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On the Prediction of Order in the σ Phases on the Basis of a Sphere-Packing Model

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Abstract

A theory for the order in σ phases based on the sphere-packing model of Wilson & Spooner [*Acta Cryst.* (1973), A**29**, 342–352] has been examined using a mathematical analysis. The analysis suggests that the prediction of order in these phases based on lattice-constant variations associated with variations in atomic diameter should be treated with caution, particularly where the results are at variance with experimentally determined results.

1. Introduction

The ordering of the σ phases has been discussed in terms of two determining factors: electronic configuration, and size of the constituent atoms. Hansen & Raman (1970) have made a study of the electron concentration and variations in the lattice parameters with composition of binary and ternary phases. Wilson & Spooner (1973) have proposed a sphere-packing model in which the occupancy of each atomic site is described in terms of an average radius calculated according to the ordering determined or assumed for that particular site.

The sphere-packing model has been used for: (i) predicting lattice parameters and order; (ii) estimating the changes in lattice parameters produced by disordering after fast-neutron irradiation; (iii) explaining the lattice parameter changes due to varying composition in binary σ phases and to the addition of a third metal.

The aim of the present work is to examine the reliability of that model in predicting order; this was suggested by the following points:

1. The sphere-packing model needs to allow for a considerable distortion of the spheres occupying the E sites.*

2. The above assumption makes it reasonable to expect a marked preference of some type of atom for these E sites. This has been verified by the present authors in the structure refinement of σ phases. Since the E–E interatomic distances are directly related to the parameter c, one should expect this parameter to be particularly sensitive to the ordering at the E sites. This sensitivity should be significantly marked in the case of alloys where the constituent atoms have rather different metallic radii; this is the case for Mo_3Co_2 which is known to be ordered as a result of single-crystal analysis (Forsyth & Alte da Veiga, 1963). However, the values of c calculated on the basis of this sphere-packing model for the ordered and the disordered schemes, 4·815 and 4·847 Å respectively, show no significant difference, the deviation being of the order of the general agreement, 1%, between observed and calculated parameters (Wilson & Spooner, 1973, Table 2).

3. The σ phase Nb_2Al was studied by Brown & Forsyth (1961) using the X-ray single-crystal technique. The final F_o and $(F_o - F_c)$ Fourier projections clearly show that the structure is ordered; however, to support the theory, an order which is different from that experimentally determined has to be assumed.

The formulae derived by Wilson & Spooner (1973) are the starting points for the mathematical analysis carried out in the next sections.

2. Calculation of parameters *c* and *a*

The model creates the σ phase from three types of panel, each of which consists of spheres in contact; from these panels the estimates c_1, c_2 and c_3 are obtained and a final estimate, c_0, of the parameter c is given by the weighted mean:

$$c_0 = (c_1 + 4c_2 + 2c_3)/7, \qquad (1)$$

where

$$c_1 = 2(r_A + r_B)\cos\theta_1 \quad \text{and} \quad \sin\theta_1 = r_B/(r_A + r_B)$$

$$c_2 = (r_B + r_C + 2r_D)\cos\theta_2 \quad \text{and}$$

$$\sin\theta_2 = (r_B + r_C)/(r_B + r_C + 2r_D)$$

$$c_3 = 4r_E,$$

r_i (i stands for each of the five atomic sites A, B, C, D and E) being the radii of the spheres forming the panels.

* The notation used by Wilson & Spooner (1973) has been adopted throughout the present work.

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For a particular alloy, the r_i are derived from the metallic radii of the constituent atoms and the occupancy of the atomic sites.

If the structure is randomly disordered, it is assumed that the radii of all the atoms have the same average value, r, which is determined solely by the atomic percentage composition of the alloy. On this assumption the above formulae give for the estimated value of c, now denoted by c':

$$c' = 3{\cdot}6172r. \tag{2}$$

The increment, δc_0, of the value of the function $c_0 = f(r_i)$ for increments δr_i of the variables can be given, to first-order approximation, by Taylor's theorem:

$$\begin{aligned}\delta c_0 = {} & \tfrac{2}{7}(r_A + r_B)[r_A(r_A + 2r_B)^{-1/2}]\,\delta r_A \\ & + \tfrac{2}{7}\{r_A[r_A(r_A + 2r_B)]^{-1/2} \\ & + 2r_D[r_D(r_B + r_C + r_D)]^{-1/2}\}\,\delta r_B \\ & + \tfrac{4}{7}r_D[r_D(r_B + r_C + r_D)]^{-1/2}\delta r_C \\ & + \tfrac{4}{7}(r_B + r_C + 2r_D)[r_D(r_B + r_C + r_D)]^{-1/2}\delta r_D \\ & + \tfrac{8}{7}\delta r_E.\end{aligned} \tag{3}$$

