THE CRYSTAL STRUCTURES OF TWO INTERMETALLIC COMPOUNDS

BY JAMES B. FRIAUF

Introduction

The elementary constituents of alloys can be divided into three general classes:[1] pure metals and metalloids, solid solutions and intermetallic compounds. The application of x-ray methods to the study of these constituents has led to the determination of the crystal structures of the metals commonly used in alloys and has thrown considerable light on the structure of solid solutions and some of the intermetallic compounds. In order to obtain more information regarding the structure of the third class of constituents, the crystal structures of two of the intermetallic compounds formed by copper, Cu_2Mg and $CuAl_2$, have been determined by x-ray methods. Cu_2Mg is one of the two compounds formed in the copper–magnesium system.[2,3] $CuAl_2$ is the most important intermetallic compound formed in the copper-aluminum system[4,5,6,7] and is likewise an important constituent in duralumin and some of the other light alloys.

Crystals of these intermetallic compounds were formed by melting together the necessary amounts of the constituent metals and slowly cooling the melt in an electric furnace. In this way a coarsely crystalline mass was obtained from which individual crystals were separated for the production of Laue and rotation photographs.

The Crystal Structure of Cu_2Mg

The size and shape of the unit cell for crystals of this compound were determined from data furnished by powder and rotation photographs taken with the K-radiation from molybdenum. The observed spacings, d, from a powder photograph are shown in the second column of Table I. Comparison with the charts of Hull and Davey[8] shows that these spacings are among those to be expected from a face-centered cubic lattice. The indices of the reflecting planes are shown in the first column of the table,

[1] Jeffries and Archer, "The Science of Metals," McGraw-Hill Book Co., Inc., New York, 1924, p. 219.

[2] Sahmen, Z. anorg. Chem., 57, 1 (1908).

[3] Urasow, J. Russ. Phys.-Chem. Soc., 39, 1566 (1907).

[4] Carpenter and Edwards, Proc. Inst. Mech. Eng., (London), 71, 57 (1907).

[5] Curry, J. Phys. Chem., 11, 425 (1907).

[6] Gwyer, Z. anorg. Chem., 57, 113 (1908).

[7] Stockdale, J. Inst. Metals, 31, 275 (1924).

[8] Hull and Davey, Phys. Rev., 17, 549 (1921).

and the values for the side of the unit cube computed from the observed spacing of a plane and its indices are given in the third column. The mean of these values for the side of the unit cube is 6.99 Å., which is in agreement with values of 6.98 Å. and 7.00 Å., obtained from another powder photograph and from a rotation photograph taken with one of the crystals used for producing the Laue photographs. The mean of these three values gives 6.99 Å. for the side of the unit cube. This unit cell is also in agreement with the data from the Laue photographs.

TABLE I

OBSERVED SPACINGS FROM A POWDER PHOTOGRAPH

hkl	d	a
111	4.045	7.007
220	2.473	6.995
113	2.107	6.987
222	2.019	6.995
400	1.745	6.979
133	1.604	6.992
151–333	1.345	6.990
440	1.236	6.992
135	1.184	7.008
260	1.100	6.957
226	1.055	6.997

Cubic axes, $a = 6.99$ Å.

The density of the compound was found to be 5.85 by a direct determination in a specific gravity bottle. The computed number of molecules in the unit cube is 8.00.

The Laue photographs obtained from crystals of this compound have the symmetry to be expected from the point groups T^d, O, or O^h. No first-order reflections were found from any planes save those with all indices odd; consequently only atomic arrangements based on a face-centered cubic lattice were considered.

Reference to a tabulation of the results of the theory of space groups[9] shows that the possible atomic arrangements which must be considered are those which arise from space-groups T_d^2 and O_h^7 (or O^4). The structures which may be obtained from T_d^2 contain a variable parameter and should give second-order reflections from planes having two indices even and one odd, except for special values of the parameter. No second-order reflections were found from any such planes, although a number were in a position to produce a reflection at a favorable wave length. It is consequently concluded that the parameter must have a value close to the special values which give zero intensity of reflection for planes of this kind. With this restriction on the value of the parameter, certain of the structures

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[9] Wyckoff, "The Analytical Expression of the Results of the Theory of Space Groups," The Carnegie Institution of Washington, Washington, 1922.

obtained from T_d^2 can be readily eliminated, and the others can be shown to be indistinguishable from the structures obtained from O_h^7.

