Acta Cryst. (1956). **9**, 297

The Crystal Structure of the Co–Cr σ Phase

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(*Received* 28 *October* 1955)

The crystal structure of a σ-phase Co–Cr alloy containing 53·3 weight% Cr has been determined with moderate accuracy. The tetragonal unit cell with $a = 8{\cdot}81$, $c = 4{\cdot}56$ Å contains 30 atoms ($\sim Co_{13}Cr_{17}$), and the space group is probably $P4/mnm$–D_{4h}^{14}. The strongly pseudo-hexagonal structure consists of flat 'main' layers of atoms in planes $z = 0$, $c/2$ and flat 'subsidiary' layers in planes $z = c/4$, $3c/4$; the atoms in the latter also form straight columns parallel to [001]. There is some evidence for an ordered distribution of Co and Cr atoms in the atomic sites.

The structure is compared with other known σ-phase structures and with that of β-U.

1. Introduction

The occurrence of the σ-phase structure in a number of binary and ternary alloy systems, and its technical importance in relation to the physical properties of alloy steels, have been discussed in many publications in recent years. The X-ray powder pattern of the σ phase is distinctive and has been widely used for the identification of the phase. Its characteristic feature is a cluster of six strong lines with spacings near 2 Å, but the pattern as a whole is very complex and numerous attempts to deduce from it the unit-cell dimensions and space-group symmetry were unsuccessful.

Only fairly recently, with the use of single-crystal methods, has the atomic structure of the σ phase been determined. Preliminary results obtained in three concurrent though independent researches were published by Shoemaker & Bergman (1950) on σ-FeCr; by Dickins, Douglas & Taylor (1951*a*, *b*) on the fundamental similarity between the σ-phase structure and that of β-U (Tucker, 1950*a*, *b*); and by Kasper, Decker & Belanger (1951) on σ-CoCr. A full account of the refinement of the structure of σ-FeCr, and of an examination of σ-FeMo, has now been published by Bergman & Shoemaker (1954), and Kasper, Decker, Belanger & Waterstrat (1952) have described a refinement of the structure of σ-CoCr. Decker, Waterstrat & Kasper (1954) have described a probable ordering scheme for σ-MnMo. The final outcome of a prolonged discussion of the details of the β-U structure (Tucker, 1954) is of great interest for comparison with the σ-phase structure.

The present paper reports the refinement, to a moderate degree of accuracy, of the structure of a σ-CoCr alloy, and an attempt to decide whether there is any ordering of Co and Cr atoms in the phase sites. Full details of the experimental measurements and their interpretation being available elsewhere (Dickins, 1955), the present account is restricted to an outline of the procedure followed in the analysis and a discussion of the results obtained.

2. The approximate structure

We have described in our earlier papers (Dickins *et al.*, 1951*a*, *b*) the procedure leading to the determination of the true unit cell, the possible space groups, and the cell contents for σ-FeCr and σ-CoCr alloys. Comparison with the corresponding data obtained by Tucker (1950*a*, *b*) for β-U at once suggested that the structures must be similar. This was fully confirmed by comparison of the observed intensities of the first thirty lines at the low-angle end of the σ-phase pattern with intensities calculated for Tucker's β-U structure. This comparison rests on the implicit assumption that all the atoms in the σ-phase alloy are—at least to a first approximation—indistinguishable. Recognition of the basic identity of β-U and σ-phase structures provided a convenient starting-point for the process of refinement of the latter, and obviated the necessity for the usual process of analysis of Patterson syntheses in the search for an approximate structure.

Our measurements have been made on a σ-CoCr alloy (kindly supplied by A. G. Metcalfe) containing 53·3 weight% Cr, i.e. 56·4 atomic% Cr. The tetragonal unit cell with

$$a = 8{\cdot}81 \pm 0{\cdot}01,\ c = 4{\cdot}56 \pm 0{\cdot}01\ \text{Å},$$

contains 30 atoms, i.e. approximately $Co_{13}Cr_{17}$, which would require 56·7 atomic% Cr. Reflexions ($0kl$) being absent when l is odd, the possible space groups are $P4/mnm$, $P4nm$ and $P\bar{4}n2$.

