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Heats of formation of bcc binary alloys

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We apply the method of Bozzolo, Ferrante, and Smith for the calculation of alloy energies for bcc elements. The heat of formation of several alloys is computed with the help of the Connolly-Williams method within the tetrahedron approximation. The dependence of the results on the choice of different sets of ordered structures is discussed.

I. INTRODUCTION

Recently, a semiempirical method for calculating defect energetics in metallic alloys was introduced by Bozzolo, Ferrante, and Smith (BFS).¹ This technique, which builds on the ideas of equivalent crystal theory (ECT),² was successfully applied to the study of heats of formation and lattice parameters of fcc alloys as a function of alloy composition. The BFS method is a quantitatively accurate and computationally simple technique for determining the energetics of ordered multicomponent structures. Although there have been extensive calculations for fcc alloys, similar results for bcc alloys have been limited. Since alloys of bcc metals are important in structural materials, this paper represents an effort to develop an approach for the calculation of defect energies in these alloys. In order to accomplish this goal we apply the BFS method to the study of bcc-based binary alloys using the method of Connolly and Williams (CWM)³ for the study of the energetics of disordered structures within the tetrahedron approximation.

In Sec. II we review the BFS method and discuss the application of the CWM method to several choices of ordered structures. Next, an application of the method is presented for calculating the heat of formation of selected binary alloys of Cr, Fe, V, and Mo as a function of composition in Sec. III. Conclusions are drawn in Sec. IV regarding the prediction of the possible ordered structures which are present in the bcc compounds.

II. FORMALISM

In BFS,¹ the energetics of binary alloys is described in terms of pure metal properties and only two experimen-

tally (or theoretically) determined alloys properties. We build on the formulation of ECT by dividing the total energy of the alloy into a chemical energy and a strain or structural energy.^{1,4,5} The strain energy associated with a given atom is computed as if all of its neighbors were of the same atomic species. It arises from neighbor locations being different from in the elemental single-crystal environment. The remainder of the total energy is defined to be the chemical energy, which is due to some of an atom's neighbors being of a different atomic species. We now proceed to outline the procedure for calculation of heats of formation versus concentration for alloys with multiple atomic species. With this procedure, the binding energy curve as a function of volume is obtained, from which the bulk properties of specified alloys can be extracted. The application of this technique to different crystallographic structures is straightforward. In this paper we concentrate on bcc based binary alloys.

Consider a cell containing N_X atoms of atomic species X (X = A, B, ...), so that the total number of atoms in this cell is given by $N = \sum_X N_X$. The heat of formation of this cell is

$$\Delta E_{\text{cell}} = E_{\text{cell}} - \sum_{X} N_X E_X , \qquad (1)$$

where E_{cell} is the total energy of the cell and E_X is the cohesive energy of an atom of species X in a pure crystal of its own species. If E'(i, X) denotes the energy of the *i*th atom in the cell $(i = 1, ..., N_X)$ of species X then

$$\Delta E_{\text{cell}} = \sum_{X} \sum_{i=1}^{N_X} e_{i,X} , \qquad (2)$$

where the energy difference $e_{i,X} = E'(i,X) - E_X$, has a

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strain and a chemical energy contribution, linked by a coupling factor $g_{i,X}$ that ensures that the chemical energy contribution vanishes for large interatomic distances:

$$e_{i,X} = e_{i,X}^{S} + g_{i,X} e_{i,X}^{C}$$
(3)

In order to compute the strain energy, $e_{i,X}^S$, we just "flip" every atom surrounding atom (i,X) into an atom of the same species X, and perform a regular ECT calculation.² The equivalent lattice parameter $a_{i,X}^S$ is determined by solving the appropriate ECT equation applied to atom (i,X) in the defect (but pure) crystal:

$$8R_{1}^{p_{\chi}}e^{-\alpha_{\chi}R_{1}} + 6R_{2}^{p_{\chi}}e^{-(\alpha_{\chi}+1/\lambda_{\chi})R_{2}} = \sum_{j}r_{j}^{p_{\chi}}e^{-[\alpha_{\chi}+S_{\chi}(r_{j})]r_{j}}$$
(4)

