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The Crystal Structure of Na_2Cd_{11}

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The structure of Na_2Cd_{11} is cubic, space group *Pm*3, with three formula units of Na_2Cd_{11} per unit cell of edge $a_0 = 9{\cdot}605 \pm 0{\cdot}003$ Å. The compound is isostructural with Mg_2Zn_{11} and $Mg_2Cu_6Al_5$. The structure has been refined by least-squares techniques with the use of an almost complete set of three-dimensional Mo $K\alpha$ intensity data. The values of the bond numbers and atomic valences obtained indicate that electron transfer has occurred between sodium and cadmium atoms and also between crystallographically different cadmium atoms in this structure.

Introduction

The most cadmium-rich compound in the Na–Cd system has been assigned the various compositions: $NaCd_4$ (Kurnakow & Kusnetzow, 1907), $NaCd_5$ (Mathewson, 1906), $NaCd_6$ (Jänecke, 1928), and Na_2Cd_{11} (Ewing & Pauling (EP), private communication). The composition Na_2Cd_{11} was deduced from a synthesized structure model which, shortly after its derivation, was found to correspond to that worked out independently by Samson (1949*a*,*b*) for Mg_2Zn_{11} and $Mg_2Cu_6Al_5$. In 1957, an X-ray diffraction study of this compound was carried out at the California Institute of Technology by one of us (C-h.W.). Fair agreement between observed and calculated structure factors of *hk*0 reflections was obtained for the model proposed by EP. The intensity data, which had been obtained with the use of copper radiation and a large crystal of irregular cross-section, suffered badly from absorption effects, and the best agreement index *R* that could be obtained was 0·20.

We have now carried out least-squares refinements of the structure with the use of a new, almost complete set of three-dimensional intensity data of good quality.

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Experimental

An alloy of approximate composition Na_2Cd_{11} was prepared by melting pieces of sodium and cadmium together in a sealed Pyrex tube filled with argon gas; vigorous shaking assured homogeneity of the melt. The ingot contained well-formed cubic crystals which, however, were too large to yield accurate data. Since attempts to grind spheres were unsuccessful, a small fragment of about $0{\cdot}05 \times 0{\cdot}04 \times 0{\cdot}02$ mm was used for the X-ray photography.

The intensities were estimated visually from equi-inclination Weissenberg photographs of layer lines 0 to 4 obtained with the multiple-film technique, the films being interspersed with copper foil to yield a film factor of about 3·6 for zirconium-filtered Mo $K\alpha$ radiation. Each intensity value is an average of three independent measurements, one made by C-h.Wong, the second by C. Chieh and the third by T. Chen. To minimize absorption errors each observer measured the reflections for two quadrants of reciprocal space and averaged the two values. The intensities of the symmetrically dependent reflections *hkl*, *lhk* and *klh* were not averaged until later (see *Refinement*). Lorentz and polarization corrections were applied in the standard manner. The value of μR is 0·7; since the range of observation was only 33° ($4° < \theta < 37°$), absorption effects were neglected (Evans & Ekstein, 1952).

Table 1. *Initial and final positional parameters and temperature factors for* Na_2Cd_{11}

Atom	Number of atoms	Point set		*x*	*y*	*z*	Temperature factors B(Å^2)
Cd(1)	1	(*b*) $\frac{1}{2}\frac{1}{2}\frac{1}{2}$	initial				2·0
			final				1·86(17)
Cd(2)	12	(*k*) $\frac{1}{2}xz$, *etc.*	initial		0·243	0·343	2·0
			final		0·2344(4)	0·3426(4)	2·09(5)
Cd(3)	8	(*i*) *xxx*, *etc.*	initial	0·222			2·0
			final	0·2184(3)			3·01(7)
Cd(4)	6	(*g*) $x\frac{1}{2}0$, *etc.*	initial	0·170			2·0
			final	0·1614(6)			2·66(8)
Cd(5)	6	(*e*) *x*00, *etc.*	initial	0·235			2·0
			final	0·2318(5)			2·40(8)
Na	6	(*f*) $x0\frac{1}{2}$, *etc.*	initial	0·312			2·0
			final	0·3105(22)			0·95(32)

The lattice parameter a was determined from a Straumanis-type powder photograph taken in a camera of 10 cm diameter. The sample consisted of annealed 325-mesh filings. A least-squares refinement gave $a = 9{\cdot}605 \pm 0{\cdot}003$ Å ($\lambda = 1{\cdot}5418$ Å). The density measured by displacement of bromoform is 7·31 g.cm^{-3}.

