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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 $0{\cdot}517_5$ Fe, $0{\cdot}311_3$ Cr, $0{\cdot}078_8$ Ni, $0{\cdot}073_5$ Mo and $0{\cdot}018_9$ 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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studies of a comparable phase (Algie & Hall, 1966), a strong preference was observed for Fe atoms to occupy 12-coordinated sites [the *A* and *D* sites, special positions 2(*a*) and 8(*i*)(2) in space group $P4_2/mnm$, respectively], while Cr atoms were distributed about equally on the 15-coordinated *B* sites [special positions 4(*f*)] and the 14-coordinated *C* and *E* sites [special positions 8(*i*)(1) and 8(*j*), respectively].

The present paper presents results of a continuation of the second set of experiments – a study of average site preferences in a chemically complex σ phase containing Fe, Cr, Ni, Mo and Mn. As in part I, an extensive set of conventional Mo $K\alpha$ Bragg diffraction data and more limited sets of SR data at Fe and Cr *K* edges were measured from a single crystal of the phase. The following sections describe the preparation of the alloy, the collection of the diffraction data and the results of their analyses by least-squares methods and vector-density maps.

2. Experimental

(*a*) *Alloy preparation*

A large specimen of 316 stainless steel, purchased for reactor irradiation studies, was found to contain precipitates of a σ phase after a series of heat treatments. The chemical composition of the precipitate particles, estimated by electron microprobe techniques, was Fe 51, Cr 31, Ni 8, Mo 8 and Mn 2 at.%. An alloy of this composition was prepared by mixing high-purity metal powders, arc-melting the mixture and quenching. X-ray powder diffraction photographs of the as-quenched sample showed that only a σ phase was present. Chemical analyses of the arc-melted alloy gave (all $\pm 0{\cdot}0_8$ at.%) Fe $51{\cdot}7_5$, Cr $31{\cdot}1_3$, Ni $7{\cdot}8_8$, Mo $7{\cdot}3_5$ and Mn $1{\cdot}8_9$ at.%. The sample was easily crushed, and small crystals suitable for Mo $K\alpha$ data collection were selected and mounted. The crystal chosen for the experiment had linear dimensions of 20–50 μm and a volume of 33×10^3 μm^3.

(*b*) *Collection of diffraction data*

Conventional Mo $K\alpha$ [$\lambda(K\alpha_1) = 0{\cdot}709300$ Å] Bragg diffraction data were collected from this crystal with the same automated diffractometer and under the same experimental conditions described in part I. Lattice parameters of the tetragonal unit cell, determined from high-angle reflection centering data, were $a_0 = 8{\cdot}839\,(2)$ and $c_0 = 4{\cdot}5973\,(9)$ Å. About 4000 individual reflection intensities were recorded with an average precision of <1% for the group of intense reflections and ~15% for the group of more numerous weak reflections (see part I). After averaging replicate measurements ($R_w \simeq 7\%$), a total of 3347 observations remained.

SR diffraction data from the same crystal were collected with the CAD-4 diffractometer at the Stanford Synchrotron Radiation Laboratory (Phillips, Cerino & Hodgson, 1979). Again, experimental conditions generally paralleled those described in part I. The Fe *K*- and Cr *K*-edge energies were estimated from measurements of relative linear absorption *vs* incident photon energy with a powdered sample of the alloy and with Fe and Cr metal foils used as calibrations. Bragg intensities were recorded at 7107 (8) eV [$1{\cdot}744_5\,(2_0)$ Å] and 5980 (7) eV [$2{\cdot}073_3(2_4)$ Å] ($1\,\mathrm{eV} = 1{\cdot}602 \times 10^{-19}$ J); Fe and Cr *K* edges in the alloy were measured at 7115 (3) and 5990 (3) eV, respectively. A total of 275 observations were made at the Fe *K* edge and 130 at the Cr *K* edge; averaging of replicate measurements reduced these numbers to 114 and 83.

(*c*) *Data reduction and analysis*

International Tables for X-ray Crystallography (1974) supplied all physical constants, atomic scattering factors at the high energy limit, and mass-absorption coefficients and dispersion correction terms at the Mo $K\alpha$ energy. At SR energies, absorption coefficients were obtained by interpolation of tabulated values, while dispersion terms were calculated by a modified Cromer & Liberman (1970) method (see Table 1 for values).

