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# Structure of $NaCd_2$: An Alternative Path to a Trial Structure

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## Abstract

A new derivation of a trial structure of the $NaCd_2$ compound is described. It is based on the application of the stochastic method in a form which is particularly useful in the derivation of trial structures of intermetallic compounds of high crystal symmetry for which the radius ratios of the component metals are of the appropriate magnitudes. In this form the initial assumption is made that the structure is tetrahedrally close-packed and that the coordination polyhedra are all the usual with coordination numbers 12, 14, 15 and 16, respectively. These restrictions are first invoked in the search for the correct structural arrangements along the symmetry axes. Only those arrangements are considered which have small packing strains along these axes when calculated using the metallic radii for coordination number 12.

## 1. Introduction

In his determination of the crystal structure of the $NaCd_2$ compound, Samson (1962) arrived at a trial structure with the space group $Fd\bar{3}m$, with $a = 30.56$ Å, and 1192 atoms in the unit cell. He arrived at this structure relying on a new method he developed in which the Friauf polyhedron plays a dominant role. Yang, Andersson & Stenberg (1987) undertook a determination of the structure using an entirely different method developed by Yang & Andersson (1987). They arrived at the same trial structure which they referred to as the 'ordered part' of the structure. Their method, although entirely different, also utilizes the Friauf polyhedron in developing the trial structure.

In this paper yet another method of finding a trial structure and its application to the $NaCd_2$ compound are described. The resulting trial structure confirms the results of the previous investigators with respect to the atomic coordinates, but not in every case with respect to the type of atom in the different positions.

The method is a form of the stochastic method which has been used by Pauling (1955) with great success in the determination of many crystal structures. The stochastic method works best for crystals of high symmetry, especially cubic crystals. In the form used in this investigation, its application is restricted to a certain class of structures, but this restriction also makes the method more powerful.

## 2. The method

The method employed is based on the assumption that the structure is tetrahedrally close-packed (t.c.p.; Shoemaker & Shoemaker, 1988) and that each coordination polyhedron is one of the 'normal' coordination polyhedra with coordination numbers (CN) 12 (icosahedron), 14, 15 and 16 (Friauf polyhedron), respectively (Frank & Kasper, 1958, 1959). Before the method can be employed, the unit cell, space group and metallic radii must be known. Diffraction intensities are not needed.

Ideally the metallic radii should be those for the actual coordination numbers of the different atoms, but these numbers are not known initially. In their absence the radii for coordination number 12 may be used. The Pauling radii for ligancy 12 (Pauling, 1960) were used in the determination reported in this paper.

The structure is usually most easily determined if the atomic arrangements on and in the immediate vicinity of the symmetry axes are first determined. The location of an atom on such an axis is fully described by just one parameter. Along such an axis there is a sequence of single atoms and groups of atoms. For example, on a threefold rotation axis these groups must be triads and on a twofold rotation axis they must be dyads, and the atoms in each of these groups must be in contact with each other in order for the structure to be t.c.p. The problem is to find the correct sequence of single atoms and such groups subject to the restrictions imposed by the atomic radii and by the geometry of the coordination polyhedra of the atoms located on the axis. These restrictions are often severe and greatly reduce the number of arrangements that need be considered. A useful criterion is the packing strain along the axis. The correct arrangement typically has a packing strain of only a few per cent. Once the correct arrangement has been found, the coordination polyhedra of all the atoms located on the axis are also known. The approximate coordinates of several more atoms can therefore be calculated. The coordinates of the remaining atoms in the unit cell, if any, are then often easy to determine.

It should be noted that in certain cases there is more than one possible orientation of a polyhedron about a symmetry axis. This is the case when two Friauf polyhedra share a hexagonal face. Such uncertainty does not occur in the structure determination described here.

It is possible that more than one arrangement have acceptably small packing strains. That with the smallest

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strain is then likely to be correct, but if the strains are all very small, the selection of the correct arrangement may have to await the determination of other parts of the structure. The different parts must fit together.

