On crystal structure of Cd–Zr intermetallic compounds.

By Arunsingh* and B. Dayal, *Department of Physics, B.H.U., Varanasi-5, India*

Three compounds of the Cd–Zr system were prepared and their crystal structures are reported. A possible reason for the tetragonal to cubic transformation of one of the phases is also given.

The present alloys from metals of widely differing melting points were prepared by compacting, in a narrow capillary tube, appropriate weights of powdered Cd and Zr metals of 99·9% purity and a 10 amp current at 2 volts was passed through the mixture for about 2 hr. It resulted in the formation of the alloy as a very fine powder.

In all, three intermetallic compounds, *viz.* Cd_3Zr, Cd_2Zr and Cd_2Zr_3, were detected and they were studied by the standard powder technique with filtered Cu $K\alpha$ radiation. The powder photographs were interpreted by the normal procedure and intensity calculations were made. The lattice parameter, density and number of molecules per unit cell are summarized in Table 1.

(i) Cd_3Zr

Out of various possibilities for the Zr and Cd atomic positions for this phase, the one for which the intensities would agree well with the observed intensities is the arrangement in which Zr atoms occupy the corners and Cd atoms are located at the faces. Based on this arrangement we have calculated the intensities which are given in Table 2. The agreement is reasonably good.

The above compound is isostructural with $CuTi_3$ and since the special condition $h+k=2n$ is satisfied, it is proposed to assign space group $P4/mmm$ to this phase.

(ii) Cd_2Zr

In this case also, various possibilities for atomic positions were tried. Table 3 compares the calculated and observed intensities for this structure. As is evident, the agreement is good. In the proposed structure Zr atoms occupy the cube corners and Cd atoms are at four of the faces, *i.e.* $\frac{1}{2}0\frac{1}{2}$ and $0\frac{1}{2}\frac{1}{2}$ or equivalent positions.

The probable space groups are $Pa3$ or $Pn3$ as they satisfy the special condition $h+k$, $k+l$, $l+h=2n$.

(iii) Cd_2Zr_3

Many structures were tried for this intermetallic compound, but only the following arrangement of atoms gave consistent results. Here it is presumed that Zr atoms

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* On leave from Government College, Shahdol (M.P.) India.

Table 2. *Observed and calculated 'd' spacings and intensities for* Cd_3Zr

Line number	Observed 'd'	Calculated 'd'	hkl	I_{calc} ($\times 10^5$)	I_{obs}
1	2·491	2·527	111	30·0	VS
2	2·191	2·208	200	10·3	S
3	2·139	2·154	002	4·8	m
4	1·555	1·561	220	3·37	m
5	1·534	1·542	202	6·4	S
6	1·322	1·328	131	7·5	VS
7	1·299	1·304	113	3·5	S
8	1·258	1·264	222	3·01	S
9	1·101	1·104	400	1·1	W
10	1·074	1·076	004	0·52	W
11	1·010	1·012	331	1·89	m
12	0·9982	1·001	313	3·75	S
13	0·9868	0·9875	420	1·87	m
14	0·9795	0·9822	402	1·87	m
15	0·9692	0·9679	204	1·87	m
16	0·8978	0·8974	422	3·96	S
17	0·8878	0·8863	224	2·0	m
18	0·8484	0·8492	151	4·62	S
19	0·8421	0·8426	333	2·4	m
20	0·8285	0·8305	115	2·19	m
21	0·7810	0·7805	440	4·96	S

Table 3. *Observed and calculated 'd' spacings and intensities for* Cd_2Zr

Line number	d_{obs}	d_{calc}	hkl	I_{calc} ($\times 10^5$)	I_{obs}
1	2·566	2·572	111	17	VS
2	2·178	2·189	200	8·3	S
3	1·546	1·547	220	5·4	S
4	1·318	1·319	113	10·3	VS
5	1·265	1·264	222	1·74	W
6	1·094	1·094	400	0·88	VW
7	1·007	1·004	331	3·07	S
8	0·9802	0·9787	420	3·06	S
9	0·8937	0·8935	422	3·25	VS
10	0·8418	0·8424	333	3·93	VS
			115		

occupy cube corners and are also situated halfway along the *a* and *c* axes. The Cd atoms are located at the centre of the '*a c*' face and at the body centre. The atomic coor-

