

Pseudopotential study of the structural properties of bulk Li

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The phase stability of the hcp, fcc, and bcc structures of Li is studied using the pseudopotential density-functional total-energy calculation scheme. The order of the crystal energy at zero pressure is $E_{\text{hcp}} < E_{\text{fcc}} < E_{\text{bcc}}$. The two closed-packed structures (fcc and hcp) are fairly stable compared to the bcc structure for all volumes considered, i.e., there is no pressure-induced bcc transition from either hcp or fcc. The energy difference between hcp and fcc is very small and a hcp-to-fcc transition occurs at a pressure of about 15 kbar. Unlike a previous pseudopotential calculation, which predicted a fcc-to-bcc transition, but no hcp-to-fcc transition, the present result on the transitions is in good agreement with existing all-electron calculations.

I. INTRODUCTION

As a prototype of simple metals, lithium has been extensively studied both theoretically and experimentally, beginning with the pioneering calculation of its cohesive properties by Wigner and Seitz¹ in the 1930s. However, the current understanding of the equilibrium crystal structure of this simple alkali metal is incomplete. Although it has been known that there is a martensitic phase transition from bcc to a close-packed structure as decreasing temperature at normal pressure, the specific form of the close-packed phase is not determined conclusively.^{2,3} Moreover, the stability of close-packed phases under pressure is still a subject of further investigation.^{4,5}

In the theoretical part, there have been a number of total energy calculations within the local density approximation⁶ to determine the stable phase of Li among the bcc, fcc, and hcp structures at zero temperature.⁷ Most of the theoretical studies agree that the order of the equilibrium phases is hcp, fcc, and bcc in increasing order. However, there is a qualitative difference in the phase stability of Li between a recent first-principles pseudopotential calculation⁹ and all-electron calculations.¹⁰⁻¹³ Dacorogna and Cohen's pseudopotential calculation⁹ predicted a fcc-to-bcc phase transition and no hcp-to-fcc transition under pressure. On the other hand, recent linear-muffin-tin-orbital (LMTO)¹² and full-potential linear-augmented-plane-wave (FLAPW)¹³ calculations have predicted a hcp-to-fcc phase transition, but no fcc-to-bcc transition. Thus the existing pseudopotential result for the possibility of the phase transitions (fcc-to-bcc and hcp-to-fcc) is just the opposite to the all-electron calculations.

This work was strongly motivated by the above-mentioned conflict of the pseudopotential result with the all-electron calculations. In this paper, we investigate the phase stability of the hcp, fcc, and bcc structures of Li under external pressure using the pseudopotential density-functional total-energy calculation scheme. We find that the order of the crystal energy at zero pressure is $E_{\text{hcp}} < E_{\text{fcc}} < E_{\text{bcc}}$, which is consistent with the earlier

theoretical studies. Unlike the previous pseudopotential result of Dacorogna and Cohen,⁹ however, our calculations predict that a hcp-to-fcc phase transition takes place at a pressure of about 15 kbar and there is no fcc-to-bcc phase transition over the range of pressure considered. Thus we show that, contrary to the previous pseudopotential calculation, the present pseudopotential results for the phase transition agree well with the all-electron calculations.

The rest of the paper is arranged as follows. The calculational procedure is described in Sec. II. In Sec. III, the total-energy results for the hcp, fcc, and bcc structures of Li are presented and compared with other theoretical results. A summary is given in Sec. IV.

II. PSEUDOPOTENTIAL DENSITY-FUNCTIONAL TOTAL-ENERGY SCHEME

In the present study, the total energies of the system are calculated within the local density approximation⁶ (LDA) and norm-conserving pseudopotential scheme^{14,15} using a momentum-space formalism.¹⁶ We treat the many-electron interactions with the LDA using the Ceperley and Alder exchange-correlation functional parametrized by Perdew and Zunger.¹⁷ The nonlocal atomic pseudopotentials of Li are generated from the ground-state atomic configuration by the generalized norm-conserving pseudopotential scheme of Hamann and co-workers.^{14,15} Since the overlap of the *s* valence electron with the core ones is not negligible in alkali metals, the partial-core correction scheme proposed by Louie, Froyen, and Cohen¹⁸ is employed in order to improve the transferability of the atomic pseudopotentials of Li. We use the partial-core cutoff radius of 1.6 a.u.

