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Magnesium–Cadmium Alloys. IV. The Cadmium-Rich Alloys; Some Lattice Parameters and Phase Relationships between 25 and 300°. Structure of the $MgCd_3$ Superlattice. Schottky Defects and the Anomalous Entropy[1]

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The lattice parameters of cadmium and three magnesium–cadmium alloys were determined between 25° and 300°. The structure of the $MgCd_3$ superlattice was established. Schottky defects to the extent of 1 to 2% were found in the alloys, accounting for the previously observed anomalously high entropy of formation of the cadmium-rich alloys. Between 75 and 100% cadmium there exists only one phase at temperatures above 80°. Below 80° the intermediate phase $MgCd_3$ (ordered) and the saturated primary solid solution of magnesium in cadmium (disordered) coexist. The heterogeneous region extends from 75 to 84% cadmium at 25°. The variation of axial ratio with composition, temperature and degree of order is discussed in terms of (1) the variation in lattice energy with composition and (2) a postulated special short range force acting between adjacent cadmiums in the $00l$ plane.

Introduction

Recently a rather extensive study of the solid binary alloys of the magnesium–cadmium system was undertaken in this Laboratory. The changes in volume,[2] entropy,[3] free energy[3] and enthalpy[4] associated with the formation of these alloys from their constituents have been reported. The present paper gives an account of some of the crystallographic characteristics of the cadmium-rich alloys, about which, due to the conflicting results reported by earlier investigators, little could previously be regarded as firmly established.

Experimental

Apparatus.—The measurements are all based on powder patterns taken with nickel-filtered copper radiation. Some of the room temperature patterns were obtained using an ordinary 114-mm. Debye camera. The remainder and the high temperature measurements were made with a modified Unicam 19-cm. high temperature camera.

The modifications consisted in a slight change permitting Straumanis[5] loading and two minor alterations intended to improve the measurement and control of temperature. First, in view of the low upper limit of temperature it proved possible to operate the heater elements from a 110-volt supply, which was carefully stabilized. Second, the thermocouple circuits were altered so as to eliminate junctions of dissimilar metals inside the camera and to enable an ice-bath to be used as a reference. Thermocouple voltages were read using a White 100,000-μv. range double potentiometer allowing temperatures to be read easily to 0.1°. The camera cooling water was circulated from a water-bath whose temperature was maintained constant to ±0.02°.

The thermocouples were calibrated against the melting points of benzoic acid, tin and lead, the calibrations being made with the materials at the point normally occupied by the diffraction sample. The melting point samples were all supplied by the National Bureau of Standards. The metals were standard melting point samples with certified melting points. The benzoic acid was a sample intended for use as a combustion calorimeter standard. One additional calibration point was obtained by allowing the camera to come to equilibrium with the water circulated from the constant temperature bath.

During operation the sample temperature was constant in most cases to ±1° or less. Extreme variations were no more than ±2° during exposures of 30 to 50 hours.

The lines of the X-ray pattern were measured by means of a 60-cm. vernier caliper (Starrett Co. No. 122 M) mounted on a viewing box as suggested by Klug.[6] The scale was graduated in 0.5-mm. divisions and provided vernier readings to 0.02 mm.

Calculations.—Extrapolations to Bragg angle $\theta = 90°$ were made by Cohen's method,[7] providing correction terms for eccentricity, film shrinkage and absorption. The wave lengths for copper radiation used were those given by Siegbahn,[8] $CuK_{\alpha 1} = 1.537395$ kx. and $CuK_{\alpha 2} = 1.54132$ kx.

Handling of Samples.—The present work was undertaken with the belief that failure to guard the alloys against atmospheric corrosion was largely responsible for the conflicting results obtained earlier in independent studies of the low temperature phase relationships, variation of lattice parameters with composition, etc., for the magnesium–cadmium system. Considerable effort was made in this study to keep the alloys free of contamination.

The samples used were portions of the alloys prepared and analyzed in connection with the thermodynamic studies of this system.[3,4] Diffraction samples were prepared by filing the bulk alloys under an atmosphere of purified argon or helium. Provisions were made for screening the filings to a size not exceeding 200 mesh, strain-annealing and transferring to a glass capillary (Vycor or Corning 7070, 0.3–0.5 mm. diameter, wall thickness about 0.01 mm.) which was then sealed off for use in the diffraction camera, all without exposure of the filings to air. This practice was followed initially. Later it was found that the strain-annealed samples could be transferred to the capillary tubes in the open air without affecting the diffraction pattern. This procedure was followed in several cases.

