

the specific heats of the various liquids to better than 0.5%. The specific heats measured by previous investigators, although their mutual discordance makes a comparison difficult, are in fair agreement with those here reported.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

SOLID CADMIUM AMALGAMS. AN X-RAY PROOF OF THE COMPOUND Cd_3Hg

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The possible existence of a compound between cadmium and mercury has been a question of interest for many years. The evidence has been conflicting. If the thermodynamic activity of cadmium is defined as unity for the pure liquid, it is found for liquid cadmium amalgams that the ratio of activity to mole fraction for cadmium is less than unity over the whole concentration range. The same is true of mercury when the activity of pure liquid mercury is taken as unity. Hildebrand, Foster and Beebe¹ found that the vapor pressures of mercury over liquid cadmium amalgams at 323° were less than corresponded to the mole fraction; and Richards and Forbes,² who measured concentration cells of cadmium amalgams at room temperature, obtained electromotive force values too large. Both of these criteria indicate an affinity between the two components, which should be manifested in complex or compound formation.³

On the other hand, microscopic or thermal analyses of solid alloys of cadmium with mercury have hitherto not brought to light any compound. The constitution diagram, based largely on the work of Bijl and of Mehl and Barrett,⁴ shows three solid solutions but no compounds. The stability of any compound which may exist should certainly be greater in the solid than in the liquid state. As the evidence from electromotive force and vapor pressure data is quite trustworthy it was a matter of considerable interest to make an x-ray study of certain amalgam compositions which had not been thoroughly investigated.

R. F. Mehl⁵ made x-ray patterns of ten alloys of Cd-Hg and reported that those containing more than 60 weight per cent. (73 atomic per cent.)

¹ Hildebrand, Foster and Beebe, *THIS JOURNAL*, **42**, 545 (1920).

² Richards and Forbes, *Carnegie Instit. Pub. No. 56* (1906).

³ The causes of deviations from ideal solution behavior are given detailed treatment in J. H. Hildebrand, "Solubility," The Chemical Catalog Company, New York, 1924, and in recent journal articles by Professor Hildebrand.

⁴ Bijl, *Z. physik. Chem.*, **41**, 641 (1902). Mehl and Barrett, *A. I. M. M. E. Tech. Pub. No. 225* (1929).

⁵ Mehl, *THIS JOURNAL*, **50**, 381 (1928).

of cadmium showed an hexagonal close-packed lattice of axial ratio 1.89, while those containing 23 to 50 weight per cent. (64 atomic per cent.) of cadmium were face-centered tetragonal, with axial ratio 0.52. Since McKeehan and Coffi⁶ and a number of subsequent workers had shown that pure mercury possessed a rhombohedral lattice, $a = 3.00$, $\alpha = 70^\circ 32'$, R. F. Mehl and C. S. Barrett examined the structure of the solid solutions terminal to pure mercury and found that up to 3.5 atomic per cent. of cadmium, the rhombohedral structure persisted. Their work extended the range of face-centered tetragonal solid solutions down to 12 atomic per cent. of cadmium. The range from 3.5 to 12 was two-phase.

Experimental Part

In order to test the possibility of a new crystal phase in the immediate vicinity of a possible compound Cd_3Hg (75 atomic per cent. of cadmium) three alloys were prepared containing 70, 75 and 80.8 atomic per cent. of cadmium, respectively. These alloys were weighed from pure metals, sealed in Pyrex tubes which were then evacuated; they were melted and held as liquids at $285\text{--}295^\circ$ for four hours. They were then cooled quickly to avoid segregation, and the solids tempered at 145 to 149° for twenty-eight hours. The following day filings were made and these filings sealed up and evacuated as before, and tempered at $145\text{--}149^\circ$ for forty-four hours. This treatment avoids oxidation or volatilization and ensures the formation of the most stable crystal phase at the annealing temperature.⁷

Powder x-ray diagrams of these three alloys, each mixed with a small quantity of finely ground sodium chloride were made using a Siegbahn type metal x-ray tube⁸ with copper target, and a new type of camera developed by the writer.⁹ On account of the rather high absorption coefficient of mercury for CuK radiation about seven hours exposure was required. Mehl, using a larger camera with the more penetrating MoK radiation, required about twenty-four hours for his exposures. A film was also made on filings of pure cadmium mixed with sodium chloride.

