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Brief Reports

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Low-pressure crystalline phases of lithium

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Systematic study of equilibrium and low-pressure crystalline phases in Li using the full-potential linearized augmented-plane-wave technique (as embodied in the code WIEN) gives hcp < fcc < bcc as the equilibrium energetic ordering. The equilibrium hcp phase stability is enhanced slightly by relaxation from the ideal c/a ratio. The first pressure-induced phase transition is hcp→fcc at a compression of $V/V_0=0.79$. These results confirm, in whole or in part, the predictions of all other studies of the low-pressure crystalline phase ordering of Li except for one. The one anomalous calculation [H. Bross and R. Stryczek, Phys. Status Solidi B **144**, 675 (1987)] finds bcc to be the most stable phase up to a compression $V/V_0 \approx 0.28$. That result is traced to a peculiar dependence of the total energy of bcc alkali metals upon the details of the Brillouin-zone scan used in the calculation.

A recent calculation of the $T=0$ K phases of Li by Bross and Stryczek[1] using the modified augmented-plane-wave (MAPW) method found the bcc phase to be stable with respect to the fcc phase over the compression range $0.28 \leq V/V_0 \leq 1$. That result contradicts three prior calculations.[2-4] One of those[4] considered hcp as well and found that the $P=0$ energetic preference of phases is hcp < fcc < bcc. Though Ref. 4 used a pseudopotential technique, two other groups did independent all-electron calculations.[5,6] Both confirmed the hcp < fcc < bcc ordering.

Reference 1 suggested that the other calculations were flawed by some unspecified inadequacy in methodology [linear-muffin-tin-orbital (LMTO), pseudopotential, and augmented-spherical-wave (ASW) methods were used in Refs. 2, 4, and 5, respectively]. Presumably, the same reasoning would apply to the subsequent Ref. 6, which used the LMTO method also. Nothing was said in Ref. 1 as to why the LCGTO (Ref. 3) calculation (which is all electron and full potential) might have suffered a parallel failure.

Shortly after Ref. 6 appeared, we did an all-electron full-potential linearized augmented-plane-wave (FLAPW) calculation and found the same ordering. At the time we did not publish it (though some results were quoted in Ref. 7). However, Sigalas *et al.*[8] have recently published APW (and LAPW) calculations for Li in cubic structures only and found fcc < bcc. They did not note that, in consonance with prior work, their result is a direct contradiction of Ref. 1 nor did they comment on any of the other prior work.

The most direct test of the methodological critique voiced in Ref. 1 would be a careful full-potential LAPW calculation with a completely independent code which can handle hcp, fcc, and bcc structures. We provide such results here and diagnose the probable cause of the anomalous result of Ref. 1.

The calculations presented here used the Hedin-Lundqvist (HL) local-density approximation[9] (LDA) and the linearized augmented-plane-wave method in its full-potential form (hence FLAPW) as embodied in the WIEN code.[10] Scalar-relativistic corrections were included. For the sake of reproducibility we list the relevant parameters of choice. The largest plane-wave vector $K_{\max}$ was determined by $R_{\mathrm{MT}}K_{\max}=8.00$ with R_{MT} the muffin-tin radius (touching spheres), a choice which consistently yielded total energies converged to within 0.01 mRy. The highest angular momentum component in the sphere was $L=12$. Brillouin-zone (BZ) scans of 259, 240, and 91 points were used in the irreducible wedges of, respectively, the hcp, fcc, and bcc systems. (All BZ scans included the vertices of the irreducible wedge of the BZ and used a uniform mesh along each of the reciprocal lattice vector directions.) The relatively small number of bcc points is a direct consequence of the high stability of $E_{\mathrm{tot,bcc}}$ with respect to meshes above about 50 points in the irreducible wedge, a behavior which has been pointed out in Ref. 4 (see their Fig. 1). As previously remarked in Ref. 6, it turns out to be important that these BZ scans are at much higher point densities than were used in Ref. 1.

Because we need only to confirm one or the other order of $P=0$ phases and the appropriate location of the first pressure-induced transition, a grid of eight volumes proved adequate. The hcp phase was assumed to have the ideal ratio $c/a=\sqrt{8/3}$, as in Ref. 6, for the initial calculations.

In Table I we give the calculated total energies as a function of V/V_0. We find $V_0=128.16$ a.u.^{3}/atom for the lowest-energy phase, hcp. The highest-energy phase at $P=0$ is bcc, in contradiction with Ref. 1 and agreement with Refs. 2–6 and 8. Relaxation of c/a at this volume causes the hcp phase to become very slightly more favored energetically (by about 0.002 mRy) with $c/a=1.003\sqrt{8/3}$. The only reported calculation of c/a gives[4] a coefficient of 0.996 and quotes the experimental coefficient of 1.002. Obviously, the shift from ideal hcp is itself small and characterized by a small, difficult-to-calculate energy difference. The first pressure-induced transition is hcp→fcc at $V/V_0=0.79$, in good agreement with the value 0.73 found by both Refs. 5 and 6.

The calculated V_0 corresponds to a nearest-neighbor spacing $a_{\mathrm{NN}}=5.66$ a.u. This value is matched quite nicely by the fcc $a_{\mathrm{NN}}=5.61$ a.u. of Ref. 3 (which could not treat hcp and used a slightly different choice of local-density model). Reference 1, on the other hand, finds a somewhat contracted $V_0=124.49$ a.u.^{3}/atom and, since their result for the $P=0$ phase is bcc, $a_{\mathrm{NN}}=5.45$ a.u.