Five groups of samples were studied. Their compositions in per cent.[9] were as follows: 100.0, 90.6, 78.0, 75.2 and 25.2. For simplicity these will be referred to as Cd, 90, 78, 75 and 25, respectively.

The heat treatments to relieve strains were 10 hr. at 300° for 25, 78 and 90, 12 hr. at 275° for 75 and 30 hr. at 225° for Cd. In addition 25 was placed in an oven at 125° and reduced to room temperature over a period of 3 days to develop the ordered structure existing below 150°.

To increase the probability that equilibrium between phases near 25° was established 75, 90 and a portion of 78 (78A) were aged at room temperature for 9 months prior to use. Their low temperature diffraction patterns were obtained first and then the temperature was raised. As the other portion of 78 (78B) was examined first at 299°, it was used about a week after its strain-anneal was completed.

Experimental Results

Lattice Parameters at Various Temperatures.—The unit cell dimensions of Cd, 75, 78 and 90 were determined as a function of temperature. The results, based on from 4 to 7 resolved doublets at Bragg angles ranging from 61 to 82°,

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[1] From a thesis submitted to the University of Pittsburgh by Donald A. Edwards in partial fulfillment of the requirements for the Doctor of Philosophy degree, February, 1952.

[2] J. M. Singer and W. E. Wallace, *J. Phys. Colloid Chem.*, **52**, 999 (1948); Paper I.

[3] F. A. Trumbore, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 132 (1952); Paper II.

[4] T. M. Buck, Jr., W. E. Wallace and R. M. Rulon, *ibid.*, **74**, 136 (1952); Paper III.

[5] M. Straumanis, *J. Applied Phys.*, **20**, 726 (1949).

[6] H. P. Klug, *Ind. Eng. Chem.*, **12**, 75 (1940).

[7] M. V. Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935).

[8] M. Siegbahn, "Spektroskopie der Roentgenstrahlen," 2nd ed., Springer Verlag, Berlin, 1931, p. 175.

[9] Percentages throughout will signify atomic percentages. Unless otherwise stated they will mean per cent. cadmium.

are summarized in Table I; 25 was examined only at 25°; its unit cell dimensions are given in Table V. The uncertainties listed are probable errors obtained, except for Cd at 25°, by establishing the probable errors in the constants[10] in Cohen's analytical function. As these calculations are rather tedious, they were made for only a portion of the determinations. Since the ones so treated were representative, the precision indices undoubtedly indicate roughly the precision of the rest. For Cd at 25° the lattice parameters reported are the mean of seven exposures each on a different sample. The probable errors were computed in the usual way from the scatter of the individual results.

TABLE I

UNIT CELL DIMENSIONS AT VARIOUS TEMPERATURES

Temp., °C.	a in kx.	c in kx.	c/a
	Pure Cadmium		
25	2.9734 ± 0.0001	5.6073 ± 0.0001	1.8858 ± 0.0001
68	2.9764	5.6200	1.8882
123	2.9799 ± .0000	5.6360 ± .0002	1.8913 ± .0001
222	2.9876	5.6636	1.8957
296	2.9956 ± .0000	5.6737 ± .0002	1.8940 ± .0001
	90.6% Cadmium		
26	2.9939 ± 0.0000	5.5047 ± 0.0002	1.8386 ± 0.0001
50	2.9960	5.5102	1.8392
149	3.0052 ± .0000	5.5320 ± .0003	1.8408 ± .0001
255	3.1067	5.5472	1.8388
297	3.0224 ± .0001	5.5511 ± .0005	1.8366 ± .0002
	78.0% Cadmium		
25[a]	6.2194 ± 0.0002	5.0350 ± 0.0001	0.8096 ± 0.0000
	3.0197 ± .0001	5.3864 ± .0002	1.7838 ± .0001
33[b]	3.0322	5.3371	1.7602
43[b]	3.0382	5.3240	1.7524
62[b]	3.0427	5.3173	1.7476
153[b]	3.0528 ± .0000	5.3317 ± .0002	1.7466 ± .0001
264[b]	3.0708	5.3375	1.7381
299[b]	3.0717 ± .0000	5.3435 ± .0002	1.7396 ± .0001
	75.2% Cadmium		
25	6.2209 ± 0.0001	5.0348 ± 0.0001	0.8093 ± 0.0000
50	6.2182	5.0478	.8118
66	6.2185	5.0605	.8138
75	6.2177	5.0709	.8156
	3.0561	5.2756	1.7262
86	3.0628	5.2524	1.7150
94	3.0647	5.2547	1.7146
141	3.0683 ± .0001	5.2665 ± .0001	1.7164 ± .0001
197	3.0724	5.2771	1.7176
245	3.0808	5.2857	1.7156
296	3.0867 ± .0001	5.2901 ± .0002	1.7138 ± .0001

[a] Alloy 78A. [b] Alloy 78B.