The lines on the films forming the sodium chloride pattern were easily identified. Using the known lattice constant $a = 5.628 \text{ \AA}$. for sodium chloride, the true angles of reflection 2θ were calculated¹⁰ from the Bragg equation

$$N\lambda = 2d \sin \theta$$

and a plot was made for each film of observed 2θ versus correction (difference between true and observed 2θ). These calibration curves were then used in getting the correct 2θ values for all the lines due to the alloys

⁶ McKeehan and Coffi, *Phys. Rev.*, **19**, 444 (1922).

⁷ The alloys were kindly prepared by Dr. B. E. Lauer.

⁸ Siegbahn, "Spectroscopy of X-Rays," Oxford University Press, 1925.

⁹ Taylor, *Rev. Sci. Instruments*, **2**, 751 (1931).

¹⁰ For a cubic lattice $\sin^2 \theta = (\lambda^2/4a^2)(h^2 + k^2 + l^2)$.

These angles are recorded in subsequent tables together with appropriate calculations. The letters v.w., m, st, signify very weak, medium, strong.

TABLE I
DATA ON PURE CADMIUM (HEXAGONAL)

2θ corrected	$\sin^2\theta$	$\sin^2\theta$ (calcd.)	Index hkl	Intensity
34.50	0.0879	0.0895	100, 010	v.w.
38.50	.1087	.1083	$\bar{1}11, 101$	m
47.85	.1644	.1647	012	w
60.90	.2568	.2588	103	w
62.30	.2676	.2685	110	w
68.70	.3184	.3177	$\beta 104$	v.w.
71.85	.3438	.3437	112	m
73.10	.3547	.3580	200	w
77.50	.3918	.3905	104	w
81.95	.4300	.4290	$\beta 203$	v.w.
90.60	.5052	.5097	$\beta 210$	w
92.95	.5257	.5273	203	m
98.15	.5709	.5697	105	m
104.40	.6243	.6265	210	w
106.70	.6437	.6453	211	m
108.05	.6549	.6590	204	w
113.35	.6982	.7017	212	m

Values of $\sin^2\theta$ (calcd.) for the CuK_α lines are obtained from the quadratic equation for an hexagonal lattice

$$\begin{aligned}\sin^2\theta &= 0.0895(h^2 + hk + k^2) + 0.0188l^2 \\ &= \frac{\lambda^2}{3a^2}(h^2 + hk + k^2) + \frac{\lambda^2}{4c^2}l^2\end{aligned}$$

using $\lambda = 1.539 \text{ \AA.}$, $a = 2.97 \text{ \AA.}$, $c = 5.61 \text{ \AA.}$, $c/a = 1.89$. The good agreement (average deviation = 0.3%) of calculated and observed values of $\sin^2\theta$ shows that these lattice constants a and c are correct within 0.2%.

Since the wave lengths of CuK_α and CuK_β lines are 1.539 and 1.388 \AA. , the ratio of $\sin^2\theta$ for these two lines reflected from a given plane is $(1.539)^2/(1.388)^2 = 1.229$. The CuK_β lines may be readily identified by use of this constant. Thus for the 104 plane, $0.3905/1.229 = 0.3177$. Observed $\sin^2\theta = 0.3184$.

The values of $\sin^2\theta$ (calcd.) for the CuK_α lines were obtained from the relation

$$\sin^2\theta = 0.0893(h^2 + hk + k^2) + 0.01846(1^2)$$

Setting $\lambda^2/3a^2 = 0.0893$ and $\lambda^2/4c^2 = 0.01846$ gives $a = 2.963 \pm 0.005 \text{ \AA.}$, $c = 5.645 \pm 0.008 \text{ \AA.}$, $c/a = 1.91$.

It may be seen that the 80.8 atomic per cent. cadmium amalgam has the same hexagonal close-packed structure as pure cadmium, with a slightly greater axial ratio. For the solid solution $c/a = 1.91$, for pure cadmium $c/a = 1.89$. This conclusion checks the results of Mehl, and also of C. v.

Simson,¹¹ who found the hexagonal structure in an amalgam containing 82 atomic per cent. cadmium.

