The Ordering of the σ Phases Cr₂Ru and Cr₂Os

By L. M. Alte da Veiga, M. M. R. R. Costa, M. J. M. de Almeida, L. R. Andrade and
A. Matos Beja

Grupo de Estruturas dos Materiais, Departamento de Física, Universidade de Coimbra, Coimbra, Portugal

Abstract

Two σ-phase structures, Cr_2Ru and Cr_2Os, have been studied using X-ray single-crystal diffraction techniques. The ordering determined has been compared with those of other σ phases and $A15$ structures. Although atoms of both kinds occupy every atomic position, a significant departure from complete disorder was detected. This is particularly important in the 14-fold J atomic positions which are associated with bond angles of 180°: the marked preference of the smaller Cr atoms for these sites indicates that their occupancy appears to be determined by the electronic factor. [Crystal data: Cr_2Ru:space group $P4_2/mnm$, $a = b = 9.0635$ (5), $c = 4.7430$ (5) Å; Cr_2Os:space group $P4_2/mnm$, $a = b = 9.0500$ (2), $c = 4.6900$ (4) Å.]

1. Introduction

The σ-phase structure has thirty atoms per unit cell distributed amongst sites of coordination numbers 12 (A, I_1), 14 (I_2, J) and 15 (G).

A detailed description of this structure based on the early work of Shoemaker & Bergman (1950), Bergman & Shoemaker (1951, 1954), Dickins, Douglas & Taylor (1951) and Kasper, Decker & Belanger (1951), and also an account of its physical properties, have been given by Sinha (1972).

The ordering of σ phases and related structures has been extensively investigated in attempts to infer a general scheme for the occupancy of the atomic sites. Since their composition is not stoichiometric, complete atomic ordering is not to be expected, in general, although a trend towards ordering at some atomic positions has been observed. However, the detection of small amounts of order requires precise measurements which in most cases are not available.

The atomic ordering in binary σ phases is normally ascribed to the following two factors: the electron concentration and the sizes of the constituent atoms. In fact, most of these phases are of type (A,B) where A is a transition metal belonging to the Cr group or to its

left in the periodic table and B is, in most cases, a transition metal to the right of the Cr group;* on the other hand, A atoms are generally larger than B atoms, $(R_A/R_B) > 1$. In the early determinations of the ordering of these phases it was found that the larger atoms occupy the highest, 15-coordinated sites, G, whereas the smaller prefer the lowest, 12-coordinated sites, A and I_1, and both constituent atoms occupy the 14-coordinated positions, I_2 and J (Kasper, 1956). Owing to its stoichiometric composition, σ-Nb_2Al is completely ordered, with the larger Nb atom occupying the G, I_2 and J positions (Brown & Forsyth, 1961).

With ordering in these phases attributable to both electronic and size factors, it should be possible to decide which factor is the more important by studying alloys in which the relative sizes of the constituent atoms are the reverse of those mentioned above, $(R_A/R_B) < 1$, as in Cr_2Ru, Cr_2Os, Cr_2Re and $CrMn_3$, where the 'A' atom, Cr, is smaller than the 'B' atom, Ru, Os, Re or Mn.

Waterstrat & Kasper (1957) reported that no strong ordering was apparent from the measured intensities on powder photographs of Cr_2Re, Cr_2Ru and Cr_2Os, but pointed out that their measurements were not accurate enough to detect small amounts of ordering.

A study of the σ phases and those having the $A15$ type of structure (Alte da Veiga, 1963) based on the comparison of their cell dimensions, c and a respectively, showed similar contractions of the corresponding interatomic distances. Assuming that the stoichiometric $A15$ structures are fully ordered, Alte da Veiga inferred the same ordering for the σ phases or, at least, a similar occupancy of the atomic sites for which the interatomic distances show contractions of the same order.

Spor, Claus & Beck (1967) reinvestigated the σ phase Cr_2Re and pointed out that, when $(R_A/R_B) < 1$, the ordering scheme depends on the magnitude of this ratio: in the case of Cr_2Re, for which the size difference between the constituent atoms is large $(R_A/R_B = 0.93)$, the ordering is essentially determined by the size factor,

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* Phases containing only A metals, (A,A), are not known, and only a few (B,B) phases have been found; the B atom can be Al, as in σ-Nb_2Al.

whereas in $CrMn_3$, where $(R_A/R_B) = 0.99$, the electronic factor predominates. According to these authors, it would be desirable to re-examine Cr_2Ru and Cr_2Os for which the ratio R_A/R_B takes intermediate values, 0.96 and 0.95 respectively; this might help in establishing the size ratio for which the changeover from size-controlled to electronic-structure-controlled ordering occurs in σ phases.

