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Influences of Lattice Sinks and Defect Interactions on Solutes in Compounds

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ABSTRACT

A thermodynamic model for the site preference of dilute solutes in ordered compounds was developed recently. The model is extended here in two ways to help interpret experimental results from this laboratory. (1) A preference for solutes to occupy sites in 'sinks' such as grain boundaries rather than regular lattice sites is included using a simple model. A wide range of site preference behavior is found; for example, a solute may switch between substitutional and sink sites with changing composition. (2) The effect of an attractive interaction between solute and defect on the site preference is examined. Conditions are established under which a solute can be stabilized by association with a defect on a site where the solute would otherwise not be found.

INTRODUCTION

Preferences of solutes among inequivalent lattice sites in a compound affect a variety of physical and mechanical properties. One needs to understand the underlying thermodynamics in order to interpret site preference observations and make predictions. Recently, we developed a thermodynamic site-preference model applicable for compounds of any structure and encompassing both substitutional and interstitial sites [1]. The model has been used to help explain some aspects of experimental observations of the site preference of dilute indium solutes in five aluminides and galliumides having the Ni_2Al_3 crystal structure [2]. This crystal structure has one Ni-site and two inequivalent Al-sites. Observations were made using the method of perturbed angular correlation of gamma rays (PAC), in which lattice locations of indium solutes were determined through measurements of nuclear quadrupole interactions. Solutes in each of the five phases were found to switch sites as the composition changed from one side of the stoichiometric composition to the other. Indium solutes in transition-metal (TM) rich phases were found to occupy one of the two inequivalent sites of the trivalent element (Wyckoff notation 2d). Solutes in TM-poor galliumides were observed instead on the TM-sublattice [2], whereas solutes in TM-poor aluminides exhibited a strongly inhomogeneous signal indicating that they had been expelled from normal lattice sites to 'lattice sinks' such as grain boundaries [2].

The thermodynamic model [1] was developed for systems in which interactions among solutes and intrinsic defects (vacancies, antisite atoms and host interstitials) can be ignored. Such a model is applicable as a first approximation for intermetallic compounds in which coulomb interactions are screened by conduction electrons. The model may also apply for ionic and semiconducting compounds in which defects and solutes have the same charges as atoms they replace.

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The present paper extends the model in two ways. First, we seek to understand conditions under which a solute may switch between substitutional and 'sink' sites with changing composition, as described above for the aluminides. Second, we seek to include the influence of defect-solute interactions on site selection using a simple model. This is motivated by PAC experiments on indium solutes in NiAl [3,4,5], CoAl [5] and FeAl [6], systems that have the CsCl structure and wide phase fields for which deviations from the stoichiometric composition are accommodated by transition-metal (TM) vacancies (V_{TM}) and TM-antisite atoms (TM_{Al}), respectively, for TM-rich and TM-poor compositions. From observed defect-induced nuclear quadrupole interactions, it is known that indium predominantly localizes on the Al-site in (TM) rich compositions where it binds with near-neighbor TM-vacancies with association energies close to 0.2 eV [3-6]. Nuclear quadrupole interactions measured using PAC in TM-poor NiAl and FeAl clearly show that indium probes continue to reside on the Al-site when they have with one or more Ni-vacancies in the first neighbor shell. Note that for a composition of 49 at.% TM, the TM-vacancy concentration is quite large (~4 at. %) and the site fractions of indium probes having at least one vacancy neighbor is of order 80% or greater. In the CsCl structure, atoms of one element are surrounded by atoms of the other, so that In_{Ni} probes can only have second-neighbor V_{Ni}'s, making vacancy-solute interactions much smaller. Therefore it is plausible that isolated indium solutes in Ni-poor NiAl may reside on a TM-site but that the energy will be reduced when it moves to an Al-site with one or more neighboring Ni-vacancies. Before turning to the extensions, we first review the model and its principal results.

