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An Alternative Description of the Structure of NaCd$_2$

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Abstract

A new description of the ordered part of the crystal structure of NaCd$_2$ is proposed. A framework of cadmium Friauf polyhedra, related to but different from that of Cu$_4$Cd$_3$, interpenetrates a partially disordered sodium-cadmium structure. Using matrix algebra developed for the coincidence site lattice theory, atomic coordinates can be calculated which are very close to those experimentally determined.

Introduction

The crystal structure of NaCd$_2$ (β-Mg$_2$Al$_3$ is isostructural) is cubic, $Fd3m$, with $a = 30{\cdot}56$ Å, and approximately 1192 atoms in the unit cell, as determined by Samson (Samson, 1962, 1965). According to Samson's description, the unit cube contains 672 icosahedra, 252 Friauf polyhedra, and 244 miscellaneous, more or less irregular polyhedra.

Derivation and description

From Samson's data for β-Mg$_2$Al$_3$ the structure was plotted with cubic axes. Two different building blocks consisting of Friauf polyhedra were derived, and these could be joined together in the space group $Fd3m$. The derived structure contained the cadmium atoms numbered 1, 2, 3, 4, 5 and 6 (from the structure of NaCd$_2$) and is shown in Fig. 2. These building blocks are red, yellow and green, the red and yellow building blocks being identical units, but in opposite orientations.

In a parallel article (Yang & Andersson, 1987), we give an exact and general description of the cubic structures that contain building blocks, using matrix algebra and symmetry considerations. It was also pointed out that this method could be used for a direct determination of complex structures. It was decided to carry out a test on NaCd$_2$, as Samson's structure determination of this compound had resulted in a relatively high R factor, *viz.* 0·17. Crystals of NaCd$_2$ were prepared in silica tubes. Complete data were collected using a Nicolet diffractometer with Mo $K\alpha$ radiation, from a suitable crystal sealed in a glass capillary.

From the general formula

$$a = n(2^{1/2})d/3$$

as derived by Yang & Andersson (1987), d is the shortest interatomic distance and was determined from the three-dimensional Patterson synthesis to be 0·09744 Å; $n = 21{\cdot}77 \approx 22$. The space group of NaCd$_2$ is $Fd3m$, which is composed of 16 building blocks of two types.

The nearest two building blocks are those located at (000) and ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) respectively. We assume that the building block around (000) is ($KLPQS$); then that around ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$) must be $-(KLPQS)$. The interface between these two building blocks is the (111) lattice plane through ($\frac{1}{8}\frac{1}{8}\frac{1}{8}$). Let ($xyz$) be the coordinates of the atoms in the interface. Then

$$(x\mathbf{a}+y\mathbf{b}+\mathbf{c})(\mathbf{a}+\mathbf{b}+\mathbf{c}) = x+y+z = 3/8$$

and

$$t_1+t_2+t_3 = 4n(x+y+z) = 33.$$

The only building block in Table 2 of our parallel paper (Yang & Andersson, 1987) which has $t_1+t_2+t_3=33$, *i.e.* coordinates (23 11 $\bar{1}$) or (11 11 11), is (4, 3, 1). The interface of two building blocks, as shown in Fig. 1, consists of these two independent coordinates according to symmetry operations.

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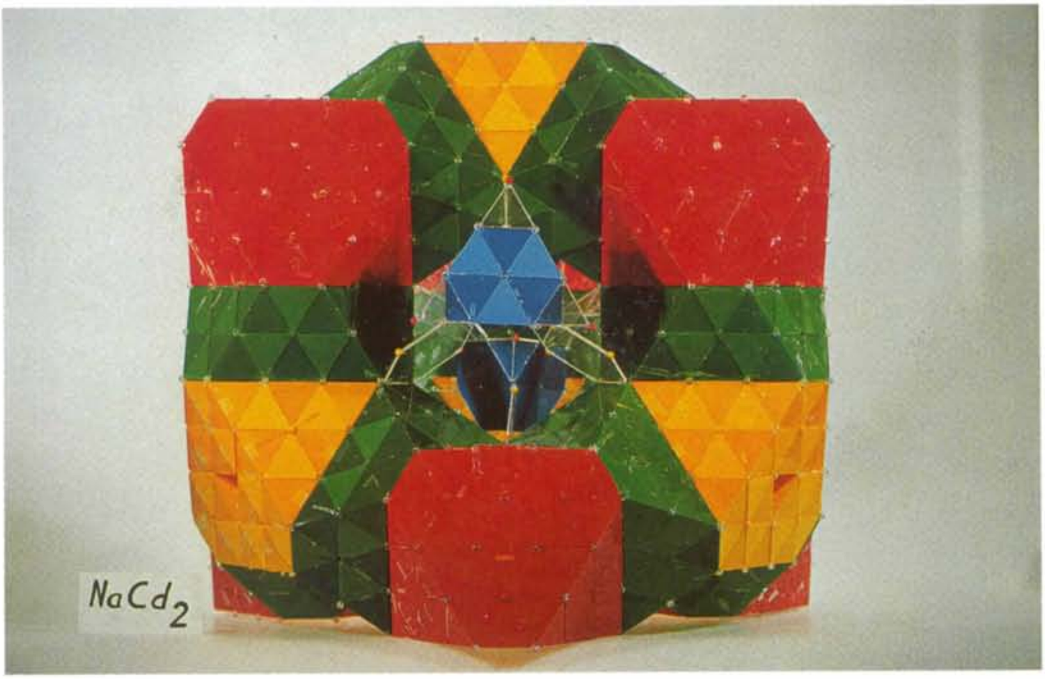