(see Ref. 2 for details) where the quantities p_X , α_X , λ_X , and S_X are defined in Ref. 2. The sum on the right-hand side (rhs) of Eq. (4) runs over all neighbors of atoms (i, X)at a distance r_j . Equation (4) is solved for the lattice parameter of the equivalent crystal $a_{i,X}^S [=(2\sqrt{3}/3)R_1$ $=R_2]$. Consequently,

$$e_{i,X}^{S} = E_{C}^{X} [1 - (1 + a_{i,X}^{S*})e^{-a_{i,X}^{S*}}],$$

$$a_{i,X}^{S*} = (a_{i,X}^{S} - a_{e}^{X})/l_{X},$$
(5)

where a_e^X denotes the lattice constant of a pure X crystal, E_C^X is the corresponding cohesive energy, and l_X is a scaling length.²

In Eq. (3) the strain and chemical energies are coupled nonlinearly. The coupling function $g_{i,X}$ guarantees that the chemical contribution will vanish with increase in interatomic spacings, as it should. We define the coupling function in terms of the scaled equivalent lattice parameter of the strained crystal as

$$g_{i,X} = e^{-a_{i,X}^{S*}}$$
 (6)

For the chemical energy contribution $e_{i,X}^C$ we keep the actual chemical composition of the cell (i.e., A, B, C in proper proportions for the alloy), but we force the atoms surrounding atom (i,X) to be located in the lattice sites of a pure crystal of species X. Thus, we are including the effect of changing a neighbor to an A, B, or C atom. Two similar ECT calculations are then performed:

$$e_{i,X}^{C} = e_{i,X}^{C}(\{\Delta_{Y,X}\}) - e_{i,X}^{C}(0) .$$
⁽⁷⁾

For the first term, $e_{i,X}^{C}(\{\Delta_{Y,X}\})$, the chemical perturbation is included in the appropriate values of the set of parameters $\{\Delta_{Y,X}\}$ which include the effects of changing the atomic species of a neighbor,¹ where Y denotes the atomic species of a given neighbor of atom (i,X). The second term is a reference energy term included in order to free the chemical energy from any structural defect information, retaining only the contribution of the chemical composition of the surrounding of atom (i,X). It is obtained by a similar procedure, but setting all the perturbative parameters $\{\Delta_{Y,X}\}$ equal to zero. In the absence of defects, as in the case examined in this paper, this second term is always zero. In order to determine the parameters $\Delta_{Y,X}$ and $\Delta_{X,Y}$ for a given pair of atomic species (X, Y), two experimental values of *any* property of the $X_x Y_{1-x}$ alloy are needed. We choose to use the experimental heats of solution in the dilute limit which in most cases are readily available.⁶

The equivalent lattice parameter $a_{i,X}^{C}$ is obtained by solving the corresponding ECT equation²

$$8R_{1}^{p_{\chi}}e^{-\alpha_{\chi}R_{1}} + 6R_{2}^{p_{\chi}}e^{-(\alpha_{\chi}+1/\lambda_{\chi})R_{2}}$$

= $\sum_{Y}N_{XY}r_{1}^{p_{\chi}}e^{-(\alpha_{\chi}+\Delta_{Y\chi})r_{1}}$
+ $\sum_{Y}M_{XY}r_{2}^{p_{\chi}}e^{-(\alpha_{\chi}+1/\lambda_{\chi}+\Delta_{Y\chi})r_{2}}$, (8)

where R_1 and R_2 are the nearest-neighbor and nextnearest-neighbor distances in the equivalent crystal of lattice parameter $a_{i,X}^C$. The first term in the chemical energy, $e_{i,X}^C(\Delta_{Y,X})$ is then given by

$$e_{i,X}^{C}(\Delta_{Y,X}) = \gamma_{i,X} E_{C}^{X} [1 - (1 + a_{i,X}^{C*})e^{-a_{i,X}^{C*}}],$$

$$a_{i,X}^{C*} = (a_{i,X}^{C} - a_{e}^{X})/l_{X},$$
(9)

with $\gamma_{i,X} = 1$ if $a_{i,X}^{C*} > 0$ and $\gamma_{i,X} = -1$ otherwise.