Table 1. *Crystal data*

Compound	Lattice type	a	b	c	Density	Number of mols. per unit cell
Cd_3Zr	Tetragonal	4·4151	—	4·307	6·85	0·80
Cd_2Zr	Cubic	4·3768	—	—	6·55	1·03
Cd_2Zr_3	Orthorhombic	7·86	6·52	5·30	3·69	1·2

Table 4. *Observed and calculated 'd' spacings and intensities for* Cd_2Zr_3

Line number	d_{obs}	d_{calc}	hkl	I_{calc} $(\times 10^5)$	I_{obs}
1	2·784	2·777	021	2·06	W
2	2·548	2·509	220	24·7	VS
3	2·447	2·455	012	5·8	mS
			310	---*	
4	2·337	2·375	301	0·12	W
5	2·214	2·197	202	14·5	S
6	2·162	2·174	030	2·0	a
7	1·888	1·902	410	2·6	mS
		1·902	230	2·6	
8	1·615	1·617	322	0·75	m
		1·617	421	0·75	
		1·614	203	0·37	
9	1·572	1·571	500	0·17	m
		1·578	402	4·7	
10	1·549	1·553	023	0·32	m
		1·545	232	2·6	
11	1·462	1·449	241	0·52	m
		1·457	430	1·1	
		1·464	303	0·26	
12	1·366	1·368	521	0·42	W
		1·371	033	---*	
13	1·341	1·336	323	0·38 (?)	S
		1·339	341	0·38	
14	1·320	1·313	403	0·15	m
		1·313	004	1·24	
15	1·284	1·280	610	0·68	W
		1·287	413	0·16	
16	1·041	1·037	115	0·09	W
		1·041	424	2·6 (?)	
		1·041	153	0·09	
		1·040	334	0·09	
		1·039	721	0·20	
		1·041	542	0·20	
17	1·022	1·021	712	---*	W
		1·023	205	0·10	
		1·023	443	0·20	
18	1·010	1·014	253	0·08	W
		1·010	215	0·08	
19	0·9947	0·9974	730	0·04	W
		0·9950	244	2·5 (?)	
20	0·9802	0·9806	731	0·08	VW
		0·9806	434	0·75	
21	0·9668	0·9658	801	0·09	W
		0·9672	524	0·18	
22	0·9076	0·9067	170	0·04	m
		0·9105	741	0·78	
23	0·8814	0·8824	831	0·09	m
		0·8833	006	0·70	
24	0·8580	0·8584	803	0·11	m
		0·8565	704	0·11	
		0·8606	544	0·22	
		0·8553	636	0·86	

* Calculated value negligibly small.

dinates will be as below:

Zr	000	$\frac{1}{2}$00	00$\frac{1}{2}$
Cd	$\frac{1}{2}$0$\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	

In Table 4 are listed the calculated intensities and observed intensities. The agreement between these data is good enough to justify the proposed structure. Other possible arrangements of atoms lead to calculated intensities which are in variance with the observed values and, therefore, the proposed structure seems to represent the correct arrangement of atoms.

Very sharp lines were obtained in the cases of Cd_3Zr and Cd_2Zr but the pattern from Cd_2Zr_3 was comparatively diffuse.

Discussion

The structures clearly suggest that it is the Cd atom which diffuses in the Zr matrix because in all three structures we find Zr atoms occupying the corners. As a result of the interdiffusion of Cd atoms the shape and size of the matrix have changed in accordance with the local changes in the energy of the lattice.

We have seen for the tetragonal phase that $c/a = 0.97$, which almost corresponds to a strained cube. From density measurements the number of atoms per unit cell is found to be ~ 0.80. This suggests that the structures contain voids and that the presence of relatively heavy Cd atoms on the '$a\,b$' face strains the cube; hence the c axis is compressed and the a axis elongated. We find confirmation of this model in the cubic phase (which is obtained by reducing the Cd content) where removal of the Cd atom from the $a\,b$ face causes the tetragonal phase to revert to the cubic phase.

It was observed that on holding the tetragonal phase at a higher temperature ($>250\,^{\circ}$C) the Cd atom is released by this phase which then transforms itself into the cubic phase (Pietrokowsky, 1954). This further confirms the above contention.

We may mention here that Cd_2Zr is a valency compound and hence the more stable.

Lastly, Cd_2Zr_3 seems to possess a defect structure; hence we may suggest that a few Cd or Zr atoms may be randomly distributed in some cells to give approximately 1·2 atoms per unit cell.

Reference

PIETROKOWASKY, P. (1954). *Trans. A.I.M.E.* **200**, 219.