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The Crystal Structure of $BaCd_{11}$

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The crystal structure of $BaCd_{11}$ (and isotypic $SrCd_{11}$, $CeZn_{11}$, $LaZn_{11}$, $PrZn_{11}$) was determined from Weissenberg diagrams. The unit cell is body-centered tetragonal, $a = 12{\cdot}02$, $c = 7{\cdot}74$ Å for $BaCd_{11}$, $Z = 4$, and the space group is $I4/amd$. The positions of the atoms were determined from electron-density projections on the (001) and (010) planes. The barium atom is surrounded by 22 cadmium neighbors; the cadmium atoms have 12–14 nearest neighbors.

Introduction

Crystal structure investigations of intermetallic compounds have revealed the existence of a series of compounds of the same structure and composition as that noted for $NaZn_{13}$ (Zintl & Haucke, 1937*a*, *b*; Ketelaar, 1937; Baenziger & Rundle, 1949). The physical properties and structural arrangement of the elements which yield this series of isostructural compounds suggest that the systems of Ba–Cd, Sr–Cd, Ce–Zn and others might possibly exhibit this phase. Examination of the region corresponding to the 1:13 phase of these systems has revealed that the compounds of AB_{11} composition occur instead.

Experimental procedures

The alloys were prepared by placing the metals in a molar ratio of 1:13 in a vycor tube and heating to 750–800° C. in an electric furnace. All preparations were carried out in a nitrogen or argon atmosphere to prevent excessive oxidation. A single crystal of the $BaCd_{11}$ compound was obtained by stirring the molten mixture until the melt had solidified.

X-ray diffraction patterns of powder specimens of the samples were taken using Cu $K\alpha$ radiation and a Debye–Scherrer camera of diameter 114·6 mm. The single crystal of the $BaCd_{11}$ compound was sufficiently well defined to allow optical alignment about the natural axes for rotation and equi-inclination Weissenberg diagrams. The zero-, first-, second-, third- and fourth-layer diagrams about [001], and the zero- and first-layer diagrams about [100] were taken using copper radiation. These diagrams were used to facilitate indexing the diagrams obtained from molybdenum radiation, which was used to record intensity data. The use of the unfiltered molybdenum radiation was designed to reduce serious absorption effects which were noted on the films exposed to copper radiation. The intensities of 103 reflection from the zero- and first-layer diagrams about [001] and the zero layer about [100] were estimated from multiple films by visual comparison with a scale of known intensity values.

X-ray data

The powder diffraction patterns of the compounds $BaCd_{11}$, $SrCd_{11}$, $CeZn_{11}$, $LaZn_{11}$ and $PrZn_{11}$ exhibit a marked similarity with regard to the position and the relative intensities of the lines, indicating that the compounds are isostructural. The lines on the films were indexed with the aid of the approximate cell dimensions determined from the single-crystal diagrams. The dimensions of the body-centered tetragonal unit cell are:

	a (Å)	c (Å)	Vol. (Å^3)	ϱ_x (g.cm.$^{-3}$)	ϱ_m (g.cm.$^{-3}$)
$BaCd_{11}$	12·02	7·74	1118	8·15	8·2
$SrCd_{11}$	12·02	7·69	1111	7·91	—
$LaZn_{11}$	10·68	6·87	784	7·27	—
$CeZn_{11}$	10·66	6·86	780	7·32	—
$PrZn_{11}$	10·65	6·85	777	7·35	—

The densities were calculated on the basis of four formula weights per unit cell.

Only the following characteristic reflections appear in the single-crystal diagrams of $BaCd_{11}$: (hkl) with $h+k+l = 2n$, $(hk0)$ with $h = 2n$, $k = 2n$, (hhl) with $2h+l = 4n$, $l = 2n$, $(0kl)$ with $k+l = 2n$. These absences are characteristic for space groups $I4/amd$ and $I4_1/a$ (diffraction symmetry $4/mmm$). In single-crystal pictures taken with copper radiation, mirror planes parallel to [001] seemed to be absent at low angles, but present at high Bragg angles, indicating that the apparent diffraction symmetry $4/m$ was due to irregular absorption in the imperfectly shaped crystal. In diagrams taken with molybdenum radiation, the relative spot intensities had changed so that true mirror planes now seemed to be present. It was assumed, therefore, that if absorption did not take place, the diffraction symmetry would be $4/mmm$. The subsequent structure determination was carried out on this assumption, using the space group $I4/amd$ as representative of the symmetry of the structure.

