

## The Sigma Phase Revisited: an Alternative Path to a Trial Structure

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### Abstract

A new derivation of a trial structure of the sigma phase is described. It is based on the stochastic method in a form which is particularly useful in the derivation of trial structures of high symmetry, provided that the radii of the component metals are of the appropriate relative magnitudes. In this form the initial assumption is made that the structure is tetrahedrally close-packed and that the coordination polyhedra are normal 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

The crystal structure of the sigma phase has tetragonal symmetry with the space group  $P4_2/mnm$ . The structure is tetrahedrally close-packed and the coordination polyhedra are all of the 'normal' type with coordination numbers 12, 14 and 15 (Bergman & Shoemaker, 1954). The polyhedron with coordination number 16 is not utilized. It should, therefore, be possible to derive a trial structure using the method recently described by Bergman and used by him in the derivation of a trial structure of the  $\text{NaCd}_2$  compound (Bergman, 1996). The method is very simple and will now be described.

The initial assumption is made that the structure is tetrahedrally close-packed and that the coordination polyhedra are all of the normal type with coordination number 12, 14, 15 or 16 (Frank & Kasper, 1958, 1959). The radius ratios of the component metals must, of course, be in the appropriate range. The metallic radii for coordination number 12 may be used.

The structure determination begins with the search for the correct structural arrangement along one of the symmetry axes. This arrangement is usually that with the smallest packing strain along the axis. The choice of symmetry axis should be such as to exploit other symmetry elements as much as possible. A good choice is an axis which is perpendicular to a mirror plane or lies in a mirror plane, or, better still, both. The trial structure can sometimes be completed without much difficulty when only one of the symmetry axes is

investigated in this way. This was the case in the structure determination reported here. A corresponding investigation of a second, possibly even a third, axis may, however, often be necessary. When the structural arrangements along the symmetry axes have been found, it is often quite simple to find the locations of the remaining atoms in the unit cell.

The unit-cell dimensions and the space group must be known. When there is more than one possible space group, the correct one can be selected with considerable confidence in a manner to be described later.

As will be shown in this paper, the correct trial structure of the sigma phase can be derived with great ease using this method. As the structure is relatively simple, the method is not put to a very severe test. Its successful application to the problem of the much more complicated  $\text{NaCd}_2$  structure (Bergman, 1996) is, therefore, far more significant. This application is also more instructive in its use. The method is described in considerable detail in the referenced paper on the  $\text{NaCd}_2$  structure. The ease with which the trial structure of the sigma phase can be found with the use of this method is, however, also evidence of its usefulness.

### 2. Determination of the trial structure

The unit-cell dimensions used in this determination are those of the sigma phase with a composition given approximately by the composition  $\text{Fe}_8\text{Cr}_7$  (Bergman & Shoemaker, 1954),

$$a = 8.7995, c = 4.5442 \text{ \AA}.$$

The metallic radii for coordination number 12 are 1.26 and 1.28 Å for iron and chromium, respectively (Pauling, 1960). Because the radii are so similar, the weighted average of 1.27 Å can be used. The trial structure cannot then differentiate between the two types of atoms in the different crystallographic positions.

The space groups requiring consideration are  $P4_2/mnm$ ,  $P4_2nm$  and  $P4n2$  (Bergman & Shoemaker, 1954). Of these, the first is the most likely and is assumed to be correct. This matter will be discussed further in a later section.

In space group  $P4_2/mnm$  there is a twofold rotation axis along the  $c$  axis at  $(0, 0, z)$  and a  $4_2$  axis at  $(0, \frac{1}{2}, z)$

(Hahn, 1995). The search for a trial structure is more efficient if it begins with the determination of the atomic arrangement along the twofold axis, because there are two diagonal mirror planes through  $(0, 0, z)$  which restrict the possible orientations of all coordination polyhedra which have their centers on the axis.

### 2.1. The arrangement along the twofold rotation axis

The arrangement along the twofold rotation axis must be a string of single atoms and dyads of atoms. The centroids of the dyads are located on the axis with the atoms in each dyad in contact with each other. The dyad axes are perpendicular to the twofold axis. The dyads can have two orientations differing by a rotation of  $90^\circ$ . Each dyad must be located on one of the mirror planes through  $(0, 0, z)$ .

It is readily seen that, with the given  $c$  dimension of the unit cell, the best packing along the axis is obtained when single atoms alternate with dyads. The packing strain is 3.2% (stretching). A single atom may then be placed either at  $(0, 0, 0)$  or at  $(0, 0, \frac{1}{2})$ . All other  $z$  coordinates can be rejected, because there are also mirror planes coinciding with and parallel to the  $xy$  plane through the points  $(0, 0, 0)$  and  $(0, 0, \frac{1}{2})$ , respectively. The first position is arbitrarily chosen. The corresponding point set is labeled *A* in Table 1. A dyad will then be located with its centroid at  $(0, 0, \frac{1}{2})$ . The corresponding point set is labeled *B* in Table 1 and all the dyads are then in the same rotational orientation about the axis. All of them could also be rotated  $90^\circ$  about the axis, but this would not lead to a different structural arrangement. The coordinates of point set *B* could also have been given as  $(x, -x, \frac{1}{2})$  with  $x$  equal to 0.102.

### 2.2. The location of the remaining atoms in the unit cell

The atoms in set *A* are located at points which have symmetry  $mmm$ . Its coordination polyhedron must then be of the coordination number 12 type (icosahedron), because among the four coordination polyhedra only this polyhedron has three mirror planes at right angles to each other. When the polyhedron is completed, the approximate coordinates of two more point sets are obtained. These sets are shown as point sets *D* and *E* in Table 1. The  $z$  coordinate of point set *E* must be approximately  $\frac{1}{4}$ , because there is compressional strain (11.8%) along the straight lines parallel to the  $z$  axis through the atoms in this set.

