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Simplified pseudopotential expansion theory for Al-Li alloys

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A new pseudopotential expansion theory is developed for nearly-free-electron alloys. This theory includes local-density-dependent corrections to the usual pair potentials, to take into account long-wavelength charge-density fluctuations. A simplified treatment of the nonlocality of the pseudopotential is presented as well. Using this theory, the heat of formation and lattice constant are calculated for several ordered and disordered phases of Al-Li alloys. The importance of the local-density correction and the nonlocal pseudopotential terms to the atomic bonding in these alloys is analyzed, and the results are compared with experiments. The dominant exothermic contribution to the heat of formation comes from the nonlocality of the Li pseudopotential. Inclusion of the local-density and nonlocal pseudopotential terms results in considerably improved heats of formation. The concentration dependence of the calculated heats of formation and ordering energy is consistent with experiment and more accurate density-functional band-structure calculations. The results for the lattice constants of the ordered compounds agree well with experiment, and the experimentally observed lattice contractions of the solid solutions are also found. However, the failure of our method in constructing an accurate phase diagram from the calculated heats of formation indicates that further improvements, including higher-order terms in the strong Al pseudopotential, are needed.

I. INTRODUCTION

The properties of Al-Li alloys are currently attracting attention from both the materials-science and physics communities. Besides being promising lightweight alloys for the aerospace industry,[1] they show several properties of fundamental interest. Some examples are the lattice contraction of the Al-rich solid solution relative to the Vegard's-law prediction,[2] the possible existence of a miscibility gap in the random solid solution according to simple model calculations,[3] and more recently observed Al-Li-Cu quasicrystal structures.[4] A quantitative understanding, at the microscopic quantum-mechanical level, of the Al—Li bond is important for understanding all of these properties of Al-Li alloys. In this paper we present a theoretical model for Al-Li alloys based on the local pseudopotential expansion theory[5] with two modifications: *local* electronic-density-dependent corrections, and a simplified treatment of the nonlocality of the pseudopotentials. Although the usual pseudopotential expansion theory has been quite successful in dealing with simple nearly-free-electron metals and some of their alloys,[6–8] we face two main difficulties in applying the theory to Al-Li alloy systems. First, the high electronic density of Al ($z=3$) and the large difference in electronic densities of Al and Li ($z_{\rm Al}-z_{\rm Li}=2$) render the second-order perturbation expansion insufficiently accurate to reproduce the actual local electronic density distribution and bonding energy in the alloy system. Second, the importance of the nonlocality of the pseudopotential, especially for Li, causes some commonly used local model potentials[9–11] to fail in dealing with several alloy properties.

The above difficulties have been discussed by several authors[12–16]. For example, a fourth-order local pseudopotential expansion has been used to study the atomic-volume contraction of a single Li atom soluted in Al solid.[16] Hafner[12] has developed a method for constructing optimized pseudopotentials for alloy systems which are alloy-composition dependent. Another method has been developed[13–15] for treating the high-order nonlinear screening effects on the basis of a self-consistent density-functional calculation. These methods have been employed in calculations for Mg-Li alloy systems.[12,17] The results, such as the heat of formation and the phase diagram of random solid solution, agree well with experiments. However, applications of these methods to alloy systems have been limited and it is often hard to glean from the calculations the underlying physics which governs the atomic bonding. To our knowledge they have not been applied to Al-Li alloys.

We develop in this paper a simple method which addresses in a transparent fashion two important aspects of atomic bonding in Al-Li alloys: the effect of the *local* density on the one-body terms and pair potentials, and the effects of the nonlocality of the pseudopotentials of Al and Li. It was pointed out by Harrison[18] that there may, in general, exist a local-electronic-density-dependent interatomic pair potential which takes into account the nonlinear screening effects beyond the second-order terms in perturbation theory. In this paper we show (Sec. II) that by introducing an intermediate Hamiltonian for the alloy system and performing successive second-order expansions, we can actually construct such local-density-dependent pair potentials for alloys. We also develop a simplified scheme for including the effects of the pseudopotential nonlocality on the bonding energy. We construct (Sec. III) new nonlocal model pseudopotentials for Al and Li from *ab initio* calculated pseudopotentials[19] and compare them with some previously used nonlocal model potentials.[15] The importance of the above effects for the Al-Li bonding are evaluated through explicit calculations and discussed in Sec. IV. Calculations are performed for the heat of formation and lattice constant of several ordered and disordered phases of Al-Li alloys, and the results are compared with experiments. Finally, Sec. V summarizes our conclusions and discusses future extensions and applications.

II. LOCAL-DENSITY CORRECTIONS TO SECOND-ORDER PERTURBATION EXPANSION

The usual second-order pseudopotential expansion theory[5,6,8,20] for an A-B alloy gives an expression for the total energy of the following form:

$$E=E_0(\bar{\rho}_0)+E_s(\bar{\rho}_0,s) \ , \tag{1}$$

with

$$E_0(\bar{\rho}_0)=\bar{z}E_j(\bar{\rho}_0)+\tfrac{1}{2}\bar{v}_a B_j(\bar{\rho}_0) + \tfrac{1}{2}[c_A\phi_{\rm bs}(\mathbf{R}=0)+c_B\phi_{\rm bs}^{BB}(\mathbf{R}=0)] \ , \tag{2a}$$

$$E_s(\bar{\rho}_0,s)=\frac{1}{2N_{\rm ion}}\sum_{\mathbf{R}\neq\mathbf{R}'}\sum_{\alpha\beta} n^{\alpha}(\mathbf{R})n^{\beta}(\mathbf{R}')\phi^{\alpha\beta}(\bar{\rho}_0,\mathbf{R}-\mathbf{R}') \ , \tag{2b}$$

