same five-dimensional space group because the electron diffraction patterns are similar to those of the 7*a* structure except for the difference in the wavevectors and *N*/*M* varies continuously with the chemical composition (Hirabayashi *et al.*, 1970). This suggests that the five-dimensional space groups of these two structures are the same and a series of incommensurate structures with $3/7 < N/M < 4/9$ have the same space group. These are expected to have similar structures.

In order to confirm this, we calculated the Fourier amplitude of the 9*a* structure given by Hirabayashi *et al.* (1970) and confirmed that the distribution of Au atoms is well approximated by (2). This shows that their five-dimensional structures are isomorphic with each other. The Fourier amplitudes P_0 and P_1 of this structure are listed in Table 1.

Summary and concluding remarks

We carried out a five-dimensional analysis of the 7*a* structure based on the theory of modulated structure analysis and obtained essentially the same result as in the more sophisticated analysis based on the usual three-dimensional symmetry. It was shown that the 9*a* structure has the same five-dimensional space group as the 7*a* structure and has a similar five-dimensional structure. The present paper demonstrates that the refinement can be carried out by using only observed reflections and parameters mainly contributing to these reflections. This saves much computing time and reduces effort in analyses of commensurate structures without accompanying higher-order harmonics.

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Atom Distributions in Sigma Phases.
I. Fe and Cr Atom Distributions in a Binary Sigma Phase Equilibrated at 1063, 1013 and 923 K*

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Abstract

Extensive single-crystal Mo *Kα* Bragg-diffraction data sets were collected and analyzed from sigma (σ) phases with compositions near $Cr_{48}Fe_{52}$ that had been annealed at three temperatures (1063, 1013 and 923 K) within the region of σ-phase metastability. Precisions of measurement varied from <1% for the relatively few intense diffraction maxima to ~10–20% for the more numerous weak reflections. No clear indication of the absence of a center of symmetry was found in any data set, or in any of the results obtained by least-squares refinements of parameters assuming space group $P4_2/mnm$. Average site-occupation parameters of limited precision (±5–10%) were derived for the five independent sites occupied in the σ structure during the refinement based on each data set. The crystal from the alloy equilibrated at 1013 K was also studied using synchrotron-radiation (SR) Bragg diffraction at photon energies just below the Fe and Cr *K* absorption edges, where relative differences ($\Delta|f|/|f|$) in the atomic scattering factors of Fe and Cr approach 20–35%. (For Mo *Kα* radiation, $\Delta|f|/|f|$ is 8–11%.) Site-occupation parameters derived from the less numerous

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SR diffraction data show greater precision (±1–2%) than the conventional data results, but do not differ significantly from them. Variations in site-occupation parameters with equilibration temperature are small (<2 e.s.d.) for the three temperatures studied. The distributions are in reasonably good agreement with results of neutron powder diffraction experiments on comparable materials. A marked preference for Fe atoms to occupy the two 12-coordinated sites is found, with Cr atoms distributed about equally among the one 15- and two 14-coordinated sites. Difference vector density maps computed from $[F^2_{\rm obs}({\rm SR}) - F^2_{\rm calc}$ (average occupation of all sites)] give useful indications of the actual atom distributions.

1. Introduction

(*a*) *Scope of experiments*

Scattering contrast between elements that are near-neighbors in the Periodic Table can be heightened by selecting photon energies close to absorption edges where anomalous-dispersion effects for one atomic species are appreciable. This series of experiments is designed to compare the capabilities of conventional metal-target X-ray and edge-tuned synchrotron-radiation (SR) diffraction techniques in quantitative estimations of site-occupation parameters for phases that contain near-neighbor transition metals. Single-crystal diffraction methods are chosen because some of the phases to be examined seem too structurally complex to attack with powder methods. Bragg scattering alone is measured, so that results describe average distributions, not local deviations from averages. Technologically important phases are studied, and comparisons of results with those given by other experimental techniques are made whenever possible.

The first experiment dealt with the distribution of iron and cobalt ions on the tetrahedral and octahedral sites of a $CoFe_2O_4$ spinel crystal (Yakel, 1980). Results showed that, with a relative difference $(\Delta|f|/|f|)$ of 3–5% in atomic scattering factors for the metal atoms, a limited (819 observations of 36 independent reflection intensities), fairly precise $[\sigma(I)/I \sim 4\%]$ conventional Cu $K\alpha$ Bragg diffraction data set could not be used to fix the single site-occupation parameter for the structure with accuracy or precision. With 290 comparably precise SR Bragg diffraction data measured just below the Fe and Co K absorption edges $(\Delta|f|/|f| \sim$ 15–25%), this parameter was fixed to ±1% at a value in agreement with results of neutron diffraction and Mössbauer spectroscopy experiments (Satya Murthy, Natera, Begum & Youssef, 1970; Sawatzky, van der Woude & Morrish, 1968).

The second set of experiments, an initial group of which is reported here, uses conventional Mo $K\alpha$ and edge-tuned SR diffraction data to measure average distributions of near-neighbor transition metals on the occupied atomic sites of σ phases. It is thus an extension of the experiments in which Dickens, Douglas & Taylor (1956) used suitably chosen characteristic X-ray energies to study order in a (Cr,Co) σ phase.

(*b*) *Structure of σ phases*

Basic features of the crystal structure of σ phases have been known for 30 years (Shoemaker & Bergman, 1950; Tucker, 1950; Bergman & Shoemaker, 1954). Because of the generally undesirable effects produced by the appearance of σ phases in many steels, there is still considerable interest in determining all possible variations in structural detail that may be shown by particular σ phases under particular conditions of formation or heat treatment. Useful reviews of progress in understanding the occurrence, structures and properties of σ phases have appeared periodically (Hall & Algie, 1966; Sinha, 1972).

