An Ionicity-Modified Pair Potential Model Analysis of the Sigma Phase Structure

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Comparison of observed lattice parameters with those predicted by an ionicity-modified pair potential model yields the conclusion that stable sigma phases must contain an element that can undergo a stabilizing crystal field distortion when occupying E-type sites; conversely, sigma phases that do not contain such a component will not be stable. It is proposed that only "exotic" elements belonging to the Ti, Cr, V, and Mn columns of the periodic table can be stabilized by such crystal fields. Consequently, such "exotic" elements should be present as components in other TCP structures having D_{2d} point symmetry. Indeed, every known phase of such structures contains at least one such "exotic" element. A positive excess entropy also contributes to the stability of some sigma phases at elevated temperatures. A crystal field-, ionicity-modified pair potential model has been developed which yields values of lattice parameters, site positioning parameters, site order parameters, and energy of formation which are in good agreement with observed values.

Introduction

This paper reports the results of part of an investigation which has the general objective of providing a means of predicting the free energy of the sigma phase structure for multicomponent alloy systems. It is intended to use this capability in applications involving superalloys and stainless steels as a rigorous alternative to the PHACOMP procedure (*1*) of predicting the $(\gamma + \gamma')/\sigma$ boundary and also in applications associated with superconductor alloy development to discover means of altering the $A15/(A15 + \sigma)$ phase boundary in order to stabilize the stoichiometric composition of the $A15$ structure in alloy systems that exhibit this equilibrium.

The particular objective of the present work was to evaluate the source of stability of the sigma phase structure for binary alloys. For those binary alloys involving combinations between early and late transition elements (our so-called Class II combinations) previous

applications of an ionicity-modified pair potential model has been able to yield acceptable predictions for the lattice parameters and relative stabilities of *cubic* structures (*2–6*) *without the use of adjustable parameters*. We have applied this model to the sigma phase structure and have found, as we show here, discrepancies between the predicted results and experimental values of the two lattice parameters, and predicted and observed relative stabilities, although those for the seven site positioning parameters and the four independent site order parameters were in fair agreement.

An analysis of the results suggested that improvement of the predictions might be achieved by further modification of the ionicity-modified pair potential model to allow for the effect of noncubic symmetry about an atom at an E-type site on the pair potential parameters. Indeed, such a modification, as we show below, was found to yield results that are consistent with experiment.

In the course of this research we have found that application of the crystal field-, ionicity-modified pair potential model not only resulted in a quite acceptable quantitative description of the lattice parameters, site parameters, site order parameters, and energy of formation, but that our understanding of the physical factors contributing importantly to the stability of the sigma phase structure has been significantly enhanced. In particular, it is now apparent why all sigma phases contain an element from either the Ti, V, Cr, or Mn columns in the periodic table—only such elements yield crystal field stabilization of the sigma phase when they occupy the E-type sites. These elements have sufficient d electrons and holes in the appropriate energy levels. The other transition elements apparently do not satisfy these requirements.

Another concept of equal importance that we came to understand in the present research is that certain sigma phases are stabilized at elevated temperatures by a positive excess entropy. Additional insights into the chemistry and physics of bonding in the sigma phase structure, which application of the pair potential model developed, are discussed in the text.

Isotropic Pair Potential Model (Ionicity-Modified)

There are 13 independent parameters associated with the sigma phase structure $(D8_b)$:[1] two lattice parameters (a and c), seven site positioning parameters, and four site order parameters. At equilibrium and at $0°K$, the lattice energy must be at a minimum with respect to each of these independent parameters! The lattice energy can be expressed as an analytic function of these parameters in the ionicity-modified pair potential model. Thus, in principle, it is possible to arrive at the values of these parameters corresponding to the minimum in the energy.

For all the parameters except the site order parameters, the energy can be differentiated and set equal to zero to find the values corresponding to the minimum energy. However, the energy does not exhibit a minimum with respect to the site order parameters. It is found, as expected, that the minimum energy corresponds to long-range order rather than partial order. There are a limited number of long-range-ordered configurations. The energy is thus determined for all these configurations and the values to be reported are for the ordered configuration having the lowest energy, except as specifically noted in the text.

The first model we have used for the lattice energy is that described in Ref. (2). In this model, it is assumed that the pair potential parameters (α and β) representing the interatomic potentials are isotropic, i.e., independent of orientation. The pair potentials are ordinary 4–8 inverse power Lennard-Jones potentials,[2] except that the repulsive potential (β) is modified to take into account any electron transfer induced by differences in electronegativity of the unlike atoms. This unique modification has been shown to be responsible for the dramatic success of this otherwise classical model in providing quantitative predictions of the lattice parameters of hundreds of intermetallic phases and their relative stabilities (2–6).

The equations for the sigma phase structure and the computer programs for their solution are given in Ref. (7). The input data appear in Ref. (2, Appendix 1). No adjustable parameters enter into this model. It is assumed, however, that the electron transfer to (or from) a given component due to the electronegativity difference between this component and its conjugate in the binary sigma phase is independent of the site occupied by the component atom in the unit cell of this

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[1] See the Appendix for a description of the $D8_b$ structure.

[2] $\phi_{ij} = -(\alpha_{ij}/r_{ij}^4) + (\beta_{ij}/r_{ij}^8)$, where ij denote the type of atom at the center of coordinates (i) and at the site (j) in the coordination shell, where the separation between these atoms is r_{ij}.

structure. The unmodified pair potential parameters between like atoms are obtained by fitting to the lattice parameter and cohesive energy of the corresponding pure component in a metallic reference structure. Those between unlike atoms are suitable averages of the parameters for the conjugate pure components (2).

The results obtained are given in square brackets in Tables I to III for the known binary sigma phases, excluding those containing Mn, Al, and Au. Previous experience has shown that when these elements are combined with transition elements factors extraneous to the pair potential model affect the lattice parameters and hence such data cannot be used to evaluate the model.

The data in Table I yield root-mean-square deviations between predicted[3] and observed lattice parameters as follows:

$$\left[\overline{\left(\frac{\Delta a}{a} \right)^2} \right]^{1/2} = 1.06\%,$$

$$\left[\overline{\left(\frac{\Delta c}{c} \right)^2} \right]^{1/2} = 1.97\%.$$

These values exceed those found previously (2–6) on application of the model to cubic structures for the same class (II) of component combinations, which uniformly were less than 0.5%. Hence, it is apparent that some factor that affects the lattice parameters is not taken into account in the isotropic model.