The ideal structure (Fig. 1) may be imagined as produced by starting with hexagonal close-packed sheets in the planes $z = 0$ and $z = c/2$, successive hexagonal sheets being oriented at 90° to each other in conformity with the tetragonal symmetry. (This accommodation of a hexagonal atomic pattern within the overall tetragonal symmetry of the cell is a striking

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feature of the structure.) Certain atoms are then displaced from the close-packed sheets to the planes $z = c/4$ and $z = 3c/4$ midway between, forming columns parallel to the c axis. The 11 atoms (per unit cell) in each of the planes $z = 0$ and $z = c/2$ are said to constitute the 'main layers', the 4 atoms in each of the planes $z = c/4$ and $z = 3c/4$ constitute the 'subsidiary layers', in conformity with the notation used for β-U (Tucker, 1954).

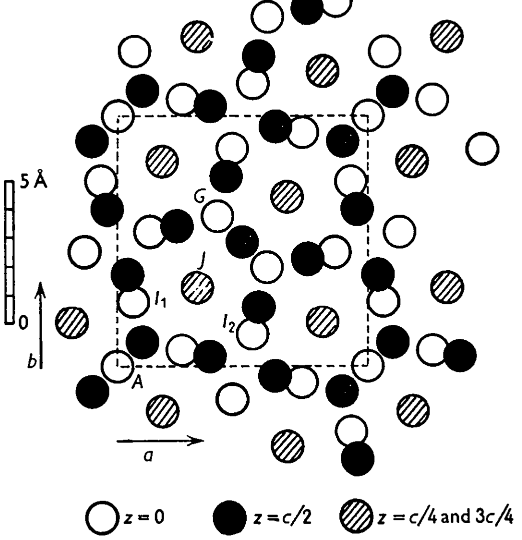

Fig. 1. The structure of σ-CoCr. Atomic coordinates are given in Table 1.

Refinement of a number of σ-phase structures is desirable in order to determine the significance of any variations in detail between one and another, and for accurate comparison of the alloy phases with the element structure β-U. The process of refinement for σ-CoCr is required to provide information on a number of points. First there is the selection of the correct space group from the three which are in conformity with the systematic absences in X-ray reflexions; with this is associated a decision on whether the atoms in 'main' and 'subsidiary' layers lie exactly in the planes $z = 0$, $c/2$ and $z = c/4$, $3c/4$ or are slightly displaced from them; also whether the 'columns' parallel to c are accurately straight, or slightly staggered. Secondly there is the problem of the distribution, in the sites of the phase-structure, of the Co and Cr atoms which are assumed indistinguishable in describing the approximate structure. In this connection a precise determination of the electron distribution in the cell would be most desirable, as would a detailed examination of the thermal vibrations of the atoms occupying sites of different types, and the correlation of both electron distributions and thermal vibrations with the coordination system.

3. Refinement of the structure

Ordering of Co and Cr atoms is discussed in § 4; throughout the present section the assumption of 30 identical atoms per unit cell is retained, and an averaged atomic f-curve is used corresponding to the composition of the alloy.

The degree of refinement achieved in this case is rather severely limited by the accuracy of the experimental measurements of intensity of X-ray reflexion. The fundamental difficulty is that of obtaining single crystals of suitable size and shape: for with a crystal so small that absorption is negligible, a large number of weak reflexions are not observed; while with a bigger crystal the application of the necessary absorption correction is subject to considerable uncertainty and inaccuracy since the material is too hard and brittle to permit control of the dimensions of the specimen. (Similar difficulties were encountered, in even more acute form, in Tucker's work with β-U.)

Oscillation photographs around [001] and [110] axes and Weissenberg photographs around [001] were taken with two crystals, using Mo $K\alpha$ radiation (filtered with Zr) and the standard multiple-film technique. Intensities were estimated visually by comparison with a standard scale, and corrections were applied for α-doublet separation and Lorentz and polarization factors. A complicated series of correlations and cross-checks, based on a systematic treatment of all the observations for each set of photographs, was devised to deal with the uncertainties associated with absorption effects. The observed intensities thus obtained were scaled, in the usual way, to give F_o by comparison with F_c in the course of the structure-refinement. This scaling operation effectively introduces an empirically determined isotropic temperature-factor and it may be noted here that the accuracy of the work did not justify any attempt to consider separately the temperature vibrations of individual atoms.

