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Room Temperature Lithium Phases from Density Functional Theory

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Abstract

Metallic lithium is a promising electrode material for developing next generation rechargeable batteries, but it suffers from dendrite formation upon recharging. This compromises both efficiency and safety of these systems. The surface phenomena responsible for dendrite formation are difficult to characterize experimentally making it important to use Quantum Mechanics (QM) to provide the understanding needed to design improved systems. The most accurate practical level of QM for such studies is the PBE form of density functional theory (DFT.) We report here an assessment of the accuracy for PBE to predict the most stable four phases of bulk lithium. PBE predicts three phases, bcc, fcc, and hcp, to be nearly equal in stability (within 5 meV.) Including the zero point energy and enthalpy corrections at standard conditions (298 K and 1 atm) we predict bcc most stable, fcc at 0.0029 eV, hcp at 0.0036 eV, and cI16 at 0.0277 eV.

Indeed their experimental free energies under ambient conditions differ only by a few meV, with bcc considered most stable. Experimentally, the fourth phase becomes stable at high pressure ($> 30 - 40$ GPa) and low temperature (< 200 K.) In order to use QM calculations to predict growth mechanisms, it is essential to bias the calculations by imposing the desired crystal structure in the underlying layers. We consider that this will allow QM studies of dendritic growth to be studied in conditions far from the crystalline phase due to the lower surface energy of bcc.

Introduction

Metallic lithium electrodes^{1,2} are very attractive for use in rechargeable batteries, but it is very important to understand crystal growth under electrochemical conditions in order to avoid dendrite formation. This has led to several computational studies aimed at understanding structural, chemical, and electrochemical properties of metallic lithium and its surfaces, both clean and covered by solid electrolyte interfaces (SEI).³⁻⁷ Mostly these investigations⁸⁻¹⁰ rely on the use of density functional theory (DFT) to obtain the quantum mechanical description of the system. In order to

assess the reliability of these DFT methods for predicting growth, it is important to establish how well DFT describes the stability of various phases of bulk Li under ambient conditions.

The most stable phase for lithium at room temperature and pressure, denoted β , has the body centered cubic (*bcc*) structure but this phase is only slightly more stable than several other phases, namely

1. the face centered cubic (*fcc*) γ phase,
2. the low temperature phase α , originally considered as hexagonal closest packed (*hcp*),¹¹ then found to be *9R*,¹² and recently referred to as *hR9*,¹³ *hR3*,¹⁴ or, again, *9R*.¹⁵
3. three more phases are expected to have similar free energy at room conditions.¹⁵ Two of them, *hcp* and *hR1* are structurally similar to *9R*. The remaining one, called *cI16*, has a distorted *bcc* structure and is observed experimentally at pressures of 40 to 60 GPa.

Based on the experimental phase diagram,¹³ the γ phase becomes more stable than β at high pressure (above 6.6 GPa at 300K) and less stable than the α phase at low temperature (below 70 K). Experimentally some or all of these phases may be found in any particular sample depending on the history of the sample, indicating that these three forms all have similar cohesive energies. Several other high pressure phases are known and some of them may also be present locally at ambient conditions under some circumstances. The possibility of adopting different local conformations plays an important role in describing the surface and its evolution during crystal growth in electrochemical processes. In particular, such phases may be relevant for formation of dendrites during electrochemical lithium deposition.

Our aim here is to assess how well PBE,^{16,17} the most practical accurate form of DFT, describes the relative stability of these phases. To this end, we performed periodic plane wave PBE on the *bcc*, *fcc*, *hcp*, and *cI16* phases of lithium, followed by a computation of the phonon density of states (PDOS) to estimate zero point energy (ZPE) and statistical thermodynamic contributions to the free energy to obtain the stability under ambient conditions.