THERMODYNAMIC MODEL

The model [1] considers binary compounds of arbitrary composition containing trace amounts of solute. This is in accord with PAC experiments, in which indium solute concentrations were about 10 parts-per-billion. We specialize the model here for an equiatomic compound AB whose crystal structure has one site per element (e.g. CsCl) and whose phase field has a finite width spanning the stoichiometric 1:1 ratio. We also ignore interstitial sites for defects or solutes in the following. The composition will be written $A_{1+2x}B_{1-2x}$, in which x indicates the deviation from stoichiometry and will be assumed to be fixed. Thus, intrinsic elementary defects to consider are antisite atoms A_β and B_α and vacancies V_α and V_β, in which subscripts identify A- and B-type sublattices. The concentration of solute is assumed to be sufficiently low that host element and intrinsic defect concentrations are undisturbed.

The model is based on development of an equation of constraint among concentrations of intrinsic defects. For the AB phase, the equation is found by methods of ref. [1] to be given by

$$2[B_\alpha]+(1-2x)[V_\alpha]+4x=2[A_\beta]+(1+2x)[V_\beta], \qquad (1)$$

in which square brackets indicate fractional concentrations of defects on the indicated sublattices. Additional relations among defect concentrations are obtained by considering the various combinations of elementary defects that can be thermally activated without altering the average composition. In the present instance, these include the antisite atom pair (A_β+B_α), Schottky vacancy pair (V_α+V_β), and triple defect ($2V_\alpha$+A_β). These three combinations can be formed by thermal activation, with equilibrium constants K respectively given by $K_{2A}=\exp(-G_{2A}/k_BT)=[A_\beta][B_\alpha]$, $K_{2V}=\exp(-G_{2V}/k_BT)=[V_\alpha][V_\beta]$, and

$K_3 = \exp(-G_3/k_BT) = [V_\alpha]^2[A_\beta]$ using the law of mass action. The *K*'s are expressed in terms of free energies of formation of the combinations, which in turn are sums of free energies of formation of the elementary defects, for example $G_{2A} = G(A_\beta) + G(B_\alpha)$. Eq. 1 can be rewritten in terms of a selected defect concentration using relations for the three *K*'s given above. This leads to a polynomial equation in the defect concentration of interest that in turn can be solved for given values of the *K*'s and *x*. For example, $[V_\alpha]$ is obtained by solution of the quartic equation

$$2\frac{K_{2A}}{K_3}[V_\alpha]^4 + (1-2x)[V_\alpha]^3 + 4x[V_\alpha]^2 - (1+2x)K_{2V}[V_\alpha] - 2K_3 = 0\,. \qquad (2)$$

It is easy to show from eq. 2 that $[V_\alpha]$ decreases monotonically with increasing *x*. Using above relations for the three *K*'s, $[B_\alpha]$ also decreases and $[A_\beta]$ and $[V_\beta]$ increase monotonically with *x*.

Partition of a solute *S* between the two substitutional sites is established by reactions that transfer the solute from one site to the other. Thus, for example,

$$S_\beta + A_\alpha \to S_\alpha + A_\beta\,, \qquad K_a = \frac{[S_\alpha]}{[S_\beta]}[A_\beta] = \exp(-G_a/k_BT)\,, \qquad (3)$$

in which the equilibrium constant K_a is again obtained using the law of mass action. From eq. 3, the ratio of site-fractions of solute S on sublattices β and α is found to be

$$R_\alpha^\beta \equiv \frac{f_\beta}{f_\alpha} = \frac{[S_\beta]}{[S_\alpha]} = [A_\beta]\exp(+G_a/k_BT) = \frac{[V_\beta]}{[V_\alpha]}\exp(+G_b/k_BT)\,. \qquad (4)$$

The last result on the right is an example of an alternate expression obtained using the transfer reaction: $S_\beta + V_\alpha \to S_\alpha + V_\beta$. 'Free energies of transfer' such as G_a can be written in terms of energies of formation of the elementary defects, for example $G_a = G(S_\alpha) - G(S_\beta) + G(A_\beta)$.

