Thermodynamically stable lithium silicides and germanides from density-functional theory calculations

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High-throughput density-functional-theory (DFT) calculations have been performed on the Li-Si and Li-Ge systems. Lithiated Si and Ge, including their metastable phases, play an important technological role as Li-ion battery (LIB) anodes. The calculations comprise structural optimisations on crystal structures obtained by swapping atomic species to Li-Si and Li-Ge from the X-Y structures in the International Crystal Structure Database, where X=\{Li,Na,K,Rb(Cs)\} and Y=\{Si,Ge,Sn,Ph\}. To complement this at various Li-Si and Li-Ge stoichiometries, ab initio random structure searching (AIRSS) was also performed. Between the ground-state stoichiometries, including the recently found Li17Si4 phase, the average voltages were calculated, indicating that germanium may be a safer alternative to silicon anodes in LIB, due to its higher lithium insertion voltage. Calculations predict high-density Li13Si4 and Li6Ge2 P4/nnm layered phases which become the ground state above 2.5 and 5 GPa respectively and reveal silicon and germanium’s propensity to form dumbbells in the Li3Si, x=2.33–3.25 stoichiometry range. DFT predicts the stability of the Li11Ge6 Cmmm, Li12Ge7 Pnma and Li2Ge3 P321/2 phases and several new Li-Ge compounds, with stoichiometries Li5Ge2, Li13Ge5, Li8Ge3 and Li113Ge4.

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I. INTRODUCTION

Lithium-ion batteries (LIBs) are the secondary (rechargeable) battery of choice for portable electronic devices due to their high specific energy (energy per unit weight) and energy density (energy per unit volume). LIBs have the highest capacity of all the commercially available battery technologies and are now being deployed in hybrid and all-electric vehicles. 1 There is substantial interest in enhancing the capacity of LIBs, driven by the economic and environmental advantages of increasing the range of electric vehicles, and enabling longer-life portable electronic devices.

Lithium intercalated graphite is the standard LIB negative electrode material due to its good rate capability and cyclability, but demand for even higher performance LIBs has motivated the investigation of other materials. Silicon is an attractive alternative since it has ten times the gravimetric and volumetric capacity of graphite (calculated from the initial mass and volume of silicon) but, unlike graphite, silicon undergoes structural changes on lithiation. 2 The negative electrode may be studied using a half-cell containing lithium and silicon. The term “anode” applies to the negative electrode during LIB discharge only, so to avoid confusion we refer to lithiation and delithiation of the silicon half-cell which corresponds to charging and discharging the LIB respectively. The first lithiation of the cell at room temperature involves the conversion of crystalline silicon (c-Si) into an amorphous lithium silicide phase (a-Li3Si) 3 The onset of amorphization depends on the lithiation rate and has been measured at y \approx 0.3 in micron-sized (325 mesh) silicon clusters after irreversible SEI (solid-electrolyte interphase) formation has been taken into account. 4 Below a discharge voltage of 50 mV the a-Li3Si crystallizes to form a metastable Li15Si4 phase which may become non-stoichiometric, Li15±δSi4, at deep discharge. 5 However, at temperatures above 100°C it is possible to form the most lithiated crystalline phase, Li21Si4, electrochemically. 6 Full lithiation of silicon leads to a drastic volume expansion of 270–280%, 6 which generates considerable mechanical stress. Hysteresis in the capacity/voltage profile occurs due to a combination of mechanical stress and different reactions taking different structural pathways on lithiation and delithiation. The microscopic mechanisms underlying these phenomena are still not entirely clear. 7 a-Li3Si has been studied in situ using nuclear magnetic resonance (NMR), 8 X-ray diffraction (XRD), 9,10 and electron energy loss spectroscopy (EELS). 11 These studies along with ex situ NMR and PDF (pair-distribution function) studies of XRD data suggest that silicon forms small clusters and isolated atoms during lithiation. The clusters that form only break apart into isolated silicon atoms at the end of the lithiation process (below 80 mV). 12

Many of the disordered structures that form during lithiation can be approximated by the Li-Si ground-state and metastable crystalline phases. For instance, the crystalline phases have been used as a first step in understanding charge transfer 13 and average lithiation voltages. 14 To gain insight into the possible types of silicon clusters present and their environments in a-Li3Si, various crystalline phases have been investigated and categorized using NMR 15 and ab initio theoretical techniques. 16–18 These c-Li3Si phases have previously been well categorized using density-functional theory (DFT) 16–19; however new insights into the most lithi-
ated phases and the ability to synthesize Li$_x$Si$_7$ through ball milling have suggested that the system is far from fully understood. The most recent phase diagram of the Li-Si system shows, in ascending lithium content order, ε-Si, Li$_x$Si$_1$, Li$_2$Si$_7$, Li$_7$Si$_3$, Li$_{11}$Si$_3$, Li$_{15}$Si$_3$, Li$_{22}$Si$_5$, and β-Li$_4$Si$_3$. Additionally investigations by Zeyliger and coworkers have presented a high-temperature Li$_{14}$Si$_8$ phase and suggested Li$_{17}$Si$_4$ as the correct stoichiometry of Li$_{21}$Si$_5$/Li$_{22}$Si$_5$.

