

First-principles study of solute-dislocation interaction in aluminum-rich alloys

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The strain dependence of the solution energy of substitutional species is derived by expanding the binary alloy energy with respect to concentration and strain to the second order. Within the approximation of small strain and concentration inhomogeneities, the energy change is found to be proportional to the solute-induced stress, and the strain dependence of the solute energy is equivalent to that from the misfit model for solute atoms. However, the solute induced stress is easily calculated from first principles, and it is computed for Ag, Cu, Fe, Li, Mg, Mn, Si, and Zn atoms in aluminum. The results are used to estimate the solute-dislocation interaction energy. The enhancement of the solute concentration near a dislocation core and the role of dislocations on precipitation of these solutes are discussed.

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I. INTRODUCTION

The last decade has seen great strides in the development of alloy theory (see, e.g., Ref. 1). Increasingly complex problems in metallurgy which until recently were considered well beyond the scope of first-principles-based computational materials science, such as predictions of precipitate shapes,² matrix-precipitate interfacial energies, and composition profiles,³ are just some of the problems that have been tackled with surprising success. Here, first-principles calculations of the technologically important problem of solute-dislocation interactions are reported. This interaction is the key to understanding solid solution hardening in some of the most common alloys such as copper-nickel and α brass (copper-zinc). In many precipitation strengthened alloys too, such as common aluminum alloys, solid solution hardening plays a significant role. To the best of the authors' knowledge, up to present there have been no attempts to compute the solute-dislocation interaction from first principles.

The frequent observation of precipitates near dislocation lines raises the question of what makes the dislocation line a preferred site for precipitation. Two mechanisms have been proposed: namely, the reduction of the precipitation nucleation barrier⁴ and the locally enhanced solute concentration near a dislocation. The nucleation barrier for forming a stable precipitate increases with the precipitate-alloy interface energy. In some regions near the dislocation, the difference between the crystal structures of the precipitate and the alloy is reduced by the dislocation strain, and the interface energy and the nucleation barrier are consequently reduced. On the other hand, there is an interaction between the dislocation and the solute atom. The dislocation-solute interaction attracts solute atoms to the dislocation, forming a so-called Cottrell atmosphere of solute atoms.^{5,6} The enhancement of the solute concentration proportionally increases the probability of precipitation near the dislocation.

The origin of the dislocation-solute interaction can be divided into three effects: namely, the size misfit effect,⁵ the modulus effect,⁷ and the electrostatic interaction.⁸ In insulators and semiconductors, dislocations and solute atoms may have electric charges, and therefore they interact through

their electric fields. In metallic alloys, however, strong screening effectively eliminates the electrostatic solute-dislocation interaction.

By acting as a source of the strain field, dislocations interact with solute atoms in metallic alloys. The size misfit effect has been derived from an elastic continuum model, in which the solute atom is represented by an elastic inclusion in a hole in the host material. The size difference between the inclusion and the hole gives rise to a strain dependence of the inclusion energy, proportional to the size difference.⁹ When the difference in the elastic moduli of the host and the inclusion is taken into account, there is an additional strain dependence proportional to the difference in the elastic moduli. Physically, this effect can be understood as an attraction of species which soften the elastic moduli towards areas of high strain because such species accommodate the strain field at a lower elastic energy cost. This effect is referred to as the modulus effect.⁷ For an isotropic material, in the linear elastic approximation, the size misfit effect depends on the hydrostatic component of the strain alone; therefore it does not contribute to the interaction of the solute atom with the screw dislocation, whose strain field is purely shear. However, the modulus effect plays a role for screw and edge dislocations, even in the isotropic approximation.

In this work, we consider the binary alloy energy in the presence of the inhomogeneous strain field from a defect, by defining an energy density, which is expanded to the second order in the local concentration, the local strain, and their gradients. The strain dependence of the solution energy thus derived is equivalent to the size misfit effect. However, our result is in a form that is easily calculated by a standard electronic structure approach. The modulus effect is excluded because, as will be shown, it first appears upon expanding the energy up to third order in concentration and strain. The optimum concentration profile resulting from the inhomogeneous strain is also derived. Based on the results of the electronic structure calculations of aluminum-rich alloys containing Ag, Cu, Fe, Mg, Mn, Li, Si, and Zn solute atoms, the contribution of the size misfit effect to the dislocation-solute interaction of these solute atoms and their distribution around an edge dislocation is calculated. The comparison of

the computed result with experiment shows that for some solute atoms, the size misfit effect contribution is the main part of the dislocation-solute interaction. The role of dislocations in enhancing the segregation and the precipitation of solutes in aluminum is discussed.

