A Sphere-Packing Model for the Prediction of Lattice Parameters and Order in σ Phases

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A model is presented for the determination of the unit-cell size for ordered and disordered binary σ phases from a geometry assuming spherical atoms. The basis of the calculations is the assumption of an average radius of the atoms occupying each of the five crystallographic sites in the unit cell. The model is then used to predict the changes in lattice parameters produced by fast-neutron irradiation and by the addition of a third element in some ternary σ phases. The calculated parameters are compared with experimental results.

Introduction

Stüwe (1959) has shown that the σ phase can be regarded as a sphere-packing structure, and demonstrated the approximate validity of this approach by calculating, with considerable accuracy, the values of the *a* and *c* parameters of many binary σ phases. Frank & Kasper (1959) have also emphasized the sphere-packing nature of this and related phases composed of transition-metal atoms. Although Stüwe did not take into account the effect of ordering on the calculated values of *a* and *c*, it is reasonable to suppose that a change in the order of a σ phase consisting of dissimilar spherical atoms would show lattice-parameter changes. It is the purpose of this paper to show how the size of the unit cell for the ordered and disordered binary σ phase can be determined from geometry assuming spherical atoms. The model is then used to predict the changes in lattice parameter produced by (i) fast-neutron bombardment, (ii) the inclusion of a non-transition element in the σ phase, and (iii) the replacement of one element by another to create ternary σ phases. The results obtained are compared with experimental results.

Lattice parameters of the σ phase

The σ-phase structure can be constructed in an approximate way by superimposing a hexagonal close-packed layer of atoms on a similar close-packed layer and rotating the former by 90° relative to the latter (Frank & Kasper, 1959). Missing sites exist in each of the two layers which, after the stacking process, lie in vertical rows which would form empty 'tubes' in the structure if they were not filled with atoms of either component (denoted X or Y) of the binary system. The tetragonal symmetry which the structure possesses can be derived from the hexagonal symmetry of the approximate close-packed layers by a shear stress which is applied to each layer after stacking. The resulting shear leads to better packing of the dissimilar X and Y atoms which are contained in each layer. In the unit cell of 30 atoms, five distinct crystallographic sites are

recognized, each being distinguished by its atomic surroundings and coordination number. The lattice coordinates, occupancy and coordination number of each site are given in Table 1 for the σ phase FeCr, as determined by Bergman & Shoemaker (1954). The structure determinations of other σ phases show minor changes in the coordinate values. Also included in the Table 1 is the general ordering scheme found in many σ phases (Spooner & Wilson, 1964), the larger atom being designated X and the smaller Y.

In spite of the tetragonal symmetry of the structure, the atoms in the horizontal layers which contain the *A*, *B*, *C* and *D* sites display a quasi-hexagonal symmetry about the vertical rows of *E*-type atoms, as shown in Fig. 1. Because of the much shorter bond between *E*-type atoms, Stüwe (1959) assumed that these atoms played very little part in controlling the *a* parameter of the unit cell. Accordingly, Stüwe calculated this parameter by assuming sphere packing for the *A*, *B*, *C* and *D*-type layer atoms only. Furthermore, Stüwe assumed that the ordered nature of the σ phase did not affect the average radius of the atoms estimated from the atomic percentage composition. We believe that the *E*-type atoms have the effect of contracting the size of the pseudo-hexagonal rings which are a feature of the layers and must therefore be taken into account in estimating the size of the unit cell from geometrical considerations. This view was also adopted in a study of the effect of neutron irradiation on the Zr_4Al_3 structure (Wilson, Wilson, Joksimovic & Westphalen, 1973). In order to substantiate this claim and determine the effect of disordering on the size of the unit cell, it is proposed to calculate the *a* and *c* parameters for the known ordered binary σ phases on the basis of sphere packing taking into account, not only the size of the *E* atoms, but also the ordered nature of the phase. The lattice parameters of a disordered phase are given by assuming an average radius for all the atoms in the unit cell based on the binary composition.

Basis of calculation of unit-cell parameters

The contents of a unit cell of the σ-phase structure

might be described as consisting of interlocking hexagonal rings of A, B, C and D-type atoms surrounding the four pairs of E-type atoms situated at $z=\frac{1}{4}$ and $z=\frac{3}{4}$. More fundamentally, the structure is seen as a face-centred tetragonal lattice, each lattice point being associated with a structural unit consisting of atoms $DDADD$ at $z=\frac{1}{2}$ and atoms $CCBBCC$ at $z=0$, together with two pairs of E-type atoms symmetrically disposed on either side of the unit. This complex configuration of atoms appears at the centre of the unit cell and at each corner in Fig. 1. The presence of the fourfold screw axes at the mid-points of the sides of the unit cell in Fig. 1 ensures that the central structural unit is oriented at right angles to those located at the corners of the cell. The departure from true hexagonal symmetry surrounding the rows of E-type atoms is a consequence of the requirement for packing atoms of different size. In the related structure adopted by Zr_4Al_3, the hexagonal symmetry is retained because each layer consists of one type of atom only (Wilson, Thomas & Spooner, 1960; Wilson et al., 1973). Although this fundamental difference exists, the stacking of the layers of the σ phase is similar to that of the Zr_4Al_3 structure in so far as one layer is rotated by 90° relative to the

next and packing difficulties in the vertical direction are avoided by creating missing sites in each layer prior to stacking. This permits the vertical rows of E-type atoms to be sited in the vacant tubes formed by the alignment of the missing layer sites. The rows of E-type atoms threading the close-packed layers appear to bind the two layers together.

The geometrical disposition of atoms surrounding the E sites is such that if the E-type atoms are in contact with their neighbours they cannot be spherical but must have an oblate spheroidal shape. This distortion of E-type atoms is marked by their short interatomic distance which is approximately 12% less than the sum of the Goldschmidt radii. The size of the unit cell suggests that the atoms in the horizontal layers are also deformed slightly in accommodating the rows of E-type atoms so that their atomic radii are effectively decreased in the xy plane. Although the layer structure and stacking are similar to Zr_4Al_3, they are not the same because the departure from hexagonal symmetry leads to an inexact placing of the atoms of one layer above the hollows of the layer below. This imperfect form of stacking is in accordance with the distortion of the atoms in the vertical direction and has the merit of providing a flexibility in the ratio of X:Y atoms which can be accommodated in each layer and hence the wide range of composition generally found in the binary σ phase.

