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Triple-defect complexes in the *B*2 intermetallic compound NiAl

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The present study combines a theoretical model on the basis of the Bethe-Bragg-Williams approximation with literature data on the pair-interaction energies in β'-NiAl with *B*2 (CsCl) structure. In this intermetallic compound, the most interesting point defect complexes are the triple defects since they have been supposed to be mainly responsible for the concentration dependence of the Ni self-diffusion coefficient in the temperature range between 1000 and 1300 K, which is nearly constant for Al-rich and stoichiometric alloys and shows a pronounced increase with increasing Ni content on the Ni-rich side of the composition range. The theoretical composition dependence of the concentration of triple-defect complexes, derived in the present work, and the experimental Ni diffusivities from the recent literature show excellent correlation, thus pointing to an important contribution of the triple-defect diffusion mechanism in *B*2 NiAl.

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I. INTRODUCTION

Due to its physical and mechanical properties, which include high melting point, low density, and good oxidation and corrosion resistance, the intermetallic compound β'-NiAl with *B*2 (CsCl) structure is an attractive material for a wide range of engineering applications. It exhibits a homogeneity range extending several atomic percent on either side of the stoichiometric composition and is highly ordered up to the melting point. β'-NiAl (from now on simply "NiAl") has traditionally been considered to be a typical "triple-defect" *B*2 compound, dominated by Ni vacancies in Al-rich compositions and Ni antisites in Ni-rich compositions.[1–5] According to *ab initio* calculations[4] and EAM (embedded-atom method) potentials,[1] Al antisite defects and vacancies on the Al sublattice are highly unfavorable, and their concentrations are therefore supposed to be very low throughout the entire phase field.[6] In contrast to these results, several authors[7–10] claimed recently that antistructure Al atoms may play a much more important role in Al-rich alloys than had been assumed before. Nevertheless, in the present study we will follow the arguments by Mishin *et al.*[1] whose results clearly point to a rather negligible role of Al antistructure atoms in Al-rich NiAl alloys compared to Ni vacancies, differing in concentration by nearly three orders of magnitude.

Although NiAl has been studied extensively over the recent years, a consistent picture for the Ni self-diffusion mechanisms in this compound has not yet emerged. According to calculations by Mishin and Farkas[11] and by Mishin *et al.*,[12] based on the EAM and based on first principles, several atomic mechanisms of long-range diffusion can operate concurrently in NiAl, i.e., cyclic nearest-neighbor (NN) jump mechanisms that depend on the occurrence of isolated Ni vacancies, and the next-nearest neighbor (NNN) vacancy mechanism in which Ni vacancies jump on their own simple cubic sublattice. Of course, the NNN vacancy mechanism depends on the occurrence of isolated Ni vacancies, too.

According to Mishin *et al.*,[12] these diffusion mechanisms should apply to stoichiometric NiAl and Al-rich compositions. However, it is clear that the diffusivities should correlate with the vacancy concentration, i.e., in Al-rich compositions, all vacancy mechanisms based on Ni vacancies should lead to high Ni diffusivities, a prediction that was not supported by the recent diffusion study of Frank *et al.*[13] Their experimental results imply that it is mainly the same diffusion mechanism that operates on both sides of stoichiometry. This hypothetical mechanism was identified as the triple-defect mechanism (see, for example, Stolwijk *et al.*[14]), where long-range diffusion is based on three-jump cycles that depend on the occurrence of triple-defect complexes. A triple-defect complex is defined here as a juxtaposition of one Ni antisite defect and two Ni vacancies.

It is still an open question if triple-defect complexes do really exist as isolated entities in a highly ordered intermetallic phase like NiAl. Usually, such point defect complexes have been assumed to be totally dissociated, and interactions between their constituents have been neglected (Wagner and Schottky,[15] Meyer and Fähnle,[16] Mishin *et al.*[12]).

In order to investigate the degree of dissociation of the triple-defect complexes in highly ordered "triple-defect" *B*2 phases, a new statistical-thermodynamic approach, the "defect correlation model" (DCM) is developed in the present work. Compared with the cluster expansion technique,[17,18] the proposed model is simpler. It can be used for large defect concentrations near the critical temperature of the order-disorder transition, but it is also applicable for highly ordered alloys with small defect concentrations. The model is able to predict the composition and temperature dependence of the thermodynamic properties and point defect concentrations, and the composition and temperature dependence of the equilibrium concentrations of bound triple-defect complexes (in an ideal three-dimensional crystal).