Two distinct atomic arrangements may be obtained from O_h^7 (or O^4). One of these gives results which are not in agreement with the data. In the other the atoms have the following positions.

Mg: 0, $1/2$, $1/2$; $1/2$, 0, $1/2$; $1/2$, $1/2$, 0; 0, 0, 0; $1/4$, $3/4$, $3/4$; $3/4$, $1/4$, $3/4$; $3/4$, $3/4$, $1/4$; $1/4$, $1/4$, $1/4$.

Cu: $1/8$, $3/8$, $7/8$; $7/8$, $1/8$, $3/8$; $3/8$, $7/8$, $1/8$; $3/8$, $5/8$, $3/8$; $1/8$, $5/8$, $1/8$; $1/8$, $1/8$, $5/8$; $5/8$, $1/8$, $1/8$; $5/8$, $5/8$, $5/8$; $7/8$, $3/8$, $1/8$; $1/8$, $7/8$, $3/8$; $3/3$, $1/8$, $7/8$; $5/8$, $3/8$, $3/8$; $7/8$, $5/8$, $7/8$; $7/8$, $7/8$, $5/8$; $5/8$, $7/8$, $7/8$; $3/8$, $3/8$, $5/8$.

This structure gives predicted intensities which are in qualitative agreement with the observed intensities as shown in Table II, which contains

TABLE II
DATA FROM A LAUE PHOTOGRAPH

hkl(n)	d/n	λ	I	S²	hkl(n)	d/n	λ	I	S²
133	1.60	0.37	100	27	557	0.70	0.44	10	27
112 (2)	1.42	.37	40	9	034 (2)	.70	.32	0	0
135	1.18	.41	82	27	134 (2)	.68	.46	2	9
335	1.06	.47	95	90	159	.68	.37	16	90
113 (2)	1.05	.48	125	215	377	.68	.39	15	90
155	.98	.39	37	27	359	.65	.37	5	27
023 (2)	.97	.31	0	0	234 (2)	.65	.31	0	0
123 (2)	.93	.40	8	9	125 (2)	.64	.38	2	9
355	.91	.36	57	90	179	.61	.33	4	27
137	.91	.46	62	90	559	.61	.43	3	27
157	.81	.34	37	90	035 (2)	.60	.37	1	9
012 (4)	.78	.42	67	135	379	.59	.42	8	90
357	.77	.35	11	27	122 (4)	.58	.37	11	135
124 (2)	.76	.33	0	0	579	.56	.34	5	90
233 (2)	.74	.31	3	9	013 (4)	.55	.42	13	314
139	.73	.44	25	90	779	.52	.37	1	27

data from a Laue photograph taken with the incident beam of x-rays nearly perpendicular to a (111) plane of the crystal. The first column contains hkl, the indices of the form to which the reflecting plane belongs, followed by the order of reflection, n, if this is different from unity; the second column, the spacing of the plane divided by the order of reflection; the third column the wave length of the x-rays producing the reflection; while the fourth and fifth columns contain the observed intensity, I, and the square of the amplitude factor, S. The greatest intensity of reflection is for wave lengths between 0.35 Å. and 0.40 Å. and the data have been given for these wave lengths when possible. The observed intensities are visual estimates made by comparison with a plate which had been given a series of known exposures. The structure factors have been computed on the assumption that the scattering powers of copper and aluminum atoms are proportional to their atomic numbers. The agree-

ment is probably as good as can be expected because of the approximations involved in the computation of S, and since none of the other possible structures is satisfactory, it is concluded that the proposed structure gives the atomic arrangement in crystals of Cu_2Mg.

The atoms in this crystal have the same arrangement that has been found for the metallic atoms in spinel,[10,11] $MgAl_2O_4$, and in the complex cyanides of potassium with zinc, cadmium and mercury,[12] $K_2Zn(CN)_4$, $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$.

