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Ab initio calculation of the static structural properties of Al

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The static structural properties of Al are calculated using the self-consistent pseudopotential approach with local-density-functional expressions for the exchange and correlation energies. The only input parameter is the atomic number. Calculated values for the lattice constant, bulk modulus, and cohesive energy agree with experimental values within $<1\%$, $\sim 1\%$, and $\sim 7\%$, respectively.

I. INTRODUCTION

Successful *ab initio* calculations of the structural properties of the group-IV covalent elements have recently been reported.[1] The methods employed were the local-density-functional (DF) formalism[2] for the total energy, angular-momentum-dependent (nonlocal) pseudopotentials to represent the core—valence-electron interactions, and a self-consistent approach to the electron-electron interactions among the valence electrons. We have applied the same approach to calculate the lattice constant, bulk modulus, and cohesive energy of Al in the fcc structure. Excellent agreement with experimental values is also obtained.

Al is chosen as a prototype metal to test the free-electron model (FEM) which is usually assumed to represent an adequate description of this material. Many calculations of the structural properties of metals have been formulated using a free-electron gas subject to a weak potential, and these calculations are carried to second order in perturbation theory.[3] To test the validity of the FEM approach and other methods, we have made detailed comparisons between the results of this paper and those of other authors using different techniques.

The rest of the paper is organized as follows: The calculational procedure is described in Sec. II. Results are presented in Sec. III. The cohesion of metals is discussed in Sec. IV.

II. CALCULATIONAL PROCEDURE

First, the pseudopotentials for Al are determined using the method of Hamann, Schlüter, and Chiang.[4] These *ab initio* psuedopotentials require no experimental input. The only requirement is that they reproduce the all-electron results in the atomic limit. The atomic calculations are performed using the DF formalism with the Wigner interpolation formula for the exchange and correlation.[5] The same functional is used for the crystal calculation. The potentials are nonlocal (i.e., angular-momentum dependent) and are generated with a given atomic electronic configuration, in our case ($3s^1 3p^1 3d^1$). To ensure that these potentials can accurately simulate core-valence interactions, they are used to calculate the valence eigenvalues and excitation energies for different atomic configurations. The results agree very well with the all-electron values (see Table I), and the valence

TABLE I. Eigenvalues and excitation energies of the pseudoatom for different atomic configurations. The values in parentheses are deviations from the all-electron results.

Configuration	Eigenvalues (in Ry) 3s	 3p	 3d	Excitation energy (ΔE_{tot})
$3s^2 3p^1$	−0.5802	−0.2133		0
	(−0.0019)	(+0.0002)		
$3s^1 3p^1 3d^1$	−0.8479	−0.4346	−0.0605	0.7010
	(0.0)	(0.0)	(0.0)	(+0.0014)
Al^{3+}				3.9109
				(−0.035)

pseudo-wave-functions are within 1% of the true valence wave functions outside the core region.

The crystal wave functions are obtained by solving the Schrödinger equation using a plane-wave (PW) basis. Plane waves with energy $(\vec{k}+\vec{G})^2$ up to $E_{\text{cut}}=12$ Ry are included in the basis, which corresponds to a $\sim 80\times 80$ Hamiltonian matrix. The charge density is represented by wave functions at 45 k points in the $(\frac{1}{48})$ irreducible Brillouin zone. The convergence of calculated quantities with respect to E_{cut} and number of k points will be discussed later. The total energy per atom is calculated in the momentum representation and is given by[6]

$$E_{\text{tot}}=\Omega_a\left[\sum_{i,\vec{G}}|\psi(\vec{k}_i+\vec{G})|^2(\vec{k}_i+\vec{G})^2+\sum_{\vec{G}\neq 0}S(\vec{G})V^L_{\text{ion}}(\vec{G})\rho(\vec{G})\right.$$
$$+\sum_{i,l,\vec{G},\vec{G}'}S(\vec{G}'-\vec{G})\psi^*(\vec{k}_i+\vec{G})\psi(\vec{k}_i+\vec{G}')V^l_{\text{nl}}(\vec{k}_i+\vec{G};\vec{k}_i+\vec{G}')$$
$$\left.+\tfrac{1}{2}\sum_{\vec{G}\neq 0}V_H(\vec{G})\rho(\vec{G})+\sum_{\vec{G}}E_{\text{xc}}(\vec{G})\rho(\vec{G})+\alpha_1 Z+\gamma_{\text{Ewald}}\right], \tag{1}$$