The diffraction patterns revealed that all phases in all the samples were hexagonal and all except 78 below 62° and 75 between 65 and 86° were homogeneous. In 78 two hexagonal phases coexisted between 25 and 62°. From a comparison of unit cell dimensions at 25° with those obtained for alloy 75 one of the phases in 78 appeared to be the ordered intermediate phase $MgCd_3$. The other phase was a disordered solution and was taken to be the saturated solution of magnesium in cadmium. For the ordered phase the diffraction lines were so indistinct at temperatures above 25° that the lattice parameters could not be evaluated.[11] Heterogeneity in 75 will be discussed later.

Structure of the $MgCd_3$ Superlattice.—Dehlinger[12] established the structure of the Mg_3Cd superlattice from single crystal work. He found the powder diffraction patterns for Mg_3Cd and $MgCd_3$ (for which he was unable to obtain single crystals) to be similar and from this assumed the two superlattices to have the same structure. Riederer[13] repeated Dehlinger's work for the two alloys and verified the unit cell dimensions and structure for Mg_3Cd. For $MgCd_3$, however, considerably different unit cell dimensions were reported by Riederer and this, of course, casts doubt on the structure postulated by Dehlinger. To clarify the situation diffraction patterns were obtained for the carefully prepared[14] and aged sample 75. As it was convenient, a Mg_3Cd sample was examined in the same series of experiments primarily for the purpose of obtaining better estimates of its unit cell dimensions.

$MgCd_3$ and Mg_3Cd (for simplicity AB_3) both show the same systematic extinctions, $hh\overline{2h}l$ and $hkil$ with $h - k = 3n$ both absent for $l = 2n + 1$. Space groups showing only these extinctions are $C\bar{6}c2$, C6cm, C6/mcm and C6/mmc[15] with A atoms in the twofold positions and B atoms in the sixfold positions. To decide which of these possibilities is appropriate for AB_3 one must examine the intensity of the diffraction lines. For $C\bar{6}c2$, C6cm and C6/mcm the structure factors for reflections $2\ 0\ \bar{2}\ 1$ and $2\ 0\ \bar{2}\ 3$ reduce to zero for any arrangement of the constituents in the unit cell. These reflections are observed, however, to be strong. The space group is accordingly C6/mmc.

For C6/mmc a preliminary inspection of the intensities reveals that A must be in the twofold positions $^1/_3$, $^2/_3$, $^1/_4$ and $^2/_3$, $^1/_3$, $^3/_4$, while B must be in the sixfold positions: $x, 2x, {^1/_4}$; $2\bar{x}, \bar{x}, {^1/_4}$; $x, \bar{x}, {^1/_4}$; $\bar{x}, 2\bar{x}, {^3/_4}$; $2x, x, {^3/_4}$; $\bar{x}, x, {^3/_4}$. The structure for Mg_3Cd obtained by Dehlinger is obtained if $x = {^5/_6}$. This arrangement of matter within the unit cell gives an agreement between calculated and observed intensities estimated visually which is entirely satisfactory. A similar situation exists for $MgCd_3$, with magnesium and cadmium, of course, interchanged.

The Order–Disorder Transition Point for $MgCd_3$.—The series of determinations of unit cell size of 75 was begun at 25° and the temperature was raised progressively. The diffraction patterns revealed the presence of the ordered and disordered types of structures over a temperature range extending from 65 to 86°. The intensity of the superlattice lines decreased throughout this temperature interval while the lines characteristic of the disordered phase steadily increased in intensity. At 75° the intensities of the lines of the low- and high-temperature forms were about equal. After the pattern at 296° was obtained, the temperature was lowered to re-examine the sample at 65 and 75°. The region of coexistence of the ordered and disordered forms was then depressed so that the pattern for 65° resembled that obtained at 75° as the temperature was raised. Hysteresis effects of this nature are not surprising in solid state transitions occurring at these low temperatures.

