of the cyclic permutation of the *hkl* indices resulting from the threefold axis, the layer lines had many reflexions in common, which more or less cancelled out the absorption effects.

The diagrams showed Laue symmetry $\frac{m}{2}\bar{3}$; the lattice was primitive. The only systematic absences appeared to be $h00$ for $h=2n+1$, which would point to $P2_13$. However, since many reflexions were absent especially at low scattering angle, the halving of the (100) planes could be accidental so that $Pm3$ and $P23$ could not be excluded.

Location of the indium atoms

The three-dimensional Patterson function was computed. The vector pattern revealed a deformed rocksalt structure. But – as was to be expected – the Patterson maps showed considerable overlap, the contours being elongated (Fig. 1). In fact, interpretation at first sight seemed doubtful, especially in view of the uncertainty about the space group. Nevertheless, we succeeded in interpreting the Patterson function on the basis of $P2_13$. With 32 molecules in the cell, this means that both In and Cl must have at least two special fourfold positions 4(*a*), as well as possibly two general twelvefold positions 12(*b*).

First an attempt was made to find the parameters of In by deforming the sodium chloride structure. Taking for In the positions of Na in the rocksalt structure with a doubled cell constant, the choice of the origin leads to two possible sets of parameters, which, on being varied in the space group $P2_13$, result in quite different deformations of the sodium chloride structure. These two possibilities are given in Table 1. Note that, with In in positions (*a*), the Cl are expected in (*b*), and *vice versa.*

Table 1. *Two possible sets of parameters in the undeformed* NaCl *structure*

(*a*)	12 (I)	$00\frac{1}{4}$	(*b*)	12 (I)	$\frac{1}{4}\frac{1}{4}0$
	12 (II)	$00\frac{3}{4}$		12 (II)	$\frac{3}{4}\frac{3}{4}0$
	4 (III)	$\frac{1}{4}\frac{1}{4}\frac{1}{4}$		4(III)	000
	4 (IV)	$\frac{3}{4}\frac{3}{4}\frac{3}{4}$		4 (IV)	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$

As shown for instance in Fig. 1, the Patterson map indicates deviations of about 10° from the rocksalt configuration, at least for the In atoms. An interpretation of the highest peaks proved possible only on the basis of case (*b*) for the twelvefold indium positions. Rough parameters could be assigned to In in 12 (I) and 12 (II). Two high peaks not yet accounted for were interpreted as an overlap of two Harker vectors and a non-Harker vector of the fourfold positions. All the expected In–In vectors could then be identified in the Patterson function, as shown for example in the section $w=0$ (Fig. 1). The positional parameters of In were then already very close to the final ones listed in Table 2.

Table 2. *The atomic parameters for* InCl

	x	*y*	*z*
$\mathrm{In_{I}}$	+0·2487	+0·2212	−0·0292
$\mathrm{In_{II}}$	+0·7520	+0·7780	+0·0280
$\mathrm{In_{III}}$	+0·0320	+0·0320	+0·0320
$\mathrm{In_{IV}}$	+0·4690	+0·4690	+0·4690
$\mathrm{Cl_{I}}$	−0·0528	+0·0040	+0·3040
$\mathrm{Cl_{II}}$	+0·0500	−0·0097	+0·8025
$\mathrm{Cl_{III}}$	+0·2029	+0·2029	+0·2029
$\mathrm{Cl_{IV}}$	+0·7983	+0·7983	+0·7983

Location of the Cl *atoms*

Three-dimensional structure factors were calculated, the phases being determined by In only. When on this basis a three-dimensional Fourier synthesis was computed, the Cl atoms in the fourfold positions could be easily found, but the electron density for the Cl atoms in twelvefold positions was spread over a number of lower peaks. Of these peaks the highest were identified as the Cl positions and, after a cycle of structure factors, the second three-dimensional Fourier synthesis confirmed this choice. As expected, these positions are close to set (*a*) in Table 1.