The trial structure

The observed Laue symmetry is $m3$; since there are no systematic extinctions, the space group is $P23$ or $Pm3$. The structure model devised by EP corresponds to $Pm3$ with three formula units of Na_2Cd_{11} per unit cell and a calculated density of 7·21 g.cm^{-3}, in fair agreement with the measured value. The relative intensities of the powder lines were very similar to those reported by Samson (1949*b*) for Mg_2Zn_{11}.

The distribution of atoms and the approximate positional parameters for the trial structure were derived on the basis of Pauling's (1947) metallic radii; they are given in Table 1.

Refinement of the structure

The structure was refined with least-squares calculations; the quantity minimized was $\Sigma w(F_o - F_c)^2$ and the weighting system was that proposed by Hughes (1941). The scattering factors for cadmium were taken from Thomas & Umeda (1957) and those for sodium from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955). Individual isotropic temperature factors were included in the refinement.

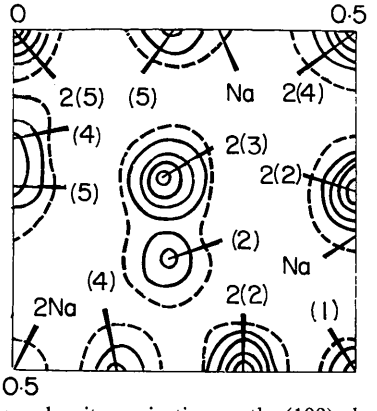

Fig. 1. Electron density projection on the (100) plane. Contours are at 20 e.Å^{-2}. Dashed lines indicate zero contours. The numbers in parentheses correspond to the atom numbers of Table 1.

Table 2. *Observed and calculated structure factors*

The four columns in each group represent k, l, $3|F_o|$, and $3\ F_c$.

The three small-angle reflections marked with an asterisk were estimated from a Weissenberg photograph taken with copper radiation and were not included in the refinement calculations.

h = 0

0	1	432*	-16
0	2	283	-273
0	3	567	-570
0	4	1896	2157
0	5	713	684
0	6	885	954
0	7	893	-939
0	8	974	948
0	9	541	583
0	10	343	340
0	11	406	-393
0	12	467	435
1	1	348*	396
1	2	210	-229
1	3	<72	-64
1	4	387	-409
1	5	244	295
1	6	134	121
1	7	172	163
1	8	138	-200
2	1	643	629
2	2	222	223
2	3	<77	-59
2	4	254	271
2	5	<96	79
2	6	199	-243
2	7	464	625
2	8	158	229
2	9	198	-182
2	10	<143	-84
2	11	<153	24
2	12	199	127
2	13	211	237
3	1	98	-98
3	2	707	778
3	3	242	-228
3	4	364	-370
3	5	353	-375
3	6	331	362
3	7	300	330
3	8	<126	-6
3	9	372	-437
4	1	894	891
4	2	1048	-999
4	3	452	501
4	4	655	720
4	5	963	1081
4	6	169	137
4	7	159	-135
4	8	246	292
4	9	676	785
4	10	<148	-94
4	11	<156	-30
4	12	<167	155
4	13	270	258
5	1	244	243
5	2	466	-447
5	3	155	-157
5	4	<106	-25
5	5	406	423
5	6	178	169
5	7	173	-172
5	8	167	-98
5	9	229	200
6	1	164	-136
6	2	477	493
6	3	673	-673
6	4	829	953
6	5	203	-166
6	6	213	250
6	7	<134	-93
6	8	519	533
6	9	259	-232
6	10	203	231
6	11	245	-225
6	12	257	240
7	1	191	162
7	2	331	349
7	3	<118	66
7	4	494	-566
7	5	203	-166
7	6	<134	-16
7	7	506	511
7	8	242	-190
7	9	254	-298
7	10	<162	-100
7	11	209	197
8	1	219	199
8	2	124	-153
8	3	126	175
8	4	322	376
8	5	278	268
8	6	231	210
8	7	<147	-51
8	8	228	259
8	9	265	247
9	1	<132	56
9	2	158	-115
9	3	<137	+66
9	4	<140	90
9	5	244	201
9	6	274	256
9	7	210	-173
10	1	382	398
10	2	372	-341
10	3	<145	-6
10	4	244	268
10	5	439	400
10	6	258	184
10	7	<162	91
10	8	<168	71
10	9	175	200
11	1	<151	-7
11	2	216	194
11	3	<155	-140
11	4	204	-177
11	5	<162	-140
11	6	<166	-7
11	7	209	169
11	8	<177	-66
11	9	235	-219
12	1	<161	-81
12	2	<162	172
12	3	<164	-43
12	4	227	259
12	5	<170	-74
12	6	213	206
12	7	<179	-55
12	8	226	216

