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The Crystal Structure of the Cadmium–Magnesium Alloy, CdMg

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The crystal structure of an alloy of cadmium–magnesium containing 50·3 atomic % cadmium has been determined accurately. The structure, which is orthorhombic, is isomorphous with AuCd and has unit-cell dimensions $a = 5{\cdot}0051$, $b = 3{\cdot}2217$, $c = 5{\cdot}2700$ Å, the space group being *Pmma*. There are two cadmium atoms in 2(*e*) and two magnesium atoms in 2(*f*) with $z_1 = 0{\cdot}177$ and $z_2 = 0{\cdot}682$.

Atomic scattering factors are given for both cadmium and magnesium at room temperature.

Introduction

It is known that the alloy CdMg has a disordered close-packed hexagonal structure at high temperatures (Hume-Rothery and Raynor, 1940), and that a transformation takes place when the temperature drops below 250° C. (Grübe & Schiedt, 1930; Riederer, 1937). Dehlinger (1930) has observed by means of an X-ray investigation that below this temperature the structure is ordered, and it has been reported by Riederer (1937) that this ordered structure is orthorhombic, the unit-cell dimensions being $a = 10{\cdot}65$, $b = 6{\cdot}38$, $c = 5{\cdot}05$ Å. Recent work by Lipson & Steeple (1951) has shown that ordered CdMg is orthorhombic and isomorphous with AuCd (Ölander, 1932), the unit-cell being much smaller than that quoted by Riederer. It is the purpose of this paper to determine the structural parameters accurately, as this work was not undertaken by Ölander.

Experimental details

The materials used in the preparation of the alloy were cadmium of 99·98% purity and magnesium of 99·95% purity. These components were melted under flux in an iron crucible and, after being cast in a thick copper mould, the alloy was homogenized by heat-treatment for 60 hr. at 380° C. in an evacuated silica tube. A chemical analysis showed that the alloy contained 50·3 atomic % cadmium.

X-ray powder photographs were obtained with a 19-cm. powder camera and filtered Cu $K\alpha$ radiation; the cylindrical specimen was prepared from filings which had been quenched from 200° C. after having been annealed at that temperature for 40 hr.

X-ray data

The unit-cell dimensions at 18° C. are

$$a = 5{\cdot}0051 \pm 0{\cdot}0003\,,$$
$$b = 3{\cdot}2217 \pm 0{\cdot}0002\,,$$
$$c = 5{\cdot}2700 \pm 0{\cdot}0003 \text{ Å}\,.$$

The ($hk0$) reflexions are absent when h is odd, confirming the space group *Pmma* found by Ölander. The density of the alloy is 5·333 g.cm.$^{-3}$ giving two atoms each of cadmium and magnesium per unit cell.

Determination of lattice parameters

There was considerable overlap of reflexions at high values of the Bragg angle θ and some difficulty was experienced in unequivocally indexing the reflexions by trial. Since the peak-to-peak distances of the overlapping reflexions were required to be known in order to separate as many of these reflexions as possible, it was necessary to determine the lattice parameters accurately. It was also necessary, for the purpose of intensity calculations, to index without ambiguity those reflexions which could not be separated. Refinement was accomplished by using Cohen's (1935) analytical extrapolation on those reflexions for which θ exceeded 60° and which could be indexed unambiguously by trial. The results are shown in Table 1 from which it can be seen that no systematic difference was then present between the observed and calculated values of $\sin^2\theta$, the only error being a random one arising from inaccuracies in the measurement of the powder films.

Table 1. *Comparison of* $\sin^2\theta_o$ *and* $\sin^2\theta_c$.

The values of $\sin^2\theta$ obtained from Cohen's extrapolation are shown under Corrected $\sin^2\theta_c$. The Cu $K\alpha_2$ wavelength has been converted to Cu $K\alpha_1$, wavelength 1·54050 Å.

hkl	$\sin^2\theta_o$	Corrected $\sin^2\theta_c$	Diff. $\times 10^5$
$331\alpha_1$	0·74976	0·74960	+16
$331\alpha_2$	0·74933	0·74960	−27
$332\alpha_1$	0·81360	0·81354	+ 6
$134\alpha_1$	0·88026	0·88027	− 1
$430\alpha_1$	0·89379	0·89370	+ 9
$522\alpha_1$	0·90642	0·90646	− 4
$504\alpha_1$	0·93420	0·93408	+12
$415\alpha_1$	0·97026	0·97024	+ 2
$514\alpha_1$	0·99094	0·99106	−12
			±10

Determination of the structure

The intensities were measured by means of a microphotometer, and a graph of intensity against distance was plotted; from this graph it was possible to determine the intensities of some of the overlapping reflexions. In all, about sixty general reflexions were available for the determination of the structure.

