JOURNAL OF MATERIALS SCIENCE 12 (1977) 1653–1658

Order in NbAl and TaAl type σ phases

C. G. WILSON, F. J. SPOONER
Physics Department, Royal Military College of Science, Shrivenham, UK

The lattice parameter changes with varying composition of the binary σ phases NbAl and TaAl are explained in terms of changes in occupancy of the various crystallographic sites using geometrical formulae derived from a sphere packing model. These order changes throughout the composition range are shown to be mainly caused by the replacement of transition metal atoms by Al atoms in the C-type crystallographic sites, stressing the importance of this site in the stability of the σ phase. The Al occupancy of these sites is closely linked to the composition range of these phases.

1. Introduction

A recent paper by Brown and Worzala [1] on resistivity and lattice parameter variations in Nb_2Al-type σ phases has led the authors to examine further the importance of the σ phase as a sphere packing structure. In an earlier paper [2], attention was focused on a geometrical model for the calculation of the lattice parameters a_0 and c_0 of the unit cell of the σ phase. Spherical atoms were assumed and an average radius for each of the crystallographic sites, A, B, C, D and E, was adopted depending on the site occupancy. In discussing the many σ phases it is normal to refer to the larger and smaller atom types as X and Y respectively. One of the important features of this geometrical model was the ability to predict the changes in a_0 and c_0 when a disordered σ phase was ordered or when the composition of the binary phase XY was changed in the ordered or disordered state. In addition, the variation in lattice parameter was calculated when a ternary σ phase was produced by the substitution of one of the binary components with a third element. One of the examples discussed in [2] was the variation in lattice parameters, produced by progressively substituting Ta for Nb in the binary σ phase Nb_2Al. The experimental results reported by Brown and Worzala [1] are particularly relevant to this earlier study and it is the purpose of this paper to suggest order schemes for the NbAl/TaAl type σ phases in the compositional ranges used by Brown and Worzala [1].

2. Lattice parameters and order schemes

2.1. The geometrical formulae

The crystallographic site occupancy by X- or Y-type atoms determines the average atom radius to be associated with that site. Using the normal 12 co-ordination Goldschmidt radii, Wilson and Spooner [2] determined the parameters a_0 and c_0 for a given σ phase XY from the formulae:

$$a_0 = \frac{a_1 + a_2 + a_3}{3},$$

where

$$\frac{a_1}{2} = (r_A + 2r_D + r_C)\cos(45^\circ - \phi) - \frac{r_B r_C}{\sqrt{2}\,(r_B + 2r_C)} \text{ and } \sin\phi = \frac{r_D}{r_A + r_D},$$

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

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

$$c_0 = \frac{c_1 + 4c_2 + 2c_3}{7},$$

where

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

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

$$c_3 = 4r_E.$$

TABLE I Order schemes and lattice parameters for stoichiometric compounds [2]

	a_0 (obs) (Å)	c_0 (obs) (Å)	Crystallographic site A		B		C		D		E		a_0 (calc) (Å)	c_0 (calc) (Å)
			X	Y	X	Y	X	Y	X	Y	X	Y		
Nb_2Al	9.943	5.186	1	1	4	0	4	4	4	4	7	1	10.034	5.238
Ta_2Al	9.870	5.215	2	0	2	2	0	8	0	8	8	0	9.953	5.246

r_A, r_B, etc, represent the atomic radii associated with each crystallographic site, A, B, etc, respectively. These formulae are based on the geometrical disposition of the atomic sites in the body centred tetragonal unit cell which is adopted by the σ phase structure.

In [2], Wilson and Spooner adopted the order scheme in Table I for the σ-Nb_2Al and σ-Ta_2Al structures reported by Hansen and Raman [3]. The calculated values of a_0 and c_0 were within 1% of the observed values but, more importantly, the differences in a_0 and c_0 for the two phases were in reasonably good agreement, considering the simple nature of the model used. It should be pointed out that the order scheme chosen for Nb_2Al was not that suggested by Brown and Forsyth [4]; this could not account for the observed differences in a_0 and c_0. The order schemes were chosen by Wilson and Spooner [2] to reproduce the variations in a_0 and c_0, not only for the two different binary σ phases Nb_2Al and Ta_2Al but also for the intermediate ternary phase $Nb_{34}Ta_{34}Al_{32}$.