σ phases have a tetragonal structure with 30 atoms distributed on five special positions of space group No. 136 (D^{14}_{4h}, $P4_2/mnm$), in a unit cell with $c/a \sim$ 0·51–0·54 and $c \sim$ 4·5–5·2 Å. Early suggestions that the symmetry center might be absent were shown to be improbable for alloy σ phases (Dickens, Douglas & Taylor, 1956; Forsyth & d'Alte da Veiga, 1963), but uncertainty still exists for the only known elemental σ-phase, β-uranium (Tucker & Senio, 1953; Thewlis & Steeple, 1954; Steeple & Ashworth, 1966; Donohue & Einspahr, 1971).

The σ structure belongs to a class that has been termed 'tetrahedrally close-packed' (t.c.p.) (Shoemaker & Shoemaker, 1969). By adopting arrangements that leave only irregular tetrahedral interstices between atoms of slightly different size, these structures achieve denser packing than could be obtained if geometrically close-packed structures were formed. Atomic coordination numbers of 12, 14, 15 and 16 may occur, and systematic classifications of t.c.p. structures have been proposed based on the manner in which the corresponding coordination polyhedra interpenetrate (Frank & Kasper, 1958, 1959). In the generalized σ structure, four of the five atoms in the asymmetric unit lie in 'primary' layers perpendicular to the tetragonal c axis. The remaining atom, in special position 8(j) (the so-called E site), forms sparsely populated 'secondary' layers that interleave the primary nets. Short 'major' bonds (Frank & Kasper, 1958) connecting atoms with 15- and 14-fold coordinations [in special positions 4(f) (the B site) and 8(i)(1) (the C site), respectively] form a 'major skeleton' in each primary layer; major bonds connecting 14-coordinated E-site atoms in successive secondary layers form linear arrays parallel to $\mathbf{c}$. Atoms with

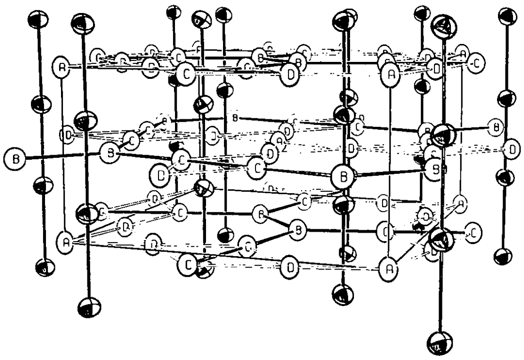

Fig. 1. A view of the atomic arrangement in the σ phase. All positional and thermal-vibration parameters are taken from the final cycle of the least-squares refinement based on the Mo *K*α diffraction data from the 1013 K crystal. Atoms on sites *A*–*D* are labeled; those on *E* sites are shown with thermal-ellipsoid sections. The unit cell, with **c** nearly vertical, is outlined by thin stick bonds connecting *A* sites. Thick solid bonds delineate the 'major skeleton'; open bonds represent other near-neighbor interatomic distances.

12-fold icosahedral coordination [in special positions 2(*a*) (the *A* site) and 8(*i*)(2) (the *D* site)] are linked to neighbors by somewhat longer 'minor' bonds only. Fig. 1 shows many of these details of the σ structure.

Component elements in alloy σ phases are frequently 3*d*, 4*d* and 5*d* transition metals. Combinations of Group V*b* or VI*b* elements with those in Group VII*b* or VIII are typical. Composition ranges are often broad and not centered on simple stoichiometries, so that complete atomic ordering on the sites described above is unlikely. Single-crystal and powder X-ray, and powder neutron diffraction experiments on binary alloy phases with favorable atomic scattering factor differences have shown that partial ordering does occur (Kasper & Waterstraat, 1956; Dickens, Douglas & Taylor, 1956; Forsyth & d'Alte da Veiga, 1963; Spooner & Wilson, 1964). Electron-deficient (usually larger) Group V*b* or VI*b* atoms tend to occupy the 15-coordination sites, and electron-rich (usually smaller) Group VII*b* or VIII atoms tend to occupy the 12-coordinated sites. The driving force for ordering thus includes both electronic and size effects, the former dominating unless the size of the electron-rich atoms greatly exceeds that of the electron-poor atoms [*e.g.* (Cr,Re) σ, where Re atoms preferentially occupy the 15-coordinated *B* sites (Spooner & Wilson, 1964)].

(*c*) *Purpose of this paper*

The primary question to be addressed by the present group of experiments was outlined in § 1(*a*). To answer it, occupation parameters in a (Cr,Fe) σ single crystal with composition near $Cr_{48}Fe_{52}$ annealed at 1013 K are compared after estimation from (i) conventional Mo *K*α Bragg diffraction data, and (ii) SR diffraction data collected with photon energies just below the Fe and Cr *K* edges. As a secondary question, one may also ask if the state of order in this phase depends to any measurable degree on the annealing temperature. To answer it, σ crystals of nearly the same composition (48% Cr) were annealed at 1063 and 923 K. Occupation parameters estimated from conventional diffraction data alone are reported for these crystals.