An examination of the individual deviations yields the results

$$\frac{\overline{\Delta a}}{a} = -0.44\%; \qquad \frac{\overline{\Delta c}}{c} = 1.49\%.$$

These values for the deviations strongly suggest that a crystal field effect (4, 5) is operative in the sigma phase structure. We consider this possible effect in greater detail in the next section.

[3] Parameters identified by the superscript * are predicted values. The observed values are denoted by a subscript xp, referring to experimental values.

The data in Table II suggest that the isotropic pair potential model yields fairly good predictions for the site positioning parameters.[4] Also, the data in Table III reveal fairly good agreement between the predicted and observed site order parameters for some alloys but not for others.

The inadequacy of the lattice parameter predictions and the need to describe the lattice energy of the sigma phase as accurately as possible in order to satisfy the objective of this investigation provided the thrust to modify the isotropic pair potential model. These modifications and the accompanying results are described in the succeeding sections.

Anisotropic Pair Potential Model

The greatest deviation from cubic point symmetry occurs at the E-type sites of the sigma phase unit cell.[4] Although the point symmetry at these sites is strictly monoclinic, it is closely approximated by the tetragonal symmetry, D_{2d} ($\bar{4}2m$). The fact that the point symmetry of the B atoms at the AB_3 composition in the $A15$ structure is also D_{2d} suggested to us that we ought to apply to the sigma phase the modification of the pair potential model previously found to yield an acceptable description of the energy of formation and lattice parameter of $A15$ phases (2). This modification is the alteration of the Gordy electronegativity of the B atoms when on B-type sites in the $A15$ structure, according to $x^{**} = 0.68\ x^*$, where $x^* = x - 0.5$ (Gordy electronegativity) and x is the Pauling electronegativity. The effect of altering the electronegativity of B-type atoms on E-type sites in the sigma phase structure was therefore evaluated. We found the unexpected result that this modification produced lattice parameter predictions in worse agreement with experiment than that found for the isotropic model!

The next modification to the pair potential model we tested is based on another result

[4] See the Appendix for definition of site positioning parameter.

TABLE I

PREDICTED LATTICE PARAMETERS AND COMPARISON WITH OBSERVED VALUES (Å)

	Alloy[a]			a^*	a_{xp}	c^*	c_{xp}	v'
	A	B						
				[8.943]		[4.651]		
43.5	V	Co	56.5	8.898	8.843	4.590	4.586	0.5
				[8.997]		[4.734]		
50	V	Fe	50	9.005	8.956	4.635	4.627	0.42
				[8.982]		[4.756]		
57.5	V	Ni	42.5	8.996	8.954	4.653	4.635	0.42
				[9.374]		[5.008]		
25	V	Re	75	9.551	9.36	4.812	4.86	0.42
				[9.374]		[5.008]		
75	Re	V	25	9.426	9.36	4.890	4.86	0.50
				[9.280]		[4.833]		
50	Mo	Fe	50	9.207	9.218	4.812	4.813	0.675
				[9.260]		[4.927]		
60	Mo	Co	40	9.265	9.229	4.825	4.827	0.625
				[9.558]		[5.074]		
72	Mo	Ir	28	9.615	9.631	4.945	4.957	0.525
				[9.537]		[5.059]		
66.7	Mo	Os	33.3	9.588	9.624	4.938	4.944	0.5
				[9.541]		[5.057]		
40	Mo	Re	60	9.576	9.59	4.994	4.982	0.2
				[9.541]		[5.057]		
60	Re	Mo	40	9.579	9.59	4.962	4.982	0.42
				[9.472]		[5.040]		
63.5	Mo	Ru	36.5	9.517	9.557	4.918	4.933	0.525
				[8.744]		[4.62]		
52.3	Cr	Co	47.7	8.761	8.75	4.544	4.54	0.42
				[8.817]		[4.663]		
46.5	Cr	Fe	53.5	8.856	8.80	4.550	4.544	0.5
				[9.089]		[4.669]		
66.7	Cr	Os	63.3	9.089	9.107	4.669	4.696	0
				[9.216]		[4.905]		
40	Cr	Re	60	9.235	9.30 (9.29)	4.894	4.85 (4.831)	0.65
				[9.018]		[4.675]		
66.7	Cr	Ru	33.3	—	9.068	—	4.704	—
				[9.730]		[5.166]		
60.5	Nb	Ir	39.5	9.769	9.847	5.044	5.053	0.325
				[9.744]		[5.169]		
60	Nb	Os	40	9.782	9.858	5.049	5.066	0.325
				[9.835]		[5.230]		
62	Nb	Pt	38	9.874	9.91	5.112	5.13	0.3

TABLE I—*Continued*

	Alloy[a]			a^*	a_{xp}	c^*	c_{xp}	v'
	A	B						
45	Nb	Re	55	[9.661] 9.676	9.789	[5.133] 5.087	5.099	0.1
55	Re	Nb	45	[9.661] 9.704	9.789	[5.133] 5.061	5.099	0.2
65.1	Nb	Rh	34.9	[9.718] 9.771	9.835	[5.201] 5.059	5.083	0.325
75	Ta	Ir	25	[9.838] 9.888	9.928	[5.246] 5.135	5.159	0.25
75	Ta	Os	25	[9.852] 9.890	9.934	[5.249] 5.160	5.189	0.2
80	Ta	Pt	20	[9.943] 9.984	10.12	[5.295] 5.206	5.20	0.2
40.8	Ta	Re	59.2	[9.620] 9.650	9.69	[5.125] 5.033	5.04	0.2
70	Ta	Rh	30	[9.747] 9.795	9.863	[5.224] 5.106	5.131	0.25
75	W	Os	25	[9.590] 9.636	9.659	[5.104] 5.001	5.001	0.42
50	W	Re	50	[9.594] 9.608	9.627	[5.065] 4.990	5.015	0.42
75	Zr	Ir	25	[10.434] 10.532	10.78 (10.504)	[5.584] 5.376	5.618 (5.355)	0.4
45.5	Re	Fe	54.5	[9.208] 9.099	9.02 (9.08)	[4.739] 4.715	4.69 (4.72)	0.975
60	Tc	Cr	40	[9.140] 9.147	9.217	[4.856] 4.796	4.803	0.35
40	Cr	Tc	60	[9.140] 9.150	9.217	[4.856] 4.849	4.803	0.30
30	Mo	Tc	70	[9.487] 9.487	9.509	[4.962] 4.962	4.945	0
70	Tc	Mo	30	[9.487] 9.487	9.509	[4.962] 4.962	4.945	0
50	Tc	Fe	50	[9.099] 9.099	9.077	[4.773] 4.773	4.756	0
60	Re	Cr	40	[9.216] 9.222	9.30 (9.29)	[4.905] 4.815	4.85 (4.831)	0.6
50	Re	W	50	[9.594] 9.628	9.627	[5.065] 5.008	5.015	0.2
59.2	Re	Ta	40.8	[9.620] 9.674	9.69	[5.125] 5.038	5.04	0.2

[a] A is "exotic" element. Numbers represent atomic percent of adjacent component.

