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Vacancies in ordered and disordered binary alloys treated with the cluster expansion

A. Van der Ven and G. Ceder
Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

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First-principles investigations of the thermodynamics of binary alloys using a cluster expansion have so far neglected the presence of vacancies. Here, we invoke a local cluster expansion as a perturbation to the standard binary cluster expansion to model the equilibrium vacancy concentration in a binary alloy as a function of temperature and alloy composition. We apply this approach to a first-principles investigation of the fcc $Al_{1-x}Li_x$ alloy (for x less than 0.3) which at $x=0.25$ exhibits $L1_2$ superstructure ordering. The equilibrium vacancy concentration is predicted to be sensitive to the bulk alloy composition x in the ordered $L1_2$ phase, varying by more than an order of magnitude in a narrow interval of x at intermediate temperatures. Both in the solid solution and in the ordered $L1_2$ phase, the vacancy prefers a nearest neighbor shell rich in aluminum. In the $L1_2$ ordered phase, the vacancy predominantly occupies the lithium sublattice. The type of short-range order around a vacancy should affect the mobility of the constituents of the alloy and hence its interdiffusion coefficient.

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I. INTRODUCTION

Most crystalline solids contain vacancies. While vacancies are often not favored energetically, they nevertheless exist because of configurational entropy. The presence of vacancies plays a crucial role in determining important properties of a solid. Atomic migration in many solids occurs by exchanges with vacancies with the resulting diffusion coefficient often proportional to the vacancy concentration. The existence of vacancies is also key in creep phenomena and in the annealing out of dislocations of work hardened metals. It is well known that the vacancy concentration in pure metals or stoichiometric oxides depends exponentially on the vacancy formation energy ΔE^V (typically positive) according to $e^{-\Delta E^V/kT}$ where k is the Boltzmann constant and T is the temperature.

In alloys with configurational disorder among its constituents, varying degrees of long- and short-range order can exist as a function of temperature and alloy composition. ΔE^V will then depend on the local arrangement of the different atoms around the vacant site. The vacancy may, for example, prefer to be surrounded by one particular specie over the others. Hence the vacancy concentration should be a function of the alloy composition as well as the degree of short range order.

The cluster expansion developed for alloy theory[1,2] is becoming an invaluable tool for predicting the thermodynamic properties of multicomponent solids from first-principles. This technique has enabled the first-principles prediction of alloy phase diagrams[3–11] and equilibrium short range order.[13] The cluster expansion offers a computationally tractable link between accurate first-principles calculations of total energies and statistical mechanics techniques for multicomponent solids. In studies of metallic alloys though, the role of vacancies are frequently neglected. For bulk thermodynamic properties, this is a reasonable approximation since the small vacancy concentrations in metals contribute negligibly to the free energy. Nevertheless, kinetic properties such as diffusion coefficients are much more sensitive to the equilibrium vacancy concentration.

In this paper, we investigate the vacancy concentration dependence on temperature and alloy concentration in the fcc based Al-Li alloy from first-principles using the cluster expansion formalism. To this end, we introduce a local cluster expansion technique to model the configuration dependent vacancy formation energy and combine it with the traditional binary cluster expansion for the vacancy-free alloy.

At low Li composition x, $Al_{1-x}Li_x$ alloys are stable in the fcc structure. Stoichiometric LiAl forms a superstructure ordering on the bcc lattice. At $x=0.25$ the alloy is metastable in the $L1_2$ phase (also referred to as δ') which is an ordered superstructure of fcc. Precipitation of δ' is exploited in thermomechanical hardening of dilute Al-Li alloys for aerospace applications.[14] The study of the order-disorder transformation in dilute fcc Al-Li alloys, which leads to δ'-phase formation, has been the subject of much investigation, both experimentally and theoretically.[15,16,3,7,17–19] The most rigorous first-principles study of phase stability in the Al-Li alloy was performed by Sluiter *et al.*[7] by implementing cluster expansions in combination with the cluster variation method (CVM) to calculate finite-temperature free energies. Theoretical treatments of the kinetics of δ' precipitation have typically relied on phase-field continuum models which requires as input interdiffusion coefficients.[17–19] Knowledge of the equilibrium vacancy concentration is a first step in arriving at diffusion coefficients from first-principles.