h = 1

1	1	283*	-302
1	2	231	-221
1	3	277	-270
1	4	628	676
1	5	<104	12
1	6	359	-364
1	7	390	-413
1	8	250	283
1	9	180	138
1	10	<157	27
1	11	216	-193
2	2	251	-235
2	3	932	950
2	4	524	-508
2	5	131	-108
2	6	<94	33
2	7	<102	-77
2	8	169	-174
2	9	264	274
2	10	194	+174
2	11	<137	90
2	12	<146	-21
3	2	562	-555
3	3	<74	65
3	4	<102	91
3	5	<95	-23
3	6	424	-456
3	7	370	-349
3	8	<125	68
3	9	180	175
3	10	145	-172
3	11	190	-135
3	12	<164	-20
4	2	142	156
4	3	336	333
4	4	378	370
4	5	446	451
4	6	301	-308
4	7	340	374
4	8	<145	0
4	9	194	196
4	10	244	213
5	2	139	-97
5	3	236	-248
5	4	663	673
5	5	165	171
5	6	310	-326
5	7	267	-234
5	8	269	267
5	9	172	136
5	10	<169	104
5	11	193	-143
6	2	<94	26
6	3	303	298
6	4	<127	-93
6	5	245	-228
6	6	<141	136
6	7	227	-219
7	2	201	-204
7	3	<116	-46
7	4	<136	94
7	5	225	-205
7	6	210	-139
7	7	424	-378
8	2	168	168
8	3	191	207
8	4	188	185
8	5	231	182
8	6	<157	-109
8	7	201	215
9	2	<148	-118
9	3	<145	-113
9	4	331	343
9	5	197	185
9	6	303	-290
10	2	205	-137
10	3	273	265
11	2	208	-138
11	3	<171	24
11	4	<176	24
11	5	<179	-79
11	6	<184	-53
11	7	232	-209

h = 2

2	2	922	-1087
2	3	1572	-1606
2	4	262	252
2	5	<88	27
2	6	554	-536
2	7	509	-496
2	8	234	-221
2	9	258	-254
2	10	<131	67
2	11	419	-362
2	12	256	-219
3	3	97	-92
3	4	246	-252
3	5	766	940
3	6	736	-822
3	7	<107	112
3	8	277	-311
3	9	383	397
3	10	366	-342
3	11	<141	21
3	12	236	-220
3	13	354	260
4	3	140	128
4	4	412	-433
4	5	498	-524
4	6	466	536
4	7	<111	-45
4	8	<119	20
4	9	191	-214
4	10	166	-142
4	11	<143	-9
4	12	201	200
5	3	<92	73
5	4	275	-240
5	5	170	-177
5	6	134	124
5	7	<116	80
5	8	<123	84
5	9	<132	-95
5	10	231	-233

h = 3

3	3	389	320
3	4	116	-111
3	5	167	167
3	6	<113	-92
3	7	<121	-100
3	8	<129	-108
3	9	170	187
3	10	<148	27
4	4	386	397
4	5	<110	32
4	6	593	-632
4	7	<125	46
4	8	<134	118
4	9	<143	40
4	10	<152	-16
4	11	157	-119
4	12	<178	-56
5	3	136	145
5	4	220	215
5	5	192	-188
5	6	236	229
5	7	246	219
5	8	138	101
5	9	181	-157
5	10	240	240
6	4	<117	63
6	5	<123	-111
6	6	380	-383
6	7	530	-567
6	8	<144	-16
6	9	216	220
6	10	213	-226
6	11	225	-237
7	4	154	168
7	5	172	-129
7	6	182	181
7	7	345	-378
8	4	260	305
8	5	<138	119
8	6	<143	5
9	5	<147	19
9	6	<153	-12
9	7	251	267
10	4	<153	-13
10	5	<156	-70
10	6	228	-214
10	7	235	-196
11	4	<161	-10
11	5	<165	-43
11	6	<169	93
11	7	179	-155
12	4	190	162
12	5	<173	52
12	6	178	-197

