

Brief Reports

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Energetics and lattice relaxation of light impurities in aluminum

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We present results of calculations for a series of impurities He, Li, Be, B, C, N, O, F, and Ne in an Al lattice, using the spherical-solid model. The relaxation displacements of the ions around the impurities at the octahedral site (i) vary rather smoothly with the impurity atomic number and (ii) show some structure. These results cannot be correlated with the size of the impurity in its atomic state, but involve the details of the density displaced in the host.

We present in this Brief Report extensions of our previous calculations on the energetics of a single H impurity in an Al host^{1,2} to He, Li, Be, B, C, N, O, F, and Ne impurities in Al. Our motivation is to understand if there are strong correlations between impurity lattice coupling (i.e., heat of solution, diffusion barrier, and lattice relaxations) and the shell structure of the impurities, to see if the calculated charge densities around the impurities can succeed in the prediction of such fine details of ground-state properties of impurity-host coupling (even in simple metal hosts like Al), and to encourage more experimental measurements in such systems. Our previous applications to H in Al (Refs. 1 and 2) provided good agreement with the experimental measurements³ but a more comprehensive study is certainly needed; this we present here.

Of course, such a low-symmetry problem has not been solved exactly and a variety of methods have been suggested⁴⁻⁶ whose value strongly depends on the nature of the host lattice. When the primary interest is the ground-state energy and lattice relaxations, we found^{1,2} that the *long-range* part of the impurity potential and the corresponding *long-range* part of the induced charge density are crucial for any reliable results. Our spherical-solid model^{1,2} (SSM) focuses on that feature and is probably best suited for simple metal hosts like Al, although extension of it to nonsimple metals has been suggested.⁷ For metals with a large number of *d* electrons, clusterlike calculations have been widely applied.⁴⁻⁶

We briefly describe the SSM. The SSM is a refined ver-

sion of the jellium model: In fact, SSM uses two successive calculations for extracting the electronic response, one for the lattice with the impurity at the center and one for the perfect lattice. The difference in the electron densities, n_1 and n_0 , respectively, is expected to give an accurate estimate of the density displaced by the impurity in the real system. Now, each of these two calculations uses the lattice potential:

$$\left\langle \sum_i V(\mathbf{r}-\mathbf{R}_i) \right\rangle_{\text{sph av}}, \quad (1)$$

i.e., the spherical average of a superposition of pseudopotentials

$$V(q) = -\frac{4\pi Z}{q^2 \Omega_0} \cos(qR_c) e^{-(q/q_0)^2} \quad (2)$$

of the smoothed Ashcroft form. Z is the valence charge of Al ($Z=3$), Ω_0 the unit-cell volume, $R_c=1.09$ a.u. the core radius, and q_0 the damping momentum. The fully-self-consistent densities $n_1(r)$ and $n_0(r)$ were obtained using the standard techniques for solving the jellium impurity problem, i.e., solution of the one-particle Schrödinger equations (for angular momenta up to 10) within a very large sphere, calculation of phase shifts, iteration of the Coulomb potential, etc. The Hedin-Lundqvist form of the exchange-correlation energy was used in these computations; its replacement by the Wigner formula produced only small change. With the help of the densities n_1 and n_0 , the total energy of the impurity in the lattice can be computed through the relation

TABLE I. Heats of solution for substantial impurities, as calculated in the present work, and compared to other published results.

	ΔH_{sub} (eV)				Ref. 9
	Present work				
He	0.85				0.77
Li	-1.27				
	Lattice relaxation				
	λ_1 (%)	λ_2 (%)	λ_3 (%)	λ_4 (%)	ΔE_{rel} (eV)
He	-1.67	-0.41	-0.07	-0.32	-0.076
Li	-1.74	-0.13	-0.17	-0.28	-0.080

$$E_{\text{imp}} = [E_1(n_1, \{\mathbf{R}_i\}) - E_0(n_0, \{\mathbf{R}_i\})]_{\text{SSM}}, \quad (3)$$

where E_1 is the energy of the system with the impurity Z_1 at the center and E_0 the energy of the perfect lattice. By subtracting the energy of the impurity atom in its free atomic or molecular state, one gets the heat of solution ΔH . In Ref. 2, we estimated the contribution of non-spherical terms in the densities to be small. This was done by calculating the higher-angular-momentum components ($l=4$ and 6) in the cubic-symmetry expansion of the density, as given by the density-functional equations based on the gradient expansion of the kinetic-energy functional. In the present applications, we assumed that the same conclusion still holds.