The electron wave functions are expanded in a plane-wave basis set which contains plane waves with the kinetic energy up to $E_{\text{pw}} = 15$ Ry. The charge density is obtained from the wave functions calculated at a uniform grid of *k* points in the Brillouin zone. As pointed out by Dacorogna and Cohen,⁹ it is very difficult to pin down the extremely small energy difference (order of 0.01 mRy/atom) between different phases of the alkali metals. To describe such a small energy difference accurately, we

consider the fcc and hcp structures in a same hexagonal supercell which includes six atoms, i.e., the hexagonal-layer stacking sequence is *ABCABC* for fcc and *ABABAB* for hcp. In this way, we can treat the two different crystal structures with the same plane-wave basis and \mathbf{k} -point sampling. A uniform grid of 1728 \mathbf{k} points in the Brillouin zone is used in the bcc structure and 288 \mathbf{k} points in the hexagonal (fcc and hcp) supercell structures. We continue the self-consistent iterations until the total energy becomes stable within 10^{-6} Ry/atom.

III. RESULTS

Total energies for the hcp, fcc, and bcc structures are calculated at nine different atomic volumes around the experimental one (see Table I). The equilibrium atomic volume, bulk modulus, and cohesive energy of each crystal structure are given in Table II by fitting to Murnaghan's equation of state.¹⁹ At equilibrium, the total crystal energy increases in the order of $E_{\text{hcp}} < E_{\text{fcc}} < E_{\text{bcc}}$. We find in Table I that the bcc structure is unstable compared to the hcp and fcc structures for all volumes considered (at equilibrium, $E_{\text{bcc}} - E_{\text{fcc}} = 0.54$ mRy). The hcp and fcc structures are energetically comparable at all volumes considered: at equilibrium hcp is slightly more stable than fcc ($E_{\text{fcc}} - E_{\text{hcp}} = 0.02$ mRy), but an energy crossing occurs in the volume range of $V/V_0 = 0.85 \sim 0.90$. We estimate a pressure-induced hcp-to-fcc transition at around $V = 117.9$ a.u. (where the calculated pressure is 15 kbar).

In the present calculation, the energy difference between hcp and fcc at equilibrium is very small (~ 0.02 mRy). Hence, we considered the further stabilization of the hcp crystal via the relaxation of the c/a ratio for a given atomic volume. At the equilibrium volume, the relaxation energy amounts to 0.008 mRy/atom at $c/a = 1.646$ (ideal $c/a = 1.633$). We expect from this result that the optimization of the c/a ratio slightly enhances the hcp stability and, as a result, the above-mentioned hcp-to-fcc transition would take place at a little smaller volume (and higher pressure).

To check the effect of the partial-core correction on the structural properties of Li, we have also performed the total-energy calculation for the hcp, fcc, and bcc structures using pseudopotentials without the partial-core correction. The calculated structural properties are given

TABLE I. Calculated total energies of Li (Ry/atom) as a function of relative atomic volume (V/V_0 , where $V_0 = 132$ a.u.) in the hcp, fcc, and bcc structures.

V/V_0	hcp	fcc	bcc
0.75	-0.620 350	-0.620 436	-0.619 605
0.80	-0.622 313	-0.622 358	-0.621 621
0.85	-0.623 621	-0.623 636	-0.622 981
0.90	-0.624 334	-0.624 327	-0.623 733
0.95	-0.624 593	-0.624 575	-0.624 035
1.00	-0.624 477	-0.624 452	-0.623 944
1.05	-0.624 078	-0.624 052	-0.623 565
1.10	-0.623 430	-0.623 403	-0.622 937
1.15	-0.622 617	-0.622 592	-0.622 140

TABLE II. Structural properties of Li in the hcp, fcc, and bcc structures. The equilibrium atomic volumes (V_{eq}), bulk moduli (B), and cohesive energies (E_{coh}) are obtained by fitting the data in Table I to Murnaghan's equation of state. The results obtained from the calculations with no partial-core correction are given for comparison in the parentheses.

	hcp	fcc	bcc
V_{eq} (a.u.)	126.45 (117.81)	126.28 (117.55)	127.59 (118.46)
B (kbar)	152 (149)	151 (147)	153 (149)
E_{coh} (mRy)	137.01 (139.78)	136.99 (139.77)	136.45 (139.19)

in the parentheses of Table II. Comparing these to the partial-core results, we can estimate the effect of the partial-core correction on the structural properties. We find that the partial-core correction increases the equilibrium atomic volumes of various structures by about 7%. From the nearly identical bulk moduli and unaffected energy differences between the phases, however, we conclude that the results on the phase stability and transition under pressure change little by the partial-core correction.