Ordered σ phases

The binary σ phase is often found to be an ordered structure and experimental results show that atomic radius plays a large part in the ordering process (Hall & Algie, 1966; Spooner & Wilson, 1964), the general rule being that the larger atoms occupy those sites which have a larger coordination number. It is found that the A and D-type sites have similar ordering tendencies and are predominantly occupied by the smaller Y atoms, whilst the B and C sites have similar ordering tendencies with the larger X atoms occupying most of the sites. The E sites are predominantly occupied by the larger X atoms. The fractional occupation of each site by X or Y atoms depends on the composition of the σ phase. In the atomic configuration associated with each lattice point, the two triangles of A and D sites appear to retain a close-packed equilateral structure which is only possible if the atoms occupying these positions have the same radii. Likewise, the structure motif CCB–BCC, consisting of B and C atoms, can only contribute to the quasi-hexagonal symmetry
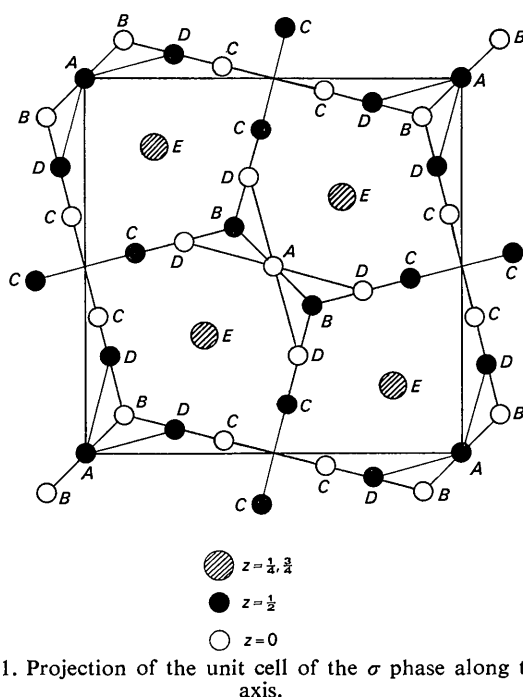
Fig. 1. Projection of the unit cell of the σ phase along the c axis.

Table 1. *Lattice coordinates, occupancy and coordination number for σ-FeCr*

Crystal site	Number of atoms	Coordinates	Coordination Number	Ordering scheme
A	2	$0,0,0$	12	Mainly Y
B	4	$x,x,0$ ($x=0.4$)	15	Mainly X
C	8	$x,y,0$ ($x=0.467$, $y=0.133$)	14	X+Y, mainly X
D	8	$x,y,0$ ($x=0.733$, $y=0.067$)	12	Mainly Y
E	8	x,x,z ($x=0.183$, $z=0.25$)	14	X+Y, mainly X

of the structure if their atomic radii are similar. This kind of correlation is important since it implies that the ordering phenomenon exerts some influence on the size of the unit cell, as will be apparent later. In the ensuing calculations it is assumed that the atoms occupying a particular site have an average radius determined by the fractional occupancy of the constituent elements.

Calculation of the c parameter

The configuration of atoms at each lattice point [Fig. 2(a)] comprises five vertical panels together with two vertical rows of E-type atoms. The centre panel consisting of $BBABB$ type atoms is joined to four symmetrically disposed panels consisting of $BCDBC$ atoms, as illustrated in Fig. 2(b) and (c). An estimation of the c parameter is obtained by supposing that each vertical panel and each vertical row of E-type atoms consists of spheres in contact, the radius of each atom r_A, r_B ... etc. being that derived from the ordering scheme as explained earlier. If the panels and rows are constructed independently in this fashion, three possible values of the c parameter are obtained from the following relations (see Fig. 2):

for panel $BBABB$: $c_1 = 2(r_A + r_B) \cos \theta_1$,

$\qquad$ where $\sin \theta_1 = r_B/(r_A + r_B)$

for panel $BCDBC$: $c_2 = (r_B + r_C + 2r_D) \cos \theta_2$,

$\qquad$ where $\sin \theta_2$

$\qquad = (r_B + r_C)/(r_B + r_C + 2r_D)$.

N.B. B and C are assumed to have a common radius of $\frac{1}{2}(r_B + r_C)$ for each row of E atoms: $c_3 = 4r_E$. In creating the σ phase from these elements of structure, c_1 and c_2 are increased whilst c_3 is reduced, the changes involved being a manifestation of the stresses produced when they are brought together. At each lattice point there are one $BBABB$ and four $BCDBC$ panels together with two EE rows, so that the formula:

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

is taken as an estimate of the final c parameter. The weighting used in this formula reflects the influence that each subunit of structure has on determining the height of the unit cell.

Calculation of the a parameter

In order to calculate the a parameter by a similar
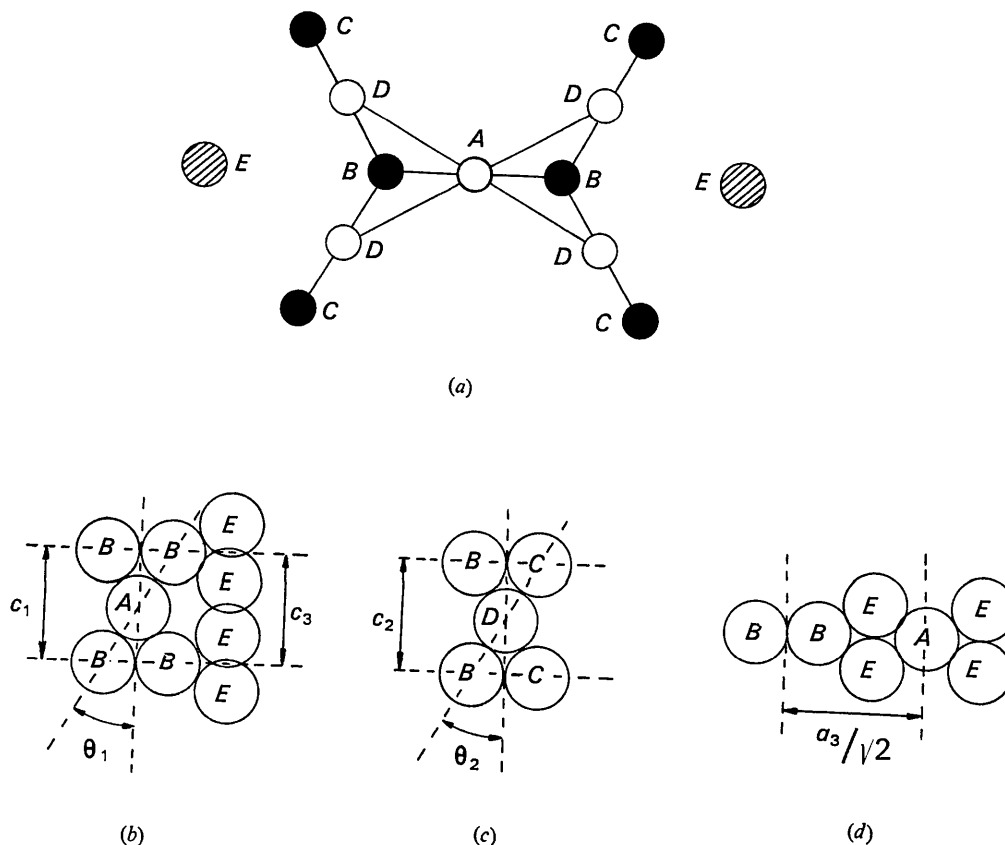