TABLE II

PREDICTED SITE POSITIONING PARAMETERS AND COMPARISON WITH OBSERVED VALUES

Alloy[a] A B	X_{B}^{*}	$X_{B,xp}$	X_{C}^{*}	$X_{C,xp}$	Y_{C}^{*}	$Y_{C,xp}$	X_{D}
	[0.4015]		[0.5367]		[0.1322]		[0.0665]
Mo Co	0.3998	0.3973	0.5355	0.5365	0.1306	0.128	0.0658
	[0.4010]		[0.5367]		[0.1327]		[0.0667]
Cr Co	0.3995	0.3984	0.5363	0.5373	0.1309	0.1291	0.0659
		(0.397)		(0.537)		(0.129)	
	[0.4009]		[0.5376]		[0.1329]		[0.0665]
Cr Fe	0.4002	0.3981	0.5370	0.5368	0.1315	0.1316	0.0667

Alloy[a] A B	$X_{D,xp}$	Y_{D}^{*}	$Y_{D,xp}$	X_{E}^{*}	$X_{E,xp}$	Z_{E}^{*}	$Z_{E,xp}$
		[0.2552]		[0.3171]		[0.2498]	
Mo Co	0.067	0.2557	0.255	0.3166	0.318	0.2499	0.250
		[0.2617]		[0.3181]		[0.2497]	
Cr Co	0.0654	0.2622	0.260	0.3173	0.316	0.2497	0.250
	(0.066)		(0.2596)		(0.3174)		(0.250)
		[0.2638]		[0.3182]		[0.2495]	
Cr Fe	0.0653	0.2628	0.2624	0.3184	0.3177	0.2494	0.2476

[a] See Table I for compositions and the Appendix for definition of site positioning parameters.

found to hold in previous work. Namely, that the attractive pair potential parameter tends to be insensitive to alteration in the electron screening (2, 3, 6), whereas the repulsive pair potential parameter is sensitive to this variable. The effect of a change in point symmetry of a transition atom's environment from cubic to tetragonal is to remove the degeneracies associated with the e_g and t_{2g} symmetry states. This transition develops A_1 and B_1 symmetry states for the e_g state and B_2 and E states from the t_{2g} state. In the particular case of the E sites in the sigma phase unit cell, it is likely that the A_1 state is increased in energy, while the B_1 and B_2 states are stabilized. Electron transfer from the A_1 state to the B_1 and B_2 states will cause the isoelectron density contour about atoms that can exhibit such electron transfer to change from spherical to that of an oblate spheroid. This process can be described in the pair potential model as follows.

First, let us denote elements that can exhibit this crystal-field-induced electron transfer by the term "exotic" elements. We believe that the elements in the Ti, V, Cr, and Mn columns of the periodic table are the only transition elements which can be "exotic" in the sense described.

Let D^* be the atomic diameter of an "exotic" element prior to crystal-field-induced change of shape. Let D_c be the minor axis of the oblate spheroid that is oriented parallel to the c direction of the sigma phase unit cell, i.e., parallel to the string of atoms on E-type sites. Also, let D_a equal the major axis of the oblate spheroid that is oriented perpendicular to the c axis of the sigma phase unit cell. If v' is the number of electrons transferred out of the A_1 state, $v'/2$ is transferred to the B_1 state and $v'/2$ to the B_2 state. Then, according to Ref. (2),

$$D_c' = D^*/(1 + 1.5\ s\ v'/x^* D^*),$$
$$D_a' = D^*/(1 - 1.5\ s\ v'/2\ x^* D^*).$$

TABLE III

PREDICTED SITE ORDER PARAMETERS[a] AND COMPARISON WITH OBSERVED VALUES[b]

Alloy		at.% B $\left(\dfrac{\text{predicted}}{\text{observed}}\right)$	f_A	f_B	f_C	f_D	f_E
A	B						
Mo	Ir	28	[0]	[1]	[1]	[0.2]	[1]
			0	1	1	0.2	1
		28	0.5	1	1	0.19	0.88
V	Ni	42.5	[0]	[1]	[1]	[0]	[0.66]
			0	1	0.66	0	1
		43.3	0.15	1	0.70	0.13	0.94
Mo	Os	33.3	[0]	[1]	[1]	[0]	[1]
			0	1	1	0	1
		35.0	0.25	1	0.94	0.06	0.88
Cr	Ru	33.3	[1]	[0]	[0.25]	[1]	[1]
			1	0	0.25	1	1
		36.5	0.635	0.635	0.635	0.635	0.635
Cr	Os	33.3	[1]	[0]	[0.25]	[1]	[1]
			1	0	0.25	1	1
		37	0.63	0.63	0.63	0.63	0.63
Cr	Co	47.7	[0]	[1]	[1]	[0]	[0.46]
			0	1	0.46	0	1
		47	0	1	1	0	0.5
Mo	Co	40	[0]	[1]	[1]	[0]	[0.75]
			0	1	0.75	0	1
		40	0	1	0.88	0	0.88
Nb	Ir	39.5	[0]	[1]	[1]	[0]	[0.77]
			0	1	0.77	0	1
		39.5	0	1	0.88	0	0.88
Nb	Os	40	[0]	[1]	[1]	[0]	[0.75]
			0	1	0.75	0	1
		40	0	1	1	0	0.75
V	Fe	50	[0]	[1]	[1]	[0]	[0.375]
			0	1	0.375	0	1
		40	0.15	1	0.81	0.15	0.75
Mo	Fe	50	[0]	[1]	[1]	[0]	[0.375]
			0	1	0.375	0	1
		50	0	0.75	0.75	0	0.75
Cr	Fe	53.5	[0]	[1]	[1]	[0.24]	[0]
			0	0	0.74	0	1
		54	0.3	0.55	0.45	0.35	0.5
Nb	Re	[c] 55	[0]	[1]	[0.19]	[0]	[1]
			0	1	0.19	0	1
		[d] 55	0	1	1	0.19	0
		55	0	1	0.59	0	0.59