Although it was pointed out by Meyer and Fähnle[19] that the vibrational term of the effective defect formation entropy should be included in accurate calculations for a typical triple-defect structure, a comparison of results by Mishin *et al.*[1] showed clearly that neglecting the vibrational entropy term still leads to very reasonable defect concentrations. Therefore, we will, for simplicity, neglect the influence of the vibrational entropy term in the present investigation.

Since the DCM describes the behavior of the lattice gas of point defects on the basis of the Bragg-Williams pair-

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interaction model it depends on the input of reasonable and consistent pair-interaction energy parameters. These parameters are taken from the EAM calculations by Mishin and co-workers.[1,11] The reliability of these four parameters in combination with the proposed model equations is tested by comparing the calculated Al activities and vacancy concentrations with well-established experimental data and with other theoretical results, respectively.

II. SHORT-RANGE ORDERING OF POINT DEFECTS

Usually, Wagner-Schottky-type models,[15,16] as well as Bragg-Williams-type models,[2,3,20] are based on the assumption of noninteracting defects and are therefore valid only for small defect concentrations, i.e., close to the stoichiometric composition and far from the critical temperature T_c of the order-disorder transition. In the case of NiAl with a homogeneity range between about 46 and 59 at. % Ni at 1000 K,[21] the point defect concentrations are relatively small, and therefore Wagner-Schottky-type models or Bragg-Williams-type models, respectively, have traditionally been used for the theoretical description of this phase,[2,3,16] yielding generally good results. In both of these approaches, any point defect complexes can occur only in a purely random way.

On the other hand, a certain degree of short-range order of the point defects, resulting in higher than random concentrations of bound triple-defect complexes, is to be expected in NiAl, since attractive binding energies of defect pairs on nearest-neighbor sites have been reported repeatedly. Unfortunately, there is no consensus in the literature about the absolute value and even about the sign of the binding energy of a nearest-neighbor pair of an Ni vacancy and an Ni antistructure atom. Recently, Fähnle *et al.*[4] obtained, by *ab initio* calculations, a value of −0.1 eV for the binding energy of a nearest-neighbor pair of an Ni vacancy and an Ni antistructure atom. Mishin and Farkas[11] obtained, by the EAM method, a value of −0.013 eV for the same defect pair. Frank *et al.*[13] reported a value of −0.17 eV for the binding energy of a triple-defect complex, formed by two Ni vacancies and one Ni anti-structure atom in nearest-neighbor positions. In contrast, Korzhavyi *et al.*[7] found a repulsive interaction of 0.009 eV between an Ni vacancy and an Ni antistructure atom in nearest-neighbor positions.

It has been pointed out earlier[13,22,23] that the interaction between atomic defects might be important in intermetallic compounds, an effect which is not included in the theories based on independent, i.e., noninteracting defects. In the present work, a Bethe-Bragg-Williams-type grand-canonical formalism,[20,24,25,38] the DCM, is used to derive expressions for the thermodynamic functions and the concentrations of bound point defect complexes in the pure triple-defect $B2$ structure (a defect structure that was defined by Wasilewski[26]). According to this defect structure, only Ni antistructure atoms and Ni vacancies are considered in the present study, neglecting—for simplicity—both the Al antistructure atoms and the Al vacancies. However, the model equations could, if necessary, be expanded to consider four types of point defects, namely vacancies and antistructure atoms on both sublattices. This will be the topic of further research.

III. DERIVATION OF THE MODEL EQUATIONS

We consider a rigid, body-centered-cubic (bcc) lattice divided into two interpenetrating simple cubic lattices referred to as the α and β sublattices. Each of the two sublattices consists of N lattice sites. Corresponding to the triple-defect mechanism, an α sublattice site can be occupied either by an A atom or by a B atom (corresponding to an antistructure atom), whereas a β sublattice site can be occupied either by a B atom or by a vacancy. Antistructure atoms on the β sublattice, vacancies on the α sublattice, and atoms in interstitial positions are not allowed (i.e., we consider a pure "triple-defect" structure).