The appearance of superlattice lines in a sample on cooling to 75° indicates that the ordered phase $MgCd_3$ is stable to at least that temperature and possibly a few degrees higher. In the discussion which follows the order–disorder transition temperature will be taken as 80°. This estimate corresponds rather well with previous estimates made from electrical resistance determinations by Grube and Schiedt[16] and Stepanov and Kornilov[17] yielding 70–80° and 80°, respectively, and from a recent determination of specific heats in which a peak value at 77.7° was observed.[18]

Discussion of Results

Provisional Values for the Primary Solid Solubilities of Magnesium in Cadmium at Various Temperatures.—Hume-Rothery and Raynor[19] have conclusively demonstrated that magnesium and cadmium exhibit complete solid state miscibility for temperatures in excess of 255°. At lower temperatures the superlattices based on Mg_3Cd, MgCd

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[10] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 249.

[11] The difference in age of samples 78A and 78B undoubtedly affected the sharpness of the lines.

[12] U. Dehlinger, *Z. anorg. allgem. Chem.*, **194**, 223 (1930).

[13] K. Riederer, *Z. Metallkunde*, **29**, 423 (1937).

[14] This sample was prepared by filing under an atmosphere of exceptionally pure helium gas, the initial evaporate from a large batch of liquid helium.

[15] Space groups C6mc and $C\bar{6}2c$ also show the observed extinctions and should be considered as possibilities. However, when tbe parameters are established from the intensities, these two become identical with C6/mmc for this particular structure.

[16] G. Grube and E. Schiedt, *Z. anorg. allgem. Chem.*, **194**, 190 (1930).

[17] N. I. Stepanov and I. I. Kornilov, *Ann. secteur anal. phys. chim., Inst. chim. gen.* (*U.S.S.R.*), **10**, 79, 98 (1938).

[18] K. G. Khomayakov, V. A. Kholler and V. A. Troskina, *Vestnik Moskov Univ.*, **5**, No. 6, Ser. Fiz-Mat. i. Estest Naik, **4**, 43 (1950).

[19] W. Hume-Rothery and G. V. Raynor, *Proc. Roy. Soc.* (*London*), **174A**, 471 (1940).

and $MgCd_3$ appear with effects on the solid solubilities yet to be clarified. The diffraction characteristics of 78 below 50° indicate a heterogeneous region, in contradiction with the observations of Grube and Schiedt, who concluded that a homogeneous phase extends from 0–61% magnesium.[20]

The data given in Table I may be employed to determine approximate and provisional values for the primary solid solubilities of magnesium in cadmium at several temperatures. For pure cadmium, the alloy 90 and the disordered phase of the alloy 78, the unit cell dimensions at various temperatures between 25 and 75° were read from a large scale plot of the a- and c-values *versus* temperature. For alloy 75 the curves, showing the unit cell dimensions *versus* temperature for the high-temperature form, were extrapolated down to room temperature to estimate the dimensions of the unit cell in the alloy with frozen-in disorder. For each of the temperatures selected isotherms were drawn showing a and c *versus* composition. Using the known lattice constants of the saturated solution its composition at various temperatures could be read from the several isotherms. The solubilities thus obtained are given in Table II. The lack of agreement between solubilities determined from the a- and c-isotherms is due in part to inaccuracies in the isotherms introduced by the extrapolation procedure involved in their construction.

TABLE II

PRIMARY SOLID SOLUBILITIES OF MAGNESIUM IN CADMIUM

Temp., °C.	Magnesium, % From a	From c	Average
25	16.8	15.4	16.1
35	19.8	19.0	19.4
50	20.8	19.8	20.3
65	21.1[a]	20.4[a]	20.8[a]
75	21.3[a]	20.4[a]	20.8[a]

[a] These points are out of the two-phase region and hence the solutions are no longer saturated.

Above 65° Table II shows a "solubility" which is invariant with temperature. This shows that above 65° the sample was out of the two-phase region, which was also indicated by the absence of lines characteristic of $MgCd_3$ in the diffraction pattern. Consequently, above 65° the phase referred to in Table II is no longer a saturated solution and its composition should be identical with the gross composition 78.0%, as indicated by the chemical analysis. The discrepancy of 1.2% again reflects the errors in the isotherms. In view of these discrepancies the reported solubilities must be regarded as merely provisional in nature.