Germanium is another choice of anode for LIB with a theoretical capacity of 1568 mAh g$^{-1}$ some 5 times greater than carbon. Its lithium diffusivity at room temperature is 400 times greater than silicon$^{45}$; however it is scarcer and consequently more expensive. About the Li-Ge phase diagram, more crystalline phases occur during electrochemical lithiation of germanium than silicon; XRD and HRTEM measurements show that during lithiation of germanium at room temperature, the Li-Ge system progressed through Li$_9$Ge$_4$, Li$_7$Ge$_2$, and Li$_{13}$Ge$_2$ around 350 $^\circ$C. We then turn our attention to Li-Ge which has not been analyzed using computational search methods before and present the new structures, Li$_7$Ge$_2$, Li$_{13}$Ge$_5$, Li$_8$Ge$_3$, and Li$_{15}$Ge$_4$. The average voltages for the Li-Si and Li-Ge systems are presented including the Li$_{17}$Si$_4$ and Li$_{11}$Si$_3$ phases. The conclusions of the simulations are given in Sec. VI.

II. METHODS

Ab initio random structure searching (AIRSS) has been successful in predicting the ground-state structures of high-pressure phases of matter$^{34-35}$. More recently it has also been applied to the Li-P system$^{36}$ and defects in technologically relevant ceramics$^{37,38}$ semiconductors$^{39,40}$ and LIBs$^{41,42}$. Since in an AIRSS calculation each random starting configuration is independent from another, the search algorithm is trivially parallelisable, making high-throughput computation straightforward. AIRSS searches were performed for stoichiometries Li$_x$Si$_y$ and Li$_x$Ge$_y$ where $x, y = 1-8$.

Relaxations were performed using the stoichiometric crystal structures of Li-Si, Li-Ge, Li-Sn, Li-Pb, Na-Si, Na-Ge, Na-Sn, Na-Pb, K-Si, K-Ge, K-Sn and K-Pb. First, the structures were obtained from the International Crystallographic Structure Database (ICSD). Second, for each structure the anions were replaced with Li and the cations replaced with {Si,Ge}. The structures were relaxed to local-energy minima using forces and stresses calculated by DFT.

Calculations were performed using the plane wave CASTEP DFT code$^{43}$. The PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional was used with Vanderbilt “ultrasoft” pseudopotentials. The Li-Si system required a basis set containing plane waves with energies of up to 400 eV and a Monkhorst-Pack (MP) grid corresponding to a Brillouin zone (BZ) sampling grid finer than $2\pi \times 0.05\AA^{-1}$. The Li-Ge system required a 600 eV planewave cutoff with harder pseudopotentials and a BZ sampling finer than $2\pi \times 0.03\AA^{-1}$.

We define the formation energy per atom of a compound Li$_n$X$_m$, where $X = \{Si,Ge\}$ as,

$$E_f/A = \frac{E(Li_nX_m) - n\mu_{Li} - m\mu_{X}}{n+m},$$

(1)

where $E(Li_nX_m)$ is the total DFT energy of a given structure, $Li_nX_m$ and $\mu_{Li}$ and $\mu_{X}$ are the chemical potentials of atomic species Li and X in their ground state elemental structure. To compare the stabilities of different stoichiometries we plot the formation energy per atom, $E_f/A$ versus the fractional concentration of lithium in a compound where,

$$C_{Li} = \frac{n}{n+m}.$$  

(2)

and, as above, $n$ and $m$ are the number of atoms of Li and X in a compound respectively. Drawing a convex hull from $(C_{Li}, E_f/A) = (0,0)$ to $(1,0)$, that is, between the chemical potentials, reveals the stable zero Kelvin structures at the vertices of the tie-lines.