$$\phi_{\rm bs}^{\alpha\beta}(\bar{\rho}_0,\mathbf{R})=\int d^3r\, d^3r'\chi[\bar{\rho}_0,\mathbf{r}-\mathbf{r}']v_{\rm ps}^{\alpha}(\mathbf{r})v_{\rm ps}^{\beta}(\mathbf{r}'-\mathbf{R}) \ , \tag{2c}$$

and

$$\phi^{\alpha\beta}(\bar{\rho}_0,\mathbf{R})=\frac{z_\alpha z_\beta}{R}+\phi_{\rm bs}^{\alpha\beta}(\bar{\rho}_0,\mathbf{R}) \ . \tag{2d}$$

Here $\bar{\rho}_0$ is the average density of conduction electrons, $E_j(\bar{\rho}_0)$ and $B_j(\bar{\rho}_0)$ are the total energy and bulk modulus of jellium at this density, v_a is the average atomic volume, $\bar{z}=c_Az_A+c_Bz_B$ is the average number of conduction electrons, α and β are labels for the two types of ions, i.e., $\alpha,\beta=A$ or B, and $n^{\alpha}(\mathbf{R})$ are distribution functions of ions of type α: $n^{\alpha}(\mathbf{R})=0$ or 1 depending on the ionic arrangement. The subscripts "bs" and "ps" denote "band-structure" and "pseudopotential," respectively.

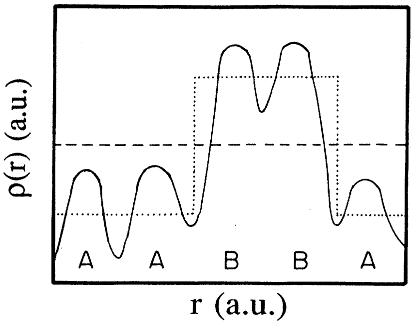

FIG. 1. Illustration of intermediate Hamiltonian. Solid curve, actual density ρ_{AB}; dotted curve, density in intermediate system ρ_i; dashed curve, uniform electron gas $\bar{\rho}_0$.

The main difficulty in applying the second-order expansion formalism given by Eqs. (1) and (2) to an alloy system results from the fact that local-electronic-density fluctuations from the average bulk density are often large (they are large in the Al-Li alloy since $z_{\rm Al}-z_{\rm Li}=2$). Such large density fluctuations render the second-order expansion from the jellium electron-gas model insufficiently accurate to reproduce the real electronic density of an alloy system.[5] The basic idea behind our method for obtaining corrections to the usual second-order expansion is illustrated in Fig. 1: We introduce an intermediate system between the jellium electron-gas potential and the complete ionic pseudopotential. This intermediate system has a nonuniform positively charged background and has an electronic density ρ_i which is closer than the uniform electron gas to the real density ρ. The density ρ_i generates an intermediate pseudopotential and Hamiltonian. We perform successive second-order expansions from the jellium electron gas via this intermediate system, to obtain corrections to the usual second-order expansion results,

$$H_i=T+V_i \ , \tag{3}$$

where T is the electron kinetic-energy operator. The forms of the intermediate pseudopotentials $v_i(\mathbf{r})$ used in our calculations will be specified later.

With the intermediate Hamiltonian H_i defined, we thus obtain

$$E[V]=E[V_i]+\int d^3r\,\rho_i\Delta V + \tfrac{1}{2}\int d^3r\, d^3r'\chi[\rho_i,\mathbf{r},\mathbf{r}']\Delta V(\mathbf{r})\Delta V(\mathbf{r}') \ , \tag{4a}$$

and

$$E[V_i]=E[V_0]+\int d^3r\bar{\rho}_0\Delta V_i + \tfrac{1}{2}\int d^3r\, d^3r'\chi[\bar{\rho}_0,\mathbf{r},\mathbf{r}']\Delta V_i(\mathbf{r})\Delta V_i(\mathbf{r}') \ . \tag{4b}$$

Here $\Delta V=V-V_i$, $\Delta V_i=V_i-V_0$, and χ denotes the electronic susceptibility of the inhomogeneous and uniform electron gases, respectively, in Eqs. (4a) and (4b). Substituting Eq. (4b) into Eq. (4a) and using $\rho_i(\mathbf{r})=\int d^3r'\chi[\bar{\rho}_0,\mathbf{r},\mathbf{r}']\Delta V_i(\mathbf{r}')$, we obtain an expression for the total energy $E[V]$:

$$E[V]=E[V_0]+\int d^3r\,\bar{\rho}_0\Delta V_0+\tfrac{1}{2}\int d^3r\, d^3r'\chi[\bar{\rho}_0,\mathbf{r}-\mathbf{r}']\Delta V_0(\mathbf{r})\Delta V_0(\mathbf{r}') \tag{5a}$$

$$+\tfrac{1}{2}\int d^3r\, d^3r'(\chi[\rho_i,\mathbf{r},\mathbf{r}']-\chi[\bar{\rho}_0,\mathbf{r},\mathbf{r}'])\Delta V(\mathbf{r})\Delta V(\mathbf{r}') \ . \tag{5b}$$