From the approximate structure it is obvious that the atoms are clearly resolved in projection on (001); the refinement of the x and y coordinates was therefore carried out in the usual way by means of a series of F_o and $(F_o - F_c)$ syntheses in this projection. This procedure is especially convenient for this structure, in which x and y coordinates of the atoms are certainly very close to those appropriate to the centrosymmetrical space group $P4/mnm$; for a slight departure from these positions, such as would be compatible with the space group $P4nm$, would be revealed (for example) in the case of the atoms J by elliptical electron-density contours corresponding to two nearly-overlapping atoms, instead of the circular contours of a pair of atoms exactly superposed (cf. Kasper *et al.*, 1952 and private communication, and see § 5(ii), below). No such systematic departures from normal circular contours were observed for any atom, so that in this projection the structure conforms to the

Table 1. *Atomic coordinates*

σ-CoCr			σ-CoCr (Kasper)		σ-FeCr		β-U	
Atom	Type	Parameters	Atom	Parameters	Atom	Parameters	Atom	Parameters
A	2(a)	(0, 0, 0; ½, ½, ½)	I	—	A	—	I	—
G	4(g)	$x(G)$ = 0·3984	II	0·3969	B	0·3981	II	0·3967
I_1	8(i)	$x(I_1)$ = 0·0654	IV	0·0662	D	0·0653	V	0·0608
		$y(I_1)$ = 0·2596		0·2604		0·2624		0·2646
I_2	8(i)	$x(I_2)$ = 0·5373	III	0·5370	C	0·5368	IV	0·5383
		$y(I_2)$ = 0·1291		0·1287		0·1316		0·1333
J	8(j)	$x(J)$ = 0·3174	V′ V″	0·3063 0·3256	E	0·3177	III	0·3183
		$z(J)$ = 0·250		0·25		0·2476		0·2300

The first three columns, headed 'σ-CoCr', refer to the authors' analysis. Notation, for space group $P4/mnm$–D_{4h}^{14}, as in *International Tables* (1952), p. 236, for type atoms (g) $x, \bar{x}, 0$; (i) $x, y, 0$; (j) x, x, z. Probable error in x, y (see text) estimated as ±0·001, which corresponds to ±0·01 Å (approx.).

Remaining columns contain information on other σ structures, parameter values being given in form comparable with those for authors' σ-CoCr.

(i) Kasper's σ-CoCr is based on $P4nm$; his division of our group (8) J into two groups (4) V′ and (4) V″ is discussed in the text (§ 5(ii)).

(ii) σ-FeCr from Bergman & Shoemaker (1954); probable error 0·0006 for all except $x(C)$ 0·0007.

(iii) Parameters for β-U from Tucker & Senio (1953).

Table 2. *Determination of z coordinates*

		From $hk0$ (cf. Table 1)			From $hk3$				
Atom	z (approx.)	x	y	Peak height	x	y	Peak height	cos $2\pi.3z$	z
A	0	0	0	462	0	0	(462)	—	0
G	0·5	0·1016	0·1016	403	0·1017	0·1017	−352	−0·874	0·50±0·03
I_1	0	0·0654	0·2596	441	0·0654	0·2601	430	0·975	0·00±0·01
I_2	0·5	0·0373	0·3709	376	0·0365	0·3685	−362	−0·963	0·50±0·01
J	0·25	0·3174	0·3174	817	(0·3174) 0·323	(0·3174) 0·323	−1 12	−0·001	0·25 ±0·000 0·25 ±0·001

The atoms G and I_2 in this table are not the same as the type atoms for which coordinates x and y are quoted in Table 1; in each case they are related by the symmetry operations of the space group.

Peak heights in the generalized ($hk3$) projection are scaled so that atom A is the same as in the ($hk0$) projection. Atomic coordinates x and y deduced from the ($hk3$) projection agree closely with those from ($hk0$) for atoms A, G, I_1, I_2; for J the electron density −1 is observed in ($hk3$) at the position corresponding to the atomic coordinates computed from ($hk0$), and 12 is the height of a small peak in the near neighbourhood. (Two atoms are superposed in the ($hk0$) projection to give peak height 817 for J.)