TABLE III—*Continued*

Alloy A B	at.% B $\left(\dfrac{\text{predicted}}{\text{observed}}\right)$	f_A	f_B	f_C	f_D	f_E
Mo Re		[1]	[0]	[0.25]	[1]	[0]
	c 60	1	0	0	0.25	1
	d 60	1	0	0.25	1	0
	55	0	0.75	0.50	0.19	0.63
		[0]	[1]	[1]	[0]	[0.21]
Re Fe	54.5	0	1	0.21	0	1
		0	1	0.66	0	0.66
		[1]	[0]	[0]	[1]	[0.25]
Cr Re	c 60	1	0	0	1	0.25
	d 60	1	0	0.25	1	0
	63	0.10	0.90	0.18	0.14	0.43
	63	0.68	0.08	0.14	0.60	0.46
	63	0.75	0.19	0.28	0.50	0.34
	63	0	1	0	0	0.91
	63	0.37	0.37	0.37	0.37	0.37

[a] Probabilities that A component occupies the type of site denoted by subscriptions A, B, C, D, and E.

[b] Observed values are copied from "Topologically Close-Packed Structures of Transition Metal Alloys," by A. K. Sinha, *Progr. Mat. Sci.* **15**, 79 (1972).

[c] A atom exotic.

[d] B atom exotic.

The corresponding pair potential parameters are then given as follows: (a) The attractive parameter, α, is unchanged; (b) the repulsive parameter β^* is now given by

$$\beta^* = m\, \alpha S_m (D'^*)^{n-m}/n\, S_n,$$

where[5]

$$(D'^*)^2 = \left(\frac{\sin^2 \theta}{D_a'^2} + \frac{\cos^2 \theta}{D_c'^2}\right)^{-1},$$

[5] This expression for D'^* is an approximation. To be consistent with our previous use of the repulsive parameter, the appropriate value of D'^* to use for a particular interatomic repulsion is the distance between centers of the atoms when they are "in contact," that is, when their surfaces defining the classical turning points (i.e., the radii of maximum electron density) are tangent to each other while their centers are on the line defined by their positions in the crystal structure. Let the components of the binary alloy be denoted by subscripts 1 and 2 and suppose that component 2 is the "exotic element." Then, according to Ref. (2), the atomic diameter of 2 in the alloy is given by $D_2^* = D_2^0/(1 - 0.75\, s_2(x_2 - x_1)/x_2^*\, D_2^0)$. Values are given in Ref. (2, Appendix 1) for the

and where θ is the angle between the c axis and the direction along which β^* is applicable.

We have made use of this relationship and have modified our pair potential model of the sigma phase structure, limiting this modification of the repulsive parameter to "exotic" elements whenever these elements appear in E-type sites. The full description of the model is given in Ref. (7). Our plausibility argument for applying this modification only to the "exotic" elements is that only such elements have enough d electrons to transfer and also have an insufficient number of them

screening constant per electron (s), the electronegativity (x), and the atomic diameter in the reference structure (D^0). The inverse power exponents m and n are taken to equal 4 and 8, respectively. The attractive pair potential parameter, α, applicable to each bond is defined in Ref. (2). for the bond between like 2-type atoms, for example, $\alpha_{22} = -4E_2^0 D_2^{04}/N\, S_m$, where N is Avogadro's number. The structure sums S_m and S_n applicable for an $A2$ reference structure and corresponding to an average sum over 13.47 atoms are 11.23 and 9.86, respectively.

that there will be holes in the B_1 and B_2 states in which electrons can transfer; i.e., only these elements are likely to be stabilized by the crystal field into the oblate spheroidal atom shape.

Our first concern is whether the modified model can reproduce the observed lattice parameters and order and site positioning parameters. Accordingly, we modified the BINARY SIGMA PROGRAM applicable to the isotropic model to take into account the effect of the crystal field on the repulsion parameter of "exotic" atoms in E-type sites. This new program is called BINARY SIGMA-ANISOTROPIC. We treated the parameter v' as the adjustable parameter, which was varied until for the most stable state the corresponding a and c lattice parameters were in best agreement with the experimental values. Thus, the a and c lattice parameters are best values obtained by adjustment of the v'. This adjustment results in the *prediction* of values for the order and lattice site parameters. We shall show that the order and lattice site parameter values obtained with use of the crystal field modified program are consistent with the experimental values.

However, let us first consider the nature of the agreement obtained for the c and a parameters because it is not necessary that a single adjustable parameter model produces agreement for two independent variables with the observed values. Table I lists the best values obtained through use of the BINARY SIGMA-ANISOTROPIC program (the unbracketed values) and the observed values. As shown, the rms deviations between observed and calculated results have been reduced to

$$\left[\overline{\left(\frac{\Delta a}{a}\right)^2}\right]^{1/2} = 0.53\% \text{ and } \left[\overline{\left(\frac{\Delta c}{c}\right)^2}\right]^{1/2} = 0.45\%.$$

Thus, the crystal field distortion of E-sited "exotic" atoms leads to a more accurate model description of the lattice parameters. That is, the BINARY SIGMA-ANISOTROPIC program yields lattice parameters that are consistent with the observed values, whereas the

BINARY SIGMA-ISOTROPIC program does not. Although an adjustable parameter is partly responsible for this improvement, it is not wholly responsible because a single-parameter adjustment has yielded acceptable results for two independent parameters.

Predicted values of the site order parameters for the anisotropic model (the unbracketed values) are compared to experimental values in Table III. The changes for the systems listed in Table III do not involve any change in the degree of agreement with observation previously obtained for the isotropic model, which was acceptable. Also, as shown by comparisons of bracketed and unbracketed values in Table II, both models yield good approximations for the site positioning parameters.

It is possible that further modification of the model to take into account possible crystal field distortions due to noncubic point symmetry at the other sites of the sigma phase unit cell would lead to still further improvement of the model. Also, the model, as developed, involves central forces and the crystal field distortion certainly sets up noncentral repulsive forces, the consideration of which would lead to the definition of all parameters, i.e., no more adjustable parameters.[6] However, such additional modifications were not undertaken in the present investigation because it was concluded that the effort required was not justified.

Energy of Formation

The pair potential model not only yields values of lattice parameters but it also predicts energies of formation. Table IV lists the predicted energies of formation for those ordered configurations predicted to be stable at 0°K. We comment later on these values.

Some energies of formation have been measured at elevated temperature. These

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[6] The possibility that the energy is minimized with respect to the crystal field parameter, v', has been considered and found to be valid for the $A15$ structure in a separate investigation (12). It is thus likely to be valid for the $D8_b$ structure as well.