The first part of $E[V]$, Eq. (5a), is the same as the result from the usual second-order expansion in Eq. (1), and the second part of $E[V]$ gives correction terms due to the local-density fluctuations in alloys. The total energy per ion E can be written as

$$E=E_0(\bar{\rho}_0)+E_s(\bar{\rho}_0,s)+\Delta E_0(\bar{\rho}_0,\rho_i)+\Delta E_s(\bar{\rho}_0,\rho_i,s) \ , \tag{6}$$

where E_0 and E_s are defined in Eq. (1). Here the correction terms ΔE_0 and ΔE_s are given by

$$\Delta E_0(\bar{\rho}_0,\rho_i)=\frac{1}{2N_{\mathrm{ion}}}\sum_{\mathbf{R}}\sum_{\alpha} n^{\alpha}(\mathbf{R})\Delta\phi^{\alpha\alpha}(\bar{\rho}_0,\rho_i,\mathbf{R},\mathbf{R}')\ , \tag{7a}$$

$$\Delta E_s(\bar{\rho}_0,\rho_i,s)=\frac{1}{2N_{\mathrm{ion}}}\sum_{\mathbf{R}\neq\mathbf{R}'}\sum_{\alpha\beta} n^{\alpha}(\mathbf{R})n^{\beta}(\mathbf{R}')\times\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\rho_i,\mathbf{R},\mathbf{R}')\ , \tag{7b}$$

where

$$\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\rho_i,\mathbf{R},\mathbf{R}')=\int d^3r\, d^3r'(\chi[\rho_i,\mathbf{r},\mathbf{r}']-\chi[\bar{\rho}_0,\mathbf{r},\mathbf{r}'])\times\Delta v_{\mathrm{ps}}^{\alpha}(\mathbf{r}-\mathbf{R})\Delta v_{\mathrm{ps}}^{\beta}(\mathbf{r}'-\mathbf{R}') \tag{7c}$$

and $\Delta v_{\mathrm{ps}}=v_{\mathrm{ps}}-v_i$.

To apply Eq. (6) to a physical system, one needs to choose an approximate form for $\chi[\rho_i,\mathbf{r},\mathbf{r}']$, and to make a particular choice of V_i. For the susceptibility, we make the ansatz

$$\chi[\rho_i,\mathbf{r},\mathbf{r}']=\chi^h[[\rho_i(\mathbf{r})+\rho_i(\mathbf{r}')]/2,\ \mathbf{r}-\mathbf{r}']\ , \tag{8}$$

where the homogeneous dielectric susceptibility χ^h is obtained[21,22] from the free-electron jellium model.[23] This ansatz has previously been used successfully for studies of metallic surfaces and molecular hydrogen.[21,22]

The intermediate potential is chosen such that it produces an electronic density which approximates the exact density better than does the uniformly averaged bulk electronic density, and which has less rapidly oscillating features than the exact density. The alloy-induced electronic density fluctuations are dominated by wavelengths larger than the Wigner-Seitz radius. Therefore, a plausible way to construct the intermediate potential for an ion of type α, $v_i^{\alpha}(\mathbf{r})$, is to smear out the ion charge $+z_{\alpha}$ uniformly into a sphericalized atomic cell with volume equal to v_{α}. This definition of the intermediate potential implies that $v_{\mathrm{ps}}^{\alpha}(\mathbf{r})-v_i^{\alpha}(\mathbf{r})=0$ in the region outside the atomic-volume sphere $r>R^{\alpha}$. Using the ansatz in Eq. (8) we can then write the pair-potential correction in Eq. (7c) as

$$\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\rho_i,\mathbf{R},\mathbf{R}')=\int_{r\leq R_a}d^3r\int_{r'\leq R_a}d^3r'\{\chi^h[[\rho_i(\mathbf{r}+\mathbf{R})+\rho_i(\mathbf{r}'+\mathbf{R}')]/2,\ \mathbf{r}-\mathbf{r}'+\mathbf{R}-\mathbf{R}']-\chi^h[\bar{\rho}_0,\ \mathbf{r}-\mathbf{r}'+\mathbf{R}-\mathbf{R}']\}\Delta v_{\mathrm{ps}}^{\alpha}(\mathbf{r})\Delta v_{\mathrm{ps}}^{\beta}(\mathbf{r}')\ . \tag{9}$$

An important simplification can be obtained by observing that the pair-potential correction term $\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\rho_i,\mathbf{R},\mathbf{R}')$ depends only on the densities $\rho_i(\mathbf{r}+\mathbf{R})$ and $\rho_i(\mathbf{r}'+\mathbf{R}')$ inside the Wigner-Seitz spheres $r\leq R_a$ and $r'\leq R_a$, where the two ions α and β are centered, respectively. Since the electronic density in these two regions is determined primarily by the contribution from the center ion and the tails from its nearest neighbors, we replace in Eq. (9) the densities $\rho_i(\mathbf{r}+\mathbf{R})$ and $\rho_i(\mathbf{r}'+\mathbf{R}')$, which depend on locations of all the other ions, by approximate averaged local densities $\bar{\rho}_i^{\alpha}(\mathbf{R})$ and $\bar{\rho}_i^{\beta}(\mathbf{R}')$, which depend only on the nearest neighbors. The averaged density $\bar{\rho}_i^{\alpha}(\mathbf{R})$ in the atomic cell $|\mathbf{r}-\mathbf{R}|\leq R_a$ of an ion of type α is defined as follows.

