X-Ray Studies of Fused Salt Systems. IV. Cadmium Iodide

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An analysis of the X-ray diffraction pattern of fused CdI_2 is reported. The shortest Cd–I distance is found to be 2.90 Å. and the shortest I–I distance, 4.75 Å. Most of the features of the radial distribution curve can be accounted for on the simple hypothesis that the liquid is a loose and expanded imitation of the solid with the same octahedral coördination scheme and short-range order. There appears, however, to be a considerable proportion of linear I–Cd–I molecules present as well. The effect of neglecting the contribution of the glass container to the total diffraction pattern of liquids so contained is discussed.

Earlier communications from this Laboratory[2] have described the structures of fused InI_3 and SnI_4. It was thought that a similar study of the iodide of cadmium, adjacent to indium and tin in atomic number, might be of interest. A special interest attaches to this substance in the liquid state because the atomic arrangements in the solid[3] and vapor[4] are very unlike. The results of the present study indicate that fused CdI_2 is a curious transition between solid and vapor, exhibiting in major part an arrangement analogous to that of the crystal. This quasi-crystalline arrangement is occasionally interrupted by a small proportion of linear CdI_2 molecules, similar to those found in the vapor.

Experimental

The experimental arrangement and procedure have been described before.[5] Reagent grade CdI_2 was placed in a Pyrex glass tube of 0.04 cm. inside diameter and 0.003 cm. wall thickness. Two exposures were made using crystal monochromated Mo-$K\alpha$ radiation at 40 kv. and 20 ma., one for 119 hours and the other for 188 hours, the CdI_2 being held at 450° during exposure. The diffracted radiation was recorded photographically and conversion to intensity effected by means of a Leeds and Northrup recording microphotometer. The intensities from both sides of each film were averaged and the two averages brought to the same relative scale on consideration of the unequal total radiation received by the sample during the two unequal exposures. No serious difference appeared in the two patterns so produced, and all four readings were accordingly averaged to produce the final intensity curve. The raw intensity curve was corrected in the usual way (see, however, the later section on "The Glass Correction") and converted to absolute intensities by matching, at large diffraction angle, to the calculated scattering of independent Cd and I atoms. These two scattering curves, calculated independent coherent and corrected experimental, are shown in Fig. 1. Both curves are scaled on the basis of the coherent scattering from one CdI_2 unit.

The approximate density of fused CdI_2 was determined by measuring the height of liquid salt of known weight in a calibrated tube at 450°. The average of three independent determinations was 4.19 ± 0.02 g./cc.

The radial distribution function was computed from the data of Fig. 1 and the liquid density in the usual way. Numerical integrations were evaluated by the International Business Machines' CPC electronic computer, adapted to carry out summations according to the trapezoidal rule. The radial distribution curve is shown in Fig. 2. The "effective" atomic numbers of Cd and I were taken as equal to their actual atomic numbers.

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(2) R. E. Wood and H. L. Ritter, This Journal, 74, 1760, 1763 (1952).

(3) G. Hägg, R. Kiessling and E. Linden, Arkiv. Kemi Mineral. Geol., 16B, No. 4 (1942).

(4) O. Hassel and L. C. Strömme, Z. physik. Chem., B38, 466 (1938); M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 37, 406 (1941).

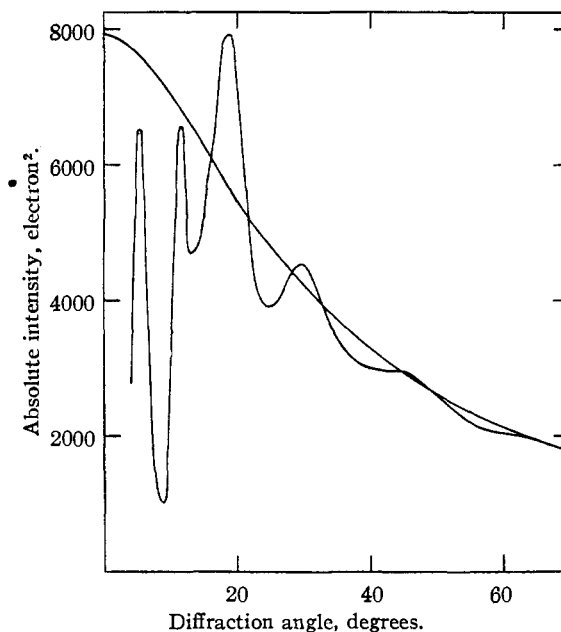(5) R. L. Harris, R. E. Wood and H. L. Ritter, This Journal, 73, 3151 (1951).

Fig. 1.—Corrected experimental and independent coherent scattering from liquid CdI_2. The vertical scale is on the basis of one CdI_2 unit.
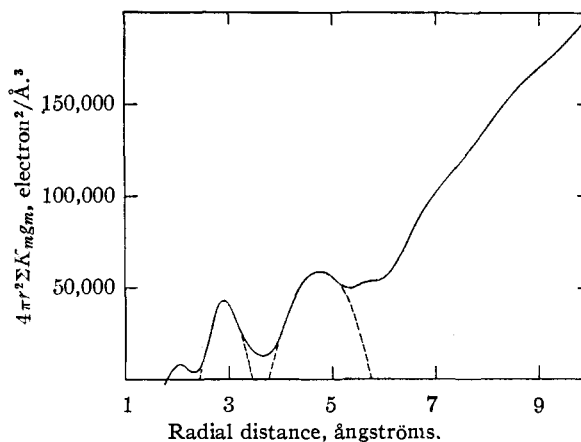

Fig. 2.—Radial distribution curve for liquid CdI_2.