An error of ±0·01 in z corresponds to ~ ±0·05 Å.

space group $P4/mnm$. In the later stages of the refinement, it was necessary to substitute in the syntheses F_c for F_o for 6 of the strongest reflexions, obviously too weak on account of extinction. The atomic peaks were located both graphically, and analytically by the method of Ladell & Katz (1954); the final parameters are given in Table 1. During the refinement process the agreement factor R fell from ~30% only to a little below 25%—a sufficient indication that only moderate accuracy can be claimed for the 'refined' structure, though it must not be forgotten that the R factor would be too high if, contrary to the assumption of 30 identical atoms per unit cell, there were in fact a high degree of order in the distribution of Cr and Co atoms.

It remained to determine the z coordinates of the atoms and to decide whether or not the structure is centrosymmetrical. From the approximate structure it is known that the atoms lie in a series of layers either flat or nearly so: for such structures statistical methods are unreliable, and would not be regarded as adequate to establish with certainty the presence or absence of a centre of symmetry. Nevertheless, it was thought to be possibly significant that one such test (Howells, Phillips & Rogers, 1950) clearly indicated centrosymmetry, which would correspond to the choice of space group $P4/mnm$. If this is actually the space group, atoms AGI_1I_2 (of Table 1) must lie exactly in the planes $z = 0$, $c/2$ and the main layers are flat, but no symmetry restriction is placed on the z coordinates of atoms J, known to lie in or near planes $z = c/4$, $3c/4$. Without assuming this space group, the z coordinates were directly determined by the method of generalized projections (see, for example, Lipson & Cochran, 1953), reflexions ($hk3$) being used to prepare a projection for comparison with the ($hk0$) projection. (The ($hk5$) projection, more sensitive, in principle, for determining z coordinates, was not used because the intensity measurements were thought to be too unreliable.) Table 2 shows that the heights of the well-defined peaks, in the ($hk3$) projection, corresponding to atoms AGI_1I_2, indicate z coordinates 0 or $c/2$ within the limits of accuracy of the method, which are rather poor for these z values. The peak corresponding to atom J has almost disappeared in the ($hk3$) projection, indicating a z coordinate very close to $c/4$; for this value of z the method is very sensitive.

Thus the atomic positions conform to the symmetry of $P4/mnm$, both main and subsidiary layers are flat, and the vertical columns formed by atoms in the subsidiary layers are straight. Estimates of the accuracy of the final atomic coordinates, on which these statements are based, are given in Tables 1 and 2; those for x and y coordinates are deduced from a consideration of the later stages of the refinement process (see also Dickins, 1955).

4. Ordering of Co and Cr atoms

So far the unit cell has been assumed to contain 30 identical atoms. Since the atomic numbers of Co (27) and Cr (24) are not very different, any ordering will be difficult to detect. Since there are no detectable 'superlattice reflexions' any proposed ordering schemes must conform to the space-group symmetry. Table 3 lists perfectly ordered distributions of Co and Cr atoms, compatible with $P4/mnm$, which are in reasonable agreement with the composition $Co_{13}Cr_{17}$ (approx.) of the alloy examined. Either partial or complete ordering in accordance with one of these or other similar schemes might be detected.

Table 3. *Possible ordering arrangements in $P4/mnm$*

Arrangement	Co atoms	Cr atoms
I	$2A, 4G, 8I_1 = 14$	$8I_2, 8J = 16$
II	$2A, 4G, 8J = 14$	$8I_1, 8I_2 = 16$
III	$2A, 4G, 8I_2 = 14$	$8I_1, 8J = 16$
IV	$8I_2, 8J = 16$	$2A, 4G, 8I_1 = 14$
V	$8I_1, 8I_2 = 16$	$2A, 4G, 8J = 14$
VI	$8I_1, 8J = 16$	$2A, 4G, 8I_2 = 14$

For Mo $K\alpha$ radiation, used in the structure refinement described in § 3, the atomic scattering factors at low glancing angles for Co and Cr differ by about 3 units. Any considerable degree of ordering might therefore be revealed directly by differences in electron contents and in peak heights for different atoms in the (001) projections. The peak heights for ($hk0$) and ($hk3$) projections (Table 2) suggest that atoms A and I_1 are Co, atoms G and I_2 are Cr, while atoms J might be Co and Cr in equal proportions, randomly distributed in this group of equivalent sites. Since no detailed examination of thermal motions of individual atoms has been attempted (§ 2, above), only general qualitative information can be anticipated, at the best. Peak heights for atoms in special symmetry positions are often inaccurate; the indication for atoms A should therefore be accepted with particular caution. The accuracy of the experimental measurements does not justify any attempt to count electrons in atomic peaks.