First, we define an electronic density $\rho_i^{\alpha}(\mathbf{r}-\mathbf{R})$ induced by a single ion α at $\mathbf{R}$,

$$\rho_i^{\alpha}(\mathbf{r}-\mathbf{R})=\int d^3r'\chi^h[\bar{\rho}_0,\ \mathbf{r}-\mathbf{r}']v_i^{\alpha}(\mathbf{r}'-\mathbf{R})\ . \tag{10}$$

Then we define an averaged "central density" $\bar{\rho}_c^{\alpha}(\mathbf{R})$ and an averaged "tail density" $\bar{\rho}_t^{\alpha}(\mathbf{R})$ as

$$\bar{\rho}_c^{\alpha}(\mathbf{R})=\int_{|\mathbf{r}-\mathbf{R}|\leq R_a}d^3r\,\rho_i^{\alpha}(\mathbf{r}-\mathbf{R})\Big/\frac{4\pi}{3}R_a^3\ , \tag{11a}$$

$$\bar{\rho}_t^{\alpha}(\mathbf{R})=\int_{|\mathbf{r}-\mathbf{R}|> R_a}d^3r\,\rho_i^{\alpha}(\mathbf{r}-\mathbf{R})\Big/\frac{4\pi}{3}R_a^3\ . \tag{11b}$$

The averaged local density $\alpha\bar{\rho}_i^{\alpha}(\mathbf{R})$ is simply equal to its central density plus the tail densities from its nearest neighbors, i.e.,

$$\bar{\rho}_i^{\alpha}(\mathbf{R})=\bar{\rho}_c^{\alpha}(\mathbf{R})+\frac{1}{N_{\mathrm{NN}}}\sum_{\mathbf{R}_{\mathrm{NN}}}\sum_{\beta} n^{\beta}(\mathbf{R}+\mathbf{R}_{\mathrm{NN}})\bar{\rho}_t^{\beta}(\mathbf{R}+\mathbf{R}_{\mathrm{NN}})\ , \tag{12}$$

where N_{NN} is the number of neighboring ions around ion α and $\mathbf{R}_{\mathrm{NN}}$ are the neighboring ion-position vectors.

Using $\bar{\rho}_i^{\alpha}(\mathbf{R})$ in Eq. (9), we now have a simplified expression for the correction term in the form of a pair-potential correction $\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\bar{\rho}_i^{\alpha}(\mathbf{R}),\bar{\rho}_i^{\beta}(\mathbf{R}'),\mathbf{R}-\mathbf{R}')$, which depends on the bulk averaged density $\bar{\rho}_0$ as well as on the local averaged densities $\bar{\rho}_i^{\alpha}(\mathbf{R})$ and $\bar{\rho}_i^{\beta}(\mathbf{R}')$ determined by the charges of ions α and β, and their nearest neighbors:

$$\Delta\phi^{\alpha\beta}(\bar{\rho}_0,\bar{\rho}_i^{\alpha}(\mathbf{R}),\bar{\rho}_i^{\beta}(\mathbf{R}'),\mathbf{R}-\mathbf{R}')=\int_{r\leq R^{\alpha}}d^3r\int_{r'\leq R^{\beta}}d^3r'\{\chi^h[[\bar{\rho}_i^{\alpha}(\mathbf{R})+\bar{\rho}_i^{\alpha}(\mathbf{R}')]/2,\ \mathbf{r}-\mathbf{r}'+\mathbf{R}-\mathbf{R}']-\chi^h[\bar{\rho}_0,\ \mathbf{r}-\mathbf{r}'+\mathbf{R}-\mathbf{R}']\}\Delta v_{\mathrm{ps}}^{\alpha}(\mathbf{r})\Delta v_{\mathrm{ps}}^{\beta}(\mathbf{r}')\ . \tag{13}$$

III. PSEUDOPOTENTIAL MODEL AND NONLOCAL CORRECTIONS

The pseudopotentials we use for Al and Li are adapted from the *ab initio* calculations by Bachelet *et al.*[19] For simplicity, we make the following modifications.

(a) We approximate the pseudopotentials $v_l(r)$ by the approximations $\bar{v}_l(r)$, which have the form of some standard model potentials[5]

$$\bar{v}_l(r)=\begin{cases}-\bar{V}_l(R_c), & r\leq R_c\\ -z/r, & r>R_c\end{cases} \tag{14}$$

where

$$-\overline{V}_l(R_c)=\int_{r\le R_c} d^3r\, v_l(r)\Big/\left[\frac{4\pi}{3}R_c^3\right] . \tag{15}$$

Here, R_c is the "core radius," which will be determined later.

(b) With $\overline{v}_l(r)$ defined in Eqs. (20) and (21) we write the pseudopotential $\hat{v}_{\text{ps}}$ as a local potential plus nonlocal corrections inside the core region, i.e.,

$$\hat{v}_{\text{ps}}=v_{\text{loc}}(r)+\Delta\hat{v}_{\text{nloc}} . \tag{16}$$

We take

$$v_{\text{loc}}(r)=\overline{V}_{l=0}(r)=\begin{cases}-\overline{V}_0(R_c), & r\le R_c\\ -z/r, & r>R_c\end{cases} \tag{17}$$

so that

$$\Delta\hat{v}_{\text{nloc}}=\sum_{l,m}\Delta\overline{v}_l(r)|lm\rangle\langle lm| \tag{18a}$$

and

$$\Delta\overline{v}_l(r)=\begin{cases}-\Delta\overline{V}_l(R_c)\equiv-[\overline{V}_l(R_c)-\overline{V}_0(R_c)], & r\le R_c\\ 0, & r>R_c .\end{cases} \tag{18b}$$

