

SITE PREFERENCE MODEL FOR HYPERFINE IMPURITIES IN COMPOUNDS

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A thermodynamic model for site preferences of solute atoms in ordered binary phases is applied in this paper for substitutional and interstitial sites of the Cu_3Au , or $L1_2$, structure. Site preferences are found to depend on formation energies of combinations of elementary point defects and on energies for transfer of solutes among different sites. The composition dependence in compounds having a wide phase field is examined in detail. A phenomenology of site preference behavior is outlined for regular lattice sites as well as for non-lattice sites such as grain boundaries.

Lattice locations of impurity probes used in hyperfine measurements are often not well known. Frequently, signals are attributed to particular sites based on simple comparisons of atomic volumes and charges of solute and host atoms. However, such comparisons are simplistic because site-preferences can change with composition, especially near stoichiometry [1]. The present work was motivated by perturbed angular correlation studies showing that In probes in five phases having the Ni_2Al_3 structure switch sites in a narrow composition range near the 40:60 ratio [1]. To interpret the measurements, we developed a thermodynamic model [2]. The model was applied in [2] for substitutional and interstitial sites in a binary 1:1 phase such as CsCl (B2) and for substitutional and empty-lattice sites in the Ni_2Al_3 structure. In the present paper, it is applied for the Cu_3Au ($L1_2$) structure. The model is more general than earlier models restricted to substitutional sites [3].

Lattice locations occupied by impurity probes can in principle be distinguished through hyperfine interactions. In particular, electric-field gradients at sites depend on local point symmetries. Consider the A_3B (Cu_3Au) structure shown in the inset of Fig. 1. The structure has three equivalent α -sublattices and one β -sublattice, normally occupied by A-atoms and B-atoms, respectively. In addition, the unit cell has four octahedral interstitial sublattices, of which one is surrounded by a regular octahedron of 6 A-atoms and the three others are equivalent sites surrounded by distorted octahedra of 4 A-atoms and 2 B-atoms (designated as sites τ). For simplicity in the following, we will assume that the regular-octahedral interstitial site remains unoccupied in systems of interest and can be ignored. The three sites of interest are then the α and distorted-octahedral sites τ , both having tetragonal point symmetry, and the β -site, having cubic point symmetry. Hyperfine measurements should therefore reveal no quadrupole interaction for solutes on β -sites and two distinct, axially-symmetric quadrupole interactions for probes on α or τ sites. This approach has been used for example to determine the substitutional sites occupied by ^{181}Hf in Ni_3Al [4] and by ^{111}In in Fe_3Sn [5] using PAC.

Defect concentrations. Consider a compound of composition $\text{A}_{3+4x}\text{B}_{1-4x}$, in which x marks the deviation from the stoichiometric 75:25 composition. Our approach is to develop an equation of constraint among defect concentrations for the phase and composition in question and to use the law of mass action to describe defect formation and solute transfer among sites [2]. Here, six elementary defects are considered: vacancies and antisite atoms on the two substitutional sublattices and host atoms on the interstitial sublattice. Subscripting the atom or defect symbol by the sublattice on which it sits, of the six defects, three (V_α , B_α , B_τ) are possible structural defects in B-rich compounds ($x < 0$) and three others (V_β , A_β , A_τ) in A-rich compounds ($x > 0$). The equation of constraint is derived from the specified ratio of

elements and numbers of sublattices. For $A_{3+4x}B_{1-4x}$, with the three sites of interest given above, and for a negligible solute concentration, it is found by methods of ref. 2 to be:

$$3[B_\alpha] + 3(\frac{1}{4} - x)[V_\alpha] + 3(\frac{3}{4} + x)[B_\tau] + 4x = [A_\beta] + (\frac{3}{4} + x)[V_\beta] + 3(\frac{1}{4} - x)[A_\tau], \quad (1)$$

in which opposing structural defects have been grouped on opposite sides of the equation. Thermal defects are created in combinations of opposing structural defects that preserve composition. Out of 3x3 possible combinations, five are listed in Table 1 with their formation reactions out of the perfect lattice (0). Also given are expressions of equilibrium constants for the formation reactions in terms of powers of concentrations of the constituent elementary defects. (Concentrations are defined with respect to the total number of sites on a sublattice.) The 4-vacancy is the generalization of the Schottky defect in an elemental solid and the 5-defect is one of two types of mixed vacancy-antisite combinations. The four remaining defect combinations can be derived from the five listed in the table.