III. VOLTAGES

We calculate average voltages in an LIB anode using DFT total energies by assuming that all the displaced charge is due to Li and that the reaction proceeds sequentially through the phases on the tie-lines of the convex hull, i.e. it is a succession of two-phase reactions.$^{44}$ The voltage is given by,

$$V = -\frac{\Delta G}{\Delta x},$$

(3)

where the Gibbs free energy change, $\Delta G$ is in eV and $\Delta x$ is the change in the number of lithium atoms per silicon atoms in the 2 phases. The Gibbs free energy is composed of a number of terms,

$$\Delta G = \Delta E + P\Delta V - T\Delta S,$$

(4)

where $\Delta E$ is the total electronic energy, and $P$, $\Delta V$, $T$, and $\Delta S$ are the pressure, change in volume, thermodynamic temperature and change in entropy respectively. Due to the difficulty in calculating $\Delta G$ we make the approximation, previously applied to the Li-Si system, that $\Delta G \approx \Delta E$ since $\Delta E$ is of the order of a few electron volts, $P\Delta V \approx 10^{-5}$ eV and $T\Delta S \approx 0.06$ eV at 425$^\circ$C.$^{45-47}$
IV. RESULTS - LITHIUM SILICIDE

We find on the convex hull, shown Fig. 1, in increasing lithium content order; diamond-structure *Fd*3m c-Si; the *I*41/*a* Li1Si1 phase which has recently been synthesized at ambient pressure and is discussed in Sec. IV A; the *Pm*3m Li12Si7 phase which contains silicon 5-membered rings and 4-membered stars, which have been studied using NMR; the Li7Si3 and Li5Si2 phases with *P*3212 and *R*3m symmetries respectively discussed further in Sec. IV B; the *Pbam* Li13Si6 phase; the metastable *I*2/amd Li15Si4; and the Li17Si4 *F*3m symmetry phase discussed further in Sec. IV C.

For Li15Si4, Mulikan analysis yields a charge of 0.15$|e|$ and −0.57$|e|$ per Li and Si respectively; in agreement with Bader analysis that Li is a cation and contrary to the reports that Li is anionic.

The average voltage was calculated between all adjacent pairs of stable Li-Si phases on the convex hull including both the Li17Si4 phase and Li13Si4 phase recently synthesized at ambient pressure. Voltages were obtained from the DFT total energies, as described in Sec. III, and referenced to lithium metal. The potential composition curve is presented in Fig. 2 as is in agreement with previous experimental and theoretical work.

A. Li1Si1 layered structures

We find a set of structures with Li1Si1 stoichiometry, listed in Table II all within ~0.1 eV/f.u. of the ground state. The DFT ground state at 0 GPa is a *I*41/*a* phase comprising a 3-fold coordinated silicon network hosting lithium tetrahedra similar to the {4Li,V} Zintl defect in silicon. Recently the *I*41/*a* phase has been synthesized via ball-milling and shown to be stable under ambient conditions. Mulikan analysis yields a charge of 0.34|$|e|$ for each Li and −0.34|$|e|$ for each Si establishing Li as cationic contrary to a previous analysis.

DFT predicts a novel *P4/mmm* phase with a formation energy of 0.07 eV p.f.u. at 0 GPa. It is a layered structure comprising a two-dimensional (non-tetrahedrally) four-fold coordinated silicon lattice with lithium intercalated between the silicon sheets. Since the silicon is four-fold coordinated it gains less of the lithium’s charge than in the layered structures, see Fig. 2. The *I*41/*a* phase recently synthesized at ambient pressure is stable at high pressure; however Li17Si4 *I*41/*amd* is not globally stable over the pressure range we studied (between 0 and 10 GPa).

The *P51m1* phase contains 6 membered rings of 3-fold coordinated silicon atoms in layered sheets, see Fig. 2. The silicon network is isostuctural to silicene, a silicon analogue of graphene. We calculate that silicene and a phase based on the *P4/mmm* silicon network are 0.63 and 0.89 eV p.f.u. respectively above the *Fd*3m ground state. When lithiated both layered structures are only 0.07 eV above the (*I*41/*a*) ground state. Given the interest in silicene our layered compounds might provide an alternative route to layered silicon.

![Figure 1](image-url) - Formation enthalpy per atom versus the fractional lithium concentration of a Li-Si compound (blue boxes). The tie-line (blue line) shows the convex-hull obtained by joining together the globally stable structures predicted by DFT. Between the species swapping technique and AIRSS we recover the known stable phases, Li1Si1, Li12Si7, Li7Si3, Li13Si4, Li15Si4 and Li17Si4. The searches also find the Li5Si2 phase predicted by Tipton et al. and low-lying metastable phases with stoichiometries Li5Si3 and Li13Si5 are also predicted.