Success in the use of the method can be expected only when all the interstices in the structure are tetrahedral and the coordination polyhedra are all of normal type. The method may, however, also be useful in the determination of structures in which a few of the coordination polyhedra are not of normal type and in which the tetrahedra are quite distorted. In these cases, when the inevitable impasse is encountered in the use of the method, the determination can still be completed without much difficulty by first completing the parts which are well behaved. Completion would require the acceptance of coordination polyhedra other than the normal ones in the trial structure. Some bond lengths may then be abnormal.

## 3. Determination of the trial structure

As already mentioned, Pauling's CN 12 radii were used in the calculation of strain along the symmetry axes. They are 1.896 and 1.508 Å for sodium and cadmium, respectively.

The following can thus be stated with reference to the atomic arrangement at the points $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$:

(1) If an atom is located at one of these points, then it must have a CN 16 coordination polyhedron and it can be assumed to be a Na atom. It can also be assumed that the equivalent 12 of the 16 atoms described by the polyhedron are Cd atoms. There are two possible orientations of the polyhedron differing by a rotation of 90° about the $z$ axis.

(2) If one of these points is not occupied by an atom, then it must be the centroid of a tetrahedral group of four atoms, which can be assumed to be Cd atoms. The possibility that they are Na atoms is rejected as poor packing efficiency cannot be avoided when Cd or Na atoms are added to such a tetrahedron (achieving close-packing of regular tetrahedra about a central tetrahedron of the same size is fraught with the same difficulty as achieving close-packing of spheres about a central sphere of the same size). There are two possible orientations of the tetrahedron differing by a rotation of 90° about the $z$ axis.

(3) It is very unlikely that the core groups of atoms at $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are of the same type (both tetrahedral groups of Cd atoms or both Na atoms with CN 16 coordination polyhedra). It can, therefore, be assumed that one of the positions is occupied by four Cd atoms in a tetrahedral group and the other by a sodium atom with a CN 16 coordination polyhedron.

The following can be stated about the coordination polyhedra of atoms located at *other* points:

(1) If an atom has a CN 16 coordination polyhedron, it can be assumed to be a Na atom.

(2) If an atom has a CN 15 coordination polyhedron, it is most likely a Na atom.

(3) If an atom has a CN 12 coordination polyhedron, it can be assumed to be a Cd atom unless all, or almost all, atoms in the coordination shell are Na atoms.

### 3.1. *The arrangement along the threefold rotation axis*

There are centers of symmetry at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ and $(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$. The arrangement along the axis must be a string of single atoms and triads of atoms with the centroids of the triads on the axis. In these triads the atoms are in contact with each other. It is immediately clear that:

(1) Two triads cannot be located next to each other.

(2) A triad cannot be located at a center of symmetry.

(3) The coordination polyhedron of an atom located on the axis must have a threefold axis coinciding with the axis.

(4) If an atom is located at a center of symmetry, then its nearest neighbors must be triads and its coordination polyhedron must be a CN 12 polyhedron.

3.1.1. *The segments* $(0,0,0)$–$(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ *and* $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$–$(\frac{5}{8}, \frac{5}{8}, \frac{5}{8})$. The length of these segments is 6.62 Å. Since this distance is very short (only about two atom diameters), the number of atomic arrangements that needs to be considered is small. A cadmium tetrahedron can arbitrarily be placed at $(0, 0, 0)$. There are two possible orientations differing by a rotation of 90°. Both must be considered. The arrangement along the segment $(0, 0, 0)$–$(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ with the smallest strain is then found to be the following:

Tetrahedron at $(0, 0, 0)$–triad–single atom at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$.