(a)

(b) $\qquad$ (c) $\qquad$ (d)

Fig. 2. (a) The configuration of the atoms. (b), (c) different ways of atomic packing, showing estimates of c. (d) Atomic packing showing one estimate of a.

synthesis of structural elements we note that each lattice-point configuration is joined to its neighbour by C-C-type atom linkages. The C-atom linkages can be regarded as pairs of spherical atoms which make contact at the fourfold screw axes of the unit cell, so that the size of the unit cell is simply related to the size of the basic configuration unit. In isolation, and in the absence of E-type atoms, the configuration unit would have a size determined by close packing in the constituent panels which were considered in estimating c_0. If we ignore the presence of the E-type atoms and assume C-C-type atom linkages between adjacent configuration units we can obtain two possible formulae for the value of a as follows. Referring to triangle $AC'P$ ($z = \frac{1}{2}$) in Fig. 3, one estimate for a is given by:

$$\frac{a_1}{2} = (r_A + 2r_D + r_C) \cos(45° - \varphi) - \frac{r_B r_C}{\sqrt{2}(r_B + 2r_C)}$$

where $\sin \varphi = r_D/(r_A + r_D)$.

In this formula the second term corrects for the fact that the C' atom connected to A does not lie on the unit-cell boundary. Likewise from triangle ABP, in which $B\hat{A}P = 45°$,

$$PB^2 = (r_B + 2r_C)^2 = a^2/4 + r_B^2 - 2(a/2)r_B \cos 45°,$$

whence, the second possible value of the a parameter, say a_2, is given by:

$$a_2 = \sqrt{2} \cdot r_B + \sqrt{2r_B^2 + 16(r_C^2 + r_B r_C)}.$$

In the absence of E-type atoms a reasonable value for the a parameter would be given by $\frac{1}{2}(a_1 + a_2)$, the average of the two possible values of a reflecting the adjustments which would follow when two layer structures are superimposed. The effect of inserting rows of E atoms can be taken into account by supposing that the E atoms, together with adjacent A and B atoms, form vertical connecting planes along the diagonals of the unit cell. In these independently devised configurations the E atoms can be conceived as spheres in contact with the A and B atoms, as shown in Fig. 2(d). From this diagram, a third estimate of the side of the unit cell is obtained:

$$\frac{a_3}{\sqrt{2}} = \sqrt{(r_A + r_E)^2 - r_A^2} + \sqrt{(r_B + r_E)^2 - r_E^2} + r_B$$

i.e.

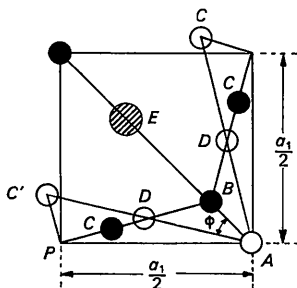$$a_3 = \sqrt{2} \cdot r_B + \sqrt{2r_A^2 + 4r_A r_E} + \sqrt{2r_B^2 + 4r_B r_E}.$$

Fig. 3. Atomic packing showing one estimate of a.

The influence of the E atoms in determining the final value of a is taken into account by using the average of these three estimates, i.e.

$$a_0 = \tfrac{1}{3}(a_1 + a_2 + a_3). \tag{2}$$

Effect of disorder on a_0 and c_0 – lattice changes

Both the formulae for a_0 and c_0 are simplified considerably for a σ phase with random order, for then the radii of all the atoms have the same average value which is determined solely by the atomic percentage composition of the alloy. Thus, for the above, using r to represent the random-order atomic radius:
i.e.

$$c_1' = 4r \cos 30° \ (\sin \theta_1 = r/2r = 0.5 \text{ and } \theta_1 = 30°),$$
$$c_1' = 4r\sqrt{3}/2 = 2\sqrt{3}r = 3.4641r,$$
$$c_2' = 4r \cos 30° = 3.4641r,$$
$$c_3' = 4r,$$

whence

$$c' = (c_1 + 4c_2 + c_3)/7 = 25.3205r/7 = 3.6172r.$$

Likewise:

$$a_1' = 4r \cos 15° - \sqrt{2}r = 7.2560r,$$
$$a_2' = (\sqrt{2} + \sqrt{34})r = 7.24515r,$$
$$a_3' = (\sqrt{2} + 2\sqrt{6})r = 6.3131r,$$

and

$$a' = \tfrac{1}{3}(a_1 + a_2 + a_3) = 6.9381r.$$

Results and discussion

Ordered and disordered binary σ phases

The calculated values of a and c using the above equations are presented in Table 2 together with the observed values, the latter being taken from Hall & Algie (1966) except where noted.

A few discrepancies were apparent in the initial calculations on ordered phases which could not be accounted for, especially for those phases involving Mn as the Y component. This was thought to be due to the use of the normally accepted values for the Goldschmidt atomic radii. Using the generally accepted atomic radius of 1.35 Å for Mn gave calculated values for a_0 and c_0 which differed from the observed values by as much as 5%. In order to obtain agreement to within 1%, the atomic radius was taken as 1.27 Å. It is clear from the work of Chessin, Arajs & Miller (1970) that the atomic volumes of the transition elements in the first long period do not follow the same variation with atomic number as the Goldschmidt radii. Using this value of 1.27 Å for r_{Mn} and the following, somewhat smaller atomic radii for the remaining transition elements in this period, gives a similar size order to that used by Chessin et al. in their study of lattice-parameter changes in solid solutions, $r_{Ni} = 1.24$, $r_{Co} = 1.25$, $r_{Fe} = 1.26$, $r_{Mn} = 1.27$, $r_{Cr} = 1.28$, $r_V = 1.33$ Å, and at the same time gives calculated values of a_0 and c_0 which are within 1% of the observed values. Kitchingman (1968) has suggested that transi-