As shown in Refs. 8 and 9, the calculation of the lattice relaxation around the impurity is based on approximations consistent with the above SSM picture. The ionic

displacements are assumed to be radial:

$$\mathbf{R}'_i = (1 + \lambda_i) \mathbf{R}_i \quad (4)$$

in each shell of ions. The energy of the real relaxed lattice is written as

$$E_1(n'_1, \{\mathbf{R}'_i\}) = [E_1(n_1 + \rho_1, \{\mathbf{R}'_i\}) - E_0(n_0 + \rho_0, \{\mathbf{R}'_i\})]_{\text{SSM}} + E_0(n'_0, \{\mathbf{R}'_i\}), \quad (5)$$

which means that, once again, the difference in energies is accurately evaluated in the SSM. The relaxation of ionic position induces changes in the spherical densities, respectively, ρ_1 and ρ_0 . Now, Eq. (5) is expanded to second order in the λ 's. The change in the ionic potential is

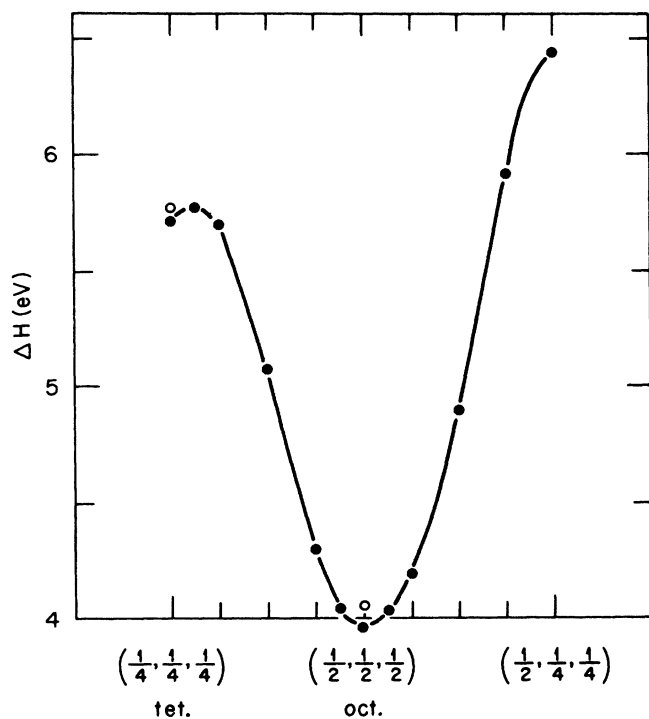


FIG. 1. Variation of the heat of solution for a He impurity in Al, as a function of its position in the lattice. Lattice relaxation not included. +, present work; o, results of Ref. 9.