2. Experimental

(*a*) *Preparation of the alloy*

A physical mixture of high-purity iron and chromium metals (48 wt% Cr) was arc-melted and quenched. The alloy was then heat-treated in pure argon at 1773 K for 48 h and furnace-cooled. Large α (b.c.c.) grains were nicked with a sharp tool, after which the alloy was encapsulated in a quartz tube under vacuum and heat-treated at 1013 K for 170 h. X-ray powder diffraction patterns of the brittle product showed that only a σ phase was present. Portions of the alloy were re-encapsulated and annealed at 1063 and 923 K for periods of 350 and 1400 h, respectively. Chemical analyses of each portion for Fe and Cr gave the following Fe-atom percentages (all ±0·5%, balance Cr): 52·2 (1063 K), 51·8 (1013 K), 50·5 (923 K). Irregularly shaped single crystals with average linear dimensions <50 μm were culled from crushed pieces of each of the annealed samples.

(*b*) Mo *K*α *data collection*

Conventional Mo *K*α [$\lambda(K\alpha_1) = 0{\cdot}709300$ Å] diffraction data were collected under similar conditions for each of the three crystals selected. An automated Picker diffractometer was used with the following specifications: a take-off angle of 1·8°; a receiving slit opening equivalent to 1·9°; a θ–2θ step-scanning mode with a 2σ step size of 0·02°; a counting time of 1 s per step, with background counts accumulated for 25 s at the beginning and end of each scan; an angular range of $3° \leq 2\theta \leq 128$–$130°$. Observations were recorded with unfiltered radiation, but a few likely to be affected by β interference were remeasured with Nb-filtered radiation.

Table 1 summarizes the lattice parameters computed by least-squares fits of high-angle reflection centering data, and the statistics of the observed data sets for each crystal. In assessing the overall precisions of these sets, one should note that typical diffraction data for a σ crystal present an unusual distribution of observed intensities. A relatively small group of reflections has intensities much above the average, while those of a larger group are well below average. There are relatively few reflections with intermediate

Table 1. *Lattice parameters and data-collection statistics for* (Cr,Fe) *σ crystals*

Annealing temperature (K)	1063 (5)*	1013 (5)	923 (5)
At.% Fe (measured)	52·2 (5)	51·8 (5)	50·5 (5)
a_o (Å)	8·7961 (4)	8·7968 (5)	8·7966 (6)
c_o (Å)	4·5605 (3)	4·5585 (3)	4·5582 (3)
Crystal volume ($\times 10^3$ μm^3)	32 (4)	36 (4)	79 (8)
Total No. of observations (excluding standards)	8089	8152	7459
Average precision (%) for observations with $I > \sigma(I)$	12	16	12
Total No. of observations after averaging replicates and removing space-group absences	7262	7552	6727
R_w (replicates) (%)	7	9	7
No. of observations with $I > \sigma(I)$	5314	5355	4804
Total No. of observations after averaging space-group equivalents	1676	1674	1726†
R_w (equivalents) (%)	6	7	6
No. of averaged observations with $I > \sigma(I)$	1419	1409	1470

* Estimates of error in the last significant digit are given in parentheses.

† The data set for the crystal annealed at 923 K extended to 130° (2θ) rather than 128°.

intensity. With a fixed counting time per step for all scans, the experimental precision of intensity estimates for the strong group is likely to be high (in the present case <1%), while the precision for the weak group is much less (~10–20%).

(*c*) *Synchrotron-radiation data collection*

Bragg diffraction data from the crystal annealed at 1013 K (hereinafter, the 1013 K crystal) were also measured with SR on the CAD-4 diffractometer at the Stanford Synchrotron Radiation Laboratory. General considerations for such experiments have been set forth by Phillips, Cerino & Hodgson (1979) and by Yakel (1980). Particular conditions for this experiment included: 2·06–2·07 GeV (1 eV = 1·6 × 10^{-19} J) stored electron energy; flat Ge (111) crystals in (1,—1) geometry monochromating the photon beam from a focusing mirror set for a 10 keV cut-off; an N_2-filled ionization chamber measured the incident-beam intensity.

To fix edge energies, relative linear absorption *vs* photon energy data were recorded around Fe *K* and Cr *K* edges by measuring the intensity of the monochromated incident beam transmitted through a powdered sample of the σ alloy and through Fe and Cr foils. The Fe *K* edge energy was estimated at 7113 (2) eV [1·7430 (5) Å compared to 1·7435 Å* for elemental iron], and the Cr *K* edge at 5988 (3) eV [2·0705 (10) Å compared to 2·0702 Å for elemental chromium]. Diffraction data were collected at monochromator settings corresponding to photon energies of 7905 eV (1·747$_4$ Å) and 5977 eV (2·074$_3$ Å), where large changes are expected in real dispersion terms but not in imaginary terms. A third data set was collected at 5636 eV (2·200$_0$ Å). Uncertainties in photon energies at the diffracting sample were estimated to be ±10 eV.

In view of the bimodal character of the distribution of σ-phase diffraction intensities, reflections to be scanned with SR were divided into two sets: a group of 18 relatively intense reflections, with a symmetry equivalent for each (based on $P4_2/mnm$), for a total of 36; and a group of 118 relatively weak but observable reflections with no symmetry equivalents. All scans were performed in the θ–2θ mode over a 1° (2θ) interval; 2θ (max.) was ~120°. Intense reflections were measured with a 3·8° (θ) min^{-1} prescan speed, a maximmum counting time of 2 min for the final scan, and with a precision of 2·5% required for $\sigma(I)/I$ from the final scan. Weak reflections were measured with a maximum time of 5 min for the final scans, which were performed regardless of the results of prescans. Precisions of intensity measurements for this group averaged ~15%. Complete intensity profile data were written to a disk file for each scan, and incident intensities, monitored every 10 s, were written to a companion file. Useful data for 198 reflections at 7095 eV, 105 at 5977 eV, and 96 at 5636 eV were recorded. After averaging of replicate measurements (R_w ~ 4%), the numbers of reflections at the respective energies were 154, 104 and 91; after averaging equivalents (R_w ~ 2%), the numbers were 135, 84 and 73.