Computational Methods

All computations were performed using the Quantum Espresso (QE) suite.¹⁸ In particular, the PW code was used for geometry optimizations and quantum mechanical energies, PHonon for phonon computations, Q2R for transformation of the dynamical matrix from reciprocal to real coordinates, and MATDYN to interpolate the dynamical matrix on a finer grid and compute the phonon density of states (PDOS).

The ultrasoft pseudopotential used for lithium is `li_pbe_v1.uspp`. Details on its optimization are reported in reference.¹⁹ Cutoffs for the plane-waves basis set were chosen at 58 and 600 *Ry* for the wave function and the density, respectively. A Gaussian smearing factor of 0.001 *Ry* was applied to determine band occupation near the Fermi energy. All computations were performed on cubic or orthorhombic cells, rather than the primitive cell.

For computations of wave function, energy, and cell parameters, the Brillouin zone was sampled with a Monkhorst-Pack grid of *k*-points with origin shifted from the Γ -point. Cutoffs and grid dimensions were determined so that cell optimizations would yield both minimal values for the energy and minimal absolute values for the stress, up to changes of 0.002 Å in the cell parameter.

For the *bcc* system, we find reasonable convergence in the values of energy and stress with a grid of 12x12x12 reciprocal space points. This corresponds to 10x10x10, 14x8x8, and 6x6x6 grids for *fcc*, *hcp*, and *cI16* systems, respectively. Phonon computations were performed at the DFT level on grids of reciprocal space points similar to those used for the wave function description, i.e. 12x12x12 for *bcc*, 10x10x10 for *fcc*, 14x8x8 for *hcp*, and 6x6x6 for *cI16*. These grids were not shifted from the Γ -point. Following the approach recommended in the user's guide to the PHonon code,¹⁸ the dynamical matrices thus obtained were Fourier transformed to force constants in real space. These were then interpolated on a finer grid, containing four times as many grid points in each direction, and the resulting mesh was then used to compute the PDOS.

This procedure was not followed for the phase *cI16* as the room pressure computation yielded imaginary frequencies, indicating a geometric instability. In this case, we computed the dynamical matrices on a coarser grid of 4x4x4 reciprocal points and removed the modes with imaginary

frequency for PDOS computation. These amount to an integrated PDOS of 0.712 modes out of 48 expected for a 16 atom cell. The cI16 results are hence not physically accurate and reported only for comparison.

Surface energies (SE) were computed for two dimensional periodic slabs with two to N_{MAX} layers, where N_{MAX} is the number required to reach a thickness of approximately 20 Å. N_{MAX} varies between nine and 27, depending on the surface considered. These SE depend on the number of layers used but converge to a limit for infinitely thick slabs. We estimate this limit by taking the average value of the six thickest slabs for each surface. The corresponding standard deviation measures the oscillations within this set and provides an estimate for the error associated to the use of finite slabs. Other sources of error are ignored in this context.

Results and discussion

Table 1: Results from PBE calculations at the optimized structures. Cell parameters a and computed relative energies for the phases of Li considered. The ΔE do not contain ZPE or thermal corrections. A negative value indicates that the phase is more stable than bcc . Experimental relative energies are not available. See text for details.

phase	cell parameter a (Å)				error (%)	volume error (%)	computed ΔE (bcc=0.0) (meV)
	computed		exp. ^a				
	0 K	298 K ^b	0 K ^b	298 K			
<i>bcc</i>	3.435	3.482	3.4615	3.5093	0.7	2.3	0.0000
<i>fcc</i>	4.324	4.384	4.328	4.388	0.1	0.3	-0.8066
<i>hcp</i>	3.058	3.100	3.069	3.111	0.3	1.1	-0.3859
<i>cI16</i>	6.865	6.960	—	—	—	—	-0.0173

^a From ref. 20; ^b Extrapolation based on the *bcc* thermal expansion coefficient

PBE optimization yields for the four phases of lithium considered the cell parameters and relative energies reported in Table 1. These are compared to experiment at 0 K using the thermal (linear) expansion coefficient of $46 \cdot 10^{-6} K^{-1}$ ²⁰ for *bcc* to account for expansion of the computed cell from 0 to 298.15 K. We did not correct the experiment for zero point energy (ZPE) which generally causes an increase in the cell parameters. Comparing the computed cell parameters to

the 0 K experimental parameters we find errors of less than 1% resulting in densities up to 2.3% higher than experiment.