Site-fraction ratios R_α^β are illustrated in Figure 1 (left) under the assumption that only triple-defects are thermally activated to an appreciable concentration, using G_3= 1.6 eV and a range of values of G_a. As can be seen, the ratios increase monotonically with *x*, in the same way as $[A_\beta]$, and, on a logarithmic scale, increase step-wise near stoichiometry. The dashed horizontal line indicates the unity ratio. Vertical positions of the R_α^β curves are controlled by solute site energies via G_a. Observed trends demonstrate a universal tendency for solutes to prefer the site of the element in which there is a deficiency. A solute whose R_α^β crosses unity will be observed to switch sites as the composition changes (see, e.g., curves for G_a= 0.4-1.2 eV in the figure.) Since there is only one type of site for each host element, $R_\alpha^\beta = f_\beta/f_\alpha = f_\beta/(1-f_\beta)$, which one can solve to obtain $f_\beta = R_\alpha^\beta/(1+R_\alpha^\beta)$. Obviously, f_β is close to 1 or 0 for R_α^β much greater or less than 1. Composition dependences of f_β corresponding to ratios in Figure 1 (left) are shown in Figure 1 (right). As can be seen, solutes are found on the α-site for x<0 and the β-site for x>0 for intermediate values of G_a, whereas for G_a<0 or G_a >1.6 eV, solutes are found on the α- or β-site, respectively, independent of composition.

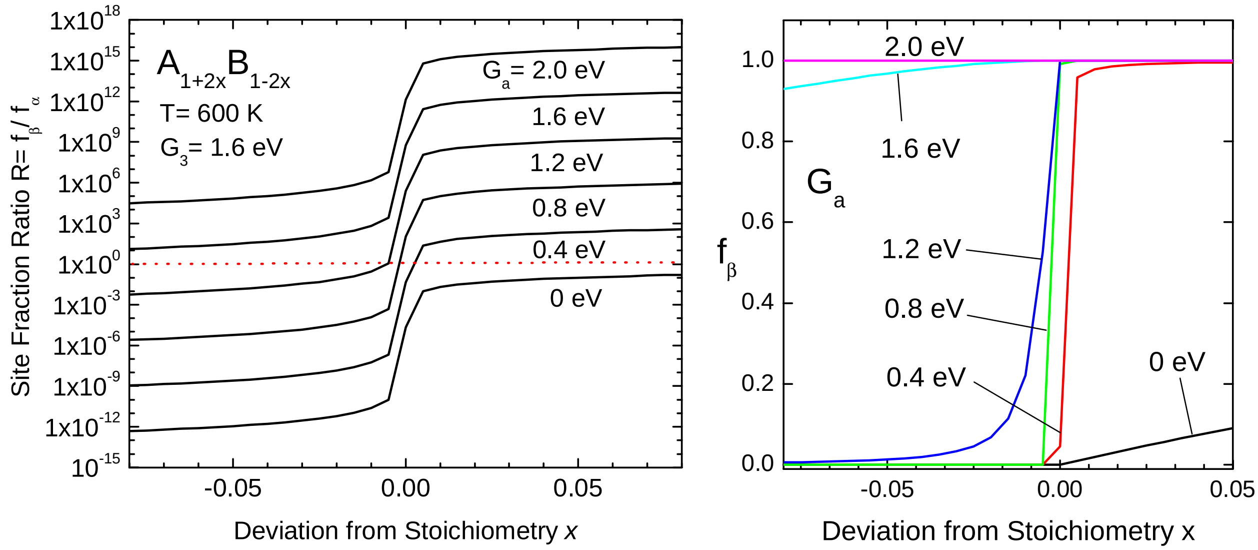

Figure 1. Site preferences of a solute on sites β and α in the CsCl phase at 600 K as a function of the deviation from stoichiometry. Thermal activation of triple defects with a formation energy G_3= 1.6 eV is assumed. (Left) Logarithmic plot of site-fraction ratio, with curves shown for six values of the transfer energy G_a between 0 and 2.0 eV. (Right) Fractions of solutes on β-site derived from data shown in figure at left.