(*d*) *Data reduction and analyses*

All physical constants and atomic scattering factors at the high-energy limit were taken from *International Tables for X-ray Crystallography* (1974). The same source provided mass-absorption coefficients and dispersion-correction terms at the Mo *Kα* energy. For SR diffraction data, mass-absorption coefficients were estimated by extrapolation of tabulated values for nearby characteristic radiations. Dispersion-correction terms at each SR energy, computed with the modified Cromer & Liberman (1970) method developed by the author (Yakel, 1980), are listed in Table 2. Probable

Table 2. *Anomalous-dispersion corrections to atomic-scattering factors for* Fe *and* Cr *at X-ray energies used in this experiment*

Energy (eV)	λ (Å)	f' (Fe)	f'' (Fe)	f' (Cr)	f'' (Cr)
5636	2·200$_0$	−1·46	0·84	−2·63	0·70
5977	2·074$_3$	−1·68	0·77	−6·40	0·71
7905	1·747$_4$	−5·81	0·63	−0·80	3·17
17444	0·71073	0·301	0·845	0·284	0·624

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* Values are taken from *International Tables for X-ray Crystallography* (1974, Table 1.1B).

errors in values of f' and f'' near the absorption edges are estimated to be ±0·5 and ±0·1 e, respectively. Note that $\Delta|f|/|f|$ values are 8–11% for Mo $K\alpha$ radiation, and 25–30% for edge-tuned SR.

Conventional Mo $K\alpha$ intensity data, with backgrounds subtracted by the data-collection program (Busing, Ellison, Levy, King & Roseberry, 1968), were converted to relative $F^2_{\rm obs}$ values by corrections for Lorentz–polarization and absorption effects. The latter correction used the *ORABS* program (Shoemaker, 1966; accession No. 362), with crystal shapes approximated as polyhedra bounded by plane surfaces. Isotropic-extinction corrections were computed with the Coppens & Hamilton (1970) algorithm in least-squares calculations using the full replicate-averaged Mo $K\alpha$ data sets. Extinction corrections were applied to all $F^2_{\rm obs}$ values (including SR data) prior to averaging of symmetry equivalents.

Initial reduction of SR intensity data were made with a program, *CAD-4DR*, developed by and available from the author. In these calculations it was assumed that the incident-beam's electric vector was completely polarized in a direction perpendicular to the scattering plane.

Parameters were refined by iterative full-matrix least-squares calculations that minimized squares of residuals between observed and computed F^2 values (*XFLS* program, Shoemaker, 1966; accession No. 389). Weights assigned were $w_i = 1/\sigma_i^2 = 1/[\sigma^2_{\rm stat} + (0{\cdot}035F^2_{\rm obs})^2]$, where $\sigma^2_{\rm stat}$ was the variance based on counting statistics. Atomic position parameters reported for a $Cr_{46{\cdot}5}Fe_{53{\cdot}5}$ σ phase (Bergman & Shoemaker, 1954), with random site-occupation parameters, were assumed initially. Observed F^2 values greater than or equal to $\sigma(F^2_{\rm obs})$ were included in the least-squares analyses. When site-occupation parameters were varied, Mo $K\alpha$ data with $(\sin\theta)/\lambda \le 0{\cdot}35$ Å^{-1} were excluded from the refinement in an effort to minimize possible charge-transfer effects.

Parameter refinements based on the Mo $K\alpha$ data in space group $P4_2/mnm$ included adjustment of a scale factor, seven positional parameters for five independent atom sites, 18 anisotropic thermal vibration parameters, and, in the final cycles, four site-occupation parameters for Fe. The number of Fe atoms on the fifth site was fixed to give the observed composition; the number of Cr atoms on each site was taken as the full multiplicity of the site less the number of Fe atoms on it (*i.e.* it was assumed that no significant number of vacancies existed on any site). The site with constrained Fe occupation could be chosen as any one of the five, though analyses of any given data set in fact converged to the same final parameters regardless of which site occupancy was constrained.

Parameter refinements based on the SR data from the 1013 K crystal were carried out only in the centrosymmetric group, and included adjustment of only scale factors and four of five site-occupation parameters. All other parameters were fixed at values given by the refinement based on Mo $K\alpha$ data from this crystal. These calculations combined the data observed at the three SR energies, with appropriate definitions of fixed dispersion-correction terms at each.

Parameter refinements based on a portion ($3° \le 2\theta \le 90°$) of the replicate-averaged Mo $K\alpha$ data set from the 1013 K crystal were also carried out in space groups $P4_2nm$ (C^4_{4v}) and $P\bar{4}n2$ (D^8_{2d}). Atoms that had been constrained to lie in mirror planes in the centrosymmetric calculations were given small arbitrary displacements at the start of each noncentrosymmetric refinement. In the case of C^4_{4v}, the choice between $F^2_{\rm obs}(hkl)$ and $F^2_{\rm obs}(hk\bar{l})$ was arbitrarily fixed; calculations with positive or negative z displacements tested the possibility that the 'crystal' studied was a single polar domain. The possibility that the 'crystal' had a composite domain structure was not tested for either noncentrosymmetric group. Unconstrained refinements of all variables eventually gave physically untenable thermal-vibration parameters for one or more atoms related by pseudosymmetry in each case. Successful convergences were obtained only through the imposition of artificial constraints on one or more components of thermal vibration of the related atoms.