The total PBE energy per Li atom is almost the same for the four phases, corresponding to a cohesive energy of 1.53 eV at the DFT level. The functional PBEsol²¹ also predicts nearly identical energies for *bcc*, *fcc*, and *cI16*, with *hcp* only slightly less stable. A brief comparison of PBE and PBEsol is reported in the Supporting Information. When zero point energy and thermal contributions to the enthalpy are included as described in the next section, assuming a perfect crystal for the solid and a perfect gas for the isolated Li atoms, the standard enthalpy of formation for atomic lithium is estimated as $\Delta_f H^\circ(\text{Li}_{(g)}) = 1.51 \text{ eV}$, which is 8% smaller than the experimental value of 1.65 eV. Phonon computations were performed as described in the Methods section for *bcc*, *fcc*, and *hcp*. Indicating the PDOS as $g(\bar{\nu})$, where $\bar{\nu}$ indicates the wavenumber, the zero point energy (ZPE), Helmholtz free energy F , and internal energy U are obtained as

Normalization

$$3N = \int_0^\infty g(\bar{\nu}) d\bar{\nu}, \quad (1)$$

Zero Point Energy

$$ZPE = \frac{hc}{2} \int_0^\infty \bar{\nu} g(\bar{\nu}) d\bar{\nu}, \quad (2)$$

Thermal Contribution to F

$$F = k_B T \int_0^\infty \ln \left(1 - e^{-\frac{hc\bar{\nu}}{k_B T}} \right) g(\bar{\nu}) d\bar{\nu}, \quad (3)$$

Thermal Contribution to U

$$U = hc \int_0^\infty \frac{\bar{\nu} e^{-\frac{hc\bar{\nu}}{k_B T}}}{\left(1 - e^{-\frac{hc\bar{\nu}}{k_B T}}\right)} g(\bar{\nu}) d\bar{\nu}, \quad (4)$$

where N is the number of atoms per unit cell, h is Planck's constant, c is the speed of light, k_B is Boltzmann's constant, and T is the temperature. The computed PDOS's for each phase are reported in the Supporting Information. The corresponding thermal corrections are reported in Table 2.

Table 2: Zero point energy (ZPE) and thermal corrections for the systems considered. The final free energy at standard conditions is lowest for *bcc*, in agreement with experiment. All numbers are in *meV* (per Li atom) and refer to $T = 298.15$ K.

system	ΔE	ZPE	F ^a	U ^a	TS	PV	H	G
<i>bcc</i>	0.0000	39.8647	-40.6713	44.6825	85.3537	0.0130	84.5602	-0.7936
<i>fcc</i>	-0.8066	40.7277	-37.8049	44.0624	81.8673	0.0217	84.0051	2.1379
<i>hcp</i>	-0.3859	40.7667	-37.6098	44.0450	81.6548	0.0130	84.4388	2.7840
<i>cI16</i> ^b	0.0173	52.7699	-25.8971	35.8405	61.7376	0.0130	88.6407	26.9031

^a Does not include ZPE. ^b Values of ZPE, F, U, H, and G for *cI16* are obtained neglecting vibrational modes with imaginary frequency.