We assume that not only the long-range order of the A and B atoms on the two sublattices is established $(T \ll T_c)$, but also "short-range order" of point defects (i.e., Ni vacancies and Ni antistructure atoms), whereby the interacting point defects occupy nearest-neighbor positions in the crystal lattice. The pairwise interaction energies are assumed to be constant and independent of the occupancy of any other nearest-neighbor positions. In order to describe the degree of point defect short-range order, we use a simple approach by dividing the β sublattice into cubes.[24,25] Each of these cubes consists of eight β sublattice sites with a single α sublattice site in the central position of the cube. The cubes form a simple cubic lattice with a total number of $N/8$ lattice sites. Following the arguments in Ref. 25, there are altogether 512 different types of cube occupying the $N/8$ lattice sites, as defined in Table I. A mean-field approximation is introduced by assuming that the state of thermodynamic equilibrium is characterized by a set of 512 equilibrium numbers of the 512 different cubes. The numbers of cubes with a given number of vacancies on the β sublattice sites are[25]

$$n_{i\mathrm{A}} + n_{i\mathrm{B}} = n_i \quad (i = 0,1,\ldots,8). \tag{1}$$

The total internal energy of the crystal is described by the sum of pair interactions between all atoms and vacancies in the system. Each arrangement of the atoms on the lattice sites, corresponding to a given set of 512 numbers of the 512 different cubes (i.e., corresponding to a given configuration) is assumed to be associated with the same total internal energy value E, the same total number of A atoms N_A, and the same total number of B atoms N_B. The grand potential Ω can therefore be expressed by

$$\begin{aligned}\Omega(N_1 \cdot \cdot \cdot N_{512}) &= E(N_1 \cdot \cdot \cdot N_{512}) - kT \ln W(N_1 \cdot \cdot \cdot N_{512}) \\ &\quad - \mu_\mathrm{A}\frac{N_\mathrm{A}(N_1 \cdot \cdot \cdot N_{512})}{N_\mathrm{L}} - \mu_\mathrm{B}\frac{N_\mathrm{B}(N_1 \cdot \cdot \cdot N_{512})}{N_\mathrm{L}},\end{aligned} \tag{2}$$

where W is the total number of possible arrangements of the atoms on the lattice sites, k is Boltzmann's constant, E is the internal energy, T is the temperature, μ_A and μ_B are the chemical potentials of the two alloy components, N_A is the total number of A atoms, N_B is the total number of B atoms, and N_L is Avogadro's number; the numbers N_1 through N_{512} are the numbers of the different cubes of types 1 through 512.

TABLE I. Properties of the 512 different types of β-sublattice cubes, as explained in the text.

Cube	Number of vacancies on β sites of cube	Number of B atoms on β sites of cube	Atom on the central α site of cube	Number of cube types	Total number
0A	0	8	A	1	n_{0A}
0B	0	8	B	1	n_{0B}
1A	1	7	A	8	n_{1A}
1B	1	7	B	8	n_{1B}
2A	2	6	A	28	n_{2A}
2B	2	6	B	28	n_{2B}
3A	3	5	A	56	n_{3A}
3B	3	5	B	56	n_{3B}
4A	4	4	A	70	n_{4A}
4B	4	4	B	70	n_{4B}
5A	5	3	A	56	n_{5A}
5B	5	3	B	56	n_{5B}
6A	6	2	A	28	n_{6A}
6B	6	2	B	28	n_{6B}
7A	7	1	A	8	n_{7A}
7B	7	1	B	8	n_{7B}
8A	8	0	A	1	n_{8A}
8B	8	0	B	1	n_{8B}

Let $x=N_V^{\beta}$ be the number of vacancies on the β sublattice. Assuming random distribution of the vacancies on the β sublattice, one can calculate the numbers of cubes with a given number of vacancies on the β sublattice referred to the number of those without a vacancy on the β sublattice, (n_i/n_0)

$$\frac{n_i}{n_0}=\binom{i}{8}\left(\frac{x}{N-x}\right)^i \quad (i=1,2,\ldots,8). \tag{3}$$

The cubes are situated on $N/8$ lattice sites, therefore, we have

$$\sum_{i=0}^{8} n_i=\frac{N}{8}. \tag{4}$$

The grand potential can be expressed as a function of the following parameters and variables:

$$\Omega=\Omega(T,N,\mu_A,\mu_B,\varepsilon_{AB},\varepsilon_{BB},\varepsilon_{VA},\varepsilon_{VB},n_{0B},$$
$$n_{1B},n_{2B},n_{3B},n_{4B},n_{5B},n_{6B},n_{7B},n_{8B},x), \tag{5}$$

where $\varepsilon_{AB},\varepsilon_{BB},\varepsilon_{AV},\varepsilon_{BV}$ are the pair interaction energies between A and B atom, two B atoms, A atom and vacancy, and B atom and vacancy, respectively.