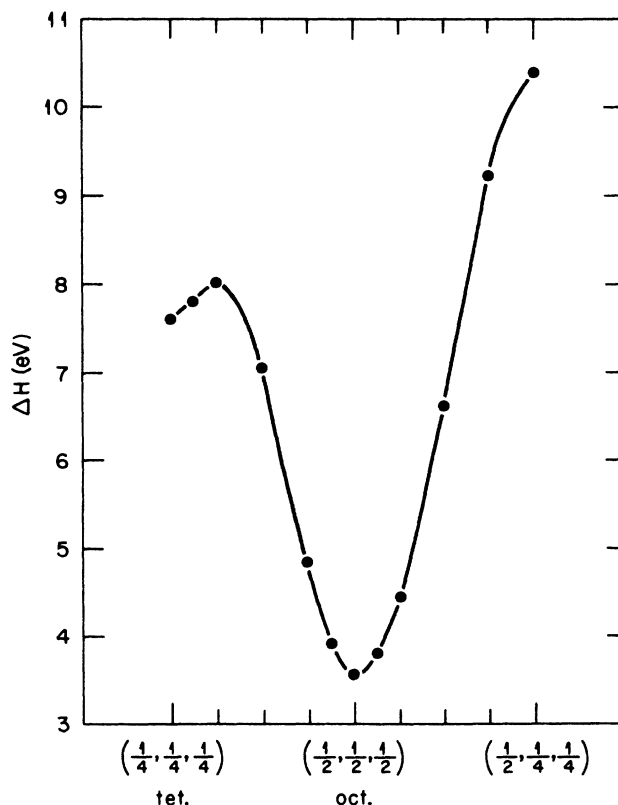


FIG. 2. Same as Fig. 1, but for a Li impurity.

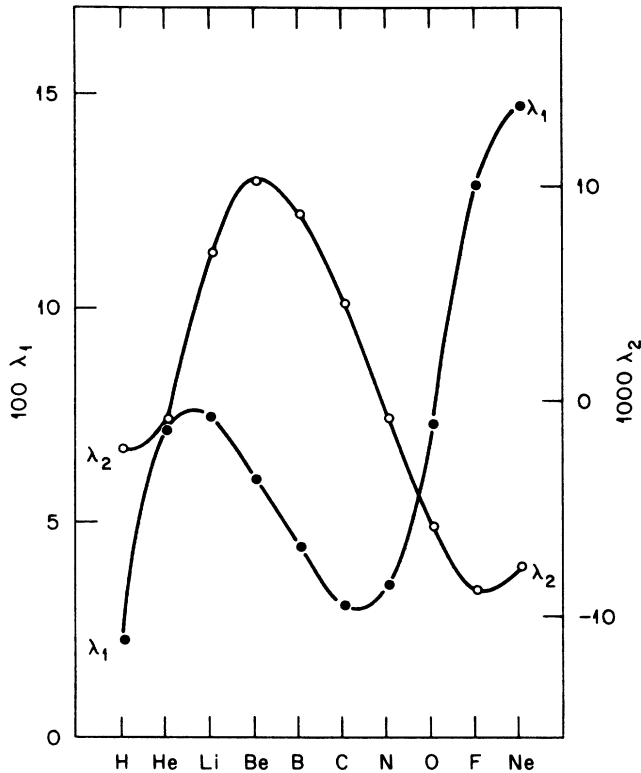


FIG. 3. Lattice relaxation, first (λ_1) and second (λ_2) shells for impurities ranging from H to Ne at the octahedral site.

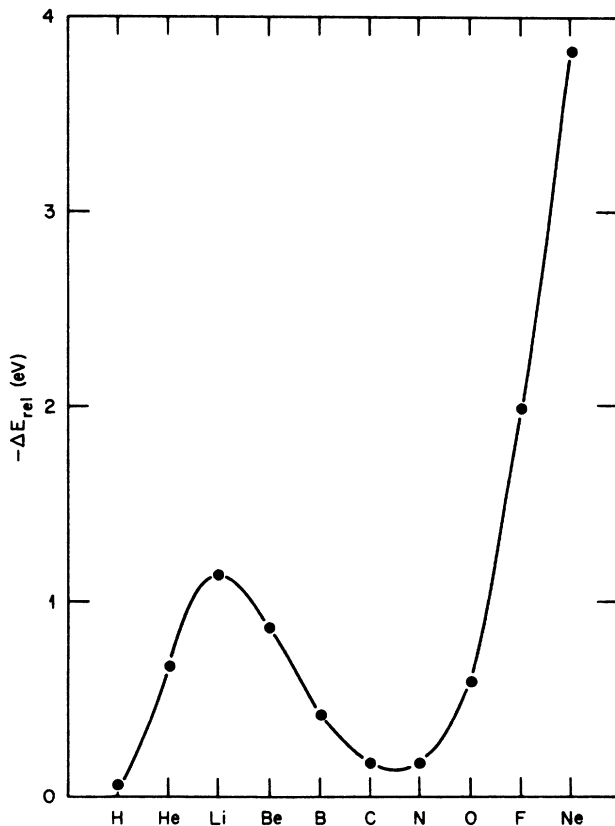


FIG. 4. Lattice-relaxation energy for impurities ranging from H to He, at the octahedral site.