Table 1.
Equilibrium defect combinations in the A_3B structure (Cu_3Au , $L1_2$.)

Equilibrium defect	Formation reaction	Equilibrium constant
4-vacancy	$0 \rightarrow 3V_\alpha + V_\beta + uc$	$K_{4V} = [V_\alpha]^3 [V_\beta] = \exp(-G_{4V} / k_B T)$
Antisite pair	$0 \rightarrow A_\beta + B_\alpha$	$K_{2A} = [A_\beta][B_\alpha] = \exp(-G_{2A} / k_B T)$
5-defect	$0 \rightarrow 4V_\alpha + A_\beta + uc$	$K_5 = [V_\alpha]^4 [A_\beta] = \exp(-G_5 / k_B T)$
Frenkel-A	$0 \rightarrow A_\tau + V_\alpha$	$K_{2FA} = [A_\tau][V_\alpha] = \exp(-G_{2FA} / k_B T)$
Frenkel-B	$0 \rightarrow B_\tau + V_\beta$	$K_{2FB} = [B_\tau][V_\beta] = \exp(-G_{2FB} / k_B T)$

The dominant defect combination will generally be the one having the lowest free-energy of formation per defect and will be comprised of elementary defects that appear as structural defects on opposing sides of the stoichiometric composition at low temperature. The notation $+uc$ indicates reactions in which a new unit cell is created. Free-energies of defect formation are equal to sums of energies of the constituent defects plus, if a new unit cell is formed, the (negative) cohesive energy of a unit cell; e.g., $G_{4V} = 3G(V_\alpha) + G(V_\beta) + G_{uc}$. Equation 1 can be reexpressed as a polynomial equation in the concentration of any selected elementary defect using formation reactions in Table 1. For a given set of K 's and x , the resulting equation can be solved to obtain the defect concentration, after which the others can be obtained using mass-action relations given in Table 1.

Solute site fractions. Equilibration of solutes S among sites takes place through transfer reactions such as

$$S_\beta + A_\alpha \rightarrow S_\alpha + A_\beta, \quad K_a = \frac{[S_\alpha]}{[S_\beta]} [A_\beta] = \exp(-G_a / k_B T), \quad (3)$$

in which $[S_\alpha]$ is the fractional concentration of solute on the α -sublattice, etc. The energy of solute transfer can be seen to be $G_a = G(S_\alpha) - G(S_\beta) + G(A_\beta)$. A second transfer reaction is

$$S_\alpha \rightarrow V_\alpha + S_\tau, \quad K_d = \frac{[S_\tau]}{[S_\alpha]} [V_\alpha] = \exp(-G_d / k_B T), \quad (4)$$

in which $G_d = G(S_\tau) - G(S_\alpha) + G(V_\alpha)$. Site-fraction ratios R can now be expressed in terms of defect concentrations and equilibrium constants for transfer reactions:

$$R_\alpha^\beta \equiv \frac{f_\beta}{f_\alpha} = \frac{[S_\beta]}{3[S_\alpha]} = \frac{1}{3}[A_\beta]K_a^{-1} = \frac{1}{3}\frac{[V_\beta]}{[V_\alpha]}K_b^{-1}; \tag{5}$$

$$R_\tau^\alpha \equiv \frac{f_\alpha}{f_\tau} = \frac{[S_\alpha]}{[S_\tau]} = [V_\alpha]K_d^{-1}, \quad R_\tau^\beta \equiv \frac{f_\beta}{f_\tau} = \frac{[S_\beta]}{3[S_\tau]} = \frac{1}{3}[V_\beta]K_e^{-1}. \tag{6}$$