TABLE IV

ENERGIES OF FORMATION FOR MOST STABLE STATE AT $0°K$ PREDICTED BY
"BINARY SIGMA-ANISOTROPIC" PROGRAM (cal/g-atom)

Alloy[a]					Alloy[a]			
A	B				A	B		
43.5	V	Co	56.5	−3570	45	Nb	Re	55	−5935
50	V	Fe	50	−4725	65.1	Nb	Rh	34.9	−8520
57.5	V	Ni	42.5	−2045	75	Ta	Ir	25	−5790
25	V	Re	75	+1580	75	Ta	Os	25	−3195
50	Mo	Fe	50	−4360	80	Ta	Pt	20	−3320
60	Mo	Co	40	−2880	40.8	Ta	Re	59.2	−7710
72	Mo	Ir	28	−630	70	Ta	Rh	30	−7525
66.7	Mo	Os	33.3	+65	75	W	Os	25	−405
40	Mo	Re	60	+2485	50	W	Re	50	−290
				+1000	75	Zr	Ir	25	−6975
63.5	Mo	Ru	36.5	−1270	45.5	Re	Fe	54.5	+1315
52.3	Cr	Co	47.7	+30	60	Re	Cr	40	−2765
46.5	Cr	Fe	53.5	−625	55	Re	Nb	45	−5450
66.7	Cr	Os	33.3	+205	60	Re	Mo	40	+1005
60.5	Nb	Ir	39.5	−8710	75	Re	V	25	−1385
60	Nb	Os	40	−5980	40	Cr	Re	60	+1455
62	Nb	Pt	38	−6890	66.7	Cr	Ru	33.3	+485

[a] Numbers in this column represent atomic percent of adjacent component.

values are listed in Table V along with the predicted values that correspond to the partial order observed for specimens equilibrated at nearly the same temperature used in the measurements of the energy of formation. As shown, the agreement between these values is extremely good. However, it should be noted that the observed order does not correspond to that for the configuration predicted to be stable at these temperatures, as is shown in Table VI. The energies of formation corresponding to the predicted stable configurations are 505 cal/g-atom (2120 J/g-atom) for Co–Cr and −625 cal/g-atom (−2615 J/g-atom) for Fe–Cr. Given the uncertainty in the absolute value of the predicted energy of formation no significance can be assigned to the agreement or disagreement between these calculated and their associated experimental values. Certainly, it is desirable to have a comparison of predicted and observed values for many more phases before a conclusion is drawn relative to this question.

The result that several systems exhibit positive values for their predicted energy of formation (see Table IV) led us to investigate whether or not the phase diagrams for these systems indicate a low-temperature instability for the sigma phase. One such system, $OsCr_2$, does, in fact, exhibit a eutectoid transformation with the sigma phase stable at high temperature.

A further investigation of the propensity of the sigma phase to exhibit a eutectoid transformation at low temperature revealed 10 such systems out of a total of 26. This frequency (0.385) may be compared with those corresponding to other TCP (topologically close packed) phases, i.e., for $C15$ only 3 out of 66 phases decompose at low temperature (a frequency of 0.045) and for $A12$ only 1 out of 10 phases was found to decompose at low temperatures (a frequency of 0.1).

This result indicates that for many systems, the sigma phase is unstable with respect to a mixture of bounding phases and entropy must

TABLE V

COMPARISON OF EXPERIMENTAL AND COMPARABLE PREDICTED ENERGIES OF FORMATION
(BINARY SIGMA-ANISOTROPIC PROGRAM)

Alloy		%B	ΔE^* (cal/g-atom (J/g-atom))	ΔE, xp (cal/g-atom (J/g-atom))
A	B			
Cr	Co	47.7	805[a] (3370)	900[b] (3760)
Cr	Fe	53.5	850[c] (3558)	1037[d] (4340)

[a] For a partially ordered array where the probabilities of occupation of the A, B, C, D, and E sites by Cr are 0,1, 0.73, 0, 0.73, respectively. This arrangement is close to the ordered arrangement corresponding to an unknown temperature. The predicted stable array at 1473°K is different, however (see Table VI).

[b] Measured at 1473°K.

[c] For a random distribution. However, the model predicts a partially ordered array to be more stable.

[d] Measured at 1060°K. The observed site occupation probabilities at 923°K correspond to nearly complete disorder.

TABLE VI

COMPARISON OF PREDICTED FREE ENERGIES[a] FOR PARTIALLY ORDERED, FULLY ORDERED, AND COMPLETELY
DISORDERED STATES (BINARY SIGMA-ANISOTROPIC PROGRAM)

Alloy		Equilibration temperature (°K)	ΔF^* (cal/g-atom (J/g-atom))			
A	B		Fully ordered	Partially ordered		Random
Cr	Co	1473	−510 (1) (−2135)	−900 (3) (−3765)	65 (5) (270)	−145 (−605)
Cr	Fe	1060	−745 (2) (−3955)	−1455 (4) (−6090)		−270 (−1130)

Site occupation probabilities for Cr component

	f_A	f_B	f_C	f_D	f_E
(1)	0	1	0.46125	0	1
(2)	0	0	0.74375	0	1
(3)	0.35	0.35	0.35	0.35	1
(4)	0.27	0.27	0.27	0.27	1
(5)	0	1	0.73	0	0.73

[a] The free energies given in the table are equal to ΔE^* (0°K) predicted by the BINARY SIGMA-ANISOTROPIC PROGRAM minus $T\Delta S_m$, where ΔS_m is the configurational entropy due to a random arrangement of the two components on the partially occupied sites.

contribute significantly to the stability of the sigma phase, but not to the bounding phases at the elevated temperatures at which the sigma phase is stable. The suspicion that there may be a positive excess entropy of formation associated with the sigma phase structure is supported by the experimental result for the Co–Cr system, where a value of 3.803 ± 0.8 J/g-atom/°C has been measured (8) (1473°K), and by the fact that the observed molar volume of formation of the sigma phase structure is positive for many systems (see Table VII). Incidentally, the latter fact does not seem to be appreciated in view of the

