The Journal of the American Chemical Society

with which has been incorporated

The American Chemical Journal

(Founded by Ira Remsen)

VOL. 45 DECEMBER, 1923 No. 12

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 28]

THE CRYSTAL STRUCTURE OF MAGNESIUM STANNIDE

By Linus Pauling

Received May 21, 1923

Introduction

The temperature-composition diagram[1] of the binary system, magnesium-tin, shows a pronounced maximum corresponding to the composition Mg_2Sn. This compound is described[2] as cubic with octahedral habit and complete octahedral cleavage. For the purpose of obtaining information regarding the nature of intermetallic compounds, crystals of magnesium stannide, Mg_2Sn, have been investigated by means of X-rays, resulting in a complete determination of their structure. No crystal structure determination for an intermetallic compound has been previously reported.

By melting the calculated amounts of magnesium and tin in an iron crucible under a mixture of potassium and magnesium chlorides, and cooling slowly, a mass of magnesium stannide was obtained from which individual crystals could be cleaved. The X-ray data were obtained from Laue and spectral photographs, treated as described by Dickinson.[3] I wish to express my thanks to Dr. Roscoe G. Dickinson for his advice and active interest in this research.

The Determination of the Structure

Spectral data from a (111) face of a crystal of magnesium stannide are given in Table I. Using the value of 3.591 for the density,[2] these data place $n^3/m = 0.248$ for the first reflection. No reflections were found on the Laue photographs with values of $n\lambda$ less than 0.26 Å. U., calculated for the unit containing four Mg_2Sn, with $n = 1$, and $d_{100} = 6.78 \pm 0.02$ Å. U.

---

[1] Kurnakow and Stepanow, *Z. anorg. Chem.*, 46, 177 (1905).

[2] Sustschinsky, *Z. Krist.*, 38, 265 (1904).

[3] Dickinson, This Journal, 44, 276 (1922).

As the lower limit of X-rays present in the spectrum was 0.24 Å. U., a larger unit of structure is not indicated.

A symmetrical Laue photograph through the (111) face showed a trigonal axis and three reflection planes; consequently only arrangements derived from point-groups T_d, O and O_h were treated. No planes but those with all indices odd gave values of $n\lambda$ less than 0.50, although a large number of other planes were in positions favorable for reflection, so treatment was given only to arrangements based on a face-centered lattice. There are three ways[4] of arranging $4Mg_2Sn$ with these restrictions, irrespective of any assumptions regarding the equivalence of atoms of one element. These are

I Sn at 000, ½½0, ½0½, 0½½
Mg at ¼¼¼, ¼¾¾, ¾¼¾, ¾¾¼, ¾¾¾, ¾¼¼, ¼¾¼, ¼¼¾
II Sn at 000, ½½0, ½0½, 0½½
Mg at ¼¼¼, ¼¾¾, ¾¼¾, ¾¾¼, ½½½, ½00, 0½0, 00½
III Sn at 000, ½½0, ½0½, 0½½
Mg at ¾¾¾, ¾¼¼, ¼¾¼, ¼¼¾, ½½½, ½00, 0½0, 00½

The intensity of the third order (111) reflection is greater than that of the second order, and the structure factor, $S = \sqrt{A^2 + B^2}$, must be greater for the third order. For Arrangements II and III, the corresponding values are

$$n = 2,\ \ A = 4\overline{Sn},\ \ B = 0;\ \ n = 3,\ \ A = 4\overline{Sn} - 4\overline{Mg},\ \ B = \pm 4\overline{Mg}.$$

On the very safe assumption that an atom of tin scatters X-rays more strongly than an atom of magnesium, the value of S for the third order is less than that for the second order, eliminating these two arrangements.

For Arrangement I reflecting planes may be divided into three classes, which have the following values of S.

Class I: hkl one odd, two even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{Sn} - 8\overline{Mg}$
Class II: hkl all odd; $n = 1$, $S = 4\overline{Sn}$
Class III: hkl two odd, one even; $n = 1$, $S = 0$; $n = 2$, $S = 4\overline{Sn} + 8\overline{Mg}$.

On the previously made assumption regarding relative reflecting powers, the values for the structure factor of the classes of planes increase in this

TABLE I

REFLECTION DATA FOR Mg_2Sn, (111) FACE

X-rays reflected Å. U.	Angle of reflection	$\frac{d_{111}}{n}$ Å. U.	$I_{observed}$	S
$Mo\beta_1$ = 0.6311	4° 37′	3.918	strong	$4\overline{Sn}$
$Mo\alpha_1$ = 0.7078	5° 11′	3.921		
$Mo\beta_1$	9° 16′	½ × 3.920	weak	$4\overline{Sn} - 8\overline{Mg}$
$Mo\alpha_1$	10° 26′	½ × 3.913		
$Mo\beta_1$	14° 3′	⅓ × 3.899	medium	$4\overline{Sn}$
$Mo\alpha_1$	15° 46′	⅓ × 3.913		
$Mo\beta_1$	18° 52′	¼ × 3.902	medium	$4\overline{Sn} + 8\overline{Mg}$

---

[4] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," *Carnegie Inst. Pub.*, 1922.

order: I, II, III. Intensity data showing the extent of the agreement with this structure are given in Tables I and II. In comparing intensities of two planes reflecting at the same wave length, if the intensity of the plane with the smaller value of d/n is larger than that of the other, the structure factor of the first must be greater than that of the second. No intensity relations not accounted for by the above arrangement were observed.