When the corresponding group of atoms centered at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , which is rotated  $90^\circ$  about the  $z$  axis, is completed, the arrangement becomes as shown in Fig. 1. On examination of Fig. 1 it is seen that ten of the atoms in the coordination shell of the atoms in set *E* are already in place. Four of them are in the plane  $z = 0$  and four in the plane  $z = \frac{1}{2}$ . The shell can be completed by adding two atoms in each of these two planes. Two six-

Table 1. Trial structure parameters

The space group (no. 136) is  $P4_2/mmm$  (Hahn, 1995). Refined structure parameters (Bergman & Shoemaker, 1954) are shown in parentheses.

Point set	$x$	$y$	$z$
<i>A</i> 2( <i>a</i> )	0, 0, 0		
<i>B</i> 4( <i>f</i> )	$x, x, 0$	0.398 (0.3981)	
<i>C</i> 8( <i>i</i> )	$x, y, 0$	0.483 (0.4632)	0.129 (0.1316)
<i>D</i> 8( <i>i</i> )	$x, y, 0$	0.721 (0.7376)	0.075 (0.0653)
<i>E</i> 8( <i>j</i> )	$x, x, z$	0.177 (0.1823)	0.250 (0.2524)

atom rings, one in each plane, are then formed and the shell becomes a coordination number 14 shell (shells with coordination number 12, 15 and 16 cannot be accommodated). When the shell is completed, the approximate coordinates of the atoms in set *C* of Table 1 are found. This completes the trial structure.

Here, it should be noted that since the symmetry of the points in set *E* is  $m$ , and all the four coordination polyhedra have a mirror plane, they are all candidate coordination polyhedra, even when deformed (with preservation of the mirror plane), unless it can be shown that one or more must be rejected because of spacial restrictions imposed by atoms already placed (atoms in sets *A*, *B*, *D* and *E*).

### 3. Discussion

The trial structure agrees quite well with the refined structure (Bergman & Shoemaker, 1954) and can, therefore, be used as a starting point for a refinement. As was mentioned by Bergman (1996) in an earlier

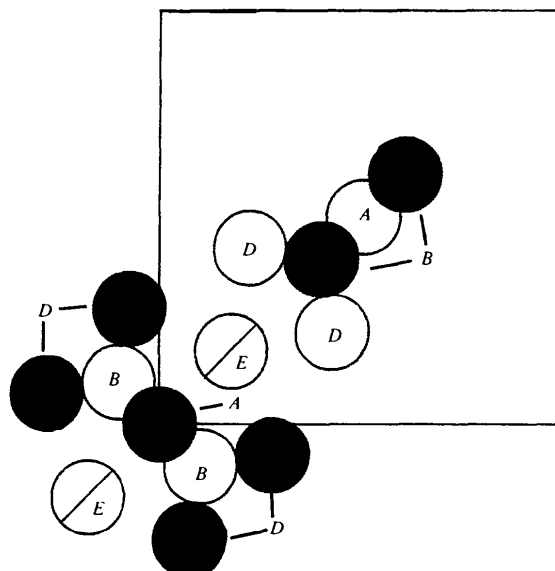


Fig. 1. Arrangement after completion of icosahedra. Filled circles: atoms in the planes  $z = 0, 1, \dots$ ; open circles: atoms in the planes  $z = \frac{1}{2}, \dots$ ; slashed circles: atoms near the planes  $z = \frac{1}{4}, \frac{3}{4}, \dots$ . Partial projection of the unit cell on  $(0, 0, 1)$ .

paper, the *T* phase and *R* phase structures could also have been obtained by the use of the same method. It is perhaps possible that several of the other now known tetrahedrally close-packed structures could have been found with less effort using this method.

The space group was assumed to be  $P4_2/mnm$  following the rule that among the possible space groups, the correct one has the largest number of points in the general position (the number of points is 16, 8 and 8, respectively, for the three possible space groups). In intermetallic compounds this rule seems to hold with

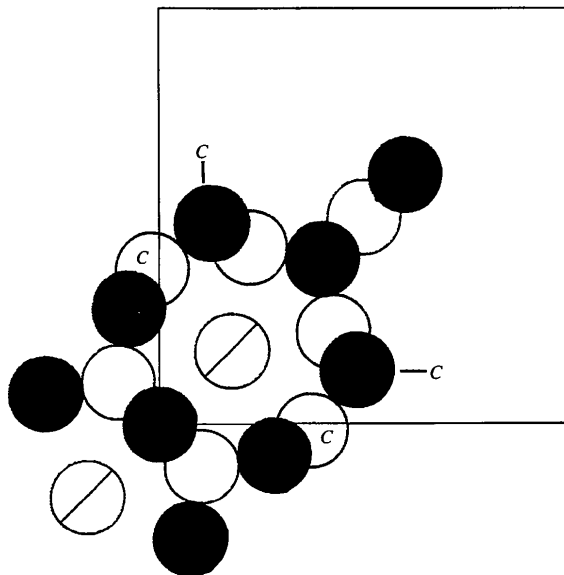


Fig. 2. The completed trial structure. Partial projection of the unit cell on (0, 0, 1).

few exceptions. That this is the case may simply be a reflection of the tendency of metals to form structures of high symmetry. This tendency is well known and has been discussed by Laves (1956). The work done by Yakel (1983) provides further evidence that the space group assumed in this investigation is the correct one.

It is interesting that among the 23 tetrahedrally close-packed structure types identified by Shoemaker & Shoemaker (1988) only two do not follow the rule discussed above and these two both contain silicon in the examples given. Silicon is not a metal and its crystal structure is of the diamond type. This may explain why the rule fails.

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