The least distance between two magnesium atoms is 3.03 Å., between two copper atoms, 2.47 Å., and between a copper and a magnesium atom, 2.90 Å. The corresponding values found by adding the radii which magnesium and copper atoms have in metallic magnesium and copper are 3.22 Å., 2.55 Å. and 2.88 Å.

The Crystal Structure of CuAl₂

The crystal structure of this compound has been the subject of two previous investigations. Owen and Preston[13] used the powder method and concluded that one molecule of $CuAl_2$ is contained in a tetragonal unit cell with $a = 4.28$ Å. and $c = 2.40$ Å. Somewhat later, Jette, Phragmén and Westgren[14] obtained Laue and rotation photographs from crystals of this compound and found it necessary to use a larger tetragonal unit cell which contains four molecules and has the dimensions, $a = 6.052$ Å. and $c = 4.878$ Å. The atomic arrangement was not determined in detail but was said to be body-centered with the symmetry of one of the crystal classes, V^d, D_4, C_4^v or D_4^h.

In the present investigation, the size and shape of the unit cell were determined from rotation photographs taken with the K-radiation of molybdenum. If a rotation photograph of a tetragonal crystal rotating about a vertical axis which coincides with the c axis of the crystal is taken on a flat photograph plate perpendicular to the incident beam of x-rays, it can be shown that[15]

$$\frac{l\lambda}{c} = \frac{V}{(V^2 + H^2 + D^2)^{1/2}} \tag{1}$$

where l is the third Miller index of the plane which produces a given spot on the photograph; λ, the wave length of the x-rays; c, the height of the unit cell; D, the distance from the crystal to the plate; and V and H the vertical and horizontal coördinates of the spot measured from the place where the incident beam of x-rays strikes the plate. Table III contains

[10] Bragg, *Phil. Mag.*, **30**, 305 (1915).

[11] Nishikawa, *Proc. Tokyo Math. Phys. Soc.*, **8**, 199 (1915).

[12] Dickinson, THIS JOURNAL, **44**, 774 (1922).

[13] Owen and Preston, *Proc. Phys. Soc. London*, **36**, 14 (1923–24).

[14] Jette, Phragmén and Westgren, *J. Inst. Metals*, **31**, 193 (1924).

[15] Ewald, "Kristalle und Röntgenstrahlen," Julius Springer, Berlin, 1923, p. 270.

the data from a rotation photograph taken with the crystal oriented in this way.   The first column contains the Miller indices, h, k, l, of the form to which the reflecting plane belongs; the second column, the values of $V(V^2 + H^2 + D^2)^{-1/2}$, computed from the observed quantities, V, H and D; the third column, the values of the second column divided by l; while the fourth and fifth columns contain, respectively the observed spacing, d, and the spacing computed for a tetragonal unit cell with $a = 6.04$ Å. and $c = 4.86$ Å.   Since λ and c are constants and l is an integer, Equation (1) requires that the observed values of $V(V^2 + H^2 + D^2)^{-1/2}$ should be integral multiples of the constant λ/c.   The constancy of the values in the third column of the table shows that this condition is satisfied and their mean gives 4.86 Å. for the least value which can be assumed for c.   Integral multiples of this are also possible.   The data from this photograph and from a number of others taken with the crystal rotating about different crystal axes, indicate that the smallest unit cell which is possible has $a = 6.04$ Å. and $c = 4.86$ Å.   No data were found on the rotation or the Laue photographs which would necessitate the use of a larger unit cell. These values for the dimensions agree well with those obtained by Jette, Phragmen and Westgren.

TABLE III

DATA FROM A ROTATION PHOTOGRAPH

hkl	$\dfrac{V}{(V^2 + H^2 + D^2)^{1/2}}$	$\dfrac{V}{l(V^2 + H^2 + D^2)^{1/2}}$	Observed spacing	Calcd. spacing
110	0		4.266	4.271
211	0.1468	0.1468	2.360	2.361
220	0		2.135	2.136
112	.2916	.1458	2.110	2.112
310	0		1.906	1.910
222	.2912	.1456	1.604	1.604
312	.2919	.1460	1.500	1.502
411	.1460	.1460	1.402	1.403
213	.4392	.1464	1.391	1.389
420	0		1.351	1.351
332	.2916	.1458	1.232	1.228
510	0		1.182	1.185
422	.2929	.1464	1.180	1.180
521	.1454	.1454	1.095	1.093
413	.4373	.1458	1.086	1.087
440	0		1.071	1.068
512	.2904	.1452	1.064	1.065
530	0		1.037	1.036
622	.2918	.1459	0.891	0.889

Tetragonal axes, $a = 6.04$ Å.; $c = 4.86$ Å.