Table 3. *Parameters for* (Cr,Fe) *σ phases annealed at three temperatures*

Estimates of error in the last significant digit are given in parentheses. Fixed parameters are: site A ($x = y = z = 0$); site B ($y = x$, $z = 0$); sites C and D ($z = 0$); site E ($y = x$).

Site	Wyckoff notation and multiplicity	Parameter	1063 K	1013 K	923 K
Positional parameters					
B	4(*f*)	x	0·39875 (5)	0·39875 (6)	0·39864 (4)
C	8(*i*)	x	0·46351 (4)	0·46349 (6)	0·46349 (4)
		y	0·13131 (4)	0·13123 (6)	0·13122 (4)
D	8(*i*)	x	0·73921 (4)	0·73935 (6)	0·73933 (4)
		y	0·06608 (4)	0·06611 (6)	0·06609 (4)
E	8(*j*)	x	0·18274 (3)	0·18267 (4)	0·18267 (3)
		z	0·25166 (9)	0·2519 (1)	0·25202 (9)
Thermal vibration parameters*					
A	2(*a*)	β_{11}	0·00103 (3)	0·00103 (4)	0·00098 (3)
		β_{33}	0·0059 (2)	0·0063 (3)	0·0057 (2)
		β_{12}	0·00004 (4)	0·00009 (6)	0·00008 (3)
B	4(*f*)	β_{11}	0·00138 (3)	0·00137 (4)	0·00136 (2)
		β_{33}	0·0054 (2)	0·0061 (2)	0·0055 (2)
		β_{12}	0·00014 (3)	0·00018 (4)	0·00015 (3)
C	8(*i*)	β_{11}	*0·00122 (3)*	*0·00119 (4)*	*0·00117 (2)*
		β_{22}	0·00117 (3)	0·00114 (4)	0·00115 (2)
		β_{33}	0·0060 (1)	0·0060 (1)	0·0054 (1)
		β_{12}	0·00002 (2)	0·00003 (3)	0·00003 (2)
D	8(*i*)	β_{11}	0·00103 (3)	0·00105 (4)	0·00098 (2)
		β_{22}	0·00112 (3)	0·00112 (3)	0·00112 (2)
		β_{33}	0·0053 (1)	0·0056 (1)	0·00512 (9)
		β_{12}	0·00003 (2)	0·00003 (3)	0·00001 (2)
E	8(*j*)	β_{11}	0·00139 (2)	0·00139 (2)	0·00142 (1)
		β_{33}	0·0043 (1)	0·0045 (1)	0·00396 (8)
		β_{12}	−0·00002 (2)	−0·00003 (3)	−0·00001 (2)
		β_{13}	−0·00029 (3)	−0·00027 (3)	−0·00031 (2)

* Parameters β_{ij} appear in temperature-factor expressions of the form $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - 2hk\beta_{12} - 2hl\beta_{13} - 2kl\beta_{23})$. Fixed parameters are: sites A and B ($\beta_{22} = \beta_{11}$, $\beta_{13} = \beta_{23} = 0$); sites C and D ($\beta_{13} = \beta_{23} = 0$); site E ($\beta_{22} = \beta_{11}$, $\beta_{23} = \beta_{13}$).

3. Results and discussion

(*a*) *Parameters, measures of agreement, and symmetry*

Structural parameters computed in the final least-squares cycle with the Mo $K\alpha$ data set from each of the three crystals studied are listed in Table 3.* Site-occupation parameters computed in the same cycle are given in Table 4, together with those derived in the refinement based on SR data from the 1013 K crystal. Measures of agreement are collected in Table 5. These results refer in all cases to refinements assuming space group $P4_2/mnm$.

Measures of agreement obtained in artificially constrained refinements in space groups $P4_2nm$ and $P\bar{4}n2$ of the Mo $K\alpha$ data from the 1013 K crystal differ so slightly from those obtained in the centrosymmetric refinement that they cannot be claimed to support the hypothesis that the space group of this σ phase is noncentrosymmetric. As noted by Forsyth & d'Alte da Veiga (1963), the electron density projection onto the *ab* plane can also serve as a test for the center's absence since the phases of all *hk*0 reflections are 0 or 180° for any of the three space groups. The shape of the maximum representing the *E*-site atom [position 8(*j*) in $P4_2/mnm$] might then be elongated in the direction of the *ab* face diagonal (suggesting $P4_2nm$), or perpendicular to that diagonal (suggesting $P\bar{4}n2$). Sections through this maximum in the projection computed with the Mo $K\alpha$ data set from the 1013 K crystal have widths parallel and perpendicular to the face diagonal that differ by only 4%. Generalized projections, as used by Dickens, Douglas & Taylor (1956), also failed to show any significant departures from a layering of atoms at $z = 0, \frac{1}{4}, \frac{1}{2}$ and $\frac{3}{4}$. One concludes that, within the precision of the current measurements, the space group of the binary (Cr,Fe) σ phase studied here is $P4_2/mnm$.

Table 5. *Indices of agreement for refined structures of* (Cr,Fe) *σ phases annealed at three temperatures*

Definitions of indices are the standard ones used by crystallographers; see Brown & Chidambaram (1969), for example, for specific equations. Values without parentheses are computed for all reflections; values in parentheses are computed for reflections with $F^2_{\rm obs} \geq \sigma(F^2_{\rm obs})$. All refinements are in space group $P4_2/mnm$.