Altogether we have ten independent equilibrium conditions

$$\left(\frac{\partial\Omega}{\partial n_{iB}}\right)=0 \quad (i=0,1,\ldots,8), \tag{6}$$

$$\left(\frac{\partial\Omega}{\partial x}\right)=0. \tag{7}$$

W, the total number of arrangements in Eq. (2) is given by

$$W=\frac{\left(\frac{N}{8}\right)!}{n_0!\left[\left(\frac{n_1}{8}\right)!\right]^8\left[\left(\frac{n_2}{28}\right)!\right]^{28}\left[\left(\frac{n_3}{56}\right)!\right]^{56}\left[\left(\frac{n_4}{70}\right)!\right]^{70}\left[\left(\frac{n_5}{56}\right)!\right]^{56}\left[\left(\frac{n_6}{28}\right)!\right]^{28}\left[\left(\frac{n_7}{8}\right)!\right]^{8}n_8!}\times r^8,$$

with

$$r = \frac{n_0!}{n_{0A}!\cdot n_{0B}!} \times \left[\frac{\left(\frac{n_1}{8}\right)!}{\left(\frac{n_{1\mathrm{A}}}{8}\right)!\left(\frac{n_{1\mathrm{B}}}{8}\right)!}\right]^{8} \times \left[\frac{\left(\frac{n_2}{28}\right)!}{\left(\frac{n_{2\mathrm{A}}}{28}\right)!\left(\frac{n_{2\mathrm{B}}}{28}\right)!}\right]^{28} \times \left[\frac{\left(\frac{n_3}{56}\right)!}{\left(\frac{n_{3\mathrm{A}}}{56}\right)!\left(\frac{n_{3\mathrm{B}}}{56}\right)!}\right]^{56} \times \left[\frac{\left(\frac{n_4}{70}\right)!}{\left(\frac{n_{4\mathrm{A}}}{70}\right)!\left(\frac{n_{4\mathrm{B}}}{70}\right)!}\right]^{70}$$
$$\times \left[\frac{\left(\frac{n_5}{56}\right)!}{\left(\frac{n_{5\mathrm{A}}}{56}\right)!\left(\frac{n_{5\mathrm{B}}}{56}\right)!}\right]^{56} \times \left[\frac{\left(\frac{n_6}{28}\right)!}{\left(\frac{n_{6\mathrm{A}}}{28}\right)!\left(\frac{n_{6\mathrm{B}}}{28}\right)!}\right]^{28} \times \left[\frac{\left(\frac{n_7}{8}\right)!}{\left(\frac{n_{7\mathrm{A}}}{8}\right)!\left(\frac{n_{7\mathrm{B}}}{8}\right)!}\right]^{8} \times \frac{n_8!}{n_{8\mathrm{A}}!\, n_{8\mathrm{B}}!}. \tag{8}$$