**Table II** - Li-Si phases predicted by DFT calculations.

| Phase      | Form. Enthalpy (eV/atom) | Li
|------------|-------------------------|-----|
| Li1Si1     | −0.2                    | 1   |
| Li7Si3     | −0.3                    | 7   |
| Li5Si2     | −0.3                    | 5   |
| Li12Si7    | −0.3                    | 12  |
| Li13Si5    | −0.1                    | 13  |
| Li15Si4    | 0.0                     | 15  |
| Li17Si4    | 0.1                     | 17  |
TABLE I: Low-energy Li$_1$Si$_1$ metastable phases. The structures are shown in Fig. 2 with formation energy $E_f$ per formula unit relative to the energy of the ground states. We calculate that P4/mmm is the most stable above 2.5 GPa.

| $E_f$ (eV/f.u.) | Symmetry | Volume ($\AA^3$/f.u.) | Description |
|----------------|----------|------------------------|-------------|
| 0.00           | I$4_1$/a | 31.3                   | Li tetrahedra in a 3-fold coordinated Si network |
| 0.05           | R$\overline{3}$ | 33.1                   | Distorted Li octahedra 3-fold coordinated Si network |
| 0.07           | P4/mmm   | 27.8                   | Flat Si sheets comprising 4 membered rings |
| 0.07           | P$\overline{1}$ | 31.7                   | Buckled Si sheets comprising 8 and 4 membered rings |
| 0.07           | P$\overline{3}$m1 | 34.1                   | Li intercalated silicene |
| 0.08           | P2/m     | 28.1                   | Li$_1$Sn$_7$-like 2.39 Å dumbbells and isolated atoms |
| 0.11           | I$4_1$/amd | 28.1                   | Isostructural with Li$_4$Ge$_1$ high-pressure phase |

B. Li$_7$Si$_3$ and Li$_5$Si$_2$

Lithium’s position in the crystal lattice can be difficult to establish due to its low XRD scattering factor. Furthermore, Li$_7$Si$_3$ has partially occupied lattice sites making it difficult to model using DFT. Its structure may be represented as a supercell of R$\overline{3}$m Li$_5$Si$_3$ in which lithium atoms have been removed from certain lattice sites. By choosing different combinations of lithium sites in the supercell, models of Li$_7$Si$_3$ can be produced with P$\overline{3}$m1, C$\overline{2}$/m Cm and P$\overline{3}$12 symmetries. The latter, labeled “#2” by Dahn et al., is found on the convex hull.

It is unsurprising that at zero Kelvin, DFT also predicts that the R$\overline{3}$m Li$_5$Si$_2$ phase to be stable since it contains entirely occupied lithium sites. Tipton et al. also found this phase to be stable using DFT.

C. Most lithiated phases

The most lithiated stable Li-Si phase has been the subject of debate. XRD measurements predict that Li$_{21}$Si$_{13}$ is stable at room temperature and Li$_{22}$Si$_{15}$ at 415°C. Previous DFT calculations predict Li$_{15}$Si$_{13}$ to be the stabler phase, even after the inclusion of temperature dependence using the harmonic approximation. The combined AIRSS/species-swapping technique predicts Li$_{15}$Si$_{13}$ and Li$_{12}$Si$_{13}$ to be locally stable but above the convex hull. The Li$_{17}$Si$_{14}$ phase is on the convex hull, and it has the same crystal structure as F$\overline{3}$m Li$_{17}$Pb$_4$, as discovered independently by Zeilinger et al. Zeilinger et al. also predict a Li$_{4.11}$Si high-temperature phase which they model using Li$_{16}$Si$_{14}$ and Li$_{16.5}$Si$_{14}$ phases. We include Zeilinger et al.’s models in Fig. 1 although DFT predicts that they are not on the tie-line.

D. Repeating units – Silicon dumbbells

We also find a R$\overline{3}$m Li$_5$Si$_3$ and a P$\overline{3}$m1 Li$_{12}$Si$_{14}$ phase close above the tie-line. They belong to the set of structures in the range Li$_7$Si$_3 \rightarrow$ Li$_{13}$Si$_5$, which all contain silicon dumbbells. The dumbbells are aligned in parallel with various numbers of collinear lithium atoms between them forming one-dimensional repeating sequences, see Table II. The 1D linear repeating chains are thus packed alongside each other realizing the three-dimensional structure. For example, since Li$_7$Si$_3$ comprises (5×Li + Si-Si) and (4×Li + Si-Si) sequences in a ratio of 2:1, it is equivalent to the Li$_5$Si$_2$ phase with lithium vacancies. Li$_{15}$Si$_{13}$ comprises sequences of atoms with the repeating unit (5×Li + Si-Si) and the Li$_{15}$Si$_{13}$ is similar but with atoms in a (4×Li + Si + 4×Li + Si-Si) repeating unit; it is isostructural with a Li$_8$Pb$_3$ phase. The Li$_{13}$Si$_5$ phase is isostructural with the Li$_{13}$Sn$_5$ phase and has two different repeating units (5×Li + Si) and (4×Li + Si-Si) in a ratio of 1:2.