In this paper we are concerned with calculating the heats of formation of the bcc-based ordered binary alloys $A_x B_{1-x}$. If no relaxation of the individual atomic sites is allowed, the calculation of the strain energy for atom (i, X) in the bulk of the alloy with lattice parameter r is particularly simple: solving Eq. (4) is unnecessary as the atom (i, X) finds itself embedded in a pure crystal X with lattice parameter r. Thus, the strain energy is simply the energy needed to expand or compress the crystal X [i.e., setting $r_1 = (\sqrt{3}/2)r$ and $r_2 = r$ in Eq. (4)]. Consequently,

$$e_X^S = E_C^X [1 - (1 + a_X^{S*})e^{-a_X^{S*}}],$$

$$a_X^{S*} = (r - a_e^X)/l_X,$$
(10)

where r is the actual interatomic distance of the alloy. Within this approximation, the second term in the chemical energy [Eq. (7)] vanishes, leaving us only with the computation of the first term, $e_X^C(\Delta)$. For a given ordered structure m, the ECT equation for the equivalent lattice parameter a_X^C [Eq. (9)] is

$$8R_{1}^{p_{X}}e^{-\alpha_{X}R_{1}} + 6R_{2}^{p_{X}}e^{-(\alpha_{X}+1/\lambda_{X})R_{2}}$$

$$= N_{XX}r_{1}^{p_{X}}e^{-\alpha_{X}r_{1}} + N_{XY}r_{1}^{p_{X}}e^{-(\alpha_{X}+\Delta_{YX})r_{1}}$$

$$+ M_{XX}r_{2}^{p_{X}}e^{-(\alpha_{X}+1/\lambda_{X})r_{2}}$$

$$+ M_{XY}r_{2}^{p_{X}}e^{-(\alpha_{X}+1/\lambda_{X}+\Delta_{YX})r_{2}}$$
(11)

with $R_1 = (\sqrt{3}/2)R_2$; $R_2 = a_X^C$; $r_1 = (\sqrt{3}/2)r_2$; $r_2 = a_e^X$. The parameters p_X , α_X , and λ_X are listed in Ref. 2 and the coefficients N_{XX} , N_{XY} , M_{XX} , and M_{XY} depend on the different ordered structures considered.

As in previous applications we will use the heats of solution in the dilute limit as the experimental input for determining the parameters Δ_{AB} and Δ_{BA} . In order to compute the heats of formation of the disordered alloys,

TABLE I. Correlations included in the tetrahedron truncation of the CWM for some structures on the bcc lattice. The ξ_i with increasing index *i*, correspond to the empty cluster, the point, the nearestneighbor (NN) pair, the next-nearest-neighbor (NNN) pair, the triangle formed by two NN pairs and one NNN pair, and the tetrahedron formed by four NN pairs and two NNN pairs.

Structure	Composition	٤o	<u></u> لاً	<u>ل</u> ء	5 3	5 4	٤s
bcc	A	1	1	1	1	1	1
DO_3	A_3B	1	$\frac{1}{2}$	0	0	$-\frac{1}{2}$	-1
<i>B</i> 2	AB	1	ò	-1	1	Ő	1
B32	AB	1	0	0	-1	0	1
DO_3	AB_3	1	$-\frac{1}{2}$	0	0	$\frac{1}{2}$	-1
bcc	В	1	-1	1	1	-1	1

v

we use the Connolly-Williams method.³ This method is based on a formal expression for the total energy first derived by Sanchez,⁷ where the total energy of a particular configuration m of a binary alloy consisting of atoms Aand B on a lattice of fixed symmetry is given by

$$\Delta E_m(r) = \sum_{\gamma} v_{\gamma}(r) \xi_{\gamma}^m , \qquad (12)$$

where $v_{\gamma}(r)$ are many-body potentials, the ξ_{γ}^{m} are multisite correlation functions defined on a γ -type cluster, ris the lattice parameter, and the sum includes all γ -type clusters on the lattice. The multisite correlation functions are defined as

$$\xi_{\gamma} = \frac{1}{N_{\gamma}} \sum_{\{n_i\}} \sigma_{n_1} \cdots \sigma_{n_{\gamma}} , \qquad (13)$$

where σ_n is a spinlike variable which takes the values +1 and -1 depending on whether the lattice point *n* is occupied by an *A* or *B* atom, and N_{γ} is the total number of γ -type clusters.