Fig. 2. The structure of $NaCd_2$. The building block (4, 3, 1) consists of one red or yellow unit and four half green units. The blue Friauf polyhedron + red balls constitute the (3, 0) building block.

The building block (4, 3, 1) has 11 independent positions. The coordinates of the building block (4, 3, 1) were derived from $4n = 88$ and the structure of the block was changed so that it consisted of Cd Friauf polyhedra, with sodium in the center. These coordinates were tried as a structure model in a least-squares refinement, which gave $R = 0{\cdot}26$. The rest of the atoms of $NaCd_2$ were obtained using a difference synthesis, and the final R factor was 0·12, using 892 reflections. We noticed, as did Samson, a partial decomposition of the crystal during the data collection.

Calculated and observed atomic parameters are given in Table 1. Our investigation does indeed confirm the original structure determination by Samson, whose parameters are also given in Table 1. It is interesting to note that our coordinates give a lower R factor, and are also closer than Samson's to the ideal derived value. From Table 1, we find that the percentages of the average atomic deviation of building blocks (4, 3, 1) and (3, 0) are 2·6 and 3·6 respectively, according to our data; however, Samson's are 3·6 and 6·0.

The major framework of the structure of $NaCd_2$ is now extremely easy to understand. Building blocks (4, 3, 1) are put together by simple face sharing, according to the symmetry of the crystal. The similarity with the structure of Cu_4Cd_3 is also obvious: the T_d polyhedron of the (4, 3, 1) block is the same as in the (4, 5, 1) block of Cu_4Cd_3.

The space group $Fd3m$ is common for the so-called interpenetrating structures, typical examples of which are the structures of zeolite N and W_3Fe_3C. In order to describe this kind of structure, we have introduced the use of differential geometry and minimal surfaces (Andersson, Hyde & von Schnering, 1984; Hyde & Andersson, 1984, 1986). In this space group, we showed that one part of a structure is situated on one side of the so-called Schwartz F surface, while another part is situated on the other side of the surface. Fig. 2 shows the fully ordered framework of red, yellow and green building blocks which are situated on one side of such a surface. The other part of the structure, now on the other side of the surface, contains the partial disorder. The positions of Cd(8),

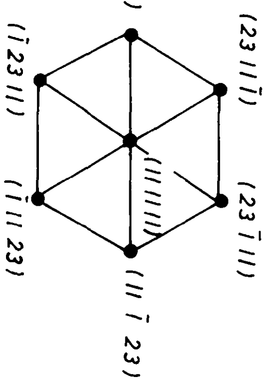

Fig. 1. Interface of two building blocks in $NaCd_2$.