where Ω_a is the atomic volume, Z is the valency, the $\vec{G}$'s are reciprocal-lattice vectors, and $S(\vec{G})$ is the structure factor. The quantities $\psi(\vec{k}_i+\vec{G})$, $V_H(\vec{G})$, $\rho(\vec{G})$, $E_{\text{xc}}(\vec{G})$, $V^L_{\text{ion}}(\vec{G})$, and $V^l_{\text{nl}}(\vec{k}_i+\vec{G};\vec{k}_i+\vec{G})$ are the Fourier transforms of the wave function, the Hartree potential, the charge density, the exchange-correlation energy, the local part of the pseudopotential, and the nonlocal part of the pseudopotential, respectively. The index i represents both the wave vector $\vec{k}_i$ and the band index n and runs over all occupied states. α_1 and γ_{Ewald} are[6]

$$\alpha_1=\lim_{G\to 0}\left[V^L_{\text{ion}}(\vec{G})+\frac{8\pi Z}{\Omega_a G^2}\right]$$
$$=\frac{1}{\Omega_a}\int\left[V^L_{\text{ion}}(r)+\frac{2Z}{r}\right]d^3r\ , \tag{2}$$

$$\gamma_{\text{Ewald}}=\frac{1}{2}\left[\sum_v\frac{2Z^2}{|\vec{R}_v|}-\frac{1}{\Omega_a}\int\frac{2Z^2}{r}d^3r\right], \tag{3}$$

where the $\vec{R}_v$'s are the lattice vectors to the ionic sites. Equation (1) can be written symbolically as

$$E_{\text{tot}}=E_K+V^L_{\text{ion}}(\vec{G}\neq 0)+V_{\text{nl}}+\tfrac{1}{2}V_H(\vec{G}\neq 0)$$
$$+E_{\text{xc}}+\alpha_1 Z+\gamma_{\text{Ewald}}\ , \tag{4}$$

where E_K is the kinetic energy. To avoid the double sum in Eq. (1), an alternative form for the total energy is used,[6]

$$E_{\text{tot}}=\frac{Z}{N}\sum_i\epsilon_i-\Omega_a\left[\frac{1}{2}\sum_{\vec{G}\neq 0}V_H(\vec{G})\rho(\vec{G})+\sum_{\vec{G}\neq 0}\mu_{\text{xc}}(\vec{G})\rho(\vec{G})\right]$$
$$+\sum_{\vec{G}}E_{\text{xc}}(\vec{G})\rho(\vec{G})+\alpha_1 Z+\gamma_{\text{Ewald}}\ , \tag{5}$$

where N is the number of occupied states; therefore, the first term is $Z\bar{\epsilon}$ where $\bar{\epsilon}$ is the average eigenvalue. The exchange-correlation potential is defined by

$$\mu_{\text{xc}}=\frac{\partial}{\partial\rho}E_{\text{xc}}[\rho]\ . \tag{6}$$

The calculation is iterated until E_{tot} is self-consistent to 10^{-6} Ry. The self-consistent pseudopotential method is described elsewhere.[7]

Since Al has partially filled bands, the special point schemes[8] are not very useful for the evaluation of $\sum_i\epsilon_i$; many eigenvalues are needed, and the following method is used. Eleven radial directions in the irreducible Brillouin zone are chosen, and eigenvalues and wave functions are calculated at four k points along each direction and at Γ yielding 45 k points in total. Using these calculated eigenvalues, we numerically interpolate along each direction. For Al, where the bands are generally spherical, such an interpolation along radial directions is expected to be good. For each direction, 200 points are interpolated, and the $\sum_i \epsilon_i$ is evaluated by a discrete sum with appropriate weighting factors. The method is tested for a free-electron band, and it yields good results.