Reduction of conventional and SR diffraction data to relative F^2_{obs} values utilized the computer programs cited in part I. The Coppens & Hamilton (1970) algorithm was employed to calculate isotropic extinction corrections in the course of least-squares analyses based on the complete Mo $K\alpha$ data set. These corrections were applied to all F^2_{obs} values (including those from SR data) prior to averaging of symmetry equivalents in space group $P4_2/mnm$. After this averaging ($R_w \simeq 6\%$ for all data sets), there were 1750, 86 and 73 observations [1284, 83 and 69 with $I \geq \sigma(I)$] in the Mo $K\alpha$, SR (Fe *K*) and SR (Cr *K*) data sets, respectively.

Refinement of all parameters proceeded from an initial model for the σ structure with atom coordinates taken from Bergman & Shoemaker (1954) and with chemical-average atoms at every site. Variable parameters were adjusted by iterative full-matrix least-squares

Table 1. *Anomalous-dispersion terms at X-ray energies used in this experiment*

	$E = 5980$ eV		$E = 7107$ eV		$E = 17444$ eV	
	f'	f''	f'	f''	f'	f''
Cr	−6·787	0·612	−0·747	3·206	0·284	0·624
Mn	−2·381	0·703	−1·665	3·706	0·295	0·729
Fe	−1·802	0·818	−7·694	0·636	0·301	0·845
Ni	−1·325	1·032	−1·857	0·803	0·285	1·113
Mo	−0·671	4·339	−0·583	3·372	−1·825	0·688

calculations that minimized squares of residuals between observed and computed F^2 values [*XFLS* program (Shoemaker, 1966)]. Weights assigned were $w_i = 1/\sigma_i^2 = 1/[\sigma^2_{\rm stat} + (NF^2_{\rm obs})^2]$, where $\sigma^2_{\rm stat}$ were variances based on counting statistics and N was 0·04 for the Mo $K\alpha$ data and 0·05 for the SR data sets.

For purposes of this refinement, the 25 nominally adjustable site-occupation parameters for a σ-phase structure (space group $P4_2/mnm$) with five constituent elements were reduced to 12 by assuming that only the Fe-, Cr- and Mo-atom occupation parameters on four of the five atomic sites were variable. The analyzed chemical composition supplied constraints fixing the other 13 distribution parameters. Assumptions implicit in the imposition of such constraints are that (i) there is no way to distinguish between Ni and Mn atoms from the given data, and (ii) there are no significant concentrations of vacancies or interstitials in the structure.

Model refinements based on the Mo $K\alpha$ data set eventually included adjustments of a scale factor, 7 atomic coordinates, 18 anisotropic thermal-vibration parameters, and (in the final cycles) site-occupation parameters for Mo atoms on four of the five atom sites. The number of Mo atoms on the arbitrarily chosen fifth site was constrained to give the observed Mo content of the phase and all other atoms were assigned to the five sites in proportion to the analyzed composition. While it was possible to extend the calculations based on the conventional data alone to include adjustments of both Mo- and Fe-atom site-occupation parameters, improvements in measures of agreement were not obtained. When the list of variables was further expanded to embrace Mo-, Fe- and Cr-atom distribution parameters, singularities occurred in the determinant of normal-equation coefficients.

At this stage, the SR data sets were introduced into the calculations. With coordinates, thermal-vibration and Mo-atom site-occupation parameters fixed at values given by the refinement based on the Mo $K\alpha$ data alone, the SR data sets were successfully used to adjust occupation parameters for Fe and Cr atoms on four of the five atom sites. Again, the numbers of Fe and Cr atoms on the fifth site were constrained to give the observed composition, and (Ni + Mn) atoms were assigned to the balance of the sites in proportion to the elemental analyses.* The procedure was iterated by inserting the distribution parameters thus obtained into the refinement based on the Mo $K\alpha$ data alone and readjusting the atomic coordinates, thermal-vibration and Mo-atom site-occupation parameters. Three sets of least-squares cycles computed in this fashion sufficed to give convergence of all varied parameters.