E, the total internal energy in Eq. (2) is the sum of all pair energies, so that

$$\frac{E}{8} = n_{0\mathrm{A}}8\varepsilon_{\mathrm{AB}} + n_{0\mathrm{B}}8\varepsilon_{\mathrm{BB}} + n_{1\mathrm{A}}(7\varepsilon_{\mathrm{AB}} + \varepsilon_{\mathrm{AV}}) + n_{1\mathrm{B}}(7\varepsilon_{\mathrm{BB}} + \varepsilon_{\mathrm{BV}}) + n_{2\mathrm{A}}(6\varepsilon_{\mathrm{AB}} + 2\varepsilon_{\mathrm{AV}}) + n_{2\mathrm{B}}(6\varepsilon_{\mathrm{BB}} + 2\varepsilon_{\mathrm{BV}}) + n_{3\mathrm{A}}(5\varepsilon_{\mathrm{AB}} + 3\varepsilon_{\mathrm{AV}})$$
$$+ n_{3B}(5\varepsilon_{\mathrm{BB}} + 3\varepsilon_{\mathrm{BV}}) + n_{4\mathrm{A}}(4\varepsilon_{\mathrm{AB}} + 4\varepsilon_{\mathrm{AV}}) + n_{4\mathrm{B}}(4\varepsilon_{\mathrm{BB}} + 4\varepsilon_{\mathrm{BV}}) + n_{5\mathrm{A}}(3\varepsilon_{\mathrm{AB}} + 5\varepsilon_{\mathrm{AV}}) + n_{5\mathrm{B}}(3\varepsilon_{\mathrm{BB}} + 5\varepsilon_{\mathrm{BV}}) + n_{6\mathrm{A}}(2\varepsilon_{\mathrm{AB}} + 6\varepsilon_{\mathrm{AV}})$$
$$+ n_{6\mathrm{B}}(2\varepsilon_{\mathrm{BB}} + 6\varepsilon_{\mathrm{BV}}) + n_{7\mathrm{A}}(\varepsilon_{\mathrm{AB}} + 7\varepsilon_{\mathrm{AV}}) + n_{7\mathrm{B}}(\varepsilon_{\mathrm{BB}} + 7\varepsilon_{\mathrm{BV}}) + n_{8\mathrm{A}}8\varepsilon_{\mathrm{AV}} + n_{8\mathrm{B}}8\varepsilon_{\mathrm{BV}}. \tag{9}$$

N_{A}, the total number of A atoms, is given by

$$N_{\mathrm{A}} = N - 8\cdot\sum_{i=0}^{8} n_{i\mathrm{B}}, \tag{10}$$

and N_{B}, the total number of B atoms, is given by

$$N_{\mathrm{B}} = N - x + 8\cdot\sum_{i=0}^{8} n_{i\mathrm{B}} \tag{11}$$

With Eqs. (1)–(11), and using Sterling's formula, the variables $x, n_{0\mathrm{A}}\ldots\ldots n_{8\mathrm{A}}, n_{0\mathrm{B}}\ldots\ldots n_{8\mathrm{B}}$ can be calculated. The mole fraction of component A is defined as

$$x_{\mathrm{A}} = \frac{N_{\mathrm{A}}}{N_{\mathrm{A}} + N_{\mathrm{B}}}. \tag{12}$$

The total vacancy concentration c_{V} is given by

$$c_V = \frac{x}{2N}. \tag{13}$$

The activity curve of component A can be obtained by use of a form of the Gibbs-Duhem relation

$$d\mu_{\mathrm{B}} = d\mu_{\mathrm{A}}\cdot\left(\frac{x_{\mathrm{A}}}{x_{\mathrm{A}} - 1}\right) \quad (dT = 0,\ dp = 0), \tag{14}$$

with

$$\mu_{\mathrm{A}} - \mu_{\mathrm{A},0} = RT\ln\left(\frac{a_{\mathrm{A}}}{a_{\mathrm{A},0}}\right), \tag{15}$$

where a_{A} is the activity of component A, and $a_{\mathrm{A},0}$ is the activity of component A at the exact stoichiometric composition.

From Table I one can easily see that the concentration of triple-defect complexes c_{tr} is obtained as

$$c_{\mathrm{tr}} = 8\cdot\frac{n_{2\mathrm{B}}}{N}. \tag{16}$$

IV. RESULTS AND DISCUSSION

All calculations for NiAl were performed by using the following set of pair energy parameters

$$\varepsilon_{\mathrm{AB}} = -0.24\ \mathrm{eV},$$
$$\varepsilon_{\mathrm{BB}} = -0.05\ \mathrm{eV},$$
$$\varepsilon_{\mathrm{AV}} = -0.125\ \mathrm{eV},$$
$$\varepsilon_{\mathrm{BV}} = -0.013\ \mathrm{eV}, \tag{17}$$

where $\varepsilon_{\mathrm{AB}}$ and $\varepsilon_{\mathrm{BB}}$ are the pair interaction energies between atoms (A=Al, B=Ni) at the first neighbor distance reported by Mishin *et al.*[1] and $\varepsilon_{\mathrm{BV}}$ is the binding energy of an associated pair of an Ni vacancy and an Ni antistructure atom as reported by Mishin and Farkas.[11] The value for $\varepsilon_{\mathrm{AV}}$ was estimated using the Ni-Ni pair interaction by Mishin *et al.*,[1] which shows repulsive interaction energies between Ni atoms situated at the distance of next-nearest neighbors or third-nearest neighbors, respectively.

