Comments

Comments are short papers which criticize or correct papers of other authors previously published in the **Physical Review**. *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Total-energy calculations of solid H, Li, Na, K, Rb, and Cs"

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The presentation of recent augmented-plane-wave calculations of alkali-metal equilibrium crystal structures by Sigalas *et al.* [Phys. Rev. B **42**, 11 637 (1990)] ignored what is known from both non-muffin-tin- (all-electron and pseudopotential) and muffin-tin-orbital calculations about the ground-state symmetry of those metals, and in some instances contradicted it. To illustrate the problem we give a thorough summary of the situation in Li, with brief remarks on other systems.

Recently Sigalas *et al.*[1] presented augmented-plane-wave calculations of alkali-metal equilibrium crystal structures. Of course, determination of the $T=0$ K crystal structure of an alkali metal from first principles has been a challenge to condensed-matter physics from the time of Wigner and Seitz's first paper almost 60 years ago.[2] There has been substantial modern effort[3–18] which has yielded many clear-cut conclusions and left only a few unresolved problems. In that context, Ref. 1 is odd in neither citing that work nor addressing those conclusions. This is particularly striking given that in many instances the conclusions of Ref. 1 are in disagreement with prior work.

Among the findings of Ref. 1 with differ from published results are the following.

(a) Reference 1 finds that the equilibrium space group of K is fcc. Three prior calculations[7,10,17] all find bcc, the experimentally determined phase as well.

(b) Reference 1 finds that the equilibrium space group of Cs is fcc. At least one previous calculation[7] found bcc in accord with experiment.

(c) Reference 1 finds the energetic ordering of space groups in solid atomic H to be fcc below bcc, in contradiction with Ref. 15(a) but in agreement with Ref. 18.

(d) With regards to calculated 0 K structural energy differences, Ref. 1 concludes that "the LAPW results may be capable of accurately predicting transition temperatures." This conclusion ignores what is generally known about the thermodynamics of Martensitic phase transitions[19] and is inconsistent with a systematic inspection of the literature (see below).

The failure of Ref. 1 to note and analyze this collection of disparities (or even acknowledge the existence of most prior work) yields a peculiarly inaccurate representation of the current state of this venerable problem (not to mention the injustice to a veritable host of authors). It might be hoped that a case could be made for Ref. 1 as a systematic study of all the alkali metals. However, the argument fails because of the absence in Ref. 1 of orderly, thorough connection to extant knowledge and a consequent absence of the contextual value normally associated with systematic studies. From this perspective Ref. 1 seems substantially less useful and complete than the prior systematic work of Skriver[7] (unreferenced by Sigalas *et al.*[1]) Put in another way, the only reliable new results in Ref. 1 appear to be the fcc band structures of H, Na, and Rb. The first fcc Li energy bands were published in Ref. 9, while fcc bands for K are found in Ref. 17, and those for Cs in Ref. 7. None of these was referenced in Ref. 1, another example of the absence of systematic context.

To outline the actual context we shall, in what follows, focus on Li, since it is the system with which we have worked the most. Some additional remarks about the other systems are at the end.

Modern efforts to treat Li structure-energy relationships [in the local-density approximation (LDA) to density-functional theory] seem to have begun with the pseudopotential calculations of Pick[3] and Shaw.[4] (A nice summary of these is in Ref. 5.) Years later a model po-

tential[6] and then an LMTO[7] calculation appeared. While they disagreed regarding predicted high-pressure behavior, they both concurred with Pick as to the $P=0$ energetic ordering of crystalline phases: $E(\text{hcp}) < E(\text{fcc}) < E(\text{bcc})$. (Shaw had found $E(\text{hcp}) < E(\text{bcc}) < E(\text{fcc})$ but the bcc-fcc energy difference was small enough to leave the ordering in doubt. Therefore his results are omitted from the discussion that follows.)

So far as we know, the first all-electron, full-potential calculation to test the Li structural energy question was by two of us.[9] Like Ref. 1 it was restricted to systems of cubic symmetry. In agreement with earlier calculations the close-packed structure was determined to be energetically preferred to bcc, for either of the two LDA models. (Reference 9 also contains an extensive set of citations to prior theoretical work on the Li equation of state, crystal structure, one-electron properties, etc.) Shortly after Ref. 9, an *ab initio* pseudopotential study of Li, Na, and K structural energetics confirmed the $E(\text{hcp}) < E(\text{fcc}) < E(\text{bcc})$ ordering for Li.[10] Allowing for differences in LDA and techniques, the calculated lattice constants were in reasonable agreement.