Annealing temperature (K)	No. of observations	$R(F)$	$R(F^2)$	R_w	σ_1
1063	1676	0·076	0·051	0·072	1·023
	(1419)	(0·061)	(0·049)	(0·071)	(1·089)
1013	1674	0·091	0·067	0·079	1·202
	(1409)	(0·075)	(0·064)	(0·077)	(1·287)
	291*	0·051	0·065	0·097	2·163
	(261)	(0·044)	(0·065)	(0·096)	(2·271)
923	1726	0·067	0·047	0·067	1·038
	(1470)	(0·054)	(0·045)	(0·064)	(1·091)

* Synchrotron-radiation diffraction data.

Table 4. *Site-occupation parameters in* (Cr,Fe) *σ phases annealed at three temperatures*

Measured numbers of iron atoms, with an estimate of error in parentheses when possible, are listed for each site. Numbers of iron atoms for random occupation, computed from the chemical composition, are in italics.

			Site				
Composition	*T* (K)	Radiation	*A* [2(*a*)]	*B* [4(*f*)]	*C* [8(*i*)]	*D* [8(*i*)]	*E* [8(*j*)]
$Cr_{47\cdot8}Fe_{52\cdot2}$	1063	Mo $K\alpha$*	1·8 (1)	1·1 (1)	3·2 (2)	6·8 (2)	2·8 (2)
			1·04	*2·08*	*4·18*	*4·18*	*4·18*
$Cr_{48\cdot2}Fe_{51\cdot8}$	1013	Mo $K\alpha$*	1·8 (1)	1·2 (2)	3·3 (2)	7·0 (2)	2·2 (2)
		SR*	1·78 (3)	1·08 (3)	3·07 (5)	7·13 (5)	2·48 (6)
			1·04	*2·07*	*4·14*	*4·14*	*4·14*
$Cr_{49\cdot5}Fe_{50\cdot5}$	923	Mo $K\alpha$*	1·75 (8)	1·0 (1)	3·0 (2)	6·7 (2)	2·7 (2)
			1·01	*2·02*	*4·04*	*4·04*	*4·04*
$Cr_{46}Fe_{54}$	923	Neutron†	1·4	1·8	4·4	5·2	4·0
			1·08	*2·16*	*4·32*	*4·32*	*4·32*
$Cr_{40}Fe_{60}$	923	Cu $K\alpha$‡	2	0	8	8	0
			1·2	*2·4*	*4·8*	*4·8*	*4·8*

* This experiment.

† Powder diffraction data (Algie & Hall, 1966).

‡ Single-crystal diffraction data (Bergman & Shoemaker, 1954). The authors refined atomic numbers at each site rather than site-occupation parameters; the parameters in the table represent the best fit to the average atomic numbers found, given that only Cr and Fe atoms are present, and not giving great weight to the analyzed composition (46·5 at.% Cr). The 'composition' listed thus corresponds to the parameters, not to the analyzed value.

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* Lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38067 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(*b*) *Ordering of* Cr *and* Fe *atoms*

In addition to the results of the present experiment, Table 4 also lists the site-occupation parameters for a $Cr_{46}Fe_{54}$ σ phase derived from neutron powder diffraction data by Algie & Hall (1966), and for a (Cr,Fe) σ crystal studied with Cu $K\alpha$ X-ray diffraction by Bergman & Shoemaker (1954). A comparison of the six sets of parameters in this table leads to the following conclusions:

(1) While the precisions of the parameters obtained from the SR diffraction data (291 observations) for the 1013 K crystal are better by factors of 3–6 than those from the Mo $K\alpha$ data (1700 observations), the two parameter sets do not differ significantly. The largest variations are slightly larger than the e.s.d. of the Mo $K\alpha$ results.

(2) There are no clear trends in the site-occupation parameters with annealing temperature for the three crystals examined in the current experiment. If weighted averages for a given site are computed, with SR results used for the 1013 K crystal, individual parameters differ from the mean by no more than twice the mean e.s.d.

(3) Though they mirror the general site-occupation preferences obtained by Algie & Hall (1966), results of the current experiment show more extreme values. Thus, 75–90% of the icosahedrally coordinated *A* and *D* sites are occupied by Fe atoms according to this experiment, while only 60–70% are so occupied according to the earlier results. Again, the current parameters place Cr atoms on 72–75% of the 15-coordinated *B* sites and on 60–70% of the 14-coordinated *C* and *E* sites, while the earlier results place 45–55% Cr on all three sites. The current results show greater variations from the still earlier, less quantitative parameters reported by Bergman & Shoemaker (1954).

The first conclusion suggests that, provided large numbers of fairly precise conventional X-ray single-crystal diffraction data are measured, reliable site-occupation parameters may be determined for binary σ phases with $\Delta|f|/|f| \sim$ 8–11%. Instances in which the higher precision of the parameters determined with edge-tuned SR diffraction data would be of value are difficult to imagine.

The second conclusion suggests that, in the range of temperature studied, changes in atom distributions on the sites of this σ phase are unfavorable thermodynamically, or are hindered kinetically. At 1063 K, the alloy is only ~25–30 K from the upper limit of σ-phase metastability, yet no significant tendency toward disorder is observed after a heat treatment of 350 h. If this reflects a state of metastable equilibrium and not sluggish diffusion rates, one could also conclude that the non-random distribution of alloying elements in the σ structure is an essential condition for the formation of the phase, not a secondary factor contributing to stability as the temperature is lowered.