The present results for the structural energy differences at equilibrium, the possibility of the phase transitions, and the lattice constants are compared with those of the previous calculations in Table III. Although all theories used different basis sets and LDA functionals, it is remarkable that they all agree in the order of phase (hcp, fcc, and bcc in increasing order). However, in the pseudopotential calculation by Dacorogna and Cohen,⁹ a fcc-to-bcc transition and no hcp-to-fcc transition were predicted as opposed to the present pseudopotential calculation and all-electron calculations, which yield a hcp-to-fcc transition and no fcc-to-bcc transition. Note that the energy difference between bcc and fcc ($E_{\text{bcc}} - E_{\text{fcc}}$) is relatively larger than one between fcc and hcp ($E_{\text{fcc}} - E_{\text{hcp}}$) in all calculations but Dacorogna and Cohen's pseudopotential result. The probable overestimation of $E_{\text{fcc}} - E_{\text{hcp}}$ in their pseudopotential calculation may be cured by an equal treatment of fcc and hcp in a hexagonal supercell as done in our calculations. The hcp-to-fcc transition pressure is calculated by about 15 kbar in the present study, but we had better not take the number serious since we are dealing with extremely small energy differences between hcp and fcc where a small inaccuracy in total-energy calculations would result in a large error in the calculated pressure. In fact, many of the previous studies reported a wide range of different transition pressures, for example, 4 kbar by Young and Ross,²³ 210 kbar by Skriver,¹⁰ and 80 kbar by Boettger and Albers.¹² The present lattice constants of the hcp, fcc, and bcc structures are in good agreement with those of the recent FLAPW calculation.¹³ The somewhat larger lattice constants of the previous pseudopotential study can be attributed to the employed LDA functionals: the Kohn-Sham-Gaspar⁶ (KSG) and Wigner²⁴ LDA functionals usually result in a larger lattice constant than the Rajagopal-Singhal-Kimball²⁵ (RSK), Hedin-Lundqvist²⁶ (HL), and Ceperley-Alder¹⁷ (CA) ones.^{9,11} Within the

TABLE III. Calculated total-energy differences (mRy) and lattice constants (a.u.) of Li in the hcp, fcc, and bcc structures in comparison with the previous calculations and experiments. Abbreviations in the parentheses represent the used LDA exchange and correlation functionals (W=Wigner, CA=Ceperley and Alder, HL=Hedin and Lundqvist, BH=Barth and Hedin, KSG=Kohn, Sham, and Gaspar, RSK=Rajagopal, Singhal, and Kimball). PT denotes phase transition. LCGTO denotes linear combination of Gaussian-type orbitals and ASW denotes augmented spherical wave.

Method	$E_{\text{fcc}} - E_{\text{hcp}}$	$E_{\text{bcc}} - E_{\text{fcc}}$	PT _{hcp-fcc}	PT _{fcc-bcc}	a_{hcp} (c/a)	a_{fcc}	a_{bcc}
Pseudopotential ^a (W)	0.47	0.20	No	Yes	5.71 (1.630)	8.09	6.43
Present pseudopotential (CA)	0.02	0.54	Yes	No	5.63 (1.633)	7.96	6.34
LCGTO ^b							
(KSG)		0.47		No		8.28	6.59
(RSK)		0.87		No		7.94	6.32
ASW ^c (BH)	0.10	0.20	Yes	No	5.91 (1.633)		
FLAPW ^d (HL)	0.08	0.24	Yes	No	5.66 (1.638)	8.00	6.35
Experiments					5.88 (1.637) ^e		6.58 ^f

^aReference 9.

^bReference 11.

^cReference 20.

^dReference 13.

^eReference 21.

^fReference 22.

known variance due to the LDA functionals, the calculated lattice constants in Table III are in reasonable agreement.

IV. SUMMARY

We have studied the phase stability of the hcp, fcc, and bcc structures of Li using the pseudopotential density-functional total-energy calculation scheme. We find that the order of phases at zero pressure is hcp, fcc, and bcc in increasing order. A hcp-to-fcc transition occurs at pressure of about 15 kbar, but there is no fcc-to-bcc transi-

tion. Unlike a previous pseudopotential calculation resulting in a fcc-to-bcc transition and no hcp-to-fcc transition, our result for the phase transition is in good agreement with existing all-electron calculations.

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