Table 2. Binary σ phases

(i) Ordered phases

r_X	At%	X	Y	At%	r_Y	r	Observed values (Å) a	c	Calculated (Å) ordered (Wilson) a_0	c_0	Calculated (Å) disordered (Wilson) a'	c'	Calculated (Å) disordered (Stüwe) a'	c'	Reference†
1·33	50	V	Fe	50	1·26	1·295	8·956	4·627	8·994	4·666	8·985	4·684	8·871	4·623	a
1·33	62	V	Ni	38	1·24	1·2958	8·980	4·640	8·989	4·663	8·990	4·687	8·876	4·626	a
1·28	56	Cr	Co	44	1·25	1·2669	8·800	4·560	8·811	4·575	8·790	4·583	8·678	4·523	a
1·40	50	Mo	Fe	50	1·26	1·33	9·188	4·812	9·234	4·763	9·228	4·811	9·111	4·748	a
1·40	60	Mo	Co	40	1·25	1·34	9·228	4·827	9·297	4·815	9·297	4·847	9·179	4·784	a
1·47	50	Nb	Re	50	1·37	1·42	9·783	5·115	9·849	5·083	9·852	5·136	9·727	5·069	a
1·47	60	Nb	Os	40	1·35	1·422	9·858	5·066	9·885	5·084	9·866	5·144	9·741	5·077	b
1·47	60	Nb	Ir	40	1·35	1·422	9·847	5·053	9·61	5·095	9·866	5·144	9·741	5·077	a
1·28	40	Cr	Re	60	1·37	1·3358	9·230	4·800	9·303	4·809	9·268	4·832	9·150	4·769	c
1·40	45	Mo	Re	55	1·37	1·3835	9·603	4·983	9·595	5·001	9·592	5·004	9·477	4·939	c
1·40	33	Mo	Re	67	1·35	1·3799	9·572	4·976	9·572	4·985	9·574	4·991	9·452	4·926	c
1·40	65	Mo	Os	35	1·35	1·3825	9·615	4·941	9·597	4·981	9·599	5·001	9·477	4·939	b
1·40	72	Mo	Ir	28	1·35	1·386	9·631	4·957	9·628	4·995	9·616	5·013	9·491	4·946	b
1·33	19	V	Mn	81	1·27	1·2814	8·918	4·613	8·896	4·633	8·890	4·635	8·778	4·575	b
1·28	20	Cr	Mn	80	1·27	1·272	8·885	4·587	8·825	4·601	8·825	4·601	8·713	4·541	a
1·40	37	Mo	Mn	63	1·27	1·3181	9·100	4·740	9·197	4·747	9·145	4·768	9·029	4·706	a
1·37	46	Re	Fe	54	1·26	1·3106	9·020	4·690	9·163	4·712	9·093	4·741	8·978	4·679	a

(ii) Disordered phases

r_X	At%	X	Y	At%	r_Y	r	Observed values (Å) a	c	Calculated (Å) ordered (Wilson) a_0	c_0	Calculated (Å) disordered (Wilson) a'	c'	Calculated (Å) disordered (Stüwe) a'	c'	Reference†
1·47	65	Nb	Rh	35	1·34	1·425	9·835	5·083	9·872*	5·092*	9·883	5·153	9·758	5·085	a
1·40	63	Mo	Ru	37	1·34	1·3778	9·538	4·922	9·572*	4·959*	9·559	4·984	9·438	4·919	a
1·33	50·5	V	Co	49·5	1·25	1·2904	8·877	4·598	8·974*	4·537*	8·953	4·668	8·839	4·607	a
1·28	46·5	Cr	Fe	53·5	1·26	1·2693	8·799	4·544	8·803*	4·589*	8·807	4·591	8·695	4·531	a
1·47	60	Nb	Pd	40	1·37	1·43	9·890	5·110	9·919*	5·133*	9·921	5·173	9·800	5·105	a
1·46	70	Ta	Rh	30	1·34	1·424	9·863	5·131			9·880	5·151	9·754	5·084	a
1·46	75	Ta	Pd	25	1·37	1·4375	9·978	5·208			9·974	5·200	9·847	5·132	a
1·28	06	Cr	Tc	36·5	1·36	1·328	9·217	4·803			9·214	4·804	9·097	4·741	d
1·28	36·5	Cr	Ru	63·5	1·34	1·3019	9·068	4·704			9·033	4·709	8·918	4·648	a
1·40	30	Mo	Tc	70	1·36	1·372	9·509	4·945			9·519	4·963	9·398	4·898	a
1·40	60	W	Ru	40	1·34	1·382	9·554	4·972			9·588	4·999	9·467	4·934	a
1·33	25	V	Re	75	1·37	1·36	9·360	4·860	9·431*	4·906*	9·436	4·919	9·316	4·853	d
1·47	62	Nb	Pt	38	1·38	1·4338	9·890	5·110			9·948	5·186	9·822	5·119	a
1·46	40	Ta	Re	60	1·37	1·406	9·690	5·040			9·755	5·086	9·631	5·019	a
1·46	75	Ta	Os	25	1·35	1·4325	9·934	5·189			9·939	5·182	9·813	5·114	a
1·46	75	Ta	Ir	25	1·35	1·4325	9·928	5·159			9·939	5·182	9·813	5·114	a
1·46	82	Ta	Pt	18	1·38	1·4456	9·950	5·160			10·030	5·229	9·902	5·161	a
1·28	65·6	Cr	Os	34·4	1·35	1·3040	9·107	4·696			9·047	4·717	8·932	4·655	d
1·41	50	W	Re	50	1·37	1·39	9·628	5·013	9·639*	5·015*	9·644	5·028	9·522	4·962	c
1·41	73	W	Os	27	1·35	1·3938	9·659	5·001	9·639*	5·015*	9·670	5·042	9·548	4·976	a
1·41	70	W	Ir	30	1·35	1·392	9·680	4·980			9·658	5·035	9·535	4·969	a
1·37	48	Re	Mn	52	1·27	1·3180	9·140	4·750			9·144	4·767	9·028	4·705	a
1·36	60	Tc	Mn	40	1·27	1·324	9·150	4·800			9·186	4·789	9·069	4·727	a
1·36	50	Tc	Fe	50	1·26	1·31	9·077	4·756			9·089	4·739	8·974	4·677	a
1·46	69	Ta	Au	31	1·44	1·4538	10·04	5·22			10·087	5·259	9·959	5·190	a
1·46	60	Ta	Al	40	1·40	1·436	9·972	5·214			9·963	5·209	9·837	5·127	a
1·46	60	Nb	Al	40	1·40	1·4413	9·923	5·171			10·000	5·213	9·873	5·145	a
1·47	66	Nb	Al	34	1·40	1·4462	9·943	5·186	10·026*	5·201*	10·034	5·231	9·906	5·163	e

* Calculated parameters using predicted order schemes.
† The references refer to the source of observed values of the lattice parameters: (a) Hall & Algie (1966); (b) Spooner & Wilson (1964); (c) Wilson & Parselle (1965); (d) Waterstrat & Kasper (1957); (e) Brown & Forsyth (1961).