Table 3: Surface energy (*mJ/m*²) for the most stable surfaces of *bcc*, *fcc*, and *hcp* lithium in vacuum and in the presence of a medium with relative dielectric constant $\epsilon = 5$ and $\epsilon = 10$. Average values are based on ideal Wulff crystal growth. The reported mean values and standard deviations refer to sets of six values, obtained as described in the Methods section of the text.

phase		<i>bcc</i>						
surface	(100)	(110)	(211)	(111)	(120)	ave.		
$\varepsilon = 1$	463 ± 6	495 ± 3	542 ± 3	539 ± 6	504 ± 3	494		
$\varepsilon = 5$	457 ± 6	492 ± 3	524 ± 4	535 ± 6	499 ± 3	490		
$\varepsilon = 10$	457 ± 6	492 ± 3	524 ± 4	534 ± 6	499 ± 3	490		
phase		<i>fcc</i>				<i>hcp</i>		
surface	(100)	(110)	(111)	ave.	(0001)	(10 $\bar{1}$ 0)	(11 $\bar{2}$ 0)	ave.
$\varepsilon = 1$	470 ± 5	529 ± 3	506 ± 1	496	503 ± 1	496 ± 3	521 ± 3	506
$\varepsilon = 5$	470 ± 4	527 ± 3	494 ± 4	491	491 ± 4	495 ± 3	507 ± 3	497
$\varepsilon = 10$	470 ± 4	527 ± 3	494 ± 3	491	491 ± 4	494 ± 3	507 ± 3	497

We find that PBE predicts *bcc*, *fcc*, *hcp* and *cI16* to be almost degenerate at room pressure when no zero point energy is included. Analysis of the phonons indicates that *cI16* is unstable,

probably against a deformation that would bring it to *fcc*. The energy differences reported in the last column of Table 1 are insignificant: we tested these by increasing slightly the wavefunction and density cutoffs and the number of points in the Monkhorst-Pack grid for Brillouin zone sampling and obtained variations of the same order of the energy differences. We conclude that a different choice of the computational parameters, of the basis set (e.g. Gaussian instead of plane-waves) or of the DFT implementation could result in another ordering of the states considered. For all practical purposes, PBE predicts the energy of these phases to be essentially equivalent. ZPE slightly favors *bcc*: it is approximately 0.9 *meV* smaller than *fcc* or *hcp* and 13 *meV* smaller than *cI16*. In the latter case, vibrational modes with imaginary frequencies were neglected in computing ZPE and thermal contributions. When thermal contributions from the lattice vibrations are accounted for, the enthalpy for *bcc*, *fcc*, and *hcp* varies within 0.6 *meV* with *fcc* being still the most stable of these three phases. The entropy term brings *bcc* to be the most stable with the energy difference of the order of 3 – 3.5 *meV* when compared to *fcc* and *hcp* and 28 *meV* when compared to *cI16*. The enthalpy of transformation $\Delta_{tr}H^\circ$ from *bcc* to *fcc* can be estimated from the slope of the coexistence curve in the phase diagram from reference¹³ via Clapeyron's equation:

$$\frac{dP}{dT} = \frac{\Delta_{tr}H^\circ}{T\Delta_{tr}V}, \quad (5)$$

where *P* and *T* are the pressure and temperature describing the coexistence curve and $\Delta_{tr}V$ is the change in the molar volume associated with the transformation. We estimate $\Delta_{tr}H^\circ \simeq 52$ *meV* using $\Delta_{tr}V$ from our theoretical computations, and $\Delta_{tr}H^\circ \simeq 490$ *meV* using $\Delta_{tr}V$ from the experimental cell parameters. These estimates refer to a pressure of approximately 610 *GPa*. Although the first of the two estimates differs from our computational result of $\Delta_{tr}H^\circ = -0.564$ *meV* by less than 65 *meV*, it indicates that PBE fails to properly distinguish between the phases considered.

In other words, while the physical system exhibits a clear region around room temperature and 1 *atm* pressure where *bcc* is the most stable phase, including the vibrational and entropic contributions the PBE model appears to give the *fcc* and *hcp* phases essentially the same free

energy. Actually, the situation is even worse. QM calculations of growth lead directly to energies or enthalpies at 0 K. We can include the zero point energy and vibrational contributions to estimate free energies, but the predictions of where the atoms go during growth, must be based on the QM energy, which disfavors *bcc*.