3. Results and discussion

Structural parameters computed in the final pair of least-squares cycles with SR and Mo $K\alpha$ data sets from this σ-phase crystal are listed in Table 2.† Measures of agreement for the three data sets are collected in Table 3. The site-occupation parameters in Table 2 constitute one of the infrequent quantitative estimations of

Table 2. *Structural and atom-distribution parameters for a σ phase containing atom fractions of* 0·517$_5$ Fe, 0·311$_3$ Cr, 0·078$_8$ Ni, 0·073$_5$ Mo *and* 0·018$_9$ Mn

Estimates of error in the last significant figure of variable parameters are given in parentheses.

Positional parameters and thermal-vibration parameters

Site	Wyckoff notation and multiplicity	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A	2(*a*)	0	0	0	0·00130 (6)	0·00130	0·0070 (4)	0·00007 (6)	0	0
B	4(*f*)	0·39800 (6)	0·39800	0	0·00159 (4)	0·00159	0·0060 (2)	0·00015 (4)	0	0
C	8(*i*)	0·46371 (7)	0·13057 (7)	0	0·00153 (5)	0·00163 (5)	0·0067 (2)	0·00002 (3)	0	0
D	8(*i*)	0·73868 (7)	0·06572 (7)	0	0·00128 (4)	0·00141 (4)	0·0061 (2)	−0·00001 (3)	0	0
E	8(*j*)	0·18302 (5)	0·18302	0·2512 (2	0·00164 (3)	0·00164	0·0049 (1)	−0·00006 (3)	−0·0036 (4)	−0·0036

Site-occupation parameters

	Fe		Cr		Mo		(Ni + Mn)	
Site	Obs.	Random	Obs.	Random	Obs.	Random	Obs.	Random
A	1·55 (5)	1·035	0·29 (4)	0·623	0·11 (2)	0·147	0·05 (6)	0·196
B	1·27 (7)	2·070	1·33 (6)	1·245	1·28 (3)	0·294	0·11 (9)	0·391
C	3·99 (9)	4·140	3·03 (9)	2·490	0·59 (4)	0·588	0·4 (1)	0·781
D	5·2 (1)	4·140	0·56 (8)	2·490	0·00 (4)	0·588	2·2 (1)	0·781
E	3·5 (1)	4·140	4·1 (1)	2·490	0·22 (6)	0·588	0·1 (1)	0·781

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* SR diffraction data at Fe and Cr edges highlight the respective atoms in the σ phase; since no data were collected at Ni or Mn edges, the relatively small numbers of these atoms were deemed to be indistinguishable.

† Lists of squares of structure factors, scaled by 0·1, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38119 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Indices of agreement achieved at various stages of refinement*

Definitions of indices are the standard ones used by crystallographers; see Brown & Chidambaram (1969), for example, for specific equations. Values are computed for reflections with $F^2_{\text{obs}} \geq \sigma(F^2_{\text{obs}})$.

Stage	No. of observations	No. of variables	R (F)	R (F^2)	R_w	σ_1
(*a*)	1284	26	0·102	0·087	0·133	1·514
(*b*)	1284	30	0·085	0·062	0·104	1·180
(*c*)	1284	30	0·079	0·054	0·092	1·051
(*d*)	152	2	0·154	0·252	0·488	6·582
(*e*)	152	10	0·073	0·117	0·200	2·886

Stage (*a*): Mo *Kα* data; scale, structural parameters varied; chemical-average atoms at all sites.

Stage (*b*): Mo *Kα* data; scale, structural parameters, four Mo-atom site-occupation parameters varied; all other atom distribution parameters random.

Stage (*c*): Mo *Kα* data; scale, structural parameters, four Mo-atom site-occupation parameters varied; Fe-, Cr- and (Ni + Mn)-atom distribution parameters fixed at values given by last SR data analysis (stage *e*).

Stage (*d*): SR data; scale factors varied; all structural and distribution parameters fixed at values given at stage *b*.

Stage (*e*): SR data; scale, eight Fe- and Cr-atom occupation parameters varied; all other parameters fixed at values given by penultimate Mo *Kα* data analysis.

average atom distributions in multicomponent alloy phases that have moderately complex crystal structures. Therefore, some discussion of grounds for confidence in these results seems justified.