Until 1987 no all-electron, full-potential calculation had found bcc to be the energetically favored Li ground-state structure.[11] The outcome of the modified APW study in Ref. 11 was so at odds with prior calculations and its computed bcc-fcc energy difference was so large that it stimulated three independent all-electron calculations.[12–14] All three agree that the ordering is $E(\text{hcp}) < E(\text{fcc}) < E(\text{bcc})$. The work of Nobel *et al.*[14] demonstrates that the prediction of Ref. 10 is a consequence of the peculiar sensitivity of the bcc total energy to an inadequate BZ sample mesh density, a trait first discussed by Dacorogna and Cohen (see Fig. 1 of Ref. 10) and rediscovered in Ref. 1.

Table I summarizes these developments quantitatively. (Young and Ross[6] gave the energetic ordering but not the energy differences. The values for Skriver's[7] calculation were read from a figure.) There one sees that, except for the contrast with the anomalous result of Ref. 11, there is nothing new in the findings of Ref. 1 as to the energetic ordering of Li crystal structures. The APW calculation of Ref. 1 gives an fcc-bcc energy difference which is close to the magnitude of the MAPW result (with the *same* LDA) from Ref. 10 but opposite in sign. Such a large disparity is strange since the MAPW and APW methods are supposed to yield similar results.[11] Unfortunately, this one technical point, which Ref. 1 could have helped resolve, went undiscussed there. As just noted, Ref. 14 shows that the discrepancy of the MAPW results with all others is rooted in the BZ scan for bcc.

Table I also shows that the calculated fcc-bcc energy difference ranges over an order of magnitude, depending on details of the LDA, the basis set, all-electron versus pseudopotential, etc. The problem is not poor calculational quality but the fact, to paraphase Ref. 10, that this energy difference is extremely small and very sensitive to computational assumptions, hence is difficult to pin

TABLE I. Comparison of calculated structure-energy relationships for $T=0$ K Li, in order of appearance. The numeral in a structure column indicates the calculated ordering, with "1" lowest in energy and a hypen when that structure was not treated. The energies E_c are cohesive energy differences (meV/atom) with respect to the lowest-energy phase reported in a given paper. Lattice constants (a.u.) are shown only when reported for the energy minimum in that structure. KSG=Kohn-Sham-Gaspar LDA (X-alpha, alpha=2/3). RSK=Rajagopal, Singhal, and Kimball LDA. All other LDA are Hedin-Lundqvist except Dacorogna and Cohen, which used KSG plus Wigner interpolation.

	hcp	E_c	a	c	fcc	E_c	a	bcc	E_c	a
Pick[a]	1	0.0			2	1.9		3	3.3	
Shaw[b]	1	0.0			3	1.4		2	1.1	
Young and Ross[c]	1	0.0			2	+		3	+	
Skriver[d]	1	0.0			2	0.2		3	2.0	
Boettger and Trickey[e]										
(KSG)					1	0.0	8.28	2	6.8	6.59
(RSK)					1	0.0	7.94	2	12.2	6.32
Dacorogna and Cohen[f]	1	0.0	5.71	9.30	2	6.4	8.09	3	9.1	6.43
Bross and Stryczek[g]					2	34.0	7.95	1	0.0	6.29
Meyer-ter-Vehn and Zittel[h]	1	0.0	5.92	9.67	2	1.4		3	4.1	
Boettger and Albers[i]	1	0.0	5.91	9.65	2	1.0		3	3.8	
Sigalas *et al.*[j]										
APW					1	0.0	7.95	2	38.1	6.38
LAPW					1	0.0	8.01	2	6.4	6.37
Nobel *et al.*[k]	1	0.0	5.66	9.24	2	1.1	8.00	3	4.4	6.35

[a]Reference 3.
[b]Reference 4.
[c]Reference 6.
[d]Reference 7.
[e]Reference 9.
[f]Reference 10.
[g]Reference 11.
[h]Reference 12.
[i]Reference 13.
[j]Reference 1.
[k]Reference 14.

down. That being the case, the claim of Ref. 1 that the fcc→bcc transition temperatures can be equated to the calculated fcc-bcc energy difference is simply not believable.