The increment, $\delta c'$, of the value c' of the function for the randomly disordered structure is obtained from the expression of δc_0 considering that $r_A = \ldots = r_E = r$, and has the simpler expression:

$$\delta c' = \frac{2}{7\sqrt{3}}(2\delta r_A + 3\delta r_B + 2\delta r_C + 8\delta r_D) + \tfrac{8}{7}\delta r_E, \tag{4}$$

where $\delta r_i = r_i - r$ (i standing for A, ..., E) is a deviation from the random atomic radius at site i, thus giving a measure of some departure from random disorder, as r_i is the atomic radius for a particular ordering at site i. Then an estimate of c, now denoted by c_0', can be obtained from the estimated random value, c', by

$$c_0' = c' + \delta c'. \tag{5}$$

If we consider a binary alloy (X,Y), the radii of the constituent atoms being r_x and r_y, the increments δr_y may be calculated in terms of the number of atoms of each type occupying the different atomic sites. If n_x^i is the number of atoms of type X at site i (n_y^i having a similar meaning), then, for the σ phase structure:

$$\begin{aligned} & n_x^A + n_y^A = 2 \\ & n_x^B + n_y^B = 4 \\ & n_x^C + n_y^C = n_x^D + n_y^D = n_x^E + n_y^E = 8 \end{aligned} \tag{6}$$

and

$$\begin{aligned}\delta r_A = r_A - r & = \tfrac{1}{2}(n_x^A r_x + n_y^A r_y) - r \\ & = (r_y - r) + \tfrac{1}{2}n_x^A(r_x - r_y).\end{aligned} \tag{7}$$

Similar calculations for δr_B, ..., δr_E provide another way of writing the expression for $\delta c'$:

$$\begin{aligned}\delta c' = {} & \frac{1}{14\sqrt{3}}[(60 + 16\sqrt{3})(r_y - r) \\ & + (4n_x^A + 3n_x^B + n_x^C + 4n_x^D + 3{\cdot}46412n_x^E) \\ & \times (r_x - r_y)].\end{aligned} \tag{8}$$

The expressions for a_0 and a' are

$$a_0 = (a_1 + a_2 + a_3)/3, \tag{9}$$

where

$$\begin{aligned}a_1 = {} & 2(r_A + 2r_D + r_C)\cos(45 - \varphi) \\ & - 2r_B r_C/[\sqrt{2}(r_B + 2r_C)]\end{aligned}$$

and $\sin\varphi = r_D/(r_A + r_D)$

$$a_2 = \sqrt{2}r_B + [2r_B^2 + 16(r_C^2 + r_B r_C)]^{1/2}$$

$$a_3 = \sqrt{2}r_B + (2r_A^2 + 4r_A r_E)^{1/2} + (2r_B^2 + 4r_B r_E)^{1/2}$$

and

$$a' = 6{\cdot}9381r. \tag{10}$$

On the basis of considerations similar to those made for the parameter c, the following expressions may now be derived for the parameter a:

