Novel structures and superconductivities of calcium–lithium alloys at high pressures: A first-principles study

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Exposing a material to high pressures can fundamentally influence its crystal and electronic structure, leading to the formation of new materials with unique physical and chemical properties. Here, we have conducted a systematic search for Ca–Li alloys by using a global minima search based on particle-swarm optimization algorithm in combination with density functional theory calculations. We predict that Calcium and Lithium with a high Ca composition $CaLi$, Ca_2Li and Ca_3Li exist, and a strikingly decomposition-combination-decomposition oscillating behavior with pressure is revealed. All predicted Ca–Li compounds are metallic and good electron–phonon superconductors with transition temperatures (T_c) of around 8–19 K. The superconductivity mainly originates from the low-energy Ca vibrations and the pressure dependence of T_c is dominated by the phonon softening/hardening.

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1. Introduction

Elements calcium (Ca) and lithium (Li) are often considered to be simple metals with two ($4s$) and one ($1s$) conduction electrons per atom, respectively, at normal conditions. Although, there has been more and more pronounced that these materials exhibit remarkably complex behaviors under compression. Especially, high-pressure superconducting transitions were observed in Ca and Li.

At ambient pressure, Ca is not known to superconduct. The superconductivity with the critical temperature (T_c) of 1.4 K at 50 GPa has been observed [1]. The T_c in Ca increases with the pressure [2], and reaches the maximum value equal to 29 K at 216 GPa [3]-the highest value of the critical temperature for any elemental superconductor. On the other hand, Li has an extremely low transition temperature of about 0.4 mK at normal pressure [4]. When compressed, superconductivity abruptly appears at 20 GPa with $T_c = 5$ K, then rises quickly to a maximum T_c of about 14 K at 30 GPa and remains in the range of 7–12 K up to pressures over 60 GPa [5–7].

There have been several theoretical and experimental studies on structural and superconducting properties of binary compound $CaLi_2$ to pursue high temperature superconductors. Feng et al. [8]

carried out electronic structure calculations for Laves phases of $CaLi_2$ and suggested that the hexagonal structure of $CaLi_2$ is stable up to over 200 GPa but undergoes a significant lattice bifurcation around 47 GPa. They also predicted that $CaLi_2$ could be a potential superconductor under pressure due to the high density of states at Fermi level, the high dynamical scale of Li, and the favorable interlayer phonons. Superconductivity is subsequently observed to start at 10 GPa and continues to 81 GPa with a maximum T_c of 13 K at about 48 GPa in experiment [9]. Debessai et al. [10] conducted the x-ray diffraction (XRD) patterns of $CaLi_2$ up to 54 GPa and suggested that hexagonal Laves-type $CaLi_2$ undergoes a phase transition above 23 GPa and completely transforms into an orthorhombic structure at 46 GPa. The results obtained by Tse et al. [11] using both density functional and experimental XRD techniques show that the application of non-hydrostatic pressure leads to a partial decomposition of $CaLi_2$ to elemental species of Ca and Li at high pressures, and thus they suggested that superconductivity observed in $CaLi_2$ at high pressure may contain decomposed element Ca and Li. However, Xie et al. [12] performed evolutionary methodology for crystal structure prediction on $CaLi_2$ and revealed two novel structures not to decompose into pure Ca and Li at high pressures. In addition, the calculated T_c is in good agreement with experimental measurements, which indicated that the measured superconductivity is from the $CaLi_2$ compound itself.

The intricate structure evolution at high pressures, together with the remarkably high T_c observed in $CaLi_2$, stimulates our interest to explore possible structures and superconductivities in

other stoichiometric Ca—Li compounds. Here, we have performed an extensive search for energetically stable crystal structures of Ca_xLi_{1-x} binary compounds under high pressures up to 200 GPa using an effective and unbiased crystal structure prediction method based on the particle swarm optimization algorithm. Three stoichiometric Ca_xLi_{1-x} compounds have been observed to stable over a range of pressures from 30 to 120 GPa. Electronic results show that remarkably large localization of valence electrons in the interstices of the lattice for all predicted Ca—Li compounds at high pressures. It is found that *Fd*-3*m* phase of CaLi and *P*-3*m*1 phase of Ca_2Li have relatively strong electron—phonon coupling mainly originates from the low-frequency Ca vibrations, which contribute to the high superconducting transition temperatures in these compounds.

