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Ab initio statistical mechanics for alloy phase diagrams and ordering phenomena including the effect of vacancies

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The effect of vacancies on the phase diagram and the order-disorder transition of a binary alloy is studied within the framework of an *ab initio* statistical mechanics. It is shown that for systems with structural vacancies the phase diagrams are substantially modified by the vacancies, both qualitatively (appearance of new vacancy-ordered phases) and quantitatively (stabilization of phases for a wider composition range, decrease of transition temperatures). The interplay of vacancies and antistructure atoms for the order-disorder transition is elucidated.

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Intermetallic compounds have attracted considerable attention in the last years because of their potential technological application as high-temperature structural materials[1] and because there is a large variety of interesting questions concerning the fundamental physics, encompassing the phase stability and kinetics of phase transformations in the bulk[2] and, for epitaxial alloys,[3] order-disorder phenomena and segregation phenomena in the bulk and at the surface,[2,4,5] atomic defects and diffusion,[6–9] structure and dynamics of dislocations,[10,11] and the complex electronic bonding properties.[12] Concerning phase diagrams, the technologically important compounds often exhibit many stable and metastable phases, and the experimental determination of equilibrium phase diagrams is complicated and time-consuming. Therefore, theoretical support for the determination, prediction, and design of phase diagrams is highly desirable. Because the electronic properties of the intermetallic compounds often are rather complicated,[12] phenomenological and semiempirical models are not always reliable and an *ab initio* statistical mechanics is required[13,14] where the energetics is described by solving the full electronic-structure problem.

The *ab initio* statistical mechanics has been rather successfully applied to many compounds assuming in nearly all studies that each lattice site is occupied by an atom. However, it is well known[6–9] that in many intermetallic compounds (especially those with bcc-type phases) there is a high concentration of thermally excited vacancies, and in some nonstoichiometric bcc-type compounds,[6–9,15] e.g., $B2$-NiAl, there are also structural vacancies, i.e., vacancies which survive in thermal equilibrium in order to guarantee the deviations from the stoichiometric compositions when going to low temperatures. It is suggesting itself to assume that these vacancies may have a considerable influence on the form of the phase diagram and on the mechanism of thermal disordering. For instance, the $B2$ phase of NiAl is nearly exclusively confined to the Ni-rich part of the calculated phase diagram (see Fig. 2 and Refs. 14 and 16), whereas it appears also in the Al-rich part of the experimental phase diagram. Our conjecture is that for Al-rich systems the $B2$ phase of NiAl is stabilized by the occurrence of structural vacancies.[15] Furthermore, it has been suggested[17] that the Ni_2Al_3 phase which is observed experimentally when going from the Al-rich $B2$ phase to even smaller Ni concentrations may be interpreted as an ordering of vacancies in such a way that every third sheet of Ni atoms perpendicular to the cube diagonal of the $B2$ structure is absent. The vacancies are also important for the thermal disordering which proceeds[15] in $B2$-NiAl at low temperatures via the formation of triple defects (two vacancies on one sublattice and an antistructure atom on the other sublattice). We assume that this mechanism of disordering must be modified at higher temperatures because otherwise the volume expansion due to the creation of vacancies would become enormously large. The preceding discussion illustrates that vacancies should be taken into account for a calculation of the phase diagram and the thermal disordering of intermetallic compounds with high vacancy concentrations.

In the present paper we demonstrate how this may be achieved within the framework of *ab initio* statistical mechanics. The calculations are for a model system consisting of Ni and Al atoms with phases which appear only on a bcc parent lattice and which does not melt. In reality, there are also phases with other symmetries in the NiAl phase diagram, and real NiAl melts before the various ordered phases exhibit a transition to a disordered solid phase. It is the objective of our paper to elucidate qualitatively the possible effects of vacancies on the phase diagram and the mechanism of thermal disordering, rather than to obtain a realistic description of the system NiAl occuring in nature.