For suitably chosen wavelengths, anomalous dispersion may either enhance or reduce the difference in atomic scattering factors for Co and Cr. Thus for $K\alpha$ radiations from Ni, Cr and Mn the difference should be 0, 4 and 5 units instead of 3 for Mo $K\alpha$ (calculations from data given by James, 1950). Attempts to take advantage of this effect to differentiate Co and Cr atoms are, however, hindered by the much more serious effects of absorption for these wavelengths (compared with the short wavelength Mo $K\alpha$), and are subject to quite considerable uncertainty in interpretation since so little direct experimental information is available to confirm the accuracy of the calculated f-curves in the region of the absorption edges. These adverse factors should be kept in mind in assessing the significance of the following three attempts to apply the anomalous dispersion effect:

(i) A limited region of the powder pattern, including the prominent group of lines at ~ 2 Å, was measured with a proportional-counter recording diffractometer, using Ni $K\alpha$ and Mn $K\alpha$ radiations in turn. For Ni $K\alpha$ radiation, f_{Co} and f_{Cr} are supposed to be identical, so that the same F_c is obtained, irrespective of any ordering of Co and Cr atoms: for Mn $K\alpha$ radiation, f_{Co} and f_{Cr} should show a maximum difference of 5 units. The agreement between intensities calculated from the atomic coordinates of Table 1 and intensities measured with Ni $K\alpha$ radiation was not sufficiently good to justify the use of the measurements with Mn $K\alpha$ radiation in an attempt to derive detailed information about ordering, though there is some indication that ordering is probably present. (We are indebted to Dr M. G. Bown for helpful discussion of the interpretation of these measurements.)

(ii) Intensities of reflexions on zero and first layer lines in rotation photographs around [001], using the same small single crystal for Ni $K\alpha$ and Cr $K\alpha$ radiations in turn, were measured by the normal processes of eye-estimation, correlation between films etc. These measurements were used in two ways:

(a) Detailed consideration of changes in relative intensities of pairs of reflexions, with the change from Ni $K\alpha$ to Cr $K\alpha$ radiation, favours distributions I and VI of Table 3 as against II, III, IV and V and the random distribution. Bearing in mind that ordering may well be only partial—i.e. not strictly in accordance with any single scheme such as those listed in Table 3—this treatment of the measurements must be regarded as completely inconclusive.

(b) Fourier syntheses ($hk0$) and ($hk1$) from the Ni $K\alpha$ measurements show wide variations in peak heights (which should in principle be the same for all atoms, with this radiation), no doubt due to the very limited number of terms available in comparison with Mo $K\alpha$ observations. Comparison with the syntheses (of the same limited number of terms) from the Cr $K\alpha$ measurements shows *changes* in peak height to be expected for the Co–Cr distribution already suggested by the *actual* peak heights in the Mo $K\alpha$ ($hk0$) and ($hk3$) syntheses, viz. $2A$, $8I_1$ = Co; $4G$, $8I_2$ = Cr; $8J$ = 4Co, 4Cr at random. It must be added that *actual* peak heights in the Cr $K\alpha$ synthesis are not in accordance with this ordered distribution, which can only be accepted if it is assumed that while *actual* peak heights for both Ni $K\alpha$ and Cr $K\alpha$ syntheses are in error owing to the limited number of terms included, *relative* peak heights for the two radiations have real significance.

A full discussion of the experimental difficulties and of the assumptions implicit in the methods of interpretation is available elsewhere (Dickins, 1955). Pending the examination of this problem with a more powerful technique—e.g. neutron diffraction—we suggest very tentatively, on the whole of the evidence above, that there is some indication that atoms $2A$, $8I_1$ are Co, atoms $4G$, $8I_2$ are Cr, while atoms $8J$ are 4Co, 4Cr at random*; this distribution corresponds to a net composition $Co_{14}Cr_{16}$, which is close to the actual composition $Co_{13}Cr_{17}$ for the alloy examined. In view of the failure to obtain unequivocal information on ordering, we have not thought it worthwhile to calculate F values for the distribution tentatively proposed.