h = 4

4	4	178	-157
4	5	408	434
4	6	220	276
4	7	<137	26
4	8	<146	-95
4	9	314	329
4	10	<164	-77
5	5	681	631
5	6	<157	6
5	7	<156	-124
5	8	<178	194
5	9	409	398
6	5	366	-394
6	6	221	284
6	7	<148	-29
6	8	176	154
6	9	363	-411
7	5	153	213
7	6	203	-182
7	7	303	314
8	5	<150	-1
8	6	321	264
9	5	368	337
9	6	<166	123
9	7	<169	-135
9	8	179	191
9	9	246	254
10	5	224	156
12	5	189	-151
12	6	236	217
13	5	209	203

Initially, a separate scale factor was refined for each layer, with all measured data included. In four least-squares cycles, the R index for all layers taken together dropped from 0·20 to 0·11. There were no significant changes in the scale factors during the last two cycles. The average values of F_o for equivalent reflections *hkl*, *lhk* and *klh* were obtained after the layers had been brought to a common scale. The resulting 375 independent data included 118 reflections too weak to be measured.

Ten more least-squares cycles with this set of data resulted in an R index of 0·089; the final parameters are listed in Table 1. During the last three cycles the shifts in the positional parameters were less than 10^{-4} of the cell edge; in the last cycle the shift in each temperature factor was less than 0·3 of its standard deviation. The observed and calculated structure factors are given in Table 2. An electron-density projection on the (100) plane is shown in Fig. 1.

Description of the coordination shells

Cd(1) is at the center of a slightly distorted icosahedron I_1 formed by twelve cadmium atoms, 12 Cd(2), each of which in turn is surrounded by an icosahedral shell I_2. Five of the center-to-vertex distances of I_2 represent edges of I_1 and are about five per cent greater than the center-to-vertex distances of I_1 as required by the metrical nature of the icosahedron; the average center-to-vertex distance of I_2 is 4·7% greater than that of I_1 but three of its vertices are occupied by large atoms (sodium).

Each cadmium atom Cd(3) is at the center of a trigonal prism formed by 3 Cd(2) and 3 Cd(5). Out from

Table 3. *Interatomic distances, bond numbers, calculated valences, and calculated single-bond radii*

The estimated standard deviations of the distance are given in parentheses. Each single-bond radius $R(1)$ is consistent with the valence V of the atom identified in column 1.

Atom	Ligancy	Distance (Å)	Bond number (n)*	Valence V* and single-bond radius $R(1)$	Packing efficiency
Cd(1)	12 Cd(2)	2·965(3)	0·475	V = 5·70 $R(1)$ = 1·371	very high
Cd(2)	1 Cd(1)	2·965(3)	0·475	V = 4·55(4·76)	high
	1 Cd(2)	3·024(7)	0·423	$R(1)$ = 1·400	
	4 Cd(2)	3·142(4)	0·269		
	2 Cd(3)	2·960(4)	0·541		
	1 Cd(4)	2·846(6)	0·838		
	1 Na	3·371(7)	0·164(0·216)		
	2 Na	3·266(13)	0·246(0·324)		
	12				
Cd(3)	3 Cd(2)	2·960(4)	0·541	V = 3·68(3·77)	low
	3 Cd(4)	3·466(3)	0·078	$R(1)$ = 1·400	
	3 Cd(5)	2·969(3)	0·522		
	3 Na	3·535(7)	0·087(0·115)		
	12				
Cd(4)	2 Cd(2)	2·846(6)	0·838	V = 3·63(3·76)	low
	4 Cd(3)	3·466(3)	0·078	$R(1)$ = 1·400	
	1 Cd(4)	3·101(11)	0·315		
	2 Cd(5)	3·007(5)	0·452		
	2 Na	3·727(12)	0·042(0·055)		
	2 Na	3·361(20)	0·171(0·223)		
	13				
Cd(5)	4 Cd(3)	2·969(3)	0·522	V = 4·08(4·09)	normal
	2 Cd(4)	3·007(5)	0·452	$R(1)$ = 1·400	
	4 Cd(5)	3·149(5)	0·262		
	2 Na	3·941(17)	0·018(0·024)		
	12				
Na	2Cd(2)	3·371(7)	0·164	V = 2·27(2·94)	very high
	4 Cd(2)	3·266(13)	0·246	$R(1)$ = 1·572	
	4 Cd(3)	3·535(7)	0·087		
	2 Cd(4)	3·727(12)	0·042		
	2 Cd(4)	3·361(20)	0·171		
	2 Cd(5)	3·941(17)	0·018		
	1 Na	3·640(44)	0·150		
	17				