TABLE VII

Observed Relative Integral Molar Volume of Formation for Sigma Phases

$$\Delta V = V_m - X_A V_A^0 - X_B V_B^0$$

Alloy[a]				A^3 (g-atom)	Alloy[a]				A^3 (g-atom)
A		B				A	B		
43.5	V	Co	56.5	−0.31	60.5	Nb	Ir	39.5	−0.19
50	V	Fe	50	−0.42	60	Nb	Os	40	−0.03
57.5	V	Ni	42.5	−0.20	62	Nb	Pt	38	−0.15
25	V	Re	75	−0.29	45	Nb	Re	55	0.06
50	Mo	Fe	50	−0.05	65.1	Nb	Rh	34.9	−0.18
60	Mo	Co	40	−0.07	75	Ta	Ir	25	−0.04
72	Mo	Ir	28	0.15	75	Ta	Os	25	0.12
66.7	Mo	Os	33.3	0.21	80	Ta	Pt	20	0.38
40	Mo	Re	60	0.22	40.8	Ta	Re	59.2	−0.25
63.5	Mo	Ru	36.5	0.17	70	Ta	Rh	30	−0.05
52.3	Cr	Co	47.7	0.03	75	W	Os	25	0.16
46.5	Cr	Fe	53.5	−0.15	50	W	Re	50	0.21
66.7	Cr	Os	33.3	0.32	75	Zr	Ir	25	0.60 (−1.47)
40	Cr	Re	60	0.36 (0.28)	45.5	Re	Fe	54.5	−0.39 (−0.14)
66.7	Cr	Ru	33.3	0.37					

[a] Numbers in this column represent atomic percent of adjacent component.

various publications which include the sigma phase among the group of TCP structures.

A check of the validity of the calculated energies of formation can be accomplished by a comparison of these values for competing crystal structures at the same composition. That crystal structure having the lowest energy of formation (most negative value) should be the structure stable at $0°$K. Thus, calculations have been made of the energies of formation for competing structures for those component combinations that are stable in the sigma phase structure ($D8_b$). Also, both isotropic and anisotropic models were used to obtain values for the sigma phase structure. Calculations for the other structures were made using programs previously evaluated (2–5, 12, 13).[7]

[7] The logic is that if $D8_b$ is observed to be stable at the lowest possible equilibration temperature and another structure is predicted to have a lower energy of formation at $0°$K, then there exists an incorrect prediction. Thus, high-temperature $D8_b$ phases are not included in this comparison nor are those for which no phase diagrams exist.

We note in Table VIII that when use is made of the isotropic program, the incorrect relative stability is predicted for 12 out of 18 phases. Obviously, the isotropic program neglects some stabilization factor. However, use of the anisotropic program, which takes into account the crystal field stabilization at the E-type sites, improves the predictability of the relative stability, as shown in Table IX, with now 4 out of 18 phases having an incorrect prediction of the relative stability. Examination of Table IX reveals that the main disagreement involves the relative stability of the $D8_b$ and $A15$ structures. Except for CrRu, the stability of the $D8_b$ structure with respect to the $A2$, $B2$, $L1_2$, and $C15$ structures (where applicable) is correctly predicted by the anisotropic model for 17 phases out of 18. Thus, except at the AB_3 composition, the anisotropic model has a high probability of yielding the correct relative stability and probably a good estimate of the energy of formation for these homoelectronic component combinations involving only transition element components.

TABLE VIII

RELATIVE STABILITY AT 0°K OF SIGMA PHASE WITH RESPECT TO COMPETING STRUCTURES AS PREDICTED USING "BINARY SIGMA-ISOTROPIC" AND "CUBIC" PROGRAMS

Alloy[a]			Energy of formation (cal/g-atom)					
A	B		Sigma	A2	B2	A15	L1$_2$	C15
43.5 V	Co	56.5	+420	+610				
50 V	Fe	50	−1430	−1875	−2345			
57.5 V	Ni	42.5	+1080	+1670				
52.3 Cr	Co	47.7	+1665	+735				
66.7 Cr	Ru	33.3	+485	+635				−540
60.5 Nb	Ir	39.5	−4750	−5250				
60 Nb	Os	40	−1990	−2760				
62 Nb	Pt	38	−3440	−3885				
65.1 Nb	Rh	34.9	−4650	−3960				+9,345
66.7 Mo	Os	33.3	+3115	+1070				+11,775
63.5 Mo	Ru	36.5	+1950	+1280				+6,980
75 Ta	Ir	25	−2915	−3585		−11,575	−1695	
75 Ta	Os	25	−840	−1805		−9,290	−395	
70 Ta	Rh	30	−4425	−3835				
75 W	Os	25	+2475	+1060		−5,880	−80	
50 W	Re	50	+2985	+1040	+895			
45.5 Re	Fe	54.5	+1315	+3610				
60 Re	Cr	40	+1455	+3000				

[a] Numbers in this column represent atomic percent of adjacent component.

TABLE IX

RELATIVE STABILITY AT 0°K OF SIGMA PHASE WITH RESPECT TO COMPETING STRUCTURES AS PREDICTED USING "BINARY SIGMA-ANISOTROPIC" AND "CUBIC" PROGRAMS

Alloy			Energy of formation (cal/g-atom)					
A	B		Sigma	A2	B2	A15	L1$_2$	C15
43.5 V	Co	56.5	−3570	+610				
50 V	Fe	50	−4725	−1875	−2345			
57.5 V	Ni	42.5	−2045	+1670				
52.3 Cr	Co	47.7	+30	+735				
66.7 Cr	Ru	33.3	+ 485	+635				−540
60.5 Nb	Ir	39.5	−8710	−5250				
60 Nb	Os	40	−5980	−2760				
62 Nb	Pt	38	−6890	−3885				
65.1 Nb	Rh	34.9	−8520	−3960				+9,345
66.7 Mo	Os	33.3	+65	+1070				+11,775
63.5 Mo	Ru	36.5	−1270	+1280				+6,980
75 Ta	Ir	25	−5790	−3585		−11,575	−1695	
75 Ta	Os	25	−3195	−1805		−9,290	−395	
70 Ta	Rh	30	−7525	−3835				
75 W	Os	25	−405	+1060		−5,880	−80	
50 W	Re	50	−290	+1040	+895			
45.5 Re	Fe	54.5	+1315	+3610				
60 Re	Cr	40	+1455	+3000				

The phasés that yield a discrepancy in the predicted relative stability between the $D8_b$ and $A15$ structures (Ta$_3$Ir, Ta$_3$Os, and W$_3$Os) are all characterized by having the "exotic" element as the major component. This fact suggests that the $D8_b$ structure for these phases may be further stabilized by an additional crystal field distortion of the "exotic" elements that occupy the other noncubic sites in the unit cell, i.e., the B and C sites. Indeed, at the AB_3 composition there are enough exotic atoms (B component) to fully occupy the B,C, and E sites (20 out of the 30 sites per unit cell), which may be a necessary condition to achieve the crystal field distortion of atoms occupying the B- and C-type sites.