The many-body potentials $v_{\gamma}(r)$ are obtained by inversion of Eq. (12), which implies the existence of a maximum cluster γ_{max} beyond which the $v_{\gamma}(r)$ are supposed to be negligible. Thus, for a certain set of ordered structures α and by arbitrarily truncating the summation in Eq. (13), the many-body potentials are

$$\gamma(\mathbf{r}) = \begin{cases} \sum_{m} (\xi_{\gamma}^{m})^{-1} \Delta E_{m}(\mathbf{r}) , & \phi \leq \gamma \leq \gamma_{\max} , \\ 0 , & \gamma_{\max} < \gamma < \infty , \end{cases}$$
(14)

where ϕ represents the empty cluster. Recently,⁸ the CWM was extended to include more ordered structures and cluster sizes than the ones originally proposed.³ Multisite correlations for the most common bcc- and fcc-based superstructures were also given.⁸ Table I lists the correlations included in the tetrahedron truncation of the CWM for some structures on the bcc lattice. Table II shows the coefficients N_{XX} , N_{XY} , M_{XX} , and M_{XY} needed to solve Eq. (11) for all the possible ordered structures included in Table I. These ordered structures are derived from the tetrahedron cluster shown in Fig. 1: α and γ are on body centers and β and δ are on cube edges. When $\alpha = \gamma$ and $\beta = \delta$ the structure is called B2. The B32 structure is derived when $\alpha = \delta \neq \beta = \gamma$ and the DO_3 structure is obtained when $\beta = \delta \neq \alpha \neq \gamma$.

In this paper we considered different choices of ordered structures, as well as the type of clusters included in Eq. (13). Being that the experimental input is, obviously, the same for all cases studied, a comparison with available experimental data for the heats of formation of binary alloys⁶ should give us an indication of the preferred or-

Comp. M_{BA} Struct. Atom N_{AA} N_{AB} N_{BB} N_{BA} M_{AA} M_{AB} M_{BB} B B(4)bcc A(1) DO_3 AB_3 B(2)B(1)**B**2 AB A(2)B(2)**B**32 AB A(2)B(2)A(2) DO_3 A_3B A(1)B(1)A(4)bcc A

TABLE II. Coefficients N_{XX} , N_{XY} , M_{XX} , and M_{XY} for different structures and compositions. The third column indicates the atomic species of the atoms in the tetrahedron and, between parentheses, the number of atoms of that atomic species in the tetrahedron.

Struct.	Comp.	m	(i)	(ii)	(iii)
bcc	В	0	$1-4x+5x^2-2x^3$	$1-4x+7x^2-6x^3+2x^4$	$1-4x+7x^2-6x^3+2x^4$
DO_3	AB_3	1	$4x - 12x^2 + 12x^3 - 4x^4$	$4x - 12x^2 + 12x^3 - 4x^4$	$4x - 12x^2 + 12x^3 - 4x^4$
B2	AB	2			$4x^2 - 8x^3 + 4x^4$
B 32	AB	2	$8x^2 - 16x^3 + 8x^4$	$4x^2 - 8x^3 + 4x^4$	
DO_3	A_3B	3	$4x^{3}-4x^{4}$	$4x^{3}-4x^{4}$	$4x^{3}-4x^{4}$
bcc	A	4	$-x^2+2x^3$	$x^2-2x^3+2x^4$	$x^2 - 2x^3 + 2x^4$

TABLE III. Polynomials $c_m(x)$ for cases (i), (ii), and (iii).

dered structures for a given binary alloy.

The different choices are related to the two possible ordered structures at 50% composition (B2 and B32) and the corresponding pair multisite correlation functions (ξ_2) and ξ_3). We will denote the cases studied as follows: (i) B 32- ξ_2 : includes the B 32 ordered structure and the ξ_2 correlation function (nearest-neighbor pair), leaving out the B2 structure as well as the ξ_3 function (next-nearestneighbor pair); (ii) $B32-\xi_3$: includes the ordered structure B32 and the ξ_3 function, leaving out B2 and ξ_2 ; (iii) B2- ξ_2 : includes B2 and ξ_2 , leaving out B32 and ξ_3 ; and (iv) $B2+B32-\xi_2+\xi_3$: includes all the structures and functions listed in Table I. In each case, the excess energy $\Delta E_m(r)$ for the corresponding ordered structures is obtained with Eq. (2). Within the tetrahedron approximation, this calculation involves just a few atoms, as indicated in Table II.