tion elements may exist in different states with different radii which are associated with the coordination number of that state, the atomic radius decreasing with increasing coordination number. The fact that most of the atoms in the σ phase have coordination numbers greater than 12 supports
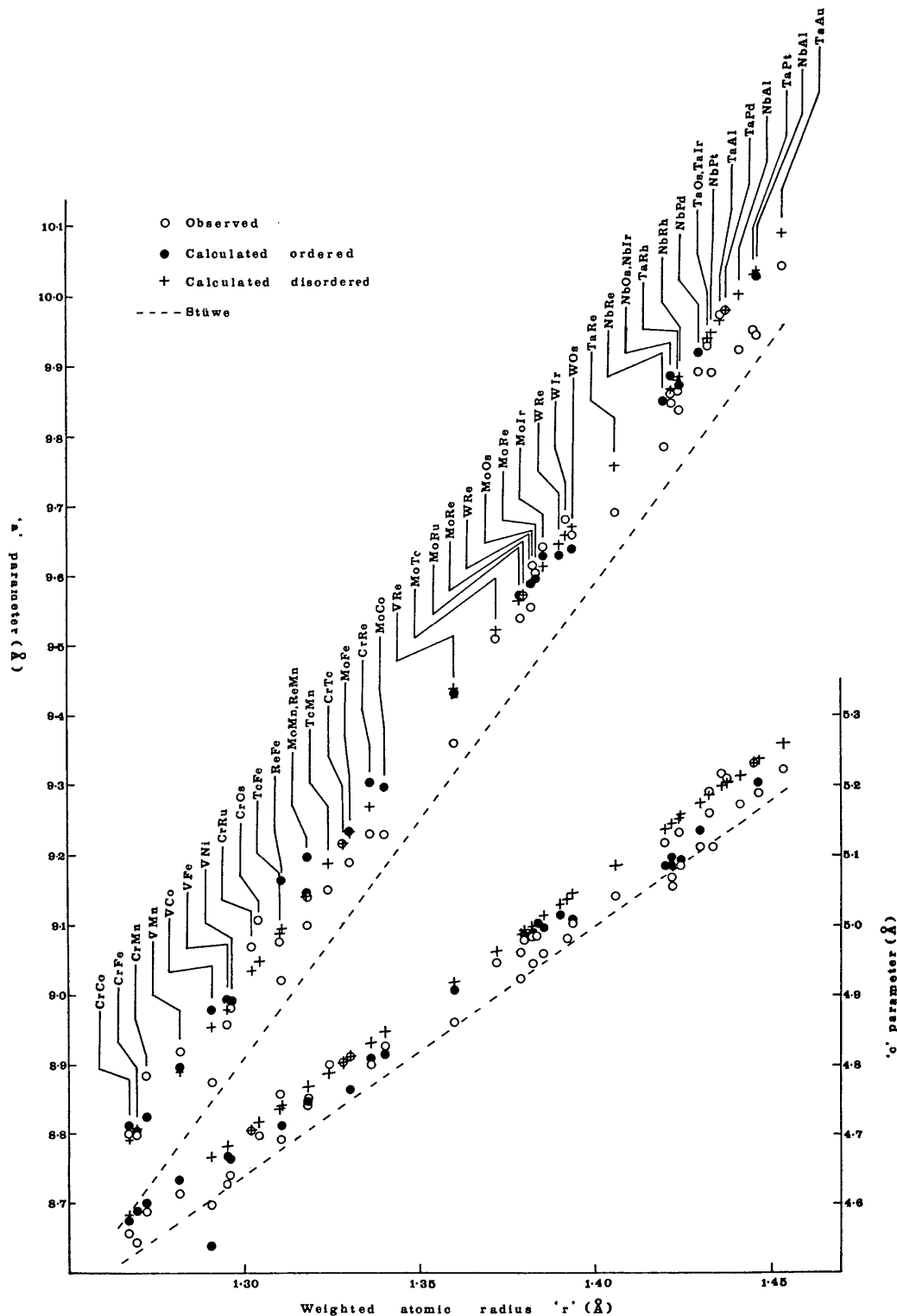

Fig. 4. Calculated values of a and c plotted against the weighted atomic radius.

the adoption of radii slightly smaller than the Goldschmidt values which are normalized to coordination number 12. Finally, it must be pointed out that 1·40 Å was used for r_{Al} instead of 1·42 Å. This value was also used in the discussion of the Zr_4Al_3 structure (Wilson, Wilson, Joksimovic & Westphalen, 1973) and is justified on the grounds that Al is not a transition metal. The reduced radius of 1·40 Å was chosen because it is similar to that found in many aluminum alloys.

It is of interest to compare the simple formulae derived above for the lattice parameters of disordered phases with those given by Stüwe (1959), namely $a' = 6·85r$ and $c' = 3·57r$. In both cases, the values of a' and c' are approximately 1% greater than those derived on a much simpler basis by Stüwe. As seen in Table 2 (ii), the calculated values of a' and c' are generally within 1% of the observed values for those σ phases whose ordering is unknown and assumed to be disordered. Thus, the new formulae appear to give better agreement than those obtained using Stüwe's formulae with the same average radii.

There were still some remaining discrepancies when the random formulae were used and these were ascribed to some degree of order. Support is given for this suggestion from the agreement obtained between calculation and observation for the *known* ordered phases using the complex formulae of equations (1) and (2), as seen in Table 2 (i). Thus, these equations might be used to predict order. This has been done for the 'disordered' phases $Nb_{65}Rh_{35}$, $Mo_{63}Mn_{37}$ etc. using simple ordering schemes based on σ phases of similar composition, as seen in Table 2 (ii). Better agreement is obtained for the calculated values a_0 and c_0 when a reasonable order scheme is adopted.

The kind of agreement overall is probably best seen in Fig. 4 where calculated and observed values of a and c are plotted against the weighted atomic radius.

Application of formulae to neutron-irradiated σ phases

The above formulae were originally developed in order to estimate the changes in lattice parameter produced by disordering after fast-neutron irradiation. The values of a and c before and after disordering by neutron irradiation of several ordered σ phases taken from Spooner's (1968) paper, together with the values calculated using the above 'ordered' and 'disordered' formulae, are given in Table 3. The most satisfactory

feature of these results is the anisotropy in the predicted *changes* of a and c. In all cases the value of c increases on disordering whilst the value of a decreases or shows a positive change which is less than the increase in c. The magnitudes of the predicted changes are generally somewhat less than the observed changes caused by neutron irradiation, and might be attributed to the fact that the alloys were not completely disordered after irradiation.

The formulae derived in the present work have given dependable results for the lattice parameters of unirradiated σ phases, have shown the extreme sensitivity in these values for small changes in the average atomic radii, and the ability to predict order in phases previously assumed to be disordered. Thus, it seems reasonable to use the formulae to predict small variations from the disordered state in irradiated σ phases in order to improve the agreement presented in Table 3, and then to see if these changes have any detrimental effect on the calculated X-ray diffraction intensities.

It should be pointed out that, in the work of Wilson & Parselle (1965) and Spooner (1968), evidence of disorder in neutron-irradiated σ phases was indicated in the changes in intensity of the X-ray diffraction lines. These intensity results suggested that the alloys were partially or wholly disordered by the irradiation, but in some instances the intensities were relatively insensitive to small changes in order and no detailed calculations were performed to link the changes in order in the various crystallographic sites with the changes in lattice parameter.

The re-ordering among the various crystallographic sites and their effect on the calculated lattice-parameter changes are presented in Table 4. It is apparent that there is considerable improvement. The calculated diffraction intensities are presented in Table 5 and no serious differences between calculation and observation have been introduced. Thus, the usefulness of the derived formulae for the calculation of lattice parameters in irradiated σ phases is demonstrated.

