UNITED STATES ATOMIC ENERGY COMMISSION

NYO-945

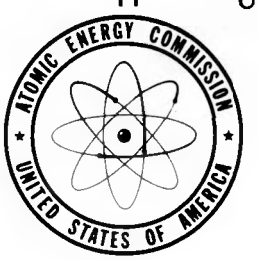
SOME CRYSTALLOGRAPHIC CHARACTERISTICS OF THE CADMIUM RICH MAGNESIUM-CADMIUM ALLOYS BETWEEN 25 AND 300°C

Progress Report for July 1, 1951 - October 1, 1951

By
W. E. Wallace
D. A. Edwards

October 5, 1951

University of Pittsburgh



Technical Information Service, Oak Ridge, Tennessee

METALLURGY AND CERAMICS

Reproduced direct from copy
as submitted to this office.

Work performed under
Contract No. AT(30-1)-647.

AEC, Oak Ridge, Tenn., 11-9-51--220-W7617

Abstract

The unit cell dimensions of pure cadmium and alloys containing 90.6, 78.0 and 75.2 atomic per cent cadmium have been determined between 25°C and 300°C. Dehlinger's proposed structure for the $MgCd_3$ superlattice was verified. The order-disorder transition temperature in $MgCd_3$ as determined by its diffraction characteristics was found to be about 65°C. The alteration in structural characteristics of $MgCd_3$ in the vicinity of its order-disorder Curie point has been determined and thermal expansivities of this alloy and the others have been reported. From the diffraction patterns a provisional estimate of the terminal solid solubility limits of magnesium in cadmium between 25 and 65°C has been made. The percentage of Schottky defects has been computed and compared with the values expected from the anomalous entropy behavior of high cadmium magnesium-cadmium alloys.

A considerable body of thermochemical and thermodynamic data for the magnesium-cadmium alloy system has been obtained in this laboratory. To interpret those results and the results of other investigations pertaining to this system which are currently underway a better understanding of its crystallographic characteristics is necessary. The present report contains an account of some of the structural characteristics of the cadmium-rich alloys between 25 and 300°C.

I. Survey of Previous Work

Hume-Rothery and Raynor[1] established that for temperatures above 255°C magnesium and cadmium exhibit continuous solid solubility, the two metals and the various alloys all crystallizing in the hexagonal system. At lower temperatures superstructures based on compositions Mg_3Cd, MgCd and $MgCd_3$ are known to exist.

Beyond that little is known with certainty about the equilibrium state of the system.

Magnesium-cadmium alloys have been studied by means of X-ray diffraction at room temperature by Natta,[2] Dehlinger,[3] Riederer[4] and Raynor.[5] Raynor's work consisted in determining lattice spacings versus composition in the high magnesium range. His work appears satisfactory in every respect. Raynor found a terminal solubility of cadmium in magnesium extending to 16%.* The other three investigators examined alloys extending over the entire composition. For the present purposes, however, reference will be made to only that part of their work relating to the high cadmium alloys.

Natta reported for alloys containing up to 15% magnesium the lattice parameters were identical with those of pure cadmium. Dehlinger examined alloys having compositions 20 and 25% magnesium. The former had unit cell dimensions differing inappreciably from pure cadmium while the latter existed as a hexagonal superlattice with a = 5.86 kx and c = 5.53 kx. Dehlinger established the structure of Mg_3Cd and from the similarity of the diffraction patterns of Mg_3Cd and $MgCd_3$ inferred the identity of the two structures. Representing both alloys as AB_3, Dehlinger placed A's at 1/2 1/2 0 and 1/6 5/6 1/2 and B's at 0 0 0, 1/6 1/3 1/2, 1/2 0 0, 2/3 1/3 1/2, 0 1/2 0, 2/3 5/6 1/2. Riederer's results for high cadmium alloys were at variance with the results of both Natta and Dehlinger. His unit cell dimensions for $MgCd_3$ differed appreciably from those observed by Dehlinger although both investigators were in agreement about Mg_3Cd. Riederer's work thus casts doubt on the structure assumed by Dehlinger for $MgCd_3$. Furthermore, in the region of zero to 19% magnesium Riederer found two types of structures, an alpha and an alpha'. The latter was characterized by unit cell dimensions which varied with

* Percentages throughout will in all cases signify atomic percentages.

composition whereas for the former the size of the unit cell was independent of composition. Both forms were hexagonal. From Riederer's paper it is not possible to decide whether he considered both, none or which of the two forms as an equilibrium phase in the magnesium-cadmium system.

From the preceding resume one notes that Natta, Dehlinger and Riederer all observed a phase in the cadmium-rich alloys for which the unit cell dimensions were independent of composition. This is indeed a surprising feature when one realizes that an alteration in composition involves the substitution of one ion for another, the two ions having Goldschmidt radii differing by roughly 5%. In their work at 310°C Hume-Rothery and Raynor observed a variation in a and c with composition at all compositions with the strongest dependence on concentration in the cadmium-rich region. It seems unlikely that a phase could exist having the characteristics of Riederer's alpha' phase and in the present work, as will be shown later, no evidence for the existence of such a phase was obtained.

In the very careful investigations of Hume-Rothery and Raynor they disposed of a number of conflicting results obtained in earlier studies by showing that it was essential to handle these alloys in an inert atmosphere to eliminate spurious effects due to atmospheric attack. It seemed likely that the aforementioned discordant results for the high cadmium alloys must be due at least in part to contamination by atmospheric attack. The present measurements were made on alloys carefully guarded against such contamination in their preparation and handling.