To obtain the equilibrium lattice constant, bulk modulus, and cohesive energy, we calculated E_{tot} for six different lattice constants and fitted the E_{tot} versus V curve with

$$E_{\text{tot}}=a\left[\frac{1}{V}-\frac{1}{V_0}\right]^2+E_0\ . \tag{7}$$

The fit is better than 5×10^{-5} Ry. The bulk modulus B^0 is given by

$$B^0=V_0\frac{\partial^2 E}{\partial V^2}=\frac{2a}{V_0^3}\ . \tag{8}$$

The cohesive energy is obtained by taking the difference between E_0 and the total energy of the atom calculated with a spin-polarized correction.[9] Our calculated spin-polarized correction is 0.186 eV. Janak *et al.*[10] and Chelikowsky[11] obtained similar corrections of 0.19 and 0.18 eV. The zero point vibrational energy of the crystal is only $\sim10^{-3}$ Ry; hence, it is not included in our calculations.

Convergence of E_{tot} with respect to E_{cut} and number of k points is examined. Changing E_{cut} from 12 to 16 Ry only changes E_{tot} by 10^{-3} Ry. The charge density is insensitive to the number of k points. E_{tot} changes by only 10^{-4} Ry going from 25 k points to 45 k points. We use the same E_{cut} and number of k points for calculations with different lattice constant to ensure the same convergence. The equilibrium lattice constant and the bulk modulus are not very sensitive to the absolute convergence as long as we maintain the same convergence for each lattice constant; hence, they are evaluated more accurately than the cohesive energy.

III. RESULTS

The calculated lattice constant, bulk modulus, and cohesive energy are shown in Table II along with experimental values[12] and results from previous calculations.[3,10,11,13] The E_{tot} versus V curve is shown in Fig. 1. To test the reliability of the fitting approach, a quadratic function of volume

$$E_{\text{tot}}=a(V-V_0)^2+E_0 \tag{9}$$

is also used, and similar agreement is obtained. When using Eq. (9), one is confined to points close

TABLE II. Lattice constant, bulk modulus, and cohesive energy of Al, calculated and experimental values. Difference between calculated and experimental values are shown in parentheses. APW denotes augmented plane-wave calculation.

	Lattice constant (Å)	Bulk modulus (Mbar)	Cohesive energy (Ry/atom)
Ashcroft *et al.*[a] (pseudopotential)		0.65 (−0.072)	0.28 (+0.03)
Ross *et al.*[b] (APW without correlation)	4.12 (+0.1)	0.93 (+0.208)	0.30 (+0.05)
Janak *et al.*[c] (APW with correlation)	4.01 (−0.01)	0.801 (+0.079)	0.282 (+0.032)
Chelikowsky[d] (renormalized atom)	4.41 (+0.39)	0.65 (−0.072)	0.219 (−0.031)
Present calculation	4.01 (−0.01)	0.715 (−0.007)	0.268 (+0.018)
Experimental values[e]	4.02	0.722	0.25

[a] Reference 3.
[b] Reference 13.
[c] Reference 10.
[d] Reference 11.
[e] Reference 12.

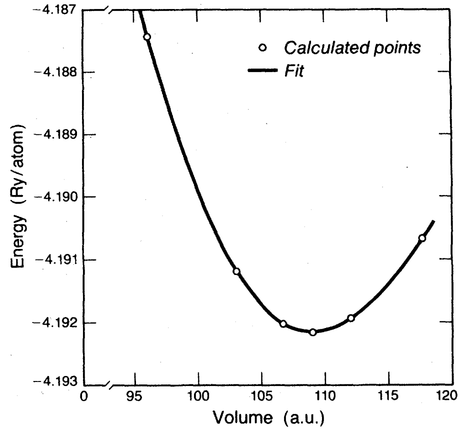

FIG. 1. Total energy versus volume. Calculated values are denoted by open circles, and the fit corresponds to the form given by Eq. (7) in the text.

to the equilibrium value. Our calculated cohesive energy differs from the experimental value by $\cong$ 0.018 Ry (Table II). This does not result from insufficient convergence accuracy since our convergence error is $\cong 10^{-3}$ Ry and increasing E_{cut} tends to lower the crystal energy.