Wilson & Spooner (1973) have proposed a model for the prediction of the unit-cell parameters and of the ordering in σ phases, based on sphere-packing considerations. A comparison between the calculated and observed values of a and c has been made by these authors for a large number of σ phases for which experimental data are available; the overall agreement was found to be better than 1%. A detailed analysis of Table 2 of their paper, however, shows that the model presented does not lead to conclusive results, as far as the prediction of ordering is concerned. This is particularly evident in the case of the σ phase Mo_3Co_2 which is known to be ordered as a result of precise measurements (Forsyth & Alte da Veiga, 1963); it happens that the difference in the atomic radii of molybdenum and cobalt is one of the largest among the known binary σ phases; therefore, a significant difference should be expected between the values of a and c when these are calculated on the assumption of an ordered structure or of a disordered one. Contrarily, a has the same calculated value, 9.297 Å, when both an ordered and a disordered structure are assumed, whilst the corresponding values for c are 4.815 and 4.847 Å, respectively. It must be emphasized that c should be particularly sensitive to ordering; however, the above values differ by less than 1%.

In order to examine the above suggestions in greater detail, a study of the two σ-phase structures σ-Cr_2Ru and σ-Cr_2Os was undertaken in our laboratory using X-ray single-crystal diffraction techniques.

Preliminary studies of the [001] projection of σ-Cr_2Ru and the ordering of σ-Cr_2Os have already been reported (Alte da Veiga, 1966; Costa, Alte da Veiga, de Almeida, Andrade & Matos Beja, 1978).

2. Experimental

The tetragonal σ phase Cr_2Ru is homogeneous over approximately 2 at.% Cr in the region of 66 at.% Cr (Pearson, 1967, p. 843). A similar type of structure occurring at high temperatures has been reported for Cr_2Os (Raub, 1957); the variation of lattice parameters for alloys with 30–32.5 at.% Os also indicates a narrow range of homogeneity (Pearson, 1967, p. 844).

Ingots of Cr_2Ru and Cr_2Os were kindly supplied by Dr M. Nevitt, Argonne National Laboratory, Illinois, USA, and by Dr R. M. Waterstrat, American Dental

Association, Washington, USA, respectively. The former alloy, containing 65.8 at.% Cr and 34.2 at.% Ru, was annealed in high vacuum for 72 h at 1573 K. The alloy $Cr_{67}Os_{33}$ was prepared by arc-melting from 99.9% and 99.999% purity Os and Cr powders, respectively, and annealed in a vacuum of 13×10^{-5} Pa for 24 h at 1673 K.

The crystal used for the study of the [001] projection of Cr_2Ru, already reported, was lost, and a different one from the same ingot was used in the present work.

Accurate lattice parameters were determined for Cr_2Ru, by the method of Farquhar & Lipson (1946), as: $a = b = 9.0635 \pm 0.0005, c = 4.7430 \pm 0.0005$ Å.

The lattice parameters of Cr_2Os were calculated, using the technique developed for the Philips automatic four-circle single-crystal diffractometer, as: $a = b = 9.0500 + 0.0002, c = 4.6900 \pm 0.0004$ Å.

The choice of the space group $P4_2/mnm$ attributed to the σ phases was justified in the course of both structure refinements.

Intensities reflected by the $(hh0)$ planes of the Cr_2Ru crystal were collected out to $(\sin \theta)/\lambda = 0.80$ Å^{-1}. Filtered Mo $K\alpha$ radiation, normal-beam Weissenberg photographs and a multiple-film technique were used. The intensities of the Bragg reflections were measured with a microdensitometer.

The collection of intensity data from the Cr_2Os specimen has been reported elsewhere (Costa et al., 1978). Data were collected on a Philips automatic four-circle diffractometer; 625 reflections, for which $|F| \geq 2\sigma$, were selected for the refinement; the remainder, labelled 'unobserved', were not included in the subsequent calculations; for 90% of these reflections, the corresponding F_c values did not exceed 5% of the highest structure factor and for the remainder, 7% of that value.

Several equivalent reflections were measured for each hkl; the mean intensity value of a group was calculated together with its standard deviation derived from those of the individual reflections; the internal agreement between equivalent reflections used in the structure refinement was within five standard deviations of the mean.

Reflections from this set of data corresponding to the zero layer line of the [001] projection were compared with those previously obtained from Weissenberg photographs. It is worth pointing out the excellent agreement between these two- and three-dimensional data sets, as shown by both the difference maps and the R factors.

In the present work the data obtained with the automatic diffractometer were used for both the two- and three-dimensional refinements.