The solubilities at 35 and 50° were based on diffraction patterns for sample 78B, a "fresh" sample since it had been in the high-temperature camera at 299° only a few days earlier. In 78B precipitation of the $MgCd_3$ may have been incomplete and the solubilities listed are perhaps too high. The solubility at 25° was based on measurements involving a well aged sample for which precipitation was presumably complete so that except for errors in the isotherms the reported solubility should be satisfactory. Taking 80° to be the transition point for $MgCd_3$, the heterogeneous region separating the ordered phase $MgCd_3$ from the saturated solution of magnesium in cadmium extends from 84 to 75% at 25°, shrinks with increasing temperature and vanishes entirely at 80°.

The solubility at 25° agrees reasonably well with the range of stability of the α' phase reported by Riederer.[13] He observed a phase boundary at 19% magnesium for an unspecified temperature near room temperature.

Heterogeneity in Alloy 75.—The observed coexistence of ordered and disordered phases could be due to an unusual dependence of free energy on the degree of order in the two phases so that there is equality of free energy for the two phases over a range of temperature. More likely the heterogeneity originates in the phase relationships discussed above. Alloy 75, containing 75.2% cadmium, probably lies in the heterogeneous region so that at 25° a small amount (2–3% of the total) of saturated solution (disordered) exists in equilibrium with the ordered phase $MgCd_3$. At 25° the minor phase escapes observation. With increasing temperature the fraction of the sample in the minor phase increases until at 65° it first becomes observable and at 75° comprises roughly half of the sample. From the a- and c-isotherms at 75° the composition of the saturated solution is estimated to be 76.4 and 76.9%, respectively. Above 75° the ordered phase has disappeared and the solution has the gross composition. The alteration in composition above 75° accounts for the unusually rapid rise in a and the anomalous fall in c in that temperature region.

Schottky Defects and the Anomalous Entropy in Magnesium–Cadmium Alloys.—The entropies of formation previously determined in this Laboratory[3] showed a surprising feature. At compositions between 78 and 100% cadmium ΔS exceeded that of random mixing.[21] One explanation advanced for the exceptionally high entropy of the alloys was that they might contain an unusually high percentage of Schottky defects, 2 to 3% being required to account for the extra entropy. The lattice spacings given in Table I together with density data at 25° obtained earlier[4] permit the estimation of the number of vacant lattice sites at 25°. The results of the calculation are given in column 4 of Table III.

TABLE III

SCHOTTKY DEFECTS AND ENTROPIES OF ALLOYING

Mole fraction cadmium	Density (g./cm.^{3}) Macroscopic	X-Ray	Vacant, %	$(S_{\text{measd}} - S_{\text{id}})$ (e.u./g. atom) Sound	Vacancies
0.75	6.955	7.074	1.7	−0.05	−0.20
.85	7.550	7.702	2.0	+ .11	− .07
.90	7.850	8.008	2.0	+ .16	− .02
.95	8.210	8.331	1.5	+ .12	− .03
1.00	8.642	8.643	0.01	.00	.00

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(20) Hume-Rothery and Rowell (*J. Inst. Metals*, **38**, 137 (1927)) concluded that cadmium dissolves only 24% magnesium at 200° but this and other conclusions about the equilibrium diagram were found invalid in the later and more careful work of Hume-Rothery and Raynor.

(21) The data were for temperatures between 270 and 300°.

The existence of vacant lattice sites to the extent shown significantly influences the entropy of the alloy system. Assuming random mixing the entropy of alloying may be computed from the usual expression

$$\Delta S_{\text{id}} = -R(N_{\text{Cd}} \ln N_{\text{Cd}} + N_{\text{Mg}} \ln N_{\text{Mg}})$$

This neglects any vibrational contribution to the entropy and is for the sound alloy, that is, one with no Schottky defects. For an alloy possessing an appreciable number of randomly distributed vacant lattice sites

$$\Delta S'_{\text{id}} = -\frac{R}{N'_{\text{Cd}} + N'_{\text{Mg}}}(N'_{\text{Cd}} \ln N'_{\text{Cd}} + N'_{\text{Mg}} \ln N'_{\text{Mg}} + N'_{\text{V}} \ln N'_{\text{V}}),$$

N'_{V} representing the mole fraction of vacancies. In Table III columns 5 and 6 the differences between the observed and calculated entropies are shown. It thus appears that the anomalously high entropies can be satisfactorily explained[22] in terms of unoccupied lattice sites if the number of defects remains about the same between 25 and 270°.

