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The Structure of the σ-Phase Nb_2Al

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The σ-phase structure of Nb_2Al has been confirmed by making single-crystal measurements. The distribution of atoms in the available sites has been determined and the atomic parameters have been refined. The relationship of this structure to other σ-phases is discussed.

1. Introduction

At least three intermediate phases exist in the niobium–aluminium system; $NbAl_3$ is tetragonal (Brauer, 1939), and Nb_3Al is cubic with the β-tungsten structure (Wood *et al.*, 1958). The third phase, Nb_2Al, was tentatively identified as a σ-phase by Corenzwit (1959) and this was subsequently confirmed by McKinsey & Faulring (1959), who made measurements on a single-phase alloy using X-ray powder methods. The occurrence of a σ-phase in which one of the constituents is not a transition metal is unexpected and it was thought that a determination of the ordering in the structure should be made.

2. Material

The material used in the present work was part of a single-phase ingot prepared by Dr McKinsey and kindly given to us by him. His analysis showed that the chemical composition of the ingot was:

Aluminium 12·97 wt.% (33·8 at.%)
Carbon 0·026 wt.%
Niobium (by difference) 87·0 wt.% (66·2 at.%) .

Gaseous impurities were estimated as less than 0·12 wt.%.

The ingot was crushed and a number of fragments examined using the Laue technique. No single crystals were found, and so the fragment which gave the simplest diffraction pattern was selected. In photographs of this fragment the reflexions from one major component could be distinguished.

3. Unit cell

The lattice constants and density of the material were determined by McKinsey & Faulring (1959) to be

$$a=9·943,\ c=5·186\ \text{Å},\ \varrho=6·87\ \text{g.cm.}^{-3};$$

these are in good agreement with a unit cell containing 10 aluminium and 20 niobium atoms, which has a calculated density of 6·89 g.cm.$^{-3}$. The reflexions recorded on Laue, oscillation and Weissenberg photographs were consistent with the space groups $P4_2nm$, $P\bar{4}n2$ and $P4_2/mnm$. The holosymmetric space group was chosen and the subsequent refinement gave no indication that this choice was wrong.

4. Refinement of the structure

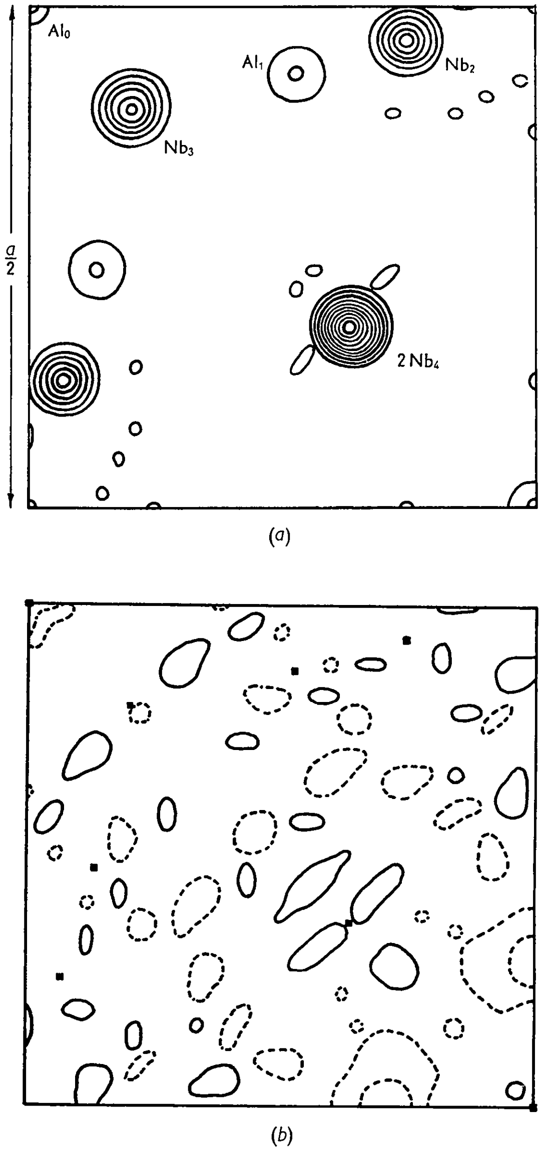
Reflexions from the zero layer of the [001] projection were recorded using the Weissenberg technique; filtered Mo $K\alpha$ radiation and a pack of five films were used. The intensities of the reflexions which extended to $\sin\theta/\lambda \sim 1·2$ Å^{-1} were measured by visual comparison with an intensity scale made with the same crystal. The intensities were corrected for Lorentz and polarization factors. Allowance was made for resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o to F_c in regions of $\sin\theta/\lambda$; for the small crystal used, the method of scaling also makes adequate allowance for the variation of absorption in the specimen. It was found that no correction for extinction was necessary.