Discussion of Results

We have demonstrated that the anisotropic pair potential model provides an acceptable quantitative description of the lattice parameters, site positioning parameters, site order parameters, and energy of formation. There is no doubt that this model gives an approximate description in that possible crystal field effects at other sites of the sigma phase unit cell have been neglected, a central force model has been used even though the repulsive forces involving nonspherical atoms are likely to be noncentral, the electronegativity-difference-induced electron transfer is averaged rather than individualized, etc. Nevertheless, it seems to be a sufficiently good approximation to use as a basis for describing the effects of adding additional components on the energy of formation. At least there appears to be no evidence to the contrary.

The anisotropic pair potential model can be used to demonstrate that the energy of formation can be sensitive to the degree and type of order when the size of the component atoms varies and is less sensitive to variation in the order parameters when the atom sizes of the components are comparable. See Table X. Thus, when the atomic radius ratio of the

components deviates from unity, the energy is minimized when sites A and D are occupied by the smaller atom and B by the larger atom.

The presence of "exotic" elements in the sigma phase structure leads to a significant stabilization of the structure. For example, for Co–Cr, the "exotic" nature of Cr (its crystal field stabilization) leads to a stabilization of the sigma phase by about 6850 J/g-atom, whereas for Fe–Mo the equivalent stabilization equals 17,690 J/g-atom. The magnitude of this stabilization is sufficient to bias the E-site occupancy in favor of the "exotic" component relative to that predicted by the isotropic

TABLE X

Dependence of Energy of Formation on Site Occupation Probability for Different Ordered Arrays (BINARY SIGMA-ANISOTROPIC Program)

ΔE (cal/g-atom)	f_A	f_B	f_C	f_D	f_E[a]
Fe Cr sigma (53.5 at.% Fe, 46.5 at.% Cr)[b]					
−520	1	1	0	0	0.99
+1055	1	0	1	0	0.49
+1565	0	1	1	0	0.24
+1225	1	0	0	1	0.49
+1730	0	1	0	1	0.24
+295	0	0	1	0	0.74
+470	0	0	0	1	0.74
+2170	1	1	0	0.99	0
+2065	1	0	1	0.49	0
+1990	0	1	1	0.24	0
−470	1	0	0	0.49	1
−555	0	1	0	0.24	1
+2050	0	0	1	0.74	0
−490	0	0	0	0.74	1
+2010	1	1	0.99	0	0
−565	1	0	0.49	0	1
−600	0	1	0.24	0	1
+2145	1	0	0.49	1	0
+2115	0	1	0.24	1	0
−625	0	0	0.74	0	1
+2090	0	0	0.74	1	0

[a] Probabilities for Cr atoms to occupy sites.

[b] Summarizing, for the components Cr and Fe of nearly equal size, the energy of formation ranges from a minimum of −625 to a maximum of +2170 cal/g-atom for variation in site occupancy.

TABLE X—*Continued*

ΔE (cal/g-atom)	f_A	f_B	f_C	f_D	f_E[c]
Fe Mo sigma (50 at.% Fe, 50 at.% Mo)[d]					
+2480	0	0	0	1	0.875
−2875	0	0	1	0	0.875
+2910	0	1	0	1	0.375
+5200	1	0	0	1	0.625
−540	0	1	1	0	0.375
+50	1	0	1	0	0.625
+1565	1	1	1	0	0.125
+4865	1	1	0	1	0.125
+1250	0	0	0	0.875	1
+5265	0	0	1	0.875	0
−2700	0	1	0	0.375	1
+1755	1	0	0	0.625	1
+2440	0	1	1	0.375	0
+5580	1	0	1	0.625	0
+2500	1	1	1	0.125	0
−2510	1	1	0	0.125	1
+5830	0	0	0.875	1	0
−3615	0	0	0.875	0	1
+4430	0	1	0.375	1	0
+7290	1	0	0.625	1	0
−4360	0	1	0.375	0	1
−1855	1	0	0.625	0	1
−3105	1	1	0.125	0	1
+5320	1	1	0.125	1	0

[c] Probabilities for Mo atoms to occupy sites.

[d] Summarizing, for the differently sized components Fe and Mo, the energies of formation range from a minimum of −4360 to a maximum of +7290 cal/g-atom with variation in site occupancy.

model. Since, in the absence of the crystal field stabilization the sigma phase is often predicted to be unstable relative to competing structures at the same composition, whereas with the crystal field stabilization the sigma phase structure is predicted to become the stable structure, the model demonstrates that the stability of the sigma phase structure depends upon the presence of components that can be stabilized by the noncubic crystal field existing at the E and other types of sites in this structure. It is plausible that only elements in the Ti, V, Cr, and Mn columns have sufficient d electrons and electron holes to exhibit the required crystal field stabilization. According to this concept, these elements—our "exotic" elements—should be required components in the observed stable sigma phases as well as in the other structures which have sites with D_{2d} point symmetry environment. This rule seems to be obeyed by the stable $A15$- and W_5Si_3-type phases; i.e., both the latter structures have sites with D_{2d} point symmetry and no such stable binary phase does not contain one of the "exotic" elements as a component! Other TCP structures, such as the $A12$ and $C15$ structures, each have associated phases that exclude the "exotic" elements ($MgCu_2$, etc., in the $C15$ structure, $Mg_{17}Al_{12}$ in $A12$)! We believe that the above concept is responsible for the speculation that electron–atom ratio has an influence on the stability of the sigma phase structure (9). That is, if one of the components is limited to a group number in the periodic table between 4 and 7 then it is likely that the average group number will exhibit a limited range of values.

If we examine the values obtained for the electron transfer between the A_1 state and the B_1 and B_2 states we find that this parameter depends primarily upon the identity of the "exotic" element although it can be influenced by the second component. Table XI lists the individual and average values obtained for this crystal field parameter. Although it is unlikely that a physical significance can be ascribed to these values, at least their magnitude is reasonable.

Wilson and Spooner (10) and Stuwe (11), before them, devised geometric models to predict lattice parameters. Also, the former were concerned with prediction of the site ordering parameters. Their predictions were in better agreement with experiment than those of Stuwe, but the margin of uncertainty was still about 1% in the lattice parameters.