II. THEORY

A. Alloy energy density function

We will consider the effect of the strain field produced by a lattice defect on the solute energy and the distribution of solute atoms in the binary alloy. The defect strain field $\epsilon^{\text{def}}(\mathbf{x})$ is inhomogeneous and is localized within a volume around the defect. In general, there may also be an external strain field ϵ^{ext} , which may be considered as homogeneous compared to the range of the defect strain field. For a nearly homogeneous alloy whose concentration is c^0 everywhere away from the defect, there is segregation of solute near the defect by the defect strain field, and therefore an excess solute concentration $c(\mathbf{x})$ is created. Choosing a volume V surrounding the defect to be large enough that both the defect strain field and the excess concentration vanish outside V , the effect of the defect strain field on the solute atoms can be derived by considering the energy of the alloy within the

volume V only. The energy is a functional of the defect strain field and the excess concentration, and can be generally written as a volume integral of an energy density function as

$$E = E[c^0 + c(\mathbf{x}), \epsilon^{\text{ext}} + \epsilon^{\text{def}}(\mathbf{x})] = V\tilde{E}^0(c^0, \epsilon^{\text{ext}}) + \int_V \tilde{E}(\mathbf{x}) d^3x. \quad (1)$$

We have separated the dependence on the external strain field and the homogeneous concentration into the first term. The integral depends directly on the defect strain field and the excess concentration only. To simplify the notation we will drop the superscript “def” and write $\epsilon(\mathbf{x})$ for the defect strain field.

The exact form of $\tilde{E}(\mathbf{x})$ is unknown; however, away from a phase transition, the alloy energy must be an analytical function of state variables. Therefore, $\tilde{E}(\mathbf{x})$ may be written as a Taylor expansion in terms of the excess concentration $c(\mathbf{x})$, the defect strain $\epsilon(\mathbf{x})$, and their derivatives with respect to the position. Assuming the case where the spatial variations are small, we retain the gradients of the fields only, and write the expansion explicitly up to the third order in the fields and the field gradients as

$$\begin{aligned} \tilde{E}(\mathbf{x}) \approx \tilde{E}(\mathbf{x}; c, c_i, \epsilon, \epsilon_i) = & c(\mathbf{x})\tilde{E}_c + \epsilon(\mathbf{x})\tilde{E}_\epsilon + \frac{1}{2}[c^2(\mathbf{x})\tilde{E}_{cc} + 2c(\mathbf{x})\epsilon(\mathbf{x})\tilde{E}_{c\epsilon} + \epsilon^2(\mathbf{x})\tilde{E}_{\epsilon\epsilon}] \\ & + \frac{1}{2} \sum_{i=x,y,z} [c_i^2(\mathbf{x})\tilde{E}_{c_i c_i} + 2c_i(\mathbf{x})\epsilon_i(\mathbf{x})\tilde{E}_{c_i \epsilon_i} + \epsilon_i^2(\mathbf{x})\tilde{E}_{\epsilon_i \epsilon_i}] \\ & + \frac{1}{6}[c^3(\mathbf{x})\tilde{E}_{ccc} + 3c(\mathbf{x})\epsilon^2(\mathbf{x})\tilde{E}_{c\epsilon\epsilon} + 3c^2(\mathbf{x})\epsilon(\mathbf{x})\tilde{E}_{cc\epsilon} + \epsilon^3(\mathbf{x})\tilde{E}_{\epsilon\epsilon\epsilon}] \\ & + \frac{c(\mathbf{x})}{2} \sum_{i=x,y,z} [c_i^2(\mathbf{x})\tilde{E}_{cc_i c_i} + 2c_i(\mathbf{x})\epsilon_i(\mathbf{x})\tilde{E}_{cc_i \epsilon_i} + \epsilon_i^2(\mathbf{x})\tilde{E}_{c\epsilon_i \epsilon_i}] \\ & + \frac{\epsilon(\mathbf{x})}{2} \sum_{i=x,y,z} [c_i^2(\mathbf{x})\tilde{E}_{\epsilon c_i c_i} + 2c_i(\mathbf{x})\epsilon_i(\mathbf{x})\tilde{E}_{\epsilon c_i \epsilon_i} + \epsilon_i^2(\mathbf{x})\tilde{E}_{\epsilon \epsilon_i \epsilon_i}] + \dots \end{aligned} \quad (2)$$

Here, to simplify the expression, we treat the strain tensor $\epsilon(\mathbf{x})$ as if it is a scalar quantity, and c_i and ϵ_i denote $\partial c / \partial x_i$ and $\partial \epsilon / \partial x_i$, respectively. \tilde{E}_α , $\tilde{E}_{\alpha\beta}$, and $\tilde{E}_{\alpha\beta\gamma}$ are the expansion coefficients and they are functions of c^0 and ϵ^{ext} . Various terms proportional to odd powers of the gradients have been eliminated because, for the cubic crystals of interest here, the energy density must be invariant under mirrors normal to the x , y , and z axes.

The strain field and the concentration that appear in Eq. (2) are the inhomogeneous strain field and the excess concentration. The coefficients \tilde{E}_c , \tilde{E}_ϵ , \tilde{E}_{cc} , $\tilde{E}_{c\epsilon}$, and $\tilde{E}_{\epsilon\epsilon}$ can be obtained from calculations pertaining to homogeneous alloys. In the limit of vanishing homogeneous concentration and external strain field, some of the coefficients can be iden-

tified with well-known alloy properties, namely the solution energy (\tilde{E}_c), the homogeneous stress (\tilde{E}_ϵ), the solute-solute interaction energy (\tilde{E}_{cc}), and the elastic modulus tensor ($\tilde{E}_{\epsilon\epsilon}$). Supercell calculations can be used to obtain the coefficients pertaining to strain and concentration. The variation of the supercell energy with respect to homogeneous strain or concentration can then be computed through finite differences although great care must be taken to eliminate systematic computational errors which can easily dwarf the quantity of interest.¹⁰ Our derivation in Sec. II B circumvents the troublesome application of the finite-difference approach by relating the strain dependence of the solute energy to the solute-induced stress which can be obtained directly, without

evaluating some small difference in total energies of two supercells.