With the pair interaction energy parameters listed above [Eq. (17)], it turns out that 0.12% of the thermally generated triple defects exist as isolated entities in stoichiometric NiAl at 1300 K, and could therefore give rise to long-range Ni self-diffusion via the triple-defect mechanism as suggested by Frank *et al.*[13] The total vacancy concentration in stoichiometric NiAl, referred to the total number of lattice sites, is found to be $\alpha = 1.5\times10^{-3}$, where α is also called the disorder parameter. This value is in good accordance with the disorder parameter obtained by Libowitz ($\alpha = 1.7\times10^{-3}$) (Ref. 27) and by Chang and co-workers ($\alpha = 2.0\times10^{-3}$) (Refs. 2 and 3) who fitted their theoretical Al activity curves to the experimental Al activities determined by Steiner and Komarek.[28]

Figure 1 shows the activity of Al in NiAl at T=1273 K as a function of composition (x_{Ni}). The theoretical curve is calculated with the pair energy parameters listed above in Eq.

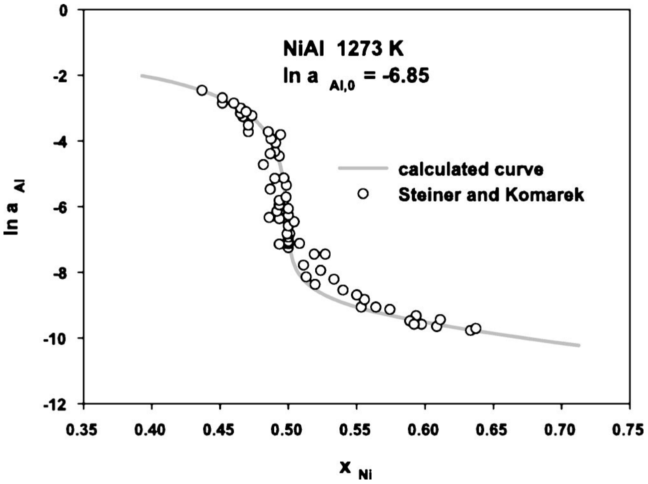

FIG. 1. Activity of Al in NiAl at 1273 K as a function of the composition x_{Ni}. The experimental data points are taken from Steiner and Komarek (Ref. 28). The theoretical curve is calculated with the pair interaction energy parameters given in the text (Eqs. (17)).

(17). It is in very good agreement with the experimental data by Steiner and Komarek[28] (which had to be shifted by 1.5 at. % due to a systematic error in the original investigation according to Ettenberg *et al.*,[29] see also Ref. 30). The Al activities determined recently by Raj *et al.*,[31] using Knudsen effusion mass spectrometry, and by Róg *et al.*,[32] using a solid-state galvanic cell technique, agree well with the isopiestic vapor pressure measurements by Steiner and Komarek[28] if the composition shift in the latter results is considered.[29,30] Note that the shape of the theoretical curve was obtained from the model calculations only and has not been fitted to the experimental results (except adjusting it to the absolute value at the exactly stoichiometric composition,[30] $\ln a_{\mathrm{Al},0}=-6.85$).

In Fig. 2, the vacancy concentration in NiAl at 1273 K is shown as a function of composition. Again, the theoretical curve, calculated with the parameters listed above in Eq. (17), is in very good accordance with the experimental data by Bradley and Taylor,[33] and by Zelenin *et al.*[34]

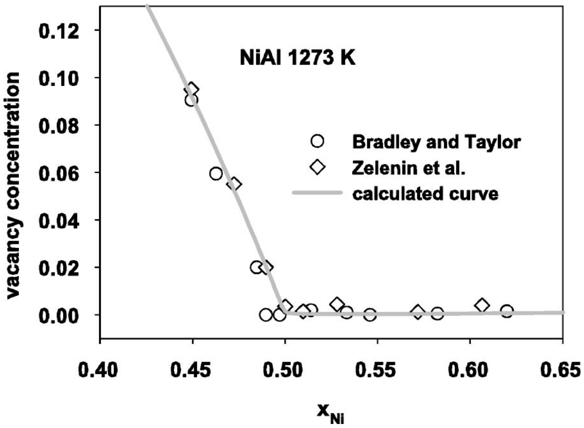

FIG. 2. Vacancy concentration (referred to the total number of lattice sites) in NiAl at 1273 K as a function of the composition x_{Ni}; experimental data points from Bradley and Taylor (○) (Ref. 33) and Zelenin *et al.* (◇) (Ref. 34). The theoretical curve is calculated with the pair interaction energy parameters given in the text [Eqs. (17)].