II. Apparatus and Equipment

The X-ray diffraction unit used in the study was a General Electric XRD-1. All exposures, except for a few preliminary ones, were made with nickel-filtered radiation from a copper-target tube.

For the pictures made at room temperatures a Von der Heyde 114 mm camera with a circular 1 mm slit was used. Since this camera permits use of the Straumanis method,[6] no calibration was required.

For those measurements at elevated temperatures the Unicam 19 cm high-temperature camera with a rectangular 1 mm slit was employed. By a slight modification it was possible to adapt this camera so as to use the Straumanis technique. Two additional modifications of the Unicam camera were made to improve the control and measurement of specimen temperatures. First, the heater elements were operated on 110 volts, instead of 220 volts, for better temperature control. This change was possible since no measurements above about 300°C were planned. The 110-volt supply was stabilized by using two constant voltage transformers in series whose output fed the primary of a variac. The camera heaters were controlled by this variac. The second modification instituted was in the thermocouple circuits. They 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. The thermocouple voltages were read on a White double potentiometer. The cooling water for the camera was circulated by a pump through a thermostatted water bath.

The thermocouples were calibrated against the melting points of benzoic acid, tin and lead. All materials were supplied by the National Bureau of Standards. The benzoic acid was a sample intended for use as a standard in combustion melting points. The melting points were observed with the materials at the point normally occupied by the diffraction sample. One additional calibration point was obtained by allowing the camera to come to thermal equilibrium with water circulated through it from a thermostatted bath.

During operation the sample temperature was constant in most cases to ± 1°C or less. Extreme variations were no more than ± 2°C 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 H. P. Klug.[7] The scale was graduated in 0.5 mm divisions and provided vernier readings to 0.02 mm.

Calculations were made by Cohen's method,[10] providing correction terms for eccentricity and film shrinkage. No correction was made for absorption since the correction was negligible for the capillaries used. The wavelengths for copper radiation were those given by Siegbahn,[11] $CuK\alpha_1$ = 1.537395 kx and $CuK\alpha_2$ = 1.541232 kx.

III. Handling of Samples

The alloys used were those prepared and analyzed in connection with thermodynamic studies of this system. The methods employed are given elsewhere.[8,9] Except for one of the samples, the filings were prepared under an atmosphere of argon by means of a mechanically driven file operating in a gas-tight metal enclosure. The reciprocating motion of the file and the adjustment of the sample holder were made possible by means of two sylphons attached to the metal chamber. During the filing process the chamber was kept filled with argon at about 5 mm above atmospheric pressure. Before introducing the argon the chamber was evacuated to a few hundredths of a micron pressure. The filings passed through a 200-mesh sieve and dropped into glass tubing so that the sample was collected without exposure to air.

In the course of the work five groups of samples were studied. Their designations for compositions in atomic per cent cadmium were as follows: Cd - 100.00, TD - 90.6, TJ - 78.0, BJ - 75.2 and TG - 25.2.

Filings from sample TJ were prepared in the argon-filled chamber described above, sealed off in vacuo, and annealed overnight at about 300°C. The tube was then opened and capillaries TJ-4 and TJ-6 were filled, exposing the filings to air for a period of at most two hours. The capillaries were then pumped out and sealed off. TJ-4 was allowed to stand for 9 months before X-ray pictures were made; TJ-6 was prepared a week before being photographed.

Filings from sample TD were prepared similarly, and after annealing at 302°C, were allowed to stand for 12 months. The glass tube was then opened and capillary TD-11 was filled, evacuated, and sealed-off.

Filings from pure cadmium were also prepared under argon. Capillary Cd-7 was annealed for 30 hours at 230°C; capillary Cd-8 was annealed for 30 hours at 220°C in the high-temperature camera before beginning the series of pictures at elevated temperatures.

Filings from sample BJ were prepared by hand in a dry box under an atmosphere of helium and were stored in a glass tube plugged with cotton in a desiccator over concentrated sulfuric acid for a period of 12 months. Capillaries BJ-1 and BJ-2 were then filled, evacuated, and sealed-off.

Except for BJ-1 and BJ-2 all capillaries were of Corning 7070 glass; capillaries BJ-1 and BJ-2 were of Vycor. The latter capillaries were superior mechanically and also in transparency to X-rays near room temperature; at temperatures near 300°C background scattering seemed greater than that for 7070 glass.

IV. Results

A. Unit Cell Dimensions at Various Temperatures

The unit cell dimensions have been determined as a function of temperature for pure cadmium, 90.6, 78.0, and 75.2 per cent cadmium. The results are

shown in Table I and graphically in Figures 1, 2, and 3. Where both high and low temperature forms occur in the same alloy the a-values of the hexagonal unit cell for the high temperature form have been doubled in order that direct comparison can be made with the low temperature form. For the high temperature disordered unit cell the true unit cell is thus only 1/4 the size indicated by the table.

The diffraction patterns of the TJ series indicated the existence of two phases for all temperatures up to and including 62°C. For one of the phases the lines were indistinct and the unit cell dimensions could only be established at 25°C. This phase was crystallographically identical with the BJ samples at 25° and was taken to be the ordered structure $MgCd_3$. The other phase was a disordered solution clearly richer in cadmium than 78.0% and was taken to be the saturated solution of magnesium in cadmium.

B. The Structure of Ordered Alloys $MgCd_3$ and Mg_3Cd

Judging from dilatometric and electrical conductivity measurements magnesium-cadmium alloys having compositions corresponding to $MgCd_3$ and Mg_3Cd develop ordered structures at reduced temperature. The Curie points have been reported to be approximately 75°C and 150°C for $MgCd_3$ and Mg_3Cd, respectively. Whereas the structure of Mg_3Cd was firmly established by Dehlinger, his proposed structure for $MgCd_3$ is open to criticism, as indicated earlier. The structures of both of these "compounds" were established in the course of the present work.