$$\begin{aligned} \Delta V(r) &= \left\langle \sum_i V(\mathbf{r}-\mathbf{R}_i-\lambda_i \mathbf{R}_i) - V(\mathbf{r}-\mathbf{R}_i) \right\rangle_{\text{sph av}} \\ &= \sum_i [\lambda_i u_i(r) + \frac{1}{2} \lambda_i^2 v_i(r)]. \end{aligned} \quad (6)$$

The induced densities $\rho_1(r)$ and $\rho_0(r)$ are obtained by linear-response theory, using a local r -dependent Thomas-Fermi response function (which takes into account the pile up of density around the impurity). The energy $E_0(n'_0, \{R'_i\})$ is the "exact" energy of the Al lattice (by exact, we mean not calculated in the SSM, but in a model correctly treating the lattice symmetries) which can be expanded to λ^2 in standard pseudopotential theory. The equilibrium values of the λ 's are obtained by minimizing the right-hand-side term of Eq. (5), i.e., solving a set of linear equations, the dimension of which is the number of shells taken into account. A more explicit expression of this linear system can be found in Ref. 9. In the present work, we included five shells of neighbors in the calculation. We expect that the assumption of radial displacements is appropriate for impurity sites having a high degree of symmetry. We therefore then per-

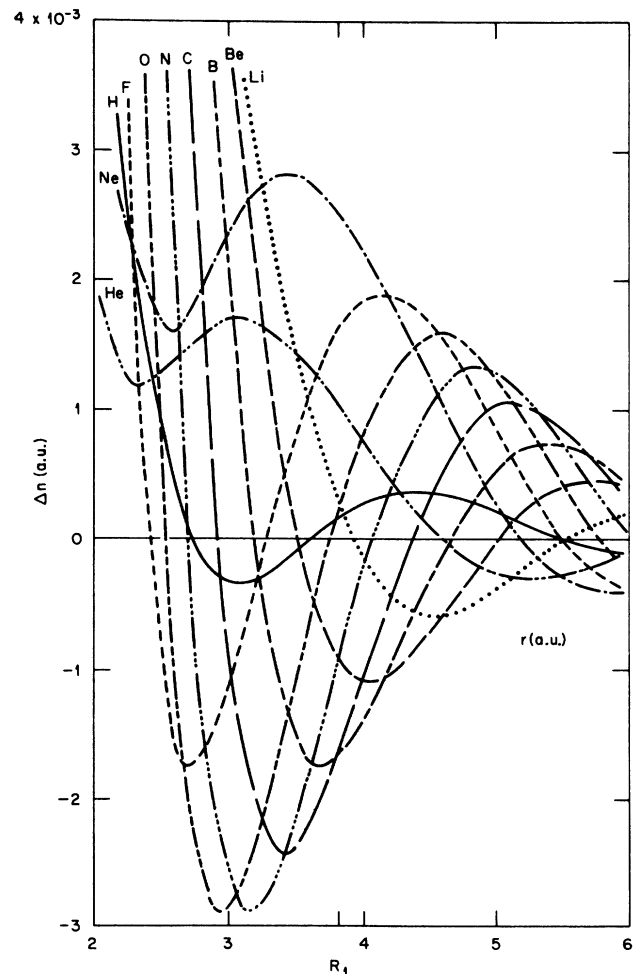


FIG. 5. Displaced electron densities $\Delta n = n_1 - n_0$ around impurities with atomic numbers ranging from 1 to 10. R_1 is the position of the first shell of Al ions.

formed the calculation for substitutional impurities and impurities in the octahedral site only.