Variation of the Lattice Parameters with Temperature.—The thermal expansivities for the several samples studied were anisotropic and strongly dependent on temperature in some cases. The temperature variation of *a* and *c* shown in Fig. 1 for alloy 75 merits some comment. (In Fig. 1 *a* for the disordered alloy is doubled.) Between 100 and 200° the increase of *a* with temperature is quite small compared to similar data either for 75 above 200° or the other specimens studied. It appears that the low thermal expansivity results from the destruction of residual order.[22a] The destruction of the superlattice is accompanied by a large decrease in *a*. It seems reasonable to suppose that a reduction in degree of short range order would also reduce *a*. Immediately above the order–disorder transition point, with increasing temperature the local order diminishes affecting *a* so as to nullify partially the normal increase of *a* with temperature. At higher temperatures local order has almost vanished and the normal expansivity is more nearly realized. Judging from Fig. 1 the influence of changing local order becomes insignificant between 150 and 200°.

The low expansivity along the *a* axis between 100 and 200° is paralleled by a high expansivity along the *c* axis, since the normal temperature effect and that due to changing local order are operating in the same direction. At higher temperatures the slope becomes smaller as the effect of changing order disappears.

Comparison with Results Obtained by Other Investigators.—The simple nature of the phase relationships deduced in this study for the alloys between 75 and 100% cadmium is in marked contrast with the complex situation which appeared to exist on the basis of the several preceding studies of these alloys. As indicated earlier Grube and Schiedt[16] concluded from resistance and expansion measurements that the primary solid solutions of magnesium in cadmium extended throughout this range. Their conclusion was reinforced by the X-ray investigations of Dehlinger[12] and Natta,[23] both of whom found this phase to possess a very unusual property in that its unit cell dimensions did not vary with (gross) composition and differed indistinguishably from the unit cell dimensions for pure cadmium.

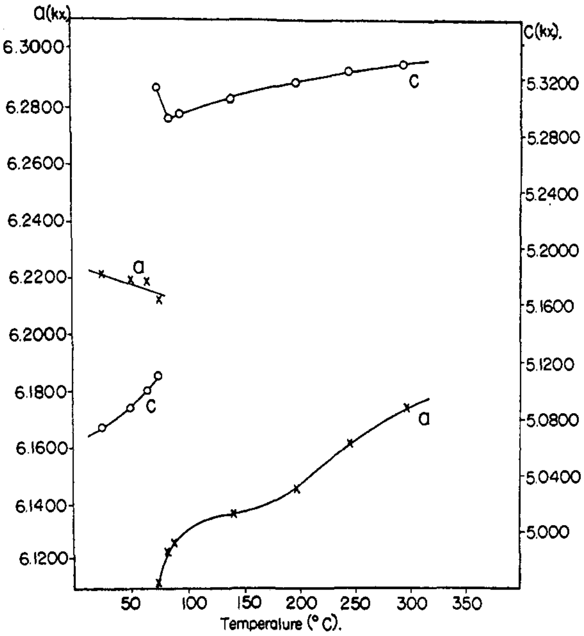

Fig. 1.—Unit cell dimensions at various temperatures for an alloy containing 75.2 atomic % cadmium. The *a*-spacings for the high temperature form have been doubled.

In this same range of composition Riederer[13] observed three phases, the intermediate phase $MgCd_3$ and two other phases which he called α and α'. The α-phase exhibited unit cell dimensions which were independent of composition and in this respect appeared to be identical with the phase observed by Natta and Dehlinger. The α'-phase had lattice parameters showing a trend with composition rather similar to that noted in the present study. Depending on the gross composition and the method of preparation Riederer observed the α- and α'-phases alone or together and all three situations occurring with and without $MgCd_3$ present.

The very careful work of Hume-Rothery and Raynor[19] revealed that the several discordant solid–liquid equilibrium diagrams for the magnesium–cadmium system were all in error due to a serious underestimation of the susceptibility of the alloys to atmospheric attack. It was pointed out by these investigators that the cadmium-rich alloys are corroded by the atmosphere more readily than the magnesium-rich alloys, including pure magnesium. The corrosion is particularly damaging at elevated temperatures. It thus appears that preparing diffraction samples by the usual practice of filing a solid alloy in the open air or sucking up the molten alloy into a small glass tube may lead to seriously contaminated samples.

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[22] The entropy deficiency in the 75 and 85% alloys undoubtedly results from partial ordering at 270° which leads to the MgCd superlattice at 50% and 255°.

[22a] The rapid increase in *a* between 75 and 94° is due to composition changes.