II. LOCAL CLUSTER EXPANSION FOR VACANCIES

A cluster expansion for a binary alloy such as Al-Li can be viewed as a generalized Ising model[1,2] where occupation variables σ_i are assigned to each crystallographic site i and take the value +1 (−1) if a Li (Al) atom resides at that site. The vector of all occupation variables corresponding to the different sites of the crystal, $\vec{\sigma}$, then uniquely characterizes

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the configuration of Li and Al atoms on the parent crystal structure. Furthermore, the occupation variables σ_i allow a convenient expansion of the configurational energy of a binary alloy in terms of polynomials, ϕ_α, of σ_i according to[1]

$$E(\vec{\sigma}) = V_o + \sum_{\alpha} V_\alpha \phi_\alpha(\vec{\sigma}). \tag{1}$$

Each polynomial basis function in the expansion, ϕ_α is simply the product of occupation variables belonging to a particular cluster of sites, α, in the crystal, i.e., $\phi_\alpha = \Pi_{i\in\alpha}\sigma_i$. The coefficients of the polynomial basis functions V_α, called effective cluster interactions (ECI), are fit to accurate first-principles energy values calculated for a variety of different arrangements of Li and Al atoms on the crystal. In this way, a cluster expansion for a particular parent crystal structure enables an accurate and rapid extrapolation of first-principles energy values for a few atomic arrangements to the energy of any arrangement of atoms on that parent crystal structure. This feature is invaluable for the calculation of thermodynamic properties of an alloy using Monte Carlo simulations.

Accounting for the presence of vacancies in a binary alloy such as Al-Li brings with it an extra level of complexity as the problem then becomes a ternary one. The occupation variable σ_i, in addition to having values of +1 (for Li) and −1 (for Al) can now also be 0 if a vacancy occupies site i. We can simplify the problem by taking advantage of the fact that vacancies are present in very dilute concentrations and are typically far enough from each other within the solid that vacancy-vacancy interactions can be neglected. The presence of vacancies in the Al-Li crystal can then be treated as a perturbation to the binary problem, whereby the energy of introducing a vacancy to the crystal only depends on the local Al-Li arrangement. This dependence can be captured with a local cluster expansion, similar to that used to describe the environment dependence of local magnetic moments,[20] local vibrational modes,[21] and activation barriers for diffusion.[22]

While in a single component solid, the vacancy formation energy can be unambiguously defined as the difference in energy of the crystal with and without a vacancy, this is not true in a multicomponent solid. Indeed, in a multicomponent solid it is not clear which specie initially occupied the site before introduction of a vacancy there. Therefore a convenient quantity to parameterize with the local cluster expansion is an *effective vacancy formation energy* (EVFE)

$$\Delta E_i^{eff} = E_i^V(\vec{\sigma}) - \frac{1}{2}[E_i^{\mathrm{Al}}(\vec{\sigma}) + E_i^{\mathrm{Li}}(\vec{\sigma})], \tag{2}$$

where $E_i^V(\vec{\sigma})$ is the energy of the crystal with configuration $\vec{\sigma}$ but with a vacancy occupying site i and $E_i^{\mathrm{Al}}(\vec{\sigma})$ $[E_i^{\mathrm{Li}}(\vec{\sigma})]$ is the energy of the crystal with configuration $\vec{\sigma}$ but with site i occupied by Al (Li). The quantity $(1/2)[E_i^{\mathrm{Al}}(\vec{\sigma})+E_i^{\mathrm{Li}}(\vec{\sigma})]$ of Eq. (2), which is an average energy, does not depend on whether Li or Al occupies site i. As a result, ΔE_i^{eff} depends on the configuration of Li and Al atoms *around* site i and can therefore be described with a local cluster expansion.

The quantity that is of relevance for purposes of determining the equilibrium vacancy concentration and short range order around vacancies with Monte Carlo techniques is the total energy of the solid for any arrangement of Al, Li, and dilute vacancies. Hence if a vacancy occupies site i, the energy $E_i^V(\vec{\sigma})$ of the crystal can be calculated by rearranging Eq. (2) and then evaluating the local cluster expansion describing ΔE_i^{eff} and the conventional binary cluster expansion Eq. (1) to evaluate $(1/2)[E_i^{\mathrm{Al}}(\vec{\sigma})+E_i^{\mathrm{Li}}(\vec{\sigma})]$. Note that $(1/2)[E_i^{\mathrm{Al}}(\vec{\sigma})+E_i^{\mathrm{Li}}(\vec{\sigma})]$ is a quantity that can be conveniently calculated with the conventional binary cluster expansion by simply evaluating it with spin $\sigma_i=0$. It should be realized that ΔE_i^{eff} has little direct physical meaning, and is primarily introduced for mathematical convenience to characterize the configurational energy of a binary solid containing vacancies. The only restriction is that vacancies are sufficiently dilute so that interactions between them can be neglected.