* Values in parentheses are calculated without the Schomaker–Stevenson correction.

the center of each of the three prism faces lies a sodium atom and out from the center of each of the three edges parallel to the prism axis lies a cadmium atom Cd(4). The coordination shell around Cd(4) is similar to that of Cd(3), except that one of the prism faces is penetrated by two sodium atoms instead of one.

Cd(5) is at the center of a tetragonal prism formed by 4 Cd(3), 2 Cd(4) and 2 Cd(5). Out from the center of each of two opposite prism faces lies a sodium atom and out from the center of each of the remaining two prism faces lies a Cd(5).

The sodium atoms are surrounded by a pentagonal prism [4 Cd(2), 4 Cd(3) and 2 Cd(4)] with two atoms, 2 Cd(2), at the poles and five atoms, Na, 2 Cd(4) and, 2 Cd(5), out from the centers of the prism faces.

A picture showing the atomic arrangement of the isostructural compound $Mg_2Cu_6Al_5$ is given by Samson (1949*a*).

Discussion of the structure

The interatomic distances are listed in Table 3 together with the bond numbers and valences calculated according to the equation $D(n)=D(1)-0{\cdot}6 \log n$ (Pauling, 1947). The single-bond radius assigned to each atom is such as to be consistent with the valence calculated for that atom (Pauling, 1949, 1960). Whenever a distance involves both Na and Cd, two values are given for the bond number and valence, one of which includes the Schomaker–Stevenson (1941) correction (0·072 Å has been subtracted from the sum of the metallic radii of the two metals).

The valence 5·70 of the icosahedral atom Cd(1) is close to the value 5·5 calculated for the zinc atom at the center of the considerably distorted icosahedron in $ZrZn_{22}$ (Samson, 1961). The icosahedral zinc atom in $NaZn_{13}$ (Shoemaker, Marsh, Ewing & Pauling, 1952) has the valence 6·0. The valence of the atom Cd(2) at the center of the icosahedron I_2 is 4·55, which is considerably lower than that of Cd(1) but higher than the 'normal' valence 4·0.

The high valence observed here for sodium, 2·27 (with the Schomaker–Stevenson correction), is explicable on the basis of electron transfer. In view of the difference in electronegativity between sodium and cadmium it seems possible that each sodium atom has received about one electron from the high-valent atoms Cd(1) and Cd(2). The valence calculated for sodium without the Schomaker–Stevenson correction, 2·94, would require the transfer of about two electrons to each sodium atom. The valences of the cadmium atoms are only very slightly altered by the Schomaker–Stevenson correction. It is possible that electron transfer has also occurred from Cd(1) and Cd(2) to Cd(3) and Cd(4), which have a slightly lower-than-normal valence.

The variations in the temperature factors of the crystallographically different atoms seem to be related to the variations in the average strengths of the bonds formed around them; the highly electropositive and hypoelectronic atoms (Na) show the smallest thermal vibration. Cadmium atoms Cd(1) and Cd(2), which are firmly packed inside icosahedral shells, have smaller temperature factors than the remaining three cadmium atoms which are less firmly packed.

The volume of the unit cell is about nine per cent smaller than the calculated sum of the atomic volumes. This reduction in volume is probably the result of the very dense packing around Cd(1), Cd(2) and around the sodium atoms.

We thank Dr Gunnar Bergman for suggesting this investigation to one of us (C-h.W.). Mr. T. H. Bergeman assisted in part of the X-ray photography and Mr. T. Chen in the collection of intensity data. We are grateful to the University authority for financial support and to members of the Computer Center of National Chiao Tung University for their assistance in the computations. We also acknowledge with gratitude many valuable suggestions and criticisms on the manuscript by Dr Sten Samson.

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