Results and Discussion

The radial distribution curve has its first prominent peak at 2.90 Å., a reasonable value for the Cd–I separation in liquid CdI_2. If the closest Cd–I distance is taken as 2.90 Å., then the area under the first peak should be $2nZ_{Cd}Z_I$, where the Z's are atomic numbers and n is the coördination number of Cd. The measured area is about 31000 elec-

tron[2], whence $n \sim 6.1$. This number suggests octahedral coördination. If the I atoms are indeed arranged about Cd in the approximate form of a regular octahedron, then there should also be an interatomic distance of $2 \times 2.90 = 5.80$ Å., corresponding to the main diagonals of the octahedron. The radial distribution curve does show a very poorly resolved peak in this neighborhood, but its prominence is far too weak to confirm the picture of iodine atoms arranged approximately at the corners of a regular octahedron having this main diagonal. For such an arrangement, moreover, there should be a prominent peak at about $2.90 \sqrt{2} = 4.1$ Å., corresponding to the octahedral edge, which does not appear. Actually, a close approach to regular octahedral coördination in liquid CdI_2, based on a Cd–I distance of 2.90 Å. could not fit other facts. Such a packing of the atoms, similar to that of crystalline CdI_2, would require a liquid density of about 6.2 g./cc., far higher than the observed density of 4.2 g./cc.

Several workers[6] have reported on the structure of crystalline CdI_2. The arrangement may be considered as a stack of two-dimensional sheets of linked CdI_6 octahedra. The octahedra are almost regular, three of the I–I distances being 4.21 Å. and the other three 4.24 Å. The density of such a configuration of atoms, regardless of the placement of the Cd atoms, is 5.71 g./cc. (i.e., the observed density of solid CdI_2). If this structure were simply expanded to a density corresponding to that of the liquid (4.19 g./cc.) the octahedral edge would become about 4.70 Å. The radial distribution curve shows a peak at 4.75 Å., and it seems reasonable to identify this observed distance with the closest I–I separation in the liquid.

In crystalline CdI_2, each I atom is surrounded by 6 I atoms at a distance of 4.21 and 6 more at a distance of 4.24 Å. Each Cd atom is surrounded by 6 other Cd atoms at 4.24 Å. In the neighborhood of 4.2 Å., then, the crystal has 12 I–I distances for each I and 6 Cd–Cd distances for each Cd. If the same packing scheme is carried over into the liquid, there should be 24 I–I distances and 6 Cd–Cd distances for every CdI_2 unit, all contributing to the area under the 4.75 Å. peak in the radial distribution curve. The area should therefore be

$$24Z_I^2 + 6Z_{Cd}^2 = 81000 \text{ electron}^2$$

The measured area under this peak is estimated as 79000 electron². It seems likely, therefore, that the scheme of atomic arrangement in liquid CdI_2 is simply an expanded and smeared out version of the solid.

If the liquid consists of a mobile collection of I atoms having a local order similar to that of the solid, the Cd atoms cannot lie at the centers of the octahedra. Such an arrangement would possess a prominent Cd–I separation of about 3.4 Å. which the radial distribution curve does not show. The Cd atoms appear to lie closer (at about 2.90 Å.) to two of the I atoms in an octahedron than to the other four. Since these latter distances (they

(6) See R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y, 1948.

would be about 3.5 to 4.0 Å.) do not appear in the curve, the Cd atom must enjoy considerable freedom in its placement within the octahedron. Presumably the Cd atom hinges more or less freely about the I–I axis it lies closest to, maintaining its distance of 2.90 Å. from these atoms. This circumstance would permit CdI_2 units to be distinctly isolable and would indicate a closer approach to pure covalency of the Cd–I bond in the liquid than in the predominantly ionic solid. The bond length of 2.90 Å. in the liquid, shorter than the 2.99 Å. reported for the solid, supports this view. The sum of the covalent radii for Cd and I is 2.76 Å. while the sum of the ionic radii is 3.13 Å. The angular CdI_2 "molecule" suggested here is thus intermediate between the 90° configuration in the crystal and the linear molecule found in the vapor. A CdI_2 molecule having Cd–I and I–I distances of 2.90 and 4.75 Å., respectively, has an I–Cd–I angle of 110°. Table I compares the configurations in the solid, liquid and vapor, and shows the gradual transition from ionic crystal to covalent vapor.