3. Refinement of structures

The reflection intensities from Cr_2Ru and Cr_2Os were corrected in the usual way for Lorentz and polari-

zation factors; allowance was made for the resolution of the $\alpha_1\alpha_2$ doublet by scaling F_o and F_c in regions of $(\sin \theta)/\lambda$. This procedure also takes into account the variation of absorption in the crystal. In view of the small dimensions and regular shape of both specimens used in the present work, no further correction was applied. The importance of dispersion corrections for Mo $K\alpha$ radiation was tested using the three-dimensional data from Cr_2Os. A refinement was first carried out neglecting the real and imaginary dispersion terms in the scattering factors. No significant variations in the ordering or in the atomic parameters were detected when a dispersion correction was introduced using the terms tabulated in *International Tables for X-ray Crystallography* (1974); the final R factor was found to decrease less than 0.1%.

Cr_2Ru

No evidence was found for serious extinction affecting even the strongest reflections. A plot of $|SF_o|$ against $|F_c|$ is shown in Fig. 1(a).

The atomic scattering factors were generated from the set of analytical constants given by Forsyth & Wells (1959) for Cr^{2+} and Ru. The structure refinement was based on $(F_o - F_c)$ syntheses.

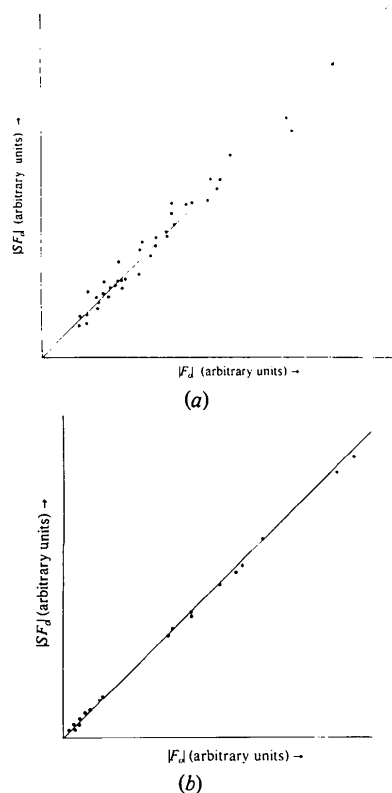The occupation of the 12-, 14- and 15-coordinated atomic sites in this σ phase were determined from the $hk0$ reflection intensities; the same data also allowed the refinement of six out of seven atomic parameters (Alte da Veiga, 1966). Only the z coordinate of the J site (z_4) remained to be determined; this could be done using data from the zero layer of the $[110]$ projection and $(F_o - F_c)$ syntheses.

The arrangement and positional parameters obtained from the study of the $[100]$ projection, together with $z_4 = 0.25$ as for σ-Mo_3Co_2 (Forsyth & Alte da Veiga, 1963), were postulated as a trial structure. The corresponding R factor was 0.11.

Futher adjustments of the atomic parameters and of the ordering previously reported were found necessary to improve the reliability factor. Tables 1 and 2 show the arrangement which gave the lowest R factor, 0.073, when reflections out to 0.80 $Å^{-1}$ in $(\sin \theta)/\lambda$, sensitive to small changes of ordering, were included. Even the low-angle-reflection intensities were sensitive to fine adjustments of the positional parameters, as reported by Alte da Veiga (1966) for σ-Mo_3Co_2. The standard deviations were estimated from the final F_o and $(F_o - F_c)$ syntheses as suggested by Lipson & Cochran (1953).

Fig. 1. (a) Plot of $|SF_o|$ against $|F_c|$ for the strongest reflections from Cr_2Ru. (b) Plot of $|SF_o|$ against $|F_c|$ for the strongest reflections from Cr_2Os.

Table 1. *Atomic parameters and their standard deviations in σ-Cr_2Ru and σ-Cr_2Os*

R factors for the atomic arrangements below are denoted as (1) corresponding to the ordering schemes (a), (b), (c) and (d), shown in Table 2, and (2) corresponding to the disordered structure.

Type	Site		σ-Cr_2Ru (a)	σ-Cr_2Ru (b)	σ-Cr_2Os (c)	σ-Cr_2Os (d)
2(a) (0,0,0)	A	–	–	–	–	–
8(i) $(x_1,y_1,0)$	I_1	x_1	0.0643 (3)	0.0624 (2)	0.0643 (2)	0.0638 (3)
		y_1	0.2585 (3)	0.2566 (2)	0.2595 (2)	0.2593 (3)
8(i) $(x_2,y_2,0)$	I_2	x_2	0.5365 (2)	0.5344 (1)	0.5350 (2)	0.5355 (3)
		y_2	0.1338 (1)	0.1317 (1)	0.1310 (2)	0.1332 (3)
4(g) $(x_3,x_3,0)$	G	x_3	0.4007 (3)	0.4000 (5)	0.4007 (4)	0.4007 (3)
8(j) (x_4,x_4,z_4)	J	x_4	0.3159 (1)	0.3159 (3)	0.3159 (4)	0.3158 (3)
		z_4	–	0.2520 (5)	–	0.2483 (12)
R factors		(1)	0.076	0.073	0.091	0.102
		(2)	0.092	0.097	0.142	0.150