The observed structure factors were corrected for multiplicity, absorption, Lorentz and polarization factors, and were then placed on an absolute scale by comparison between the observed and calculated structure factors of intensities $hk0$ with h even. For these reflexions the calculated structure factors are $\pm 2(f_{\text{Cd}}+f_{\text{Mg}})$ with k even and $\pm 2(f_{\text{Cd}}-f_{\text{Mg}})$ with k odd, and are therefore known. A straight-line graph was obtained when $\log_e (f_o/f_c)$ was plotted against $-B\sin^2\theta/\lambda^2$, and from this graph both the temperature factor and the scale factor were determined. The observed structure factors could thus be placed on an absolute scale.

The only variable atomic parameters are cadmium at z_1 and magnesium at z_2. Preliminary values of $\frac{1}{6}$ and $\frac{2}{3}$ were assigned to z_1 and z_2 respectively, since these would have been the values had the atoms been situated at the points of the close-packed hexagonal structure. This can be seen from Fig. 1, which shows the projection of the ordered orthorhombic structure on (100). With these values of z_1 and z_2 a reliability factor of 12% was obtained when the accidentally absent reflexions were not taken into account. An examination of the calculated structure factors of the absent reflexions revealed that for ($hk3$) with h odd the factors were all identically zero, whereas for ($hk4$) with h even the factors were all higher than the corresponding estimated maximum values. Accordingly z_1 and z_2 were adjusted so as to decrease the latter factors without too much increase in the former, and the resulting reliability factor was improved to 7·5%, the accidentally absent reflexions again being omitted. It should be stressed that there are only two variable parameters in the structure, and that such marked agreement between observed and calculated structure factors is not, in general, to be expected when the number of parameters is large.

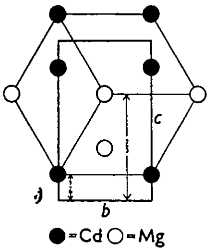

Fig. 1. Projection of the orthorhombic unit cell on (100) showing the relation of this unit cell to that of the close-packed hexagonal structure.

Refinement of the atomic parameters by the method of steepest descents

Further refinement was attempted by applying the method of steepest descents (Qurashi, 1949), the absent reflexions being given zero weight. Thirty-five reflexions were then available, and in the first instance all reflexions were considered. Further descents were then made using two separate arbitrarily chosen lists, (a) and (b), list (a) containing eighteen reflexions and list (b), seventeen. The results are shown in Table 2.

Table 2. *Application of method of steepest descents*

	All reflexions	List (a)	List (b)
Change in z_1(Cd)	0	+0·001	−0·001
Change in z_2(Mg)	+0·005	+0·004	+0·006

Each adjustment in z, however, produced no appreciable change in the reliability factor.

In order to estimate the limits of error in the values of the atomic parameters obtained by trial, the graphs of reliability factor against atomic parameter of both cadmium and magnesium in the region of the respective minima were plotted. From the graphs, the minimum value of the reliability factor when considering changes in the cadmium parameter was 7·4% at $z_1 = 0{\cdot}177\pm0{\cdot}002$, and the corresponding figures for magnesium were 7·5% at $z_2 = 0{\cdot}682\pm0{\cdot}007$; these values were accepted as being correct. The limits of error in both cases correspond to an algebraic change of ±0·1% in the value of the reliability factor. According to the geometry of the structure z_1 and z_2 should differ by exactly 0·5, and from the X-ray determination the difference is 0·505±0·009.

It will be seen that when all of the thirty-five reflexions were utilized, the method of steepest descents gave $z_1 = 0{\cdot}178$ and $z_2 = 0{\cdot}683$, which results are in excellent agreement with those obtained from the graphs. However, in view of the fact that changes in z_1 of opposite sign were produced when first the reflexions of list (a), and then those of list (b), were utilized, it would appear that the lower limit of the number of reflexions necessary for the successful application of the method is higher than is sometimes implied. Had the initial agreement between observed and calculated structure factors not been so marked, it is conceivable that, in the case of this structure, fewer than twenty reflexions would have given spurious values for the change required in z so as to effect refinement.