[23] G. Natta, *Ann. chim. applicata*, **18**, 135 (1928).

TABLE IV

UNIT CELL DIMENSIONS AT 25° OBTAINED BY DIFFERENT INVESTIGATORS

Investigator	Cadmium		90.6% Cd		84% Cd		$MgCd_3$		Mg_3Cd	
	a, kx.	*c*, kx.	*a*, kx.	*c*, kx.	*a*, kx.	*c*, kx.	*a*, kx.	*c*, kx.	*a*, kx.	*c*, kx.
Jette and Foote[24]	2.9731	5.6069								
Natta[23]	2.98	5.63	2.99	5.62	2.99	5.62				
Dehlinger[12]	2.96	5.63	2.96	5.63	2.95	5.61	5.86	5.53	6.26	5.07
Riederer[13]	2.98	5.63	2.98[a]	5.63[a]	2.98[a]	5.63[a]	6.22	5.04	6.26	5.07
			3.01[b]	5.53[b]	3.02[b]	5.40[b]				
Authors	2.9734	5.6073	2.9939	5.5047	3.016	5.376	6.2209	5.0348	6.300	5.064

[a] α-Phase. [b] α′-Phase.

The phase observed by Natta and Dehlinger and Riederer's α-phase must have been an alloy of fixed composition. As the Goldschmit radii of magnesium and cadmium differ by roughly 5%, it seems quite unlikely that a phase of variable composition could exhibit constant lattice geometry. It seems probable that the "alloy" was a contaminant of either a very dilute magnesium solution or pure cadmium. The crude methods employed in preparing the diffraction samples probably led to a leaching out of magnesium atoms at the surface by reaction with the atmosphere. Riederer's paper indicates that in general his α-phase occurred when the possibility for corrosion of the diffraction sample was greatest. Riederer, while not recognizing the α-phase as a contaminant, did regard the α′ as the stabler of the two phases.

In the present study there was no evidence of a phase corresponding to that observed by Dehlinger, Natta and Riederer (α-phase). The primary solid solutions corresponded rather well with Riederers' α′-phase.

Tables IV and V contain a summary of the unit cell dimensions obtained by various investigators. The agreement between the present results and those of Jette and Foote[24] and Riederer (except for his α-phase) is gratifying. The discrepancies between the present work and Hume-Rothery and Raynor's proved to be outside the combined errors attributed to the measurements, ranging from 0.007 to 0.58% and averaging 0.20%. Since the deviations are in different directions for the *a*- and *c*-spacings, the discrepancies cannot be attributed to errors in measuring temperature.

For the alloys an error in composition might account for the differences. In this composition range an increase in magnesium content increases the *a*-parameter and rapidly decreases the *c*-parameter. Thus a small error in composition would produce an appreciable error in the parameters. For pure cadmium the differences obviously cannot be explained by errors in composition.

At this point the source of the differences is not clear. One possibility is the different extrapolation procedures used in the two cases. Hume-Rothery and Raynor obtained their values through the Bradley and Jay[25] extrapolation; in this paper Cohen's analytical method has been used. It appears that the former method is less satisfactory, since errors are magnified in the adaptation employed by Hume-Rothery and Raynor. Even so the differences noted seem larger than anticipated. Another possible source of the difference is the entry of contaminants in one or both studies during preparation or handling of the samples. It is felt that the contaminants in this study were kept to a very low level, at least during the preparation procedure, as filings from some of the alloys were examined spectroscopically and no metallic contaminants appeared in anything other than traces. This did not exclude the possibility, however, that some nonmetallic contaminants were present in the samples.

The unit cell dimensions for pure cadmium were measured by Owen and Roberts[26] between 20 and 280°. Up to 250° there is good agreement between their results and those obtained in this study. Above 250° both *a* and *c* are larger than the present results. Extrapolating to 310° their *c*-spacing is in fair agreement with Hume-Rothery and Raynor's value while their *a*-spacing is 0.29% larger. The *a*-spacing obtained in the present study when extrapolated to 310° is between Hume-Rothery and Raynor's and Owens and Roberts' value, being 0.1% lower than the latter value. These comparisons indicate that some factor, perhaps resulting from the softness of cadmium, lessens considerably the reliability of the lattice parameters at temperatures above 250°. This factor may be the principal cause of the deviations noted in Table V.