The local pseudopotential $v_{\text{loc}}(r)$ will be treated in the total-energy calculations using the formalism developed in Sec. II. The total energy per ion due to the nonlocal part $\Delta\hat{v}_{\text{nloc}}$ in the elemental case, is calculated using a first-order perturbation expansion from the uniform electron gas, i.e.,

$$\Delta E_{\text{nloc}}(\overline{\rho}0)=\frac{1}{N_{\text{ion}}}\sum_{\mathbf{R}}\langle\Phi_0|\Delta\hat{v}_{\text{nloc}}(\mathbf{r}-\mathbf{R})|\Phi_0\rangle , \tag{19}$$

where $|\Phi_0\rangle$ is the ground-state wave function of the noninteracting electron gas and

$$\begin{aligned}\langle\Phi_0|\Delta\hat{v}_{\text{nloc}}(\mathbf{r}-\mathbf{R})|\Phi_0\rangle&=2\sum_{k\le k_F}\sum_l\epsilon_l(k) ,\\ \epsilon_l(k)&=-4\pi\Delta\overline{V}_l(R_c)(2l+1)I_l(k) ,\\ I_l(k)&=\tfrac{1}{2}R_c^3[j_l^2(x)-j_{l-1}(x)j_{l+1}(x)],\quad x=kR_c\end{aligned} \tag{20}$$

where $j_l(x)$ are spherical Bessel functions.

To include the local-density corrections in the alloy, we replace k_F in Eq. (20) by a local Fermi wave vector $k_F(\mathbf{R})$ which is determined by the local density $\overline{\rho}_i^\alpha(\mathbf{R})$ defined in Eq. (12). The nonlocal correction to the total energy from the ion at site $\mathbf{R}$ is then given by

$$\langle\Phi_0|\Delta\hat{v}_{\text{nloc}}(\mathbf{r}-\mathbf{R})|\Phi_0\rangle=2\sum_{k\le k_F(\mathbf{R})}\sum_l\epsilon_l(k) , \tag{21}$$

where $\epsilon_l(k)$ is defined in Eq. (20).

(c) The core radius R_c is determined by fitting the average bulk electronic-density parameters r_s for the pure metals (or, equivalently, the lattice constants) to the experimentally measured values, which are 2.06 for Al (fcc) and 3.25 for Li (bcc).

The values of R_c and $\overline{V}_l(R_c)$ determined for Al and Li are for Al, $R_c=1.846$ a.u., $\overline{V}_0(R_c)=1.347$ a.u., $\Delta\overline{V}_1(R_c)=0.343$ a.u., and $\Delta\overline{V}_2(R_c)=1.194$ a.u.; and for Li, $R_c=1.910$ a.u., $\overline{V}_0(R_c)=0.167$ a.u., $\Delta\overline{V}_1(R_c)=0.803$ a.u., and $\Delta\overline{V}_2(R_c)=0.342$ a.u. (We use atomic units throughout this paper: $\hbar=m_e=e=1$; distance, 1 a.u.$=0.529$ Å; energy, 1 a.u.$=27.2$ eV.)

As a check on the accuracy of our method, we have calculated the bulk moduli of Al and Li, at their equilibrium densities. We obtain $B_{\text{Al}}=2.15\times10^{-3}$ a.u. and $B_{\text{Li}}=4.27\times10^{-4}$ a.u., which are within 20% of the experimental results,[24] $B_{\text{Al}}=2.70\times10^{-3}$ a.u. (at $T=0$ K), and $B_{\text{Li}}=4.49\times10^{-4}$ a.u. (at $T=78$ K). Note that for both Al and Li, the nonlocal p component $-\Delta\overline{V}_1$ is attractive. This will be shown later to be very important in describing the atomic bonding in Al-Li alloys. We also note that band-structure calculations[25] have shown that the Fermi energies for both Al and Li are lower than the free-electron estimates: $\epsilon_F-\epsilon_F^{\text{FE}}=-0.0228$ a.u. for Al and -0.0539 a.u. for Li. In a lowest-order perturbation calculation these shifts come only from the nonlocal part of the pseudopotentials. An estimate of these reductions from our model potentials gives $\Delta\epsilon_F\cong\langle k_F|\Delta\hat{v}_{\text{nloc}}^{l=1}|k_F\rangle=-0.0135$ a.u. for Al and -0.0199 a.u. for Li. These estimated values, though they account for only about 50% of the correct magnifudes, and show that the nonlocal pseudopotentials for Al and Li from our model have the correct signs and relative strengths.

IV. CALCULATIONS FOR Al-Li ALLOYS

A. Random solid solutions, α phase

The Al-rich Li alloy α-phase Al_{1-x}-Li_x is a random solid solution on a fcc lattice.[26–28] The solid solubility of Li in Al is[28] 13.7% (atomic concentration) at $T=600\,^\circ\text{C}$, decreasing to 5.5% at $150\,^\circ\text{C}$. However, we show results for the entire concentration range because they elucidate the physical mechanisms underlying the bonding, and because metastable solid solutions and coherent ordered structures can be prepared with much higher Li concentrations. We calculate the heat of formation $\Delta H(c)$ per atom as a function of the atomic concentration c of Li.

The interatomic pair potentials $\phi^{\text{Al-Al}}(r)$, $\phi^{\text{Li-Al}}(r)$, and $\phi^{\text{Li-Li}}(r)$ at $c=0.25$ are plotted in Fig. 2(a). The local-density correction parts of the potentials $\Delta\phi^{\alpha\text{-}\beta}(r)$ at the same concentration are plotted in Fig. 2(b). The Li-Li correction $\Delta\phi^{\text{Li-Li}}(r)$ is stronger than the other two for both phases. This is due to the fact that inside the core region $r\le R_a$, $|\Delta v_{\text{ps}}|=|v_{\text{ps}}-v_i|$ for Li is larger on average than that for Al.