2.2. NbAl σ phases

The values for a_0 and c_0 for the quasi-stoichiometric Nb_2Al samples prepared by Brown and Worzala [1] are not quite the same as those quoted by Hansen and Raman [3]. The latter are in agreement with the values given by Brown and Forsyth [4], which were ascribed to McKinsey and Faulring [5]. The Nb_2Al sample, with composition 33.4 ± 0.3% Al, used by Brown and Worzala, has the experimentally determined parameters $a = 9.942$ Å, $c = 5.160$ Å (each value ± 0.002 Å). Whilst the a_0 value is the same, within experimental error, as the Hansen and Raman value, the c_0 value is significantly lower ($\Delta c_0 = 26 \times 10^{-3}$ Å). This difference in c_0 parameters is interesting and may be due to an uncertainty in the Al content of either the Hansen and Raman, or the Brown and Worzala samples; it could also result from an error in lattice parameter determination, but this does not seem likely in view of the consistent pattern of parameter measurements. We have assumed that the difference is caused by a change in order which

TABLE II Order schemes and lattice parameters for σ-NbAl alloys of varying composition

Composition (at.%)	Atoms/cell		A		B		C		D		E	
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
$Nb_{69}Al_{31}$	20.7	9.3	0.6	1.4	4	0	7.1	0.9	3	5	6	2
$Nb_{68}Al_{32}$	20.4	9.6	0.45	1.55	4	0	6.95	1.05	3	5	6	2
$Nb_{66.7}Al_{33.3}$	20	10	0.25	1.75	4	0	6.75	1.25	3	5	6	2
$Nb_{66}Al_{34}$	19.8	10.2	0.2	1.8	4	0	6.2	1.8	3.5	4.5	5.9	2.1
$Nb_{65}Al_{35}$	19.5	10.5	0.12	1.88	4	0	5.38	2.62	4.25	3.75	5.75	2.25
$Nb_{64}Al_{36}$	19.2	10.8	0.05	1.95	4	0	4.55	3.45	5	3	5.6	2.4
$Nb_{63}Al_{37}$	18.9	11.1	0	2	4	0	3.9	4.1	5.5	2.5	5.5	2.5
$Nb_{62}Al_{38}$	18.6	11.4	0	2	4	0	2.85	5.15	6.45	1.55	5.3	2.7

TABLE III Order schemes and lattice parameters for σ-TaAl alloys of varying composition

Composition (at.%)	Atoms/cell		A		B		C		D		E	
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y
$Ta_{80}Al_{20}$	24	6	0.5	1.5	4	0	8	0	4	4	7.5	0.5
$Ta_{75}Al_{25}$	22.5	7.5	0.9	1.1	4	0	6.6	1.4	4	4	7	1
$Ta_{70}Al_{30}$	21	9	1.3	0.7	4	0	4.7	3.3	4	4	7	1
$Ta_{66.7}Al_{33.3}$	20	10	1.5	0.5	4	0	3.5	4.5	4	4	7	1
$Ta_{65}Al_{35}$	19.5	10.5	1.7	0.3	4	0	2.5	5.5	4.3	3.7	7	1
$Ta_{60}Al_{40}$	18	12	2	0	3	1	0	8	6	2	7	1

may be a result of the different annealing times in the preparation of the various samples, where a slow diffusion rate in the σ phase may lead to alloys in non-equilibrium conditions as intimated by Knapton [6].

Since the differences in the a_0 and c_0 values determined by Brown and Worzala are of primary interest in this paper, a modified order scheme for Nb_2Al has been determined based on that used to explain the Hansen and Raman results. The modified scheme predicts the difference in a_0 and c_0 observed by Brown and Worzala. This order scheme is that given for the specimen with composition $Nb_{66.6}Al_{33.4}$ in Table II.

The lattice parameters measured by Brown and Worzala [1] for NbAl type σ phases of varying Al content are also given in Table II. The observed changes in a_0 and c_0 are assumed to be caused by a change in order, and order schemes are presented for each NbAl composition and values of a_0 and c_0 calculated using the Wilson and Spooner formulae. The order schemes were chosen to give calculated differences Δa_0 and Δc_0 between the measured parameters and those of the stoichiometric Nb_2Al similar in sign and magnitude. Thus, the stoichiometric σ Nb_2Al has been regarded as a standard, and since the calculated values of a_0 and c_0 for this phase are within 1% of the observed values, the calculated values for all the σ phases are determined with this accuracy. The agreement between measured and calculated differences in parameters relative to σ-Nb_2Al is excellent.