The variation of various components of E_{tot} with respect to the lattice constant is shown in Table III. The E_K and $V_{\text{ion}}^{L}(\vec{G}\neq 0)$ are evaluated explicitly while V_{nl} is deduced by subtracting all other contributions from the sum of eigenvalues. The kinetic energy increases with decreasing volume as expected. $V_{\text{ion}}^{L}(\vec{G}\neq 0)$ and $V_H(\vec{G}\neq 0)$ are very small because the charge density is quite smooth. γ_{Ewald} seems to constitute a large part of the crystal energy. However, we should not focus on γ_{Ewald} alone because it was introduced to remedy the separate divergences of the electron-electron Coulomb, the electron-ion, and the ion-ion interactions.[6] It is the combined term

$$E^{\text{Coul}} = V_{\text{ion}}^{L}(\vec{G}\neq 0) + V_{\text{nl}} + \tfrac{1}{2} V_H(\vec{G}\neq 0) + \alpha_1 Z + \gamma_{\text{Ewald}} \tag{10}$$

which has real physical meaning, and it represents the total Coulomb interaction of the ion plus electron system. Actually, a pseudoion and pseudoelectron system is being modeled. The E^{Coul} term is attractive, and it favors small volume (Table III), which counterbalances the kinetic energy. The E^{Coul} term becomes extremely repulsive when the volume is smaller than the core size because of the $\alpha_1 Z$ term.

To compare our results with the free-electron model (FEM) results, we let $\rho(\vec{G}) = (Z/\Omega_a)\delta_{\vec{0},\vec{G}}$, that is, a uniform charge density, and Eq. (5) becomes

$$E_{\text{tot}}^{\text{FEM}} = Z\bar{\epsilon} + ZE_{\text{xc}}(0) + \alpha_1 Z + \gamma_{\text{Ewald}} , \tag{11}$$

where $ZE_{\text{xc}}(0) = ZE_{\text{x}}(0) + ZE_{\text{c}}(0)$ is given (in Ry) by

$$ZE_{\text{x}}(0) = -\frac{0.916}{r_s} Z$$

and

$$ZE_{\text{c}}(0) = -\frac{0.88}{r_s + 7.8} Z , \tag{12}$$

and r_s is the electron gas parameter defined by

$$\frac{4\pi}{3} r_s^3 = \frac{\Omega_a}{Z} . \tag{13}$$

TABLE III. Trends of various energy components versus lattice constant a.

	a_1	a_2	a_3	a_4	a_5	a_6
a (Å)	3.85	3.94	3.98	4.01	4.05	4.12
E_K	1.878 727	1.795 125	1.756 653	1.730 539	1.701 096	1.650 885
$V_{\text{ion}}^{L}(\vec{G}\neq 0)$	−0.372 340	−0.351 516	−0.342 465	−0.337 015	−0.331 291	−0.323 390
V_{nl}	−0.114 289	−0.099 141	−0.094 044	−0.090 456	−0.086 713	−0.080 441
$\frac{1}{2} V_H(\vec{G}\neq 0)$	0.009 979	0.009 089	0.008 615	0.008 345	0.008 143	0.007 976
E_{x}	−1.405 876	−1.373 985	−1.358 281	−1.347 510	−1.335 195	−1.313 777
E_{c}	−0.269 113	−0.267 864	−0.267 233	−0.266 792	−0.266 281	−0.265 372
$\alpha_1 Z$	1.758 895	1.642 566	1.587 412	1.550 166	1.508 055	1.436 239
γ_{Ewald}	−5.673 395	−5.545 456	−5.482 679	−5.439 460	−5.389 751	−5.302 800
E_{tot}	−4.187 412	−4.191 182	−4.192 022	−4.192 183	−4.191 937	−4.190 678
E^{Coul}	−4.391 150	−4.344 458	−4.323 161	−4.308 420	−4.291 557	−4.266 385
$E_{\text{tot}}^{\text{FEM}}$	−3.871 985	−3.903 834	−3.916 879	−3.924 875	−3.933 114	−3.944 992

If we also assume a free-electron band, that is, $\epsilon(k)=k^2$, then

$$Z\bar{\epsilon}=\frac{2.21}{r_s^2}Z\ . \tag{14}$$

The presence of both the $\alpha_1 Z$ and γ_{Ewald} terms distinguishes this model from the jellium ion model; $\alpha_1 Z$ represents the effect of the core, and γ_{Ewald} represents the effect of localized ions. In terms of r_s,

$$\alpha_1 Z=\frac{Z}{\Omega_a}\int\left[V_{\text{ion}}^L(r)+\frac{2Z}{r}\right]d^3r\equiv\frac{V_{\text{ps}}(0)}{\frac{4}{3}\pi r_s^3}\ , \tag{15}$$