Table 1. *Calculated and observed atomic parameters*

	Experimental coordinates (Samson)			Experimental coordinates (this work)			Calculated coordinates			Calculated			Building block						Δd (Å)		
Atomic position	x	y	z	x	y	z	x	y	z	t_1	t_2	t_3	symbol	n	U	x_0	y_0	z_0	(Samson)	(this work)	Occupancy
Cd(1) in 192(i)	0·145	0·213	0·421	0·1456	0·2137	0·4207	0·1477	0·2159	0·4205	$\bar{9}$	$\bar{3}$	15	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·1120	0·0431	100% Cd
Cd(2) in 96(h)	0·125	−0·012	0·262	0·1250	0·0117	0·2617	0·1250	−0·0114	0·2614	11	$\bar{1}$	23	(4, 3, 1)	22	U_1	0	0	0	0·0259	0·0130	100% Cd
										$\overline{11}$	$\overline{23}$	1	−(4, 3, 1)		U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$			
Cd(3) in 96(g)	0·146	0·146	0·218	0·1463	0·1463	0·2176	0·1477	0·1477	0·2159	$\bar{9}$	$\bar{9}$	$\bar{3}$	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0976	0·0673	100% Cd
Cd(4) in 96(g)	0·216	0·216	0·488	0·2170	0·2170	0·4877	0·2159	0·2159	0·4886	$\bar{3}$	$\bar{3}$	21	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0188	0·0549	100% Cd
Cd(5) in 32(e)	0·216	0·216	0·216	0·2155	0·2155	0·2155	0·2159	0·2159	0·2159	$\bar{3}$	$\bar{3}$	$\bar{3}$	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0053	0·0212	100% Cd
Cd(6) in 16(c)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	$\overline{11}$	$\overline{11}$	$\overline{11}$	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0	0	100% Cd
										11	11	11	(4, 3, 1)	22	U_1	0	0	0			
Cd(7) in 32(e)	0·378	0·378	0·378	0·3799	0·3799	0·3799	0·3864	0·3864	0·3864	12	12	12	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·4446	0·2646	78% Cd, 22% Na
Na(1) in 32(e)	0·318	0·318	0·318	0·3149	0·3149	0·3149	0·3181	0·3181	0·3181	6	6	6	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0053	0·1693	100% Na
Na(2) in 96(g)	0·044	0·044	0·316	0·0431	0·0431	0·3160	0·0454	0·0454	0·3182	$\overline{18}$	$\overline{18}$	6	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0904	0·1200	14% Cd, 86% Na
Na(3) in 96(g)	0·064	0·064	0·203	0·0698	0·0698	0·2037	0·0681	0·0681	0·2045	6	6	18	(4, 3, 1)	22	U_1	0	0	0	0·1830	0·0774	100% Na
Na(4) in 48(f)	0·144	0	0	0·1364	0	0	0·1364	0	0	$\overline{10}$	22	22	−(4, 3, 1)	22	U_2	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·2322	0	100% Na
										12	0	0	(4, 3, 1)	22	U_1	0	0	0			
Cd(8) in 96(g)	0·218	0·218	0·650	0·2174	0·2174	0·6498	0·2159	0·2159	0·6477	$\bar{3}$	$\bar{3}$	$\bar{9}$	(3, 0)F	22	U_1	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0·1148	0·0912	57% Cd, 43% Na
Cd(9) in 32(e)	0·600	0·600	0·600	0·6033	0·6033	0·6033	0·6023	0·6023	0·6023	9	9	9	−(3, 0)F	22	U_2	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·1217	0·0529	50% Cd
Cd(10) in 96(g)	0·179	0·179	0·569	0·1805	0·1805	0·5687	0·1818	0·1818	0·5644	0	0	$\frac{31}{3}$									61% Cd, 39% Na
Na(5) in 8(b)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	0	(3, 0)F	22	U_1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	0	43% Cd, 57% Na
Na(6) in 96(g)	0·134	0·134	0·487	0·1382	0·1382	0·4884															18% Cd, 82% Na
Na(7) in 32(e)	0·439	0·439	0·439	0·4373	0·4373	0·4373	0·4318	0·4318	0·4318	$\bar{6}$	$\bar{6}$	$\bar{6}$	(3, 2)	22	U_1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·3811	0·2911	71% Cd, 29% Na

Cd(9) and Cd(10) are also shown in Fig. 2. Centered around $\frac{1}{4}\frac{1}{4}\frac{3}{4}$ [Na(5)] are 12 Cd(8) forming a regular Friauf polyhedron (blue), and bridging over the surface are Cd(10) (yellow balls) completing a hexagon (transparent). The corners of the hexagons (yellow balls) form a small cubic arrangement of atoms. The central position of this cube is split in two - this is Cd(9) (red balls) with 50% occupancy. In other words, the blue Friauf polyhedron is intergrown with a b.c.c. structure to form an interpenetrating network in the structure. The Cd(8) and Cd(9) atoms form a building block denoted (3, 0) in our matrix notation, as shown in our parallel paper (Yang & Andersson, 1987).

The rest of the sodium atoms, as well as some cadmium atoms, are distributed over positions given in Table 1, with disorder; this is in the channel space obvious in Fig. 1. The structure is zeolitic in its character, which is reflected in its properties; crystals react with air or moisture, and gradually decompose.

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Thermal Vibration in CsSCN Below the Structural Phase Transition at 470 K*

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Abstract

Caesium thiocyanate undergoes a phase transition at $T_c \simeq 470$ K from an orthorhombic (*Pnma*) form to a cubic modification. Single-crystal neutron diffraction data have been obtained for CsSCN within the range 300 to 441 K and, together with reported data at 453 K, are analysed to study thermal motion in the crystal preceding the onset of the phase transition. For the SCN$^-$ ions, the data are consistent with large rigid-body translations and librations, with only small contributions from internal modes. From 440 K to T_c, the SCN$^-$ ions exhibit enhanced amplitudes of translational and librational motion; the Cs$^+$ ions exhibit a concomitant anomalous increase in vibrational amplitudes. This behaviour is highly anharmonic and is indicative of the onset of the phase transition at 470 K. The mechanism suggested for the phase transition involves a sudden rearrangement of all the ions at T_c. This is in contrast with KSCN, in which the phase transition arises purely by rotational disordering of the SCN$^-$ ions.

Introduction

The thermal vibrational behaviour of solids in the vicinity of structural phase transitions may contain information on the nature of the phase transition. Presently there is a lack of both theoretical and experimental evidence on the temperature dependence of the thermal parameters obtained by Bragg diffraction from phase-transforming materials. Accurate experimental results are particularly scarce for the extended temperature region below phase transitions ($T < T_c$). See, however, the results of Lander, Brown & Faber (1982) on Cu$_3$Au. Temperature-dependent data above

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