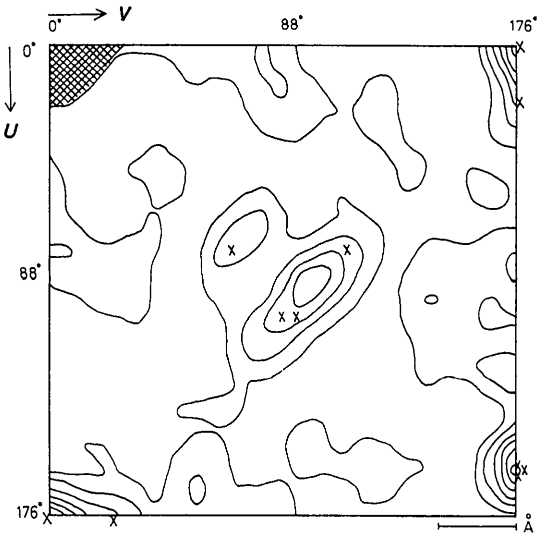

Fig. 1. Section $w=0$ of the three-dimensional Patterson synthesis of InCl. Only positive contours are drawn. The ends of the In–In vectors are indicated by crosses.

With these parameters for Cl, and after a little shifting of the In atoms, the R value worked out at 19% with an isotropic temperature factor B of 0·45 Å.

A three-dimensional difference synthesis was computed and the atoms were shifted using the relation:

$$r = \frac{\partial(\varrho_o - \varrho_c)/\partial r}{\partial^2 \varrho_o/\partial r^2}\,.$$

The final parameters are listed in Table 2; with the same value for B, the R value dropped to 17·4%, excluding reflexions 222 and 400, which are too strong to be estimated properly.

The observed and calculated structure factors are listed in Table 3.

Description of the structure

It is concluded that the structure is indeed a distorted version of the rocksalt structure, the edge of the cubic unit cell being twice as long as for an undeformed rocksalt structure. In sodium chloride, layers of Na^+ and layers of Cl^- parallel to (111) alternate. If we consider an Na^+ ion in such a layer, it is octahedrally surrounded by three Cl^- ions in each of the two adjoining layers of Cl^-. In the second sphere it is surrounded by a cubooctahedron of 12 Na^+, six of which lie in its own layer, and three in each of the nearest Na^+ layers (Fig. 2). All the Na–Na distances are equal. Now Table 4 shows that in the structure of InCl, each In atom, whether in position I, II, III or IV, has three In neighbours at a relatively short distance of about 3·65 Å and nine at a distance of about 4·7 Å. The way in which an In atom is surrounded differs for each of the four crystallographic positions. With respect to the short In–In distances, we can divide the In atoms into two groups:

(*a*) $\mathrm{In_{I}}$ and $\mathrm{In_{III}}$
(*b*) $\mathrm{In_{II}}$ and $\mathrm{In_{IV}}$.

In group (*b*) an $\mathrm{In_{IV}}$ forms a nearly regular tetrahedron with three $\mathrm{In_{II}}$; $\mathrm{In_{IV}}$ as the top corner of the tetrahedron has three $\mathrm{In_{II}}$ at distances of 3·61 Å, which, forming the basis of the tetrahedron, have mutual distances of 3·68 Å [Fig. 3(*c*), (*d*)]. Thus, in group (*b*), the short In–In distances lead to isolated tetrahedra.

The other group, (*a*), forms a rather complicated three-dimensional network of In atoms at short dis-