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Structure determination

As the first step in the structure determination, the Patterson projection on (001) was evaluated. Since a rather small number of peaks were observed for the structure (assumed to be $BaCd_{9-11}$), and since the space-group positions require a Ba atom at the origin of the unit cell, it was assumed that most of the peaks must correspond to the actual positions of atoms in the unit cell with a large amount of superposition of interatomic vectors. On this basis 4 Ba and 36 Cd atoms were placed in essentially their final positions, and an electron-density projection on (001) was evaluated, using phases calculated on the basis of this arrangement. The electron-density map showed that eight additional Cd atoms were present in positions (*d*) below, making the formula $BaCd_{11}$. The addition of the extra eight Cd atoms vastly improved the intensity agreement, and the formula $BaCd_{11}$ was later verified by density measurements. The electron-density projection (Fig. 1) was re-evaluated by including all the (*hk*0) intensity data to obtain better values of the parameters.

The *z* parameter of 0·304 for the cadmium atoms in the positions (*i*) was determined from an electron-density projection on (010) (Fig. 2). This structure was further refined by trial calculations of the structure factor for various combinations of parameters varying by 0·001 parameter units from each other. The variation in parameters used in this procedure were: x 0·119 to 0·125, y 0·200 to 0·208, z 0·302 to 0·308. The set of parameters which gave the best agreement between observed and calculated structure amplitudes is listed below. The change in the x and y parameters from the values obtained from the electron-density plots was in the same direction and of about the same magnitude as that indicated by the finite-series correction.

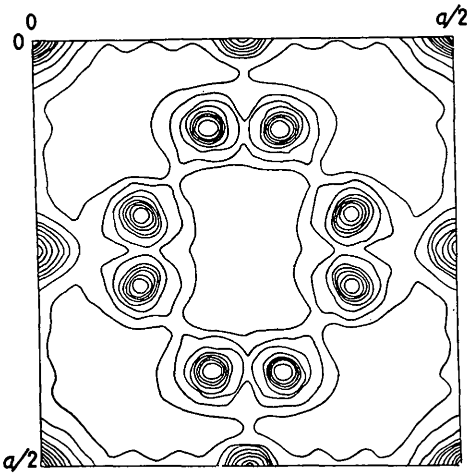

Fig. 1. Electron density of $BaCd_{11}$ projected on (001).

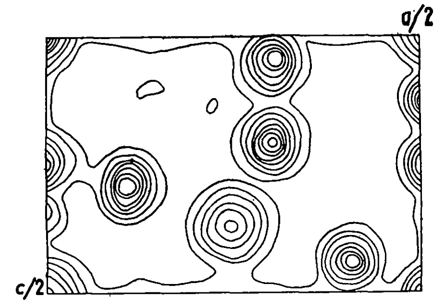

Fig. 2. Electron density of $BaCd_{11}$ projected on (010).

The atomic positions are:

$$(0, 0, 0),\ (\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) +$$

4 Ba in (*a*): $(0, 0, 0),\ (0, \tfrac{1}{2}, \tfrac{1}{4}),$

4 Cd in (*b*): $(0, 0, \tfrac{1}{2}),\ (0, \tfrac{1}{2}, \tfrac{3}{4}),$

8 Cd in (*d*): $(0, \tfrac{1}{4}, \tfrac{5}{8}),\ (0, \tfrac{3}{4}, \tfrac{5}{8}),\ (\tfrac{1}{4}, 0, \tfrac{3}{8}),\ (\tfrac{3}{4}, 0, \tfrac{3}{8}),$

32 Cd in (*i*):

$$\begin{aligned}&(x, y, z),\ (\bar{x}, \bar{y}, z),\ (x, \tfrac{1}{2}+y, \tfrac{1}{4}-z),\ (\bar{x}, \tfrac{1}{2}-y, \tfrac{1}{4}-z),\\&(\bar{x}, y, z),\ (x, \bar{y}, z),\ (\bar{x}, \tfrac{1}{2}+y, \tfrac{1}{4}-z),\ (x, \tfrac{1}{2}-y, \tfrac{1}{4}-z),\\&(y, x, \bar{z}),\ (\bar{y}, \bar{x}, \bar{z}),\ (y, \tfrac{1}{2}+x, \tfrac{1}{4}+z),\ (\bar{y}, \tfrac{1}{2}-x, \tfrac{1}{4}+z),\\&(\bar{y}, x, \bar{z}),\ (y, \bar{x}, \bar{z}),\ (\bar{y}, \tfrac{1}{2}+x, \tfrac{1}{4}+z),\ (y, \tfrac{1}{2}-x, \tfrac{1}{4}+z),\end{aligned}$$