Table 2. *Possible ordering arrangements in σ phases*

Atomic site	A		I_1		I_2		J		G	
Coordination number	12		12		14		14		15	
Occupancy	Cr	Os (Ru)	Cr	Os (Ru)	Cr	Os (Ru)	Cr	Os (Ru)	Cr	Os (Ru)
Electronic-factor order	0	2	0	8	8	0	8	0	4	0
Size-factor order	2	0	8	0	5	3	5	3	0	4
Random disorder	1.33	0.67	5.33	2.67	5.33	2.67	5.33	2.67	2.67	1.33
Cr_2Ru^a	1.5	0.5	5.2	2.8	4.8	3.2	6	2	2.5	1.5
Cr_2Ru^b	1.6	0.4	4.4	3.6	4.8	3.2	6.6	1.4	2.6	1.4
$Cr_2Os^{c,d}$	1.6	0.4	4.5	3.5	4.8	3.2	6.8	1.2	2.3	1.7
Experimental error	5%		3%		3%		3%		5%	

References: (a) Alte da Veiga (1966). (b) Present work. (c) Present work; two-dimensional data. (d) Present work; three-dimensional data.

In a further attempt to improve the agreement between the postulated and the observed structure, the temperature factors were refined. Previous $(F_o - F_c)$ syntheses showed no anisotropy of atomic thermal vibrations; hence, isotropic thermal parameters were assumed for both types of atom in the structure. A slight trend for the temperature factor of Cr to increase above the value of 0·4 used for Ru was inferred from the difference maps; however, the corresponding improvement in the R factor was hardly significant.
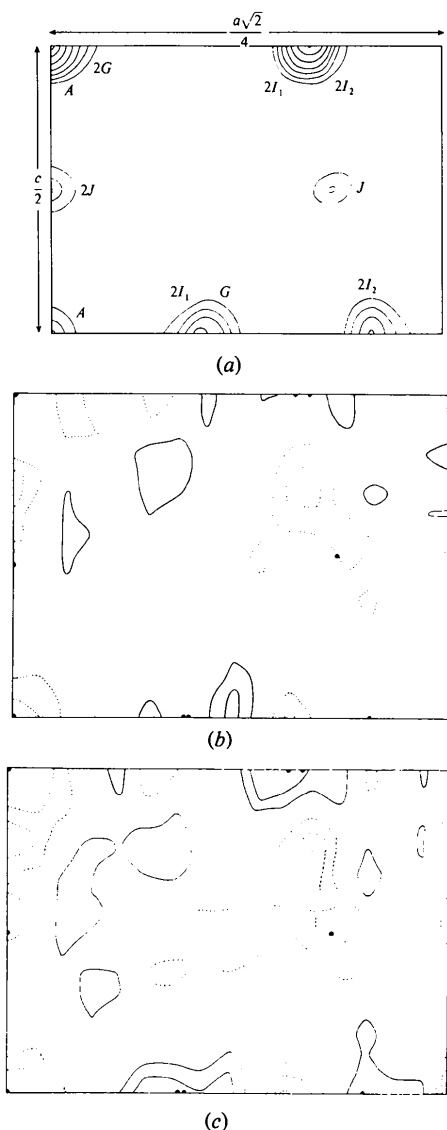

(a)

(b)

(c)

Fig. 2. Final F_o and $(F_o - F_c)$ [110] Fourier projections for σ-Cr$_2$Ru. (a) F_o for the atomic arrangement and ordering shown in Tables 1 and 2; contours are at arbitrary equal intervals. (b) $F_o - F_c$ for the atomic arrangement and ordering shown in Tables 1 and 2; contours are at $\frac{1}{10}$ those of F_o in (a); dashed lines represent negative contours. Circles mark the atomic sites. (c) $F_o - F_c$ for the atomic arrangement shown in Table 1 and a disordered structure; contours are at $\frac{1}{10}$ those of F_o in (a); dashed lines represent negative contours. Circles mark the atomic sites.

The error in the Fourier syntheses was calculated as indicated by Lipson & Cochran (1953) in order to find the significance level on the Fourier maps shown in Fig. 2(a) and (b).

The difference between the results obtained for the occupancy of a few atomic sites in the present work and in that mentioned earlier (Alte da Veiga, 1966) is well above the experimental error (Table 2). The difficulty experienced in selecting the two crystals used reflects the difficulty in growing suitable single crystals during the annealing, and the above discrepancy is most likely a consequence of different local growth conditions.*

Cr$_2$Os

Two- and three-dimensional data obtained from this alloy were processed as described above. No extinction correction was applied as suggested by the graph shown in Fig. 1(b).