$$\begin{aligned}\delta a_0 = {} & \frac{\sqrt{2}}{3}\{[r_D + (r_A^2 + 2r_A r_D)^{1/2}](r_A + r_D)^{-1} \\ & + (r_A + 2r_D + r_C)(r_A^2 + 2r_A r_D)^{-1/2} \\ & - (r_A + 2r_D + r_C)[(r_A^2 + 2r_A r_D)^{1/2} + r_D] \\ & \times (r_A + r_D)^{-2} + (r_A^2 + 2r_A r_E)^{-1/2}(r_A + r_E)\}\,\delta r_A \\ & + \frac{\sqrt{2}}{3}\{-r_C(r_B + 2r_C)^{-1} + r_B r_C(r_B + 2r_C)^{-2} \\ & + 2 + (r_B + 4r_C)[r_B^2 + 8(r_C^2 + r_B r_C)]^{-1/2} \\ & + (r_B + r_E)(r_B^2 + 2r_B r_E)^{-1/2}\}\,\delta r_B \\ & + \frac{\sqrt{2}}{3}\{[r_D + (r_A^2 + 2r_A r_D)^{1/2}](r_A + r_D)^{-1} \\ & - r_B(r_B + 2r_C)^{-1} + 2r_B r_C(r_B + 2r_C)^{-2} \\ & + 4(2r_C + r_B)[r_B^2 + 8(r_C^2 + r_B r_C)]^{-1/2}\}\,\delta r_C \\ & + \frac{\sqrt{2}}{3}\{2[r_D + (r_A^2 + 2r_A r_D)^{1/2}](r_A + r_D)^{-1} \\ & + (r_A + r_C + 2r_D) \\ & \times [1 + (r_A^2 + 2r_A r_D)^{-1/2}](r_A + r_D)^{-1} \\ & - (r_A + r_C + 2r_D) \\ & \times [r_D + (r_A^2 + 2r_A r_D)^{1/2}](r_A + r_D)^{-2}\}\,\delta r_D \\ & + \frac{\sqrt{2}}{3}[r_A(r_A^2 + 2r_A r_E)^{-1/2} \\ & + r_B(r_B^2 + 2r_B r_E)^{-1/2}]\delta r_E\end{aligned} \tag{11}$$

$$
\begin{aligned}
\delta a' = \frac{\sqrt{2}}{3}&[(3\sqrt{3}/2 - 1/2)\delta r_A \\
&+ (16/9 + 2\sqrt{3}/3 + 5/\sqrt{17})\delta r_B \\
&+ (7/18 + \sqrt{3}/2 + 12/\sqrt{17})\delta r_C \\
&+ (2 + 2\sqrt{3}/3)\delta r_D + (2\sqrt{3}/3)\delta r_E \qquad (12)
\end{aligned}
$$

$$
\begin{aligned}
\delta a' = 6{\cdot}9381(r_y - r) &+ (0{\cdot}4945 n_x^A + 0{\cdot}4885 n_x^B \\
&+ 0{\cdot}2455 n_x^C + 0{\cdot}1859 n_x^D \\
&+ 0{\cdot}0680 n_x^E)(r_x - r_y) \qquad (13)
\end{aligned}
$$

$$a'_0 = a' + \delta a'. \qquad (14)$$

The second-order terms, $\delta^2 c'$ and $\delta^2 a'$ in (5) and (14), are

$$
\begin{aligned}
\delta^2 c' = (1/21\sqrt{3}r)(&-\delta^2 r_A + 2\delta r_A \delta r_B - 2\delta^2 r_B - \delta r_B \delta r_C \\
&+ 2\delta r_B \delta r_D - \delta^2 r_C + 4\delta r_C \delta r_D - 4\delta^2 r_D) \qquad (15)
\end{aligned}
$$

and

$$
\begin{aligned}
\delta^2 a' = (\sqrt{2}/3r)[&(1/2 - \sqrt{3}/2)\delta^2 r_A \\
&+ (4/27 - 8/17\sqrt{17} - \sqrt{3}/9)\delta^2 r_B \\
&+ (4/27 - 8/17\sqrt{17})\delta^2 r_C + (-2\sqrt{3}/9)\delta^2 r_D \\
&+ (-2\sqrt{3}/9)\delta^2 r_E + (\sqrt{3}/12 - 1/4)\delta r_A \delta r_C \\
&+ (11\sqrt{3}/36 - 1/4)\delta r_A \delta r_D + (\sqrt{3}/9)\delta r_A \delta r_E \\
&+ (-4/27 + 8/17\sqrt{17})\delta r_B \delta r_C \\
&+ (\sqrt{3}/9)\delta r_B \delta r_E \\
&+ (1/4 - \sqrt{3}/12)\delta r_C \delta r_D]. \qquad (16)
\end{aligned}
$$

3. Results and discussion

Values given by the above formulae are tabulated in Table 1 for some σ phases. The phases chosen for testing the derived formulae are representative of a variety of situations regarding composition, ordering and atomic radii; amongst all σ phases, Mo_3Co_2 is one of those for which a large difference in the atomic radii of the constituent atoms occurs; attention has also been paid to the accuracy of the available data.

