Ground-state thermomechanical properties of some cubic elements in the local-density formalism

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We show that the cohesive energy, lattice constant, and bulk modulus of Li, Be, Na, Al, Ar, K, Ca, and Cu can be calculated using the local-density scheme of Kohn and Sham, to within $\sim 20\%$, ~ 0.3 Bohr radii, and $\sim 10\%$, respectively, of experimental values. These calculations are truly *a priori* in that the only inputs are the atomic number Z and the zero-point lattice properties. Self-consistent crystal calculations were performed using the muffin-tin approximation, and atomic calculations were performed using the spin-polarized exchange-correlation functional constructed by von Barth and Hedin. The results show that these approximations are adequate for computing the equilibrium properties of crystals (errors in the computed pressure-volume relations are less than ~ 10 kbar), but errors occur in the atomic calculations for atoms with more than one electron outside a closed shell, and possibly in the muffin-tin approximation for transition-element crystals.

I. INTRODUCTION

According to Hohenberg and Kohn,[1] all ground-state properties of an interacting electron system are unique functionals of the ground-state charge density. Furthermore, Kohn and Sham[2] showed that this charge density can be obtained, in principle, from a one-electron Schrödinger equation containing an effective potential, although the exact form of the exchange-correlation part of this potential (though it is a unique and problem-independent functional of the density) is not known. The calculation of excited-state properties, on the other hand, will require information (energy-dependent self-energies, vertex corrections, etc.) which is not needed for the ground-state calculation, and about which relatively little is known.[3] Thus, ground-state properties such as the cohesive energy, lattice constant, and bulk modulus can be calculated with less uncertainty than any other properties of a material.

We report here on calculations of these properties for Li, Be, Na, Mg, Al, Ar, K, Ca, and Cu in the fcc or bcc structures, using the local form of the exchange-correlation potential obtained by Hedin and Lundqvist[4] from the theory of the homogeneous electron gas constructed by Singwi *et al.*[5] The only input information required for our calculations is the atomic number Z and the zero-point lattice properties (lattice structure, Debye temperature Θ_D, and Grüneisen constant γ). By iterating the (muffin-tin) energy-band calculation to self-consistency, we find the total energy, pressure, and bulk modulus as functions of the lattice constant. We then compare these quantities at the lattice constant where the computed pressure curve passes through zero to experiment. The results are generally in very good agreement with experiment (cohesive energies are within $\sim 20\%$, lattice

constants within ~ 0.3 Bohr radii, and bulk moduli within $\sim 10\%$ of experimental values).

II. ATOMIC CALCULATIONS

The cohesive energy of a crystal is the difference in the total energy of an atom in the crystal and the energy of an isolated atom. The local exchange-correlation potential used in our calculations is rigorously valid only in the limit of slowly varying electron density, and involves serious errors both within the atomic cores, and far from the nucleus, where an electron begins to leave its exchange-correlation hole behind. To the extent that the core charge density does not change in forming the crystal, a cancellation in the cohesive energy of the errors due to the rapidly-varying core charge density can be effected by maintaining internal consistency, and performing self-consistent calculations for the isolated atoms using the same exchange-correlation functional as has been used in the crystal calculations.

Actually, atoms with electrons in other than an s^2 configuration outside a closed shell have spin-polarization effects which lower their total energy. The magnitude of this effect is not insignificant compared to the cohesive energy, as shown by Gunnarsson *et al.*[6] for sodium, using a spin-polarized exchange-correlation functional constructed by von Barth and Hedin.[7] Therefore, we have performed our atomic calculations using an exchange-correlation functional which is appropriate for spin-polarized systems. This functional has the same form as the one used by Gunnarsson *et al.*,[6] and given in Eqs. (2) and (3) of their paper. However, we have used $c_p = 0.045$, $r_p = 21.0$, $c_f = c_p/2^{1/3}$, $r_f = 2^{1/3} r_p$, so that our functional reduces to the one given by Hedin and Lundqvist[4] (which we used for the crystal calculations) whenever the spin polarization vanishes.[8]

TABLE I. Total energies of atoms (Ry).