Influence of Lattice Sinks

It may be energetically favorable for a solute to sit at a 'sink' such as the surface, an interface, grain boundary or dislocation. We shall model this phenomenon assuming the presence of one kind of sink that contains both A- and B-type sites that are normally occupied solely by A and B atoms. Equilibration of the solute between substitutional and sink sites can in that case take place via the following exchange reactions:

$$S_\alpha + A_A \rightarrow S_A + A_\alpha, \qquad K_A = [S_A]/[S_\alpha] = \exp(-G_A / k_B T), \tag{5}$$

and

$$S_\beta + B_B \rightarrow S_B + B_\beta, \qquad K_B = [S_B]/[S_\beta] = \exp(-G_B / k_B T), \tag{6}$$

in which upper-case subscripts refer to A- and B-type sites in sinks. With solutes partitioned among substitutional and sink sites, the site fraction of all solutes in sinks is given by

$$f_{\text{sink}} \equiv \frac{N_A[S_A] + N_B[S_B]}{N_A[S_A] + N_B[S_B] + N_\alpha[S_\alpha] + N_\beta[S_\beta]} = \frac{c_1 + c_2[A_B]}{c_1 + c_2[A_B] + c_3 + c_4[A_B]}, \tag{7}$$

in which the rightmost member of the equation is obtained after algebraic manipulation to show the functional dependence of f_{sink} on defect concentrations at a fixed temperature. The four coefficients c_1-c_4 depend on equilibrium constants and on the total numbers of sites N in the lattice and sinks. Examination of eq. 7 for ranges of the coefficients shows that f_{sink} may be large for x>0 or x<0 and small in the other range, be close to one or zero for all x, or have a constant value $0<f_{sink}<1$ independent of x. Thus, this simple model accommodates a wide range of possibilities. In particular, it can explain the observation that indium solutes switch in aluminide Ni_2Al_3 phases from a substitutional site for TM-rich compositions to a sink site for TM-poor compositions. Recalling that $[A_\beta]$ increases monotonically with increasing x, this scenario will occur, e.g., if c_1 and c_4 are large and c_2 and c_3 can be neglected. Inclusion of interstitial sites for defects and solutes in the model would introduce an additional term in the denominator of eq. 7 equal to $c_5[V_\alpha]^{-1}$, with which it is even possible for f_{sink} to have a maximum value close to x=0. This scenario may be relevant for small solute atoms near stoichiometric compositions.

Influence of Defect Interactions

In some systems, interactions between defects and solutes may be strong enough to modify site preference behavior. Consider a binary compound of composition $A_{1+2x}B_{1-2x}$ having the CsCl structure, with atoms of one element surrounded by atoms of the other. Let us suppose that solutes on site β interact with near-neighbor α-vacancies to form complexes ($S_\beta V_\alpha$) with association energy G_{SV}:

$$(S_\beta V_\alpha) \rightarrow S_\beta + V_\alpha, \qquad K_{SV} = \exp(-G_{SV}/k_B T) = \frac{[S_\beta][V_\alpha]}{[(S_\beta V_\alpha)]}, \tag{8}$$

whereas solutes on site α experience no interactions with defects. The ratio of site-fractions of solutes on substitutional sites β and α is then

$$R_\alpha^\beta = \frac{[S_\beta]+[(S_\beta V_\alpha)]}{[S_\alpha]} = \frac{[S_\beta]}{[S_\alpha]}(1+[V_\alpha]K_{SV}^{-1}) = [A_\beta]K_a^{-1}(1+[V_\alpha]K_{SV}^{-1})\,. \tag{9}$$

For definiteness, let us further assume that defect combinations apart from the triple defect have high formation energies and that their concentrations can be neglected. Approximate forms for defect concentrations can then be obtained from eq. 2 and from the reaction for formation of the triple defect: for x<<0, $[A_\beta] \cong K_3/16x^2$ and $[V_\alpha] \cong 4x$, and for x>>0, $[A_\beta] \cong 2x$ and $[V_\alpha] \cong \sqrt{2x/K_3}$. Interesting is the scenario for x<0 in which the solute prefers the β-site when associated with a vacancy, but the α-site otherwise. Inserting the concentration approximations for x<<0 given above into eq. 9 leads to the site-fraction ratio

$$R_\alpha^\beta \cong K_3 K_a^{-1}/16x^2 + K_3 K_a^{-1} K_{SV}^{-1}/4x \qquad \text{(x<0)}. \tag{10}$$