Finally, in Li$_{13}$Si$_4$, the one-dimensional columnar structure does not exist but Si-Si dumbbells and Si isolated atoms remain in a ratio of 1:1. At higher lithium concentrations, Li$_{15}$Si$_{13}$ forms, in which all silicon dumbbells are broken, and only isolated Si atoms remain. The propensity for silicon dumbbells to form over a wide range of stoichiometries and total energies implies that silicon dumbbells form on lithiation of silicon in a LIB anode.

| Stoichiometry | Constituent columns |
|---------------|---------------------|
| Li$_7$Si$_3$   | 2×(5×Li + Si-Si) & (4×Li + Si-Si) |
| Li$_5$Si$_2$   | (5×Li + Si-Si) |
| Li$_{15}$Si$_{13}$ | (5×Li + Si) & 2×(4×Li+Si-Si) |
| Li$_{13}$Si$_5$ | (4×Li + Si + 4×Li + Si-Si) |
In order of lithium content, the following Li-Ge phases have all been proposed: \( \text{Li}_7\text{Ge}_{12}, \text{Li}_1\text{Ge}_1, \text{Li}_{12}\text{Ge}_7, \text{Li}_{11}\text{Ge}_6, \text{Li}_{10}\text{Ge}_4, \text{Li}_9\text{Ge}_3, \text{Li}_7\text{Ge}_2, \text{Li}_{15}\text{Ge}_4, \text{Li}_{17}\text{Ge}_4 \) and \( \text{Li}_{22}\text{Ge}_5 \). Below we compare in detail the known phases to the results of the DFT searches.

\( \text{Li}_7\text{Ge}_{12} \) is the only reported phase with a ratio of Li/Ge less than 1. It has two symmetries associated with it, originally \( Pmn_2_1 \) \( \text{P}_{\text{n}} \), which was later disputed \footnote{Wen and Huggins} \footnote{Chevrier et al.}, and more recently, \( P2_1/n \) \footnote{Chevrier et al.}. Four of its lithium lattice sites are 50% occupied. We model its structure in a periodic lattice using a simulation cell containing 28 Li and 48 Ge sites. The fractionally occupied sites can be filled in a variety of ways: all sites, giving rise to a crystal symmetry \( P2_1/c \); one site \( (P1) \), four different ways (all degenerate); two sites, 6 ways \( (P_c, P_2 \text{ or } P\text{I}) \) each symmetry being doubly degenerate); three sites \( (P1) \) four ways (all degenerate); and by leaving all empty \( (P2_1/c) \) one way. A convex hull of their single point energies shows that the \( P_c \) version is the most stable, hence we use this throughout the rest of the calculations. Although not on the Li-Ge convex hull, see Fig. \ref{fig:fig3} this \( P_c \) predicted phase is close above.

V. RESULTS - LITHIUM GERMANIDE

FIG. 2: (Color online) Low-energy \( \text{Li}_x\text{Si}_x \) phases detailed in Table \ref{table:table1} with a) \( I4_1/a \), b) \( R \), c) \( P4/mnm \), d) \( P\text{mm1} \), e) \( P\text{I} \) symmetries. DFT predicts the \( P4/mnm \) phase to be stable above 2.5 GPa.

FIG. 3: (Color online) Potential-composition curves of stable structures found on the convex hull in Fig. \ref{fig:fig1} (black line) compared to experiment at 415\(^\circ\) C (red dashed line) and previous DFT-GGA calculations (blue dot-dashed line) \footnote{FIG. 2: (Color online) Low-energy \( \text{Li}_x\text{Si}_x \) phases detailed in Table \ref{table:table1} with a) \( I4_1/a \), b) \( R \), c) \( P4/mnm \), d) \( P\text{mm1} \), e) \( P\text{I} \) symmetries. DFT predicts the \( P4/mnm \) phase to be stable above 2.5 GPa.}

\begin{itemize}
  \item \textit{This work DFT-GGA}
  \item \textit{Experiment}
  \item \textit{DFT-GGA\textsuperscript{*}}
\end{itemize}

\textsuperscript{*} Wen and Huggins \textsuperscript{3} \textsuperscript{b} Chevrier et al. \textsuperscript{45}
Li$_3$Ge$_1$ has an $I4_1/a$ ground state and a $I4_1/amd$ high pressure form. DFT predicts $I4_1/amd$ and a new layered $P4/mmm$ phase at 0.012 eV/f.u. and ~0.020 eV/f.u. above the $I4_1/a$ ground state respectively. The $P4/mmm$ phase is isostructural with the Li-Si phase discussed above in Sec. IV A. DFT predicts that the system undergoes a phase transition from the $I4_1/amd$ to the $P4/mmm$ phase at 5 GPa.