(*a*) Mo-*atom distribution parameters*

Although Mo atoms comprise only 2·2 of the 30 atoms in a unit cell of this σ phase, the Mo *Kα* Bragg diffraction data appear to be remarkably sensitive to their distribution. The sensitivity can be demonstrated by comparing measures of agreement for models with and without Mo-atom ordering and by analyzing vector-density maps.

Based on the Mo *Kα* data set alone, least-squares refinements of the initial model that adjusted only scale, coordinate and thermal-vibration parameters (26 in all) converged to a weighted *R* factor of 0·133. With the addition of four Mo-atom site-occupation parameters, but with all other atom distributions fixed at random values corresponding to the analyzed chemical composition, several refinement cycles decreased this factor to 0·104 and produced an Mo-atom distribution that was distinctly non-random. The *R*-factor ratio (Hamilton, 1965), 1·283, is much larger than the significance point for the ratio $\mathscr{R}_{4,1250,0\cdot005}$ (= 1·006). Thus, the hypothesis that a model with a random distribution of Mo atoms gives agreement with observations as satisfactory as that given by the derived non-random distribution may be rejected with a very small probability of error.

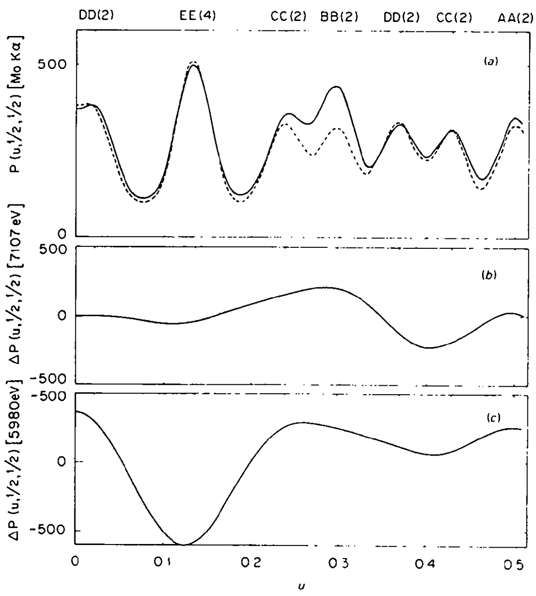

Fig. 1. (*a*) $P(u,\frac{1}{2},\frac{1}{2})$ sections of vector-density maps computed from Mo *Kα* X-ray diffraction data from the σ phase studied here (solid curve) and from a (0·482 Cr, 0·518 Fe) σ phase (dashed curve). (*b*), (*c*) $\Delta P(u,\frac{1}{2},\frac{1}{2})$ sections of difference vector-density maps computed with SR diffraction data collected at (*b*) 7107 eV and (*c*) 5980 eV from the σ phase studied here. Sections in (*a*) are drawn to the same relative scale for *P*; the sections in (*b*) and (*c*) are plotted with absolute values of ΔP. Interactions (with multiplicities) expected at discrete *u* values are indicated at the top of each graph.

Confidence in the reliability of the detailed site-occupation parameters for Mo atoms produced by the least-squares calculations is increased by the qualitative confirmation they receive from studies of variations in vector densities in the Harker section $P(u,\frac{1}{2},\frac{1}{2})$. Fig. 1(*a*) shows this section computed from scaled Mo *Kα* F^2_{obs} values for the σ phase studied here (solid curve) and for a binary (Cr,Fe) σ phase (dashed curve, from part I) where atomic scattering factors may be taken as equal, to a crude approximation. Noticeable increases in the former function near the *u* value associated with *B*—*B* vector interactions suggest that these sites are occupied by atoms with significantly greater-than-average scattering power – most probably by Mo atoms in numbers greatly exceeding random, as found in the least-squares analysis.