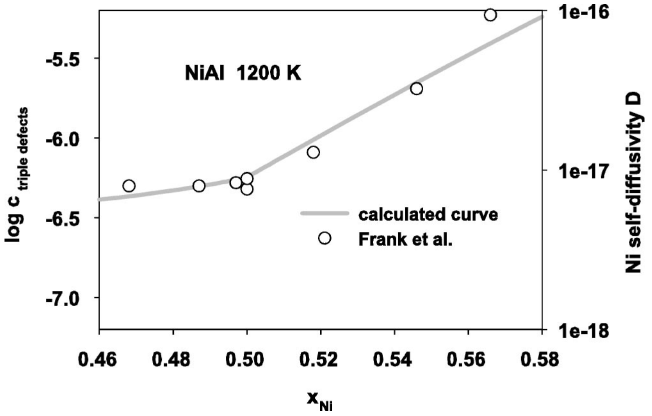

FIG. 3. Experimental values of the Ni self-diffusion coefficient D (in $m^2 s^{-1}$) in NiAl at 1200 K (○) as a function of composition according to Frank *et al.*[13] The full curve is the concentration of triple-defect complexes at the same temperature, calculated with the pair interaction energy parameters given in the text [Eqs. (17)].

In Figs. 3 and 4, the experimentally determined concentration dependence of the Ni self-diffusion coefficient in NiAl at $T=1200$ and 1300 K, respectively, by Frank *et al.*[13] are compared with the theoretical concentrations of triple-defect complexes. The theoretical curves are calculated with the parameters listed above [Eq. (17)]; they are not fitted in any way to the experimental data. One can see that the Ni self-diffusion coefficient according to Frank *et al.*[13] is proportional to the triple-defect complex concentration over a wide concentration range. This supports the suggestion by the authors[13] that the main Ni diffusion mechanism operating in NiAl involves triple-defect complexes. Frank *et al.*[13] expected a contribution of the so-called antistructure bridge mechanism[35] in Ni-rich alloys, which could explain the deviation of the data point at $x_{\mathrm{Ni}}=0.566$. The deviation at $x_{\mathrm{Ni}}=0.468$ might point to contributions of mechanisms which are based on single Ni vacancies, e.g., the next-nearest neighbor vacancy mechanism.[12]

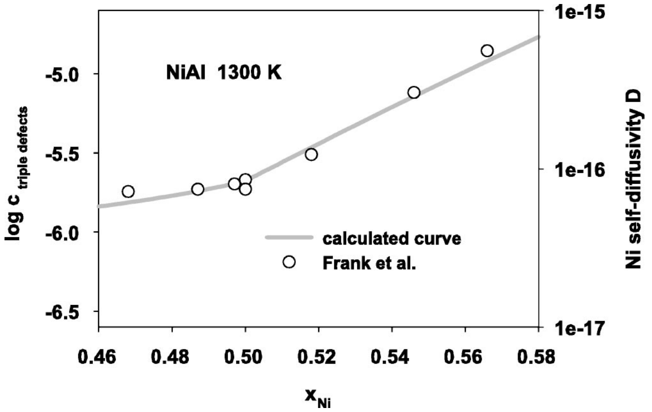

FIG. 4. Experimental values of the Ni self-diffusion coefficient D (in $m^2 s^{-1}$) in NiAl at 1300 K (○) as a function of composition according to Frank *et al.*[13] The full curve is the concentration of triple-defect complexes at the same temperature, calculated with the pair interaction energy parameters given in the text [Eqs. (17)].