with

$$x = 0{\cdot}123,\ y = 0{\cdot}205,\ z = 0{\cdot}308\ .$$

The agreement between observed and calculated values of the structure amplitudes (Table 1) calculated for all reflections (*hk*0), (*hk*1) and (0*kl*), which had indices below a value of $h^2+k^2+(9/4)l^2 = 400$, as determined by $R_1 = \Sigma||F_o|-|F_c|| \div \Sigma|F_o|$ is 0·29. Assuming that F_o for absent reflections is equal in intensity to $\frac{1}{2}F_o$ min., the value is 0·26. The agreement factor for (*h*00) reflections, for which the absorption factor varied in the most uniform fashion, was 0·16. The reason for the only mediocre agreement between calculated and observed F values is undoubtedly the neglect of absorption factors. Lorentz, polarization, and artificial temperature corrections were made.

Discussion of the structure

The structure consists of Ba atoms surrounded by a polyhedron of 22 Cd atoms. A projection of these atoms along the *c* axis is shown in Fig. 3 in which only the Cd–Cd bonds are drawn. The structure is

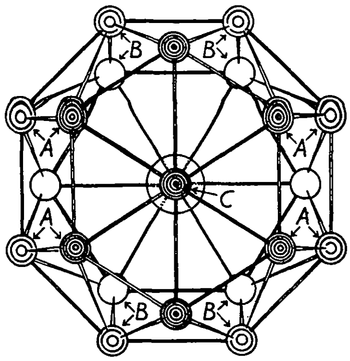

Fig. 3. Projection along *c* of atoms in the polyhedron around the Ba atom.

Table 1. *Comparison of observed and calculated structure factors for* $BaCd_{11}$

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	6	7	501	17	20	507	6	8
400	13	10	701	12	11	707	9	11
600	15	11	901	5	4	907	< 3	1
800	22	22	11,0,1	6	4	11,0,7	< 4	1
10,0,0	24	23	13,0,1	< 3	1	13,0,7	< 4	4
12,0,0	15	12	15,0,1	7	7			
14,0,0	14	12	17,0,1	8	8	008	8	7
16,0,0	17	20				208	12	17
18,0,0	2	5	202	< 1	1	408	17	20
			402	16	19	608	< 3	3
220	< 1	0	602	14	11	808	10	8
420	24	29	802	17	17	10,0,8	< 4	6
620	6	2	10,0,2	16	14	12,0,8	21	32
820	7	5	12,0,2	< 3	0			
10,2,0	< 1	0	14,0,2	13	13	211	16	22
12,2,0	16	17	16,0,2	< 4	4	411	13	12
14,2,0	7	2				611	24	24
16,2,0	< 2	3	103	11	15	811	32	36
18,2,0	< 2	2	303	8	8	10,1,1	24	26
			503	4	1	12,1,1	< 9	11
440	< 1	4	703	7	7			
640	9	7	903	13	12	321	39	40
840	27	30	11,0,3	< 3	3	521	31	34
10,4,0	5	5	13,0,3	6	5	721	< 7	4
12,4,0	20	20	15,0,3	8	9	921	< 8	0
14,4,0	6	3	17,0,3	7	6	11,2,1	23	23
16,4,0	17	18				13,2,1	26	25
18,4,0	< 2	5	004	10	9			
			204	7	6	431	49	71
660	< 1	0	404	< 2	0	631	< 6	12
860	13	10	604	10	9	831	33	34
10,6,0	< 2	0	804	< 3	1	10,3,1	< 8	5
12,6,0	9	7	10,0,4	12	9	12,3,1	10	27
14,6,0	5	0	12,0,4	< 3	2			
16,6,0	7	7	14,0,4	8	7	541	28	13
						741	40	29
880	4	3	105	5	5	941	18	23
10,8,0	17	17	305	12	14	11,4,1	< 9	15
12,8,0	9	8	505	5	5	13,4,1	10	30
14,8,0	13	14	705	6	2			
16,8,0	< 2	2	905	7	6	651	19	18
			11,0,5	7	7	851	32	46
10,10,0	7	3	13,0,5	9	10	10,5,1	< 9	5
12,10,0	8	6	15,0,5	4	5	12,5,1	32	42
14,10,0	< 2	1						
16,10,0	9	14	206	15	18	761	10	13
			406	15	16	961	10	17
12,12,0	22	32	606	7	5	11,6,1	< 9	11
14,12,0	< 2	0	806	17	17	13,6,1	< 10	9
16,12,0	< 2	3	10,0,6	< 3	2			
			12,0,6	< 3	0	871	22	21
14,14,0	< 2	2	14,0,6	< 4	2	10,7,1	24	24
16,14,0	6	11				12,7,1	31	50
			107	< 3	1			
101	2	3	307	7	8	981	32	22
301	5	3						

made up by packing the polyhedra so that the square faces, *A*, tilting up are shared by those, *B*, tilting down, leading to a two-dimensional packing of polyhedra. The polyhedra are connected in the *c* direction by sharing the atoms *C*. The neighbors of the atom *C*, projected along the *c* axis, are shown in Fig. 4. A similar projection of the cadmium atoms in positions 8(*d*) is shown in Fig. 5. A list of interatomic distances is given in Table 2.