The refinement of six atomic parameters and determination of the ordering were based on two-dimensional $(F_o - F_c)$ syntheses using data from the zero layer line of the [001] projection.

The arrangement and parameters obtained for the structure of Cr$_2$Ru were initially postulated, yielding a reliability factor of 0·13. The availability of three-dimensional data made possible the refinement of all positional parameters, including z_4, making use of full-matrix least-squares calculations, as already reported (Costa et al., 1978).

The final values of the atomic parameters and their standard deviations and of the ordering determined from both sets of data are listed in Tables 1 and 2, together with the final R factors.† The results of F_o and $(F_o - F_c)$ syntheses for the arrangement which gave the lowest R factor are shown in Fig. 3(a) and (b).

The agreement between the two- and three-dimensional refinements is generally good, except for the y_2 parameter. In an attempt to clarify this discrepancy, several refinements of the atomic parameters were carried out for different site occupancies: the refined values were found to vary only within their standard deviations. As a complementary test (also enabling the accuracy of the ordering parameters to be assessed) the atomic parameters were kept fixed, while the ordering parameters were altered in the following systematic

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(a)

(b)

(c)
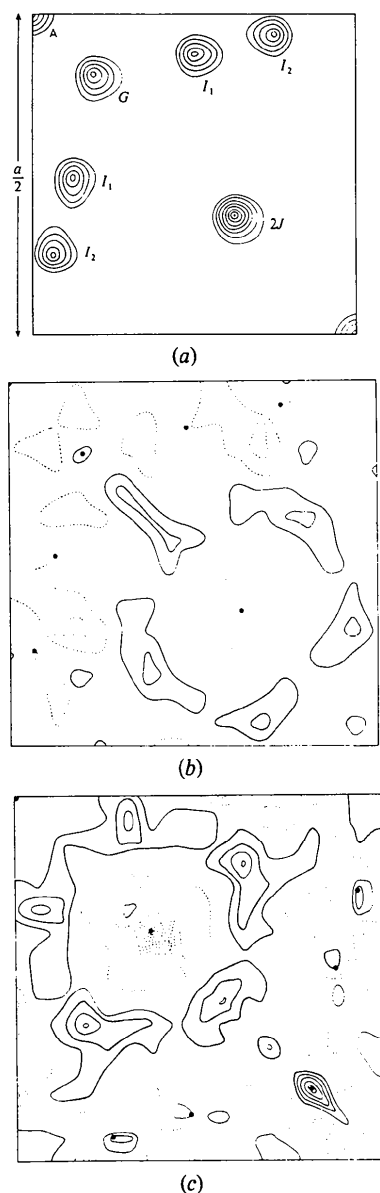
Fig. 3. Final F_o and $(F_o - F_c)$ [001] Fourier projections for σ-Cr_2Os. (a) F_o for the atomic arrangement and ordering shown in Tables 1 and 2; contours are at arbitrary equal intervals. (b) $F_o - F_c$ for the atomic arrangement and ordering shown in Tables 1 and 2; contours are at $\frac{1}{10}$ those of F_o in (a); dashed lines represent negative contours. Circles mark the atomic sites. (c) $F_o - F_c$ for the atomic arrangement shown in Table 1 and a disordered structure; contours are at $\frac{1}{10}$ those of F_o in (a); dashed lines represent negative contours. Circles mark the atomic sites.

Fig. 4. Plot of R factors against occupancies for each atomic site in the σ phase Cr_2Os.

way: for each site the occupancy was varied whilst all remaining sites were assumed to be occupied by the same type of 'compound' atom, as required by the composition of the alloy; the corresponding R factors are plotted against the site occupancies in Fig. 4; the minima of these curves occur at site-occupancy values which agree with those listed in Table 2. Although these
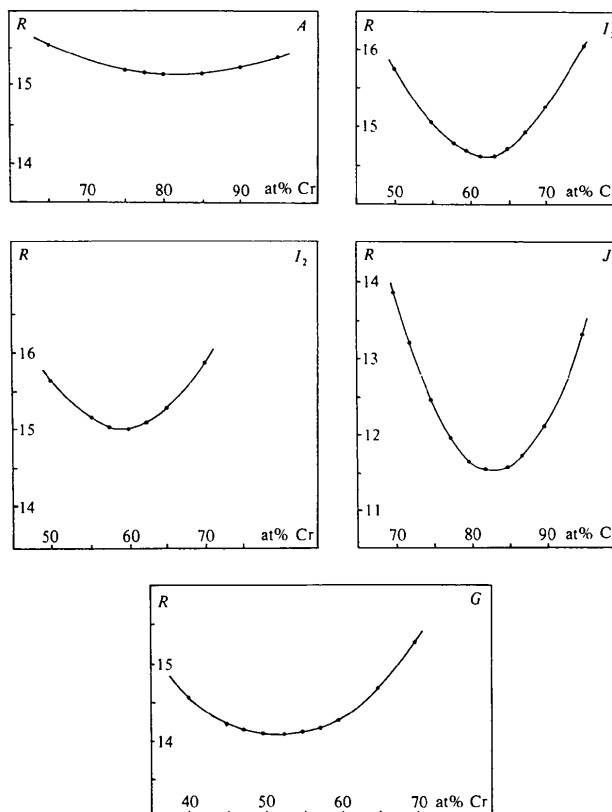
two tests do not provide an explanation for the discrepancy in y_2, they show that no interaction between atomic coordinates and site occupancies appears to have affected the final results. This conclusion is also supported by the fact that the same ordering parameters were obtained both in the two-dimensional and in the three-dimensional refinements, which were carried out in different ways, as described above.