III. FIRST-PRINCIPLES CLUSTER EXPANSIONS

A. Binary cluster expansion for fcc based Al-Li alloy

We determined the ECI of a binary cluster expansion for fcc Al-Li by fitting to fully relaxed first-principles energy values of 71 different arrangements of lithium and aluminum atoms over the fcc crystal (no vacancies). The first-principles energy values were calculated within the local density approximation (LDA) with a plane-wave pseudopotential code (Vienna *Ab initio* Simulation Package VASP[23]) using ultrasoft pseudopotentials.[24] The fit of the ECI to the LDA energies was performed with a least-squares inversion procedure whereby the ECI of a truncated cluster expansion, Eq. (1), are adjusted to minimize the least-squares error between the actual first-principles energies and those predicted by the cluster expansion (the choice of clusters used in the truncated expansion was determined by minimizing the cross validation error in a manner similar to that suggested in Ref. 11). Since the fcc based Al-Li alloys are of importance only at low Li concentration (at higher composition, the alloy is stable on the bcc lattice), we gave the first-principles energies corresponding to low composition configurations more weight in the fit of the ECI.

Also included in the fit of the ECI were "spin flip energies," energy differences between a configuration in which a particular site i contains Li and the same configuration in which the Li at site i has been replaced by Al (or vice versa). These spin flip energies were obtained from LDA, pseudopotential calculations of supercells containing 108 atoms ($3\times3\times3$ supercell of the conventional cubic fcc unit cell). Spin flip energies used in the fit included lowest order excitation energies in dilute Al and in $\mathrm{L1_2}$ $\mathrm{LiAl_3}$. Fitting to flip energies biases the cluster expansion to accurately reflect the lowest order excitation energies which play an important role in determining the thermodynamics of the solid at low temperature, especially within the ordered $\mathrm{L1_2}$ phase.

The ECI and their corresponding clusters for binary fcc Al-Li are illustrated in Fig. 1. The cluster expansion contains the first five nearest neighbor pair clusters and eight triplet clusters. As a measure of the accuracy of the cluster expan-

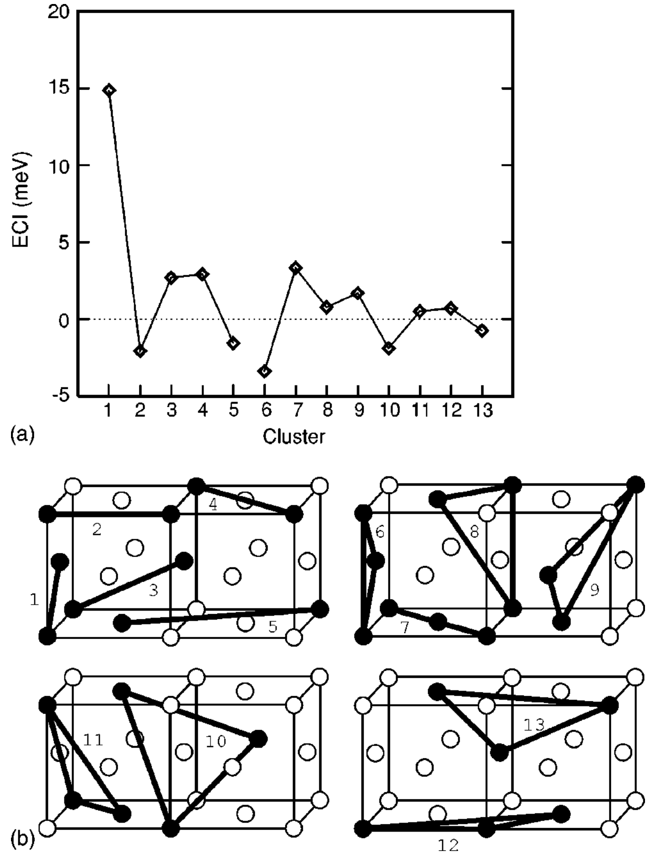

FIG. 1. Numerical values of the ECI (a) and corresponding clusters (b) of the cluster expansion of the fcc Al-Li alloy.

sion in the concentration range of relevance for fcc Al-Li, the root-mean-square difference between first-principles energies and cluster expanded energies for all structures used in the fit with composition between 0 and 0.35 is 5.6 meV per atom.