Table 3. *List of observed and calculated structure factors of* InCl

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
4	1	0	55.6	68.1	12	4	1	35.5	39.5	6	10	1	33.6	35.3
6	1	0	37.6	47.5	0	1	6	46.2	44.4	8	10	1	30.7	35.3
8	1	0	59.4	64.3	4	6	0	29.5	48.9	9	10	1	77.0	91.0
10	1	0	41.4	50.5	5	6	0	30.7	41.4	1	3	12	50.9	47.4
4	2	0	10.7	29.0	8	6	0	36.2	41.4	1	4	12	37.2	35.7
8	2	0	79.0	85.2	13	6	0	48.2	48.1	0	0	12	61.0	66.2
12	2	0	102.3	91.7	14	6	0	49.1	45.5	0	2	12	79.5	102.3
14	2	0	47.4	53.1	4	7	0	71.9	80.5	0	3	12	23.5	35.0
4	3	0	88.0	90.9	8	7	0	96.8	109.4	0	4	12	46.7	66.2
8	3	0	87.2	98.2	12	7	0	73.6	80.1	0	6	13	76.4	82.7
12	3	0	55.3	56.4	0	8	0	55.1	40.2	0	0	14	64.5	44.4
1	4	0	71.4	86.4	8	0	1	71.2	82.3	0	2	14	64.9	63.9
2	4	0	21.8	23.6	8	0	2	61.1	72.2	0	3	14	26.8	21.4
2	1	1	14.7	25.8	0	3	8	50.5	54.1	0	4	14	40.8	38.0
4	1	1	59.4	72.4	0	4	8	41.8	35.3	0	6	14	45.7	34.2
6	1	1	51.9	60.5	4	5	1	60.9	73.3	0	6	0	20.4	13.9
8	1	1	53.0	62.7	5	5	1	13.3	22.2	1	7	12	68.5	65.8
10	1	1	55.6	60.8	6	5	1	37.3	48.9	6	13	1	51.9	55.3
14	1	1	27.8	33.6	8	5	1	50.7	55.8	2	14	1	44.3	39.5
2	2	1	20.7	34.5	10	5	1	32.6	41.4	1	4	14	33.2	26.7
4	2	1	61.7	81.5	2	6	1	62.8	58.3	1	5	14	30.2	27.1
5	2	1	37.6	50.5	4	6	1	46.9	55.6	6	14	1	29.9	26.7
6	2	1	45.9	56.4	5	6	1	103.4	143.3	2	4	2	31.2	20.7
8	2	1	62.8	70.8	6	6	1	49.0	54.5	2	2	5	48.7	44.4
9	2	1	39.5	49.4	8	6	1	32.2	36.1	2	2	6	143.7	127.5
10	2	1	39.5	49.3	9	6	1	101.7	112.0	2	8	2	72.7	55.6
3	4	0	55.6	48.4	13	6	1	63.1	60.5	2	9	2	46.9	40.2
4	4	0	188.0	207.7	2	8	1	54.1	56.4	2	12	2	84.9	66.2
5	4	0	86.5	64.8	3	8	1	98.5	103.0	14	2	2	54.4	51.9
8	4	0	45.5	41.8	5	8	0	49.7	66.9	4	3	4	55.2	62.8
10	4	0	62.0	57.0	10	8	0	53.3	63.2	3	5	5	27.8	16.9
12	4	0	54.1	46.7	0	2	9	51.1	65.0	3	7	7	31.1	27.1
14	4	0	19.6	61.6	6	9	0	108.0	138.7	3	10	10	30.6	24.4
0	2	5	55.6	46.8	10	9	0	88.6	99.3	4	3	3	65.6	57.2
4	5	0	27.8	14.7	0	0	10	48.5	37.6	4	4	4	145.2	133.5
6	5	0	112.8	96.9	0	1	10	43.1	41.4	5	4	4	39.2	39.5
8	5	0	25.9	15.7	0	2	10	44.7	44.4	6	6	5	68.5	54.5
10	5	0	93.6	82.1	0	3	10	36.1	33.5	5	7	7	44.9	40.2
14	5	0	26.3	37.5	4	10	0	32.4	33.8	5	8	8	27.7	26.7
3	1	4	37.6	37.2	5	10	0	24.5	30.1	5	9	9	32.9	25.9
3	1	6	27.8	33.8	6	10	0	27.0	30.1	6	4	4	21.8	18.0
3	1	8	35.7	40.1	4	11	0	44.8	39.1	6	5	5	49.8	39.5
3	1	10	50.8	53.6	8	11	0	70.8	76.0	6	6	6	36.4	19.9
3	1	14	31.6	43.6	4	8	1	41.1	48.1	7	3	3	6.4	18.0
4	1	2	51.9	61.0	6	8	1	19.7	28.2	4	3	2	78.3	101.9
1	3	4	103.0	93.8	7	8	1	92.8	97.8	2	8	3	89.0	74.1
4	1	4	71.4	60.2	11	8	1	64.8	68.8	2	12	3	53.3	50.4
1	6	4	47.4	40.7	12	8	1	35.1	41.0	2	5	5	23.7	20.7
7	4	1	69.2	67.3	2	10	1	65.4	48.9	2	3	4	40.7	41.4
8	4	1	41.7	46.9	1	3	10	25.8	29.0	2	5	4	69.0	73.3
10	4	1	41.0	41.1	4	10	1	47.9	48.9	2	8	4	40.4	37.6
11	4	1	41.0	39.3	5	10	1	83.2	95.9	2	9	4	37.7	29.0