The curves shown in Fig. 4 indicate the sensitivity of the R factor to small variations of the individual site-occupancy parameters: as expected, for each atomic site, the shape of the corresponding curve depends on the number of equivalent positions in the unit cell. The pronounced U shape of the curve for the J site is particularly striking, reflecting a higher degree of sensitivity to small occupancy changes at these sites; this effect was noticed throughout the two-dimensional refinements of Cr_2Ru, Cr_2Os and Mo_3Co_2 (Forsyth & Alte da Veiga, 1963).

The experimental errors in the ordering parameters are listed in Table 2; these values, which were estimated from Fig. 4, agree with those inferred from the successive site occupancies postulated in the course of the two-dimensional refinements of both Cr_2Os and Cr_2Ru.

4. Discussion

The occupancies of the atomic sites according to different ordering schemes and the results found by the present authors are listed in Table 2; it is clear that the σ phases investigated are not fully ordered, but they are not randomly disordered either, as the deviation from this scheme is significant. This may be deduced also from a comparison between the R factors obtained for the ordering determined and when a disordered structure is assumed (Tables 1 and 2) as well as from a comparative analysis of the corresponding $(F_o - F_c)$ maps [Fig. 2(b) and (c) for Cr_2Ru; Fig. 3(b) and (c) for Cr_2Os]. This departure from random disorder will be discussed in detail.

In the two alloys studied the trend towards ordering is shown by the increase of Cr at the J sites, together with a decrease at I_1 and I_2. Only the occupancies of the J and I_1 atomic positions can be attributed to the electronic configuration; the size factor appears to be more effective in determining the occupancy of the I_2 sites. This may seem peculiar, since both the J and I_2 atomic positions are 14-coordinated; however, it must be stressed that the J sites form linear chains in the structure. Atoms at these sites are closely packed along the [001] direction as can be deduced from the relevant interatomic distances, which happen to be the shortest for these alloys (Table 3). Two slightly different values occur, as expected, when the z_4 parameter deviates from the ideal value of 0·25. The I_2 sites form rows GI_2I_2G of a planar net where the distances between any

Table 3. *Interatomic distances* (Å) *in* σ-Cr_2Ru *and* σ-Cr_2Os

Site	Neighbours	Interatomic distances σ-Cr_2Ru	σ-Cr_2Os	Other neighbours
A	$4 J$	2·637 (4)	2·637 (4)	
	$4 G$	2·696 (3)	2·667 (2)	
	$4 I_1$	2·393 (3)	2·417 (4)	
I_1	$2 J$	2·645 (3)	2·625 (4)	
	$2 J$	2·609 (3)	2·611 (4)	
	$2 G$	2·785 (3)	2·775 (2)	
	$2 I_2$	2·595 (2)	2·577 (4)	
	$1 I_2$	2·591 (1)	2·574 (4)	
	$1 I_2$	2·585 (2)	2·552 (2)	
	$1 I_1$	2·489 (3)	2·502 (4)	$1 A$
I_2	$2 J$	2·849 (3)	2·836 (4)	
	$2 J$	2·853 (3)	2·836 (4)	
	$1 G$	2·503 (5)	2·489 (4)	
	$2 I_2$	2·944 (1)	2·935 (2)	$2 I_1, 1 I_1,$
	$1 I_2$	2·467 (1)	2·495 (4)	$1 I_1, 2 I_2$
G	$2 J$	3·007 (5)	3·012 (4)	
	$4 J$	2·939 (5)	2·921 (4)	
	$1 G$	2·563 (6)	2·542 (4)	$2 I_2, 4 I_1, 2 A$
J	J	2·391 (3)	2·361 (8)	$1 G, 2 G, 2 I_2, 2 I_2,$
	J	2·353 (3)	2·329 (8)	$2 I_1, 2 I_1, 1 A$

pair of atoms, particularly I_2–I_2, are noticeably short compared to the sums of atomic radii of the 'compound' atoms at those sites; this has also been observed in σ-Mo_3Co_2 (Forsyth & Alte da Veiga, 1963). The abnormally short J–J distance, suggesting strong electronic bonding (Nevitt, 1962), has been associated with bond angles of 180° (Forsyth & Alte da Veiga, 1962); it is difficult, however, to explain this directional character of the bonding between identical atoms of a transition metal occupying equivalent positions in the structure.