The third conclusion supports the generally observed trend, noted in § 1(*b*), for Group VIII and VI*b* elements in binary σ phases to prefer low- and high-coordination-number sites, respectively. That the trend is more sharply defined here than has been reported for previously studied (Cr,Fe) σ phases may be due to longer times of equilibration at temperature, more precise data, or both.

(*c*) *Vector density maps*

Harker sections of the interatomic vector density maps that can be computed with diffraction data from σ phases contain information concerning both the locations and the chemical identities of atoms on the several sites of the structure. $P(u,\frac{1}{2},\frac{1}{2})$ sections are particularly useful because of their good resolution of vectors from a given site to a symmetry-related site. Fig. 2(*a*) shows this section computed from the Mo $K\alpha$ $F^2_{\rm obs}$ values for the 1013 K crystal; some indications of the site-occupation parameters obtained in the least-squares refinement based on this data set can be seen in the section.

Vector density maps computed from the SR $F^2_{\rm obs}$ values for the 1013 K crystal magnify these indications, though with necessarily poorer resolution. The evidences of relative ordering can be accentuated by

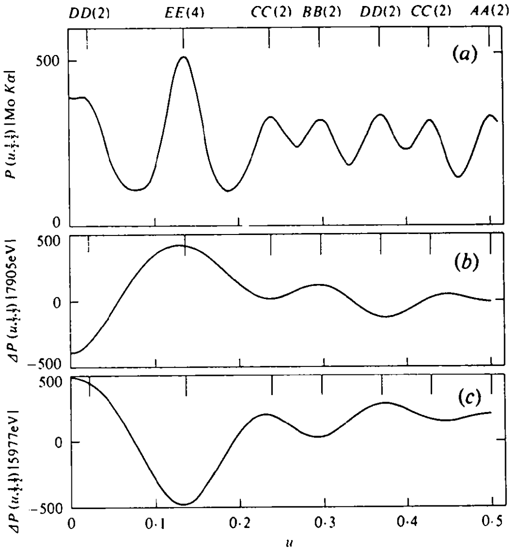

Fig. 2. Sections along the line $u,\frac{1}{2},\frac{1}{2}$ in interatomic vector density maps computed with diffraction data from the 1013 K crystal. (*a*) The vector density function computed from the Mo $K\alpha$ $F^2_{\rm obs}$ values. (*b*) The difference vector density function at the Fe *K* edge computed with coefficients defined in the text. (*c*) The difference vector density function at the Cr *K* edge. The interactions (with multiplicities) expected at discrete *u* values are indicated at the top of each graph. Scale factors have been applied to the ordinates of functions calculated with SR diffraction data to bring them into correspondence with the Mo $K\alpha$ function.

computing difference vector density maps whose coefficients are:

$$[F^2_{\mathrm{obs}}(\mathrm{SR}) - F^2_{\mathrm{calc}}(\mathrm{ave.})],$$

where $F^2_{\mathrm{calc}}(\mathrm{ave.})$ values are computed with random numbers of Fe and Cr atoms on each site. $\Delta P(u,\frac{1}{2},\frac{1}{2})$ sections from maps calculated with SR data from the 1013 K crystal at the Fe *K* and Cr *K* edges are shown in Fig. 2(*b*,*c*). Note that the difference function is positive when the scattering powers of the atoms defining the vector are greater than those of chemical-average atoms, and negative when they are less. For SR tuned just below the Fe *K* edge, the scattering power of Fe is substantially less than that of Cr. Along the $\Delta P(u,\frac{1}{2},\frac{1}{2})$ section, therefore, the function will be negative when the vector is defined by atoms on sites with more Fe than the chemical average, and it will be positive when the vector involves sites with less Fe than the average. Negative and positive regions along this section are reversed when the function is computed with SR data collected at the Cr *K* edge. These expectations are generally met by the functions plotted in Fig. 2(*b*,*c*), and again they qualitatively confirm the site-occupation parameters listed in Table 4.

Table 6. *Some interatomic distances in* (Cr,Fe) *σ phases annealed at three temperatures*

Estimates of error in the last significant digit are given in parentheses; all distances are in Å.