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	b	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$	h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
2	10	4	31.9	34.6	6	9	2	97.7	109.4	5	6	11	32.1	29.0
2	12	4	63.6	62.8	10	9	2	79.6	97.4	5	6	13	52.1	35.0
2	14	4	40.5	31.6	2	10	2	31.2	29.0	6	7	5	26.1	21.8
3	5	2	43.1	42.9	3	10	2	40.7	47.4	6	7	8	37.6	23.7
2	4	5	19.4	20.7	4	10	2	40.7	41.4	6	7	9	41.0	30.8
6	5	2	100.0	109.8	5	10	2	24.7	32.0	6	7	10	46.0	42.9
7	4	4	63.1	51.1	8	10	2	50.4	66.2	6	7	11	24.3	19.6
7	5	5	30.5	35.7	8	11	2	69.4	74.4	6	7	12	54.8	32.3
7	7	7	51.8	44.0	4	12	2	67.4	79.3	7	8	3	82.3	63.9
7	8	8	47.4	39.5	6	13	2	52.2	45.1	7	8	4	40.4	26.7
7	9	9	33.7	20.7	3	14	2	37.1	29.0	7	8	5	47.7	39.9
8	3	3	76.5	60.5	4	3	7	63.5	55.6	6	4	11	45.6	38.4
4	4	8	35.2	20.7	4	3	8	34.7	25.2	6	4	13	32.7	24.4
5	5	9	33.9	27.4	4	3	10	25.7	29.7	7	5	9	38.1	35.0
6	6	9	56.8	48.9	4	3	11	43.6	38.4	7	5	10	27.8	25.6
9	7	7	40.6	29.7	4	3	12	22.9	25.6	7	5	11	30.7	26.7
9	8	8	30.9	20.7	5	4	10	68.2	57.2	8	6	11	34.5	21.4
9	9	9	35.1	22.6	6	5	4	80.4	79.7	10	8	4	29.8	21.4
4	4	10	35.1	24.8	8	6	5	42.6	33.5	10	8	5	45.1	23.3
5	5	10	39.7	26.7	9	6	5	46.7	38.4	0	2	13	34.7	35.3
4	4	11	45.1	34.6	10	6	5	23.6	19.6	1	3	6	16.0	21.8
10	5	2	88.8	110.9	7	6	12	47.0	22.2	13	1	4	10.4	20.7
14	5	2	41.4	32.7	4	14	2	55.0	39.1	7	8	10	33.1	29.7
2	3	6	21.0	20.7	6	14	2	35.4	25.6	7	8	11	43.8	27.4
5	6	2	43.2	57.2	8	7	4	82.1	50.4	2	0	1	19.4	8.3
6	6	2	80.0	88.7	8	7	6	70.1	57.2	2	0	5	14.8	15.4
9	6	2	29.7	39.1	8	7	10	38.5	23.7	2	0	10	27.4	23.3
13	6	2	50.1	58.7	10	9	4	72.5	44.0	4	2	2	31.2	19.6
14	6	2	35.2	44.7	10	9	6	60.1	32.3	4	2	13	34.4	27.8
4	7	2	65.1	77.8	11	10	2	20.1	11.3	5	3	6	18.8	18.4
8	7	2	89.5	103.0	11	10	4	31.4	15.0	5	3	7	28.1	21.8
12	7	2	67.4	63.9	0	1	12	19.1	24.1	5	3	8	63.4	51.9
6	8	11	58.8	44.4	3	4	5	51.2	56.3	5	3	10	20.4	18.8
2	3	8	45.5	44.0	3	4	8	75.1	70.3	6	4	2	26.2	17.3
2	4	8	53.5	58.3	3	4	10	37.3	31.6	6	4	7	54.8	52.6
5	5	11	26.9	26.7	3	4	12	59.0	65.0	2	4	11	46.2	48.1
6	6	11	16.5	17.7	3	4	13	26.2	18.4	3	5	3	9.1	19.2
7	7	11	36.6	29.0	3	4	14	32.2	17.3	3	5	7	26.6	24.1
3	3	12	46.9	33.8	0	1	14	16.4	17.3	3	5	10	78.4	75.2
4	4	12	33.4	30.5	1	2	12	21.9	29.0	3	5	11	1.8	18.4
2	2	13	39.2	29.7	2	3	12	27.9	29.0	3	5	14	35.3	29.7
5	5	13	16.5	13.5	4	5	6	33.2	31.6	4	6	9	81.3	76.7
6	6	13	34.6	23.7	4	5	7	30.2	29.0	4	6	10	24.2	25.9
4	4	14	38.2	24.8	8	4	5	39.8	33.5	4	6	12	27.1	18.8
2	1	13	29.7	32.7	9	4	5	24.2	27.1	4	6	13	59.8	48.9
3	2	6	18.4	28.2	10	4	5	38.9	24.1	5	7	9	33.4	33.1
3	2	10	24.9	35.0	12	4	5	37.2	41.0	5	7	11	30.0	29.7
6	4	3	41.5	66.2	4	5	14	40.8	23.7	5	7	12	42.1	35.3
5	8	2	48.8	54.5	5	6	3	91.0	93.6	6	8	3	50.4	47.8
6	8	2	35.0	48.9	5	6	8	28.8	24.4	6	8	9	23.7	18.8
3	9	2	50.8	53.0	5	6	10	60.6	47.4					