We first carried out complete calculations for He and Li impurities in Al. The behavior of these two impurities are expected to be quite different: the solubility of He in metals is very low; on the other hand, Li and Al are known to be able to form stable alloys, so that stability is likely even in the Li low-concentration limit, at least in appropriate lattice sites. The results of our calculations for substitutional He and Li impurities are presented in Table I. The heat of solution ΔH is obtained by adding the ionization energy of the atom to the SSM impurity energy E_{imp} , defined in Eq. (3). These ionization energies are, respectively, $I = 78.88$ eV for He and $I = 101.74$ eV for Li.¹⁰ The values of ΔH_{sub} are 0.85 and -1.27 eV in He and Li, respectively, relaxation energy not included. The value found for He is in fair agreement with the result of Whitmore ($\Delta H_{\text{sub}} = 0.77$ eV), who calculated the impurity energy using a coupling-constant-integration scheme.¹¹ It is clear that Li is much more stable than He as a substitutional impurity. The lattice-relaxation results are also listed in Table I. In both cases, due to the smaller sizes of the impurities, there is a contraction of the lattice, leading to an energy contribution of the order of 10% of ΔH . The variations of ΔH with the position of the impurity in the lattice are displayed in Fig. 1 for He and Fig. 2 for Li. In both cases, the octahedral site is the most favorable one. In He, the activation energy for octahedral to tetrahedral diffusion is 1.80 eV. It may be compared with Whitmore's value, i.e., 1.70 eV. In Li, we find an activation energy of 4.45 eV for migration from octahedral to tetrahedral sites. Incidentally, in the H-Al case² we have checked the sensitivity of these results to a small variation in R_c [Eq. (2)] and found these results relatively insensitive.

Next, we discuss the lattice relaxation at the octahedral site. We find an outward displacement of the first shell of neighbors in He of $\lambda_1 = 7.3 \times 10^{-2}$, and $\lambda_1 = 7.5 \times 10^{-2}$ in Li; this is much larger than the value $\lambda_1 = 2.2 \times 10^{-2}$ we found for H.² These results are quite

surprising if one tries to understand them with a simple model relating the magnitude of the displacements to the "size" of the impurity, or the strength of impurity-lattice coupling with open- or closed-shell structure. Such a simple picture indicates that λ_1 would be smaller in a closed-shell atom like He than in H, and considerably larger in Li than in He. We found no such simple correlations for the next seven impurities up to $Z_1 = 10$. In Fig. 3 we present the variations of the displacements in the first two shells, λ_1 and λ_2 , versus the impurity atomic number. These variations are smooth and exhibit some structure. For instance, λ_1 shows a minimum near the middle of the second row. The variations of λ_1 correlate very well with those of the relaxation energy ΔE_{Rel} displayed in Fig. 4. The structure is incompatible with the simple picture previously mentioned, indicating that an interpretation based only on free-atom quantities (i.e., extension of the electron charge density) is irrelevant. Also, the position of the first shell in Al is at $R_1 = 3.82$ a.u., which is not in the asymptotic limit of the displaced density ($\Delta n = n_1 - n_0$) and therefore the results cannot be correlated with the phase shifts alone. In fact, as shown in Ref. 9, the quantity driving the first-shell displacement is

$$\frac{Z}{R_1} - \int (n_1 - n_0) u_1 d\mathbf{r}, \quad (7)$$

where u_1 is defined by Eq. (6). The continuous variation of λ_1 with Z_1 may only be understood in the light of the detailed structure of the displaced density, as shown in Fig. 5. This displaced density evolves continuously from Li to F, the amplitude of the negative oscillation going through a minimum. The cases of closed-shell impurities, Ne and He, are somewhat different since the closest mode disappears for these atoms.

The range of relaxation is very wide; it ranges from 2.2% in H to 15% in Ne. It would be very interesting to see if experimental measurements can confirm these trends as presented in Figs. 3 and 4.

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