TABLE II

LAUE PHOTOGRAPHIC DATA FOR Mg$_2$Sn. INCIDENT BEAM 12° 30′ FROM NORMAL TO (111)

hkl	$\frac{d_{hkl}}{n}$ Å. U.	λ Å. U.	$I_{observed}$	Class	*hkl*	$\frac{d_{hkl}}{n}$ Å. U.	λ Å. U.	$I_{observed}$	Class
$13\bar{3}$	1.52	0.28	2.8	II	$41\bar{2}$	0.74	0.29	0.08	I
$\bar{1}\bar{1}2$	1.38	.30	8	III	$91\bar{3}$	.71	.32	.3	II
$\bar{5}11$	1.30	.31	2.4	II	$\bar{7}71$	.68	.34	.2	II
$\bar{1}5\bar{3}$	1.15	.36	2.4	II	$50\bar{1}$	.67	.33	.4	III
$30\bar{1}$	1.07	.33	2.6	III	$\bar{1}9\bar{5}$	.66	.28	.14	II
$03\bar{2}$	0.94	.33	0.5	I	$05\bar{2}$	.63	.45	.4	I
$2\bar{3}1$	.91	.26	.4	III	$\overline{11}.1.\bar{1}$	.61	.32	.12	II
$35\bar{5}$	.88	.26	.2	II	$11.1.\bar{1}$	.61	.46	.5	II
$71\bar{3}$	.88	.31	.6	II	$11.1.\bar{3}$	.59	.31	.10	II
$\bar{3}7\bar{3}$	.83	.30	.5	II	$\bar{4}33$	.58	.48	1.0	III
$17\bar{5}$	.78	.30	.4	II					

Discussion of the Structure

The structure determined for magnesium stannide is the one known as the calcium fluoride arrangement.[5] It places eight magnesium atoms around each tin atom at the corners of a cube, and four tin atoms around each magnesium atom at tetrahedron corners. The sum of the atomic radii of magnesium[6] and tin[7] obtained from the distance between atoms in the metals is 3.01 Å. U. (from gray tin) or 2.80 (from white tin); the closest approach of tin and magnesium atoms in magnesium stannide is 2.94 ± 0.01. There is no similarity in the way in which an atom of tin or magnesium is surrounded by other atoms in the metals and in this compound.

Crystals of sodium cadmide, NaCd$_2$, reported from goniometrical measurements as cubic, were prepared by the method of Kurnakow.[8] Each of several Laue photographs taken from three different crystals with the beam perpendicular to an octahedral face showed a 3-fold symmetry axis lying in three symmetry planes. The photographs were, however, so complicated that it was not found possible to assign indices with certainty to many of the spots even on the symmetrical photographs. It was accordingly not possible to determine the apparently very complex structure.

[5] W. H. and W. L. Bragg, *Proc. Roy. Soc.*, **89A**, 474 (1913).

[6] Hull, *Phys. Rev.*, [2] **10**, 661 (1917).

[7] Bijl and Kolkmeier, *Proc. Acad. Sci. Amsterdam*, **21**, 494 (1919).

[8] Kurnakow, *Z. anorg. Chem.*, **23**, 459 (1900).

In view of the lack of a simple valence relation between the atoms, complex atom-groups may be formed in sodium cadmide in a way similar to the formation of Pb_2^- ions in a solution of sodium plumbide, $NaPb_2$, in liquid ammonia,[9] preventing a simplicity of structure.

Summary

Crystals of the intermetallic compound magnesium stannide, Mg_2Sn, have been prepared and investigated by means of Laue and spectral photographs with the aid of the theory of space-groups. The intermetallic compound has been found to have the calcium fluoride structure, with $d_{100} = 6.78 \pm 0.02$ Å. U. The closest approach of tin and magnesium atoms is 2.94 ± 0.01 Å. U.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE THEORY OF EMULSIFICATION[1]

BY PHILIP FINKLE, HAL D. DRAPER AND JOEL H. HILDEBRAND

RECEIVED JUNE 6, 1923

To disperse one liquid in another in the form of an emulsion requires the doing of work upon the system equal to the product of the interfacial tension multiplied by the increase in surface. An emulsion produced by the mechanical agitation of two pure, incompletely miscible liquids is, therefore, always unstable, the drops of dispersed liquid coalescing upon contact to decrease the interfacial area. To stabilize an emulsion a suitable third substance must be added. Many very effective emulsifiers are known but there has been thus far no altogether satisfactory way to predict the relative powers of different emulsifying agents, either to stabilize the emulsions or to determine which of the two liquids shall be dispersed in the other. Some very useful criteria yielded by experience are more in the nature of rules than theories. We will refer to some of these briefly and then proceed to elaborate an hypothesis which seems to account for the behavior of all emulsifying agents for which we have the data to apply it.

To form a stable foam or emulsion requires that the films of enclosing liquid which separate the bubbles or drops, respectively, shall be stable. This cannot be the case with a pure liquid, since a film represents a surface which is far from the minimum possible. It was shown by Rayleigh that a film is stabilized by the addition of some substance which, by virtue of high adsorption at the surface, greatly lowers the surface tension. In such a case the surface tension is larger at a fresh surface than at an old surface, at which there has been time for the adsorption to take place by diffusion,

---

[9] Kraus, THIS JOURNAL, 29, 1557 (1907).

[1] Presented at the Colloid Symposium held at Madison, Wis., in June, 1923, under the auspices of the Department of Chemistry of the University of Wisconsin.