The powder diffraction patterns of $MgCd_3$ and Mg_3Cd (for simplicity AB_3) readily index under the assumption that the crystals belong to the hexagonal system. Since the same systematic absences, h h $\bar{2}$h l and h - k = 3n, both for l = 2n + 1, occur for $MgCd_3$ and Mg_3Cd, both substances can be discussed together. The possible space groups are C$\bar{6}$c2 C6cm, C6/mcm, C$\bar{6}$2c, C6mc, C6/mmc, C6cc, and C6mcc,

Table I

Unit Cell Dimensions at Elevated Temperatures

Temperature °C	Capillary	a in kx	c in kx	c/a
		Pure Cadmium		
25	Cd-7	2.9733	5.6072	1.8858
68	Cd-8	2.9764	5.6200	1.8882
123	Cd-8	2.9799	5.6360	1.8913
222	Cd-8	2.9876	5.6636	1.8957
296	Cd-8	2.9956	5.6737	1.8940
		90.6% Cadmium		
26	TD-11	2.9939	5.5047	1.8386
50	TD-11	2.9960	5.5102	1.8392
149	TD-11	3.0052	5.5320	1.8408
255	TD-11	3.0167	5.5472	1.8388
297	TD-11	3.0224	5.5511	1.8366
		78.0% Cadmium		
25	TJ-4	6.2194	5.0350	0.8096
		6.0394*	5.3864	0.8919
33	TJ-6	6.0644*	5.3371	0.8801
43	TJ-6	6.0764*	5.3240	0.8762
62	TJ-6	6.0854*	5.3173	0.8738
153	TJ-6	6.1056*	5.3317	0.8733
264	TJ-6	6.1418*	5.3375	0.8690
299	TJ-6	6.1434*	5.3435	0.8698
		75.2% Cadmium		
25	BJ-1	6.2209	5.0348	0.8093
50	BJ-2	6.2182	5.0478	0.8118
66	BJ-2	6.2185	5.0605	0.8138
75	BJ-2	6.2177	5.0709	0.8156
		6.1122*	5.2756	0.8631
86	BJ-2	6.1255*	6.2524	0.8575
94	BJ-2	6.1294*	5.2547	0.8573
141	BJ-2	6.1365*	5.2665	0.8582
197	BJ-2	6.1448*	5.2771	0.8588
245	BJ-2	6.1616*	5.2857	0.8578
296	BJ-2	6.1734*	5.2901	0.8569

* The value of a has been doubled.

with A atoms in the two-fold positions and B atoms in the six-fold positions. Space groups C6cc and C6mcc require additional systematic absences, h k i l absent for l = 2n + 1, which were not observed. To decide which of the remaining six possibilities is appropriate for AB_3 one must examine the intensity of the diffraction lines. For $C\bar{6}c2$ 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. When the constituents are in the special positions previously indicated, space groups C6cm and C6/mcm are special cases of $C\bar{6}c2$ and hence all three of these are eliminated on the basis of the 2 0 $\bar{2}$ 1 and 2 0 $\bar{2}$ 3 reflections.

For $C\bar{6}2c$ a preliminary inspection of the intensities reveals that A must be in the two-fold positions 2/3 1/3 1/4 and 1/3 2/3 3/4, while B must be in the six-fold positions: x y 1/4; $\bar{y}$, x-y, 1/4; y-z, $\bar{x}$, 1/4; y x 3/4; $\bar{x}$, y-x, 3/4; x-y, $\bar{y}$, 3/4. The structure for Mg_3Cd obtained by Dehlinger is obtained if x = 1/6 and y = 5/6 and the origin is moved by 5/6 1/6 3/4, giving magnesium the positions 0 0 0; 0 1/2 0; 1/2 0 0; 2/3 1/3 1/2; 2/3 5/6 1/2; 1/6 1/3 1/2 and cadmium the positions 1/2 1/2 0 and 1/6 5/6 1/2. This arrangement of matter within the unit cell gives an agreement between calculated and observed intensities which is entirely satisfactory. A similar situation exists for $MgCd_3$, with magnesium and cadmium, of course, interchanged.

C. Characteristics of $MgCd_3$ Near the Order-Disorder Curie Point

The 75.2% cadmium alloy was aged for a period of 12 months after filings were prepared, thus allowing ample time for the equilibrium state to be reached. The series of determinations of unit cell size was begun at room temperature and carried to around 300°C.

The diffraction patterns revealed the presence of the ordered and disordered types of structures over a range of temperature extending from 65° to 86°C. Superlattice lines were faint at 86°C and had disappeared completely at 94°C. Certain lines characteristic of the disordered form began to appear faintly at 65°C. 75°C is the temperature at which the low- and high-temperature forms appeared to be present roughly in equal amounts. After raising the temperature for the series of pictures around 300°C, the temperature was lowered to repeat the patterns made at 75°C and 65°C. Here the temperature at which both types of structures existed simultaneously and in roughly equal amounts was 65°C. At 75°C the lines appeared similar to those produced at 65°C as the temperature was being raised.

