

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

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Using highly converged local-density-approximation calculations for K and Li, we dispute on physical grounds the claims of the preceding Comment.

The authors of the preceding Comment raise several issues, which we address in turn. The first, and perhaps the main point of their comment, has to do with referencing of previous work on the stability of the various phases of hydrogen and the alkali metals. We admit that we have not referenced all papers which could be of interest to readers of our paper (Ref. 1 in the following), and we agree that it would have been better if some of them had been referenced. However, our purpose was not to provide a review of this large field. The value of our paper is in the fact that, using the same methodology in a systematic way, we have calculated self-consistently within the local-density approximation (LDA) both the total energies and the band structures of all the alkali metals and hydrogen and we have performed parallel muffin-tin approximation and full-potential calculations to assess the effect of the muffin-tin approximation. We have not claimed that our calculations are the first or the only calculations on alkali metals. Further, many of the references of the preceding Comment are related only peripherally to our paper. For example, Refs. 2–6 of the preceding Comment do not present the results of self-consistent LDA calculations, which are the interest of our paper. Further, Ref. 14 of the preceding Comment, which is the work of two of its authors, has not to our knowledge been published, and the first reference to that work appeared more than four months after submission of our manuscript. Reference 18 of the previous comment, which also shares authors with it, has not been published either.

Regarding H, we would like to point out that while the authors of the preceding Comment agree with our findings that the fcc structure has lower energy than the bcc structure, they again make an issue of us not referencing previous work. Let us remind them that we published² augmented-plane-wave energy bands, the electronic density of states and the electron-phonon interaction for metallic hydrogen in 1977, much earlier than the papers mentioned in the preceding Comment.

The remainder of the preceding Comment questions the results and conclusions of our paper. The first of these questions regards our calculated ordering of the fcc and bcc phases. We emphasize, as we demonstrated in our paper, that the muffin-tin approximation augmented-plane-wave calculations give accurate values for the lattice parameters and bulk moduli, while the structural energy difference has the correct sign in the cases we tested, but the magnitude is unreliable. Therefore we focus on

full-potential calculations of the energy difference. Secondly, we emphasize that our paper consists of a compilation of LDA predictions, not experimental results, and that LDA predictions can disagree with experiment. First of all regarding K, our calculated energy difference between the bcc and fcc phases is very small, with the fcc phase being the stable phase. We agree with the authors of the preceding Comment that previous studies have been split over the LDA prediction for the ground state of this material. In order to resolve this we have performed LDA calculations using a highly precise full-potential extended linearized augmented-plane-wave (LAPW) method,³ with highly converged basis sets and fine Brillouin-zone samplings. This method is identical to the standard full-potential LAPW method, except that it adds local orbitals to the basis to remove any errors due to the linearization. This was important because of the small energy differences involved. The Brillouin-zone samplings were performed using 408 and 728 special k points for the fcc and bcc phases, respectively. The result of this calculation is that the fcc phase is lower than the bcc phase in agreement with Ref. 1. Although the energy difference is small (0.5 meV), we are confident that this is the correct static lattice LDA ordering.

The fact that bcc K is observed at low temperatures means, therefore, that (1) the bcc phase is stabilized by a lower zero-point energy, which is neglected in static lattice calculations (this is consistent with the observed transition to a bcc structure at higher temperature for many materials with a close-packed ground state), or (2) the LDA predicts the wrong ground state for K. This conjecture is supported by the fact that the LDA lattice parameters are significantly smaller (by 3–4 %) than experiment for the alkali metals. These contracted lattice parameters may be corrected by adding a nonlocal correction to the LDA exchange correlation potential which favors inhomogeneous charge densities. This is the known behavior of generalized gradient corrections to the LDA, for example. Such a favoring of nonuniform densities would also tend to stabilize the bcc structure.

The authors of the preceding Comment also question our calculations for Li, and our conclusion that there may be a significant correlation between the calculated bcc-fcc energy difference and the transition temperature, which may make it possible to estimate transition temperature using total-energy calculations. First of all, contrary to the claim of the preceding Comment the energy difference is an important ingredient in determining the

transition temperature. The stable phase is the phase with the lowest free energy, and this is given by $E - TS$, where E is the energy, T is the temperature, and S is the entropy. Setting the free energies equal at the transition, one obtains

$$T = \Delta E / \Delta S, \quad (1)$$

where ΔE is the energy difference between the two phases and ΔS is the entropy difference (which may be T dependent). Clearly Eq. (1) depends on the energy difference. If the entropy differences are similar for different materials, there will be a strong correlation between the transition temperature and ΔE . Secondly, the claim that there *cannot* be a strong correlation between the LDA value of ΔE and T , because previous calculations yield a wide range of ΔE , is flawed. All that this wide range really proves is that some of the previous calculations must be wrong. In order to address this issue we have performed additional more highly converged calculations for Li. These calculations were performed using the full-potential LAPW method as in Ref. 1 but with better converged Brillouin-zone samplings of 60 and 112 special points for the fcc and bcc structures, respectively. We obtain a stable fcc phase as in Ref. 1 and most previous

calculations, with a fcc-bcc energy difference of 4.2 meV/atom. Convergence tests indicate that the error arising from the discrete Brillouin-zone sampling is less than 1 meV/atom. This number is intermediate between the unpublished results of Nobel *et al.* (Ref. 14 of the preceding Comment) and the LAPW result in Ref. 1. Further, in our calculation we obtain lattice parameters of 8.00 and 6.36 a.u. in good agreement with the results of Ref. 1. These lattice parameters, like the calculated energy difference, are in substantial disagreement with the calculation of Boettger and Trickey (Ref. 9 of the preceding Comment), implying either an anomalously large sensitivity to the particular local exchange correlation potential, or numerical inaccuracies in that work. Removing the calculation of Boettger and Trickey from the "data base" considerably reduces the range of ΔE for Li. Finally, we note as we did in Ref. 1 that our conjecture of a correlation between ΔE and the transition temperature is based on calculations for two materials (Li and Na), and that it is subject to further convergence tests and calculations for more materials. Also we did not claim, and do not believe, that the correlation should be perfect. However, nothing in the preceding Comment or the calculations above demonstrates that the conjecture is incorrect.

¹M. Sigalas, N. C. Bacalis, D. A. Papaconstantopoulos, M. J. Mehl, and A. C. Switendick, *Phys. Rev. B* **42**, 11 637 (1990).
²D. A. Papaconstantopoulos and B. M. Klein, *Ferroelectrics* **16**,

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³D. Singh, *Phys. Rev. B* **43**, 6388 (1991).