TABLE II
AMALGAM CONTAINING 80.8% CADMIUM (HEXAGONAL)

2θ corrected	$\text{Sin}^2\theta$	$\text{Sin}^2\theta$ (calcd.)	Index hkl	Intensity
34.40	0.0874	0.0893	100, 010	w
38.40	.1082	.1079	$\bar{1}11, 101$	m
47.60	.1629	.1631	012	m
54.00	.2061	.2072	$\beta 103$	w
60.55	.2542	.2551	103	w
62.40	.2684	.2685	110	w
63.45	.2765	.2780	$\beta 112$	w
65.10	.2895	.2905	$\beta 200$	v.w.
71.60	.3422	.3421	112	m
73.35	.3567	.3580	200	w
81.50	.4261	.4255	$\beta 203$	v.w.
82.30	.4330	.4316	202	w
90.60	.5052	.5098	$\beta 210$	v.w.
95.50	.5479	.5495	105	w
97.20	.5627	.5629	114	m
104.85	.6281	.6266	210	w
107.10	.6470	.6449	211	m
113.40	.6986	.7001	212	m
120.0	.7500	.7519	106	m

The Tetragonal Solid Solution.—An excellent pattern of the face centered tetragonal solid solution is given by C. v. Simson for an amalgam containing 50 atomic per cent. cadmium. She tabulates values of the line position 1 on the film for a camera of radius 2.47 cm. From this one may calculate θ in the Bragg equation $n\lambda = 2d \sin \theta$. Using $\lambda = 1.539 \text{ \AA}$. for

TABLE III
FIFTY ATOMIC PER CENT. CD (F.-C. TETRAGONAL)

i (Simson)	θ	$\text{Sin}^2\theta$	$\text{Sin}^2\theta$ (calcd.)	Index hkl	Intensity
2.78	$16^\circ 06'$	0.0769	0.0767	200	v.st.
3.34	$19^\circ 22'$.1100	.1095	111	m
3.98	$23^\circ 05'$.1536	.1534	220	st
4.76	$27^\circ 37'$.2147	.2139	$\beta 131$	w
5.32	$30^\circ 50'$.2626	.2629	131	v.st.
5.67	$32^\circ 50'$.2940	.2941	$\beta 202$	w
5.79	$33^\circ 34'$.3058	.3067	400	st
6.37	$36^\circ 58'$.3617	.3615	202	m
6.60	$38^\circ 16'$.3838	.3834	240	st
6.92	$40^\circ 06'$.4150	.4163	331	st
7.15	$41^\circ 29'$.4390	.4382	222	m.st.
8.43	$48^\circ 52'$.5673	.5696	151	st
8.65	$50^\circ 08'$.5891	.5915	402	m.st.
9.57	$55^\circ 28'$.6786	.6791	113	m

¹¹ Simson, *Z. physik. Chem.*, **109**, 197 (1924).

CuK α , I have computed the corresponding values of $\sin^2 \theta$ and listed them together with the indices hkl . Table III contains this material.

Values of $\sin^2 \theta$ (calcd.) are obtained from the quadratic equation for a tetragonal lattice

$$\sin^2 \theta (\text{calcd.}) = 0.01917(h^2 + k^2) + 0.07124 l^2$$

Setting $\lambda^2/4a^2 = 0.01917$ and $\lambda^2/4c^2 = 0.07124$ give

$$a = 5.558 \pm 0.006 \text{ \AA.}, c = 2.883 \pm 0.003 \text{ \AA.}, c/a = 0.519$$

The agreement between observed and calculated values of $\sin^2 \theta$ is satisfactory so that one may have confidence in the lattice constants a and c . Mehl's lattice constants for the tetragonal solid solution are $a = 5.570 \text{ \AA.}$, $c = 2.896 \text{ \AA.}$, $c/a = 0.520$. These values are based on averages of a number of patterns representing alloys of different composition.

Amalgams Containing 70 and 75% Cadmium. New Structure.—Table IV presents $\sin^2 \theta$ values from films No. 93 and No. 92, which were made from the 70 and 75% amalgams, respectively. The fifth column gives the average or in some cases the best value, giving consideration to the intensities of the lines. The last two columns give calculated values of $\sin^2 \theta$ and the corresponding indices of the reflecting planes.