The observed structure amplitudes showed fair agreement with those calculated for the CoCr σ-phase structure determined by Dickins *et al.* (1956) (see

Table 1. *Atomic parameters in* σCoCr *and* Nb_2Al

		σCoCr		Nb_2Al		
Type		Atom	Parameters	Atom	Parameters	Standard deviation
2(*a*)	(0, 0, 0)	*A*		Al_0		
8(*i*)	$(x_1, y_1, 0)$	I_1	$x_1 = 0·0654$	Al_1	0·0665	0·0005
			$y_1 = 0·2596$		0·2615	0·0005
8(*i*)	$(x_2, y_2, 0)$	I_2	$x_2 = 0·5373$	Nb_2	0·5350	0·0002
			$y_2 = 0·1291$		0·1280	0·0002
4(*g*)	$(x_3, \bar{x}_3, 0)$	G	$x_3 = 0·3984$	Nb_3	0·3965	0·0003
8(*j*)	(x_4, x_4, z)	J	$x_4 = 0·3174$	Nb_4	0·3180	0·0002
			$z_4 = 0·250$		0·2520	0·0007

Table 1) with niobium in all the atomic sites. An F_o synthesis showed that the aluminium atoms were located principally on the A and $\mathrm{I_I}$ sites. The structure was refined using $(F_o - F_c)$ syntheses and a final R-factor of 0·085 was obtained with these sites completely filled with aluminium atoms. The final F_o and $(F_o - F_c)$ syntheses are shown in Fig. 1.

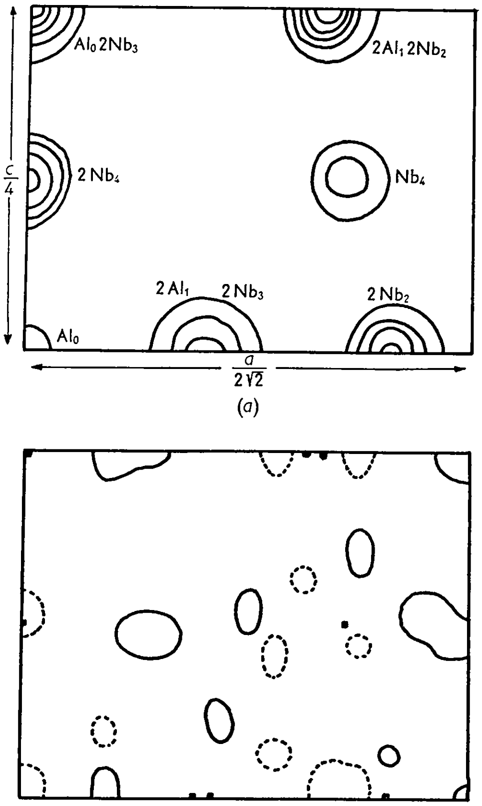


(a)

(b)

Fig. 1. Final F_o and $(F_o - F_c)$ [001] Fourier projections. (a) F_o. The contours are at equal arbitrary intervals. (b) $(F_o - F_c)$. The contour intervals are one-fifth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

Refinement of the [001] projection gave values for all the parameters except z_4. In order to determine the value of this parameter and also to give a further check on the accuracy of the structure, reflexions were recorded for the zero layer of the [110] projec-



(a)

(b)

Fig. 2. Final F_o and $(F_o - F_c)$ [110] Fourier projections. (a) F_o. The contours are at equal arbitrary intervals. (b) $(F_o - F_c)$. The contour intervals are one-fifth those of the F_o; negative contours are shown as broken lines. Squares mark the atomic sites.