All atoms are Cd atoms. The strain is 2.4% (compression). The coordination polyhedron of the single atom must then be a CN 12 polyhedron, but its orientation about the threefold axis cannot be determined until the coordination polyhedron of the atoms in the tetrahedral group has been determined. This polyhedron can be assumed to be an icosahedron since the atoms in the tetrahedral group are Cd atoms (if these atoms were Na atoms, the polyhedron could be a CN 15 polyhedron as explained earlier). The coordinates and types of atom in three different crystallographic positions are now known and are those shown for point sets $A$, $B$ and $C$ in Table 1. Completion of the icosahedron centered about the single atom then leads to the approximate coordinates of the point set $K$ in Table 1.

In the arrangement with the second smallest strain the triad consists of Na atoms. The strain is 6.7% (compression). Also, a central Cd atom with an icosahedral coordination shell in which at least six atoms are Na atoms is a highly unlikely arrangement. It is rejected.

A Friauf polyhedron must then be placed at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The central Na atom is in point set $D$ in Table 1. Both possible orientations must be considered. The only

Table 1. *Trial structure parameters*

The space group (No. 227) is $Fd\bar{3}m$ (Hahn, 1995); center of symmetry at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$.

| | Point set | | $x$ | $y$ | $z$ | Occupancy |
|---|---|---|---|---|---|---|
| *A* | 32(*e*) | *xxx* | 0.034 | | | Cd* |
| *B* | 96(*g*) | *xxz* | 0.104 | | 0.034 | Cd* |
| *C* | 16(*c*) | $\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$ | 0.125 | | | Cd* |
| *D* | 8(*b*) | $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ | 0.500 | | | Na* |
| *E* | 96(*g*) | *xxz* | 0.531 | | 0.600 | Cd* |
| *F* | 32(*e*) | *xxx* | 0.598 | | | Cd* |
| *G* | 32(*e*) | *xxx* | 0.312 | | | Na* |
| *H* | 32(*e*) | *xxx* | 0.380 | | | Cd* |
| *I* | 32(*e*) | *xxx* | 0.435 | | | Cd* |
| *J* | 48(*f*) | *x*00 | 0.134 | | | Na* |
| *K* | 96(*g*) | *xxz* | 0.07 | | 0.20 | Na |
| *L* | 96(*g*) | *xxz* | 0.63 | | 0.50 | Na |
| *M* | 96(*g*) | *xxz* | 0.044 | | 0.313 | Na* |
| *N* | 192(*i*) | *xyz* | 0.15 | 0.20 | 0.43 | Cd |
| *O* | 96(*h*) | $\frac{1}{8}, y, \frac{1}{4} - y$ | | −0.01 | | Cd |
| *P* | 96(*g*) | *xxz* | 0.216 | | 0.484 | Cd* |
| *Q* | 96(*g*) | *xxz* | 0.18 | | 0.57 | Cd |

* Data for best arrangements along the line segments and therefore probably of highest reliability. There are 1192 atoms in the unit cell. The composition of this trial structure is given by the formula $NaCd_{2.17}$.

acceptable arrangement is then found to be the following:

Single atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$–triad–single atom–center of symmetry.

The center of symmetry is vacant. Both the single atom next to it and the triad consist of Cd atoms. The strain is 4.2% (compression). The coordinates and types of atoms in two more crystallographic positions are now known and are those shown for point sets *E* and *F* in Table 1.

In the arrangement with the second smallest strain the single atom is sodium and the strain is 17% and must be rejected.

It is, however, seen that since the single atom has a single atom (an atom in set F on the other side of the center of symmetry) and a triad (atoms in set *E*) as nearest neighbors, its coordination polyhedron, if it is normal, should be of the CN 16 type. If so, the atom should be a Na not a Cd atom. However, this leads to the arrangement which was rejected because of the large packing strain. Due to this impasse it may be concluded that the polyhedron is not of the Friauf type; nor can it be one of the other 'normal' ones. The atoms in set *F* may then be Cd atoms, as shown in Table 1. A more acceptable explanation cannot be found. The actual coordination polyhedron of atoms *F* will reveal itself as the structure determination proceeds.