The calculations were performed within the framework of the real-space cluster expansion (CE) technique[18,13,14] for the energetics and of the cluster variation method[19,18,20] (CVM) for the configurational entropy. In the CE a parent lattice with N sites i is chosen and each configuration is described by assigning a spin variable S_i to each site of the lattice. For the binary system NiAl with vacancies the variable S_i exhibits the values $+1$, -1, or 0 if site i is occupied by a Ni atom, an Al atom, or a vacancy, respectively, i.e., we treat the vacancy as a third component in a ‘‘quasiternary’’ system. The energy $E(\sigma)=\Sigma_m \Sigma_s J_{ms}\phi_{ms}(\sigma)$ of each configuration σ then may be exactly described by an infinite sum of contributions arising from all possible spin clusters m on the parent lattice, i.e., nearest-neighbor pairs and further distant pairs,

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triplets of different shapes, quartets, and so on. The $\phi_{ms}(\sigma)$ are appropriate cluster functions of the spin variables of the clusters and the J_{ms} are the corresponding interaction parameters. The index s marks the different cluster functions belonging to the same cluster.[18] We confined ourselves to the tetrahedron approximation, i.e., we considered only contributions from the 21 crystallographically inequivalent cluster functions which may be formed on the smallest possible tetrahedron of the bcc parent lattice. The 21 coefficients J_{ms} of the CE were determined via the structure inversion method[21] from the calculated total energies $E(\sigma)$ for 21 periodic reference supercell configurations σ which were selected to be linear independent within the tetrahedron approximation to guarantee that the above equation for $E(\sigma)$ can be inverted for the J_{ms}. This was achieved by the following structures: bcc-Ni, $D0_3$-Ni_3Al, $B2$-NiAl, $B32$-Ni_2Al_2, $D0_3$-$NiAl_3$, and bcc-Al, as well as structures which were generated by taking an ideal 32-atom supercell of $B2$-NiAl and then replacing the central tetrahedron of the ideal $B2$ structure by a tetrahedron with, respectively, one of the 15 various tetrahedron configurations which contain at least one vacancy. The total supercell energies were determined by the *ab initio* pseudopotential method[22] with a mixed basis set of plane waves and five localized nonoverlapping d orbitals per Ni atom.[23] Because of the different atomic sizes of Al and Ni atoms, relaxation effects are essential, giving rise to volume relaxations of the supercells and structural relaxations of individual atoms in the supercells. For the volume relaxations the local relaxation approximation[24] was adopted, i.e., each total energy $E(\sigma)$ was obtained at the lattice constant for which $E(\sigma)$ is minimized. For the subsequent thermodynamic treatment this corresponds to the assumption that configuration σ appears in thermal equilibrium locally at its respective minimum energy volume; i.e., the constraints on the bond lengths exerted by the rest of the lattice are ignored. We plan to account for these constraints by adding an elastic energy term to the internal energy obtained by the incompatibility method of the stochastic elasticity theory which was already successfully used to determine atomic level internal stresses in metallic glasses.[25] Concerning the structural relaxations of individual atoms two sets of total energy data were obtained, one with and one without structural relaxations. Because the convergence of the tetrahedron approximation disapproved when taking into account the structural relaxation, we present in the following only the ‘‘unrelaxed’’ results, keeping in mind that we only want to elucidate for a model system the new qualitative features related to the effect of vacancies.

The configurational energy was represented in the CVM by a linear combination of entropies of all clusters included in the tetrahedron. The contribution of the vibrational entropy was neglected. Then the grand potential was calculated from the internal energy, the configurational entropy, and the chemical potentials μ_{Ni} and μ_{Al} (the chemical potential of the vacancy is zero because the number of vacancies cannot be prescribed independently of the state variables T, p, and N) as a function of the tetrahedron probabilities w_{ijkl}. These quantities describe the probability to find the tetrahedron in the configuration given by the subscripts (with $i,j,k,l=$Ni, Al, or vacancy), and they were determined by minimizing the grand potential with the natural iteration method.[19] Thereby one has to prescribe the symmetries of the phases which are assumed to compete for the phase diagram. In the following we consider only the phase diagram on the bcc parent lattice, and we represent the bcc lattice by a superposition of four interpenetrating fcc sublattices. Four possible symmetries were assumed, i.e., the $A2$ structure (all sublattices are crystallograpically equivalent, corresponding to a disordered bcc alloy), the $B2$ structure (respectively two sublattices corresponding to the next-nearest-neighbor distance are equivalent), the $B32$ structure (respectively two sublattices corresponding to the nearest-neighbor distance are equivalent), and the $D0_3$ structure (two sublattices are equivalent but different from the other two mutually distinct sublattices).