The analysis of Table 1 clearly shows that the second-order terms, $\delta^2 c'$ and $\delta^2 a'$, are very small, their contributions to the estimates of c and a (c'_0 and a'_0) being smaller than 0·006 and 0·01% respectively, except in Mo_3Co_2 for which both contributions are 0·04%. This fully justifies the use of first-order terms only in the calculation of c'_0 and a'_0; a comparison of these values with c_0 and a_0 shows that the overall agreement is better than 0·06%.

It is worth noting that the highest values of both $\delta c'$ and $\delta^2 c'$ occur for the alloy Mo_3Co_2; this supports the previously made statement that when the difference between the atomic radii of the constituent atoms is large, the parameter c is expected to be rather sensitive to ordering. It is not clear, in the work of Wilson & Spooner (1973) which ordering is assumed in the calculations; for instance, there is disagreement between their values for Mo_3Co_2, $c_0 = 4{\cdot}815$ and $a_0 = 9{\cdot}297$ Å, and those listed in Table 1. For the calculations carried out in the present work, the experimentally determined ordering was used.

The agreement between the observed values c and a and those calculated on the basis of the sphere-packing model is $\leq 1\%$ (Wilson & Spooner, 1973); however, both Table 2 of the paper by these authors and Table 1 of the present work show that the calculated ordered and disordered values c_0 and c'_0 (and a_0 and a'_0) also agree within 1% in most cases. This appears to indicate that the estimates of c and a are not particularly sensitive to the ordering assumed, and that a prediction of order based on the comparison of these estimates with the observed values is not meaningful.

Table 1. *Estimates of the parameters c and a* (Å) *for some σ phases*

(X,Y)	$Nb_{66}Al_{34}$[(a)]			$Mo_{60}Co_{40}$[(b)]			$Cr_{65{\cdot}8}Ru_{34{\cdot}2}$[(c)]			$Cr_{46}Fe_{54}$[(d)]		
r_x, r_y	1·48		1·43	1·40		1·25	1·28		1·34	1·28		1·26
r		1·463			1·340			1·301			1·269	
	n_x^i	r_i	δr_i	n_x^i	r_i	δr_i	n_x^i	r_i	δr_i	n_x^i	r_i	δr_i
A	0	1·43	−0·033	0	1·25	−0·090	1·6	1·292	−0·009	0·6	1·266	−0·003
B	4	1·48	+0·017	4	1·40	+0·060	2·5	1·303	+0·002	2·2	1·271	+0·001
C	8	1·48	+0·017	7	1·38	+0·040	4·8	1·304	+0·004	3·6	1·269	−0·000
D	0	1·43	−0·033	0	1·25	−0·090	4·4	1·307	+0·007	2·8	1·267	−0·002
E	8	1·48	+0·017	7	1·38	+0·040	6·6	1·291	−0·010	4	1·270	+0·001
$\delta c'$ $\delta a'$	−0·021		−0·006	−0·058		−0·002	−0·004		0·007	−0·002		−0·003
$\delta^2 c'$ $\delta^2 a'$	−0·000		−0·000	−0·002		−0·004	4×10^{-6}		3×10^{-5}	-1×10^{-6}		-3×10^{-6}
c' a'	5·292		10·151	4·847		9·297	4·704		9·020	4·591		8·806
c'_0 a'_0	5·271		10·145	4·789		9·295	4·700		9·027	4·589		8·803
c_0 a_0	5·271		10·145	4·787		9·294	4·701		9·030	4·589		8·803
c_{obs} a_{obs}	5·186		9·943	4·8269 ±0·0006		9·2287 ±0·0004	4·7430 ±0·0005		9·0635 ±0·0005	4·544		8·799

References: (*a*) Brown & Forsyth (1961); (*b*) Forsyth & Alte da Veiga (1963); (*c*) Alte da Veiga, Costa, de Almeida, Andrade & Matos Beja (1980); (*d*) Algie & Hall (1966).