The square roots of the observed and calculated intensities, including those of the overlapping reflexions, are shown in Table 3. Eye-estimated values of those reflexions, which, although visible, were either too weak, or at high angles too diffuse, to be measured by the microphotometer, are shown in brackets. The overall reliability factor was 8·0% when accidentally absent reflexions were not taken into account.

The inter-atomic distances are as follows:

Table 3. *Comparison of* $\sqrt{I_o}$ *and* $\sqrt{I_c}$

Values estimated by eye are shown in brackets.

hkl	$\sqrt{I_o}$	$\sqrt{I_c}$
001	87	67
101	179	158
010	115	116
011	121	106
002	97	102
200	186	157
111	273	277
102	168	168
201	63	58
012	74	73
210	116	117
112	109	122
211	110	107
202	110	104
003	58	71
103	< 30	21
020	90	105
301	82	84
212	72	80
013 021	126	139
113 121	97	115
203	72	82
311	171	163
302	102	100
022	63	53
220	107	120
122	114	129
004 213 221	157	167
312	75	80
104	88	107
400	79	76
014	< 25	16
401	< 25	29
303	< 25	14
222	82	89
023 014	84	111
410 204	75	69
123	< 25	19
411	64	60
313 321 402	99	103
214	< 25	20
030 223 412 322	134	142
005	(40)	32
031	(40)	39
304	83	85
105 131 024 403	125	133
015 124	119	126
032	(30)	36
420 230 314 501 115	142	159
132	52	64
413 205 421 231 323	138	143
224	< 25	29
511	124	108
502	70	68
215	90	93
422 232	100	90
033	75	79
404	< 25	21
133	< 25	26
512	67	67
305	< 30	39
331	113	112
025	(50)	47
006	(50)	58
414	< 30	11
324 503 125	123	138
106	35	37
423 233 315	163	176
332	64	73
016	67	61
513 521 116 600 034 225 206	171	174
601	(40)	32
134	94	99
430	76	76
522	134	123
610	77	99
405 040 431 333 216	142	166
504	123	118
611 041 602	107	113
424	< 40	45
234	< 40	32
141	(150)	125
306	< 75	72

Cd–Cd	3·2217±0·0002	and	3·12±0·02 Å .
Mg–Mg	3·2217±0·0002	and	3·15±0·05 Å .
Cd–Mg	3·11 ±0·04	and	3·07±0·01 Å .

Atomic scattering factors of cadmium and magnesium

Since the temperature factor had already been determined, it was considered of interest to publish the atomic scattering factors at room temperature of cadmium and magnesium. The values at the absolute zero were multiplied by $\exp(-B\sin^2\theta/\lambda^2)$, where $B = 1{\cdot}9\times10^{-16}$ cm.^{2}, and the resulting respective values of f_{Cd} and f_{Mg} for different values of $\sin\theta/\lambda$ are given in Table 4.

Table 4. *Atomic scattering factors at room temperature of cadmium and magnesium*

f_{Cd}	f_{Mg}	$\sin\theta/\lambda\times10^{-8}$ (cm.$^{-1}$)
48·0	12·0	0
36·1	8·68	0·1
25·8	5·88	0·2
18·2	4·10	0·3
12·9	2·78	0·4
9·44	1·86	0·5
6·97	1·23	0·6

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References

Cohen, M. U. (1935). *Rev. Sci. Instrum.* **6**, 68.
Dehlinger, U. (1930). *Z. anorg. Chem.* **194**, 223.
Grübe, G. & Schiedt, E. (1930). *Z. anorg. Chem.* **194**, 190.
Hume-Rothery, W. & Raynor, G. V. (1940). *Proc. Roy. Soc.* A, **174**, 471.
Lipson, H. & Steeple, H. (1951). *Nature, Lond.* **167**, 481.
Ölander, A. (1932). *Z. Krystallogr.* **83**, 145.
Riederer, K. (1937). *Z. Metallk.* **29**, 423.
Qurashi, M. M. (1949). *Acta Cryst.* **2**, 404.