B. Local cluster expansion for vacancy in fcc based Al-Li alloy

The parameters of the local cluster expansion of the effective vacancy formation energies Eq. (2) were fit to the corresponding first-principles energy values for 23 different configurations around a vacancy. The first-principles energies were calculated in 108 atom supercells (107 atoms when a vacancy was present). The shortest distance between periodic images of the vacancy in the 107 atom supercells is of the order of 12 Å. For each supercell calculation, a 4×4×4 Monkhorst-Pack *k*-point mesh was used with a broadening parameter of 0.8 eV. Based on *k*-point convergence tests, we estimate the numerical error of the supercell calculations to be of the order of 50 meV, though due to cancellation of errors when taking differences, the numerical errors of the EVFEs should be smaller. Defect calculations in the supercells were performed at constant volume (using the volume of the closest perfectly ordered configuration), but all internal coordinates were fully relaxed. Note that for every effective vacancy formation energy for a particular arrangement of Li and Al atoms, three supercell calculations are needed, namely $E_i^V(\vec{\sigma})$ (supercell with a vacancy at site i), $E_i^{\mathrm{Al}}(\vec{\sigma})$ (supercell with Al at site i), and $E_i^{\mathrm{Li}}(\vec{\sigma})$ (supercell with Li at site i).

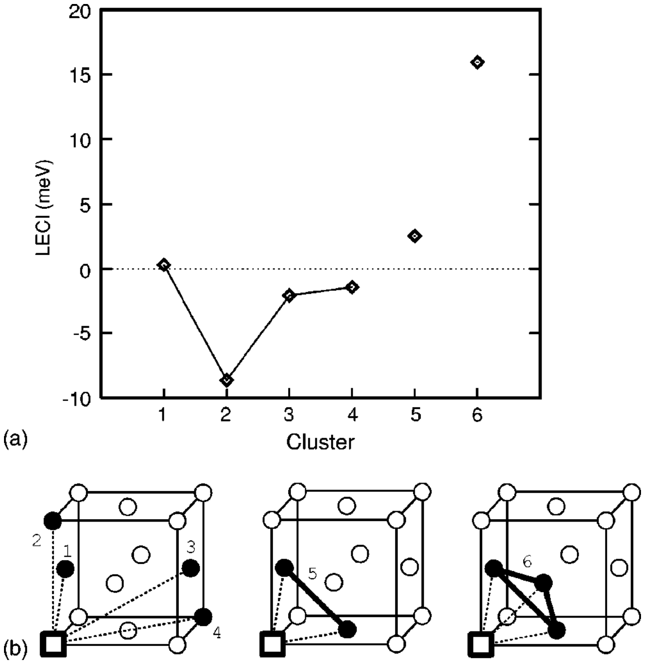

FIG. 2. Numerical values of the ECI (a) and corresponding clusters (b) of the local cluster expansion of the effective vacancy formation energy (EVFE) in the fcc Al-Li alloy. ($\sigma_i = +1$ if a Li occupies site i and -1 if Al occupies it.)

Figure 2 illustrates the ECI and the corresponding clusters for the local cluster expansion of the EVFE in fcc Al-Li. With the local cluster expansion for the EVFE and the binary cluster expansion of Fig. 1, it is possible to calculate the energy of any arrangement of Li, Al, and vacancies on the fcc lattice, provided the vacancies are separated far enough not to interact with each other. For example, the vacancy formation energy for pure Al is predicted from first-principles to be (calculated within a 107 atom supercell) 670 meV whereas the value predicted by combining the local and binary cluster expansions is 696 meV. Figure 3 illustrates the variation in energy of an isolated Li-V pair [Fig. 3(a)] and an isolated Li-Li pair [Fig. 3(b)] in pure aluminum as a function of their separation. The crosses (connected with a dashed line) correspond to the energy variation predicted from first-principles (as calculated in the 107/108 atom supercell) and the diamonds (connected with a solid line) correspond to the variation predicted with the cluster expansions. Table I compares first-principles and cluster expanded lowest order flip energies in the $L1_2$ ordered phase. Included are energy changes when replacing a Li atom on the Li sublattice of $L1_2$ by Al, $\delta E^{\mathrm{Al}}(\mathrm{Li})$, or by a vacancy, $\delta E^{V}(\mathrm{Li})$, and energy changes when replacing an Al atom on the Al sublattice of $L1_2$ by Li, $\delta E^{\mathrm{Li}}(\mathrm{Al})$, or by a vacancy, $\delta E^{V}(\mathrm{Al})$. Notice that the differences between first-principles values and the cluster expanded values are of the order of the numerical error of the first-principles supercell calculations as well as that of kT (k is the Boltzmann constant and T the absolute temperature) when T ranges between 300 and 800 K, the temperature interval of interest.