Element	E_{HF}[a]	E_{sp}[b]	δE_{sp}[c]
Li	−14.865	−14.709	0.027
Be	−29.146	−28.909	0.0
Na	−323.718	−322.902	0.024
Mg	−399.229	−398.274	0.0
Al	−483.753	−482.637	0.014
Ar	−1053.635	−1051.862	0.0
K	−1198.330	−1196.382	0.017
Ca	−1353.517	−1351.442	0.0
Cu	−3277.928	−3275.460	0.018

[a]After Mann (Ref. 9).

[b]Total energy of the spin-polarized atom in the local-density scheme.

[c]Lowering of the energy due to spin-polarization (local-density scheme). There are no spin-polarization effects for atoms with closed-shell, or s^2 outside a closed shell, configurations.

The results of our atomic calculations are given in Table I, where we show the Hartree-Fock energies obtained by Mann,[9] the total energy of the spin-polarized atom, obtained as discussed above, and the lowering of the total energy produced by the spin polarization, which we found by performing a separate self-consistent atomic calculation using the spin-unpolarized exchange-correlation functional given by Hedin and Lundqvist.[4] The relatively large differences between the Hartree-Fock and local-density total energies are similar to those found by Tong and Sham,[10] and are due to the neglect of nonlocal exchange effects in the local-density formalism. Our results for the total energy and energy of spin polarization for sodium and lithium are slightly different from those obtained by Gunnarsson et al.[6]; this is presumably due to the different values used for the constants in the exchange-correlation expression.[8]

III. CRYSTAL CALCULATIONS

The crystal calculations were performed for the bcc and fcc structures using the muffin-tin approximation. For each material, the calculation was iterated until the rms difference between input and output charge densities inside the muffin tin was less than 10^{-5} electrons. Our method of constructing the total energy and pressure from the charge density has been described in detail in an earlier paper.[11] (Briefly, the expression for the total energy is rearranged so that all contributions from the nonoverlapping cores appear in a single term, which can be calculated to the necessary accuracy by using double-precision arithmetic in the core-state calculations; and the expression for the pressure is rearranged so that the cores do not appear at all. The cancellation of large core contributions

to the pressure, which would otherwise have to be accomplished numerically, is thus effected algebraically. It is estimated that the total energies are numerically accurate to about 0.001 Ry, and the pressures to about 1 kbar.) Given the pressure $P(a)$ at several lattice constants, the bulk modulus is obtained from

$$B = -\tfrac{1}{3} a \frac{dP}{da} \tag{1}$$

by numerical differentiation.

In order to include the zero-point properties of the lattice, we use the Debye model,[12] in which the lattice motion contributes to the total energy an amount

$$E_0 = \tfrac{9}{8} k \Theta_D (\text{Ry/atom}) , \tag{2}$$

where k is Boltzmann's constant, and Θ_D is the Debye temperature. The contribution to the pressure is

$$P_0 = \gamma E_0/\Omega , \tag{3}$$

where γ is Grüneisen's constant, and Ω is the unit-cell volume; if we assume that γ is independent of volume, the lattice contribution to the bulk modulus is

$$B_0 = (1 + \gamma) P_0 . \tag{4}$$

These lattice quantities must be added to the electronic quantities to find the properties of the crystal. (For all the materials discussed here, the lattice quantities are small compared to the electronic quantities.)

In Table II, we show the values used for Θ_D and γ; we also show in this table the discontinuity in the self-consistent crystal potential at the muffin-tin radius. This quantity, weighted by the fraction of the volume to which it pertains, gives a measure of the validity of the muffin-tin approximation.

TABLE II. Lattice properties and muffin-tin discontinuity (MTD).

Element	Structure	Θ_D (K)[a]	γ[b]	MTD (Ry)[c]
Li	bcc	344	1.18	0.0273
Be	fcc	1440	1.18	0.0757
Na	bcc	158	1.31	0.0246
Mg	fcc	400	1.48	0.0595
Al	fcc	428	2.19	0.0936
Ar	fcc	93[d]	1.78[d]	0.0453
K	bcc	91	1.37	0.0210
Ca	fcc	230	1.16	0.0401
Cu	fcc	343	2.00	0.0977

[a]Reference 13.

[b]Reference 14.

[c]Discontinuity in crystal potential at muffin-tin radius.

[d]Reference 15.

TABLE III. Predicted and measured equilibrium properties.