The quality of the CE was tested by comparing for configurations which were not used as reference configurations the energies as obtained by the CE with the energies obtained by the direct *ab initio* pseudopotential calculation. Among the various tests the most important one was to calculate by the CE the defect formation parameters[9,15] for vacancies on both sublattices and for the antistructure atoms on both sublattices (these latter configurations were not included in the fit) which describe the change in energy when introducing one of these isolated defects in an otherwise perfect $B2$-NiAl. From these parameters we calculated the effective formation energies for these four defects by statistical mechanics for uncorrelated defects[9,15] and compared with the results obtained from a direct *ab initio* calculation of the defect formation parameters. The deviations were smaller than 1.5%, except for the Al antistructure atom (3.7%). These tests demonstrate that the tetrahedron CE should be accurate enough to explore the qualitative effects of the vacancies.

It should be noted that for binary systems it is the present calculational state of the art to go beyond the tetrahedron approximation, whereas there have been only extremely few attempts to do this for ternary systems. We treat our vacancy as a third component (with chemical potential zero) in a ‘‘quasiternary’’ system and we therefore confined ourselves to the tetrahedron approximation. It should also be noted that there are *ab initio* calculations in the literature[26] for the intercalation compound Li_xCoO_2 where vacancies are allowed to appear on one sublattice (the Li sublattice) of the considered phase. In this case the vacancies are treated as a second component in a ‘‘quasibinary’’ expansion. In our approach the vacancies may appear on all sublattices and we therefore are able to describe such interesting phenomena like a transition from a phase with an overall distribution of vacancies to a phase where the vacancies are condensed on one sublattice (see below).

Figure 1 shows the concentration of vacancies and antistructure atoms on the two sublattices of stoichiometric $B2$-NiAl. It should be recalled that in reality the $B2$-NiAl melts before the $B2$-$A2$ transition. The results at high temperatures therefore are not representative for real NiAl, but the qualitative effects discussed below are certainly relevant for systems with high concentrations of structural or thermal vacancies and with ordering energies smaller than the one of

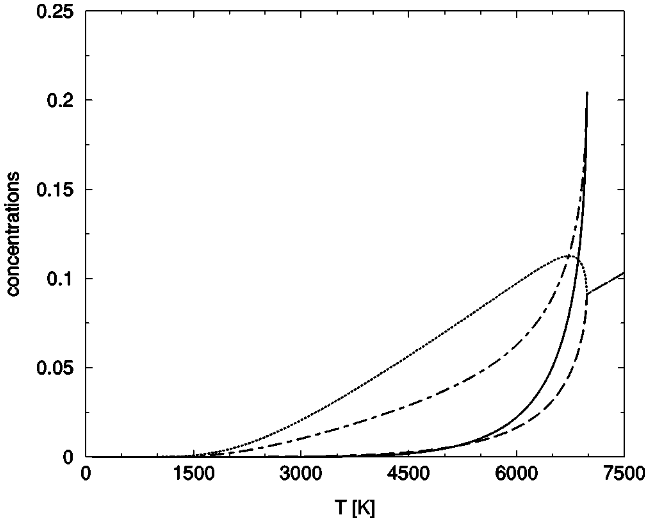

FIG. 1. The concentrations of atomic defects (normalized to the number of lattice sites) for a model stoichiometric $B2$-NiAl which does not melt before the $B2$-$A2$ transition occurs (see text) as function of temperature. Solid line: Al antistructure atom. Dash-dotted line: Ni antistructure atom. Dashed line: Al vacancy. Dotted line: Ni vacancy. The line for $T>6980$ K gives the total vacancy concentration.

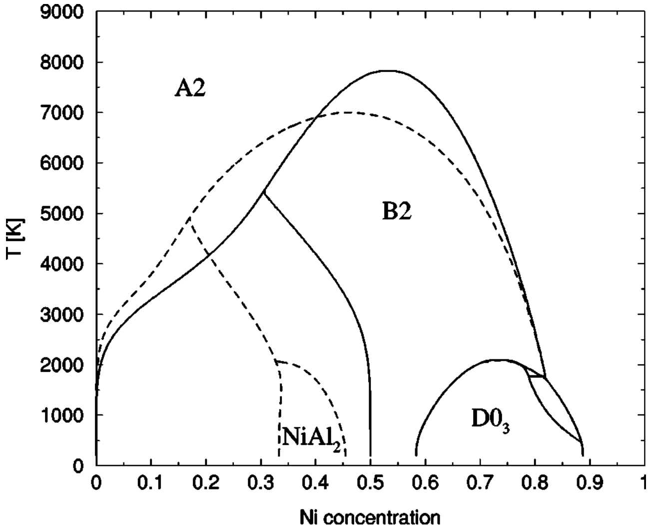

FIG. 2. The phase diagram of the system NiAl on the bcc parent lattice without (solid lines) and with (dashed lines) the effect of vacancies. Note that we found nearly the same phase boundary lines with and without vacancies for the $D0_3$ phase and the corresponding mixed phases because of the small number of vacancies at those concentrations and temperatures.

