

THE CRYSTAL STRUCTURE OF MAGNESIUM DI-ZINCIDE

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ABSTRACT

Crystals of the intermetallic compound, $MgZn_2$, were prepared and the crystal structure was determined from x-ray data furnished by Laue and rotation photographs. The crystal was found to have hexagonal axes with $a=5.15A$ and $c=8.48A$. The unit cell contains four molecules. The effect of absorption in the crystal in determining the wave-length giving a maximum intensity of reflection in Laue photographs was used to confirm the dimensions of the unit cell. The atoms have the positions:

$$Zn: u, \bar{u}, \frac{1}{4}; 2\bar{u}, \bar{u}, \frac{1}{4}; u, 2u, \frac{1}{4}; \bar{u}, u, \frac{3}{4}; 2u, u, \frac{3}{4}; \bar{u}, 2\bar{u}, \frac{3}{4}; 0, 0, 0; 0, 0, \frac{1}{2}$$

$$Mg: \frac{1}{3}, \frac{2}{3}, v; \frac{1}{3}, \frac{2}{3}, \frac{1}{2} - v; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + v; \frac{2}{3}, \frac{1}{3}, \bar{v}.$$

Where $u=0.830$ and $v=0.062$. The least distance between two magnesium atoms is $3.15A$, between two zinc atoms, $2.52A$, and between a magnesium and a zinc atom, $3.02A$.

THE constitution diagram for the binary system, magnesium-zinc,^{1,2} has a pronounced maximum corresponding to the formation of an intermetallic compound, $MgZn_2$, which forms eutectics with both constituents. Since both magnesium and zinc crystallize in the hexagonal close-packed arrangement, a determination of the crystal structure of their compound was thought to be of interest.

Crystals of the compound were formed by melting together the calculated amounts of magnesium and zinc under a molten mixture of sodium and potassium chlorides to prevent oxidation. The melt was then allowed to cool slowly in the electric furnace, about four hours being taken to cool from ten degrees above to ten degrees below the melting point of the compound, $595^\circ C$. In this way a mass of crystals was obtained from which individual crystals were separated for the production of Laue and spectral photographs.

Two rotation photographs taken with the x-rays from a molybdenum water-cooled tube on an x-ray spectrograph of the kind described by Wyckoff,³ furnished data for the determination of the size and shape of the unit cell. As no information on the crystal class or axial ratio of crystals of this compound was found in the literature, a consideration of the secondary spectra as well as of the principal spectrum was necessary in order to obtain the quadratic form which gives the spacings of the planes. These spacings can be computed from the positions of the re-

¹ Grube, Z. anorg. Chemie **49**, 80 (1906).

² Bruni and Sandonini, Z. anorg. Chemie **78**, 276 (1912).

³ Wyckoff, The Structure of Crystals (New York, 1924), p. 164.

flections on the plate and furnish information of the same nature as that available from a powder photograph.

Table I gives the data from a rotation photograph. The observed spacings are the means of those calculated from the reflections produced by the $K\alpha$ doublet and the $K\beta$ line of molybdenum for all the planes of the same form showing on the plate. These spacings were compared with the charts given by Hull and Davey,⁴ and were found to agree with the

TABLE I

Spacing between planes of magnesium di-zincide. The spacings are found to agree with the spacings for a hexagonal unit cell having $a=5.15\text{A}$, $c=8.48\text{A}$, $c/a=1.646$

Plane	Observed spacing	Calculated spacing	Plane	Observed spacing	Calculated spacing
00.1(2)	4.241A	4.240A	12.3	1.449	1.448
10.3	2.377	2.388	00.1(6)	1.411	1.413
11.2	2.204	2.201	20.5	1.351	1.350
00.1(4)	2.122	2.120	12.4	1.321	1.320
10.1(2)	1.966	1.974	11.6	1.244	1.239
10.4	1.916	1.915	20.6	1.198	1.194
20.3	1.746	1.751	20.7	1.071	1.065
12.1	1.658	1.653	00.1(8)	1.062	1.060

spacings for a hexagonal unit cell having $a=5.15\text{A}$ and $c=8.48\text{A}$. Since the crystal was rotated about one of the a axes for this photograph, the assignment of indices obtained from the chart was checked by comparing the computed values of the x and y coordinates with the observed. The fact that certain reflections could not occur because of the limited rotation of the crystal could also be used in some cases to distinguish between planes having nearly the same spacings. On another photograph taken with the crystal rotating about the c axis, only the principal spectrum was measured. This gave $a=5.15\text{A}$ which is in agreement with the value just given. The third column of the table gives the values for the spacings computed from the dimensions of the unit cell.