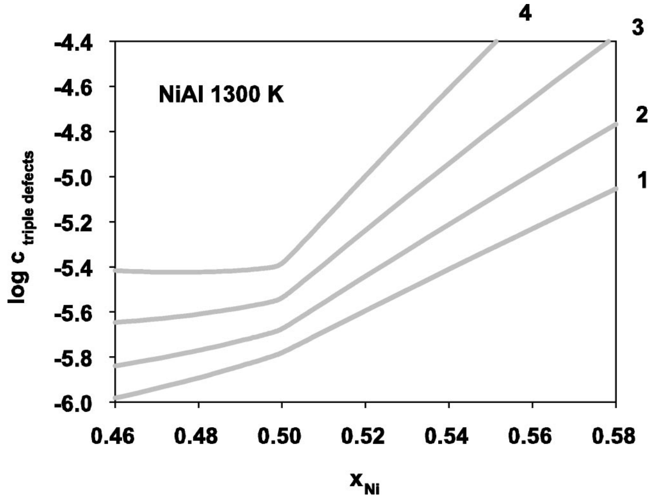

FIG. 5. Triple-defect complex concentrations vs alloy composition at 1300 K, calculated using different values of the interaction energy parameter ε_{BV}. The parameters $\varepsilon_{AB}=-0.24$ eV, $\varepsilon_{BB}=-0.05$ eV, and $\varepsilon_{AV}=-0.125$ eV are given in the text (17). Curve 1: $\varepsilon_{BV}=0$ (random distribution of point defects); Curve 2: $\varepsilon_{BV}=-0.013$ (as used in the present study); Curve 3: $\varepsilon_{BV}=-0.03$; Curve 4: $\varepsilon_{BV}=-0.05$

In Fig. 5 the concentrations of bound triple-defect complexes are compared for the case where correlations are taken into account (for different values of ε_{BV}) or are neglected (by setting the parameter ε_{BV} equal to zero). It can be shown that the defect interactions between Ni vacancies and Ni antistructure atoms have only minor effects on the Al activities and the absolute values of the equilibrium point defect concentrations, i.e., the thermodynamic properties depend solely on the three parameters (see Eqs. (17)) which are kept constant in Fig. 5. As can be seen in Fig. 5, the defect interactions exert a strong influence on the concentration of first-neighbor defect pairs and of bound triple-defect complexes. Such an effect has also been pointed out by Korzhavyi *et al.*[7]

It is interesting to note that very recently, Soule De Bas and Farkas[36] performed molecular dynamics simulations of diffusion mechanisms in stoichiometric NiAl. Their results pointed to a variety of cyclic mechanisms with the so-called six-jump cycle, originally postulated by Elcock and McCombie,[37] playing a major role, whereas the next-nearest-neighbor vacancy mechanisms turned out to be negligible. Unfortunately, only one single vacancy was introduced into the ensemble of Al and Ni atoms for the calculations which excluded *a priori* any diffusion mechanisms that might depend on triple-defect complexes.

V. CONCLUSIONS

Interactions among point defects in intermetallic compounds are generally small, therefore, in NiAl, Ni vacancies and Ni antistructure atoms are expected to move more or less independently of each other. However, even small equilibrium concentrations of point defect complexes can be of great interest, if they are involved in the diffusion mechanisms. The present study combines a statistical model (DCM) on the basis of the Bragg-Williams approach with literature data on the pair-interaction energies. The DCM is presented for the simplified case of a pure "triple-defect" *B*2 (CsCl) phase. Using pair interaction energies obtained from the EAM calculations by Mishin *et al.*,[1,11] the equilibrium vacancy concentrations and the concentration dependence of the Al activity in NiAl can be computed with good accuracy, as demonstrated in Figs. 1 and 2.

The most interesting point defect complexes in the *B*2 phase NiAl are the triple-defect complexes, consisting of two Ni vacancies and one Ni antistructure atom, since they have been supposed to be mainly responsible for the concentration dependence of the Ni self-diffusion coefficient which is nearly constant for Al-rich and stoichiometric alloys, and increases markedly with increasing Ni content on the Ni-rich side of the composition range.[13] The concentrations of these triple-defect complexes can be obtained with the DCM in a straightforward manner, with their reliability depending, of course, on the reliability of the parameter ε_{BV}, as demonstrated in Fig. 5.

It is shown that the calculated composition dependence of the triple-defect complex concentration, derived in the present work, and the Ni diffusivities, found experimentally by Frank *et al.*,[13] show a striking correlation, as can be seen in Figs. 3 and 4. This points to an important role of the triple-defect mechanism or of other mechanisms that involve complexes of antistructure atoms and vacancies in nearest-neighbor positions. On the other hand, the excellent correlation in Figs. 3 and 4 can be taken as a strong indication for the actual existence of such bound defect complexes. This would clearly indicate an attractive interaction between Ni antistructure atoms and Ni vacancies that would not be compatible with a positive interaction energy between these two defects, as reported by Korzhavyi *et al.*[7]

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