For this scenario to occur, the first term in eq, 10 must be small and the second large. At low temperature, this will arise if $G_a - G_3 < 0$ and $G_a + G_{SV} - G_3 > 0$. For NiAl, G_3~ 1.6 eV and G_{SV} =0.20 eV for an indium solute [3,5]. For $G_a = G(S_\alpha) - G(S_\beta) + G(A_\beta)$ in the range 1.4 to 1.6 eV, the solute will be stabilized on the β-site by a near-neighbor vacancy but reside on the α-site when isolated. For G_a>1.6 eV, the solute will reside on the β-site independent of the composition or of its local surroundings. For G_a<1.4 eV, the solute will always sit on the α-site. Results of a simulation of site fractions f_β for G_3= 1.6 eV, G_a=1.2 eV and four different values of G_{SV} from 0 and 0.6 eV are shown in Figure 2. The figure demonstrates that modest interactions can lead to large transfers of solute from one site to another, although fortuitous values of formation and transfer energies may be required. The PAC experiments on In solutes in Ni-poor NiAl exhibit signals interpreted in terms of one or more Ni-vacancies trapped simultaneously in the closest atomic shell [4], with binding energies of each vacancy in the range 0.15-0.2 eV. The two possible substitutional lattice sites of In probes without near-neighbor Ni-vacancies cannot be resolved in PAC experiments because both sites have cubic point symmetry. One can therefore conclude that $G_a > G_3 - G_{SV} \approx 1.4$ eV for indium solutes in NiAl.

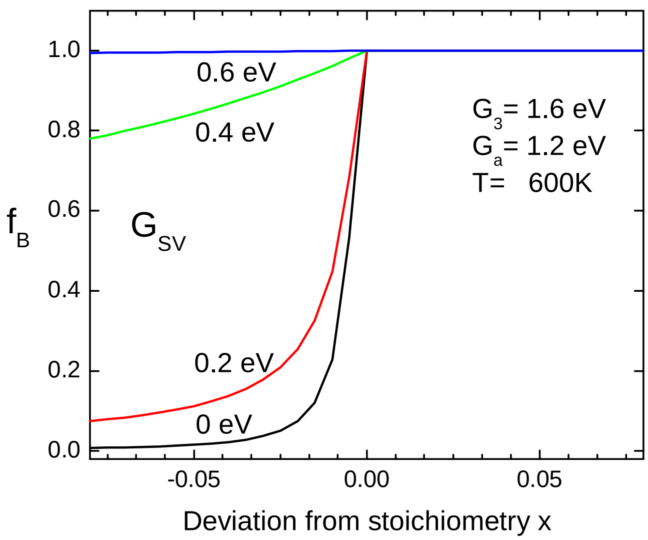

Figure 2. Site fraction of solutes on the β-site in the CsCl phase $A_{1+2x}B_{1-2x}$ as a function of *x* for four selected values of the interaction energy G_{SV} between a solute and a near-neighbor vacancy. In the absence of interaction, the solute switches to the α-site for x<0. In the presence of strong interactions, trapped vacancies stabilize the solute on site β for all compositions. Note that there is a high concentration of structural vacancies for x<0.

SUMMARY

A thermodynamic model for site selection of solutes in compounds developed in ref. [1] was extended in two ways. First, the model was generalized to treat solutes that might occupy a sink site (such as in a grain boundary) as well as regular lattice sites. A simple mechanism for equilibration of solutes among sink and lattice sites was found to accommodate a wide range of behaviors. The model provides a qualitative explanation of observations obtained from PAC experiments on aluminide phases having the Ni_2Al_3 structure. Second, the effect of interactions between solutes and defects on solute site preference was examined. It was found that defect interactions can induce solutes to switch sites, and the energy conditions under which this can happen were explored.

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