Grüttner et al. mentioned a Li$_{1.5}$Ge$_7$ phase isotopic with the corresponding Li$_{12}$Si$_7$ phase in a very brief report, but did not present any further data to support its discovery. DFT also predicts a Li$_{1.5}$Ge$_7$ Pnma phase near the tie-line.

Li$_{11}$Ge$_6$ was synthesized by Frank et al. with a molecular volume of 172.3 cm$^3$ mol$^{-1}$. Nesper et al. claim that the phase is actually Li$_3$MgGe$_6$, suggesting that since Li$_3$MgGe$_6$ has a molecular volume of 166.5 cm$^3$ mol$^{-1}$ it is unlikely that Li$_{11}$Ge$_6$ could have two more atoms per formula unit. DFT also finds a Li$_{11}$Ge$_6$ Cmcm phase slightly above the tie-line with a volume of 286.26 Å$^3$ per f.u., which corresponds to a molecular volume of 172.4 cm$^3$ mol$^{-1}$. Hence it seems entirely possible to us that Li$_{11}$Ge$_6$ Cmcm was synthesized by Frank et al. as initially proposed.

Li$_9$Ge$_4$ in the Cmcm symmetry group, have been made electrochemically and from high temperature fusion by all of our calculations show it well above the tie line, favoring disproportion into a $P321_2$ Li$_7$Ge$_3$ phase. Li$_7$Ge$_3$ with $P321_2$ symmetry was first mentioned by ref. 22 but no supporting information was given. Jain et al. found an unknown phase that they suggested was Li$_2$Ge$_3$ fitting the diffraction data to $R3m$ symmetry. Hence we suggest that Jain et al. synthesized either the Li$_2$Ge$_2$ or indeed Li$_6$Ge$_3$ phases, DFT predicting that both phases have the $R3m$ symmetry. Li$_3$Ge$_2$ is above the tie-line and Li$_{11}$Ge$_5$ and Li$_6$Ge$_3$ are all stable although to the best of our knowledge they have not previously been presented in the literature. This may be due to thermal effects, see the discussion of similar arguments for Li$_3$Si$_2$ in Sec. IV B. Li$_{17}$Ge$_5$ was predicted by St. John, et al. during electrochemical studies. They presented no crystal structure nor is there any prototype structure of {Li/Na}{Si/Ge/Sn/Pb} with this stoichiometry. DFT predicts a Li$_{17}$Ge$_4$ Pbam phase, isostructural with the Li$_{17}$Si$_4$ phase which is slightly above the tie-line and with a similar Li:Si ratio to Li$_{16}$Ge$_5$. Recently preliminary results by H. Jung et al. have produced electrochemically new phases in the Li$_2$Ge phase range whose X-ray pair distribution functions (PDF) match at least one of our predicted phases. A fuller investigation will be presented later.

The Li$_3$Ge$_2$ phase with Cmmm symmetry can be made electrochemically and by annealing from high temperature melt. DFT-GGA predicts the $P3m1$ phase above the tie-line and 0.08 eV/f.u more stable than the Cmmm phase. This discrepancy remains after using harder pseudopotentials and either the LDA exchange-correlation or the HSE06 hybrid functional. A fuller investigation into this will be presented elsewhere.

We find the well known Li$_{13}$Ge$_5$ stoichiometry $I43d$ phase stable. The most lithiated phase has been a matter of debate in all Li-Group 4 compounds including germanium. Its stoichiometry was reported as Li$_{22}$Ge$_5$ with $F23$ symmetry due to its similarity to Li$_{22}$Pb$_4$. More recently, Goward et al. studied this family of structures and show that for the Ge, Sn and Pb compounds the correct stoichiometry is Li$_{17}$Ge$_4$ with $F43m$ symmetry. $F43m$ symmetry Li$_{21}$Ge$_5$, Li$_{22}$Ge$_5$ and Li$_{17}$Ge$_4$ are found by DFT all at local energy minima. However, Li$_{17}$Ge$_4$ is on the tie-line. Fassler et al. also predict a Li$_4$Ge$_{10}$ phase analogous to the Li$_{4.1}$Si phase. We use the same model structures as in the Li$_{4.1}$Si phase for our DFT

![FIG. 4: (Color online) The Li-Ge binary composition diagram. The red squares indicate the formation enthalpy of a structure. The red line is the tie-line indicating the stable structures on 0 K predicted by DFT.](image-url)
TABLE III: Experimental and predicted phases of Li$_x$Ge system.