5. Discussion of the structure

(i) *Characteristic features*

If the space group is $P4/mnm$ the main layers must be perfectly flat, in planes $z = 0, c/2$, and the vertical columns parallel to [001] must be perfectly straight. Unfortunately, only indirect evidence is offered to prove that this is the correct choice from the three space groups corresponding to the systematic absences in X-ray reflexions. First, the use of generalized projections shows that (within the rather limited accuracy of the method) atoms G, I_1, I_2, as well as A, lie in the planes $z = 0, c/2$; secondly, in the (001) projection the peak corresponding to atom J has excellent circular contours, indicating exact superposition of successive atoms, at heights $z \sim c/4, 3c/4, \ldots$, in accordance with the mirror planes $(001)_0$ and $(001)_{\frac{1}{2}}$ of $P4/mnm$. Additional support for this choice of space group is provided by a statistical test, which alone would be inadequate to prove centrosymmetry in such a strongly layered structure. It is important to bear in mind the difficulty of determining the space group with absolute certainty, especially in comparing σ-CoCr with other σ-phase structures.

Irrespective of the choice of space group, the subsidiary layers may be either flat or crumpled. The method of generalized projections is very sensitive for the z coordinate of atoms J and fixes them very accurately in flat layers in the planes $z = c/4, 3c/4$.

Table 4 lists, for each atom, the number of contacts to nearest neighbours and the bond lengths. In view of the high coordination numbers (12, 14, 15) it is not surprising that bond lengths vary within rather wide limits (2·28–2·92 Å). The shortest bonds (2·28 Å) are between successive uniformly spaced atoms J forming the vertical columns. There is a direct correlation between coordination number and mean bond length, as shown in the last column of Table 4; that the difference between the mean values 2·50, 2·49 Å (A, I_1) and 2·71, 2·66, 2·64 Å (G, I_2, J) is significant can be seen from a scrutiny of the individual values from which they are derived.

The tentative ordering scheme proposed in § 4 on the basis of intensity measurements shows a very interesting correlation with the above coordination numbers and mean bond lengths, for atoms A and I_1 are Co, atoms G and I_2 are Cr, and atoms J are partly Co, partly Cr. For the transition elements fixed atomic radii cannot be assigned with certainty, but the difference in mean bond lengths for Co and Cr atoms in this structure is in the direction to be expected from such evidence as is available (see, for example, Hume-Rothery & Coles, 1954).

An alternative treatment of the coordination numbers and individual bond lengths uses the familiar Pauling relation $R(n) = R(1) - 0{\cdot}300 \log_{10} n$ to determine bond strength for each contact, and thence the effective 'valency' of each atom. Using single-bond radii $R(1) = 1{\cdot}157$ Å for Co and $R(1) = 1{\cdot}172$ Å for Cr, and assuming ordering as above, the 'valencies' are A 6·7, G 4·5, I_1 6·0, I_2 5·2, J 5·9; if ordering is

Table 4. *Interatomic distances in* σ-CoCr

		Interatomic distances (Å)					
Atom	Number of contacts	A	G	I_1	I_2	J	Mean
A	12		(4) 2·61	(4) 2·36		(4) 2·54	2·50
G	15	(2) 2·61	(1) 2·53	(4) 2·69	(2) 2·44	(4) 2·84 (2) 2·92	2·71
I_1	12	(1) 2·36	(2) 2·69	(1) 2·42	(1) 2·48 (2) 2·49 (1) 2·51	(2) 2·55 (2) 2·56	2·49
I_2	14		(1) 2·44	(1) 2·48 (2) 2·49 (1) 2·51	(1) 2·41 (4) 2·83	(2) 2·79 (2) 2·76	2·66
J	14	(1) 2·54	(2) 2·84 (1) 2·92	(2) 2·55 (2) 2·56	(2) 2·79 (2) 2·76	(2) 2·28	2·64

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* As seen in projection on (001)—see also § 5(ii)(b), below.

ignored in the calculation, the use of a mean single-bond radius $R(1) = 1{\cdot}165$ Å leads to nearly identical values A 6·9, G 4·4, I_1 6·1, I_2 5·0, J 5·9 (necessarily, since the single-bond radii are so nearly identical). The significant feature is that atoms G and I_2 are again differentiated from A and I_1 (and J).