3.1.2. *The line segment* $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$–$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This line segment is twice as long as the previous two, but since the configurations are already known at both ends, the number of atomic arrangements that need to be considered is again small. There are two arrangements with very small strain amounting to 0.0 and 1.0% (both compression), respectively. They must both be considered, but it turns out that the first does not lead to a structure with acceptable packing. The second arrangement presents no difficulties:

Tetrahedron at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$–single atom–single atom–single atom–single atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

The three single atoms following the tetrahedron are sodium, cadmium and cadmium, respectively, as shown for point sets *G*, *H* and *I* in Table 1, which also shows the coordinates. The coordination polyhedra are of the CN 16, CN 14 and CN 14 types, respectively.

The rejected arrangement is the same except that the atoms in set *I* are Na atoms and the single atoms in set *H* are replaced by triads of Cd atoms.

The strain is 7.1% (compression) for the arrangement with the third smallest strain. It is rejected.

Completion of the coordination polyhedra of the atoms in sets *G*, *H* and *I* leads to the approximate coordinates of the atoms in point sets *J*, *N*, *L* and *M* in Table 1.

### 3.2. *The arrangement along the fourfold inversion axis*

The arrangement along the fourfold inversion axis must be a string of single atoms and dyads. The centroids of the dyads are located on the axis with the atoms in each dyad in contact with each other and the dyad axes are perpendicular to the axis. The dyads can have two different orientations differing by a rotation of 90°.

It is then clear that:

(1) When two dyads are next to each other, they cannot be in the same orientation.

(2) If an atom has two dyads as nearest neighbors and the dyads are in the same orientation, then its coordination polyhedron is a CN 12 polyhedron. If the dyads are not in the same orientation, the polyhedron is a CN 16 polyhedron and the atom can be assumed to be a Na atom.

3.2.1. *The line segment* $(0,0,0)$–$(0, 0, \frac{1}{2})$. The length of the line segment is 15.28 Å. The number of arrangements that need be considered is small, because the arrangements of the atoms are known at both ends of the segment. Furthermore, the approximate coordinates of the atoms in set *M* are also known (pairs of atoms in this set form dyads). The only arrangement that need be considered is the following:

Tetrahedron at (0, 0, 0)–single atom–dyad–dyad–dyad–single atom at $(0, 0, \frac{1}{2})$.

Types of atoms and coordinates are those shown for point sets *A*, *J*, *P*, *M*, *E* and *D* in Table 1. The strain is 1.8% (stretching). Only point set *P* is new.

Coordinates and the types of atoms have now been determined for one more point set (*P*). In addition, the type of atom in point set *M* has been determined and the coordinates of the set calculated with smaller errors. Also, the atoms in point set *Q* are immediately found by inspection (the dyads in sets *E*, *M* and *P* determine the positions of the atoms in set *Q*). The atoms in set *J* have CN 16 coordination polyhedra.

Approximate coordinates are now known for 16 point sets. The coordination polyhedra of all atoms located on the investigated line segments are also known, except that of atoms in set *F* about which, as explained above, there is uncertainty. It turns out, however, that when the coordinates of the atoms in sets *L* and *Q* have been found, the coordination polyhedron of the atoms in set *F* is also completely described. It is not one of the four normal coordination polyhedra; it can be described as an icosahedron which has been modified to accommodate one more atom on the threefold axis. The coordination number then becomes 13. The new polyhedron has three corners at which four edges come together, four at which six edges come together and six at which five edges come together.

Finally, inspection of the atomic arrangement obtained in this way reveals voids that can be filled with the atoms in the point set labeled *O* in Table 1.

The determination of the trial structure is then complete. It agrees with the trial structure of Yang, Andersson & Stenberg (1987), described in Table 2, with one exception: in their investigation the atoms in set *I* were found to be sodium, not cadmium. It is, however, interesting that in their refined disordered structure these atoms are 71% cadmium. The trial structure also agrees completely with the ordered part of the refined structure of Yang, Andersson & Stenberg (1987). The agreement with the disordered part for sets other than *I* is also qualitative. In Samson's (1962) structure the atoms in set *I* are mostly sodium. Samson did not refine his structure.