Table 4. *Interatomic distances*

$\mathrm{In_{I}{-}In_{III}}$	3·64 Å	$\mathrm{In_{II}{-}In_{IV}}$	3·61 Å	$\mathrm{In_{III}{-}In_{I}(3)}$	3·64 Å	$\mathrm{In_{IV}{-}In_{II}(3)}$	3·61 Å
$\mathrm{In_{I}{-}In_{I}(2)}$	3·65	$\mathrm{In_{II}{-}In_{II}(2)}$	3·68	$\mathrm{In_{III}{-}Cl_{I}(3)}$	3·45	$\mathrm{In_{IV}{-}Cl_{I}(3)}$	2·93
$\mathrm{In_{I}{-}Cl_{II}}$	2·95	$\mathrm{In_{II}{-}Cl_{II}}$	2·98	$\mathrm{In_{III}{-}Cl_{II}(3)}$	2·80	$\mathrm{In_{IV}{-}Cl_{II}(3)}$	3·54
$\mathrm{In_{I}{-}Cl_{I}}$	3·42	$\mathrm{In_{II}{-}Cl_{I}}$	2·90	$\mathrm{In_{III}{-}Cl_{III}}$	3·66		
$\mathrm{In_{I}{-}Cl_{I}}$	3·25	$\mathrm{In_{II}{-}Cl_{II}}$	3·52				
$\mathrm{In_{I}{-}Cl_{I}}$	3·24	$\mathrm{In_{II}{-}Cl_{II}}$	3·45				
$\mathrm{In_{I}{-}Cl_{III}}$	2·93	$\mathrm{In_{II}{-}Cl_{III}}$	3·50				
$\mathrm{In_{I}{-}Cl_{IV}}$	3·51	$\mathrm{In_{II}{-}Cl_{IV}}$	2·91				

tances. The $\mathrm{In_{I}}$ atoms form equilateral triangles with an edge of 3·65 Å around a threefold axis. Each corner is linked to an $\mathrm{In_{III}}$ atom (Fig. 5), the $\mathrm{In_{I}}$–$\mathrm{In_{III}}$ distances being 3·64 Å. These $\mathrm{In_{III}}$ atoms lie on other threefold axes, each $\mathrm{In_{III}}$ having three $\mathrm{In_{I}}$ at 3·64 Å in the nearest layer of In atoms normal to this axis. These three $\mathrm{In_{I}}$ atoms lie around this axis forming an equilateral triangle with an edge of 4·61 Å. Thus they form with $\mathrm{In_{III}}$ a flattened tetrahedron [Fig. 3(*b*)]. Now each of these three $\mathrm{In_{I}}$ atoms belongs to a different triangle with short $\mathrm{In_{I}}$–$\mathrm{In_{I}}$ distances; thus $\mathrm{In_{III}}$ is connected with three different triangles of edge 3·65 Å, which are related to each other by the threefold axis passing through $\mathrm{In_{III}}$. In this way the $\mathrm{In_{III}}$ atoms are the nodal points in a network of triangles. Thus the short In–In distances of group (*a*) form a three-dimensional network while the isolated tetrahedra of group (*b*) are accommodated in the holes formed by this network.

Now we will consider the whole coordination of the In atoms in the four different crystallographic positions. As in the case of sodium chloride, the structure of InCl is most easily understood when viewed along one of the body diagonals of the cell. It is convenient to compare the coordination of In with the surrounding of $\mathrm{Na^+}$ in sodium chloride (Fig. 2).

We see in Fig. 3(*b*) that $\mathrm{In_{III}}$ lies at the top of a flattened tetrahedron of In atoms. One triangle of Cl is stretched out so that the three $\mathrm{In_{I}}$ atoms can draw nearer to $\mathrm{In_{III}}$ at distances of 3·64 Å. The same is seen in Fig. 3(*c*) and (*d*) for $\mathrm{In_{II}}$ and $\mathrm{In_{IV}}$. Moreover, $\mathrm{In_{III}}$ has still one Cl in the second Cl layer at a distance of 3·66 Å. All the triangles are equilateral owing to the threefold axis. The In atoms at longer distances have been omitted; their positions can be roughly deduced by comparison with Fig. 2.