Grube and Schiedt[12] reported a transformation between 70° and 80°C, their determination being based upon electrical conductivity and dilatometric measurements. Using a similar procedure Stepanov and Kornilov[13] ascribed the transition to 80°C. Very recently the specific heats of $MgCd_3$ have been determined between 25°C and 300°C by Kholler and Troshkina.[14] The typical λ-point specific heat behavior was observed with a peak value at 77.7°C. The specific heat anomaly is most pronounced between 67°C and 87°C, but is in evidence at 25°C. The specific heat behavior is consistent with the appearance of the disordered form at 65°C noted in this work.

The destruction of long range order is accompanied by an appreciable volume increase. At 75°C where ordered and disordered forms co-exist the lattice spacings are a = 6.2177 kx and c = 5.0709 kx for the ordered phase and a = 6.1122 kx and c = 5.2756 kx for the disordered phase. The unit cell of the high temperature form exceeds that of the low temperature form by 0.91 kx^3. The volume increment is 0.54%, based on the volume of the ordered phase.

D. Provisional Values for the Terminal Solid Solubilities of Magnesium in Cadmium at Various Temperatures

The data given in Table I may be employed to determine approximate values for the terminal solid solubilities of magnesium in cadmium at several temperatures. For pure cadmium and for 90.6% cadmium the unit cell dimensions at various temperatures between 25°C and 65°C can be read from a large scale plot of the a- and c-values versus temperature. For the 75.2% cadmium one may extrapolate the curve, showing the unit cell dimensions versus temperature for the high-temperature form, down to room temperature to obtain the dimensions which the unit cell would have had if it had remained in the disordered state. For each of the temperatures selected one can then draw isotherms for unit cell size versus composition.

Analysis of the diffraction patterns for the 78.0% sample shows that it is a two-phase mixture for all temperatures studied up to 65°C. On the basis of the unit cell dimensions one phase appeared to be identical with the low temperature form observed with the 75.2% alloy, that is, the ordered structure $MgCd_3$. The other phase was a disordered phase which, judging from the geometry of its unit cell, was poorer in magnesium than the gross composition of this alloy would indicate. It seems clear that this second phase was a saturated solid solution of magnesium in cadmium. From the unit cell dimensions (see Table I) its composition can be estimated at various temperatures by use of the a- and c-isotherms obtained as previously indicated. 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 isotherm introduced by the extrapolation procedure involved in their construction.

Above 65°C Table II shows a "solubility" which is invariant with temperature. This clearly indicates that above 65°C one is out of the two-phase region,

a conclusion which is borne out by the absence of lines characteristic of $MgCd_3$ in the diffraction pattern. This temperature is also consistent with that at which the disordered phase first appeared in the 75.2% alloy. Consequently, above 65°C 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 composition estimated from the lattice spacings at 65°C and above is 79.2%, the difference again arising, at least in part, from inaccuracies in the isotherms. In view of such discrepancies the solubilities reported in Table II must be regarded as merely provisional in nature.

Table II

Terminal Solid Solubilities of Magnesium in Cadmium

Temperature °C	Per Cent 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*	20.4*	20.8*
75	21.3*	20.4*	20.8*

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

E. Schottky Defects

In the determination of densities from X-ray measurements one assumes that all lattice sites are occupied. If the densities so determined are greater than those determined macroscopically it means that a number of the lattice sites are vacant. Such vacancies are called Schottky defects. The per cent of vacancies is given by

$$\% \text{ Vac.} = 100(d_{\text{x-ray}} - d_{\text{mac.}})/d_{\text{x-ray}}$$

The density from X-ray data is given by

$$d_{X\text{-}ray} = (nA)/(VN),$$

where A is the gram atomic weight, V is the unit cell volume, N is Avogadro's number, and n is the number of atoms per unit cell. The percentages of vacancies for various compositions at 25°C are given in Table III. The macroscopic densities were determined by Singer and Wallace[15] using the method of Archimedes.

Table III

Data for Estimating Schottky Defects
in Magnesium-Cadmium Alloys at 25°C

%Cadmium	Densities		$d - d$	% Vacancies
	Macroscopic	X-ray	Macroscopic X-ray	
75	6.955	7.074	0.19	1.7
80	7.250	7.392	0.142	1.9
85	7.550	7.702	0.152	2.0
90	7.850	8.008	0.158	2.0
95	8.210	8.331	0.121	1.5
100	8.642	8.643	0.001	0.01

F. Thermal Expansivities

Thermal expansivities were found to be anisotropic. Since the plots are in general non-linear, only the average expansivities over a range of temperature are presented.

Table IV

Average Linear Expansivities per °C

% Cadmium	Temperature Range	a-Direction	c-Direction
100	25 - 296	2.76×10^{-5}	4.34×10^{-5}
90.6	26 - 297	3.51	3.10
78.0	62 - 299	4.01	2.08
75.2	25 - 75	-1.0*	14.9*
	75 - 86	19.8**	-40.1**
	86 - 296	3.72**	3.41**

* Indicates low-temperature form. ** Indicates high-temperature form.

V. Discussion of Results

A. Comparison with Results Obtained in Previous Studies

1. Unit Cell Dimensions

A comparison of the results obtained in this study with those obtained by earlier observers is shown in Tables V and VI.

The agreement with the values obtained by Jette and Foote[16] for pure cadmium at 25°C is good, and the values found by Riederer for Mg_3Cd, $MgCd_3$, and the alpha'-type agree reasonably well. The "alpha-phase" found by Riederer was not observed in this study and it seems likely that this "phase" was a contaminant of pure cadmium introduced in the preparation and manipulation of the samples by Riederer and also by Dehlinger and Natta, both of whom found a "phase" having somewhat the characteristics of Riederer's "alpha-phase".