These calculations have served to justify the use of the derived formulae, but do not account completely for the observed changes. This is not surprising, since the disordering of the crystal structure is only one possible manifestation of the atomic displacements effected by fast-neutron bombardment. It is well known that point defects are also created which might aggregate

Table 3. *Effects of neutron irradiation of ordered phases*

| | | | | Observed values (Å) | | | | | | Calculated values (Å) | | | | | |
| | | | | Before irradiation | | After irradiation | | Changes ($\times 10^3$) | | Before irradiation | | After irradiation | | Changes ($\times 10^3$) | |
At. %	X	Y	At. %	a	c	a	c	Δa	Δc	a_0	c_0	a'	c'	Δa	Δc
65	Mo	Os	35	9·615	4·947	9·585	4·994	−30	+47	9·597	4·981	9·599	5·001	+2	+20
72	Mo	Ir	28	9·631	4·957	9·584	4·986	−47	+29	9·628	4·995	9·616	5·013	−12	+18
60	Nb	Os	40	9·858	5·063	9·850	5·080	−8	+17	9·885	5·084	9·866	5·144	−19	+60
45	Mo	Re	55	9·603	4·983	9·584	5·005	−19	+22	9·595	5·001	9·599	5·004	+4	+3
33	Mo	Re	67	9·572	4·976	9·561	4·993	−11	+17	9·572	4·985	9·574	4·991	+2	+6
50	W	Re	50	9·628	5·013	9·621	5·032	−7	+19	9·639	5·015	9·644	5·028	+5	+13
33	W	Os	67	9·634	4·986	9·580	5·010	−54	+24	9·634	5·009	9·645	5·029	+11	+20

Table 4. *Effects of re-ordering irradiated phases*

σ phase					Changes in site occupancy										Changes in parameter (Å × 10³)			
At.% X	X	Y	At.% Y		A-X	A-Y	B-X	B-Y	C-X	C-Y	D-X	D-Y	E-X	E-Y	Δa_0(obs)	Δa_0(calc)	Δc_0(obs)	Δc_0(calc)
65	Mo	Os	35	Ordered	0·5	1·5	4	0	7·5	0·5	0·5	7·5	7	1				
				Disordered	1·3	0·7	2·6	1·4	5·2	2·8	5·2	2·8	5·2	2·8	−30	+2	+47	+20
				Reordered	1·3	0·7	2·6	1·4	3·4	4·6	5·2	2·8	7	1	−30	−22	+47	+21
72	Mo	Ir	28	Ordered	1	1	4	0	8	0	1·5	6·5	7	1				
				Disordered	1·44	0·56	2·88	1·12	5·76	2·24	5·76	2·24	5·76	2·24	−53	−12	+29	+22
				Reordered	1·44	0·56	2·88	1·12	5·02	2·98	5·26	2·74	7	1	−53	−18	+29	+22
60	Nb	Os	40	Ordered	0	2	4	0	8	2·0	0	8	6	2				
				Disordered	1·2	0·8	2·4	1·6	4·8	3·2	4·8	3·2	4·8	3·2	−8	−19	+17	+60
				Reordered	0·8	1·2	2·7	1·3	6·5	1·5	2·5	5·5	5	3	−8	−10	+17	+25
45	Mo	Re	55	Ordered	0	2	3	1	4	4	1·5	6·5	5	3				
				Disordered	0·9	1·1	1·8	2·2	3·6	4·4	3·6	4·4	3·6	4·4	−19	+4	+22	+3
				Reordered	1	1	1	3	2	6	3·5	4·5	6	2	−19	−14	+22	+9
33	Mo	Re	67	Ordered	0	2	2	2	4	4	0	8	4	4				
				Disordered	0·66	1·34	1·32	2·68	2·64	5·36	2·64	5·36	2·64	5·36	−11	+2	+17	+6
				Reordered	0·5	1·5	1	3	2	6	1·5	6·5	5	3	−11	−12	+17	+8

in particular planes to create planar defects. Spooner (1968) has suggested that the preferential siting of such defects coupled with distortion of the kagomé layers might be partly responsible for the observed results.

The inclusion of a third element in the binary phase

In their review of the nature of the σ phase, Hall & Algie (1966) have given evidence to support the general contention that the structure of this phase is mainly governed by geometrical factors. The success achieved by Stüwe (1959) is only marred by the inability of his approach to account for the effects of ordering which is an important feature of this phase. Using the equations derived above, which are based on the average atomic radii of the atoms occupying the five different sites in the structure, the effects of replacing atoms of one element by those of another in any given site can be determined.

There are several publications on the effects of replacing one of the binary components of a σ phase by a third element, which report interesting results not hitherto explained by a simple sphere-packing theory. The applications of the present model to some of these phenomena are examined below.

Addition of a third transition metal

In the study reported by Kitchingman & Bedford (1970, 1971) the changes in lattice parameters were measured when 3·4 at. % of various transition elements were incorporated in σ-FeV in which equal atomic proportions of Fe and V were always maintained. Starting with the order scheme for σ-$Fe_{40}V_{60}$ given by Hall & Algie (1966), modified to account for the small difference in composition, the changes in a_0 and c_0 produced by the inclusion of one non-transition element atom into the σ-FeV unit cell (equivalent to 3·4 at. %) have been determined by using revised order schemes. The revised order schemes adopted for these calculations together with the observed and calculated changes in a_0 and c_0 are given in Table 6(a).

Although the choice of revised order scheme adopted for each of the ternary σ phases has been guided by a need for producing agreement between observed and calculated changes in a_0 and c_0, the revisions seem reasonable. With Ta or W as the third element (designated Z), the same revised order scheme is used. This involves slight shifts only in the V and Fe occupancy of the atomic sites and gives values for a_0 and c_0 which are in good agreement with the observed results. A slightly different order scheme is adopted for Re which has a smaller radius than Ta or W but still larger than V and Fe ($r_{Re} = 1·37$ Å). In these three cases the added transition atom tends to occupy C and E sites. The exceptional behaviour adopted by Mn in replacing one Fe atom in the A site of the assumed order scheme is in accordance with the general order behaviour of smaller atoms occupying sites with low coordination number. The value of the radius of the Mn atom used in the calculations was the same as that adopted in

earlier calculations ($r_{Mn} = 1\cdot27$ Å). The order scheme adopted for σ-VFe(Zr) is different to the rest in so far as the V:Fe occupancy of the B sites is almost reversed and the Fe content of the C sites reduced to zero. Whilst this reversal may seem to contradict the general order rule that the larger X atoms occupy the B, C and E sites with the larger coordination numbers, it is questionable whether this rule can apply when one of the σ-phase components (Zr) is not a true transition element. The normal Goldschmidt radius of $r_{Zr} = 1\cdot60$ Å has been used in these calculations and, as seen in Table 6 the Zr atom can be accommodated in the unit cell to give the observed changes in a_0 and c_0, providing the normal σ-VFe order scheme is modified. Whether the hard-sphere concept can still be maintained for σ phases containing such atoms is questionable and it would be of interest to check this revised σ-VFe(Zr) order scheme with X-ray or neutron-diffraction techniques.