Table 2. *Interatomic distances in* Nb_2Al, *together with their standard deviations*

Atom	Neighbour	Distance	Standard deviation	Other neighbours
Al_0	4 Al_1	2·683 Å	0·002 Å	
	4 Nb_3	2·973	0·003	
	4 Nb_4	2·864	0·004	
Al_1	1 Al_1	2·742	0·007	1 Al_0
	2 Nb_2	2·833	0·005	
	1 Nb_2	2·799	0·005	
	1 Nb_2	2·787	0·005	
	2 Nb_3	3·054	0·006	
	2 Nb_4	2·895	0·007	
	2 Nb_4	2·877	0·007	
Nb_2	1 Nb_2	2·639	0·004	1 Al_1 2 Al_1
	4 Nb_2	3·194	0·003	
	1 Nb_3	2·755	0·004	
	2 Nb_4	3·140	0·005	
	2 Nb_4	3·151	0·005	
Nb_3	1 Nb_3	2·911	0·006	2 Al_0 4 Al_1 2 Nb_2
	2 Nb_4	3·279	0·008	
	4 Nb_4	3·221	0·008	
Nb_4	1 Nb_4	2·614	0·007	1 Al_0 2 Al_1 2 Al_1 2 Nb_2 2 Nb_2 2 Nb_2 1 Nb_3
	1 Nb_4	2·572	0·007	

tion. These data were corrected, and the refinement was carried out, in the same way as for the [001] projection. The final R-factor for this projection was 0·099; the final syntheses are shown in Fig. 2.

The final parameters and their standard deviations are given in the last two columns of Table 1. The interatomic distances are listed in Table 2.

Discussion

The main features of the structure are substantially the same as those of the CoCr σ-phase (Dickins *et al.*, 1956). The interatomic distances are between 10 and 15% larger than those in σ CoCr mainly by virtue of the increased lattice constants. The parameter z_4 which in σ CoCr was not found to be significantly different from 0·250, was changed in this structure to 0·2520. This has had the effect of making the interatomic distances from the Nb_4 atom to atoms in the layer at $z=\frac{1}{2}$ more nearly equal to those to the equivalent atoms in the layer at $z=0$. This equalisation is achieved by making the two Nb_4–Nb_4 distances unequal.

Table 3. *Mean interatomic distances in the niobium–aluminium phases*

	$NbAl_3$	Nb_2Al	Nb_3Al
Aluminium–Aluminium	2·846 Å	2·712 Å	—
Aluminium–Niobium	2·884	2·895	2·899 Å
Niobium–Niobium	—	3·040	3·175

The compound Nb_2Al is the first σ-phase to be found in which one of the component elements is not a transition metal. The mean interatomic distances in the three known niobium–aluminium phases are given in Table 3; they suggest that the atomic interactions are comparable in all three compounds and they are not inconsistent with the generally accepted radii for the two elements. The stability of this σ-phase may therefore arise mainly from size considerations. In other σ-phase structures for which the ordering has been determined (Kasper & Waterstrat, 1956) the elements to the left of manganese in the periodic table (A) are found to occupy the 15-coordinated site, and those to the right (B) the 12-coordinated sites. Both A and B atoms may occupy the 14-coordinated sites. However, in all these structures the A atom is larger than the B atom, so that the ordering is consistent with the size factor. There are, nevertheless, three known σ-phases (ReCr, RuCr, OsCr) in which the A atom, chromium, is smaller than the B atom. An investigation of the ordering in ReCr is now being undertaken and the result should indicate whether size or some other factor is predominant in determining the ordering in the σ-phase.

The ordering found in Nb_2Al is also consistent with that which must be assumed for Nb_3Al, which has the β-tungsten structure. The atomic environments in the latter are closely similar to those of the 12- and 14-coordinated sites in the σ-phase and the two structures are frequently found in the same system. A number of compounds with the β-tungsten structure have been found in alloys between transition metals and the elements aluminium and gallium (Wood *et al.*, 1958). It is possible that further σ-phases containing only one transition metal may occur in these systems.

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