The coefficients associated with gradients of composition and strain are much more difficult to obtain and to the best of our knowledge no such *ab initio* calculations have ever been performed. The reason is that in order to impose a reasonable gradient, extremely large cells are required and proportionally the supercell energies and random errors become so large that the energies associated with the gradients are too small to be reliably extracted. Fortunately, an alternative to the supercell difference method exists. It can be shown that in the harmonic approximation the coefficients of the strain derivatives, e.g., $\tilde{E}_{\epsilon_i \epsilon_j}$, etc., can be related to the force constants.¹¹ The force constants can be obtained from first-principles calculations by linear response¹² or the so-called direct method.^{13,14} When the force constants are generalized by including a compositional component in addition to the three ordinates, chemical interaction energies can be included within the same Hamiltonian. Then, it might be possible to compute coefficients where terms pertaining to strain and composition and their gradients are mixed such as $\tilde{E}_{c_i \epsilon_j}$. Concerning this speculation, it should be emphasized that neither the formalism nor the *ab initio* calculation of the generalized force constants has been reported in the literature yet.

B. Strain dependence of the solute energy

The strain dependence of the solution energy can be obtained from the expansion of the alloy energy density, Eq. (2). Strain-induced segregation of impurities will be caused by cross terms between the concentration or the concentration gradients and the strain or the strain gradients only. This indicates that nonlinear elasticity, being at least third order in ϵ , affects the solution energy through the fourth or higher orders only. For the case where the excess concentration, the inhomogeneous strain, and their gradients are small, Eq. (2) can be truncated including only up to the second-order terms. In this case, there are only two cross terms: namely, $c(\mathbf{x})\epsilon(\mathbf{x})\tilde{E}_{c\epsilon}$ and $c_i(\mathbf{x})\epsilon_i(\mathbf{x})\tilde{E}_{c_i \epsilon_i}$. Considering the homogeneous case, the first term only matters, and the strain dependence of the solution energy is found to be proportional to

$$\{\tilde{E}_{c\epsilon}\}_{ij} \equiv \frac{\partial^2 \tilde{E}}{\partial c \partial \epsilon_{ij}} = -\frac{\partial \sigma_{ij}}{\partial c}, \quad (3)$$

where i and j represent the ordinates x , y , and z , \tilde{E} is the energy density of the alloy with a homogeneous strain ϵ^{ext} and concentration c^0 , and ϵ_{ij} and $\sigma_{ij} = -\partial \tilde{E} / \partial \epsilon_{ij}$ are the ij components of the homogeneous strain and stress, respectively. Therefore, in the linear elastic approximation, $\tilde{E}_{c\epsilon}$ can be interpreted as the stress due to a solute atom, and we will refer to this as the solute induced stress tensor. It should be stressed that this property can be computed easily from first principles. As the quantities characterizing the alloy properties must remain unchanged under the alloy symmetry operations, the symmetry consideration reduces the number of the independent and nonvanishing components of the solute-

induced stress tensor. The strain dependence of solute energy is now easily evaluated from the $c(\mathbf{x})\epsilon(\mathbf{x})\tilde{E}_{c\epsilon}$ term

$$\Delta E_s(\mathbf{x}) = -v_0 \sum_{i,j=x,y,z} \epsilon_{ij}(\mathbf{x}) \frac{\partial \sigma_{ij}}{\partial c}, \quad (4)$$

where v_0 is the atomic volume, we have written the components of the strain, explicitly, and σ_{ij} is defined in Eq. (3).

Equation (4) gives the dependence of the solute energy on the local value of the defect strain field. The dilute random alloy of a cubic material also has cubic symmetry, and the derivative of the stress tensor has one independent nonvanishing component only,¹⁵ $\partial \sigma_{xx} / \partial c = \partial \sigma_{yy} / \partial c = \partial \sigma_{zz} / \partial c$. In this case, the strain dependence is reduced to $\Delta E_s(\mathbf{x}) = -v_0 \epsilon_d(\mathbf{x}) \partial \sigma_{xx} / \partial c$, where $\epsilon_d \equiv \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$ is the hydrostatic component of the strain. This is in agreement with the misfit model for solutes derived within the approximation of linear isotropic elasticity (see, e.g., Ref. 9), which gives the strain dependence of the solute atom energy as $v_0 B \epsilon_d \epsilon_s$, where B is the bulk modulus and $\epsilon_s \equiv (v_s - v_0) / v_0$ is the size misfit between the solute and the host. The size misfit can be related to the solute-induced stress by $\epsilon_s = B^{-1} \partial \sigma_{xx} / \partial c$. While this has been derived from the isotropic model, Eq. (4) is more general and it gives the energy change in term of the solute-induced stress, which can be obtained directly from an electronic structure calculation. Using Eq. (4) the strain dependence of the solute atom energy can be calculated without any arbitrary parameters.