Element	Cohesive energy (Ry/atom)		Lattice constant (a. u.)		Bulk modulus (Mbar)	
	Expt.[a]	Theory	Expt.[b]	Theory	Expt.[c]	Theory
Li	0.122	0.121	6.60[d]	6.40	0.132	0.148
Be	0.244	0.294	6.02[e]	5.93	1.15	1.35
Na	0.083	0.081	7.98	7.69	0.085[f]	0.090
Mg	0.112	0.121	8.46[e]	8.42	0.369	0.405
Al	0.244	0.282	7.60	7.59	0.880	0.801
Ar	0.0059[g]	0.0067	10.04[g]	9.5	0.025[g]	0.060
K	0.069	0.066	9.90	9.57	0.040	0.044
Ca	0.134	0.164	10.52[d]	10.0	0.152[a]	0.167
Cu	0.257	0.309	6.81	6.79	1.42	1.58

[a]Reference 14.
[b]Reference 13.
[c]Reference 16.
[d]Room-temperature value.

[e]For same atomic volume as hcp (0 °K).
[f]Reference 17.
[g]Reference 15.

IV. RESULTS AND DISCUSSION

The predicted cohesive energies, lattice constants, and bulk moduli are compared to experiment in Table III. The theoretical cohesive energies include the lattice contribution given by Eq. (2), and the theoretical lattice constants are defined by the point where the sum of the electron pressure and the lattice pressure given by Eq. (3) passes through zero. The theoretical bulk moduli are then obtained from the slope of the total pressure curve at this point using Eq. (1).

Calculations for Be and Mg were performed for the fcc structure, whereas these materials actually crystallize in the hcp lattice. The difference in energy between these two structures should be small compared to the cohesive energy, so that a comparison of cohesive energies is meaningful. (Note that the theoretical cohesive energies for the hcp structure for these two materials will be slightly larger than the values found for the fcc structure, and the latter are already greater than the experimental values.) The pressure-volume relation may be more sensitive to crystal structure, and a comparison of the lattice constant and bulk modulus to experimental values for Be and Mg is probably less meaningful. (The "experimental" lattice constant for these two materials is that value of the lattice constant for the fcc structure which gives the same atomic volume as is observed experimentally at liquid-helium temperatures.)

With the exception of argon, the predicted bulk moduli are generally within 10% of experimental values. The results for the lattice constants show that the computed pressure-lattice-constant curves are consistently too low. One possibility is that the γ values given in Table II are too small, or that γ depends strongly on volume. Except for Be, for which a γ of 3.4 would bring the lattice constant into agreement with experiment, the values of γ

required to bring the theoretical and experimental lattice constants into agreement are much too large. Thus, the results for the lattice constants are consistent with the statement that the approximations used in the crystal calculations (muffin-tin approximation, and local exchange-correlation potential) lead to errors of the order of −10 kbar in the computed pressure-lattice constant curve for simple metals. In Table IV, we give the pressure error δP due to the lattice constant error δa, obtained from Eq. (1) according to

$$\delta P = -3B\, \delta a/a \quad . \tag{5}$$

We also give the energy error $\Omega \delta P$ in Ry/atom, obtained by multiplying by the atomic volume Ω in appropriate units. This latter quantity is a better measure of the accuracy of the muffin-tin approximation than errors in the cohesive energy, because the core contributions can be explicitly removed from the pressure expression.[11] The cohesive energy, on the other hand, contains additional uncertainties due to the use of an approximate exchange-correlation expression for the valence electrons of the isolated atom, especially far from the nucleus

TABLE IV. Pressure errors.

Material	δP(kbar)[a]	$\Omega \delta P$(Ry/atom)[b]
Li	13.2	0.012
Be	63.2	0.022
Na	9.6	0.015
Mg	5.2	0.005
Al	4.0	0.003
Ar	3.7	0.006
K	4.5	0.013
Ca	24.4	0.041
Cu	12.5	0.007

[a]δP obtained from Eq. (5).
[b]Ω is the atomic volume.

where the valence-charge density is small. Thus the errors $\Omega\delta P$ in Table IV (except for beryllium and calcium) are larger for bcc than fcc materials, reflecting the commonplace that the muffin-tin approximation should be worse in bcc materials because of their larger interstitial volume. Calcium is the only material in Table IV with a partially filled d shell, and it is possible that its relatively large value of $\Omega\delta P$ is due to the anisotropy of the d-charge density, which is ignored in the muffin-tin approximation. This suggests that the muffin-tin approximation or the local exchange-correlation potential may involve serious errors when used for energy-band calculations in transition metals. (Preliminary calculations for vanadium and chromium suggest pressure errors δP around 100 kbar and $\Omega\delta P$ values as large as 0.1 Ry.)