An examination of Table VI reveals the fact that, for the values of Hume-Rothery and Raynor, the a-parameters are consistently smaller than those presented by the authors, while the c-parameters are consistently larger. Therefore, the differences cannot be attributed to incorrect temperature measurements. For the alloys an error in composition might account for the difference. In this composition range an increase in magnesium content would increase the a-parameter

and rapidly decrease 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 extrapolation; the authors used Cohen's analytical method. It appears that the former method is less satisfactory since errors are magnified in the adaptation employed by Hume-Rothery and Raynor, although 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 non-metallic contaminants were present in the samples.

2. Structures of Mg_3Cd and $MgCd_3$

As indicated earlier the structure of Mg_3Cd determined in the present work agrees with that found by Dehlinger and also the structure found for $MgCd_3$ agrees with that postulated by Dehlinger (see Sectiin IV,B).

3. The Terminal Solid Solubility Limit of Magnesium in Cadmium at 25°C

At 25°C the solid solubility limit of magnesium in cadmium was found in this study to be 16%. This result agrees reasonably well with the value of 19% found by Riederer for "room temperature," as determined by the location of the break in his plot of lattice parameters versus composition.

B. Schottky Defects and the Entropies of Magnesium-Cadmium Alloys

It is interesting to compare the Schottky defects reported here with those postulated by Trumbore, Wallace, and Craig[8] from entropy considerations. For cadmium-rich alloys above the Curie point they found an anomalous excess entropy over the entropy of random mixing and postulated the existence of 2 to 3% vacant lattice sites as one means of accounting for this extra entropy. The percentage of vacancies found in this study is of the same order of magnitude as that postulated from entropy considerations.

Table V

Unit Cell Dimensions at 25°C Obtained by Different Investigators

Investigator	Cadmium		90% Alloy		84% Alloy		$MgCd_3$		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[16]	2.9731	5.6069								
Natta[1]	2.98	5.63	2.99	5.62	2.99	5.62				
Dehlinger[2]	2.96	5.63	2.96	5.63	2.95	5.61	5.86	5.53	6.26	5.07
Riederer[3]	2.98	5.63	2.98*	5.63*	2.98*	5.63*	6.22	5.04	6.26	5.07
			3.01**	5.53**	3.02**	5.40**				
Authors	2.9733	5.6072	2.9939	5.5047	3.016	5.376	6.2209	5.0348	6.300	5.064

* Riederer's alpha-phase ** Riederer's alpha'-phase

Table VI

A Comparison of Unit Cell Dimensions at 310°C with Values Obtained by Hume-Rothery and Raynor

% Cadmium	Hume-Rothery and Raynor[4]		Authors		% Difference	
	a(kx)	c(kx)	a(kx)	c(kx)	a	c
100	2.9913	5.6835	2.9971	5+6749	-0.19	+0.15
90.6	3.0246	5.5631	3.0248	5.5520	-0.007	+0.20
78.0	3.0700	5.3510	3.0748	5.3424	-0.16	+0.16
75.2	6.1674	5.3272	6.1762	5.2964	-0.14	+0.58

C. Thermal Expansivities Near the Curie Point

The thermal expansivities of $MgCd_3$ in the vicinity of the Curie point can be interpreted in terms of the effects of changes in long-range and short-range orders. For $MgCd_3$ Figure 3 shows that the value of the a-parameter decreases with the disappearance of long-range order. After the long-range order has disappeared a short-range order still persists. That a decrease in this short-range order tends to decrease further the a-parameter is indicated by that part of the curve where its slope is least. Beyond this point the normal effect of expansion becomes sufficiently strong, and the effect of short-range ordering sufficiently weak, to cause the curve to rise more sharply. Similarly one observes that, for the c-parameter, the effect is just the opposite, the c-parameter increasing as the long-range order disappears. A further decrease in short-range order causes the curve to rise more sharply until the flat portion of the curve is reached where the normal effect of expansion prevails.

D. Summary of Structural Characteristics of the Cadmium-Rich Magnesium-Cadmium Alloys

From the results obtained one concludes that, for the magnesium-cadmium alloys with compositions between 0 and 25% magnesium, the equilibrium state of the system between 75°C and the solidus is a single homogeneous solid phase--a solid solution, showing no long-range order, one whose crystals belong to the hexagonal system. Below 65°C two phases exist, one the compound or ordered structure, $MgCd_3$, also hexagonal, and the other a saturated solution, holding at 25°C approximately 16% magnesium. From the trend of solubilities above 25°C it would seem that at very low temperatures the "saturated" solution approaches pure cadmium, and at those temperatures only pure cadmium and $MgCd_3$ would be stable in the composition region cited.

Bibliography

1. Natta, G., Ann. Chim. applicata, 18, 135 (1928).

2. Dehlinger, U., Z. anorg. allgem. Chem., 194, 223 (1930).

3. Riederer, K., Z. Metallkunde, 29, 423 (1937).

4. Hume-Rothery, W., and Raynor, C. W., Proc. Roy. Soc. (London), 174A, 471 (1940).

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

6. Straumanis, M., J. Applied Phys., 20, 726 (1949).

7. Klug, H. P., Ind. Eng. Chem., 12, 753 (1940).

8. Trumbore, F. A., Wallace, W. E., and Craig, R. S., J. Am. Chem. Soc., in press.

9. Buck, T. M., Jr., Wallace, W. E., and Craig, R. S., J. Am. Chem. Soc., in press.

10. Cohen, M. U., Rev. Sci. Instruments, 6, 68 (1935).

11. Siegbahn, M., Spektroskopie der Rontgenstrahlen, Berlin, Springer, 2nd Ed. (1931).

12. Grube, C. and Schiedt, E., Z. anorg. allgem. Chem., 194, 190 (1930).

13. Stepanov, N. I. and Kornilov, I. I., Ann. specteur phys.-chim., Inst. Chim. gen. (U.S.S.R.) 10, 79 (1938); ibid. 10, 97 (1938).