σ phases including a non-transition element, aluminum

In their study of the occurrence of σ-phase alloys of transition elements with non-transition elements, Hansen & Raman (1970) measured the lattice parameters of many alloys derived from Al with Nb, Ta or Zr. Of interest here are the binary σ phases Nb_2Al and Ta_2Al which are able to form ternary σ phases containing Nb, Ta and Al or Nb, Zr and Al. By assuming a suitable order scheme for σ-Nb_2Al the values of a_0 and c_0 are calculated and the effect on these parameters of replacing Nb by Ta to form $Nb_{34}Ta_{34}Al_{32}$ (NbTaAl) and ultimately Ta_2Al, is investigated by using modified order schemes. In addition to this example the effect of replacing Nb in Nb_2Al by Zr is determined in a similar way. The results of these calculations together with the measured values of a_0 and c_0 obtained by Hansen & Raman are given in Table 6(b).

The variations in lattice parameter reported by Hansen & Raman for the various ternary σ phases formed by Nb, Ta and Al are interesting, for example, in the sequence Ta_2Al, $Ta_{34}Nb_{34}Al_{32}$, $Ta_{14}Nb_{54}Al_{32}$, Nb_2Al, in

which the atomic fraction of Al is almost constant, the effective replacement of Ta atoms by Nb atoms leads to a gradual increase in a_0 from 9·864 to 9·943 Å but to a decrease in c_0 from 5·215 to 5·186 Å, the intermediate c_0 values being 5·174 and 5·162 Å. Thus, whilst the a_0 parameter increases monotonically the c_0 parameter displays a minimum at the composition $Ta_{14}Nb_{54}Al_{32}$. In order to reproduce this kind of behaviour in the calculations it is not possible to use the order scheme for Nb_2Al suggested by Brown & Forsyth (1961) in which Al atoms are placed preferentially in A and D sites only. In the modified order scheme quoted in Table 6(b) Al shares A, C and D sites with Nb atoms. Again this assumption may be questioned and needs experimental justification which should be possible in this case with X-ray diffraction. However, using this initial order scheme allows progressive kinds of order schemes to be used for the ternary NbTaAl alloys and the final σ-Ta_2Al whose calculated parameters give changes Δa_0 and Δc_0 which are in approximate agreement with experiment. By the same token the parameters of the ternary alloy NbZrAl can be calculated to give changes in a_0 and c_0 which are in fair agreement with experiment.

Although agreement with changes in a_0 and c_0 is obtained, the general order rule is not obeyed and Al atoms are frequently found in sites which are normally reserved for the σ-phase component with the larger atom. In quoting these results, however, it is fair to point out that Al is not a transition-metal atom and electronic factors in addition to size factors may govern the site occupancy. Kitchingman & Bedford (1970) suggest that Al atoms should tend to destabilize the binary σ phases of transition elements and form body-centred cubic phases, a role opposite to that of Si which tends to stabilize binary σ phases. The difference in behaviour between Al and Si was attributed by Gupta, Rajan & Beck (1960) to the greater electropositivity of Al to Si. The formulae used for calculating a_0 and c_0 are based on a geometrical pattern of atoms rather than simple close packing and to this

Table 5. *Intensities*

I_O = Observed unirradiated; I = Observed irradiated; I_C = Calculated ordered; I_D = Calculated disordered; I_R = Calculated reordered

σ phase hkl	Mo65Os35 I_O	I	I_C	I_D	I_R	Mo72Ir28 I_O	I	I_C	I_D	I_R	Nb60Os40 I_O	I	I_C	I_D	I_R	Mo45Re55 I_O	I	I_C	I_D	I_R	Mo33Re67 I_O	I	I_C	I_D	I_R
101	21	–	24	2	1	16	–	16	2	2	35	19	33	2	10	12	5	12	2	2	11	–	11	2	2
111	6	–	7	–	–	6	–	5	–	–	11	3	9	–	3	3	–	2	–	–	2	–	3	–	1
311	–	3	–	6	9	–	5	–	6	6	–	–	–	8	3	4	4	3	7	10	4	8	4	7	7
002	29	16	30	24	33	21	12	22	20	26	32	26	31	28	27	25	19	29	25	35	25	25	30	25	35
112 / 410	99	81	93	102	96	78	128*	74	81	81	96	81	104	115	107	97	93	97	105	89	100	105	100	105	94
330	38	36	36	45	43	30	40	27	36	35	35	38	40	50	43	46	46	43	46	44	48	41	41	46	42
202	27	25	28	40	38	20	36	21	32	32	29	42	32	47	38	37	41	36	40	38	35	45	37	41	37
212 / 420	73	97	70	76	67	62	85	55	61	59	88	88	80	86	84	74	76	78	81	75	76	65	78	82	73
411	114	157	119	121	133	133*	175*	87	96	106	132	114	124	135	122	127	124	127	123	140	123	130	129	125	135
331	70	60	64	57	60	60	51	49	45	51	75	106	68	65	65	64	55	60	59	65	61	63	65	60	65
222	12	14	16	13	12	11	–	13	11	11	14	23	18	16	16	15	16	14	14	12	16	16	15	14	13
312 / 430	18	11	18	15	14	11	15	14	12	12	19	23	22	18	18	18	16	18	17	13	17	20	18	17	14

* Denotes overlapping impurity lines.

Table 6. *Ternary σ phases*

(a) V–Fe phases

σ phase	Site A V	Fe	Z	Site B V	Fe	Z	Site C V	Fe	Z	Site D V	Fe	Z	Site E V	Fe	Z	Observed (Å) a_0	c_0	Calculated (Å) a_0	c_0	Observed ($\times10^3$) Δa_0	Δc_0	Calculated ($\times10^3$) Δa_0	Δc_0
V Fe	0.25	1.75	—	3.35	0.65	—	5.4	2.6	—	1	7	—	5	3	—	8.949	4.622	8.995	4.666	—	—	—	—
V Fe Ta	0	2	0	3	1	0	5.75	1.55	0.7	0	8	0	5.75	1.95	0.3	8.961	4.626	9.009	4.672	+12	+4	+14	+6
V Fe W	0	2	0	3	1	0	5.75	1.55	0.7	0	8	0	5.75	1.95	0.3	8.955	4.623	8.999	4.668	+6	+1	+4	+2
V Fe Mn	0.25	0.75	1	3.75	0.25	0	4.65	3.35	0	1	7	0	4.85	1.35	0	8.953	4.623	9.000	4.668	+4	+1	+5	+2
V Fe Re	0	2	0	3.3	0.55	0	5.65	2	0.35	1	7	0	4.55	2.95	0.5	8.961	4.626	9.008	4.671	+12	+4	+13	+5
V Fe Zr	0.25	1.75	0	0.8	3.2	0	7.1	0	0.9	0.45	7.55	0	5.9	2.0	0.1	8.964	4.626	9.011	4.669	+15	+4	+16	+3