TABLE I

GEOMETRY OF THE CdI_2 "MOLECULE" IN SOLID, LIQUID AND VAPOR

	Cd–I, Å.	I–I, Å.	I–Cd–I
Solid[6]	2.99	4.23	90°
Liquid	2.90	4.75	110°
Vapor[4]	2.58	5.16	180°

At the same time, however, the presence of the shoulder in the radial distribution curve at about 5.8 Å. indicates the presence of a considerable proportion of linear I–Cd–I molecules. On the whole, the structure of liquid CdI_2 seems to be patterned largely after the octahedral arrangement of the crystal. For the most part the Cd atoms are placed eccentrically within the octahedra, forming angular I–Cd–I molecules; but the structure is widely interrupted by linear I–Cd–I units having about the same Cd–I separation.

The Glass Correction

When a non-crystalline substance is supported in a glass container, the total diffraction pattern is composed of contributions from both glass and sample. Since both patterns are diffuse, the problem of subtracting out the contribution due to the glass is a necessary but difficult one. The authors have adopted the following method for performing this correction.

Cylindrical samples of Pyrex glass of close to the optimum dimensions were prepared and exposures taken of them for measured lengths of time, T, under controlled and measured average X-ray flux, F. If there were no absorption in the glass sample, the diffracted intensity so produced would be proportional to FTS, where S is the cross-sectional area of the glass rod. The specific diffracted intensity per unit cross-sectional area, per unit time, and per unit of primary X-ray flux (any arbitrary unit of X-ray flux is suitable) is then the measured intensity, I, divided by FTS. Since the measured intensity, however, is affected by self-absorption, the true specific intensity is $I_0 = I/FTSA$, where A is the self-absorption correction. A table of I_0 as a func-

tion of diffraction angle was prepared from several such exposures.

Now if an exposure is taken of some liquid sample contained in a Pyrex tube of cross-sectional (annular) area S' for a time T' under average X-ray flux, F', in the absence of absorption, the contribution to the total pattern of the glass alone would be $I_0F'T'S'$. The radiation diffracted by the container, however, is affected by absorption—both self-absorption in the annulus and absorption in the sample core as well. This correction, $A_{a,ac}$, may be computed[7] from a knowledge of the geometry of the sample and the absorption coefficients. The extraneous contribution of the glass container may thus be computed from the standard curve, I_0, as $I' = I_0F'T'S'A_{a,ac}$. The intensity due to the sample is simply the total intensity decreased by I'. This correction may amount (particularly in the region of $\theta = 10°$ where Pyrex glass has its strongest peak) to as much as 60% of the total diffracted intensity, although its average value over the whole range of θ is less than 15% of the total.

Since this correction is such a large fraction of the observed quantity, we have been uncomfortable about the effect of errors, in the computed value of the correction, on the final calculated radial distribution curve. We estimate that the glass correction is known, in any given case, to about 10% of its own value. It is of interest to examine the effect of even larger uncertainties. Accordingly we have computed the radial distribution function for CdI_2, not only from the corrected intensity curve (Fig. 1) but also from the original uncorrected curve; from a partially corrected curve obtained by subtracting 80% of the computed glass correction; and from an overcorrected curve obtained by subtracting 120% of the computed correction. The computed radial distribution curves are shown in Fig. 3. Curve B is a repetition of Fig. 2 and the other three curves result from 0, 80 and 120% correction for glass diffraction. It is clear from this figure that an error of as much as ±20% in computing the glass contribution has very little effect on the radial distribution. Curves A, B and C agree exactly in the positions of their peaks and very closely in the areas under the peaks. Complete neglect of the correction, however, produces a radial distribution in which the peaks are noticeably shifted and in

(7) H. L. Ritter, R. L. Harris and R. E. Wood, *J. App. Physics*, **22**, 169 (1951).
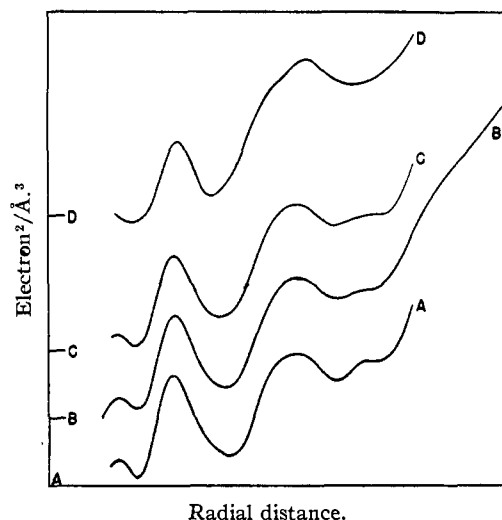

Radial distance.

Fig. 3.—Comparison of under- and overcorrection for diffuse diffraction by the container. The curves are radial distribution curves calculated on the basis of: A, 20% undercorrected; B, properly corrected; C, 20% overcorrected; D, completely uncorrected, for diffraction by the glass. The several origins are displaced vertically and only the region between 2 and 6.5 Å. is shown.

which some of the detail is definitely altered. It appears then that in this case one cannot ignore the effect of the container but that an error of more than ±20% in correcting for it is tolerable.

The relative diffractive contribution of the container can be reduced by using thinner walls or material of relatively lower atomic number. It can be completely eliminated by using a crystalline container. Attempts to reduce it by going to thinner walls have been unsuccessful. There is some reason to believe that a suitable crystalline container may eventually be contrived.

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