To determine whether PBE remains suitable to simulate growth of metallic lithium, we report in Table 3 the computed surface energies for the most likely low energy faces of *bcc*, *fcc*, and *hcp* phases. In general, surface energies depend on the medium outside the crystal. Lithium tends to interact strongly with most electrolytes, leading to donor-acceptor bonds and often to formation of a Solid-Electrolyte-Interface (SEI) layer. Although a thorough investigation of these chemical interactions is beyond the scope of this article, we include in Table 3 the surface energies in the presence of a medium with low dielectric constant, representing the liquids or gels commonly used to preserve metallic lithium. We used the Self-Consistent-Continuum-Solvation²² (SCCS) approach, that accounts for the dielectric behavior of the liquid but neglects all surface-liquid chemical interactions.

We find that for relative dielectric constants $\epsilon = 5$ and $\epsilon = 10$, solvation decreases the surface energies by a few mJ/m^2 . The effect is larger for rugged surfaces, e.g., *bcc* – (211), and smaller for flat ones, e.g., *bcc* – (100), but does not change qualitatively the energy differences between surfaces or phases.

The *bcc* phase has a slightly lower surface energy than the other forms. This is essential for small systems, such as those used to investigate surface growth with DFT methods. To quantify the importance of surface effects on phase stability, we consider a cluster with roughly spherical shape and containing N atoms. For this cluster, volume and surface area are determined by the spherical shape and the density. Two values for the vacuum ($\epsilon = 1$) surface energy were considered: the smallest value for each phase in Table 3 and the average value, based on ideal Wulff crystal^{23,24} surface exposure. Considering both Gibb's free energy for the bulk from Table 2 and the surface energies, we obtain the free energies as a function of number of atoms in the cluster, as reported in Figure 1.

Figure 1: Free energy of *fcc* and *hcp* relative to *bcc* for spherical globelets. Results are based on the lowest surface energy for each phase, or on the average surface energy, assuming ideal crystal growth.

Based on this estimate, *bcc* is significantly more stable than *fcc* or *hcp* for high surface area systems than for bulk. For instance, based on the Wulff averaged surface energies, for globelets comprising 100 atoms, corresponding to diameters of 15 – 16 Å, *bcc* is more stable than *fcc* and *hcp* by approximately 3.6 and 9.2 mJ/m², respectively. Using the lowest surface energies, these difference are 6.1 and 19.7 mJ/m² for *fcc* and *hcp*, respectively. This is more than twice the bulk values of 2.9 and 3.5 meV from Table 2.

Thus, although PBE fails to predict the correct energy difference between *bcc*, *fcc*, and *hcp*, it is suitable for simulations of compact lithium systems as long as the underlying *bcc* crystal structure is enforced during the calculation. For instance, we can investigate the surfaces for each phase by fixing some of the deeper layers to have the correct geometry.

For situations such as dendrite growth far from a well-defined periodic surface, PBE correctly predicts *bcc* as the most stable form owing to its lower surface energy. Caution should however be used due to the artificially small *fcc* energy, which may lead to erroneous configurations.

Conclusions

In this study, we investigated the accuracy of the Density Functional PBE in describing the relative stability of lithium phases near ambient conditions. The computed enthalpy of transitions appear to be significantly smaller than experimentally observed; in order to obtain the correct *bcc* ground state phase, thermal corrections for both the enthalpy and the entropy must be included in the computation, which is not practical. Hence, PBE may be used to study bulk properties for single-phase systems only if the desired crystal structure is enforced and caution should be used when comparing energies for different phases.

When surface effects are included, PBE correctly favors formation of the *bcc* phase for high surface area systems. Thus, it is reasonable to use this Functional to investigate problems such as surface growth or dendrite formation.

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Supporting Information Available

The following file is available free of charge.

- SupportingInformation.pdf: Phonon Density of States for the phases considered. Comparison with PBEsol results. Geometries for selected systems.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

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