Novel structures and high pressure superconductivity of CaLi$_2$

Auxiliary Material

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Supplementary Online Material

Detail of DFT calculations

Detailed evolutionary simulations were performed at 10, 30, 50, 80, 100, 120, 150, 180, 200, 220, and 250 GPa with system sizes of 1, 2, 3, 4, 6, and 8 formulas in the unit cell. Each generation contained between 20 and 40 structures (increasing with the system size), and the first generation was always produced randomly. All structures were locally optimized using the VASP code. In a typical evolutionary run, the lowest-enthalpy 60% of each generation were used to produce the next generation (70–80% of these were produced by heredity, and the remaining 20–30% by lattice mutation, and in addition to that the lowest-enthalpy structure survived into the next generation). Gaussian strength of lattice mutation was set to 0.5–0.55. Local optimizations performed during structure search, were done with the conjugate gradients method and were stopped when the enthalpy changes became smaller than 1 meV/cell. Usually, the structure searching simulation was stopped after we generated 1000 ~ 1200 structures (30 ~ 40 generations). Analyzing the results of evolutionary simulations, we selected a number of distinct lowest-enthalpy structures and optimized their structures as a function of pressure using VASP and very dense k-points meshes. A plane-wave kinetic energy cutoff of 500 eV was used and gave well-converged total energies (with in ~ $5 \times 10^{-3}$ eV per atom over the pressure range).
The electronic density of states has been calculated with a $24 \times 24 \times 12$ $k$ mesh generated by the Monkhorst-Pack method [1] for both structures. Phonon dispersion and electron-phonon coupling were performed with Quantum-ESPRESSO package, where the structures are fully re-optimized from PAW results. The pseudopotential for Li and Ca were generated by the Opium code [2] with $1s^22s^1$ and $3s^23p^64s^2$ as valence electrons, respectively. Based on convergence tests, we adopted a kinetic energy cutoff of 60 Ry and a $8 \times 8 \times 4$ MP mesh for Brillouin zone (BZ) integration. Phonon dynamic matrix elements were performed in the first BZ on a $4 \times 4 \times 2$ $q$ mesh. To ensure the convergence of the electron-phonon coupling matrix elements for the electron-phonon interaction coefficients, a large $16 \times 16 \times 8$ grid is required.

The structure optimizations for the elements Ca and Li were also performed with VASP code. The energy cut-off (usually the ‘high’ precision provided by the VASP is good enough) and k-point sampling are chosen such that energies are convergent within $\sim 5 \times 10^{-3}$ eV per atom over the pressure range.
**Supplementary TABLE I.** Detail of the new favored structures discovered in this work. The parameters of the $C2/c$ related to 36 GPa, while the $P2_1/c$ structure was at 55 GPa.

<table>
<thead>
<tr>
<th>Space group</th>
<th>Lattice parameters (Å)</th>
<th>$\beta$</th>
<th>Atomic coordinates (fractional)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C2/c$</td>
<td>$a = 7.8737$</td>
<td>101.7680°</td>
<td>Ca 8f 0.89094 0.11133 0.60162</td>
</tr>
<tr>
<td></td>
<td>$b = 4.6222$</td>
<td></td>
<td>Li1 8f 0.94499 0.40707 0.37001</td>
</tr>
<tr>
<td></td>
<td>$c = 8.5854$</td>
<td></td>
<td>Li2 8f 0.75201 0.66396 0.64787</td>
</tr>
<tr>
<td>$P2_1/c$</td>
<td>$a = 4.5867$</td>
<td>90.0288°</td>
<td>Ca 4e 0.91338 0.94161 0.83685</td>
</tr>
<tr>
<td></td>
<td>$b = 3.943$</td>
<td></td>
<td>Li1 4e 0.29530 0.98252 0.49770</td>
</tr>
<tr>
<td></td>
<td>$c = 7.0471$</td>
<td></td>
<td>Li2 4e 0.53887 0.52378 0.66742</td>
</tr>
</tbody>
</table>
Supplementary Fig. 1. We indeed found the trigonal structure $P-3m1$ (a) - (c) and the ideal hexagonal $P6/mmm$ (d) – (f) from the simulation. But both of them have a higher enthalpy (g) than the distorted $P2_1/c$ structure.
Supplementary Fig. 2. Theoretical and experimental equations of state of CaLi$_2$. A moderate volume overexpansion in theory is observed at high pressure, typical of GGA calculation.
Supplementary Fig. 3. (a) Enthalpy curves (with respect to the mixture of the elements) of various CaLi$_2$ structures predicted by the simulations. An orthorhombic structure $F_{dd}$ was found with a much higher enthalpy than the $P_{21}/c$ structure near 50 GPa. (b) Comparison of the experimental x-ray diffraction pattern with the theoretical pattern of predicted structures at 54 GPa. The similarity between the experimental and theoretical pattern does not preclude the proposed $P_{21}/c$ structure.
Supplementary Fig. 4. The band structure and projected DOS for $C2/c$ and $P2_1/c$ structures at 36 (a) and 60 GPa (b), respectively. The projected DOS suggests strong Ca-Li hybridization. A small peak appears at the Fermi level due to the crossing of $E_F$ by the Ca $d$-band.
Supplementary Fig. 5. Both hexagonal (a) and $C2/c$ (b) structures are dynamical unstable at 20 GPa; and $C2/c$ becomes stable near 28 GPa (c).
Supplementary Fig. 6. Calculated softening of (a) optical B_g and B_u modes in the $C2/c$ structure, and (b), (c) for TA modes in the $C2/c$ and $P2_1/c$, respectively.
Supplementary Fig. 7. Partial electron-phonon coupling parameter $\lambda_{q\nu}$ at selected pressures. The area of each red circle is proportional to the $\lambda_{q\nu}$. The left and right panels are for the $C2/c$ and $P2_1/c$ structures, respectively. It is obvious that low-frequency phonons make the most important contributions.