The Cd (or Zn) atoms form a network in which there is a nearly spherical hole for the Ba, Sr, or rare-earth atoms. The diameter of the hole depends primarily on the Cd or Zn atom size, and does not vary appreciably as metals of different size are placed in the hole. A similar situation occurs in the $NaZn_{13}$-type compounds, in which the hole depends primarily on the size of the Be, Zn or Cd atoms.

The radii of the holes in these two structures, calculated by assuming that the Be, Zn or Cd atom has the radius for 12-fold coordination as given by Pauling (1947), are listed in Table 3 together with the radii of the alkali, alkaline-earth and rare-earth atoms

Table 2. *Interatomic distances in the* AB_{11} *compounds*

Values in Ångström units

Atom	Neighbor	Distance				
		$BaCd_{11}$	$SrCd_{11}$	$LaZn_{11}$	$CeZn_{11}$	$PrZn_{11}$
A	8 B at	3·73	3·73	3·32	3·31	3·30
	2 B at	3·87	3·85	3·44	3·43	3·42
	8 B at	3·87	3·87	3·44	3·43	3·43
	4 B at	4·18	4·16	3·71	3·70	3·70
B in 4(b)	4 B at	3·16	3·16	2·81	2·80	2·80
	8 B at	3·24	3·23	2·88	2·87	2·86
	2 A at	3·87	3·85	3·44	3·43	3·42
B in 8(d)	4 B at	2·92	2·90	2·59	2·59	2·58
	4 B at	2·94	2·94	2·62	2·61	2·61
	2 B at	3·16	3·16	2·81	2·80	2·80
	2 A at	4·18	4·16	3·71	3·70	3·70
B in 32(i)	1 B at	2·92	2·90	2·59	2·59	2·58
	1 B at	2·94	2·94	2·62	2·61	2·61
	1 B at	2·96	2·96	2·63	2·62	2·62
	2 B at	3·00	2·99	2·66	2·66	2·65
	1 B at	3·03	3·02	2·69	2·69	2·68
	1 B at	3·06	3·06	2·72	2·71	2·71
	2 B at	3·24	3·23	2·88	2·87	2·86
	1 B at	3·28	3·27	2·92	2·91	2·90
	1 A at	3·73	3·73	3·32	3·31	3·30
	1 A at	3·87	3·87	3·44	3·43	3·43

Table 3. *Radii of holes for A atoms in the* AB_{13} *and* AB_{11} *structures*

Radii in metal		Radii of holes in the AB_{13} and AB_{11} structures					
Cs	2·62	—	—	—	—	$CsCd_{13}$	2·57
Rb	2·43	—	—	—	—	$RbCd_{13}$	2·57
K	2·27	—	—	KZn_{13}	2·28	KCd_{13}	2·54
Ba	2·17	—	—	$BaZn_{13}$	2·28	$BaCd_{11}$	2·19
Sr	2·14	—	—	$SrZn_{13}$	2·24	$SrCd_{11}$	2·19
Ca	1·97	$CaBe_{13}$	1·94	$CaZn_{13}$	2·22	—	—
Na	1·86	—	—	$NaZn_{13}$	2·26	—	—
La	1·86	$LaBe_{13}$	1·98	$LaZn_{11}$	1·94	—	—
Pr	1·82	$PrBe_{13}$	1·96	$PrZn_{11}$	1·92	—	—
Ce	1·81	$CeBe_{13}$	1·95	$CeZn_{11}$	1·93	—	—
Nd	1·81	$NdBe_{13}$	1·95				
Th	1·79	$ThBe_{13}$	1·96				
Zr	1·58	$ZrBe_{13}$	1·85				
U	1·42	UBe_{13}	1·92				

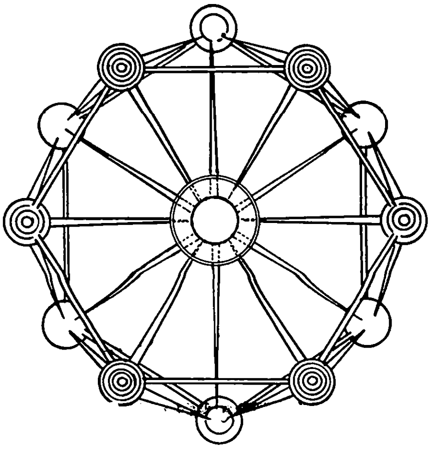

Fig. 4. Projection along c of the nearest neighbors of Cd atoms in 4(b).