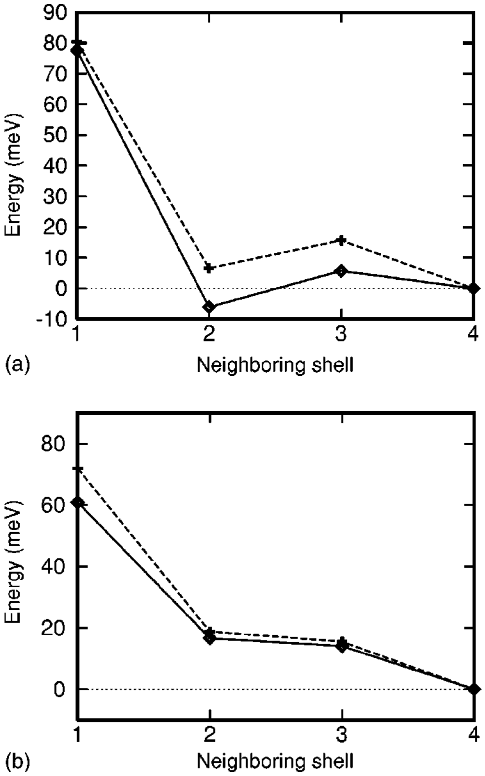

FIG. 3. Variation of the energy of an isolated (a) lithium-vacancy pair and (b) lithium-lithium pair in pure aluminum. The crosses connected by a dashed line are first-principles values (LDA, pseudopotential method) calculated within a 108 atom supercell and the diamonds connected by a solid line are values predicted with the cluster expansions of Figs. 1 and 2.

TABLE I. Comparison between cluster expanded and first-principles lowest order flip energies in the $L1_2$ ordered phase (meV). These are calculated as the change in formation energy of the solid (relative to fcc Al and fcc Li) when performing the flip.

	Cluster expanded	LDA, pseudopotential
Li→Al	584	609
Li→V	1021	1022
Al→Li	−112	−102
Al→V	955	965

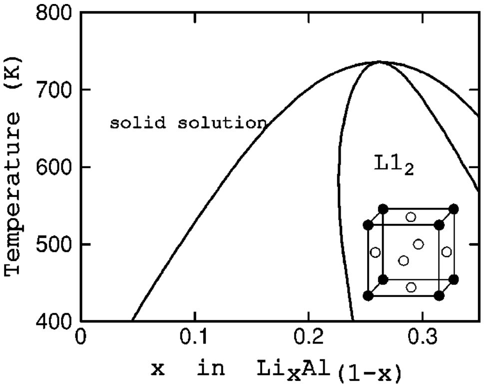

FIG. 4. Calculated fcc Al-Li phase diagram using the cluster expansion of Fig. 1.

C. Monte Carlo simulations

The binary and local cluster expansion were combined in Monte Carlo simulations to calculate equilibrium thermodynamic properties at finite temperature for the fcc Al-Li system. Monte Carlo simulations were performed in the grand-canonical ensemble. Only the binary cluster expansion was used to calculate the fcc Al-Li phase diagram (since vacancies are so dilute, they can be expected to have a negligible effect on the phase diagram). Both cluster expansions were used to calculate the equilibrium vacancy concentration and the short range order around a vacancy. At equilibrium, the chemical potential of a vacancy is zero as vacancies are not conserved. The grand canonical energy used in the Monte Carlo simulations takes the form

$$\Omega(\vec{\sigma}) = E(\vec{\sigma}) - N_{\mathrm{Al}}\mu_{\mathrm{Al}} - N_{\mathrm{Li}}\mu_{\mathrm{Li}}, \tag{3}$$

where N_{Al} and N_{Li} are the number of Al and Li atoms and μ_{Al} and μ_{Li} are their corresponding chemical potentials. The chemical potentials μ_{Al} and μ_{Li} are not independent but are related according to the Gibbs-Duhem relation

$$N_{\mathrm{Al}}d\mu_{\mathrm{Al}} + N_{\mathrm{Li}}d\mu_{\mathrm{Li}} = 0. \tag{4}$$