| Experimental Symmetry | $x$ | Stoichiometry | Predicted Symmetry |
|-----------------------|-----|---------------|-------------------|
| Fd$ar{3}$m$^0$ | 0.000 | Ge | Fd$ar{3}$m |
| Pm$ar{3}$m$^0$, P$2_1$/n$^0$ | 0.580 | Li$_7$Ge$^{12}$ | P$3$ |
| I$4_1$/a$^d$, I$4_1$/amd$^e$ | 1.000 | Li$_1$Ge$_1$ | I$4_1$/a, I$4_1$/amd$^e$, P$4$/mmm$^{**}$ |
| Pm$n^a$ | 1.710 | Li$_3$Ge$_7$ | Pnma$^a$ |
| Cm$ar{c}$m$^e$ | 1.83 | Li$_3$Ge$_6$ | Cm$ar{c}$m$^e$ |
| Cm$ar{c}$m$^{a,b,i,j}$ | 2.25 | Li$_4$Ge$_4$ | Cm$ar{c}$m$^e$ |
| P32$121/3$, R$ar{3}$m$^i$ | 2.33 | Li$_5$Ge$_3$ | P32$121$, P21/m$^*$ |
| 2.50 | Li$_3$Ge$_2$ | R$ar{3}$m$^*$ |
| 2.60 | Li$_3$Ge$_5$ | P$3$m$^1$ |
| 2.67 | Li$_5$Ge$_3$ | R$ar{3}$m |
| 3.20 | Li$_7$Ge$_5$ | |
| 3.25 | Li$_7$Ge$_4$ | Pb$m^a$ |
| Cm$ar{c}$m$^{a,b,i,j}$ | 3.50 | Li$_7$Ge$_2$ | P$3$m$^1$, Cm$ar{c}$m$^{**}$ |
| F$ar{4}$3$n^a,i,j$ | 3.75 | Li$_3$Ge$_4$ | F$ar{4}$3d |
| F$ar{4}$3$n^a$ | 4.20 | Li$_7$Ge$_4$ | F$ar{4}$3m |
| F$ar{4}$3$m^{a,b,i}$ | 4.25 | Li$_2$Ge$_5$ | F$ar{4}$3$m^*$ |
| P$ar{6}$_5/mmc$^f$ | – | αLi | P$ar{6}$_5/mmc |

Sangster and Pelton’s work was invaluable for an overview of the field.$^{58}$

$^a$ First metastable above tie-line.

$^b$ Second metastable above tie-line.

$^c$ A. W. Hull$^{59}$

$^d$ Very brief summaries are given by Grüttnet al.$^{22,60}$

$^e$ Kiefer and Fässler.$^{51}$

$^f$ E. Menges et al.$^{23}$

$^g$ J. Evers, et al.$^{24}$

$^h$ Reported in abstract by Grüttnet al.$^{22}$

$^i$ First found by Frank et al.$^{25}$, Nesper et al.$^{62}$ suggested it is actually Li$_8$MgGe$_6$.

$^j$ V. Hopf et al.$^{66}$

$^k$ Jain et al.$^{27}$

$^l$ Yoon et al.$^{28}$

$^m$ E. M. Pell finds Li$_3$Ge$_1$.$^{64}$ See Sangster et al. $^a$ and a discussion therein. St. John et al. report that they have found the Li$_3$Ge$_1$ reported earlier as Li$_{16}$Ge$_5$.$^{65}$

$^n$ V. Hopf et al.$^{29}$

$^o$ Gladyshevskii et al.$^{30}$ and Johnson et al.$^{21}$

$^p$ Goward et al.$^{32}$

$^q$ Gladyshevskii et al.$^{33}$

$^r$ Reported by Jain et al.$^{27}$ as Li$_{21.1875}$Ge$_5$

$^s$ C. S. Barrett.$^{66}$

TABLE IV: Low energy Li$_1$Ge$_1$ metastable phases, with formation energy, $E_f$ p.f.u relative to that of the energy of the ground state. The structures are isotypic of those found in Li$_1$Si$_1$, as shown in Table II and Fig. 2. DFT predicts that the P4/mmm phase is the most stable above 5 GPa.

| $E_f$ (eV/p.f.u.) | Symmetry | Volume ($\text{Å}^3$/p.f.u.) | Description |
|------------------|----------|-----------------------------|-------------|
| 0.00 | I$4_1$/a | 35.1 | Li tetrahedra in a 3-fold coordinated Ge network |
| 0.01 | I$4_1$/amd | 32.2 | Known high pressure phase |
| 0.02 | P$4_1$/mmm | 31.9 | Flat Ge sheets 4 membered rings |
| 0.03 | R$\bar{3}$ | 36.8 | Distorted Li octahedra 3-fold coordinated Ge network |
| 0.04 | P$2_1$/m | 32.1 | Isostructural with the corresponding Li$_1$Sn$_1$ phase |

VI. DISCUSSION

Crystal structures of the Li-Si and Li-Ge systems have been presented, found using both AIRSS searches and atomic species swapping of ICSD structures. Below we discuss the
structures that are likely to be thermally accessible at room temperature, that is, those at a local minima on the DFT potential energy surface which reside on, or close to, the convex hull. These structures serve as a model for the clustering and bonding behavior of electrochemically lithiated silicon and germanium.