(*b*) Fe- *and* Cr-*atom distribution parameters*

As noted in § 2(*c*), adjustments of eight Fe- and Cr-atom site-occupation parameters were made in least-squares calculations based on the SR data sets alone with all other variables fixed at values given by refinements based on the Mo *Kα* data set. Final measures of agreement achieved for the SR data after convergence of this refinement scheme are somewhat larger than might be expected for reasonably precise counter-diffractometer data (see Table 3). A possible cause for the diminished agreement may lie in uncertainties about the incident photon energy at the σ-phase crystal and hence the values of anomalous-dispersion corrections.

Nevertheless, the significance of the Fe- and Cr-atom site-occupation parameters may be judged by comparing the value of R_w for the final cycle of the refinement based on SR data (0·200) with the corresponding value for random distributions of all but Mo atoms (R_w = 0·488). The ratio, 2·4, should discourage any belief that random occupation parameters for Fe and Cr atoms are reasonable estimators of the actual distributions.

With the final Fe- and Cr-atom site-occupation parameters listed in Table 2, an adjustment of 30 scale, coordinate, thermal-vibration and Mo-atom distribution parameters based on the Mo $K\alpha$ data set gave $R_w = 0{\cdot}092$. The ratio $0{\cdot}104/0{\cdot}092 = 1{\cdot}130$ is again larger than the significance points for $\mathscr{R}_{n,1250,0\cdot005}$ even if n is 38. Thus, though the conventional data alone are considered, the hypothesis that a model with ordered Mo-atom but random Fe- and Cr-atom distributions gives agreement with observations as satisfactory as that given by the derived non-random Fe- and Cr-atom parameters may be rejected with small chance of error.

It is more difficult to test the hypothesis that some other non-random site-occupation parameters for Fe and Cr atoms may be better estimators of the actual distributions than those produced by the least-squares refinement procedure described above. Confidence in the reliability of the latter could again be increased by examining Harker sections in vector-density-maps. In part I, it was reported that difference functions $\Delta P(u,\frac{1}{2},\frac{1}{2})$ could magnify indications of site-occupation preferences in σ phases. These functions have coefficients given by $[F^2_{\text{obs}}\,(\text{SR}) - F^2_{\text{calc}}\,(\text{av.})]$ where, in the present case, F^2_{calc} (av.) is computed with random numbers of Fe, Cr and (Ni + Mn) atoms on each site, but with Mo-atom distribution parameters fixed at values given by least-squares refinements based on the Mo $K\alpha$ data set.

The difference functions for F^2_{obs} (Fe K edge) and F^2_{obs} (Cr K edge) are shown in Fig. 1(b) and (c), respectively. The difference function is positive where the scattering factors of atoms defining vectors are greater than those of average atoms but negative where they are less; at the Fe K edge $|f|_{\text{Fe}} < |f|_{\text{av}}$, while at the Cr K edge $|f|_{\text{Cr}} \ll |f|_{\text{av}}$. With allowance for the relatively poor resolution of series summed from few terms, one sees that Fe- and Cr-atom site-occupation parameters listed in Table 2 agree moderately well with features of the function generated from Cr K-edge data but rather less well with those from Fe K-edge data.

In evaluating this result, it may be noted that the features of difference vector-density function generated from data collected near a given atomic absorption edge will be most sensitive to departures from random values in the site-occupation parameters of the atom species whose scattering power is most distinguished from the average. In cases of interest here, this will usually be the species whose edge is approached. Moreover, magnitudes of differences between extrema of the function will also be proportional to squares of the difference between the scattering powers of the distinguished species and the average atom. The smaller this difference, the greater the effect that errors in observed and computed parts of the coefficients could have on the apparent features of the function. For the function in Fig. 1(b), the atoms distinguished are Fe whose derived site-occupation parameters differ from 1 ($i.e.$ random) by a maximum of 0·50 (at A sites) with a weighted mean of 0·23, and the value of $|f|_{\text{Fe}} - |f|_{\text{av}}$ is about 4 electrons. For the function in Fig. 1(c), the atoms distinguished are Cr whose distribution parameters differ from 1 by a maximum of 0·76 (at D sites) with a weighted mean of 0·48, and the value of $|f|_{\text{Cr}} - |f|_{\text{av}}$ is over 6 electrons. Thus, if the distribution parameters of Table 2 describe reality, difference vector-density functions with more pronounced extrema and with less interference from errors would be generated by Cr K-edge data than by Fe K-edge data from this σ phase. The first part of the prediction is borne out in Fig. 1(b) and 1(c); the second part may help to rationalize the lack of detailed agreement between the distribution parameters in Table 2 and the Fe K-edge function.