The particular atomic configuration associated with the J sites also occurs in the $A15$ phases where the A sites, having the same 14-fold coordination, also form linear chains (along the [100] direction). Hence, a comparison of the A–A and J–J interatomic distances is meaningful; it is of particular interest to note that these distances are respectively $a/2$ and $c/2$, thus enabling a comparison to be made even before an accurate determination of the structure is carried out. Furthermore, binary alloys possessing the $A15$ type of structure might be expected to be completely ordered, the occupancies of the A and B atomic sites being dictated by a definite stoichiometric composition A_3B. This has been observed in a number of cases; however, some degree of disorder has been found in some phases (Reuth & Waterstrat, 1968; Waterstrat & Dickens, 1974).

A comparative study of $a/2$ and $c/2$ in $A15$ and σ phases which occur in the same system was carried out by Alte da Veiga (1963); based on the assumption that the $A15$ phase Cr_3Ru was fully ordered and on the cell dimensions of Cr_3Ru and σ-Cr_2Ru, Alte da Veiga suggested that the J sites of the σ phase should be exclusively occupied by Cr. A more recent investigation of $Cr_{72}Ru_{28}$ and $Cr_{72}Os_{28}$ alloys with $A15$ type structure and compositions deviating from stoichiometry has shown that the occupancies of sites lying along linear chains are mixed (Reuth & Waterstrat, 1968). The Cr atoms, however, show in both cases a marked preference for those sites ($\sim$85 at.% Cr); the same marked preference is evidenced by the present results for σ-Cr_2Ru and σ-Cr_2Os.

The interatomic distances A–A ($=a/2$) and J–J ($=c/2$) are abnormally short when compared with the sum of the Goldschmidt atomic radii of the 'compound' atoms occupying those sites; these distances and the corresponding contractions are listed for a number of systems in which both $A15$ and σ phases occur in Table 4, which is an updated version of that given by Alte da Veiga (1963). The observed contractions were obtained from the ordering and lattice parameters determined by several authors; the values shown in the last three columns are based on three possible ordering schemes as indicated in Table 2, the differences between the calculated contractions for each alloy indicating their sensitivity to the ordering assumed.

Table 4. *Comparison of contractions in σ phases and A15 structures for systems with both types of structure*

The error in the observed contractions for $Cr_{65.8}Ru_{34.2}$ and $Cr_{67}Os_{33}$ was estimated from the accuracy of the determined occupancy as $\pm0.1\%$.

| | A15 phases | | | | | | σ phases | | | | Contraction (%) | | |
Phase	$A-A$ $(a/2)$ (Å)	Occupancy (at.% A)	Reference	Observed contraction (%)	R_A/R_B	Phase	$J-J$ $(c/2)$ (Å)	Occupancy (at.% A)	Reference	Observed	Electronic	Size	Disorder
$Cr_{72}Os_{28}$	2·3400	87·8	4	9·2	0·948	$Cr_{67}Os_{33}$	2·345	85·0	7	9·1	8·4	10·3	10·0
$Cr_{72}Ru_{28}$	2·3384	85·2	4	9·3	0·955	$Cr_{65.8}Ru_{34.2}$	2·371	82·5	7	8·1	7·4	9·0	8·9
$V_{75}Co_{25}$	2·3380	97·5	6	13·9	1·088	VCo	2·299	*91·0	5	*14·9	15·4	12·8	11·9
$V_{77.5}Ni_{22.5}$	2·3550	100	6	13·4	1·097	VNi	2·315	93·8	1	14·4	14·9	12·0	11·5
						$V_{70}Ni_{30}$	2·335	98·8	1	14·1	14·2	11·2	11·8
						$V_{65}Ni_{35}$	2·320	98·8	1	14·6	14·7	11·8	12·0
Mo_3Os	2·4845	95·3	4	11·1	1·037	$Mo_{65}Os_{35}$	$2·470_5$	87·5	2	11·4	11·8	10·6	10·7
Mo_3Ir	2·4841	96·8	4	11·2	1·037	$Mo_{72}Ir_{28}$	$2·478_5$	87·5	2	11·1	11·5	10·3	10·6
*Nb_3Rh	2·5560	*95·0	3	*12·6	1·097	*Nb_3Rh_2	2·527	*90·0	3	*13·3	14·1	11·1	10·9
Nb_3Os	2·5674	97·5	4	12·5	1·089	Nb_3Os_2	$2·531_5$	75·0	4	12·1	13·9	11·2	11·0
Nb_3Ir	2·5667	98·8	4	12·6	1·089	Nb_3Ir_2	2·525	87·5	4	13·3	14·1	11·4	11·2
Nb_3Pt	2·5762	98·3	4	12·3	1·065	*Nb_3Pt_2	2·565	*94·0	3	*12·4	12·8	10·7	10·6