The coordination of $\mathrm{In_{I}}$ is more irregular (Fig. 3*a*), as it does not lie on a threefold axis. In its own layer it is surrounded by 3 In: one at a distance of 3·64 Å, two at 3·65 Å.

$\mathrm{In_{IV}}$, lying on a threefold axis, is surrounded by equilateral triangles of Cl and In. With three $\mathrm{In_{II}}$ at 3·61 Å it forms the nearly regular tetrahedron (Fig. 3*c*, *d*). We also see that the surroundings of $\mathrm{In_{II}}$ and $\mathrm{In_{IV}}$ are about the same.

The coordinations of the Cl atoms in fourfold position are easy to describe and are given in Fig. 4. Both Cl atoms have one layer of In atoms at a shorter distance than the other, which will cause polarization of Cl. The Cl atoms in twelvefold positions are surrounded by deformed octahedra of In at distance varying between 2·80 and 3·45 Å. The shortest Cl–Cl distance is 3·92 Å.

Discussion of the structure of InCl and other compounds containing s^2 ions

It is evident from the structure of InCl that there is a special bonding between the $\mathrm{In^+}$ ions, which have

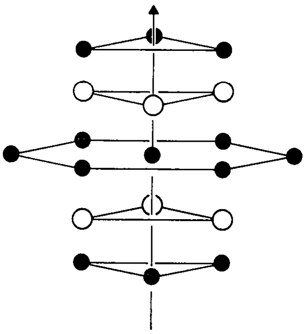

Fig. 2. The surrounding of Na in the NaCl structure viewed in layers normal to (111]. The Na atoms are indicated by solid circles.

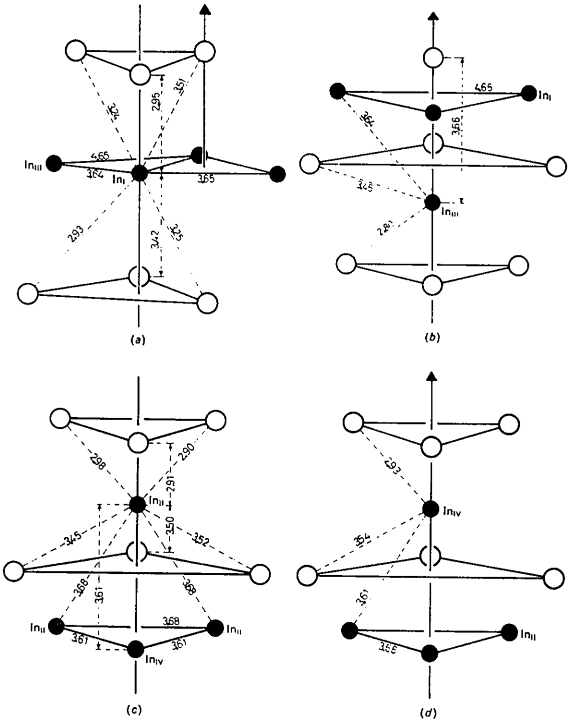

Fig. 3. The surrounding of the In atoms in different crystallographic positions viewed in layers normal to [111]. (*a*) $\mathrm{In_{I}}$ (*b*) $\mathrm{In_{III}}$ (*c*) $\mathrm{In_{II}}$ (*d*) $\mathrm{In_{IV}}$.

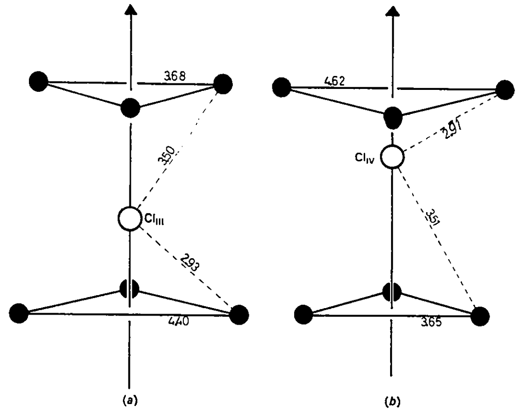

Fig. 4. The surroundings of the Cl atoms.
(*a*) $\mathrm{Cl_{III}}$ (*b*) $\mathrm{Cl_{IV}}$.

an outer s^2 shell. It is difficult to say anything about its nature. It could be that p orbitals are used in the bonding. There are several compounds, containing s^2 ions, whose structures clearly point to cation bonding.