For the homogeneous case, neglect of the third order terms means that effects such as the concentration dependence of the elastic moduli ($\tilde{E}_{c\epsilon\epsilon}$) and the strain dependence of the solute-solute interaction ($\tilde{E}_{cc\epsilon}$) are not taken into account. The third-order terms become important, even in the case of small strains and excess concentrations, when the second-order term is unusually small. The above analysis indicates that this occurs when the solute-induced stress (or misfit between solute and host matrix) is very small. Then an expansion of the energy density up to least third order is required.

C. Optimum concentration profile

As shown in the previous section the inhomogeneous strain makes the solute energy position dependent so that segregation of the solute atoms is favored. For a particular strain at a finite temperature the optimum concentration profile can be obtained by minimizing the grand potential:

$$\Omega[c(\mathbf{x}), \epsilon(\mathbf{x})] = E - TS[c'(\mathbf{x})] - \Delta\mu \int_V c(\mathbf{x}) d^3x, \quad (5)$$

where the energy E is given by Eq. (1), S is the entropy, and $\Delta\mu$ is the chemical potential difference of the solute species and the host species. The chemical potential is defined as the derivative of the Helmholtz free energy of the homogeneous alloy per atom with respect to the concentration. The Lagrange multiplier $\Delta\mu$ is needed to impose the constraint that the total number of species is held constant when optimizing the Helmholtz free energy. Note that the entropy is

written as a functional of the total concentration $c^t(\mathbf{x}) = c^0 + c(\mathbf{x})$, rather than the excess concentration $c(\mathbf{x})$.

To derive the optimum concentration profile, we write the variation of the grand potential due to the variation of the excess concentration, $\delta c(\mathbf{x})$, up to the second order in concentration, strain, and their gradients,

$$\delta\Omega = \int_V \left[\tilde{E}_c - \Delta\mu + c(\mathbf{x})\tilde{E}_{cc} + \boldsymbol{\varepsilon}(\mathbf{x})\tilde{E}_{c\varepsilon} - \sum_{i=x,y,z} c_{ii}(\mathbf{x})\tilde{E}_{c_i c_i} \right] \delta c d^3x - T\delta S. \quad (6)$$

We have applied the condition that δc vanish on the surface of V . For dilute alloys the configurational entropy is well approximated by the ideal entropy, $S[c^t(\mathbf{x})] = -k_B \int_V c^t(\mathbf{x}) \ln c^t(\mathbf{x}) + [1 - c^t(\mathbf{x})] \ln [1 - c^t(\mathbf{x})] d^3x$, and the equation governing $c(\mathbf{x})$ can be written as

$$\ln[c^0 + c(\mathbf{x})] = \frac{1}{k_B T} \left[\Delta\mu - \tilde{E}_c - \boldsymbol{\varepsilon}(\mathbf{x})\tilde{E}_{c\varepsilon} + \sum_{i=x,y,z} c_{ii}(\mathbf{x})\tilde{E}_{c_i c_i} - c(\mathbf{x})\tilde{E}_{cc} \right]. \quad (7)$$

Equation (7) has a simple solution when the first three terms on the right-hand side are much larger than the fourth and fifth terms. Neglecting the fourth and fifth terms should be valid for dilute alloys when the excess concentration and the second derivative of the concentration $c_{ii}(\mathbf{x})$ are small. Then, the total concentration profile can be written as

$$c^0 + c(\mathbf{x}) = c^0 \exp \left[\frac{\sum \boldsymbol{\varepsilon}_{ij}(\mathbf{x}) \partial \sigma_{ij} / \partial c}{k_B T} \right], \quad (8)$$

where $c^0 = \exp[-(\tilde{E}_c - \Delta\mu)/k_B T]$, and the summation is taken over all strain components, $i, j = x, y, z$. The excess concentration satisfies the boundary condition that $c(\mathbf{x}) = 0$ outside V . The total concentration is given by the Maxwell distribution with the energy given by the strain dependence of the solute energy according to Eq. (4).

For the case of higher concentration, the solute-solute interaction \tilde{E}_{cc} can be calculated by *ab initio* methods and included as a perturbative term to the solution in Eq. (8). The segregation is enhanced (diminished) when the solute-solute interaction is attractive (repulsive). Likewise the term with the second derivative of the concentration can be included perturbatively provided that $\tilde{E}_{c_i c_i}$ has been determined from calculations on inhomogeneous systems.