References (1), (2), (4), (5), (6) and (7) refer to the source of lattice parameters and occupancies; reference (3) refers to the source of lattice parameters only. (1) Kasper & Waterstrat (1956); (2) Spooner & Wilson (1964); (3) Pearson (1967); (4) Reuth & Waterstrat (1968); (5) Wilson & Spooner (1973); (6) Waterstrat & Dickens (1974); (7) Present work.

* See text.

The observed contractions show a consistent trend to deviate from those associated with random disorder and to approach the values calculated for an electronic-factor-controlled ordering (this trend being less marked in Nb_3Os_2).

The occurrence of linear chains with the same atomic configuration in A15 and σ phases suggests that alloys with similar compositions existing in both phases should have similar lattice parameters and exhibit similar contractions: this is confirmed in most cases, as shown in Table 4; the discrepancy in the case of σ-Cr_2Ru is related to the surprisingly different lattice parameters measured in the A15 and σ-phase structures. The contractions appear to depend on the A metal, decreasing as the A atomic number, and hence e/a, increases along the same period; this is in agreement with previous conclusions of Alte da Veiga (1963) and Reuth & Waterstrat (1968) for A15 phases. The latter authors infer that such contractions occur and their magnitudes vary in a similar way, even when the Goldschmidt radius ratio is close to unity. It is in evidence, in Table 4, that the observed contractions fall in four different groups, the contractions within each group being similar; in the second and fourth groups (with distinct A and B metals) similar R_A/R_B ratios occur; this suggests that the observed contractions are likely to be predominantly dependent on the type of the constituent atoms rather than on R_A/R_B.

Based on $A-B$ contact distances, Geller (1956) derived a set of effective A15 (CN 12) radii (which can be used to predict lattice parameters of A15 alloys within 0·03 Å). These have been revised by Johnson & Douglass (1973). The new values of the atomic radii of elements occupying A sites in the A15 structure,

together with the lattice parameter a, can be used to calculate the contractions in a way similar to that indicated previously. Although the values thus obtained are somewhat different from those listed in Table 4, the same type of variation is observed when the A metal varies along the same row of the periodic table.

The above considerations suggest that the data in Table 4 may be used to predict the ordering in those phases for which no experimental results are reported in the literature. This was attempted in the phases marked with asterisks; taking into account the positions of the constituent atoms in the periodic table and the similar compositions of these and other phases, the expected contractions were used to derive the probable occupancy of the J (and A) sites in the alloy.

5. Conclusions

The σ phases Cr_2Ru and Cr_2Os are not fully ordered; however, a significant departure from random disorder has been detected.

The analysis of the results obtained in the present work, taken in comparison with other relevant data, indicates that both the electron concentration and the size factor are important in determining the ordering of σ phases. The prediction of a possible cancellation of size and electronic factors for a limited range of R_A/R_B values in σ phases (A,B) (Spor et al., 1967) appears to be confirmed to a certain extent as far as the A, I_1, I_2 and G sites are concerned. However, it is clear that electronic effects are dominant in determining the occupancy of the J sites, those forming linear chains, thus associated with bond angles of 180°. This

conclusion is also supported by a comparative study of $A15$ and σ-phase structures.

It is worth pointing out that even those authors who base their predictions of ordering in σ phases on size-factor considerations assume that some overlap occurs between spheres occupying the J sites [Wilson & Spooner, 1973, Fig. 2(b)]; the need for admitting that such deformed spheres occur can only be interpreted in terms of electronic interaction between neighbouring J sites.

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Structure du Sulfate de Vanadyle Pentahydraté VO(H₂O)₅SO₄β (Variété Orthorhombique)

PAR MICHEL TACHEZ ET FRANÇOIS THÉOBALD

Université de Franche-Comté, Laboratoire de Chimie-Physique, 32 rue Mégevand, 25030 Besançon CEDEX, France

Abstract

β-VOSO$_4$.5H$_2$O is orthorhombic, space group $Pmn2_1$, with cell parameters $a = 7.234$ (1), $b = 9.304$ (1), $c = 6.184$ (2) Å, $Z = 2$, $V = 416.23$ Å^3, $d_m = 2.021$ (8), $d_x = 2.02$ Mg m^{-3}. The structure was refined to $R = 0.0335$ for 830 unique reflexions; it consists of isolated [VO(H$_2$O)$_5$]$^{2+}$ octahedra and isolated (SO$_4$)$^{2-}$ tetra-