This becomes evident if expressions (8) and (13) derived for the increments $\delta c'$ and $\delta a'$ are investigated in detail. For a given alloy, the values of r_x, r_y and r being fixed, only the n_x^i depend on the ordering assumed. However, it is clear that these can be varied without altering the value of $\delta c'$ or $\delta a'$. Taking, for example, expression (8), it may be readily seen that $\delta c'$, and hence c_0', remain the same providing the sum

$$4n_x^A + 3n_x^B + n_x^C + 4n_x^D + 3{\cdot}4641n_x^E$$

is kept constant. This is possible if an n_x^i, whose coefficient has an intermediate value, is increased (or decreased), while two others, with a higher and a lower coefficient, are decreased (or increased) in a certain way; this is, for example, the case of n_x^A, n_x^B and n_x^C, then

$$4n_x^A + 3n_x^B + n_x^C = 4(n_x^A + \Delta n_x^A) + 3(n_x^B - \Delta n_x^A - \Delta n_x^C) + (n_x^C + \Delta n_x^C),$$

which is constant for any $\Delta n_x^A = 2\Delta n_x^C$.

There is, then, an infinite number of solutions.* Table 2 shows the observed ordering in Mo_3Co_2 and two others corresponding to solutions, Δn_x^i, which are integers; both ordering 1 and ordering 2 are well away from the observed one and in marked disagreement with that observed in the σ phases; however, all three yield the same calculated value, c_0'. A final test of the equivalence between the original formulae and those derived in the present work is to use the solutions of the latter, *e.g.* ordering 1 and ordering 2, and carry out the calculations using the original expressions (1) and (9); this is done for c_0 in Table 2.

The above arguments support the conclusion that the sphere-packing model should be treated with caution when used in the prediction of order in the σ phases. This is related to the fact that it appears not to be correct to calculate the r_i taking into account the metallic radii of the constituent atoms and the occupancy of the atomic sites only, but the constraint that the r_i are radii of spheres in contact should be imposed. This restriction would forbid solutions such as those corresponding to ordering 1 and 2 of Table 2, which violate the requirement of contacting spheres. From this point of view, the assumption of the same average value, r, for the atoms at every atomic site in a randomly disordered structure is also questionable.

* Wilson & Spooner (1977, p. 1656) have pointed out the difficulty in demonstrating the uniqueness of the order schemes chosen.

Table 2. *Ordering schemes for* Mo_3Co_2 *yielding a constant* c_0'; *x and y refer to* Mo *and* Co, *respectively*

Order	n_x^A	n_y^A	n_x^B	n_y^B	n_x^C	n_y^C	n_x^D	n_y^D	n_x^E	n_y^E
Observed	0	2	4	0	7	1	0	8	7	1
1	2	0	1	3	8	0	0	8	7	1
2	0	2	1	3	8	0	2	6	7	1

Finally, it must be pointed out that the correctness of the original expressions (1) and (9), and consequently of those derived in the present work, is restricted by the assumption of independence of the variables r_i, which does not correspond to the actual physical situation.

This mathematical analysis was undertaken partly as a consequence of a referee's comment to the paper *The ordering of the σ phases* Cr_2Ru *and* Cr_2Os (Alte da Veiga, Costa, de Almeida, Andrade & Matos Beja, 1980). The authors would like to thank that referee and the referee of the present work whose comments contributed to improve the final presentation of both papers.

References

ALGIE, S. H. & HALL, E. O. (1966). *Acta Cryst.* **20**, 142.
ALTE DA VEIGA, L. M., COSTA, M. M. R. R., DE ALMEIDA, M. J. M., ANDRADE, L. R. & MATOS BEJA, A. (1980). *Acta Cryst.* B**36**, 1750–1757.
BROWN, P. J. & FORSYTH, J. B. (1961). *Acta Cryst.* **14**, 362–364.
FORSYTH, J. B. & ALTE DA VEIGA, L. (1963). *Acta Cryst.* **16**, 509–512.
HANSEN, R. C. & RAMAN, A. (1970). *Z. Metallkd.* **61**, 115–120.
WILSON, C. G. & SPOONER, F. J. (1973). *Acta Cryst.* A**29**, 342–352.
WILSON, C. G. & SPOONER, F. J. (1977). *J. Mater. Sci.* **12**, 1653–1658.