The density of $CuAl_2$ was determined by weighing in a specific gravity bottle and was found to be 4.37.   This gives 4.00 molecules in the unit cell.

The Laue photographs taken with the incident beam of x-rays perpendicular to the (001) plane have a four-fold symmetry axis and four planes of symmetry, while those taken with the incident beam perpendicular to a (100) or a (110) plane have a two-fold axis and two planes of symmetry. The atomic arrangement must consequently be obtained from some space group isomorphous with one of the point-groups V^d, C_4^v, D_4 or D_4^h, and since no reflections were observed from any planes save those for which the sum of the indices is an even number, only body-centered arrangements were considered. This restriction is in agreement with the conclusions regarding the atomic arrangement which were reached by Jette, Phragmén and Westgren.

Reference to a tabulation of the results of the theory of space groups[9] shows that there are numerous possible body-centered arrangements with four atoms of one kind and eight of another kind in the unit cell. Many of these possibilities are readily eliminated. Careful consideration of the remaining possibilities shows that the most satisfactory agreement with the data is obtained for the atomic arrangement which places the atoms in the following positions.

Cu: 0, 0, 0; 0, 0, $^1/_2$; $^1/_2$, $^1/_2$, $^1/_2$; $^1/_2$, $^1/_2$, 0.

Al: u, $u + ^1/_2$, $^1/_4$; $^1/_2 - u$, u, $^1/_4$; $\bar{u}$, $^1/_2 - u$, $^1/_4$; $u + ^1/_2$, $\bar{u}$, $^1/_4$; $u + ^1/_2$, u, $^3/_4$; u, $^1/_2 - u$, $^3/_4$; $^1/_2 - u$, $\bar{u}$, $^3/_4$; $\bar{u}$, $u + ^1/_2$, $^3/_4$.

This arrangement may be obtained from D_{4h}^{18} and equivalent arrangements may be obtained from several other space groups. One of the characteristic features of such an atomic arrangement is that it predicts zero intensity of reflection from all planes of the forms $(0kl)$ where k and l are both odd. No reflections from any planes of these forms were found on any of the photographs, although a considerable number of planes of this kind were in a position to produce reflections at favorable wave lengths. Furthermore, the copper atoms contribute nothing to reflections from planes of the forms (hkl) where l is odd, and h and k are one even and one odd. A large number of planes of this kind were present on the photographs and a consideration of their intensities enables the parameter, u, to be determined free from any uncertainty regarding the relative scattering powers of copper and aluminum atoms. In order to obtain satisfactory agreement with the data, u must be nearly equal to 0.158. Table IV contains the data from a Laue photograph taken with the incident beam of x-rays nearly perpendicular to a (110) plane of the crystal. The first column contains hkl, the indices of the form to which the reflecting plane belongs, followed by the order of reflection, n, if this is different from unity; the second column, the spacing of the plane divided by n; the third column, the wave length of the x-rays producing the reflection; while the fourth and fifth columns contain the observed intensity, I, and the square of the structure factor, S. The most intense reflections are for wave lengths