Hence in a grand canonical Monte Carlo simulation, one of the chemical potentials can be varied independently, and the other can be determined by integration of Eq. (4) (in a Monte Carlo simulation of a binary system without vacancies, the chemical potentials of Li and Al do not need to be known separately, only $\mu_{\mathrm{Li}}-\mu_{\mathrm{Al}}$ needs to be varied).

Since the local cluster expansion of the EVFE is valid only as long as vacancies are far enough apart that they do not interact with each other (this in itself depends on the extent of the cluster expansions), the Monte Carlo cell should only be so large so as to avoid the simultaneous occurrence of two vacancies in the same cell. For the temperature ranges considered here, we found that a $12\times12\times12$ cell was found small enough to effectively eliminate the occurrence of two vacancies in the Monte Carlo cell at the same time. To obtain suitably converged averages, between 200,000 and 400,000 Monte Carlo passes were needed (i.e., average number of times that each lattice site was considered for a spin flip in the Monte Carlo simulation).

IV. RESULTS AND DISCUSSION

The calculated binary fcc Al-Li phase diagram (calculated without including vacancies) in the aluminum rich region is illustrated in Fig. 4. The phase diagram was derived from free energies obtained from the binary Monte Carlo simulations (see, for example, Refs. 10 and 12). A two phase region separates a dilute solid solution of Al-Li from the $L1_2$ Al_3Li phase. Al_3Li is predicted to disorder at 735 K. The agreement between the calculated metastable phase diagram of this work and previous first-principles predictions by Sluiter *et al.*[7] is very good. In fact, even though different cluster expansions were used (through the use of different first-principles methods—LDA-pseudopotential method in this work versus LDA-LMTO ASA in Ref. 7—as well as differ-

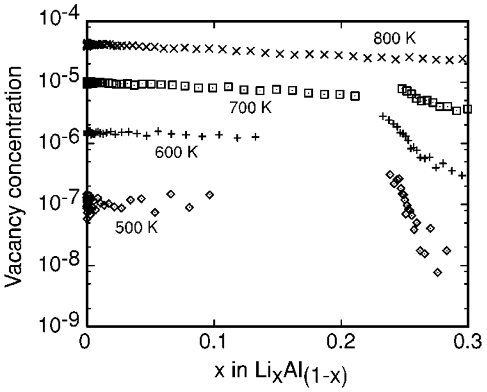

FIG. 5. Calculated vacancy concentration at different temperatures as a function of bulk concentration x in $Al_{(1-x)}Li_x$; 500 K (diamonds), 600 K (crosses), 700 K (squares), and 800 K (×'s).

ent basis functions for the cluster expansions), the predicted congruent ordering temperature and width of the two-phase region is very similar between the calculated metastable fcc phase diagram of this work and that of Sluiter *et al.*[7] The calculated metastable phase diagram is also qualitatively consistent with available experimental evidence.[25–27,15]

Figure 5 illustrates the calculated vacancy concentration as a function of x at different temperatures. Above the order-disorder transition temperature of $L1_2$, the vacancy concentration remains more or less constant as a function of x. Below the order-disorder transition, though, the vacancy concentration peaks slightly around $x=0.25$ at each temperature, but drops rapidly as the bulk concentration x is increased.

It is instructive to consider the equilibrium short range order around a vacancy in Al-Li. Figure 6(a) illustrates the fraction of lithium ions in the first four neighboring shells of a vacancy at 800 K (above the order-disorder transition temperature) as calculated with Monte Carlo simulations.[28] The first nearest-neighbor shell around a vacant site has a lithium occupancy that is significantly below the average lithium concentration of the alloy. The lithium occupancy in the second to fourth nearest-neighbor shells are closer to that of the bulk concentration x, though the second nearest-neighbor shell around the vacancy exhibits a tendency towards a slightly enhanced lithium concentration. The predicted short range order around a vacancy of Fig. 6(a) shows that the vacancies in fcc Al-Li alloys repel lithium atoms, preferring instead to be surrounded by Al in their immediate vicinity.