(ii) *Comparison with other σ-phase structures*

We are greatly indebted to Dr J. S. Kasper for information, in advance of publication, on the atomic coordinates selected after full refinement of the σ-CoCr structure originally described by Kasper *et al.* (1951; see also Kasper *et al.*, 1952). Accurate structure analyses have also been published for σ-FeCr and β-U.

(*a*) *Atomic parameters.*—The composition of Kasper's σ-CoCr alloy corresponds to unit-cell contents $Co_{14}Cr_{16}$, compared with our $Co_{13}Cr_{17}$. Atomic parameters for his structure are set out in Table 1, in a form comparable with ours. The choice of space group $P4nm$ is required* because Kasper subdivides our group (8) J into independent groups (4) V′ and (4) V″ nearly but not exactly superposed when viewed in projection along the c axis. Thus the 'vertical columns' are slightly staggered, the atoms being displaced by $\sim 0{\cdot}12$ Å from the mean axis of the column. Both main layers and subsidiary layers are perfectly flat, as in our alloy. Taking the mean value of x (0·3160) for Kasper's V′ and V″ for comparison with our $x(J)$, the differences in x and y parameters between the two structures are less than, or only slightly exceed, our estimated probable error—the difference is everywhere $< 0{\cdot}02$ Å.

The σ-FeCr alloy examined by Bergman & Shoemaker (1954) has a unit cell $a = 8{\cdot}7995$, $c = 4{\cdot}544$ Å, containing $Fe_{16}Cr_{14}$. The space group $P4/mnm$ is selected, so that main layers are flat and vertical columns are straight; from the parameters quoted in Table 1 it is seen that subsidiary layers also are effectively flat—atoms E (= J) are $\sim 0{\cdot}01$ Å above or below mean planes $z = c/4$, $3c/4$. The x and y parameters are extremely close to those for σ-CoCr except for $y(D)$ and $y(C)$, which correspond to differences of $\sim 0{\cdot}02$ Å in each case. It follows that the coordination number for each kind of atom (A, G, I_1 etc. ...) is the same, and that the bond lengths are very similar, for the two phases; in particular, there is the same correlation between coordination number and mean bond length.

Comparison with β-U is important for an understanding of the relationship between the alloy phases and the element. The unit cell, with $a = 10{\cdot}590$, $c = 5{\cdot}634$ Å, is larger in proportion to the larger size of the U atom, and the axial ratio c/a (0·532) is somewhat larger than for σ-CoCr (0·517) and σ-FeCr (0·5164). If arguments advanced by Tucker (1954) are accepted, the structure is based on $P4/mnm$ and the best available atomic parameters are those of Tucker & Senio (1953), from which those given in Table 1 are derived. The main layers are flat, the vertical columns straight, but the atoms III (with $z = 0{\cdot}2300$) are displaced by $\sim 0{\cdot}1$ Å from the mean planes of the subsidiary layers. In addition, differences in x and y parameters are appreciably larger between β-U and σ-CoCr than between σ-CoCr and σ-FeCr.

(*b*) *Ordering in σ phases.*—Pearson & Christian (1952) reported the observation of reflexions from σ-Ni–V not conforming to the space-group requirements obeyed by other σ phases, and suggested a possible explanation in terms of an ordered arrangement of Ni and V atoms. Later, however, Bland (1954) advanced an alternative explanation of the occurrence of the 'forbidden' reflexions, in terms of the Renninger (double reflexion) effect. Decker *et al.* (1954) have interpreted X-ray powder patterns of σ-MnMo (approximate composition $Mn_{19}Mo_{11}$ per unit cell) as shown in Table 5. The present discussion is confined to the cases of σ-CoCr, σ-FeCr, σ-FeMo and σ-MnMo, in which any ordering is without effect on systematic (space-group) absences in the X-ray reflexions.