14. Kholler, K. G., and Troskina, V. A., Vestnik Moskov Univ. 5, No. 6, Ser. Fiz-Mat. i Estest Naik No. 4, 43-54 (1950).

15. Singer, J. M. and Wallace, W. E., J. Phys. & Colloid Chem., 52, 999 (1948).

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

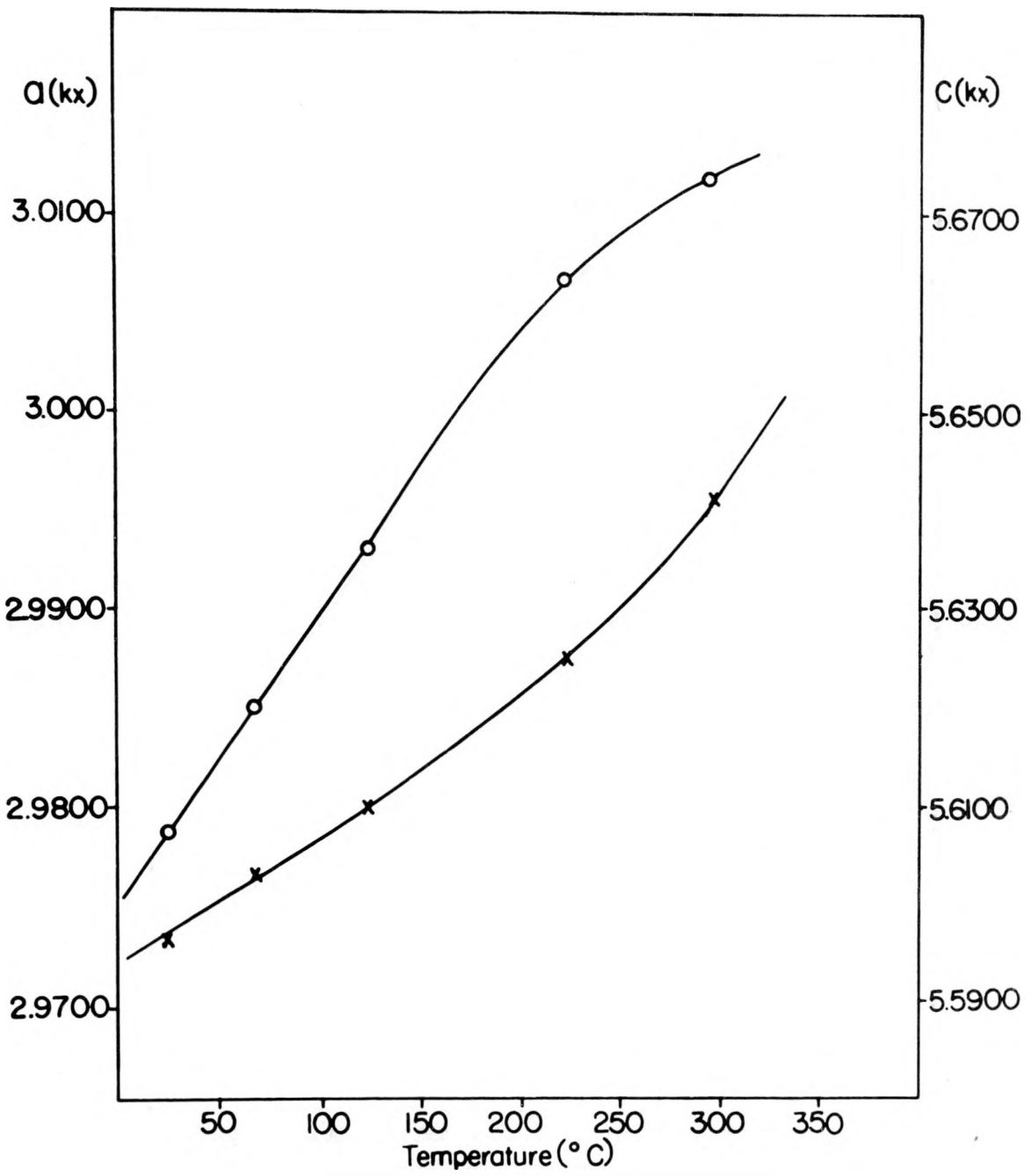


FIGURE 1. PLOT SHOWING VARIATION OF UNIT CELL DIMENSION WITH TEMPERATURE FOR PURE CADMIUM.