Following CWM, the excess energy for the disordered alloys $A_x B_{1-x}$ is given by

$$\Delta E_D(\mathbf{r}, \mathbf{x}) = \sum_{\gamma} \left(1 - 2\mathbf{x} \right)^{n_{\gamma}} v_{\gamma}(\mathbf{r}) , \qquad (15)$$

where n_{γ} is the number of sites contained in the γ cluster. For each choice of ordered structures and multisite correlation functions we have different many-body potentials:

$$v_{\gamma}(\mathbf{r}) = \sum_{m} (\xi_{\gamma}^{m})^{-1} \Delta E_{m}(\mathbf{r}) .$$
⁽¹⁶⁾

Replacing Eq. (16) in Eq. (15) we can write $\Delta E_D(r,x)$ for each one of the cases studied as

$$\Delta E_D(r,x) = \sum_m c_m(x) \Delta E_m(r) , \qquad (17)$$

where the sum runs over the appropriate ordered structures included in each case considered and the polynomials $c_m(x)$ are also dependent on the clusters and struc-



FIG. 1. Tetrahedron cluster in a bcc lattice (see text).

tures included in each case. Table III lists the polynomials $c_m(x)$ for the reduced basis sets (i), (ii), and (iii) and Table IV displays the corresponding polynomials for the general case (all structures and multisite correlation functions included in Table I). Finally, the heat of formation for a given concentration x is obtained by finding the minimum value of $\Delta E_D(r,x)$.

III. RESULTS AND DISCUSSION

In this section we present results for selected bcc-based alloys which display quite different behavior. For the four systems studied we used the experimental values of the heats of solution in the dilute limit,⁶ listed in Table V. Table VI displays the values of p, α , l, and E_C for the pure elements,² needed to solve Eqs. (5)-(11). Table VII shows the values of Δ_{AB} and Δ_{BA} one obtains with our procedure for several binary alloys A-B and for the different choices of basis sets described in the previous section.

The parameters Δ_{AB} and Δ_{BA} can be taken as "perturbations" to the pure-element α 's listed in Table VI, trying to simulate the interaction between two atoms of different species. In all cases, these quantities are small compared to the pure-element α 's, and, surprisingly, rather insensitive to the different choices of basis sets. However, these small differences translate into a noticeable change in the heat of formation versus concentration curves obtained for each choice of basis set, as can be seen in Fig. 2.

Figure 2(a) shows the results obtained for Cr-Fe alloys where the regular, symmetric behavior of the heat of formation curve is accurately reproduced by using the basis set (iii), where a B2 structure is included. Similar results were obtained for Fe-V alloys [Fig. 2(b)] where, again, basis set (iii) best approximates the available experimental values of the heat of formation.⁶ Interestingly, there is some experimental evidence that such an ordered phase exists.^{6,9}

TABLE IV. Polynomials $c_m(x)$ for case (iv).

Structure	Composition	т	(iv)
bcc	В	0	$1-4x+6x^2-4x^3+x^4$
DO_3	AB_3	1	$4x - 12x^2 + 12x^3 - 4x^4$
B2	AB	2	$4x^2 - 8x^3 + 4x^4$
B 32	AB	2	$2x^2-4x^3+2x^4$
DO_3	A_3B	3	$4x^{3}-4x^{4}$
bcc	A	4	x ⁴

TABLE V. Experimental heats of solution E_{AB} and E_{BA} .

A	В	E_{AB}	E_{BA}
Cr	Fe	0.218	0.218
Fe	v	-0.102	0.807
Cr	V	-0.088	-0.189
Cr	Мо	0.215	0.323

The predictions for Cr-Mo alloys show a drastic change in behavior as compared to Cr-Fe, although both systems display similar features in the experimental values of the heat of formation. Figure 2(c) shows the theoretical results. In this case, the basis sets (i) and (ii) which include only the B32 structure, yield comparable results.

Of the four examples shown in this work, Cr-V [Fig. 2(d)] displays the most surprising features, therefore providing a severe test to the sensitivity and accuracy of our method. In the large body of experimental data for binary alloys, Cr-V is one of the very few to display the irregularities seen in the heat of formation versus concentration curve, characterized by a sudden change in curvature for a small range of concentrations. As it was the

case for Cr-Mo, this feature of Cr-V is approximately reproduced *only* by the results generated with the choice of the basis set (ii).

The fact that we used the experimental heats of solution in the dilute limit (i.e., the derivative of the heat of formation at x = 0 and x = 1) might lead one to believe that that choice somehow predetermines the behavior of the heat of formation curves. The examples shown in this work obviously contradict this fact: all four curves (for each choice of basis set) were obtained with the *same* values of the heats of solution. However, their behavior for the whole range of concentration is quite different in each case.

The explanation for the particular features of the heat of formation versus concentration curves is not then in the heats of solution, which is our only experimental input, but in the delicate balance between the strain and chemical energies, as defined in our formalism. Except for the case of Cr-Fe, where the small lattice mismatch results in an almost negligible strain energy, in all the other cases the heat of formation predicted with our method is obtained from large competing strain and chemical energy contributions.