TABLE IV

SEVENTY AND SEVENTY-FIVE ATOMIC PER CENT. CADMIUM						
Film 93, 70% Cd Intensity	$\sin^2 \theta$	Film 92, 75% Cd $\sin^2 \theta$	Intensity	$\sin^2 \theta$ Average	$\sin^2 \theta$ (calcd.)	Index hkl
v.w.	0.0051			0.0051	0.0063	101
w	.0109	0.0109	w	.0109	.0087	200
w	.0182			.0182	.0173	220
		.0322	v.w.	.0322	.0335	222
		.0364	v.w.	.0364	.0347	400
v.w.	.0420			.0420	.0433	420
w.	.0606			.0606	.0595	422
v.w.	.0640			.0640	.0648	004
w	.0688	.0686	m	.0687	.0694	440
		.0826	v.w.	.0826	.0821	224
		.0889	m	.0889	.0867	260
w	.0978	.0992	m	.0985	.0995	404
w	.1101	.1082	m	.1091	.1081	424
w	.1262	.1265	m	.1264	.1289	462
w	.1376	.1382	m	.1379	.1387	800
		.1651	w	.1651	.1636	822
		.1770	w	.1770	.1766	752
		.1894	v.w.	.1894	.1896	842
w	.2047	.2042	m	.2045	.2035	804
v.w.	.2321	.2325	w	.2323	.2330	1002
w	.2388	.2395	w	.2392	.2382	844
		.2463	v.w.	.2463	.2460	952
v.w.	.2492			.2492	.2492	871
		.2550	v.w.	.2550	.2585	646
v.w.	.2607			.2607	.2592	008

TABLE IV (Concluded)

Film 93, 70% Cd Intensity	$\sin^2 \theta$	Film 92, 75% Cd $\sin^2 \theta$	Intensity	$\sin^2 \theta$ Average	$\sin^2 \theta$ (calcd.)	Index <i>hkl</i>
w	.2674	.2672	w	.2673	.2676	1042
		.2744	v.w.	.2744	.2765	228
w	.2808	.2828	v.w.	.2818	.2816	864
v.w.	.2950	.2956	v.w.	.2953	.2948	1060
		.3095	v.w.	.3095	.3121	1200
		.3200	v.w.	.3200	.3192	846
		.3286	v.w.	.3286	.3286	448
m	.3434	.3424	m	.3429	.3422	884
		.3467	v.w.	.3467	.3468	1240
v.w.	.3530			.3530	.3554	1080
w	.3601	.3626	v.w.	.3614	.3630	1242
					.3628	866, 1006
		.3841	v.w.	.3841	.3856	1224
v.w.	.3918	.3928	v.w.	.3923	.3914	857
v.w.	.4093	.4076	m	.4076	.4064	1262
					.4066	828
w	.4144	.4140	m	.4142	.4137	2010
					.4131	668
v.w.	.4239	.4235	v.w.	.4237	.4232	886
v.w.	.4356	.4352	w	.4354	.4335	1420, 10 100
w	.4625	.4616	w	.4621	.4614	5110
					.4608	1107
		.4660	v.w.	.4660	.4666	1226
		.4778	m	.4778	.4760	868, 1008
		.4978	w	.4978	.4983	10104, 1424
w	.5017			.5017	.5013	1086
		.5118	w	.5118	.5106	1048
		.5231	w	.5231	.5243	1444
w	.5627	.5635	w	.5631	.5636	1620
					.5611	6610
w	.5791	.5804	m	.5800	.5800	1228
					.5798	1622
					.5832	0012
		.6176	m	.6176	.6179	4012
					.6147	1088
		.6504	m	.6504	.6494	1268
					.6526	4412

The agreement between observed and calculated value of $\sin^2 \theta$ is satisfactory. For the CuK_α lines, $\sin^2 \theta$ (calcd.) = $0.002168(h^2 + k^2) + 0.00405l^2$. The lattice is body-centered tetragonal with the constants $a = 16.53 \text{ \AA.} \pm 0.3\%$, $c = 12.09 \pm 0.3\% \text{ \AA.}$, axial ratio $c/a = 0.732$. Attempts were made to derive a structure with smaller lattice constants but without success. The high order of the reflections may possibly be a factor in giving lines of low intensity.

The patterns of films 92 and 93 are practically identical. The lines on No. 92 (75% Cd) are more intense because of the lower mercury content,