This unit cell agrees with the data from Laue photographs taken with the white radiation from a tungsten target. When the wave-lengths of the x-rays producing the spots on symmetrical and unsymmetrical Laue photographs were calculated on the basis of this unit cell, no values were found less than the short wave-length limit, about 0.24A , of the x-rays used. The curves showing the intensity of reflection from different planes of the same form reflecting at different wave-lengths in unsymmetrical Laue photographs, start from the short wave-length limit, rise to a maximum between 0.36A and 0.40A , and then decrease for longer wave-lengths. The presence of a maximum intensity so far below the wave-length of the silver absorption edge is due to absorption in the crystal.

⁴ Hull and Davey, Phys. Rev. **17**, 549 (1921).

The photographic intensity, I , of the white radiation from a tungsten target operated at 50 kv can be approximately represented⁵ between the short wave-length limit, λ_0 , and the wave-length of the silver absorption edge, 0.485A, by the equation

$$I = B(\lambda - \lambda_0)$$

where B is a constant. This must be modified, however, if the crystal is strongly absorbing. For a first approximation it can be assumed that all the rays producing spots on a Laue photograph are absorbed for a distance equal to the thickness of the crystal. The absorption coefficient can be computed from data given by Richtmyer and Warburton⁶ for the atomic scattering and fluorescent absorption coefficients. Since the absorption due to scattering is small and nearly independent of the wave-length,⁶ it will have no other effect than to decrease the value of the constant, B , but the fluorescent absorption, which is proportional to the cube of the wave-length, will cause greater weakening of the longer wave-lengths and the maximum intensity is accordingly shifted to the short wave-length side of the silver absorption edge. The density of the crystal, 5.16, its thickness, about 0.3 mm, and the computed absorption coefficient give

$$I' = B'(\lambda - \lambda_0)e^{-22\lambda^3}$$

where I' is the photographic intensity of the white radiation after passing through the crystal, and B' is the constant, B , multiplied by the factor which represents the common decrease in intensity of all wave-lengths due to scattering. The curve given by this equation has a maximum at 0.36A and agrees in form with the curves showing the intensity of reflection as a function of the wave-length, thus furnishing additional evidence for the correctness of the unit cell chosen.

The density was determined by weighing in a specific gravity bottle after breaking the sample into small pieces in order to avoid, as far as possible, inclusion of blowholes. Two determinations gave 5.164 and 5.155. Using the value 5.16 for the density, the computed number of molecules in the unit cell was found to be 3.93, the deficiency from the integral number, 4, doubtless being due to the fact that the density determined by the use of a specific gravity bottle is likely to be less than the density determined by x-ray measurements, unless porosity of the sample can be completely eliminated.

Smaller unit cells, containing 1, 2, or 3 molecules were found to be inconsistent with the data available.

⁵ Wyckoff, *The Structure of Crystals* (New York, 1924), p. 142.

⁶ Richtmyer and Warburton, *Phys. Rev.* **22**, 539 (1923).

A Laue photograph taken with the incident beam of x-rays parallel to the principal axis of the crystal had a six-fold symmetry axis intersected by six planes of symmetry. The space-group giving the arrangement of atoms in the crystal must consequently be isomorphous with one of the point-groups D_3^h , C_6^v , D_6 or D_6^h . Reference to a tabulation of the results of the theory of space-groups⁷ shows the possible ways of arranging four (magnesium) and eight (zinc) atoms in the unit cell. The arrangements which are possible if it is assumed that the magnesium atoms are equivalent and that the zinc atoms are likewise equivalent, are inconsistent with the Laue data and the assumption of equivalence of all chemically like atoms must consequently be relinquished. With the freedom of choice thus allowed there are numerous ways of arranging the atoms. The zinc atoms may be in two groups, each of four equivalent positions; two groups, one of six and one of two equivalent positions; or in some other combination giving the required number of atoms. The number of possible combinations for the magnesium atoms is somewhat less. The choice of the correct atomic arrangement is simplified by the observation that many of the groups of six equivalent positions lie in a single plane parallel to the base of the unit cell. If, however, six zinc atoms which constitute more than half the reflecting power of all the atoms contained in the unit cell, are arranged in such a plane, the absence of odd order reflections from 00.1 and the observation that the fourth order reflection from 00.1 is stronger than the second order cannot be satisfactorily explained. Groups of six equivalent positions having such an arrangement are consequently excluded from further consideration.