The results[29] for the heat of formation are plotted as functions of c in Fig. 3. The solid (dashed) curve shows the results calculated with (without) the local-density corrections using Eqs. (1), (2), (6), (7), (13), and (21) [Eqs. (1), (2), and (21)], including the nonlocal pseudopotential corrections. The dotted curve shows the results with the

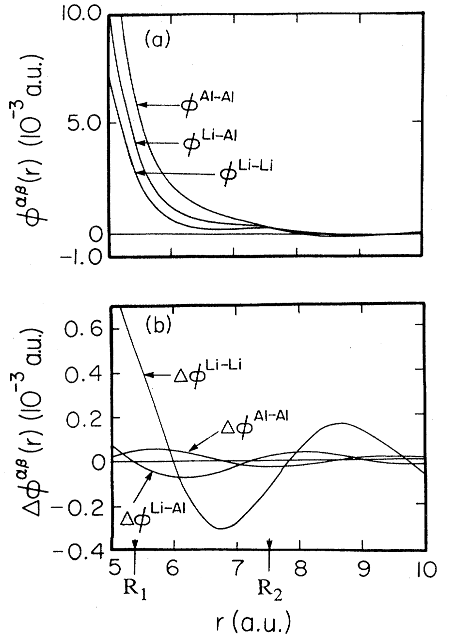

FIG. 2. (a) Interatomic pair potentials for Al-Li alloy at $c=0.25$ Li atomic concentration. (b) Local-density correction.

local-density corrections but without the nonlocal pseudopotential corrections. The magnitude of the nonlocal pseudopotential correction is clearly much larger than that of the local-density correction. Note that without the nonlocal pseudopotential correction the heat of formation would be positive; this is also true if the heat of formation is calculated with a local pseudopotential fitted to the lattice constant (the local part of our pseudopotential will, of course, obtain an incorrect lattice constant). The nonlocal pseudopotential correction provides a negative contribution to the heat of formation which is large enough to make the total heat of formation negative as well. This negative sign in the heat of formation is consistent with the observed phase diagram. The exothermic sign of the nonlocal contribution is due to the strongly attractive p component of the Li pseudopotential. Upon alloying with Al, the average electron density at a Li site becomes greater than in elemental Li. The p charge increases rapidly with the electron density, resulting in an exothermic contribution.

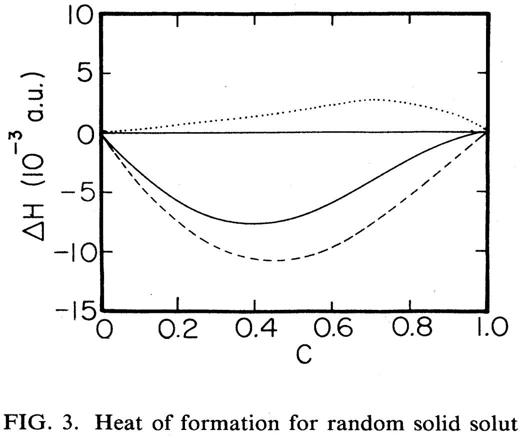

FIG. 3. Heat of formation for random solid solution: Solid curve, with both local-density and nonlocal pseudopotential corrections; dashed curve, with only nonlocal pseudopotential correction; dotted curve, with only local-density correction.

The local-density correction for the present model (cf. Fig. 3) reduces the magnitude of the heat of formation. We will show later that this reduction places our results closer to those obtained from more accurate density-functional band-structure calculations. The main contribution of the local-density corrections to the total energy in Eq. (7) comes from the one-body terms,

$$\Delta\phi^{\alpha\alpha}=\frac{1}{2}\int d^3r\,d^3r'\{\chi^h[\bar{\rho}_i^\alpha(\mathbf{R}),\mathbf{r}-\mathbf{r}'] -\chi^h[\bar{\rho}_0,\mathbf{r}-\mathbf{r}']\}\Delta v_{\text{ps}}^\alpha(\mathbf{r})\Delta v_{\text{ps}}^\alpha(\mathbf{r}')$$

[see Eq. (13)]. For the dielectric susceptibility one has $\partial\chi^h/\partial\rho<0$, since $\chi^h<0$ and a larger electron density screens more effectively. Therefore the one-body correction term $\Delta\phi^{\text{Al-Al}}$ for an Al atom lowers the total energy since the averaged local density $\bar{\rho}_i^{\text{Al}}(\mathbf{R})$ at an Al site is larger than the averaged bulk density $\bar{\rho}_0$. In contrast, $\Delta\phi^{\text{Li-Li}}$ for a Li atom raises the total energy since $\bar{\rho}_i^{\text{Li}}(\mathbf{R})$ at a Li site is smaller than $\bar{\rho}_0$. The one-body term for a Li atom dominates over that for an Al atom since, as mentioned above, $\Delta v_{\text{ps}}^{\text{Li}}$ is larger than $\Delta v_{\text{ps}}^{\text{Al}}$ inside the core region. The total energy with the local-density correction is therefore higher than that without the correction.

A surprising property of the solid solution is the contraction of the atomic volume relative to the pure Al metal. Instead of an increase in the average atomic radius in the alloy as predicted by Vegard's law (the atomic radius of Li $R^{\text{Li}}=3.25$ a.u., is larger than the atomic radius of Al, $R^{\text{Al}}=2.98$ a.u.), a decrease is observed.[2] This was studied previously using a pseudopotential expansion for a single impurity, including third- and fourth-order[16] terms. We find a contraction, relative to Vegard's law, of $(R_a-R_a^V)/R_a^V=0.13c$ for $c<0.10$, where R_a^V is the atomic volume of Vegard's law. This is in good agreement with the experimental result,[2] $(R_a-R_a^V)/R_a^V=0.11c$ (at 298 K).