D. Dislocation-solute interaction

The dislocation-solute interaction energy is obtained by inserting the dislocation strain field into Eq. (4). As we are interested in the interaction in aluminum, whose elastic tensor is almost isotropic, we will simplify the problem by using the strain field from the isotropic elastic continuum model of dislocation. In addition, as a cubic material has only one

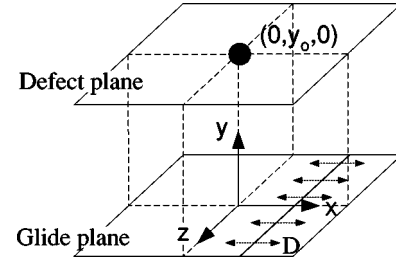


FIG. 1. Schematic diagram of the dislocation-solute interaction measurement. A dislocation on the xz glide plane interacts with a solute atom at a distance y_0 on the y axes. The dislocation line (D) is parallel to the z axes; therefore the energy is a function of the dislocation position x . The dotted arrows shows the direction of dislocation motion, and the solid circle represents the solute atom.

independent component of the solute-induced stress tensor $\partial \sigma_{xx} / \partial c$, the solute atom energy will depend on the dilation components of the strain only so that only the edge dislocation interacts with the solute atom via the size misfit effect.

The dilation component of the edge dislocation strain field is given by¹⁶

$$\varepsilon_d(x, y) = -\frac{b(1-2\nu)}{2\pi(1-\nu)} \frac{y}{x^2 + y^2}, \quad (9)$$

where b is the magnitude of the Burgers vector and ν is Poisson's ratio. The dislocation line is assumed to lie along the z axis, and the slip plane is the x - y plane. The extra half-plane is assumed to be above the slip plane; therefore the strain is compressive where $y > 0$ and expansive where $y < 0$. The solute atom with a negative (positive) solute-induced stress will have a lower energy, and therefore be attracted to the area above (below) the slip plane. As the continuum model has a singularity at the dislocation core, it is usually assumed that the strain given by Eq. (9) is not valid at distances closer to the center of the dislocation than a so-called core radius, whose length is usually taken to be comparable to the Burgers vector.

The dislocation-solute interaction energy can be measured experimentally with stress-amplitude-dependent internal friction experiments.¹⁷ In such an experiment, an applied ultrasonic wave moves a dislocation as is schematically depicted in Fig. 1. The interaction energy as a function of the dislocation position x is given by

$$U(x) = U_0 \frac{(x/y_0)^2}{1 + (x/y_0)^2}, \quad (10)$$

where the interaction strength

$$U_0 = \frac{-b(1-2\nu)}{2\pi y_0(1-\nu)} \frac{\partial \sigma_{xx}}{\partial c}. \quad (11)$$

The interaction strength is a function of the distance y_0 between the solute atom and the slip plane. To compare the calculated interaction strength with experiment, U_0 should be averaged over a range of y_0 . However, for simplicity, it can be assumed that the value of y_0 that corresponds to the minimum solute energy will contribute most to the interac-

tion so that $y_0 = +b$ ($y_0 = -b$) if the solute atom has a negative (positive) solute-induced stress.

The effect of the dislocation on the solute distribution is obtained by inserting the dislocation strain field into Eq. (8). Within the dislocation core where the continuum model is invalid, the solute concentration is assumed to be the same as the concentration just outside the core.

E. Multiple solute species

Precipitation in aluminum usually involves several atomic species. To evaluate whether a certain precipitate can form the chemical concept of “solubility limit” is helpful. For precipitation to occur the product of the concentrations of all participating species must exceed a certain limit K . Hence, to precipitate a compound $\text{Al}_p\text{X}_q\text{Y}_r$ from a solid solution,

$$c_{\text{Al}}^p c_{\text{X}}^q c_{\text{Y}}^r > K_{\text{Al}_p\text{X}_q\text{Y}_r}, \quad (12)$$

where the limit $K_{\text{Al}_p\text{X}_q\text{Y}_r}$ depends not only on the reaction product ($\text{Al}_p\text{X}_q\text{Y}_r$) but also on environmental factors such as temperature. When the concentration is greatly increased locally, such as near a dislocation that may subsequently move away, the likelihood of the limit being exceeded is also increased. While it is very difficult to exactly calculate the increased precipitation probability, a crude qualitative argument can be made. The effect of local strain fields is included by substituting Eq. (8) in Eq. (12),

$$\begin{aligned} & c_{\text{X}}^{0q} \exp \left[q \frac{\sum \epsilon_{ij}(\mathbf{x}) \partial \sigma_{ij} / \partial c_{\text{X}}}{k_{\text{B}} T} \right] \\ & \times c_{\text{Y}}^{0r} \exp \left[r \frac{\sum \epsilon_{ij}(\mathbf{x}) \partial \sigma_{ij} / \partial c_{\text{Y}}}{k_{\text{B}} T} \right] \\ & = c_{\text{X}}^{0q} c_{\text{Y}}^{0r} \exp \left[\frac{\sum \epsilon_{ij}(\mathbf{x}) [q \partial \sigma_{ij} / \partial c_{\text{X}} + r \partial \sigma_{ij} / \partial c_{\text{Y}}]}{k_{\text{B}} T} \right] \\ & > K_{\text{Al}_p\text{X}_q\text{Y}_r}, \end{aligned} \quad (13)$$