In eqs. 5 and 6, equilibrium constants not previously defined come from other solute transfer reactions, with $G_b = G(S_\alpha) - G(S_\beta) + G(V_\beta) + G(V_\alpha)$ and $G_e = G(S_\tau) - G(S_\beta) + G(V_\beta)$. Site fractions themselves are obtained from a complete set of site-fraction ratios; for example,

$$f_\beta = \frac{1}{1 + 1/R_\alpha^\beta + 1/R_\tau^\beta}. \tag{7}$$

Site-preference behavior is therefore completely specified by a set of defect energies, the cohesive energy of the unit cell, the composition (x), solute site energies, and temperature.

Numerical simulation. To illustrate possible behavior, defect concentrations and site preferences are simulated at 800 K using the set of energy parameters: $G(V_\alpha)$, $G(V_\beta)$, $G(A_\beta)$, $G(B_\alpha)$, $G(A_\tau)$, $G(B_\tau)$, $G_{uc} = 5.0, 6.0, 0.5, 2.0, -3.0, -3.0, -18.2$ eV, for which G_{4V} , G_{2A} , G_5 , G_{2FA} , G_{2FB} are, respectively, 2.8, 2.5, 2.3, 2.0, 2.3 eV. The reference state for an atom or solute is when it is removed to infinity, so that vacancy formation energies are large and positive because of the energy needed to break bonds and interstitial formation energies are negative due to bond formation. At 0.46 eV per defect, the 5-defect is the combination having the lowest formation energy, and predominant defect concentrations at low and moderate temperatures are accordingly found to be $[V_\alpha] \cong \frac{16}{3}|x|$ for $x < 0$ and $[A_b] \cong 4x$ for $x > 0$. Site preferences were simulated using equal energies for a solute on α and β sites and a smaller

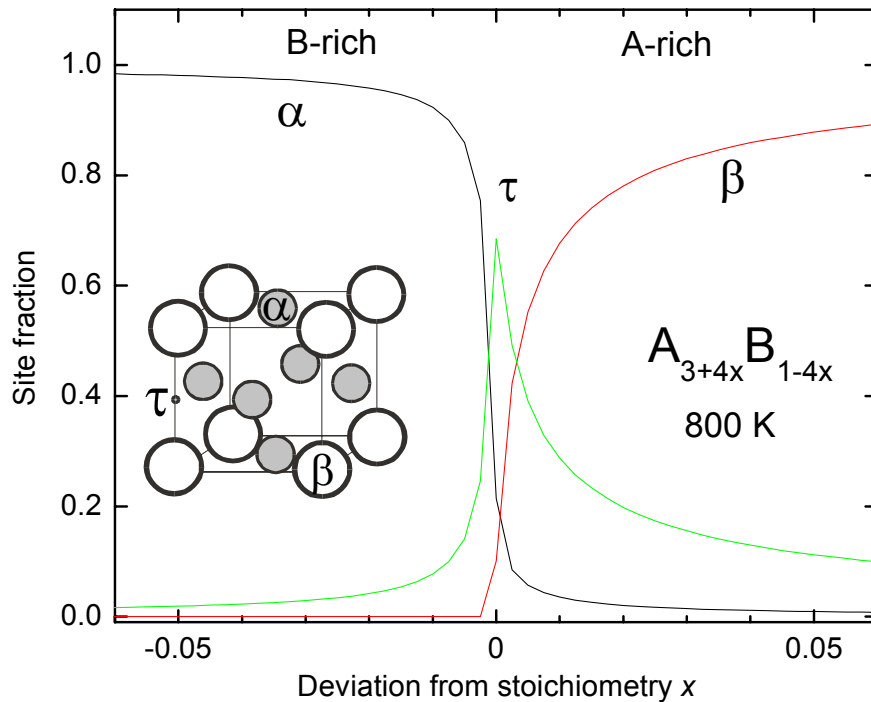


Figure 1. Solute site fractions as a function of composition in $A_{3+4x}B_{1-4x}$ at 800 K. The inset shows the crystal structure, with substitutional sites α and β , and interstitial sites τ located at centers of the cube edges.

interstitial site energy: $G(S_\alpha) = G(S_\beta) = G(S_\tau) + 4.7eV$ Fig. 1 shows results as a function of composition. As can be seen, the solute locates primarily on the β -sublattice for $x > 0$, on the α -sublattice for $x < 0$, and on the τ -sublattice close to the stoichiometric composition.