2.3. TaAl σ phases

The experimentally determined a_0 and c_0 values for the stoichiometric Ta_2Al σ phase have been determined by interpolation from the Brown and Worzala [1] results:

$$a_0 = 9.930, \quad c_0 = 5.195\,\text{Å (both} \pm 0.010\,\text{Å).}$$

The values used in Wilson and Spooner [2] were those quoted by Hansen and Raman [3]:

$$a_0 = 9.864, \quad c_0 = 5.215\,\text{Å}.$$

The differences $\Delta a_0 = +66 \times 10^{-3}$ and $\Delta c_0 = -20 \times 10^{-3}$ Å are much larger than those for Nb_2Al, and even though the uncertainty in measurement is rather large (± 0.010 Å), it is again assumed that the differences result from changes in order. To effect some meaningful discussion on ordering resulting from compositional changes in the phases, the previous Wilson and Spooner order scheme [2] for Ta_2Al has been modified so that it can reflect the differences between the parameters measured by Brown and Worzala for stoichiometric Nb_2Al and Ta_2Al, using Nb_2Al as a reference. At the same time, the new order scheme for σ Ta_2Al has been chosen so that the changes in a_0 and c_0 reported by Brown and Worzala for the TaAl σ phases of varying composition can also be

TABLE II *continued*

a_0 [1] (Å)	Obs. $\Delta a_0 \times 10^3$ (Å)	a_0 (theor) (Å)	Theor. $\Delta a_0 \times 10^3$ (Å)	c_0 [1] (Å)	Obs. $\Delta c_0 \times 10^3$ (Å)	c_0 (theor) (Å)	Theor. $\Delta c_0 \times 10^3$ (Å)
9.960	+ 17	10.060	+ 18	5.167	+ 77	5.220	+ 5
9.952	+ 9	10.053	+ 11	5.167	+ 7	5.218	+ 3
9.943	0	10.042	0	5.160	0	5.215	0
9.937	− 6	10.037	− 5	5.167	+ 7	5.219	+ 4
9.930	− 13	10.029	− 8	5.173	+ 13	5.221	+ 6
9.922	− 21	10.023	− 14	5.175	+ 15	5.227	+ 12
9.915	− 28	10.015	− 22	5.177	+ 17	5.228	+ 13
9.908	− 35	10.007	− 30	5.183	+ 23	5.233	+ 18

TABLE III *continued*

a_0 [1] (Å)	Obs. $\Delta a_0 \times 10^3$ (Å)	a_0 (theor) (Å)	Theor. $\Delta a_0 \times 10^3$ (Å)	c_0 [1] (Å)	Obs. $\Delta c_0 \times 10^3$ (Å)	c_0 (theor) (Å)	Theor. $\Delta c_0 \times 10^3$ (Å)
9.958	+ 32	10.038	+ 38	5.194	0	5.222	+ 5
9.945	+ 19	10.028	+ 28	5.194	0	5.219	+ 2
9.934	+ 8	10.012	+ 12	5.194	0	5.218	+ 1
9.926	0	10.000	0	5.194	0	5.217	0
9.913	− 13	9.994	− 6	5.200	+ 6	5.219	+ 2
9.885	− 41	9.956	− 44	5.218	+ 24	5.226	+ 9

TABLE IV Calculated lattice parameters using the order schemes suggested by Brown and Worzala [1]