Pairs	No. of atoms	(1063 K)	(1013 K)	(923 K)	(B & G)*
A–B	4	2·6050 (3)	2·6042 (4)	2·6046 (3)	2·603
A–D	4	2·3664 (4)	2·3655 (5)	2·3656 (3)	2·380
A–E	4	2·5465 (4)	2·5461 (6)	2·5463 (4)	2·542
B–A	2	2·6050 (3)	2·6042 (4)	2·6046 (3)	2·603
B–B	1	2·519 (1)	2·519 (1)	2·522 (1)	2·536
B–C	2	2·4204 (5)	2·4213 (7)	2·4206 (4)	2·414
B–D	4	2·6953 (3)	2·6938 (3)	2·6934 (3)	2·695
B–E	4	2·8348 (4)	2·8338 (6)	2·8340 (4)	2·833
B–E	2	2·9219 (6)	2·9231 (9)	2·9221 (6)	2·920
C–B	1	2·4204 (5)	2·4213 (7)	2·4206 (4)	2·414
C–C	1	2·3976 (8)	2·396 (1)	2·3962 (7)	2·404
C–C	4	2·8414 (3)	2·8401 (5)	2·8399 (3)	2·838
C–D	1	2·4920 (5)	2·4934 (7)	2·4931 (5)	2·483
C–D	1	2·4888 (5)	2·4894 (7)	2·4891 (5)	2·476
C–D	2	2·4836 (2)	2·4834 (3)	2·4832 (2)	2·470
C–E	2	2·7607 (5)	2·7614 (6)	2·7617 (4)	2·763
C–E	2	2·7707 (5)	2·7708 (6)	2·7704 (4)	2·768
D–A	1	2·3664 (4)	2·3655 (5)	2·3656 (3)	2·380
D–B	2	2·6953 (3)	2·6938 (3)	2·6934 (3)	2·695
D–C	1	2·4920 (5)	2·4934 (7)	2·4931 (5)	2·483
D–C	1	2·4888 (5)	2·4894 (7)	2·4891 (5)	2·476
D–C	2	2·4836 (2)	2·4834 (3)	2·4832 (2)	2·470
D–D	1	2·4221 (7)	2·420 (1)	2·4207 (6)	2·453
D–E	2	2·5320 (5)	2·5322 (7)	2·5319 (5)	2·538
D–E	2	2·5649 (4)	2·5648 (6)	2·5649 (4)	2·562
E–A	1	2·5465 (4)	2·5461 (6)	2·5463 (4)	2·542
E–B	1	2·9219 (6)	2·9231 (9)	2·9221 (6)	2·920
E–B	2	2·8348 (4)	2·8338 (6)	2·8340 (4)	2·833
E–C	2	2·7607 (5)	2·7614 (6)	2·7617 (4)	2·763
E–C	2	2·7707 (5)	2·7708 (6)	2·7704 (4)	2·768
E–D	2	2·5320 (5)	2·5322 (7)	2·5319 (5)	2·538
E–D	2	2·5649 (4)	2·5648 (6)	2·5649 (4)	2·562
E–E	1	2·2651 (9)	2·262 (1)	2·2607 (8)	2·253
E–E	1	2·2954 (9)	2·296 (1)	2·2975 (8)	2·294

* From Bergman & Shoemaker (1954).

(*d*) *Interatomic distances*

Closest interatomic distances about each independent atomic site were calculated with the *ORFFE* program (Shoemaker, 1966; accession No. 363); they are summarized in Table 6, together with the distances found by Bergman & Shoemaker (1954) for a (Cr,Fe) σ phase of similar composition equilibrated at 923 K. In general, agreement is good, the largest discrepancy (0·03 Å) occurring for a *D–D* distance. An analysis of these distances in terms of differing 'major' and 'minor' radii for each atom was proposed by Shoemaker, Shoemaker & Wilson (1957); it would seem to need no revision in light of the present results.

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Atom Distributions in Sigma Phases.
II. Estimations of Average Site-Occupation Parameters in a Sigma Phase Containing Fe, Cr, Ni, Mo and Mn*

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Abstract

A sigma (σ) phase with atom fractions of $0\cdot517_5$ Fe, $0\cdot311_3$ Cr, $0\cdot078_8$ Ni, $0\cdot073_5$ Mo and $0\cdot018_9$ Mn was prepared to duplicate the observed composition of a σ precipitate in a commercial 316 stainless steel. Analyses of an extensive set of conventional Mo $K\alpha$ Bragg diffraction data from a crystal of this phase gave reliable average site-occupation parameters for Mo atoms on the five independent sites of the σ structure but could not resolve the individual site preferences of the 3*d* transition elements. Synchrotron-radiation diffraction data were measured from the same crystal at photon energies just below the Fe *K* and Cr *K* absorption edges. With atom coordinates, thermal-vibration and Mo-atom-distribution parameters fixed from the refinement based on the conventional data set, the synchrotron-radiation data could be used to distinguish the average distributions of Fe, Cr and (Ni + Mn) atoms. Results indicate a marked preference for Mo atoms to occupy the 15-coordinated *B* sites, with Cr atoms located in numbers greater than random at the 14-coordinated *C* and *E* sites. Atoms of Fe and (Ni + Mn) are found to occupy preferentially the icosahedrally 12-coordinated *A* and *D* sites.

1. Introduction

The general purpose of the current experiments was outlined in the first paper of this series (Yakel, 1983; hereinafter part I). Briefly, it is to assess conditions that may require enhanced contrast among the scattering factors of near-neighbor transition metals for the accurate and precise estimation of average site-occupation parameters from single-crystal Bragg X-ray diffraction data. Changes in atomic scattering factors due to anomalous dispersion produce this contrast when the energy of the X radiation is close to that of an atomic absorption edge. Synchrotron radiation (SR) provides an intense, continuous source of X rays for these edge-tuned diffraction experiments; conventional metal-target X-ray tubes provide sources of characteristic radiation for comparative or complementary experiments.

The first set of experiments dealt with a $CoFe_2O_4$ spinel crystal (Yakel, 1980). It showed that SR diffraction data easily resolved Fe- and Co-ion distributions that could not be estimated with accuracy or precision from Cu $K\alpha$ data. The second set of experiments began with a comparison of the abilities of conventional Mo $K\alpha$ and edge-tuned SR diffraction data to distinguish site-occupation parameters in binary (Cr,Fe) σ-phase crystals (see part I). It showed that, with relative differences in atomic scattering factors ($\Delta|f|/|f|$) of 8–11% for Cr and Fe, conventional data could yield reliable, moderately precise (±5–10%) occupation parameters for Fe atoms on the five sites of the tetrahedrally close-packed σ structure (see part I for a description of this structure). SR diffraction data, with $\Delta|f|/|f| \simeq$ 20–35%, gave distribution parameters of higher precision (±1–2%) than the conventional-data results but with no significant differences. In agreement with findings of neutron powder diffraction

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