where c_{Al} has been set to unity because we are concerned with dilute alloys. It is apparent that the concentration product has been increased by the exponential factor in which the solute-induced stress is multiplied by the concentration of the atomic species in the precipitate, $q \partial \sigma_{ij} / \partial c_{\text{X}} + r \partial \sigma_{ij} / \partial c_{\text{Y}}$. This last factor will be called the “precipitation enhancement factor” (PEF). The precipitate could have been written as $\text{Al}_{2p}\text{X}_{2q}\text{Y}_{2r}$ as well, which would have given a PEF twice as large. Therefore, the PEF will be defined with respect to one solute atom: for $\text{Al}_{p/(q+r)}\text{X}_{q/(q+r)}\text{Y}_{r/(q+r)}$,

$$\text{PEF} = \frac{q}{(q+r)} \frac{\partial \sigma_{ij}}{\partial c_{\text{X}}} + \frac{r}{(q+r)} \frac{\partial \sigma_{ij}}{\partial c_{\text{Y}}}. \quad (14)$$

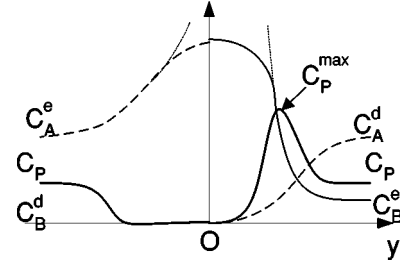


FIG. 2. Schematic plot of the product of the concentrations of two solute species A and B. It is assumed that the solute induced stresses of A and B are positive and negative, respectively, and that the magnitude of the stress of B is greater than that of A. The dashed line shows the concentration of A; the solid line shows the concentration of B. The superscripts *e* and *d* indicate the enhancement and the depletion of the solute atoms, respectively. The enhanced concentrations are assumed to deviate from Maxwell’s distribution shown by the dotted lines and asymptotically approach the solution limits at the dislocation core. The product $C_P = C_A C_B$ shown by the thick line has a maximum indicated by the arrow.

When the PEF takes values near zero, local strain fields are not likely to strongly favor precipitation by segregation, but for very positive or very negative PEF values a strong enhancement is indicated.

For the precipitation of a single species the sign of the solute induced stress $\partial \sigma_{ij} / \partial c$ determines on which side of the slip plane the precipitation is enhanced. On the other hand, the coprecipitation of solute species depends on the product of the concentrations of all species. Based on the sign of the solute-induced stress of each species, the precipitates can be classified into two types: namely, the “*s* type” when the stresses are of the same sign and the “*d* type” when the stresses have different signs. The concentrations of all species involving an *s*-type precipitate are enhanced on the same side of the slip plane, and so is their precipitation. For a *d*-type precipitate, on either side of the slip plane, there are both enhancement and depletion of solute concentrations. The precipitation is enhanced on the side of the slip plane where the concentration of the solute with the larger solute-induced stress is enhanced.

Another difference between *d*-type and *s*-type precipitates is that for *d*-type precipitates the maximal product of the concentrations can occur at some distance from the dislocation. The solute-solute interaction causes the solute concentration to deviate from Maxwell’s distribution given by Eq. (8) such that the solution limit is asymptotically approached near the dislocation core; see Fig. 2. As a result, the concentration product reaches a maximum at a distance of the order of angstroms away from the dislocation core. The maximum of the concentration product occurs on the side of the slip plane where the concentration of the solute with the larger solute induced stress is enhanced.

III. CALCULATION METHOD

The solute-induced stresses $\partial \sigma_{xx} / \partial c$ of Ag, Cu, Fe, Li, Mg, Mn, Si, and Zn in aluminum are calculated using the local density approximation of density functional theory with

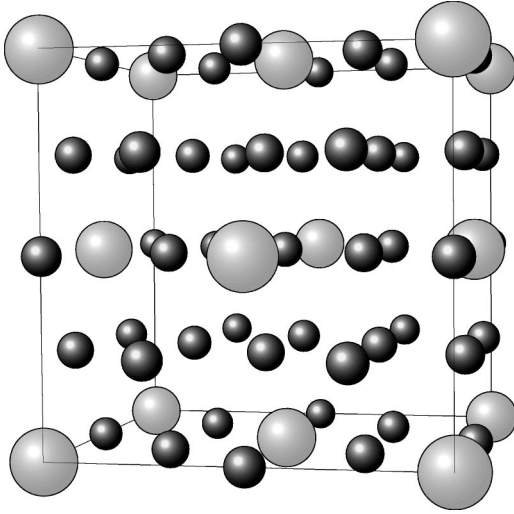


FIG. 3. Supercell of Al_7X used in the calculations with Al and X being represented by the black and the white spheres, respectively.

a pseudopotential plane-wave method.¹⁸ The supercell geometry is used and the alloys are represented by Al_{n-1}X supercells with X being one of the solute atoms, and $n=8, 27$, and 64 corresponding to the solute concentrations of 12.5, 3.7, and 1.6 at. %, respectively. As illustrated in Fig. 3, the supercell translation vectors are in the same directions as the primitive translation vectors of the face-centered-cubic lattice, with the length $n^{1/3}$ times as long, resulting in an ordered alloy where the shortest distance between the solute atoms is equal to $n^{1/3}$ times the distance between aluminum atoms.