TABLE IV

DATA FROM A LAUE PHOTOGRAPH

hkl(n)	d/n	λ	I	S²	hkl(n)	d/n	λ	I	S²
114	1.17	0.41	100	26	581	0.64	0.44	5	37
012 (2)	1.13	.45	90	20	275	.63	.45	2	13
134	1.02	.43	130	110	147	.63	.45	3	15
451	0.93	.44	30	20	392	.62	.44	20	158
125	.91	.44	32	23	583	.60	.42	4	37
154	.85	.43	50	38	185	.59	.41	2	28
235	.84	.41	1	1	257	.59	.44	3	31
453	.82	.40	14	20	590	.59	.45	9	71
145	.81	.41	12	15	176	.59	.47	10	96
116	.80	.46	60	80	138	.58	.45	11	110
370	.79	.41	70	143	592	.57	.45	5	82
231 (2)	.79	.41	64	123	376	.57	.47	2	5
103 (2)	.78	.41	60	92	043 (2)	.55	.42	5	58
372	.75	.42	6	5	158	.54	.42	4	38
136	.75	.41	16	13	594	.53	.41	5	71
273	.74	.43	8	13	358	.52	.43	5	74
232 (2)	.69	.43	8	9	304 (2)	.52	.43	7	169
473	.68	.40	4	8	252 (2)	.51	.41	4	116
572	.67	.40	16	69	178	.49	.41	1	19
127	.67	.44	5	23	503 (2)	.48	.42	3	158
156	.67	.46	20	62	738	.48	.43	2	143
374	.66	.45	32	143					

between 0.40 Å. and 0.48 Å., and have been given in this region. The observed intensities are visual estimates made by comparison with a plate which had been given a series of graduated exposures. S^2 has been given instead of S, since the crystal is probably sufficiently imperfect to give reflections more nearly proportional to S^2 than to S. S has been computed in the usual way[16] on the assumption that $u = 0.158$ and that the scattering powers of copper and aluminum atoms are proportional to their atomic numbers. The values of S^2 in the last column account quite satisfactorily for the observed intensities from planes which do not differ greatly in spacing, except that certain of the planes with l even give more intense reflections as compared to neighboring planes with l odd than is indicated by the corresponding values of S^2. Discrepancies of this kind are to be expected, however, because of the approximations underlying the computation of S. A number of theoretical and experimental investigations have shown that the scattering power of an atom is not a constant proportional to the number of outer electrons it contains, but is a function of the glancing angle, θ, which decreases as θ increases. This decrease is more rapid for atoms with a small number of electrons than for atoms with a larger number, and the relative scattering powers of two atoms will con-

[16] Wyckoff, "The Structure of Crystals," The Chemical Catalog Company, Inc., New York, 1924, p. 104.

sequently also be a function of θ. An exact evaluation of the changes which would be introduced into the calculated structure factors by this variation in scattering power cannot be made in the absence of a knowledge of the forms to be ascribed to the F curves for copper and aluminum atoms in crystals of CuAl₂, but a qualitative estimate can readily be made and shows that the changes which would be introduced into S if the variation in scattering power were taken into account are in such a direction as to bring the calculated values of S^2 into better agreement with the observed intensities. The agreement is consequently thought to be satisfactory and since there is also good agreement with a Laue photograph which was taken with the incident beam of x-rays nearly perpendicular to the (001) plane of the crystal, it is concluded that the proposed structure gives a close approximation to the atomic arrangement in crystals of CuAl₂. None of the other possible structures considered was found satisfactory.

The least distance between two copper atoms is 2.43 Å., between two aluminum atoms, 2.70 Å., and between a copper and aluminum atom 2.59 Å. These are somewhat less than the values 2.54 Å., 2.86 Å. and 2.70 Å. computed from the radii which copper and aluminum atoms have in metallic copper and aluminum.

Summary

The atomic arrangements in crystals of two of the intermetallic compounds formed by copper, Cu₂Mg and CuAl₂, have been determined by x-ray methods.

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THE REACTION BETWEEN POTASSIUM CARBONATE AND SULFUR IN ALCOHOL SOLUTION

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In his "Experiments and Notes about the Producibleness of Chymical Principles," appended to the second English edition of "The Sceptical Chymist," Oxford, 1680, Robert Boyle discusses the possibility of transmuting or changing into one another the so-called elements of the alchemists. As evidence that "a disposition to be dissoluble in this or that liquor may be acquir'd by mixture," he points[1] to the fact that, whereas neither "salt of tartar" (potassium carbonate) nor sulfur is soluble in "spirit of wine" (alcohol), "yet if this Salt and Sulphur be mixt together, spirit of Wine will in less than an hour and sometimes in less than a quarter

[1] Robert Boyle, op. cit., p. 4. Concerning the several editions of "The Sceptical Chymist," see Isis, 8, 71 (1926).