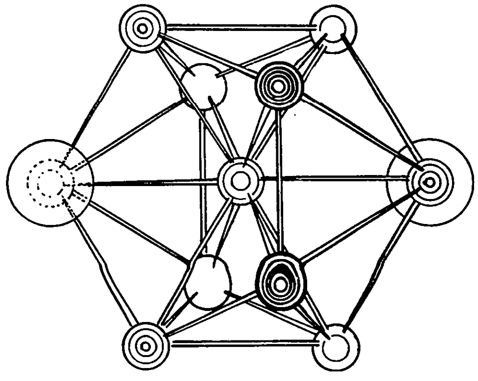

Fig. 5. Projection along c of the nearest neighbors of Cd atoms in 8(d).

in the metal. It can be seen that in each case the structure does not exist when the A atom gets too big for the hole, and that the AB_{11} structure is assumed in preference to the AB_{13} structure when the atom is too small for the AB_{13} type but fits tightly in the hole in the AB_{11} type.

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X-ray Scattering by Aggregates of Bonded Atoms. III. The Bond Scattering Factor: Simple Methods of Approximation in the General Case

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General approximate methods of calculating the bond scattering factor (defined in a previous paper) are devised: formulae are given which cover all cases arising from bonds involving (1*s*), (2*s*) and (2*p*) electrons. The approximate method is compared with the earlier rigorous method in a treatment of the hydrogen molecule and is found to be entirely adequate.

The *absolute* accuracy of the resultant effective atomic scattering factor (f^e) is carefully investigated, again in the hydrogen-molecule case, by systematic refinement of the wave function. A change of 'effective nuclear charge' in the atomic orbitals employed is found to have a considerable effect on the calculated f^e, but the introduction of a certain amount of configuration interaction (equivalent to the addition of ionic terms) is found to have a very small effect. It is concluded that the original definition of an effective scattering factor (based upon a one-configuration wave function) is completely satisfactory. More complete knowledge of the parameters in molecular wave functions is perhaps desirable; but calculations based upon quite crude estimates are likely to yield substantially correct scattering factors since the valence-electron contribution is usually relatively small. On the other hand, attempts to allow for the effect of bonding by empirical methods, using point charges in the bonds, are to be discouraged.

1. Introduction

In a preceding paper (McWeeny, 1952, hereafter II) the problem of discussing the scattering of X-rays by a molecule or lattice of *bonded* atoms has been formally solved: the conventional treatment is modified only in so far as the atomic scattering factors are replaced by certain *effective* factors which are obtained from the familiar isolated-atom factors (recently revised by McWeeny, 1951, hereafter I) by addition of appropriate corrections. The corrections incurred involve certain 'bond scattering factors'

$$f(\varrho_{AB}) = \frac{1}{S_{AB}}\int \varphi_A(\mathbf{r}_A)\varphi_B(\mathbf{r}_B)\exp\{i\varkappa\mathbf{S}.\mathbf{r}\}d\mathbf{r}\,, \quad (1)$$

and although an accurate and fairly general method of computing these quantities was developed in II, it is evident that calculations along these lines would become excessively laborious in elaborate applications; indeed, even in the case of the hydrogen molecule (II) the labour involved effectively precluded a full examination of the dependence of the results upon accuracy of the wave function.

In this paper a simple *approximate* method of evaluating the bond scattering factor is developed: the example treated in II is then re-examined for purposes of comparison and the new method is found to be entirely adequate. Briefly the method consists of replacing the hydrogen-like or Slater (1930)* atomic orbitals occurring in (1) by approximate expressions of more suitable analytical form: the integration may then be effected in simple closed form without any of the tedious expansions required by the original, accurate method. Satisfactory approximations to (1*s*), (2*s*) and (2*p*) orbitals follow in § 2 and make possible the treatment of all bonds between atoms from hydrogen to neon; there should be no difficulty in extending the method to heavier atoms but it seems clear that

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* The Slater functions are nodeless, one-term functions with a radial factor $r^n \exp\{-ar\}$.