The only structures which are possible with these restrictions and which offer any possibility of accounting for the observed intensity relations are those arising from the space-groups D_{3h}^4 , C_{6v}^4 , D_6^6 , and D_{6h}^4 . Of the structures which can be obtained from the space-groups D_6^6 and D_{6h}^4 the only one not conflicting with the data is that in which the atoms have the following positions:

$$\begin{aligned} \text{Zn: } & u, \bar{u}, \frac{1}{4}; 2\bar{u}, \bar{u}, \frac{1}{4}; u, 2u, \frac{1}{4}; \bar{u}, u, \frac{3}{4}; 2u, u, \frac{3}{4}; \bar{u}, 2\bar{u}, \frac{3}{4}; 0, 0, 0; 0, 0, \frac{1}{2} \\ \text{Mg: } & \frac{1}{3}, \frac{2}{3}, v; \frac{1}{3}, \frac{2}{3}, \frac{1}{2} - v; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + v; \frac{2}{3}, \frac{1}{3}, \bar{v} \end{aligned}$$

This arrangement is obtained by placing the magnesium atoms in one group of four equivalent positions and the zinc atoms in two groups of, respectively, six and two equivalent positions. A consideration of the type of structure involved shows that it is sufficient to consider only values of the parameters satisfying the conditions $0 \leq u \leq 0.5$ and -0.25

⁷ Wyckoff, The Analytical Expression of the Results of the Theory of Space Groups (Washington, 1922).

$\leq v \leq 0.25$. If it is assumed that there is a reasonable distance between the two magnesium atoms in the same vertical line, v will be restricted to the middle half of its possible range.

The amplitude factor, S , is computed from

$$S = (A^2 + B^2)^{\frac{1}{2}}$$

where A and B have their usual significance of sine and cosine summations,⁸ and is zero for first order reflections from planes of the forms $\{h h \cdot 2p+1\}$ irrespective of the values of u and v . No first order reflections from any such planes were found on any of the Laue photographs, although planes of the forms 22.1, 33.1, 44.3, 55.3, and 44.5 were in a position to give first order reflections at a favorable wave-length. Another characteristic feature of this structure is that the magnesium atoms contribute nothing to the amplitude factors for first order reflections from planes of the forms $\{0 3h \cdot 2p+1\}$. The intensities of such reflections are consequently useful in determining the positions of the zinc atoms, and show that u can not have values differing greatly from 0, $\frac{1}{6}$, $\frac{1}{3}$, or $\frac{1}{2}$. Consideration of the amplitude factors for other planes shows that the only values of u giving general agreement with the requirements of the Laue data are those in the neighborhood of $u = \frac{1}{6}$. The observed intensity relations for the planes 26.3, 26.5 and 26.7 can then be satisfied by giving v a small negative value.

TABLE II

Extent of the agreement between estimated intensity and amplitude factor using for the parameters the values $u=0.170$ and $v=-0.062$

Plane	Spacing	Estimated intensity	$n\lambda$	Amplitude factor	Plane	Spacing	Estimated intensity	$n\lambda$	Amplitude factor
12.1	1.65A	32	0.37	31	16.4	0.65	3	0.36	72
03.1	1.46	4	0.46	15	07.3	0.62	5	0.37	108
13.1	1.22	20	0.36	38	35.3	0.62	4.8	0.38	89
04.1	1.10	90	0.43	171	35.4	0.61	3	0.43	84
02.1(2)	1.08	70	0.76	132	26.3	0.60	5	0.36	114
23.1	1.01	12	0.41	46	22.3(2)	0.58	6	0.80	149
23.2	0.99	6	0.37	30	26.5	0.58	10	0.35	191
14.2	0.95	60	0.36	153	07.6	0.58	2.5	0.41	71
05.3	0.85	11	0.38	77	13.3(2)	0.57	9	0.74	164
33.2	0.84	36	0.38	152	35.7	0.56	1.4	0.44	68
24.1	0.84	28	0.31	170	26.7	0.55	5	0.42	136
24.3	0.81	23	0.40	116	08.3	0.55	2.5	0.30	113
12.2(2)	0.78	3	0.91	29	17.6	0.54	2.5	0.36	83
15.3	0.77	11	0.43	83	08.5	0.53	5	0.35	192
15.4	0.75	12	0.41	98	04.3(2)	0.51	5	0.73	164
03.1(2)	0.73	8	0.75	83	18.4	0.50	1	0.32	108
34.3	0.71	4.2	0.39	77	08.7	0.50	2.5	0.36	134
25.2	0.70	10	0.36	155	46.5	0.49	3	0.36	190
03.2(2)	0.70	50	0.77	237	27.8	0.48	1	0.38	149
34.4	0.69	8	0.37	111	46.7	0.47	1	0.34	134
16.3	0.66	5	0.39	98					

⁸ Wyckoff, *The Structure of Crystals* (New York, 1924), p. 107.