It is not surprising that in the refined structure of Yang, Andersson & Stenberg (1987) the atoms in sets *H* and *I* are only 78 and 71% cadmium, respectively. For both sets the coordination number is 14. In a disordered structure partial occupancy by sodium can then be expected. That the set *D* is not 100% sodium is more surprising.

Table 2. *Refined structure parameters (Yang, Andersson & Stenberg, 1987)*

| | Point set | | *x* | *y* | *z* | Occupancy (%) |
|---|---|---|---|---|---|---|
| *A* | 32(*e*) | *xxx* | 0.0345 | | | 100 Cd |
| *B* | 96(*g*) | *xxz* | 0.1037 | | 0.0324 | 100 Cd |
| *C* | 16(*c*) | $\frac{1}{8},\frac{1}{8},\frac{1}{8}$ | 0.1250 | | | 100 Cd |
| *D* | 8(*b*) | $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ | 0.5000 | | | 43 Cd, 57 Na |
| *E* | 96(*g*) | *xxz* | 0.5326 | | 0.6002 | 57 Cd, 43 Na |
| *F* | 32(*e*) | *xxx* | 0.6033 | | | 50 Cd |
| *G* | 32(*e*) | *xxx* | 0.3149 | | | 100 Na |
| *H* | 32(*e*) | *xxx* | 0.3799 | | | 78 Cd, 22 Na |
| *I* | 32(*e*) | *xxx* | 0.4373 | | | 71 Cd, 29 Na |
| *J* | 48(*f*) | *x*00 | 0.1364 | | | 100 Na |
| *K* | 96(*g*) | *xxz* | 0.0698 | | 0.2037 | 100 Na |
| *L* | 96(*g*) | *xxz* | 0.6382 | | 0.4884 | 18 Cd, 82 Na |
| *M* | 96(*g*) | *xxz* | 0.0431 | | 0.3160 | 14 Cd, 86 Na |
| *N* | 192(*i*) | *xyz* | 0.1456 | 0.2137 | 0.4207 | 100 Cd |
| *O* | 96(*h*) | $\frac{1}{8}, y, \frac{1}{4}-y$ | | 0.0117 | | 100 Cd |
| *P* | 96(*g*) | *xxz* | 0.2170 | | 0.4877 | 100 Cd |
| *Q* | 96(*g*) | *xxz* | 0.1805 | | 0.5687 | 61 Cd, 39 Na |

## 4. Discussion of the trial structure

The structure can be described relatively simply. In the space group $Fd\bar{3}m$ there are two sets of diamond positions: one set at (0, 0, 0) *etc.* and a second set at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) *etc.* The 16 points in these two sets form a body-centered cubic (b.c.c.) lattice. One can therefore imagine the unit cube consisting of 16 cubo-octahedra, eight of which contain atom arrangements of one type and the other eight arrangements of a second type. It is simple to describe these arrangements.

The first type has a core consisting of a central atom (point set *D*) surrounded by a first shell of 16 atoms (point sets *E* and *I*) at the corners of a CN 16 polyhedron. The CN 16 polyhedron has 28 triangular faces. An atom is located out from each of these faces (point sets *L*, *M* and *F*). Out from the centers of the six rings formed by atoms in point sets *L* and *M* are located four atoms (point set *H*). They are arranged tetrahedrally and are located near the centers of four of the hexagonal faces of the cubo-octahedron. The second shell is completed when 12 more atoms (point set *Q*) have been placed out from the triangles defined by the atoms in sets *E* and *M*. The atoms in set *O*, which are located near the corners of the cubo-octahedra, complete the arrangement. They may be considered as the beginning of a third coordination shell. All interstices are tetrahedral. There are 73 atoms in the arrangement.