In InBr and InI, which have the β-TlI structure, the In^+ ions form zigzag chains with short distances of about 3·60 Å, while InCl forms partly a three-dimensional network and partly tetrahedra of In^+ ions with short distances. In the first two compounds the angles between the short In–In distance vectors are about 90°; in InCl they are all about 60°, except one angle which is 79° (Table 5). The way in which the cations condense to form short distances is not the same for these compounds and seems to depend on the size of the anions. InCl does not show as strong a deviation from the sodium chloride packing as InBr and InI, whose structures can be formally derived from the sodium chloride structure by shifting two double layers with a sodium chloride arrangement with respect to each other over one fourth of the diagonal of the basis face of the cell (van Arkel, 1961). Because Cl^- is smaller, a strong deformation of the structure, as for InBr and InI, is not required to obtain short distances between the cations. Geometrically, the situation for forming cation bonding is more favourable with small anions because short cation distances are more readily obtained.

Table 5. *Angles between the short* In–In *distance vectors*

In_{I}–In_{II}–In_{I}	79° 14′
In_{III}–In_{I}–In_{I}	79 14
In_{I}–In_{I}–In_{I}	60 0
In_{II}–In_{II}–In_{II}	59 21
In_{II}–In_{IV}–In_{II}	61 18
In_{II}–In_{II}–In_{IV}	59 21

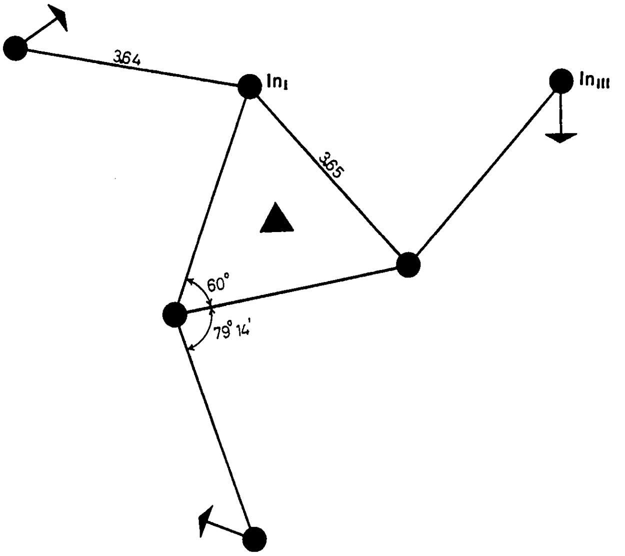

Fig. 5. The positions of In_{I} and In_{III} viewed along a threefold axis. The directions of the remaining threefold axes are indicated at the positions of the In_{III} atoms.

In the compounds GeS, GeSe, SnS and SnSe bonding between the s^2 ions is also highly probable. They have the SnS structure and resemble InBr and InI in that they have zigzag chains with short cation distances of about 3·50 Å. Summing up, the conclusion is that the InCl, β-TlI and SnS structures, as far as they are found for compounds with s^2 ions, all point to bonding between the s^2 ions. Another type of structure is found for SnO and PbO. They form layer structures. The reason why such a structure is formed is not yet quite clear and it may be that in these compounds, too, cation bonding plays a role.

Up to now evidence of this kind of bonding between s^2 ions has only been observed in compounds AB. The larger number of anions in compounds AB_n $(n > 1)$, for instance in $SnCl_2$, impedes the bonding and, on the whole, none is found for this group of compounds.

A more extensive discussion of this kind of bonding between cations with closed shells (non-bonding interactions) and of metal–metal bonding in general will be published in the near future (Kepert, Lewis, Nyholm & Vrieze, 1966).

The formation of tetrahedra is not characteristic of bonding between In^+ ions; in InCl only part of the In^+ ions form tetrahedra and in InBr and InI the In^+ ions condense by forming zigzag chains. Nevertheless it is interesting in this connection to mention some compounds containing tetrahedra of metal ions. This is true of some intermetallic compounds AB where A is an alkali metal and B an element of the fourth subgroup (Hewaidy, 1964; Witte & Schnering, 1964), for instance NaPb. One could interpret the effect as follows: the Pb atom accepts an electron from Na and thus has the same outer electronic configuration as phosphorus. The Pb^- ions can now form tetrahedra, similar to those in white phosphorus. An analogous interpretation could be advanced for the In_4 tetrahedra, In^+ now being a true metal in that it has more valence orbitals than valence electrons.