mercury being a very good absorber for CuK radiation. This accounts also for certain very weak lines on film No. 92 not appearing on No. 93 or being too faint to measure accurately. A few lines possibly belong to the hexagonal or tetragonal solid solution lattices (*cf.* Tables II and III) but this is not necessarily the case. They may be merely coincidences. If the period of tempering was not quite long enough, traces of the hexagonal or of the other tetragonal solid phase might persist. However, the great abundance of lines which are not to be ascribed to these structures show that a new crystal phase is present. The range of stability of this structure includes 70 and 75 atomic per cent. cadmium and may be a slightly wider range but does not reach 80.8% (at 147°), for the alloy of this composition annealed at the same temperature (145–149°) as the 70 and 75% alloys shows only an hexagonal pattern. Mehl examined an alloy of 60.1 weight per cent. cadmium (73 atomic per cent. Cd) which had been tempered for 120 hours at 170°. His pattern shows lines of the hexagonal lattice only. The discrepancy between his results and mine may lie in the tempering conditions. Annealing the alloy at the lower temperature would favor compound formation. It is noteworthy that whereas according to Bijl's¹² melting point diagram, a 73 atomic per cent. of cadmium alloy should be inhomogeneous, Mehl found only the pattern*of the hexagonal (α) solid solution and no tetragonal (ω). The Bijl diagram is in need of revision in this composition region, especially with regard to solid-solid equilibria.

There are other cases known where certain solid phases do not appear if the annealing temperature is too high. Thus alloys of copper with gold show two compounds, AuCu and AuCu₃ if annealed below about 400°, but these phases disappear in fifteen minutes if annealed at 400–420° and quenched in water.¹³ A comparison of the lattice constants of the new structure with those of the body-centered tetragonal solid solution (50 atomic per cent. cadmium) is instructive. For the 50% Cd alloy

$$\begin{aligned} a_1 &= 3.932 \text{ \AA.}, \text{ Mehl; } a_1 = 3.930, \text{ Simson} \\ c_1 &= 2.896 \text{ \AA.}, \text{ Mehl; } c_1 = 2.883, \text{ Simson} \\ c_1/a_1 &= 0.74 \end{aligned}$$

These values are computed from the constants of the face-centered lattice by dividing the length of the a axis by $\sqrt{2}$. For the 70 and 75% Cd alloys

$$\begin{aligned} a_2 &= 16.53 \text{ \AA.} \\ c_2 &= 12.09 \text{ \AA.} \\ c_2/a_2 &= 0.73 \end{aligned}$$

$$\text{Thus, } a_2/a_1 = 2.97 \sqrt{2} \text{ and } c_2/c_1 = 2.96 \sqrt{2}$$

Each side of the new unit cell is roughly $3 \sqrt{2}$ times that of the smaller unit. The volume of the new cell is $54 \sqrt{2}$ larger than that of the smaller

¹² Bijl, Ref. 4.

¹³ G. Borelius, C. H. Johanssen and J. O. Linde, *Ann. Physik*, **86**, 291 (1928).

cell. Since the latter contains 2 atoms, the new cell must contain 152 atoms. The observed density for the 75% Cd alloy is 10.12 g. per cc. Taking a mean atomic weight of 134.5, the number of atoms per unit cell is computed to be $150.4 \pm 1\%$. Such a cell containing 152 atoms would have 38 Cd₃Hg in the case of the 75% Cd alloy. The complexity of the atomic arrangement in the cell is probably the reason why long annealing at not too high a temperature is necessary to bring about proper orientation and distribution of the atoms.

Alloy systems furnish other examples of large cells. Thus the γ -structure in Cu-Sn alloys has a lattice constant $a = 17.91 \text{ \AA}$. and contains 416 atoms per unit cell.¹⁴ It is possible that the large complex cell found in the Cd-Hg series is an example of a "superstructure" described by Westgren.

Summary

x-Ray examination of solid cadmium amalgams, which had been annealed *in vacuo* at 147° for seventy-two hours, has demonstrated the existence of a new crystal phase, body-centered tetragonal, with lattice constants $a = 16.53 \text{ \AA}$., $c = 12.09 \text{ \AA}$., axial ratio $c/a = 0.73$. The lattice constants are probably correct to 0.3%. The structure evidently contains 152 atoms or 38 molecules of Cd₃Hg. Its composition range includes 70 and 75 atomic per cent. cadmium, and may be slightly wider. It may be regarded as Cd₃Hg or as a solid solution of Hg in Cd₃Hg. The structure is apparently derived from the ω type of solid solutions which characterize alloys poorer in cadmium (down to 12 atomic per cent.).

Confirmation of the hexagonal close-packed structures of pure cadmium and of an 80.8 atomic per cent. of cadmium amalgam has also been obtained.

The bearing of these results on the thermodynamic behavior of cadmium amalgams has been noted.

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¹⁴ A. Westgren and G. Phragmen, *Z. Metallkunde*, **18**, 279 (1926).