With the values of u and v restricted in this way it was found by trial that satisfactory agreement with the data was obtained for $u=0.170$ and $v=-0.062$. The extent of the agreement is shown in Table II, which gives the data from an unsymmetrical Laue photograph. The table shows the spacing of the plane producing the reflection, the intensity as estimated visually by comparison with a plate which had been given a series of graduated exposures, the product of the order of reflection by the wave-length producing the reflection, and the amplitude factor computed for the values of the parameters given on the assumption that the reflecting powers of the zinc and magnesium atoms are proportional to their atomic numbers. In comparing the intensities of two planes, if the plane with the smaller spacing gives the greater intensity under comparable conditions of wave-length, it must have a greater amplitude factor. As previously stated, the maximum intensity falls between 0.36A and 0.40A and the intensities in the table have been given in this region when possible.

This two-parameter structure is the simplest which will give agreement with the data available. The only other possible structures are a three-parameter structure derived from D_{3h}^4 and a five-parameter structure derived from C_{6v}^4 . Neither of these two more general structures can be eliminated, but consideration indicates that neither will give satisfactory agreement with the data except for values of the parameters which reduce them to forms closely approaching that of the two-parameter structure, and it is consequently concluded that this structure, or a more general structure, so similar as to be indistinguishable from it, represents the crystal structure of $MgZn_2$ when u and v have the values given.

This structure can be described in an alternative way without the use of a negative parameter by setting $u=0.830$ and $v=0.062$. Fig. 1 shows the arrangement of atoms in the unit cell. The least distance between two magnesium atoms is 3.15A, between two zinc atoms 2.52A and between a magnesium and a zinc atom 3.02A. The values computed from the atomic radii determined from the crystal structures of magnesium and zinc are respectively 3.22A, 2.67A, and 2.95A. If the zinc atoms at $0,0,0$ and $0,0,\frac{1}{2}$ are called zinc atoms of the first kind and the others, zinc atoms of the second kind, each magnesium atom is surrounded by three zinc atoms of the first kind and nine of the second kind, all twelve zinc atoms having very nearly the same distances from the magnesium atom. Each zinc atom of the first kind is equidistant from six zinc atoms of the second kind, while the nearest neighbors of each zinc atom of the second kind are two zinc atoms of the same kind.

Each magnesium atom in magnesium di-zincide is equidistant from

three other magnesium atoms and at very nearly the same distance from a fourth. In the structure found, these four atoms are at the corners of a tetrahedron which is so nearly regular that with changes in the values of the axial ratio and the parameter, v , of less than one percent, each magnesium atom would be surrounded by four others at the corners of a regular tetrahedron having the inclosed atom at its center. This is the arrangement which Bragg⁹ has suggested for the oxygen atoms in ice, and is given by two interpenetrating hexagonal close-packed arrangements of which one has been displaced vertically with respect to the

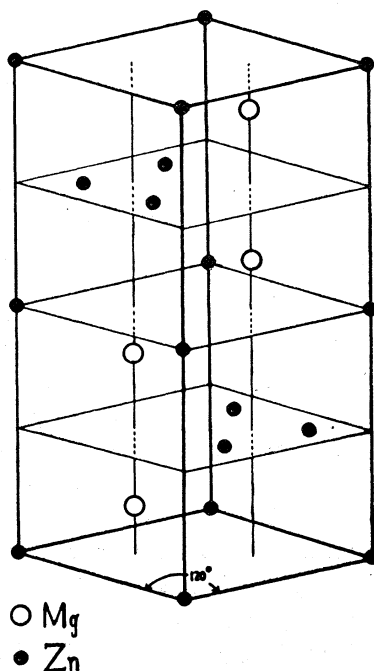


Fig. 1. Arrangement of atoms in the unit cell of $MgZn_2$.

other, through a distance equal to $\frac{3}{8}c$. There is no such obvious similarity between the way in which the zinc atoms are arranged in magnesium di-zincide and in metallic zinc, and the structure which has been found for this compound is apparently different from any which has been previously described.

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⁹ W. H. Bragg, Proc. Phys. Soc. London **34**, 98 (1922).