Composition (at.%)	Atoms/cell		A		B		C		D		E		a_0 (Å)	c_0 (Å)
	X	Y	X	Y	X	Y	X	Y	X	Y	X	Y		
σ-NbAl														
$Nb_{69}Al_{31}$	20.7	9.3	0.14	1.86	4	0	8	0	0.56	7.44	8	0	10.063	5.210
$Nb_{68}Al_{32}$	20.4	9.6	0.08	1.92	4	0	8	0	0.32	7.68	8	0	10.059	5.206
$Nb_{67}Al_{33}$	20.1	9.9	0.02	1.98	4	0	8	0	0.08	7.92	8	0	10.055	5.203
$Nb_{66.7}Al_{33.3}$	20	10	0	2	4	0	8	0	0	8	8	0	10.052	5.201
$Nb_{66}Al_{34}$	19.8	10.2	0	2	4	0	8	0	0	8	7.8	0.2	10.051	5.199
$Nb_{65}Al_{35}$	19.5	10.5	0	2	4	0	8	0	0	8	7.5	0.5	10.050	5.197
$Nb_{64}Al_{36}$	19.2	10.8	0	2	4	0	8	0	0	8	7.2	0.8	10.049	5.193
$Nb_{63}Al_{37}$	18.9	11.1	0	2	4	0	7.9	0.1	0	8	7	1	10.045	5.191
$Nb_{62}Al_{38}$	18.6	11.4	0	2	4	0	7.6	0.4	0	8	7	1	10.038	5.190
σ-TaAl														
$Ta_{79}Al_{21}$	23.7	6.3	0.74	1.26	4	0	8	0	2.96	5.04	8	0	10.050	5.218
$Ta_{76}Al_{24}$	22.8	7.2	0.56	1.44	4	0	8	0	2.24	5.76	8	0	10.040	5.210
$Ta_{73}Al_{27}$	21.9	8.1	0.38	1.62	4	0	8	0	1.54	6.46	8	0	10.027	5.200
$Ta_{70}Al_{30}$	21.0	9.0	0.2	1.8	4	0	8	0	0.8	7.2	8	0	10.016	5.192
$Ta_{66.7}Al_{33.3}$	20	10	0	2	4	0	8	0	0	8	8	0	10.004	5.182
$Ta_{64}Al_{36}$	19.2	10.8	0	2	4	0	8	0	0	8	7.2	0.8	10.001	5.175
$Ta_{61}Al_{39}$	18.3	11.7	0	2	4	0	7.3	0.7	0	8	7	1	9.989	5.172

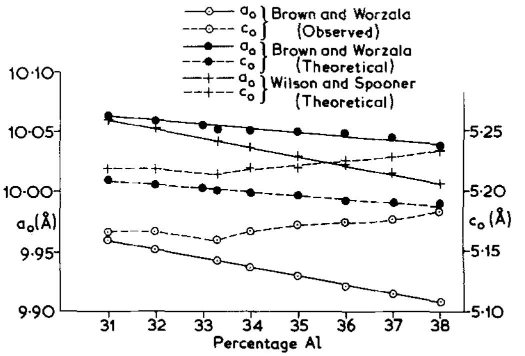

Figure 1 Lattice parameters of σ-NbAl as a function of composition.

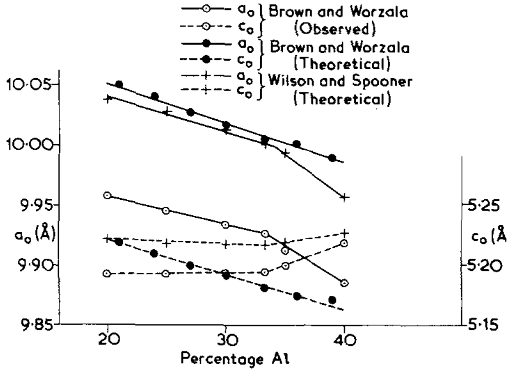

Figure 2 Lattice parameters of σ-TaAl as a function of composition.

reproduced in the calculations. The degree of success achieved is indicated in Table III. The agreement between the measured and calculated differences Δa_0 and Δc_0 is reasonably good, but not as good as that achieved with the NbAl σ phases. This is not surprising considering the relatively large uncertainties of ± 1% in atomic compositon and ± 0.01 Å in parameter measurements for the TaAl phases.

2.4. Comparison of results and the difference formulae

The values of a_0 and c_0 obtained by using the order schemes suggested by Brown and Worzala [1] have been calculated with the aid of the sphere-packing formulae (Table IV) and are plotted as a function of composition, together with the corresponding results using our order schemes, in Figs. 1 and 2. It is clear that the agreement is poor for the Brown and Worzala order schemes.