The arrangement of the second type does not have a single atom at its center and can therefore not be described similarly in terms of successive shells. At the center are four atoms (point set *A*) in a tetrahedral arrangement, followed by four atoms (point set *G*) also in a tetrahedral arrangement, but rotated 90° with respect to the first, followed by six atoms (point set *J*) in an octahedral arrangement. This group of atoms has 12 pockets in which 12 atoms (point set *B*) can be placed. On the outside of the resulting group 40 atoms can be placed, 24 in six-rings (point set *N*) near four of the eight hexagonal faces of the cubo-octahedron, 12 in four groups of three (set *K*) in triangular arrangements near the other four hexagonal faces and four (point set *C*) in a tetrahedral arrangement, each at the center of these faces. These four atoms are at centers of symmetry and shared by neighboring cubo-octahedra. Finally, a set of 12 atoms (point set *P*) near the square faces of the cubo-octahedron completes the cluster. All interstices are tetrahedral. There are 76 atoms in the cluster. The total number of atoms in the unit cell is then 1192.

The fact that the structure can be described quite simply in terms of cubo-octahedra containing atomic arrangements of two different types, both having only tetrahedral interstices, suggests that the structure could also have been found by starting with the two types of core groups – four Cd atoms in tetrahedral arrangement and a Na atom with a CN 16 coordination polyhedron, respectively – and by then adding atoms, observing tetrahedral close-packing, until the clusters met. This is undoubtedly the case, but the form of the stochastic method used here leads more directly to the correct structure.

## 5. Comments

The use of Pauling's CN 12 radii in the calculation of the strain in the structure may be questioned. A CN number between 13 and 14 would be ideal, but the effect on the calculated strain would be too small to be important.

A small error was made in the strain calculation when it was assumed that the Na atom at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ was in contact with the surrounding 12 Cd atoms. The Na atom is slightly too small for this to be the case.

The assumption that the atoms in the triads and in the dyads are in contact with each other is also an approximation.

It seems reasonable to expect that the method used here will often be found useful in the determination of t.c.p. structures, in particular those of high symmetry. It has, for example, also been shown that the crystal structures of the *T* phase, the sigma phase and the *R* phase could have been determined by its use. It is clearly more difficult to use the method when not all the coordination polyhedra are normal, but the success in the work reported in this paper suggests that the difficulties can often be overcome quite easily.

It is interesting that the trial structure was obtained without using any information about the chemical composition of the compound. The calculated formula is $NaCd_{2.17}$. Chemical analysis yielded a composition in the range $NaCd_{1.99\text{-}2.12}$ according to Samson (1962). It is therefore tempting to conclude that the structure is ordered, but the results obtained by Yang and co-workers (Yang & Andersson, 1987; Yang, Andersson & Stenberg, 1987) show that this can hardly be the case. After refinement they obtained an *R* factor of 0.12. One can perhaps say that there is a strong tendency towards order. The considerable difference in metallic radii of the two metals certainly made order seem more likely than disorder until evidence to the contrary had been found. Samson's *R* factor was 0.23 for his disordered structure. His disorder parameters are quite different, probably because he never refined his structure.

### References

Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184–190.

Frank, F. C. & Kasper, J. S. (1959). *Acta Cryst.* **12**, 483–499.

Hahn, T. (1995). Editor. *International Tables for Crystallography*, Vol. A, Fourth, revised ed. Dordrecht: Kluwer Academic Publishers.

Pauling, L. (1955). *Am. Sci.* **43**, 285–297.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 403. Ithaca: Cornell University Press.

Samson, S. (1962). *Nature* (*London*), **195**, 259–262.

Shoemaker, D. P. & Shoemaker, C. B. (1988). *Aperiodicity and Order*. New York: Academic Press.

Yang, Q. B. & Andersson, S. (1987). *Acta Cryst.* **B43**, 1–14.

Yang, Q. B., Andersson, S. & Stenberg, L. (1987). *Acta Cryst.* **B43**, 14–16.