Wilson and Spooner evaluated the lattice parameters by averaging the projected lengths of the various atomic rows that contribute to the a and c parameters. This averaging is weighted only according to the relative population of the rows. Each row length is determined by summing over the atomic radii

TABLE XI

EVALUATED NUMBER OF ELECTRONS v, TRANSFERRED FROM A_1 TO B_1 AND B_2 SYMMETRY STATES OF "EXOTIC" ELEMENT LISTED AT E-TYPE SITES IN SIGMA PHASES

"Exotic" element	Alloy			v'	$\bar{v}'$
V	43.5 V	Co	56.5	0.5	
	50 V	Fe	50	0.42	0.45
	57.5 V	Ni	42.5	0.42	
Cr	52.3 Cr	Co	47.7	0.42	
	66.7 Cr	Ru	33.3	0	0.23
	66.7 Cr	Os	33.3	0	
	46.5 Cr	Fe	53.5	0.5	
Nb	65.1 Nb	Rh	34.9	0.325	
	60 Nb	Os	40	0.325	0.32
	62 Nb	Pt	38	0.3	
	60.5 Nb	Ir	39.5	0.325	
Ta	75 Ta	Ir	25	0.25	
	75 Ta	Os	25	0.2	0.23
	80 Ta	Pt	20	0.2	
	70 Ta	Rh	30	0.25	
Zr	75 Zr	Ir	25	0.4	0.4
W	75 W	Os	25	0.42	0.42
Mo	50 Mo	Fe	50	0.675	
	60 Mo	Co	40	0.625	
	66.7 Mo	Os	33.3	0.500	0.57
	63.5 Mo	Ru	36.5	0.525	
	72 Mo	Ir	28	0.525	

of the atoms comprising the rows. Since these rows do not sum up to the same projected lengths, some are larger and some are smaller than the corresponding length at equilibrium in the sigma phase structure; i.e., at equilibrium the tensile forces of the smaller rows (extended to the average length) just balance the compressive forces due to the longer rows (compressed to the average length). However, for large strains, outside the range of Hooke's law, the compressive force corresponding to a given relative change in length exceeds the tensile force corresponding to the same length change. Linear averaging of the projected lengths of the atomic rows neglects this fact and hence the Spooner and Wilson technique should lead to the prediction of smaller lattice parameters than one in which the row lengths are weighted according to their elastic constants. Effectively, the isotropic pair potential

model accomplishes the latter type of row averaging. Hence, it is not surprising that the latter model predicts larger lattice parameters than does the Wilson and Spooner model. Because the largest strains are associated with the rows of E atoms (about 12%) the Wilson and Spooner method of averaging is equivalent to the assumption that the atoms are soft in compression. Essentially, the same result is obtained in the present model by allowing the "exotic" atoms in these rows to undergo a crystal field distortion to a more stable shape. Although much more complex, the present model has the advantage of predicting energies of formation, which is not possible to accomplish with the strictly geometrical models.

With respect to the predicted energies of formation, we may note that the existence of positive values in Table IV is still consistent with the observation of stable sigma phases because the entropy of formation is also expected to be large and positive. Such a large positive excess entropy of formation is to be expected because the large strains associated with the bonds emanating from atoms on E-type sites will of necessity produce associated diminished force constants for these bonds. These diminished force constants will contribute directly to a positive excess entropy of vibration through the relation between entropy of vibration and the force constant.

It is to be expected that this excess vibrational entropy will be sensitive to the site order parameters and thus may exert an influence on which of the latter combinations will correspond to the stable configuration at elevated temperatures. The site order parameters reported are for specimens equilibrated at elevated temperature. This concept may help explain the slight differences between observed and predicted site order parameters shown in Table III.

It should be noted that our use of a constant screening constant per outer electron per atom (s) is not strictly valid. In a supplementary investigation of the effect of intraatom electron transfer between d states on the screening of

the outer *sp* repulsive shell of electrons, it has been found that the new shape approximates that of an oblate ellipsoid, but does depart from it. This result may have consequences with respect to calculations of energy of formation, lattice parameters, and the like. Although it is possible to include this effect, as well as many of the other effects neglected in the present study (i.e., crystal field effects at other than E-type sites, minimization of the energy with respect to the crystal field parameter, v', localization of electron transfer rather than its averaging, etc.), the cost of these improvements measured in dollars of computation must be weighed relative to the benefits to be obtained. At the moment, the increase in cost by an order of magnitude occasioned by such improvements has prevented their consideration in the present investigation.

Conclusions

1. The crystal field stabilization of elements belonging to the Ti, V, Cr, and Mn columns of the periodic table only, at E-type sites in the sigma phase structure, is the significant factor responsible for the stability of the sigma phase relative to competing structures. Thus, no known sigma phase excludes these "exotic" elements; i.e., at least one such element is present as a component in every known sigma phase.

2. With one adjustable parameter, the anisotropic pair potential model yields good agreement between predicted and observed lattice parameters, site positioning parameters, site order parameters, and energies of formation.

3. The anisotropic pair potential model appears capable of generalization to account for the energy of formation of the sigma phase structure containing multicomponents to within the required accuracy.

4. Many, if not all, the sigma phases are stabilized by a high positive entropy of formation. For some of these phases, this term

is solely responsible for their observed stability.

Appendix

The sigma phase unit cell contains 30 atoms distributed on five distinct sites as follows:

$2A$ atoms in $2(a)$ $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}.$

$4B$ atoms in $4(f)$ $x, x, 0; \bar{x}, \bar{x}, 0; \frac{1}{2} + x, \frac{1}{2} - x,$
$\frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2}.$
$x_{\text{FeCr}} = 0.3981$

$8C$ atoms in $8(i)$ $x, y, 0; \bar{x}, \bar{y}, 0; \frac{1}{2} + x, \frac{1}{2} - y,$
$0; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2}; \bar{y}, \bar{x}, 0; \frac{1}{2} +$
$y, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2}.$
$x_{\text{FeCr}} = 0.5368, \quad y_{\text{FeCr}} = 0.1316$

$8D$ atoms in $8(i)'$ $x_{\text{FeCr}} = 0.0653; \quad y_{\text{FeCr}} = 0.2624$

$8E$ atoms in $8(j)$ $x, x, z; \bar{x}, \bar{x}, z; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}$
$+ z; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} + z; x, x,$
$\bar{z}; \bar{x}, \bar{x}, \bar{z}; \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2} - z;$
$\frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2} - z;$
$x_{\text{FeCr}} = 0.3177; \quad z_{\text{FeCr}} = 0.2476$

Figure 24 of Ref. (*14*) illustrates the positions of the atoms in the unit cell. Another review of the sigma phase structure is that of Hall and Algie (*9*).

Acknowledgments

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