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Site ordering in some σ phase structures.

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Since the first determination in 1951 of the atomic positions in the σ-phase structure, many investigations have shown that the atomic sites are not randomly occupied. In particular, Bergman & Shoemaker (1954) with (Fe–Cr)σ and (Fe–Mo)σ, Decker, Waterstrat & Kasper (1954) with (Mn–Mo)σ, and Dickins, Douglas & Taylor (1956) with (Co–Cr)σ found indications that this was so. Later, neutron diffraction, applied by Kasper & Waterstrat (1956) to a study of (Fe–V)σ, (Ni–V)σ, and (Mn–Cr)σ phases, clearly revealed the type of ordering in these particular alloys.

The σ-phase structure is tetragonal with 30 atoms per cell, distributed amongst one group of twofold (*A*), one fourfold (*B*) and three eightfold sites (*C*, *D*, *E*). If the atoms of Group VA and VIA metals making up the structure are called type *X*, and the 'long period' elements type *Y*, then it is found that type *X* atoms show a preference for the *B* sites, while type *Y* atoms prefer sites *A* and *D*. Sites *C* and *E* show mixed occupancy depending on the limitations set by the composition of the alloy. This scheme has recently been extended and reviewed by Spooner & Wilson (1964).

In an attempt to examine further ordering in these more complex structures an X-ray and neutron-diffraction investigation was undertaken on four more of these compounds: (Mn–V), (Mn–Cr), (Co–Cr), and (Fe–Cr) σ phases. Of these the first had not been investigated previously, while the (Fe–Cr) and (Co–Cr) systems had only received X-ray examination and the results could be considered of low accuracy. The (Mn–Cr) system was included as a check.

All alloys were argon-arc melted, high purity materials being used. The first three alloys were crushed and, apart from slight oxidation evident in (Mn–Cr), were all single phase and used without further heat treatment. The (Fe–Cr)σ alloy was annealed in vacuo at 650 °C to induce the α–σ transformation. Some α phase remained in the neutron diffraction sample, but this did not greatly interfere with measurements.

X-ray intensities for powder samples were determined by means of a horizontal diffractometer, proportional counter and linear amplifier, while the neutron-diffraction runs were carried out at the Australian Atomic Energy Commission's Research Establishment at Lucas Heights.

For each reflexion $B_i=0$, so that the structure factors become:

$$F_{hkl}=A_Af_A+A_Bf_B+A_Cf_C+A_Df_D+A_Ef_E$$

and the problem resolves into determining the values of f_i for the five sites. Two methods were tried with the X-ray data. The first, a trial-and-error method, involved calculating all the intensities for many different values of f_i, subject to the proviso that the values tried should fit the composition of the alloy. An IBM 1620 computer was programmed to do this, restricting itself to ten different values of f_i for each site, and printing answers only when reasonable correlation was achieved. The second method involved forming five ratios with respect to the 411 line, thereby yielding five simultaneous equations in f_i which could then be solved. (Some minor simplifying assumptions need be made on the variation of f_i with θ).

Neither of these two methods yielded very clear answers. The trial-and-error method gave correlations which varied only slowly as the degree of order changed, while the simultaneous equations gave solutions outside the allowable range, owing to the inherent statistical inaccuracy in the line intensities coupled with the closely similar scattering factors.

The neutron-diffraction results, on the other hand, gave a clearer picture of the structure, despite poorer resolution in the diffraction pattern, because the nuclear scattering amplitudes varied widely in the four cases. The 002 line was taken as a standard for intensities and the sets of simultaneous equations so obtained were solved. Subsequent refinement gave the site occupancy shown in Table 1.

The results in Table 1 conform to the generally accepted scheme of ordering, except that in the (Mn–V) and (Mn–Cr) samples, where the proportion of *X* atoms is low, the *B* sites are no longer so clearly preferred by these atoms. The (Co–Cr) and (Fe–Cr) results given here differ somewhat from those of the original investigations, but the (Mn–Cr) values agree within experimental error with the results of Kasper & Waterstrat (1956).

In conclusion, it may be pointed out that absolute intensity determinations would be of considerable advantage in this type of work. As well as eliminating the compounding of errors in forming the intensity ratios, it may be shown, for example, that the 002 intensity will yield the ordering in the *E* sites directly, and this fact alone would greatly diminish subsequent calculations.

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Table 1. *Ordering schemes for σ phases*

σ phase		Composition		Site *A*		Site *B*		Site *C*		Site *D*		Site *E*	
X	*Y*	at. %*X*	at. %*Y*	*X*	*Y*	*X*	*Y*	*X*	*Y*	*X*	*Y*	*X*	*Y*
V	Mn	19	81	0·0	2·0	1·8	2·2	1·2	6·8	0·0	8·0	2·7	5·3
Cr	Mn	20	80	0·2	1·8	1·4	2·6	1·2	6·8	0·4	7·6	2·8	5·2
Cr	Fe	46	54	0·6	1·4	2·2	1·8	3·6	4·4	2·8	5·2	4·0	4·0
Cr	Co	61	39	0·7	1·3	3·8	0·2	6·8	1·2	3·0	5·0	4·0	4·0

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