A phenomenological model calculation has been recently made for the metastable phase diagram of Al-Li alloys.[3] In this model short-range order in the solid phases was taken into account within the tetrahedron approximation of the cluster-variation method and the Ising parameters for the ordering energy were fitted to the observed phase diagram. For the Al-Li fcc-based structures, the model parameters were fitted to the order-disorder congruent temperature and other aspects of the observed phase diagram, phase, and the experimental α solvus concentration. The calculated free energy of the fcc random solid solution implied the existence of a metastable miscibility gap below 400 K. However, from our calculated heats of formation shown in Fig. 3, there is no evidence for the existence of this miscibility gap. On the Al-rich side, the heat of formation is a monotonically decreasing function of the concentration with positive curvature, which precludes a miscibility gap.

B. Ordered structures

1. *Al-Li phase* (β)

The observed ordered stable Al-Li β phase has a $B32$ or Na-Tl structure,[26] which is a superstructure of the bcc lattice. For the heat of formation[30] we find $\Delta H_{B32} = -11.70$ mH/atom. The lattice contraction is also found in the $B32$ structure, $\Delta R^{\text{Al}}/R^{\text{Al}}$ $[=(R_a - R_a^{\text{Al}})/R_a^{\text{Al}}] = -0.0123$; the experimental result is -0.0091 (calculated from the data in Ref. 26).

In order to compare the ordering energies we also treat two other hypothetical ordered structures for Al-Li, the CsCl structure and AuCu structure.[26] The heat of formation is found to be -9.52 mH for CsCl and -11.11 mH for AuCu. We find that $\Delta H_{B32} < \Delta H_{\text{AuCu}} < \Delta H_{\text{Cscl}}$, is consistent with experiment. This ordering can be understood from the numbers of like and unlike neighbor atoms in each structure: six and eight, respectively, for the CsCl structure (including both first and second neighbors); four and eight for the CuAu structure; and four and ten for the $B32$ structure. In the alloy, unlike neighbors are preferred, explaining the stability of the $B32$ structure.

2. *Al_3Li*

This is a metastable ordered phase with the $AuCu_3$ structure.[26] The heat of formation we calculate is -9.68 mH for Al_3Li, and the lattice contraction (relative to Vegard's law) we find for Al_3Li is $\Delta R^{\text{Al}}/R^{\text{Al}} = -0.0103$, where the experimental value is -0.0096 (from data in Ref. 26). For comparison we also calculate the heat of formation of the hypothetical compound $AlLi_3$ with the same $AuCu_3$ structure: $\Delta H = -5.69$ mH.

3. *Al_4Li_9 δ phase*

The atomic basis of the structure[26] consists of 26 atoms, 8 Al and 18 Li. Each atom has 14 neighbors. All Al atoms have 12 Li and 2 Al neighbors. For Li atoms there are four different cases: 4 AL+10 Li, 5 Al+9 Li, 6 Al+8 Li, and 7 Al+7 Li. We find that $\Delta H = -5.15$ mH (the random fcc solid solution at the same concentration has $\Delta H_{\text{random}} = -4.42$ mH). The equilibrium atomic radius we find is $R_a/R_a^{\text{expt}} = 0.992$.

C. Discussion

In Fig. 4 we plot the results for the heats of formation we calculate for ordered and disordered structures versus atomic concentration. All of the ordered structures are stable relative to the random solid solution with the same concentration. Full potential linearized augmented-plane-wave (FLAPW) density-functional-band structure calculations have been performed for three ordered structures: Al_3Li, AlLi, and $AlLi_3$.[31] These results are plotted in Fig. 4 for comparison. One can see that our results overestimate the magnitudes of the heats of formation, although the local-density correction has reduced the magnitudes considerably (Fig. 3). However, the overall trend of the present values agrees with the band-theoretic values. We find the same asymmetry in both ordered and disordered phases with respect to the equiatomic concentration, with the Al-rich side having lower (more exothermic) heats of formation. Similar asymmetries in the heat of formation, with lower values on the side of the higher valence element, have been found in theoretical calculations[8,17] as well as experiments[32] for the random solid solutions of AlMg and MgLi. A major contribution to this asymmetry in the case considered here comes from the nonlocal pseudopotential contribution, which as mentioned above is the dominant exothermic contribution. A first-order expansion of the spherical Bessel functions in Eq. (21) shows that the slope of the heat of formation from the nonlocal pseudopotential $\Delta\bar{v}_1(r)$ part is proportional to $|2k_F^5/\partial c|$. If one used Vegard's law, one would have $\partial k_F^5/\partial c = 5/3k_F^5(\Delta z/z + \Delta V_a/V_a) \propto k_F^5$; therefore the more rapid change in k_F^5 with concentration for Al-rich alloys will lower the heat of formation relative to the Li-rich case.

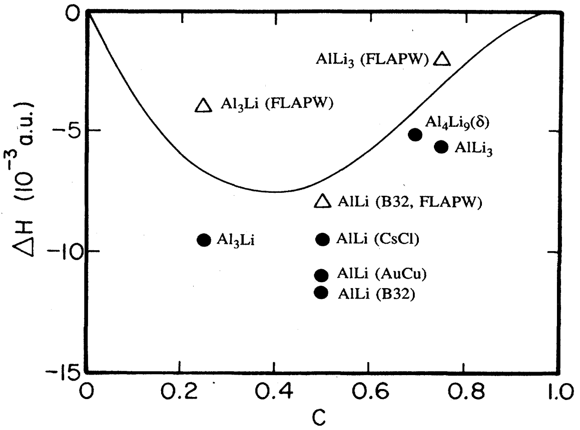

FIG. 4. Heats of formation of random solid solution and several ordered structures: Solid curve, random solid solution (fcc); ○, ordered structures; △, FLAPW calculations (Ref. 31).