Tetrahedra of metal ions also occur in metal carbonyl complexes such as $Co_4(CO)_{12}$, $Co_4(CO)_5(SC_2H_5)_7$, $Rh_4(CO)_{12}$ and the $Ni_4(CO)_9^{2-}$ ion, and in $\{(C_2H_5)_2NCS_2Cu\}_4$ and $(CH_3Li)_4$. In all these compounds the tetrahedra are more or less stabilized by bridging groups, forming a unit with the tetrahedra. The formation of complex groups In_4Cl_n stabilizing the tetrahedral conformation of In is much less evident. Besides, only part of the In^+ ions form tetrahedra.

For a better understanding of the structure of InCl we have to take into account the Coulomb energy, the bonding energy of the cations and the polarization energy. The deformation, caused primarily by cation bonding, is very unfavourable for the Coulomb energy, which would benefit by an undeformed sodium chloride structure. The loss in Coulomb energy is compensated for by extra bonding energy of the cations as well as by a gain in polarization energy. This cooperation of important effects may evidently lead to the complicated structure observed. Under these circumstances condensation of the In^+ ions in this special way may just result in a minimum free energy of the compound.

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Configuration of the Cyanide Ion in Potassium Zinc Cyanide
A Neutron Diffraction Study

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A single-crystal neutron-diffraction study of the structure of cubic ($a = 12·53$ Å) potassium zinc cyanide, $K_2Zn(CN)_4$, has been made with a view to studying the coordination of the cyanide ion in a complex metal cyanide. Four possible structural models have been tested on the basis of 96 *hhl* intensities. Model I, involving a freely-rotating cyanide ion, was ruled out quite easily. The other three models were refined by the method of least squares with individual isotropic temperature factors, and model II, with the cyanide-ion coordination of the type Zn–C–N–K–N–C–Zn, was found to give the best agreement between the observed and calculated structure factors. Model III, with the inverse coordination involving interchange of the C and N atoms, as well as model IV, with disordered cyanide ions, could be rejected. The structure has been further refined on the basis of model II with anisotropic thermal parameters. Zinc is tetrahedrally coordinated to four cyanide ions and the Zn–C–N group is linear. The C–N distance corrected for thermal motion is $1·157 \pm 0·009$ Å. Six nitrogen atoms form a trigonal antiprism around potassium.

Introduction

The coordination of the cyanide ion in metal cyanides is a problem that has attracted the attention of investigators from various fields including X-ray diffraction, spectroscopy, and, more recently, neutron diffraction. In the case of alkali cyanides such as KCN (Sequeira, 1965), NaCN and RbCN (Bijvoet & Lély, 1940), and CsCN(Lély, 1942) which are cubic in their room-temperature phases, the question of specific coordination with the alkali metal ion does not arise, the neighbouring sites to the metal ion being statistically shared by C and N. In other cyanides, particularly the complex cyanides, it is often assumed that the polyvalent metal-ion coordination is with the carbon atom; this assumption is found in many textbooks of chemistry (Pauling, 1960). It may be mentioned here that on the basis of his infrared studies, Jones (1957*a*) has attempted to determine the cyanide-ion coordination in a series of cyanides, and although his studies favour the polyvalent metal-ion coordination with the carbon atom his rejection of the alternative coordination seems somewhat tentative.

It should be of interest to obtain conclusive evidence from diffraction studies regarding this point. In view of the fact that carbon and nitrogen have nearly the same X-ray scattering amplitudes, recent attempts to distinguish between carbon and nitrogen in X-ray structure determinations have been based on indirect criteria such as the reasonableness of the temperature factors (Rossmann, Jacobson, Hirshfeld & Lipscomb, 1959; Emerson & Britton, 1963) or the reasonableness of the bond-angles (Cromer, 1957) or bond lengths (Cromer & Larson, 1962), and have not been absolutely convincing. In a recent X-ray investigation of $CuCN . NH_3$, Cromer, Larson & Roof (1965) have refined the structure for two alternative orientations of the cyanide group (involving interchange of the C and N atoms) and have chosen one of them on the basis of a marginally better *R* index and more sensible thermal param-