The tendency of a vacancy to repel lithium is already clear from the variation in energy between an isolated vacancy-Li pair in pure Al [see Fig. 3(a)]. The variation in energy of Fig. 3(a) was calculated within LDA, but an almost identical trend is predicted with the generalized gradient approximation (GGA). Fig. 3(a) shows that the energy of the solid drops by almost 80 meV when an isolated Li adjacent to a vacancy is taken to the fourth nearest neighbor shell of the vacancy. The nearest-neighbor repulsion between a vacancy and lithium persists even in the nondilute regime. In fact, in the ordered phase the preference of the vacancy for a particular environment is even more pronounced. As illustrated in Fig. 6(b), the Monte Carlo simulations predict that the vacancy almost exclusively occupies sites on the Li sublattice of $L1_2$ Al_3Li. The Li sublattice sites of $L1_2$ are completely surrounded by Al in their first nearest-neighbor shell, making it possible for the vacancy on that site to avoid lithium as a nearest neighbor. (A Li sublattice site in perfectly ordered $L1_2$ $LiAl_3$ has all Li atoms as second and fourth nearest neighbors, and all Al as first and third nearest neighbors.)

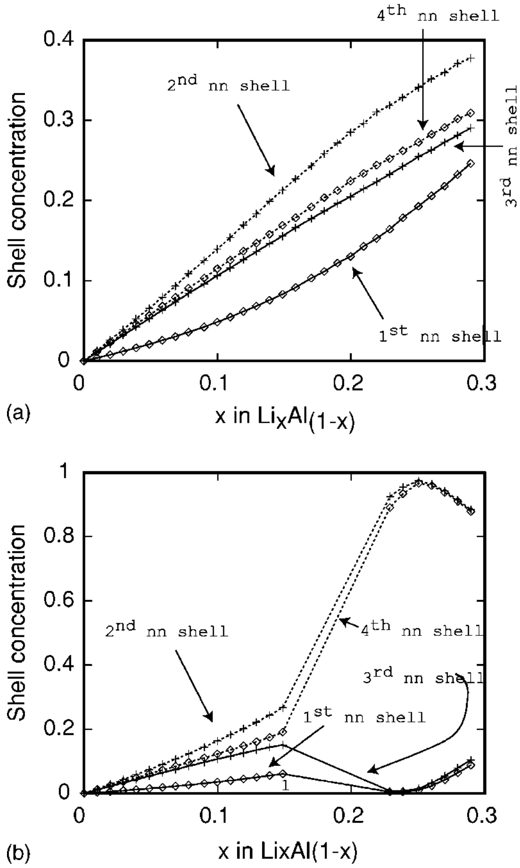

FIG. 6. Short range order correlations around a vacancy. The lithium concentration in the first nearest-neighbor shell (diamonds connected with a solid line) is lower than the bulk concentration. The concentration in the second nearest-neighbor shell (crosses connected with a dashed line), third nearest-neighbor shell (crosses connected with a solid line), and fourth nearest-neighbor shell (diamonds connected with a dashed line) are also illustrated. (a) is at 800 K, above the order-disorder transition temperature and (b) is at 600 K. In the ordered $L1_2$ phase, the vacancy prefers the lithium sublattice as these sites are surrounded by aluminum in the first nearest-neighbor shell.

Within an Al rich fcc phase, the vacancies have similar short range ordering tendencies as the Li atoms. This is evident in Fig. 3 which illustrates the variation of the energy with distance of isolated Li-vacancy and Li-Li pairs in pure aluminum. Furthermore, the vacancy predominantly occupies the lithium sublattice as opposed to the Al sublattice in the ordered $L1_2$ $LiAl_3$ phase.

At finite temperature, the ordered phase is not perfect, but exhibits slight disorder whereby some Al occupies sites of the Li sublattice and vice versa. This disorder reduces the number of Li sublattice sites that have an all aluminum

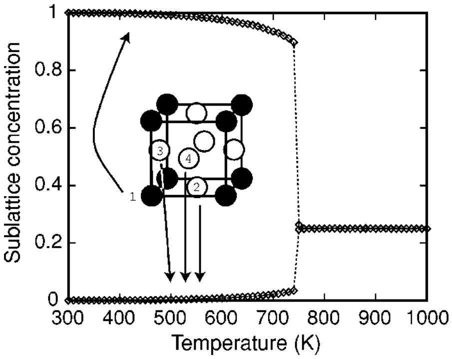

FIG. 7. Variation with temperature of sublattice concentrations in Al_3Li $L1_2$. At low temperature, Al_3Li is characterized by pefect $L1_2$ ordering, but as the temperature increases sublattice disorder becomes non-negligible.