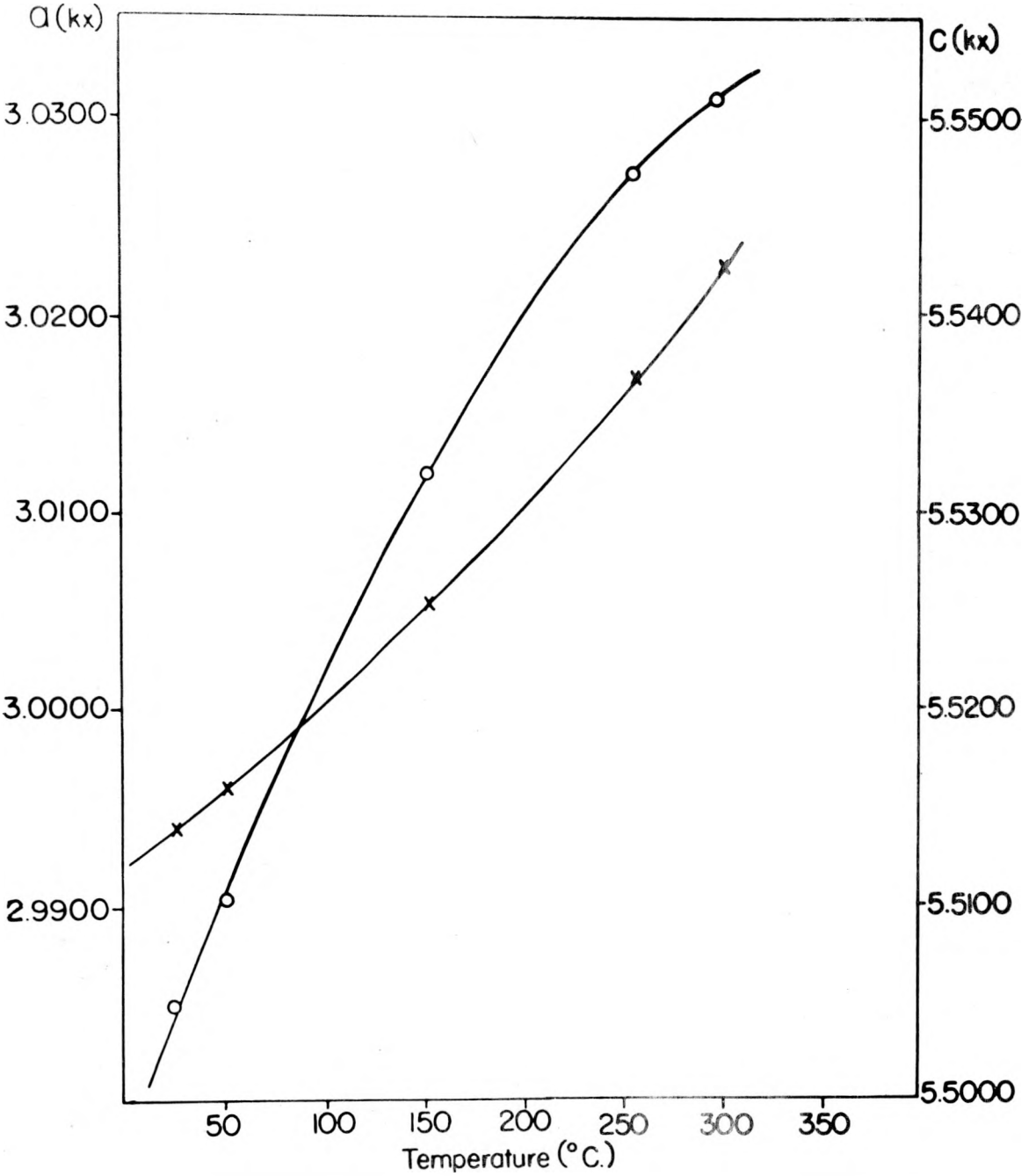


FIGURE 2. PLOT SHOWING VARIATION OF UNIT CELL DIMENSION WITH TEMPERATURE FOR 90.6 ATOMIC PERCENT CADMIUM.