For each n , the energy of the Al_n supercell as a function of the lattice parameter is calculated and fitted to Birch's equation of state¹⁹ and the lattice parameter of aluminum is determined from the minimum of the energy. The Al_{n-1}X supercells are set to have the same lattice parameter as aluminum. The electronic structure is optimized, and the stress tensors are calculated from the partial derivatives of the energy with respect to the atomic positions. While the Al_{n-1}X supercell size and shape are fixed, the atomic positions are relaxed with a conjugated gradient method¹⁸ minimizing the forces between atoms.

The calculations are performed with constant cutoff energies of 300 eV for expanding the wave functions and 400 eV for the augmentation charges. These are large enough for the ultrasoft pseudopotentials²⁰ used in the calculations. The reciprocal space integrations are performed in the irreducible part of the first Brillouin zone of the supercell on k -point meshes, which are equivalent to 54 872 k points in the first Brillouin zone of the primitive cell of aluminum. The number of k points has been tested to be adequate in our earlier work.²¹

IV. RESULTS AND DISCUSSION

The average value of the solute induced stress $\partial\sigma_{xx}/\partial c$ calculated using three supercells of different sizes for each solute species is shown in Table I. Figure 4 shows that the deviation of the values from different supercell sizes from

TABLE I. Calculated solute-induced stress $\partial\sigma_{xx}/\partial c$ and the dislocation-solute interaction strength.

Solute species	$\partial\sigma_{xx}/\partial c$ (kbar)	Interaction strength (eV)	
		Calculated	Experimental ^a
Ag	41.04	0.031	0.135
Cu	-338.21	0.256	0.195
Fe	-710.79	0.537	—
Li	-41.90	0.032	—
Mg	239.69	0.181	0.19
Mn	-652.85	0.493	—
Si	-121.42	0.092	—
Zn	-92.10	0.074	0.11

^aData from Ref. 17.

the mean value is small, compared to the mean value, for most solute species except Li and Ag. It is evident that the supercell size does not significantly affect the results. As the solute concentration differs considerably between the three supercell sizes, this also implies that the second derivative $\partial^2\sigma_{xx}/\partial c^2$ is small justifying expanding the alloy energy up to second-order in strain and concentration only. As was mentioned in Sec. II B, the second-order expansion of the alloy energy is likely to fail when the solute misfit or alternately the solute-induced stress is very small, as turns out to be the case for Ag and Li.

The calculated solute-induced stresses are negative for Cu, Fe, Li, Mn, Si, and Zn, indicating that these solutes decrease the lattice parameter, while the solute-induced stresses of Ag and Mg are positive, so that Ag and Mg increase the lattice parameter. Figure 5 shows that the sign and magnitude of the calculated stress qualitatively correspond with the experimental²² volume misfit defined as $\lim_{c \rightarrow 0} V^{-1} dV/dc$, where V is the alloy atomic volume.

The dislocation-solute interaction strength calculated from the solute-induced stress of each solute species is shown in Table I. The results are in good agreement with existing experimental data of Cu, Mg, and Zn, but not the result of Ag. The discrepancy of the result most likely arises from truncating the third-order terms from Eq. (2), i.e., neglecting the modulus change effect. The excellent agreement

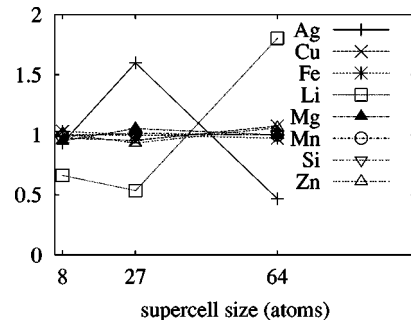


FIG. 4. Deviation of the solute-induced stresses calculated with different supercells from the mean value. The vertical axes shows the ratio of the solute induced stress calculated with a particular supercell to the average value.

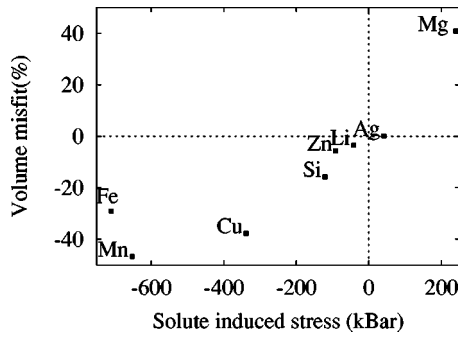


FIG. 5. Correlation between the calculated solute-induced stress and the experimental (Ref. 22) volume misfit defined as $\lim_{c \rightarrow 0} V^{-1} dV/dc$, where V is the alloy atomic volume.

between the calculated and experimental results for Cu, Mg, and Zn suggests that the size misfit effect accounts for the major part of the dislocation-solute interaction for these solute atoms in aluminum.