nearest-neighbor shell. Figure 7 illustrates the sublattice concentrations of Al_3Li $L1_2$ as a function of temperature calculated with canonical Monte Carlo simulations (without vacancies) at $x=0.25$. Already at 600 K, almost 3% of the Li sublattice is occupied by Al atoms at the stoichiometric composition of 0.25. The number of antisite defects above 500 K greatly exceeds the equilibrium number of vacancies. Above the order-disorder phase transition (T around 735 K), long-range order disappears, and the sublattice concentrations reduce to the bulk concentration of 0.25.

While the variation of the vacancy concentration with alloy concentration is not as large as predicted within the low temperature expansion approximation for the $L1_2$ $ScAl_3$ alloy by Woodward *et al.*,[29] the present results for Al-Li show that the vacancy concentration can vary by more than an order of magnitude over a small interval of alloy composition. Furthermore, the strong preference of the vacancy for a particular environment, both in the disordered phase and in the ordered $L1_2$ phase, can be expected to have important consequences on the mobility of Li and Al within the solid for diffusion with a vacancy mechanism. As the vacancy prefers aluminum rich environments, Li has less access thermodynamically to the vacancy, meaning that Li is essentially deprived of a diffusion mediating defect.

The advantage of using a *local* cluster expansion to parameterize the EVFE is that we can avoid a ternary treatment of the problem. This is possible because typical vacancy concentrations in metallic alloys are very low. A ternary cluster expansion would require many more terms in order to obtain a similar quantitative accuracy as the current approach. Furthermore, in order to fit a ternary cluster expansion to a solid containing two species and a vacancy, ordered superstructures with nondilute vacancy concentrations would be needed. Many of such configurations are unlikely to be stable in first-principles calculations, especially if relaxations are accounted for, complicating the determination of the ECI. Nevertheless, the current approach is valid only in the limit of a dilute vacancy concentration.

While LDA (as well as GGA) first-principles calculations and the cluster expansion based on LDA calculations predict that a vacancy energetically repels lithium from its first nearest-neighbor shell, Ceresara *et al.*[30] concluded from resistivity measurements that vacancies in Al-Li alloys bind lithium atoms. Resistivity measurements, however, offer indirect evidence about vacancy-impurity interactions and are based on assumptions that are difficult to quantify. Neglected are the effects on resistivity of grain boundaries and dislocations.[31] Furthermore, models used to extract impurity-vacancy binding energies from resistivity measurements neglect interactions between impurities and grain boundaries or dislocations.[31] Other factors can also affect measurements. While Ceresara *et al.*[30] took precautions to minimize lithium loss during heat treatment of their Al-Li alloys, the volatility of Li at elevated temperature can lead to significant Li loss that is accompanied by the injection of vacancies through the Kirkendall effect in excess of the equilibrium vacancy concentration.[32,33] An enhanced vacancy concentration in Al-Li alloys over that of pure Al implies a tendency of lithium to bind vacancies. Yet if the enhancement occurs due to kinetics associated with lithium loss, the apparent binding is not a thermodynamic quantity and cannot be compared with the first-principles results of this work. Nevertheless, given the apparent contradiction between conclusions drawn from resistivity measurements and both LDA and GGA calculations for Li-vacancy interactions in dilute Al-Li alloys, other experimental probes that investigate the interactions between impurities and vacancies should be considered. Another factor that should be considered, but was neglected here, is the effect of atomic vibrations on the interactions between vacancies and impurities. The contribution to the free energy of vibrational degrees of freedom in solids with dilute impurities has been shown to be large.[34]

V. CONCLUSION

We have introduced a local cluster expansion as a purturbative correction to the traditional binary cluster expansion in order to model a dilute concentration of vacancies in binary alloys from first-principles. Applied to fcc Al-Li alloys, we find that the vacancy concentration is very sensitive to the degree of local order and to the bulk concentration of the alloy. Furthermore, we find that in Al-Li alloys, the vacancies repel lithium, preferring a local environment rich in Al. This feature can be expected to have an important impact on the transport properties of Li and Al in this alloy.

ACKNOWLEDGMENTS

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