NiAl so that the order-disorder transition is further advanced than in NiAl (e.g., $B2$-CoAl, $B2$-NiGa) or even complete (e.g., $B2$-FeAl). The order-disorder transition in our model system is complete at about 6980 K, i.e., above this temperature there is the disordered $A2$ phase for which we cannot distinguish between the two sublattices and for which we can define just a total concentration of vacancies. The figure clearly demonstrates the above expected change in the mechanism of thermal disordering with increasing temperature: At low T the concentration of Ni vacancies is twice as large as the concentration of Ni antistructure atoms, i.e., triple defects are excited. In contrast, close to the transition temperature the thermal excitation of antistructure atoms on both sublattices dominates, the Ni vacancies are partially refilled and therefore their concentration decreases, and the concentration of Al vacancies increases strongly. From the temperature dependence of the defect concentrations at low temperatures we obtained the effective formation energies for the vacancies and antistructure atoms, and the results were in very good agreement with those obtained by *ab initio* statistical mechanics for uncorrelated defects,[15] i.e., for the low-defect-concentration regime of the stoichiometric compound the defect-defect interactions can be neglected. It should be noted that the concentrations of atomic defects have been calculated not only by the statistical mechanics of uncorrelated defects[15] but also by the CVM, describing the energetics by an empirical pair-interaction model including fitting parameters.[27] Because of the complex electronic structure, such a pair-interaction model is not reliable in NiAl,[12] and we therefore apply in the present letter the *ab initio* CVM to a system for which the effect of vacancies is essential.

In Fig. 2 the principal effects of vacancies on the phase diagram are explored by considering the phases of our model system which appear with and without vacancies. For the Al-rich part of the phase diagram the calculations yield a high concentration of structural vacancies. This is in line with the results of the *ab initio* statistical mechanics of uncorrelated defects,[15] i.e., vacancies appear to be structural defects not only for low defect concentrations. The vacancies have essentially three effects on the phase diagram.

(i) The $B2$ phase is stabilized by the vacancies, i.e., it extends to lower Ni concentrations.

(ii) There is a new phase (which we call the $NiAl_2$ phase) which results from an ordering of Ni vacancies on third-nearest-neighbor sites (the interaction of two Ni vacancies is repulsive for the next-nearest-neighbor sites). It may be conceived as a $D0_3$ structure for which at the composition $NiAl_2$ one sublattice is totally empty due to the ordering of vacancies. The transition from the $NiAl_2$ phase to the $B2$ phase with increasing temperature corresponds to a continuous order-disorder transition of the vacancies. When increasing the Ni concentration, this empty sublattice is gradually filled by Ni atoms. The $NiAl_2$ structure resembles the experimentally observed Ni_2Al_3 structure (see above) in the sense that both structures represent a vacancy ordering on third-nearest-neighbor sites, albeit the details of the structures being different. (It should be noted that we find an even more stable phase than this $NiAl_2$ phase when we allow that all fcc sublattices are crystallographically inequivalent. This corresponds to the so-called $F\overline{4}3m$ symmetry group. The phase boundaries for this phase, however, are hard to locate by our natural iteration algorithm.)

(iii) The transition temperature for the $B2$-$A2$ phase transition is lowered by the vacancies. To conclude, we have performed for an ordered binary compound an *ab initio* calculation of a phase diagram and of an order-disorder transition which includes the influence of vacancies in a general manner, i.e., treating the vacancy as third component of a ‘‘quasiternary’’ system. The vacancies modify the phase diagrams quantitatively (stabilization of phases for a wider composition range, decrease of transition temperatures) and qualitatively (appearance of new vacancy-ordered phases) and have a considerable effect on the order-disorder transition. Therefore they should be taken into account in all systems with high vacancy concentrations. For instance, it would be highly interesting to investigate by our formalism the experimentally observed[28] order-disorder transition of the abundant vacancies in the technologically important refractory titanium monocarbide TiC_{1-x} with $x \approx 0.4$. Furthermore, we are convinced that vacancies have an essential effect also on the ordering and segregation phenomena at the surfaces of alloys with high vacancy concentrations and therefore should be included in a future development of an *ab initio* statistical mechanics for surfaces.

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