The dislocation-solute interaction favors solutes with positive (negative) solute-induced stress at the dilated (compressive) area near an edge dislocation. The enhancement of the solute concentration due to the dislocation strain field is calculated for dilute alloys using Eq. (8). To illustrate the result, the region where the concentration of each solute is 10 times the concentration far away from the dislocation (c^0) is shown in Fig. 6. The regions where the solute concentration enhancement is 10 times for Ag, Li, Zn, and Si are within the core of the dislocation, where the continuum model is invalid. At the dislocation core radius the concentration enhancement of Ag, Li, Zn, and Si is 2.05, 2.08, 5.03, and 8.42 times, respectively. The energies of Fe and Mn are most affected by the strain, and their concentrations are most enhanced on the compressive side of the slip plane and are most depleted on the other side.

As discussed previously, the extend to which strain might enhance precipitation through local concentration buildup can be qualitatively described by the PEF [Eq. (14)]. In Table II, the PEF as computed with the solute induced stress from Table I is listed. It is readily apparent that precipitates in-

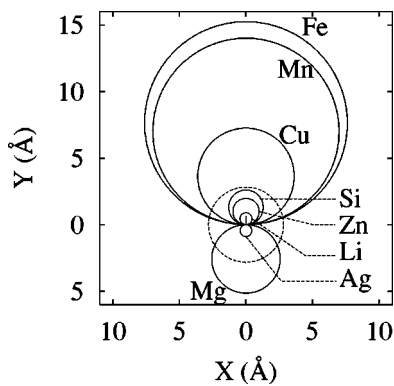


FIG. 6. Region around an edge dislocation where the concentration of each solute species is 10 times the concentration away from the dislocation. The dislocation core at (0,0) is represented the dotted circle with the radius equals to the magnitude of the Burgers vector. The extra-half plane is assumed to be on the $y > 0$ side.

TABLE II. Types and “precipitation enhancement factors” (PEF), as defined in Sec. II E, of common precipitate phases in aluminum alloys.

Precipitate	Type	PEF (kbar)
Ag_2Al	<i>s</i>	41
AgMg	<i>s</i>	140
Cu_2Al	<i>s</i>	-338
$(\text{CuFe})\text{Al}_6$	<i>s</i>	-525
Cu_2FeAl_7	<i>s</i>	-462
$(\text{CuFeMn})\text{Al}_6$	<i>s</i>	-567
$(\text{CuFeMn})_3\text{Si}_2\text{Al}_{15}$	<i>s</i>	-486
CuMgAl_2	<i>d</i>	-49
CuMg_4Al_6	<i>d</i>	124
$\text{Cu}_2\text{Mg}_8\text{Si}_6\text{Al}_5$	<i>d</i>	32
$\text{Cu}_2\text{Mn}_3\text{Al}_{20}$	<i>s</i>	-527
$\text{Cu}_5\text{Zn}_2\text{Al}_3$	<i>s</i>	-268
FeAl_3	<i>s</i>	-711
$(\text{FeMn})\text{Al}_6$	<i>s</i>	-682
FeSiAl_5	<i>s</i>	-416
Fe_2SiAl_8	<i>s</i>	-514
LiAl_3	<i>s</i>	-42
Mg_2Si	<i>d</i>	119
Si	<i>s</i>	-121

volving combinations of iron, manganese, copper, and silicon are much affected by localized strain fields, while precipitates involving silver and lithium or combinations of copper, magnesium, and silicon tend to be much less affected. Experimentally it is known that precipitation in aluminum-lithium and aluminum-magnesium alloys is quite homogeneous, while precipitation in aluminum-copper alloys is quite sensitive to the presence of stresses and grain boundaries. However, for iron and manganese a comparison with experiment is quite difficult because these elements have very low solubilities in aluminum.²³

V. CONCLUSION

The strain dependence of the solute atom energy has been derived by expanding the binary alloy energy to the second order in the concentration and the strain. The result is equivalent to the size misfit model effect, but the present form relates the solute energy change to the solute induced stress, which can be calculated directly within standard electronic structure methods. The solute-induced stress is calculated for Ag, Cu, Fe, Li, Mg, Mn, Si, and Zn atoms in aluminum-rich alloys, using the local density approximation of density functional theory with a pseudopotential plane-wave method. The order of the solute atoms according the magnitude of the solute induced stress is Ag, Li, Zn, Si, Mg, Cu, Mn, and Fe, with a positive sign for Ag and Mg and a negative sign for the others. The dislocation-solute interaction strength obtained from the calculated solute-induced stress is in good agreement with experimental data for Cu, Mg, and Zn, suggesting that the size misfit effect is the domi-

nant part of the dislocation-solute interaction for these solutes in aluminum. For elements that have almost no lattice mismatch with aluminum, the modulus change effect may be important. This appears to be the case for Ag where the calculation differs significantly from the experimental result. Near an edge dislocation, the concentrations of Fe, Mn, Cu, and Mg are expected to be significantly enhanced from the values far away from the dislocation. The effect is moderate for Si and Zn and very small for Li and Ag. The sign suggests that Ag and Mg prefer to be on the opposite side of the dislocation slip plane from the other solute atoms. The local enhancement of solute concentrations might assist in nucle-

ation of precipitates. It has been shown that precipitation of Fe and coprecipitation of Fe and Mn with various other alloying elements and of Fe and Si should be most enhanced by segregation due to the presence of strain fields from lattice defects, while precipitation of Ag-, Li-, and Mg-based compounds should be least affected.

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