The order schemes that we propose are obtained by inspection. Owing to the complex nature of the geometrical formulae given previously it is not easy to give a convincing demonstration of the uniqueness of the order schemes chosen. The variations in a_0 and c_0 as a function of small changes in site occupancy are most easily followed by using the following difference formulae which are derived from the formulae for a_0 and c_0:

$$\Delta a_0 = 1.2\Delta r_A + 1.95\Delta r_B + 1.91\Delta r_C + 1.3\Delta r_D + 0.6\Delta r_E$$

$$\Delta c_0 = 0.33\Delta r_A + 0.5\Delta r_B + 0.32\Delta r_C + 1.3\Delta r_D + 1.2\Delta r_E.$$

These formulae give the changes produced by the transfer of atoms from one crystallographic site to another, and, providing a reference order scheme is available for one composition, a unique sequence of order schemes can be chosen to conform to the pattern of changes recorded for a_0 and c_0 of different compositions. In this deductive process it is assumed that changes in a given site occupancy by a given component increase or decrease monotonically. It is possible to reproduce the variation in a_0 and c_0 for different σ phase compositions by choosing random variations in site occupancy but this would represent unusual alloying behaviour.

3. Discussion

Although the binary σ phase is not properly understood, the two factors which govern the stability of the phases produced by transition metals are electronic and atomic size. The average number of electrons outside the closed shells and sub-shells per atom (electron:atom ratio) in these phases is found to lie between 5.6 and 7.4 [7]. Furthermore, the two components of the phase σ XY are distinguished by the difference in their own electron:atom ratio, X being less than 7 and Y greater than 7. From the early studies of ordering in σ phases, Kasper and Waterstrat [8] deduced that X type atoms preferentially occupy B sites, Y atoms preferentially occupy A and D sites and the remaining C and E sites have mixed X and Y occupancy. The B sites have the largest co-ordination number (CN = 15), the A and D sites the smallest (CN = 12) and both C and E sites an intermediate value (CN = 14). Since the radius of X-type atoms is usually greater than that of Y atoms, an atomic size correlation is also associated with ordering. However, exceptions are known, such as σ-CrMn and σ-CrRe, in which $r_X < r_Y$ and the so-called inverse ordering occurs with the smaller Cr atoms occupying A and D sites. This points to the size factor being dominant in ordering these phases [9]. Frank and Kasper [10] regard the σ phase as a packing sequence of Kagomé nets of spherical atoms and point the importance of atomic size in determining the ordering appropriate to the packing requirements. Thus, for transition metal σ phases atomic size is probably the more important parameter controlling the stability of the ordered state.

The geometrical sphere-packing model proposed by the present authors [2] attempts to take into account the distortion of spherical atoms which fill the available space by using a weighted average for the relations between lattice parameters and atomic size derived from the simple packing of the structure elements. This is a phenomenological device which avoids uncertain knowledge of the forces between neighbouring atoms and the atomic compressibilities. The model ignores any electronic factors which may affect the occupancy of a given site. This is important in discussing the application of the model to the two binary σ phases with X = Nb or Ta, and Y = Al, in which the Y component is a non-transition metal. Since the electron:atom ratio for both of these phases is well below the average of 6.5 for transition metal σ phases (4.3 for both Nb_2Al and Ta_2Al), the role of the electronic factor in determining stability becomes obscure. If it be assumed that the size factor is the most important ordering parameter, Al atoms would be expected to occupy the A and D sites, since $r_{Al} < r_{Ta} < r_{Nb}$, and Nb or Ta to occupy B sites with mixed occupancy of C and E sites. It is also reasonable to suppose that a non-transition element such as Al would not dominate E sites because of the excess contraction required.

The results of the present work show that the order schemes for the stoichiometric σ-Nb_2Al and σ-Ta_2Al are not dissimilar. The large B and E sites are occupied predominantly by the larger Nb and Ta atoms as expected, the D sites of each alloy have mixed occupancy, but the behaviour is different in the A and C sites: Nb_2Al has Al dominant in A sites and Nb dominant in C sites, whilst Ta_2Al has a similar mixed occupancy in C and D sites but the larger Ta atoms occupy most of the smaller A sites. A difference in order behaviour of the two stoichiometric alloys is suggested by the experimental evidence presented by Brown and Worzala [1] in which Nb_2Al alone shows a marked peak in resistivity at the stoichiometric composition corresponding to the decrease in c_0 at this composition.

As the composition of each type of σ phase changes from the stoichiometric form, the general pattern of behaviour tends to be similar. Towards the Al-rich side of stoichiometry each σ phase tends to transfer transition elements from C sites to D sites. On the opposite side of stoichiometry the opposite behaviour occurs, and the ordering schemes are similar at the end of the composition range and support the expected behaviour of X atoms occupying B sites and Y atoms occupying A sites, but C and E sites are dominated by X and D sites are mixed. For σ-$Ta_{79}Al_{21}$ (at.%) the order scheme is very similar to that suggested by Brown and Worzala to explain their results.