Pending detailed publication by Kasper on the refinement of his σ-CoCr structure, the only available information about ordering concerns the 'staggering' of atoms V′ and V″ in the vertical columns which results in elongation of the contours of the corresponding (double) peak in the (001) projection (see Kasper *et al.*, 1952, and Tucker & Senio, 1953, pp. 758–9) and is attributed to alternation of Co and Cr atoms along the columns. Decker *et al.* (1954) also refer to the difference in x parameter for these atoms, depending on the type of atom occupying the site. Such an ordered distribution in sites V′ and V″ is

Table 5. *Ordering in σ phases*

Number of atoms	σ-CoCr*		σ-CoCr†		σ-MnMo‡		σ-FeCr§		σ-FeMo§	
2	A	Co	I		I	Mn	A	Fe	A	Mo
4	G	Cr	II		II	Mo	B	Cr	B	Mo
8	I_1	Co	IV		IV	Mn	D	Fe	D	Fe or Fe, Mo
8	I_2	Cr	III		III	5 Mn, 3 Mo	C	Fe	C	Fe
8	J	4 Co, 4 Cr	$\left\{\begin{matrix}V' \\ V''\end{matrix}\right\}$	4 Co, 4 Cr	V	4 Mn, 4 Mo	E	Cr	E	Mo

The atoms for each structure are named in accordance with the usage of the authors: cf. Table 1.

* Present authors. † Kasper *et al.*, 1951, 1952. ‡ Decker *et al.*, 1954. § Bergman & Shoemaker, 1954.

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* Decker *et al.* (1954) refer to the σ-CoCr structure in terms of space group $P4/mnm$ but with x-parameter for atoms V which depends upon the kind of atom occupying the site.

compatible with our suggestion that atoms (8) J may comprise 4Co, 4Cr, but in our structure analysis the evidence indicates that in our crystals the two kinds of atoms are seen exactly superposed in projection on (001).

For σ-MnMo the allocation of atoms corresponds to our allocation for sites A, G, I_1, J but site I_2 (Cr in our σ-CoCr) contains both Mn and Mo (approximately 5Mn+3Mo) in σ-MnMo. Decker *et al.* (1954) also point out the differences in the sizes of the 'holes' available for atoms in sites II (large), I, IV (small), and III, V (medium)—cf. § 5(i), above.

For σ-FeCr and σ-FeMo the ordering schemes shown in Table 5 are deduced directly from least-squares analysis of their measured intensities by Bergman & Shoemaker (1954), who point out that the conclusions for σ-FeCr are less reliable than for σ-FeMo and also emphasize the likelihood that ordering in any σ-phase structure is only partial. They also point to the difference in axial ratio c/a (FeCr, 0·5164; FeMo, 0·5237) in support of their allocation of Cr and Mo atoms, in the two alloys, in positions $J(E)$ which form the vertical columns. It will be profitable to consider the extension of this argument to β-U (c/a 0·532) when the structure is better understood, possibly in relation to the general problem of the nature of ordering forces. In this connexion it is interesting to note that the correlation between coordination number and mean bond length (discussed in (i) above in relation to ordering in σ-CoCr), and the effective 'valencies' (computed from the Pauling relation by Bergman & Shoemaker) corresponds with the proposed ordered distribution in σ-FeCr only for atoms A, G, I_1, but breaks down with I_2. Too much weight should not be attached to any of these correlations, however; it is to be hoped that more reliable information may be forthcoming from neutron-diffraction studies.

6. Conclusion

It is to be hoped that as more structures related to the σ phases are examined (see, for example, Brink, Shoemaker & Fox, 1955) the basic geometry governing their formation will become clear. In the meantime a thorough examination of ordering in different σ-phase alloys may lead to a better understanding of the conditions governing the occurrence of this structure in binary and ternary systems. The meaning to be attached to the Brillouin zones corresponding to groups of prominent lines in the X-ray pattern (Douglas, 1951; Bergman & Shoemaker, 1954) seems unlikely to emerge until much more fundamental treatments of the electronic systems of transition-metal atoms are forthcoming.

We acknowledge our indebtedness to Dr J. S. Kasper for information on the progress of his refinement of the σ-CoCr structure, and to Dr C. W. Tucker and Dr D. P. Shoemaker for valuable discussions of the problem in the earlier stages of our work. Many friends helped us in trying to obtain suitable samples of σ-phase alloys, especially Mr D. A. Oliver. The σ-CoCr alloy specimen used in our experiments was supplied by A. G. Metcalfe, Department of Metallurgy, University of Cambridge. One of us (G. J. D.) acknowledges with gratitude the award of a Bursary by the British Iron and Steel Research Association.

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