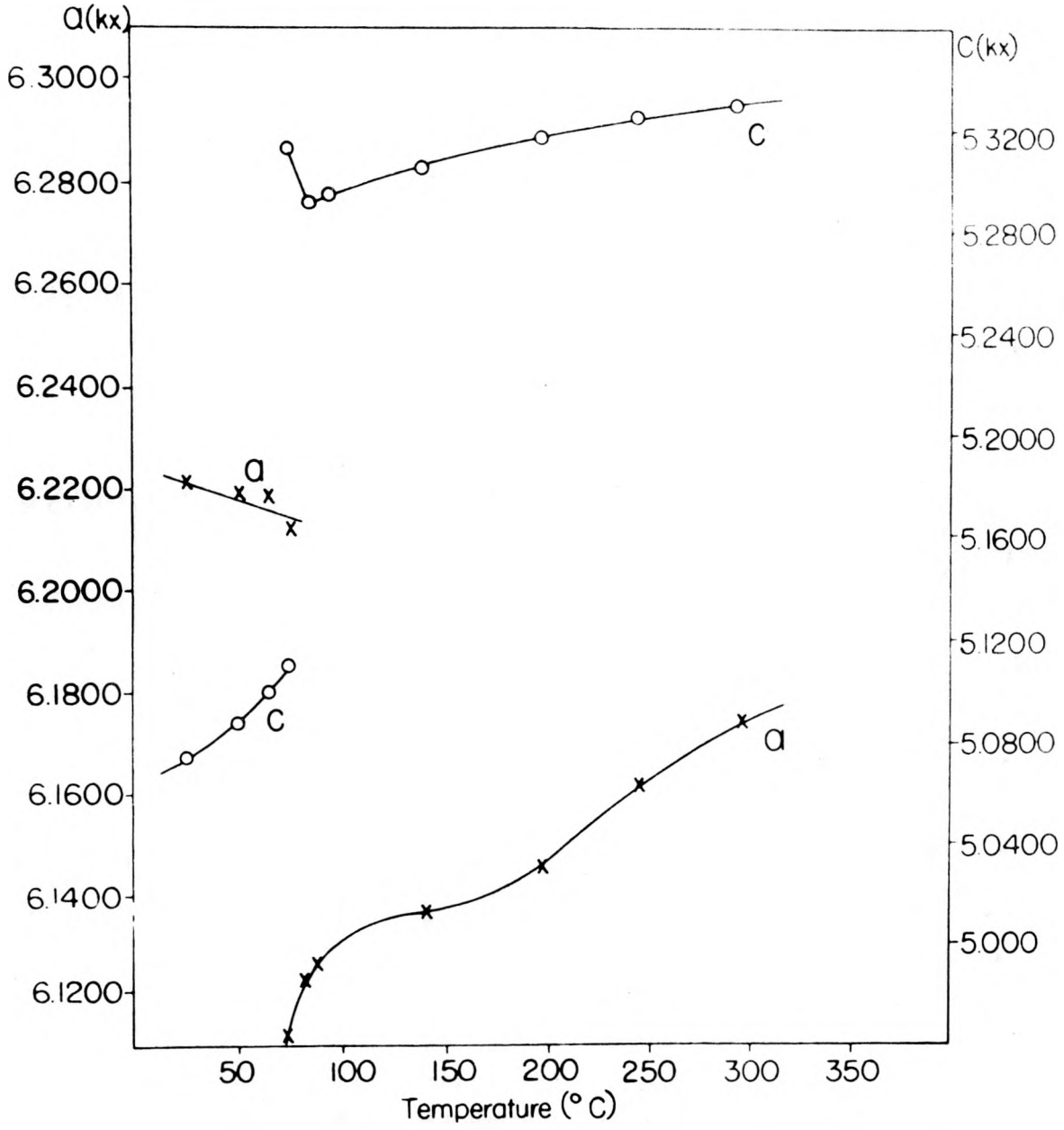


FIGURE 3. PLOT SHOWING VARIATION OF UNIT CELL DIMENSION WITH TEMPERATURE FOR 75.2 ATOMIC PERCENT CADMIUM.

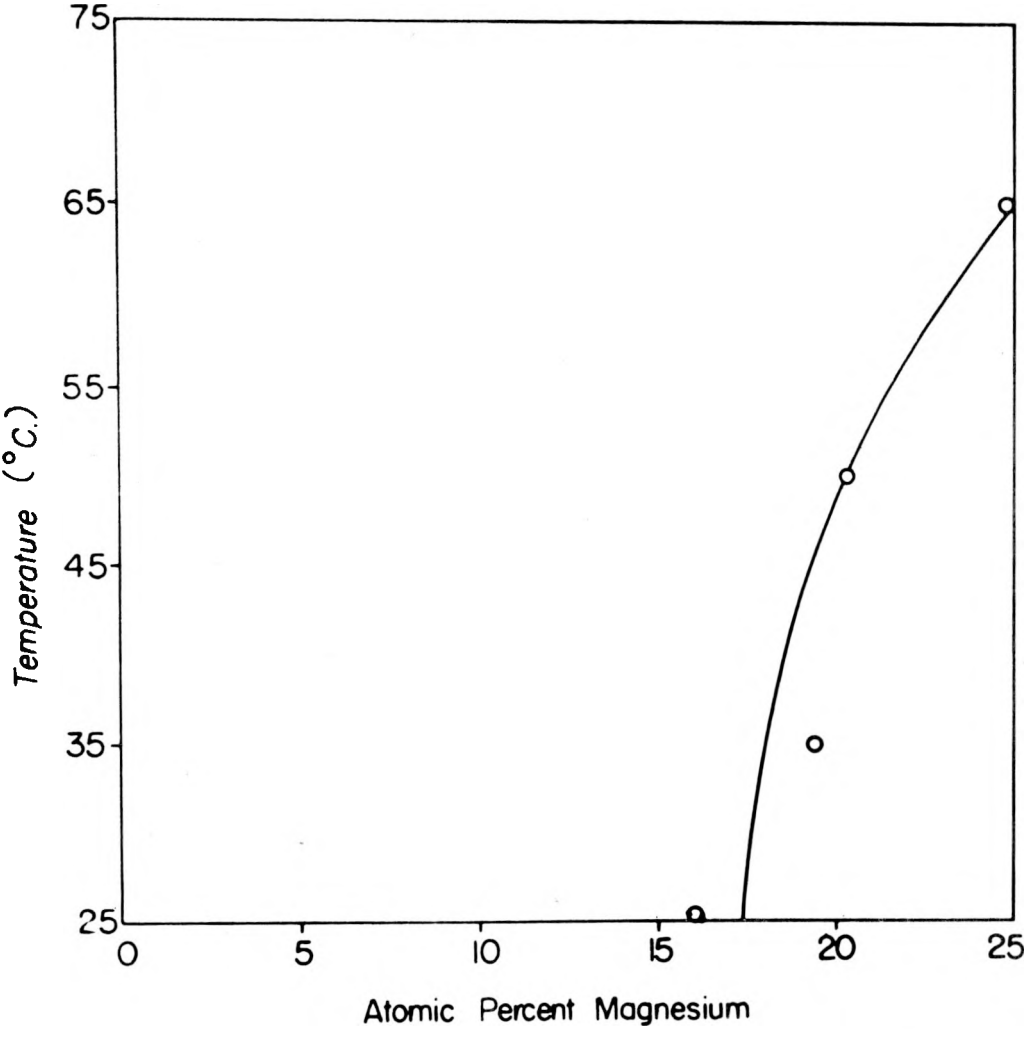


FIGURE 4. PLOT SHOWING PROVISIONAL VALUES FOR TERMINAL SOLID SOLUBILITIES OF MAGNESIUM IN CADMIUM AT VARIOUS TEMPERATURES.

END OF DOCUMENT