The apparent discrepancy of the V_0's in Refs. 4 and 6 with our results is resolved upon observing that they used the Wigner interpolation (WI) and Kohn-Sham-Gaspar (KSG) local-density models, respectively. Reference 4 determined the shift in lattice parameter in going from WI to HL in bcc Na as $\Delta a/a=-0.012\,38$. Assuming the same shift for their hcp calculation gives $a=5.6998$ a.u. and $V_0=130.70$ a.u.^{3}/atom, very close to our result. Similarly, the V_0 in Ref. 6 corresponds to a hcp $a_{\mathrm{NN}}=5.86$ a.u. virtually identical with the KSG result for fcc in Ref. 3. Thus the shift in V_0 between this work and Refs. 4 and 6 is purely a manifestation of the different local-density models employed. Experience shows that though the choice of LDA affects the calculated V_0, it typically does not reorder the predicted sequence of crystalline phases.

Table II compares calculated equilibrium-energy differences. The only evident oddity is that the pseudopotential calculation overestimates the magnitude of the fcc-hcp energy splitting. Otherwise, the four calculations that treat bcc, fcc, and hcp are in good agreement.

TABLE II. Calculated total-energy differences (mRy) for equilibrium Li for the present work (FLAPW), Ref. 4 (PW), Ref. 5 (ASW), Ref. 6 (LMTO), and Ref. 8 (APW).

Method	$E_{\mathrm{hcp}}-E_{\mathrm{fcc}}$	$E_{\mathrm{bcc}}-E_{\mathrm{fcc}}$
FLAPW	-0.08	$+0.24$
PW	-0.47	$+0.20$
ASW	-0.10	$+0.20$
LMTO	-0.06	$+0.23$
APW		$+0.28$

The consistency of our calculations with all prior ones except for Ref. 1 (and consistency with Ref. 8 also) shows that the LDA prediction of the ordering of $T=0$ K Li equilibrium phases is hcp < fcc < bcc, not bcc < fcc as in Ref. 1. The difference apparently does not arise from use of the APW method, as had been surmised in Ref. 1. Since their $P=0$ fcc result is essentially identical with both ours and that of Ref. 3 while their bcc result differs notably, the most likely source of the discrepancy is a flaw in the Ref. 1 bcc calculation.

This suspicion can be focused by consideration of Fig. 1 of Ref. 4, which shows a 1-mRy downward notch in the total energy at a 20-point BZ scan for bcc Li and stable results only for scans of 44 and more points. (Reference 8 rediscovered the same peculiar sensitivity.) Our calculations are similarly sensitive to inadequate BZ scan density for the bcc phase. In fact, we can reproduce the prediction of Ref. 1 that bcc is stable relative to fcc at V_0 by using relatively coarse BZ scans, e.g., 20 and 30 points in the irreducible wedges of the fcc and bcc phases, respectively.

In that case we obtain 0.06 mRy for $E_{\mathrm{fcc}}-E_{\mathrm{bcc}}$ as opposed to Ref. 1, which gets 3.5 mRy. However, Ref. 1 used a special-point scheme. In the present context, the very nature of such specialized schemes is to optimize the energy recovered from a coarse BZ grid in a *given* symmetry. There is nothing in special-point methods which is specifically designed to offset the kind of sensitivity to scan density first pointed out in Ref. 4. (In fact, such methods appear to be better adapted to the energy bands of insulators and semiconductors than to Fermi surfaces.) With that appraisal in mind, the $E_{\mathrm{fcc}}-E_{\mathrm{bcc}}$ difference calculated here for a coarse scan is in reasonable accord with the coarse special-point value found in Ref. 1. We conclude that the incorrect equilibrium-phase ordering

TABLE I. Calculated total energies (Ry) for Li at the compressions shown, with $V_0=128.16$ a.u.^{3}/atom in the hcp phase.

V/V_0	$-E_{\mathrm{hcp}}$	$-E_{\mathrm{fcc}}$	$-E_{\mathrm{bcc}}$	Favored phase
1.1111	14.833 905	14.833 823	14.833 585	hcp
1.0000	14.834 639	14.834 557	14.834 322	hcp
0.9764	14.834 606	14.834 527	14.834 292	hcp
0.9444	14.834 432	14.834 363	14.834 116	hcp
0.8889	14.833 716	14.833 664	14.833 389	hcp
0.7222	14.826 704	14.826 737	14.826 304	fcc
0.5556	14.805 153	14.805 352	14.804 729	fcc

found in Ref. 1 for $P=0$ Li most probably resulted from use of an inadequate BZ scan.

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[1] H. Bross and R. Stryczek, Phys. Status Solidi B **144**, 675 (1987).

[2] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).

[3] J. C. Boettger and S. B. Trickey, Phys. Rev. B **32**, 3391 (1985).

[4] M. M. Dacorogna and M. L. Cohen, Phys. Rev. B **34**, 4996 (1986).

[5] J. Meyer-ter-Vehn and W. G. Zittel, Phys. Rev. B **37**, 8674 (1988); W. G. Zittel, Ph.D. thesis, 1986, pp. 75–89.

[6] J. C. Boettger and R. C. Albers, Phys. Rev. B **39**, 3010 (1989).

[7] J. C. Boettger, S. B. Trickey, F. Müller-Plathe, and G. H. F. Diercksen, J. Phys. Condens. Matter **2**, 9589 (1990).

[8] M. Sigalas, N. C. Bacalis, D. A. Papaconstantopoulos, M. J. Mehl, and A. C. Switendick, Phys. Rev. B **42**, 11 637 (1990).

[9] L. Hedin and B. I. Lundqvist, J. Phys. C **4**, 2064 (1971).

[10] P. Blaha, K. Schwarz, P. Sorantin, and S. B. Trickey, Comput. Phys. Commun. **59**, 399 (1990).