Solid argon is unique among the materials considered here, in that its pressure–lattice constant relation has a large second derivative. Shifting the P-vs-a curve upwards by 4 kbar not only brings the lattice constant into agreement with experiment, but also reduces the theoretical bulk modulus to about 35 kbar, in much better agreement with experiment.

The cohesive-energy results are somewhat poorer for elements with more than one electron outside a closed shell. As mentioned above, we believe that this is due to errors in the atomic calculations rather than in the crystal calculations. As further evidence, the computed crystal energy is almost independent of the lattice structure if the atomic volume is kept fixed (this rule leads to lattice constants which are quite close to the ones giving zero pressure for the two cubic lattices considered). This energy difference was found to be 9×10^{-4} Ry/ atom for beryllium and 6×10^{-4} Ry/atom for sodium, with fcc lying lower than bcc in both cases. These energy differences are beyond the estimated accuracy of the calculations, and should not be taken to indicate the relative stability of the fcc structure; but they are so much smaller than the errors in the cohesive energies that the latter are almost certainly due to errors in the atomic calculations. Thus, there appear to be effects, beyond the spin-polarization effect, which must be taken into account in the local-density scheme for configurations with more than one electron outside a closed shell.

The cohesive energies obtained here are compared to those found in earlier calculations[18-22] and to experiment in Table V. Most of these calculations arrived at a cohesive energy based on a spin-unpolarized atomic calculation. To provide the reader with a basis for comparison, we have subtracted the energy of spin polarization given in Table I from the cohesive energies of these authors. Since they used different approximations for the

TABLE V. Comparison of cohesive energies (Ry/atom).

Material	Expt.[a]	This work[d]	Previous work	Previous work[c]
Li[d]	0.122	0.121	0.124[e]	...
Li	0.122	0.121	0.148[b]	0.121
Na	0.083	0.081	0.096[b], 0.102[f]	0.072, 0.078
K	0.069	0.066	0.075[b]	0.058
Ar	0.0059[g]	0.0066	0.0060[h]	...
Cu	0.257	0.309	0.281[i]	0.263

[a]Reference 14.

[b]Reference 19.

[c]For purposes of comparison, the spin-polarization energies given in Table I have been subtracted from the cohesive energies found by those authors who used unpolarized atomic calculations (see text).

[d]Using spin-polarized atomic calculation.

[e]Reference 18.

[f]Reference 20.

[g]Reference 15.

[h]Reference 21.

[i]Reference 22.

exchange-correlation potential, the energies in the last column of Table V are not necessarily the same as the cohesive energies that these authors would have obtained had they performed spin-polarized atomic calculations. The energies given in the last column of Table V are probably reasonable estimates, however.

The calculation of Ching and Callaway[18] for Li was a non-muffin-tin calculation using the $X\alpha$ method[23] with $\alpha = \frac{2}{3}$; Averill's calculations[19] on the alkali metals, the calculations of Trickey et al. on Ar,[21] and those of Snow on Cu,[22] were all muffin-tin calculations using the $X\alpha$ method with the "virial" α,[24] and Tong's calculation[20] on Na was performed using a cellular method and an interpolated form for the exchange-correlation potential. Where these authors have computed lattice constants and bulk moduli, the agreement of these quantities with our results is comparable to the agreement between cohesive energies appearing in Table V.

In summary, we have shown that the equilibrium properties of simple metals can be computed from first principles with good accuracy using the local-density scheme of Kohn and Sham. Because the pressure-volume relation of a crystal can be calculated with no reference to the atom, agreement of the lattice constant and bulk modulus with experiment constitutes a better test of the muffin-tin and local exchange-correlation approximations for crystals than does the cohesive energy.

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