(c) *Comparisons of distribution parameters with those in binary σ phases*

Atom-distribution parameters reported in Table 2 also gain credibility when compared with corresponding parameters observed for binary σ phases. The bar graphs in Fig. 2 display preference ratios of observed random site-occupation parameters for the

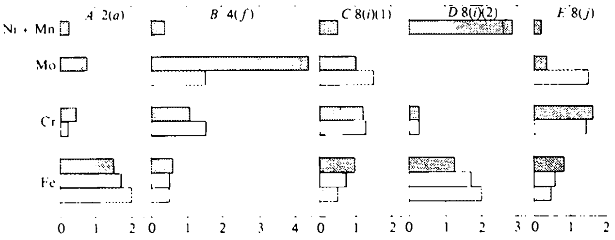

Fig. 2. Bar graphs showing site-occupation preference ratios (observed: random distribution parameters) for the five atom sites of the σ phase. Values of the ratio are plotted horizontally for the four atom species indicated at the left. Cross-hatched bars give values for the σ phase reported here; open bars give values for the (0·482 Cr, 0·518 Fe) σ phase annealed at 1013 K and reported in part I; diagonally lined bars give values for a (0·5 Fe, 0·5 Mo) σ phase reported by Wilson & Spooner (1963).

five atomic sites of the centrosymmetric σ structure. Results from part I for a 51·8 at.% Fe (Cr,Fe) σ phase, from Wilson & Spooner (1963) for a 50 at.% Fe (Fe,Mo) σ phase, and from the present experiment are shown.

Preferences for Group VIII elements to occupy icosahedrally 12-coordinated *A* and *D* sites are common to all the plotted results. In the binary phases, Group VI*b* elements occupy the one 15-coordinated and two 14-coordinated sites (*B* and *C*, *E*, respectively) in the asymmetric unit with approximately equal probability. Results of the present experiment show that, when both Cr and Mo atoms are present, Mo atoms tend to segregate to 15-coordinated *B* sites with fewer than random numbers at *C* and *E* sites. The Cr atoms displaced from *B* sites appear at *A* and *E* sites in proportions greater than those measured for the binary (Cr, Fe) σ phase, while the *C*-site occupancy remains about the same. These trends suggest that when two Group VI*b* elements are present in a σ phase, the larger atom will preferentially occupy the site with highest coordination number. Kasper (1954) found a similar trend in a (Cr,Fe,Mo) χ phase, another tetrahedrally close-packed structure.

The disproportionately large number of (Ni + Mn) atoms at *D* sites compared to *A* sites is more unexpected and less easy to explain. It might be supposed that the distributions could change somewhat if it were possible to distinguish between the scattering powers of Ni and Mn atoms. It might also be supposed that relatively small variations in the Fe-atom distributions could significantly affect the (Ni + Mn)-atom distributions. Since the Fe-atom distributions cannot be confirmed in detail from the difference vector-density maps, this possibility cannot be eliminated. If one did assume that the actual Ni-atom distributions were reflected in the derived (Ni + Mn)-atom values listed in Table 2, one would be forced to look for causes of preferential occupation in the fact that *A* and *D* sites, while both 12-coordinated, differ in such details as site symmetry and contact distances to nearest neighbors.

4. Conclusions

Results of the experiment described in this paper show that:

(i) when more than two constituent elements are near-neighbor members of the same period, the distribution parameters for polycomponent transition-metal phases may not be recoverable from conventional X-ray diffraction alone;

(ii) least-squares analyses of combinations of conventional and edge-tuned SR diffraction data should determine most of the distribution parameters in such cases, even when elemental concentrations are of the order of 10 at.%;

(iii) the distribution parameters so determined have statistical significance; they are consistent with some qualitative features of directly calculable vector-density maps, and they are compatible with corresponding parameters reported for chemically simpler systems. In sum, they appear to be reasonable estimates of the actual distributions.

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