The most striking feature of the two sets of order patterns is the gradual replacement of transition metal atoms by Al as the composition range is traversed from small to high Al content. The B and E sites are relatively unaffected. The behaviour of D sites shows a marked replacement of Al by Nb in NbAl phases and a smaller kind of change for TaAl phases. The A sites in NbAl phases gradually fill with Al atoms and fill with Ta atoms in TaAl phases. As shown in Fig. 1,the experimental results show a decrease in a_0 with increasing Al content in each type of σ phase, but the c_0 parameter tends to increase beyond the stoichiometric Nb_2Al or Ta_2Al compositions. The difference formulae show that a variation in C occupancy produces a large change in a_0 but a small change in c_0, whilst a variation in D occupancy produces the same change in a_0 and c_0. Thus, these two sites govern the lattice parameter changes. The E sites are relatively unchanged throughout both composition ranges, which is not surprising if it is assumed that Al atoms cannot be compressed to the extent that is required in this structure. However, if the E sites remain unchanged and are mostly filled by transition metal atoms they must relax slightly as c_0 increases beyond the stoichiometric composition. This relaxation can be effected, and at the same time the a_0 values can decrease with increasing Al content, if the transition metal atoms in C sites are replaced by smaller Al atoms. The C sites are unique since they form tetrahedra about the vertical four-fold inverse or rotation axes in the unit cell, with one tetrahedron per unit cell surrounding each four-fold axis. These tetrahedra link the planar arrays of A, B and D sites from adjacent cells and act like anchor pins. Thus, if the non-transition metal atoms are much less capable of being compressed (vertically) than the transition metal atoms, which certainly occurs in C sites, though to a lesser extent than E sites, the gradual replacement of C sites by Al can reproduce the observed behaviour. The smaller changes in A and D sites allows the planar arrays to adjust to the new spatial requirements.

Although this argument is plausible, it does not account for the different behaviour in the A sites of the two sets of σ phases. The gradual increase of Ta in A sites with increasing Al content in TaAl phases is expected as a consequence of replacing D sites with Ta in the quasi-tetrahedral arrangement of A, B and D sites. The opposite behaviour with NbAl phases is understandable because it is accompanied by increasing Al content in E sites. Whilst the TaAl σ phase order schemes seem to be anomalous in permitting the larger Ta atoms to dominate A and D sites at the Al-rich end of the composition range, this behaviour is simpler than that of NbAl σ phases and leads to the wider range of 20 to 40 at.% Al for TaAl compared to 31 to 38 at.% Al for NbAl.

4. Conclusions

(1) The Wilson–Spooner sphere-packing model of the σ phase can give a good account of the order associated with the NbAl and TaAl σ phases and reproduces the variations in the associated lattice parameters.

(2) The variation in order throughout the composition range is mainly caused by the smaller Al atoms replacing transition metal atoms in C sites, the required stability being achieved by packing without compression in these sites.

(3) The range of composition of the two phases is linked to the permissible Al content in C sites, which is a maximum in TaAl phases but is restricted in NbAl phases.

5. References

1. P. W. BROWN and F. J. WORZALA, *J. Mater. Sci.* **11** (1976) 760.
2. C. G. WILSON and F. J. SPOONER, *Acta. Cryst. A* **29** (1973) 342.
3. R. C. HANSEN and A. RAMAN, *Z. Metallk.* **61** (1970) 115.
4. P. J. BROWN and J. B. FORSYTH, *Acta, Cryst.* **14** (1961) 362.
5. C. R. McKINSEY and G. M. FAULRING, *ibid* **12** (1959) 701.
6. A. G. KNAPTON, *J. Inst. Metals* **87** (1958) 28.
7. E. O. HALL and S. H. ALGIE, *Met. Rev.* **11** (1966) 61.
8. J. S. KASPER and R. M. WATERSTRAT, *Acta. Cryst.* **9** (1956) 289.
9. R. W. SPOR, H. CLAUS and P. A. BECK, *X-ray Anal.* **10** (1967) 213.
10. F. C. FRANK and J. S. KASPER, *Acta. Cryst.* **12** (1959) 483.

Received 24 September and accepted 14 October 1976.