For example, application of the recipe from Ref. 1 to the full-potential, all-electron calculations *alone* give predictions ranging from 31 to 142 K, see Table I. For another, that recipe and the LAPW calculation of Ref. 1 gives 72 K while the FLAPW calculation of Ref. 13 using the *same* LDA gives 39 K. In addition to this severe pragmatic difficulty, the claim is also not sustainable on fundamental thermodynamic grounds. For many years, it has been known that temperature-induced transitions of the type considered by Ref. 1 are driven by the entropy differences between the various phases.[19] Thus even if the exact 0 K structural energy difference were known, the procedure used in Ref. 1 would not be a reliable method for predicting the transition temperature.

As to calculated lattice constants, the most straightforward comparison is with calculations that used LDA models beyond simple KSG (Kohn, Sham, and Gaspar). For systems of cubic symmetry, the relevant previous calculations are Ref. 9 [all-electron, Gaussian orbitals, Rajagopal, Singhal, and Kimball (RSK) LDA] and Ref. 10 (pseudopotential, plane waves, KSG plus Wigner interpolation LDA). For a_{fcc} those give 7.94 (Ref. 9) and 8.09 a.u. (Ref. 10) versus the APW and LAPW values 7.95 and 8.01 a.u., respectively, from Ref. 1. The corresponding a_{bcc} comparison is 6.32 and 6.43 a.u. versus 6.38 and 6.37 a.u. from Ref. 1. Clearly there is little new in Ref. 1 calculations of cubic Li lattice constants beyond simple confirmation of the well-known fact that diverse modern techniques for solving the Kohn-Sham equations agree within about 0.15 a.u. in the prediction of lattice constants.

Reference 1 gives fcc and bcc bulk moduli at $P=0$, again without comparison to prior results. Table II makes the comparison for some readily available values. For all except Ref. 1's LAPW calculation $K_{0,\mathrm{fcc}} > K_{0,\mathrm{bcc}}$. Otherwise, the results for calculations using LDA's beyond the KSG model agree to within the known precision of computed bulk moduli (which is determined by the rather low precision of extracting the second derivative of energy with respect to cell volume).

Reference 1 also presents band structures for fcc and bcc Li. As noted, the first published self-consistent energy bands for energy-optimized fcc Li were Fig. 1 of Ref. 9. Except for the somewhat smaller energy range for the APW bands from Ref. 1 (Fig. 2, upper panel), they appear to be substantially identical to those of Ref. 9.

TABLE II. Comparison of calculated bulk moduli (kbar) for equilibrium Li at $T=0$ K.

	hcp	fcc	bcc
Boettger and Trickey[a]			
(KSG)		187	147
(RSK)		168	158
Dacorogna and Cohen[b]	137	138	130
Sigalas *et al.*[c]			
APW		156	148
LAPW		147	151

[a]Reference 9.
[b]Reference 10.
[c]Reference 1.

In the same vein, we note that a similarly large and thorough body of work on solid H (atomic and also molecular) was omitted from consideration or citation in Ref. 1. Without any attempt at completeness, we note the extensive work of Freeman's group[15] and of Cohen's group,[16] both of which have addressed specifically the H structure-energetics ordering problem. With a colleague, two of us have recently revisited the atomic H problem as well.[18] It is particularly striking that Ref. 1 omits comparison with Ref. 15(a). That prior paper found the order of atomic H crystalline phases to be $E(\mathrm{sc}) < E(\mathrm{hcp}) < E(\mathrm{bcc}) < E(\mathrm{fcc})$ while Ref. 1 finds $E(\mathrm{fcc}) < E(\mathrm{bcc})$. Reference 18 finds $E(\mathrm{sc}) < E(\mathrm{hcp}) E(\mathrm{fcc}) < E(\mathrm{bcc})$. Finally, a somewhat similar critique could be made with regard to the heavier alkali metals treated in Ref. 1; see Refs. 7, 8, and 10. Reference 1 reports, for example, a bcc-fcc energy difference for Rb which is far larger in magnitude than the previously reported value but fails to note or analyze the disparity.[8]

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