(b) Nb–Al phases

σ phase	Site A Nb	Al	Ta	Site B Nb	Al	Ta	Site C Nb	Al	Ta	Site D Nb	Al	Ta	Site E Nb	Al	Ta	Observed (Å) a_0	c_0	Calculated (Å) a_0	c_0	Observed ($\times10^3$) Δa_0	Δc_0	Calculated ($\times10^3$) Δa_0	Δc_0
Nb_2Al	1	1	—	4	0	—	4	4	—	4	4	—	7	1	—	9.943	5.186	10.039	5.238	−73	−12	−36	−11
$Nb_{34}Ta_{34}Al_{32}$	0	1	1	1.5	0.5	2	2	4	2	3	3.5	1.5	3.5	1	3.5	9.870	5.174	10.003	5.227	−79	+29	−86	+8
Ta_2Al	—	0	2	—	2	2	—	8	0	—	0	8	—	0	8	9.864	5.215	9.953	5.246	—	—	—	—

σ phase	Site A Nb	Al	Zr	Site B Nb	Al	Zr	Site C Nb	Al	Zr	Site D Nb	Al	Zr	Site E Nb	Al	Zr	Observed (Å)	Calculated (Å)	Observed ($\times10^3$) Δa_0	Δc_0	Calculated ($\times10^3$) Δa_0	Δc_0
$Nb_{53.5}Zr_{13.5}Al_{33}$	0	2	0	0	4	0	4	0	4	4	4	0	8	0	0	9.952 5.174	10.068 5.238	+9	−12	+29	0

(c) Phases including Si

σ phase	Site A Cr/V	Fe	Si	Site B	Fe	Si	Site C	Fe	Si	Site D	Fe	Si	Site E	Fe	Si	Observed (Å) a_0	c_0	Calculated (Å) a_0	c_0	Observed ($\times10^3$) Δa_0	Δc_0	Calculated ($\times10^3$) Δa_0	Δc_0
$Cr_{50}Fe_{50}$	0.8	1.2	—	3	1	—	4	4	—	3	5	—	4.2	3.8	—	8.798	4.558	8.816	4.593	—	—	—	—
$Cr_{46.5}Fe_{46.5}Si_7$	0.25	1.75	0	1	3	0	4	4	0	2.9	5	2.1	7.8	0.2	0	8.780	4.570	8.804	4.603	−18	+12	−12	+10
$V_{47}Fe_{53}$	0.25	1.75	—	3	1	—	5	3	—	1	7	—	4.85	3.15	—	8.943	4.619	8.975	4.661	—	—	—	—
$V_{42.3}Fe_{47.7}Si_{10}$	0	2	0	2	2	0	4.5	3.5	0	0	5	3	6.19	1.81	0	8.906	4.625	8.939	4.670	−37	+6	−36	+9

The observed values in this table were taken from the following references:

(*a*) Kitchingman & Bedford (1971)
(*b*) Hansen & Raman (1970)
(*c*) Aronnson & Lundström (1957), Gupta, Rajan & Beck (1960)

extent, therefore, the sites occupied by atoms are not dictated by the need to fit into the pattern. It is assumed that any apparent misfit caused by smaller atoms lying in larger sites will be supported by appropriate electronic forces between atoms as implied in the disordered binary σ phases created by neutron irradiation.

The addition of silicon

The role of silicon dissolved in binary σ phases has been considered by Aronnson & Lundström (1957) and Gupta, Rajan & Beck (1960). In the earlier work of Aronnson & Lundström the lattice parameters of the σ phase containing equal atomic percent of Fe and Cr and varying quantities of dissolved Si were measured up to the solubility limit of 14 at. %. The order scheme for the equiatomic σ phase $Fe_{50}Cr_{50}$ has been determined by Algie & Hall (1966) so that this system offers a good test for the calculation of lattice-parameter changes caused by the admixture of silicon. To illustrate the application of the formulae for a_0 and c_0, calculations are made for one σ phase only. The values of a_0 and c_0 for this representative phase containing 7 at. % Si were obtained from the curves given by Aronnson & Lundström showing the variation of a_0 and c_0 with increasing Si content. The Si content in this phase corresponds to 2·1 atoms of Si per unit cell. The revised order scheme for the phase which gives agreement with the observed values for the changes in a_0 and c_0 (Δa_0 and Δc_0) is given together with the calculated and observed values of a_0 and c_0 for the phases with and without Si in Table 6(c).

The work of Gupta et al. (1960) is complementary to that of Aronnson & Lundström and they report values of lattice parameters for the binary σ phase FeV containing various amounts of dissolved silicon. Again to demonstrate the ability of the formulae to calculate the changes in a_0 and c_0, one composition only containing 10 at. % of Si is chosen. For calculating Δa_0 and Δc_0 the order scheme for σ-FeV is the same as that used for the calculations above, slightly modified to take into account the different composition. The revised order schemes assumed for the σ phases containing Si are chosen to give approximate agreement with the approximate observed values of a_0 and c_0 as shown in Table 6(c). In all the calculations the atomic radius of Si was assumed to be $r_{Si} = 1·30$ Å. This is somewhat lower than the normally quoted Goldschmidt radius ($r_{Si} = 1·34$) but is in keeping with the reduced values of r_V ($= 1·33$) and r_{Fe} ($= 1·26$) chosen for the earlier binary σ-phase calculations, and still larger than $r_{Cr} = 1·28$ Å.

The observed changes in lattice parameters on incorporating Si into both σ-FeV and σ-FeCr are anisotropic with a reduction in a_0 and an increase in c_0. The evidence cited by Aronnson & Lundström (1957) and Gupta et al. (1960) supported the suggestion that the Si atoms occupied D-type sites in the unit cell, but, on the simple sphere-packing model of the σ phase

proposed by Stüwe (1959) the presence of Si atoms in such sites was bound to give increased values of a_0 and c_0, unless the radius of the Si atoms was assumed to be less than that of the atoms replaced. Although the value of r_{Si} used here is less than normal, it is still intermediate between that of V and Fe in the σ-FeV phase and greater than that of Fe and Cr in the σ-FeCr phase. The calculated changes Δa_0 and Δc_0 for both examples have the correct sign and agree approximately with experiment, with the added Si atoms assuming D-type sites in the unit cells. In each case, however, the order schemes required to achieve this approximate kind of agreement assume that the smaller Fe atoms replace one or more of the larger Cr or V atoms in the B sites of the unit cell. It is interesting to note that a similar re-ordering pattern is used in both cases.

Conclusions

The calculation of the lattice parameters of the σ phase has been made solely on the basis of the average radius of atoms occupying each of the possible five sites in the unit cell. In all cases the calculated values are within 1 % of the observed values of a_0 and c_0. The model is most successful in offering an explanation of the changes in lattice parameter which occur when the σ phase is reordered and emphasizes the importance of order in this phase.

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