The heat of formation ΔH_{B32} for the $B32$ structure and the ordering energy $\Delta H_{B32} - \Delta H_{\text{CsCl}}$ have previously been calculated using several more sophisticated methods: FLAPW by Guo *et al.*,[31] linear muffin-tin orbital (LMTO) by Christensen,[33] linear combination of atomic orbits (LCAO) by Hafner and Weber,[34] and a third-order local pseudopotential expansion by Maknovetskii and Krasko.[35] Their results are compared with ours and experiment[36] in Table I. Our estimate of ΔH_{B32} is within 30% of the experimental value and exceeds the FLAPW estimate by 40%. The ordering energy obtained by the present method is 30% below the FLAPW result (which is probably the most accurate). The third-order local pseudopotential expansion and the LCAO calculations obtain much larger discrepancies.

As another comparison of our results with experiment, we estimate the ordering transition temperature of the metastable ordered structure Al_3Li with an effective Ising model for the order-disorder transition[37]

TABLE I. Calculated heat of formation of the $B32$ structure and the ordering energy $\Delta H(B32)-\Delta H(\text{CsCl})$.

Method	$\Delta H(B32)$ (10^{-3} hartree/atom)	$\Delta H(B32)-\Delta H(\text{CsCl})$ (10^{-3} hartree/atom)
FLAPW[a]	-8.0	-3.3
LMTO[b]	-7.75	-2.9
LCAO[c]	-11.2	-0.6
Third-order pseudopotential		
Expansion theory[d]		-0.3
This work	-11.70	-2.2
Expt.[e]	-9.3 ($T=298$ K)	

[a] Reference 31.
[b] Reference 33.
[c] Reference 34.
[d] Reference 35.
[e] Reference 36.

$$E_{\text{order}}=\frac{J}{4}\sum_{i,j}\bar{\sigma}_i\bar{\sigma}_j \; . \tag{22}$$

Here $\bar{\sigma}_i$ is defined as

$$\bar{\sigma}_i=\begin{cases}2c & \text{for Al sites ,}\\ -2(1-c) & \text{for Li sites ,}\end{cases} \tag{23}$$

where c is the Li atomic concentration and only nearest-neighbor contributions are included. The ordering energy per ion for Al_3Li is $-\frac{5}{4}J$. The ordering energy we calculate is $E_{\text{order}}=-2.93$ mH for Al_3Li, which yields $J=2.34$ mH. The transition temperature is given by[37] $T_c=0.935J/k_B$ so that $T_c=690$ K for Al_3Li. This is quite close to the value estimated from the phase diagram in Ref. 3, $T_c \cong 800$ K.

The primary failure of our calculations for these structures is that we cannot construct an accurate phase diagram for the Al-Li alloy. From the results shown in Fig. 4 we find Al_3Li to be stable and Al_4Li_9 to be metastable or unstable, inconsistent with the observed stability of the Al_4Li_9 phase. These discrepancies are probably due to some inaccuracies in our method for dealing with the strong scattering pseudopotential of Al. The local-density-dependent corrections in our method include only the higher-order terms due to the inhomogeneity of the electronic density in the alloys. The remaining higher-order terms will lead to three- and four-body potentials or effectively angular forces. These are expected to be very important in stabilizing complex chemically specific structures such as the Al_4Li_9 structure.

V. CONCLUSIONS

In this paper we have developed a physically transparent pseudopotential expansion theory for nearly-free-electron alloys. Our method includes important modifications to the previously used local pseudopotential theories. We have used our approach to calculate the heats of formation and lattice constants of several ordered and disordered phases of Al-Li alloys and found considerable improvements over the previous approaches. Although our method does not have the quantitative accuracy required to calculate phase diagrams, it has the advantage of being orders of magnitude faster than band theoretic techniques, because no matrix diagonalizations are performed. Therefore believe that it can be of considerable utility in treating other Al-Li alloy properties, such as liquid structure and the atomic configurations around dislocations and grain boundaries. The local-density-dependent pair potential developed here also has potential advantages for treating many other inhomogeneous electronic systems, such as metallic surfaces and bulk solids containing point defects. For example, it is well established[38] that in the case of the Al vacancy, neglect of local corrections to the pair potential can lead to large errors in the calculated formation energy. Because the standard pseudopotential expansion theory does not treat strongly inhomogeneous systems accurately, they have often been treated with empirical pair and higher-order[39,40] potentials, which are based on arbitrary assumptions about the functional form of the potentials. The analysis presented here may well provide a useful alternative description for such systems.

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[29] We have found that our results are not sensitive to the cutoff distance in the summations of the pair potentials when it is larger than five neighbor shells. We include ten neighbor shells in the fcc lattice; for the other ordered structures we use a supercell approximation. The supercells for the $AuCu_3$ and $B32$ structures include $7\times7\times7$ unit cells, for the δ phase $3\times3\times3$ unit cells.

[30] We treat the first- and the second-neighbor shells as being in one shell for the CsCl structure and the $B32$ structure (both are bcc). The averaged "tail density" from an atom in the second neighboring shell is about 80% of that in the first neighboring shell for a bcc lattice.

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