The Li-Si system was used to validate our method: DFT finds all of the known phases as local energy minima including independently uncovering the Li$_{17}$Si$_4$ phase. For the Li-Ge system, DFT finds Li$_3$Ge$_2$, Li$_8$Ge$_3$, Li$_{13}$Ge$_5$ and Li$_{13}$Ge$_4$ locally stable and, to the best of our knowledge, these have not been presented in the literature before. DFT predicts that Li$_7$Ge$_{12}$ and Li$_{11}$Ge$_6$ are local energy minima; the former having Pc symmetry and the latter Cmcm. It was reported that Li$_{11}$Ge$_6$ may be produced from a high-temperature melt but this has been disputed. Also at local energy minima are the Li$_{12}$Ge$_7$ Pma and Li$_7$Ge$_3$ P32$_1$2 phases, which were suggested by Grütter but without presenting the crystal structure. An unknown phase was found by heating ball milled Li-Ge, its XRD pattern fits an Li$_7$Ge$_3$ phase with R$\bar{3}$m symmetry. Since DFT and Grütter both predict Li$_7$Ge$_3$ has P32$_1$2 symmetry, we propose that the unknown phase may be either the Li$_5$Ge$_2$ or Li$_8$Ge$_3$ phases which have a similar stoichiometry to Li$_7$Ge$_3$ and both of which DFT predicts to have R$\bar{3}$m symmetry.

For the Li-Si and Li-Ge structures on the tie-lines, the average voltages were calculated relative to lithium metal. This included for the first time Li$_{17}$Si$_4$ and Li$_{11}$Si$_1$. The average voltages are in good agreement with both previous calculations and experiment. They are higher in Li-Ge than Li-Si, implying that germanium has a lower energy density than silicon. However the higher insertion voltage is safer during lithiation, reducing the chance of lithium plating which can result in dendrites short circuiting the cell. Lithium in germanium also has higher diffusivity than in silicon.

Li$_3$Si$_1$ was previously only synthetisable at high pressure but has recently been synthesized by highly energetic ball milling, remotivating interest in the high-pressure phases. AIRSS searches predict a selection of higher energy Li$_3$Si$_1$ and Li$_3$Ge$_3$ phases. At lower pressures three-dimensional three-fold coordinated silicon/germanium networks were prevalent. However, at higher densities, both silicon and germanium exhibited a $P4/mmm$ structure comprising flat sheets of four-fold coordinated silicon and germanium atoms respectively. These became the most stable phase of Li$_3$Si$_1$ and Li$_3$Ge$_3$ at 2.5 GPa and 5 GPa respectively. Given the interest in silicene our layered compounds might provide an alternative route to layered silicon.

A LIB does not necessarily have time to equilibrate thermodynamically over large length scales. The ability to generate a wide range of locally-stable low-energy structures above the ground state allows us to visualize the types of clusters which form in the LIB during cycling. Over a lithiation range of Li$_{1-x}$Si, $x = 2.33 - 3.25$ we found that the structures present exhibited Si-Si dumbbells. At higher lithiation all of the silicon dumbbells break up and the crystalline Li$_{13}$Si$_4$ phase forms. Since these dumbbells were seen in both ground state and metastable phases is seems likely that they will exist in LIB anodes, probably in a lower symmetry solid solution. Furthermore we find the analogous dumbbell containing structures in the Li-Ge system.

Above we have demonstrated that the combination of both atomic species swapping the ICSD phases and AIRSS is a powerful tool for predicting the crystal structures of LIB electrode materials. A refinement to the method combines these two techniques by using results of the AIRSS searches as inputs to the species swapping technique. For example, the low-energy structures found by AIRSS in Li$_3$Si$_1$ were re-optimized as candidate Li$_3$Ge$_3$ phases in the Li-Ge system.

Our method has only provided results of the stable and metastable structures at 0 K, of course, the effect of temperature could be included post hoc using phonon calculations within the harmonic approximation and beyond. Our method serves as a crucial first step in ab initio materials discovery and design.

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Since the Li$_{16.5}$Si$_4$ model contains partially occupied Li sites we extended the cell in the $a$ direction fully occupying four 8g and two 4c sites before optimizing the geometry using DFT.

Confusingly Sangster and Pelton$^{58}$ report that Nesper et al. claim it is the Li$_8$MgSi$_6$ phase.