TABLE V

A COMPARISON OF UNIT CELL DIMENSIONS AT 310° WITH VALUES OBTAINED BY HUME-ROTHERY AND RAYNOR

Cadmium, %	Hume-Rothery and Raynor[19]		Authors	
	a, kx.	*c*, kx.	*a*, kx.	*c*, kx.
100	2.9913	5.6835	2.9971	5.6749
90.6	3.0246	5.5631	3.0248	5.5520
78.0	3.0700	5.3510	3.0748	5.3424
75.2	3.0837	5.3272	3.0881	5.2964

Dependence of Axial Ratio on Temperature and Composition.—The anomalously high axial ratio in pure cadmium is well known. The departure from 1.63, the value for close packed spheres or atoms possessing spherically symmetrical force fields, indicates that an atom is more tightly bonded to its neighbors in the 00*l* plane than to an adjacent atom above or below the plane. The same situation to a lesser degree exists in the disordered cadmium-rich alloys, whereas in the ordered alloy (disregarding the double of the *a*-spacing) a normal axial ratio is realized. The strong dependence of the axial ratio on order and also the more moderate alterations due to changing temperature and composition are of interest, especially since they may shed some light on

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(24) E. R. Jette and F. Foote, *J. Chem. Phys.*, **3**, 605 (1935)

(25) A. J. Bradley and H. Jay, *Proc. Phys. Soc. (London)*, **44**, 563 (1932).

(26) E. A. Owen and E. W. Roberts, *Phil. Mag.*, **22**, 290 (1936)

the directional character of the forces around a cadmium atom in the crystal.

Thermochemical evidence indicates[3,4] that the cadmium lattice becomes increasingly stronger as magnesium is substituted for cadmium, the lattice energy increasing from 26.8 to 30.6 kcal./g. atom on passing from cadmium $MgCd_3$. The fall in axial ratio with increasing magnesium content results from this increased cohesion. The experiments of Bridgeman[27] on the linear compressibilities of single crystals of cadmium have shown that the direction of easy compression is parallel to the hexagonal axis. Thus on the application of a uniform external pressure distances along the hexagonal axis will be preferentially reduced and the trend will be toward a normal axial ratio and equalization of distance between a cadmium atom and each of its twelve neighbors. Increased cohesion should have an effect similar to that of a uniform external pressure. The levelling effect of increasing cohesion is exhibited by the variation of axial ratio with composition and also by the influence of temperature and degree of order on c/a. In general cohesion increases as temperature is reduced. For a pure metal this is merely a reduction in vibrational energy. With some alloys, however, order develops and the cohesive energy increases more rapidly with decreasing temperature. The rapid drop in c/a for $MgCd_3$ on passing through the Curie point merely parallels the rapid rise in cohesive energy.

On this basis it appears that c/a should increase with increasing cadmium content, temperature and degree of disorder. Examination of Table I reveals that these expectations are borne out experimentally except for cadmium between 222 and 296° and for the alloys of composition 90.6, 78.0 and 75.2% cadmium at temperatures 149 to 297°, 62 to 264° amd 197 to 296°, respectively.[28] The reversal in temperature coefficient for cadmium is small but undoubtedly real.[26] The fall in reversal temperature between cadmium and the 90.6% alloy undoubtedly continues to higher magnesium concentrations, being obscured in the 78.0% alloy by phase segregation and changing composition and in the 75.2% alloy by the variation of short range order.

It is suggested that the increase in thermal expansivity along the a axis at temperatures around 300° is a property which originates in some special kind of interaction which makes the spacing between cadmium in the $00l$ plane anomalously small. This special interaction is short range compared to the "normal" interaction and preferentially disappears as the average interatomic distance increases. At sufficiently high temperatures the solid is expanded to the point where the restraint imposed by the special interaction disappears, whereupon the thermal expansivity perpendicular to the hexagonal axis rapidly increases.[26] Concurrently, the expansivity along the hexagonal axis might be expected to diminish sharply.[28] The fall in inversion temperature with composition can then be viewed as a dilution effect to which the special interaction should be particularly sensitive. In this sense the replacement of a small cadmium atom by a large magnesium atom expands the lattice and has the effect of an increase in temperature.

The same conclusions can be reached by postulating special repulsion between an atom and an adjacent atom above or below the $00l$ plane. This possibility seems less likely, however, than that outlined above.

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(27) P. M. Bridgeman, *Proc. Am. Acad. Arts Sci.*, **60**, 342 (1925).

(28) Results for alloy 75 between 75 and 95° and for alloy 78 below 62° are not included in the discussion since composition and temperature are both changing.