35. *The Structure of Germanous Iodide.*

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A modified method of preparing germanous iodide is described. *X*-Ray investigation shows the crystal structure of the substance to be the *C*.6 type, and therefore establishes the existence of the germanous ion. The radius of this ion for sodium chloride type structures is estimated to be 0·98 A.

Similarities in the behaviour of germanous and stannous compounds and the close resemblance of germanous iodide to lead iodide (Brewer and Dennis, *J. Physical Chem.*, 1927, **31**, 1526; Brewer, *ibid.*, p. 1817) make it of interest to examine further the evidence for the existence of a germanous ion, and the existence of an " inert pair " of electrons in this element (cf. Sidgwick, *Ann. Reports*, 1933, **30**, 123). We have therefore investigated the crystal structure of germanous iodide.

Hydrated germanous hydroxide was prepared by a modification of the method of Dennis and Hulse (*J. Amer. Chem. Soc.*, 1930, **52**, 3553), involving reduction of a solution of germanium tetrachloride by hypophosphorous acid at 90° in an atmosphere of nitrogen, and subsequent precipitation of the hydroxide by aqueous ammonia. The hydroxide was filtered off in a nitrogen atmosphere, and dissolved in hot concentrated hydriodic acid from which the free iodine had been removed by warming with the minimum quantity of hypophosphorous acid. On cooling the solution, crystals were obtained in very thin, six-sided plates which were optically uniaxial with fairly strong negative double refraction. They decomposed slowly in air.

Oscillation photographs taken with copper radiation gave for the hexagonal cell size $a = 4{\cdot}13$, $c = 6{\cdot}79$ A., and a calculated density for one molecule per unit cell of 5·37. The dimensions, which are near to those required for a hexagonal close-packing of iodine ions, suggest that the structure is the *C*.6 (so-called cadmium iodide type) of Ewald and Hermann's " Strukturbericht." The layer character of the structure is shown by the flakiness of the crystals, the negative double refraction, and certain peculiarities in the *X*-ray reflexions. Photographs obtained with extremely thin, hexagonal plates oscillated about the *a* axis show moderately sharp *hki*0 reflexions, but *hkil* spots are spread out into streaks along Debye–Scherrer curves. The effect varies from crystal to crystal but sometimes the streaks may reach nearly half way to adjacent layer lines. It may be explained by bending of the crystal, with slipping of the layers of the structure over each other so that, although the normal to a plane 0001 or *hkil* varies in direction from one portion of the crystal to another, there is very little bending of *hki*0 planes.

No weak reflexions that would require an enlargement of the unit cell similar to that found for cadmium iodide by Hassel (*Z. physikal. Chem.*, 1933, *B*, **22**, 333) were observed, but if present they would be very diffuse and difficult to detect. There were no systematic absences of spectra, and the space group may therefore be one of the large number of hexagonal-latticed groups of the trigonal and hexagonal systems satisfying this condition. None of the hexagonal groups will give a structure compatible with intensities and probable interatomic distances, and the others are either excluded on similar grounds or all lead to a *C*.6 structure belonging to the trigonal system.

The inequalities to be expected in relative intensities of certain *hkil* and $hki\bar{l}$ reflexions for a *C*.6 structure were not observed, but the observations are consistent with this structure twinned on the basal plane. For many planes the relative intensities could not be estimated accurately owing to the varying diffuseness of the spots; the general regularities in relative intensity are, however, in good agreement with calculation; *e.g.*, $0h\bar{h}0$ is always very weak unless $h = 3n$, and $hh\overline{2h}0$ is strong for all values of *h*. These data are explained by a cell with Ge at 000 and 2I at $\frac{1}{3}\frac{2}{3}z$ and $\frac{2}{3}\frac{1}{3}\bar{z}$. That *z* is very close to 0·25 is shown by other regularities, and particularly by the relative intensities in the series 000*l* for which calculated and observed values are given in the table.

Relative intensities of 000*l*.

l	1.	2.	3.	4.	5.	6.	7.	8.
Obs.	m	vs	m	vs	vvw	m	w	ms
Calc.	7·9	16·3	1·3	13·5	0·4	1·8	0·25	8·1

Each germanium has six iodine neighbours at 2·94 A. from it, arranged octahedrally, and each iodine has three equidistant germanium neighbours at this distance. In this type of structure the binding between atoms in the layers is ionic, but the distance is decreased under the influence of co-ordination number and polarisation forces, and the result therefore provides evidence for the existence of the germanous ion. The Ge–I separation of 2·94 A. is very much greater than the distance 2·57 A. found in the covalent germanium tetraiodide (Jaeger, Terpstra, and Westenbrinck, *Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 747).

An estimate of the radius of the germanous ion as it would be in a sodium chloride type structure may be made from the results as follows. It is assumed that the departure of the germanium–iodine separation in this structure from the sum of the ionic radii (for sodium chloride structures) is the same as in cadmium iodide, *viz.*, a decrease of 7½%, and we therefore obtain for the sum of the germanous and the iodine radius the value 3·18 A. By subtraction of the iodine radius, 2·20 A. (Goldschmidt), the germanous ion radius is found to be 0·98 A.

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