Figure 3 displays these contributions for the four systems considered in Fig. 2, showing the results obtained



FIG. 2. Heat of formation (in eV/atom) vs concentration for different bcc-based alloys. In all cases, the solid squares indicate experimental values, and the different curves indicate the results obtained using the basis sets and correlation functions described in the text: (i) $B32-\xi_2$ (long-dashed line), (ii) $B32-\xi_3$ (short-dashed line), (iii) $B2-\xi_2$ (solid line), and (iv) $B32+B2-\xi_2+\xi_3$ (dotted line) for (a) Cr-Fe, (b) Fe-V, (c) Cr-Mo, and (d) Cr-V.

Element	р	l	α	λ	Cohesive energy	Lattice constant
Cr	6	0.254	2.889	0.714	4.10	2.88
Fe	6	0.277	3.124	0.770	4.29	2.86
v	6	0.305	2.726	0.857	5.31	3.03
Мо	8	0.262	3.420	0.736	6.82	3.15

TABLE VI. Input parameters for bcc elements.

with the best basis sct choice for each system, as discussed before. The apparent similarity seen in Cr-Fe and Cr-Mo for their heats of formation, arises from quite different strain and chemical energy contributions: while the positive chemical energy is mainly responsible for the heat of formation for Cr-Fe alloys [Fig. 3(a)], a large negative chemical energy in Cr-Mo [Fig. 3(c)] is necessary to balance a large strain-energy contribution, absent in Cr-Fe. Also, the symmetry seen in the heat of formation curve for Cr-Mo is a result of completely different regimes in the strain and chemical energies: linear for Morich systems and with a pronounced curvature for Crrich alloys. Figure 3(b) shows, for Fe-V, how the chemical energy is solely responsible for the axis crossing seen in the heat of formation curve.

As noted before, Cr-V provides the appropriate

grounds for testing the sensitivity of this method. Figure 3(d) displays the strain and chemical energy contribution for the Cr-V systems. One can see how a barely noticeable flattening in the chemical energy contribution is the source of the unusual feature seen in the heat of formation curve. These results correspond to the basis set (ii), which best approximates the experimental results. Finally, Fig. 4 expands on the results shown in Fig. 3(d) in that the strain and chemical energy contributions are displayed for all four basis sets used in this work. The strain-energy contribution (independent of Δ_{CrV} and Δ_{VCr}) shows small differences due to the choice of different ordered structures. The chemical energy term dictates the behavior of the heat of formation as a function of concentration: the asymmetry seen in Fig. 3(d) arises from the chemical behavior of the B32 structure.



FIG. 3. Strain energy (in eV/atom) (long-dashed line) and chemical energy (short-dashed line) contributions to the heat of formation (solid curve) for (a) Cr-Fe, (b) Fe-V, (c) Cr-Mo, and (d) Cr-V.

A	В	Basis set	Δ_{AB}	Δ_{BA}
		(i)	0.0445	0.0277
Cr	Fe	(ii)	0.0443	0.0279
		(iii)	0.0447	0.0275
		(iv)	0.0448	0.0274
		(i)	0.0751	-0.0644
Fe	v	(ii)	0.0757	-0.0647
		(iii)	0.0768	-0.06515
		(iv)	0.0775	-0.0649
		(i)	-0.0228	-0.0215
Cr	v	(ii)	-0.0230	-0.02115
		(iii)	-0.0222	-0.0226
		(iv)	-0.0217	-0.0221
		(i)	-0.0246	-0.0060
Cr	Мо	(ii)	-0.0248	0.0060
		(iii)	-0.0238	-0.0143
		(iv)	-0.0230	-0.0075

TABLE VII. Parameters Δ_{AB} and Δ_{BA} .



FIG. 4. Strain and chemical contribution (in eV/atom) to the heat of formation of Cr-V for different choices of ordered structures (see text): (i) long-dashed curves, (ii) solid curves, (iii) short-dashed curves, and (iv) dotted curves. The sum of these pairs of curves are shown in Fig. 2(d).

IV. CONCLUSIONS

In this paper we applied the semiempirical method of Bozzolo, Ferrante, and Smith to the study of bcc-based alloys. The method was used to compute the total energy of ordered structures. The energetics of disordered alloys was studied with the CWM and several choices of basis sets were considered. Good agreement with experimental results is obtained for certain choices of basis sets. The partition of the heat of formation into strain and chemical contributions provide some insight in the physical behavior of the systems studied.

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