Discussion. The phenomenology of site-preference behavior is now summarized.

1. Monotonic variations of substitutional fractions f_α and f_β with composition. Eq. 7 and a similar equation for f_α can be written directly in terms of defect concentrations: $f_\beta = 1/(1 + 1/K_a^{-1}[A_\beta] + 3/K_e^{-1}[V_\beta])$, $f_\alpha = 1/(1 + K_a^{-1}[A_\beta] + 1/K_d^{-1}[V_\alpha])$. f_β will tend to be larger when $[A_\beta]$ or $[V_\beta]$ is large, that is, for $x > 0$ where A_β or V_β are possible structural defects. Similarly, f_α will be large if $[A_\beta]$ is small and if $[V_\alpha]$ is large, that is for $x < 0$. Because of the monotonic variations of defect concentrations with x , f_α or f_β likewise can only vary monotonically with x . These features are illustrated in the figure.
2. Preference for interstitial or empty-lattice sites at stoichiometry. The interstitial site-fraction can be written $f_\tau = 1/(1 + K_d^{-1}[V_\alpha] + K_e^{-1}[V_\beta])$. It will be large when $[V_\alpha]$ and $[V_\beta]$ are both small, which as shown in Fig. 1 can occur near the stoichiometric composition since the vacancy species are structural defects on opposing sides of the stoichiometric composition whose concentrations increase with the deviation from stoichiometry. Alternatively, one term in the denominator may remain much less than one for all compositions, in which case f_τ may remain large on only one side of stoichiometry.
3. Generality of results. The trends described above are found to be independent of crystal structure or of the types of structural or thermal defects present in a particular phase.
4. Inequivalent sites for an element. Solute exchange between inequivalent sublattices of the same element leads to a site-fraction ratio that is independent of composition. For example, the Ni_2Al_3 structure has two sublattices β_1 and β_2 with relative numbers of sites 1:2, for which the site-fraction ratio is $R_{\beta_1}^{\beta_2} \equiv f_{\beta_2} / f_{\beta_1} = 2 \exp(+ (G(S_{\beta_1}) - G(S_{\beta_2})) / k_B T)$.
5. Existence and observability of site-switching. Whether a solute switches sites depends on solute-transfer and defect-formation energies. When solute site-energies sufficiently favor one site, its site fraction will dominate for all compositions. Consider the simple situation in which only substitutional sites are occupied in the A_3B structure. If either the antisite-pair or 5-defect is dominant, it can be shown that (i) solutes will exclusively occupy β -sites when $G_a > G_{2A}$ or G_5 , (ii) solutes will switch from β -sites for $x > 0$ to α -sites for $x < 0$ if $0 < G_a < G_{2A}$ or G_5 , and (iii) solutes will occupy only α -sites if $G_a < 0$. Such conditions can still be specified when more than two sites are available. Site-switching can be observed only if the width of the phase field is finite and overlaps the composition range in which site-switching would occur theoretically.
6. Competing non-lattice sites. In addition to regular lattice sites, solutes may occupy sites in lattice sinks such as grain boundaries, interfaces or dislocations. Using a simple thermodynamic model for sites in a lattice sink that allows for exchange reactions between solutes on regular crystal sites and in the lattice sink, it can be shown that a wide variety of site preference behavior is possible, including large site fractions in lattice sinks for either $x > 0$, $x < 0$, all x , or with a maximum near $x = 0$, just as for interstitial sites.

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