and

$$\gamma_{\text{Ewald}}^{(\text{fcc})}=-\frac{1.79175}{r_s}Z^{5/3}\ . \tag{16}$$

For the Ashcroft potential,[3] $V_{\text{ps}}(0)=4\pi r_c^2$, where r_c is the core radius. With the Al potential used here, $V_{\text{ps}}(0)=56.394\,68$ Ry. We have calculated $E_{\text{tot}}^{\text{FEM}}$ (Table III). The equilibrium lattice constant deduced from $E_{\text{tot}}^{\text{FEM}}$ is 4.40 Å (error = 10%) while the bulk modulus is 1.1 Mbar (error = 50%). The terms neglected in the FEM are

$$\frac{1}{2}\sum_{\vec{G}\neq 0}V_H(\vec{G})\rho(\vec{G})+\sum_{\vec{G}\neq 0}[E_{\text{xc}}(\vec{G})-\mu_{\text{xc}}(\vec{G})]\rho(\vec{G})\ , \tag{17}$$

and the correction to the free-electron band arising from the presence of the ionic potential. Usually, these terms, called the band-structure term,[3] are approximately accounted for by perturbation theory to second order and linear screening.

We have investigated how well the individual energy components are given by the FEM (Table IV). Both E_x and E_c agree quite well with the FEM while $Z\bar{\epsilon}$ seems to deviate. However, if the eigenvalues are measured with respect to the bottom of the band, $\epsilon_i'=\epsilon_i-\epsilon(k=0)$, then $Z\bar{\epsilon}'$ is in better agreement with the FEM. Although the agreement with the FEM is quite good, the value of the bulk modulus depends on a detailed balance between different energy components and a high degree of accuracy is required.

IV. DISCUSSION

It is instructive to examine how the various energy components contribute to the cohesion of Al. The energy components of the atom and the solid are shown in Table V. As discussed before, the terms V_{ion}^L, V_{nl}, $\frac{1}{2}V_H$, $\alpha_1 Z$, and γ_{Ewald} are combined together under E^{Coul}, for the atom $\alpha_1 Z$ and γ_{Ewald} are zero. The kinetic energy increases from the atom to solid because the density is increased. There is a gain in Coulomb energy going from atom to solid; E^{Coul} is more negative in the solid because the electrons feel the presence of other ions. However, this gain is not enough to overcome the increase in kinetic energy. Therefore, the exchange term is essential for the cohesion of the metal.

A point which should be mentioned is that the kinetic energies in Table V are really those of the pseudo-valence-electrons in the atom and in the solid. Individually, they do not represent the kinetic energy of the true valence electrons. However, since only the part of the wave function outside the core is modified in going from the atom to the solid, the difference between the pseudokinetic energies should reproduce the true difference.

In summary, we have calculated the structural properties of Al from first principles. The results agree very well with the experimental values. The trends of the various energy components were examined and found to be qualitatively described by the free-electron model. The bulk modulus, which depends on the detailed balance between different energy components, requires accurate calculation. The contribution to the cohesion from various en-

TABLE IV. Comparison with FEM.

	a_1	a_2	a_3	a_4	a_5	a_6	FEM
r_s	1.9707	2.0162	2.0393	2.0555	2.0745	2.1085	
r_sE_x	−0.9235	−0.9234	−0.9233	−0.9233	−0.9233	−0.9234	(−0.916)
$(r_s+7.8)E_c$	−0.8765	−0.8765	−0.8765	−0.8765	−0.8765	−0.8765	(−0.88)
$r_s^2\bar{\epsilon}$	1.7960	1.8145	1.8221	1.8269	1.8320	1.8391	(2.21)
$r_s^2\bar{\epsilon}'$	2.0995	2.1087	2.1125	2.1149	2.1175	2.1212	(2.21)

TABLE V. Contributions to cohesive.

	Atom (Ry)	Solid (Ry)	Δ (Ry)
E_K	1.249 304	1.730 539	$+0.481\,235$
E^{Coul}	$-3.973\,150$	$-4.308\,420$	$-0.335\,270$
E_x	$-0.949\,340$	$-1.347\,510$	$-0.398\,170$
E_c	$-0.237\,756$	$-0.266\,792$	$-0.029\,036$
E (spin polarization)	(-0.0137)		$(+0.0137)$
E_{tot}	$-3.924\,640$	$-4.192\,183$	$-0.267\,543$

ergy components was also examined. The exchange contribution is essential to the cohesion of metals.

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