1.1. Computational details

Stable high-pressure structures of Ca_xLi_{1-x} compounds are explored by using an unbiased structure prediction method based on the particle swarm optimization algorithm as implemented in CALYPSO (crystal structure analysis by particle swarm optimization) code [13,14]. The most significant feature of this methodology is the capability of predicting the stable structure with only the knowledge of the chemical composition. This method has been successfully used to predict structures of many novel compounds under pressure [15–22]. Several predictions of the high-pressure structures were confirmed by independent experiments [15,16,20]. The structure predictions were performed using a unit cell containing up to four Ca_xLi_{1-x} units and at pressures ranging from 0 to 200 GPa. The underlying *ab initio* structural relaxations and the electronic properties calculations were performed within the framework of density functional theory (DFT) [23,24] as implemented in the VASP (Vienna Ab initio Simulation Package) code [25]. The generalized gradient approximation within the framework of Perdew—Burke—Ernzerhof [26] was used for the exchange-correlation functional, and projector augmented wave (PAW) potentials [27] were used to describe the ionic potentials. In the PAW potential for Ca, the 3*s*, 3*p* and 4*s* orbitals and for Li, the 1*s* and 2*s* orbitals were treated as valence. The cutoff energy for the expansion of the wavefunction into plane waves was set at 400 eV, and appropriate Monkhorst—Pack (MP) *k* meshes [28] were chosen to ensure that all enthalpy calculations converged to better than 1 meV per atom. The electron localization function (ELF) was also calculated using VASP. As implemented in VASP, it ranges from 0.5 (free electron gas) to 1 (localized electrons).

The lattice dynamics and electron—phonon coupling (EPC) of Ca—Li are calculated using the pseudopotential plane-wave method within the density functional theory [23,24] and density functional perturbation theory [29] as implemented in the QUANTUM-ESPRESSO package [30]. The convergence in the plane wave basis set and *k*-point sampling has been carefully examined by employing higher kinetic energy cutoffs and dense *k*-point sets for all structures of Ca—Li compounds, where the converged structures from PAW calculation are fully reoptimized with internal forces convergence threshold to 1×10^{-4} eV/Å. In order to approximate the exchange-correlation functional, the PBE parametrization has been used. Convergence tests gave the choice of E_{cutoff} of 450 eV and $2\pi \times 0.02$ Å MP grids for the electronic Brillouin-zone integration for all structures. Phonon frequencies were calculated based on the density functional linear-response method [31,32]. $4 \times 4 \times 4$, $3 \times 3 \times 2$, $3 \times 3 \times 2$, $3 \times 3 \times 2$, and $2 \times 2 \times 2$ *k* meshes in the first BZ were used in the interpolation of the force constants for the phonon dispersion curves and electron—phonon coupling calculations for *Fd*-3*m* structure of CaLi, $P2_1/m$, *P*-3*m*1, and *C*2/*m* structures of Ca_2Li and *C*2/*m* structure of Ca_3Li, respectively. 8 *q*-points for *Fd*-3*m* phase of CaLi, $P2_1/m$, *P*-3*m*1, and *C*2/*m* phases of Ca_2Li and 6 *q*-

points for *C*2/*m* phase of Ca_3Li were used in the electron—phonon coupling constants calculations. The accuracy of the interpolation was also examined by comparing the results with phonon frequencies computed directly at selected *q* points. In the electron—phonon coupling calculations, convergence to the zero-limit was achieved with $8 \times 8 \times 8$, $6 \times 6 \times 4$, $6 \times 6 \times 4$, $6 \times 6 \times 4$, and $4 \times 4 \times 4$ *k* meshes employing Gaussian function broadening with a half-width of 0.04 Ry for *Fd*-3*m* phase of CaLi, $P2_1/m$, *P*-3*m*1, and *C*2/*m* phases of Ca_2Li and *C*2/*m* phase of Ca_3Li, respectively. The strain-stress method was used to calculate the elastic constants of Ca—Li compounds [33].

2. Results and discussions

The phase stabilities of Ca—Li systems are investigated by calculating the formation enthalpy in a pressure range of 0—200 GPa. For the most stable structures at a given pressure, the enthalpy of formation of Ca_xLi_{1-x} per atom is calculated using the following formula: $h_f(Ca_xLi_{1-x}) = h(Ca_xLi_{1-x}) - xh(Ca) - (1 - x)h(Li)$. The enthalpies of Ca and Li are those of the most stable known structure at given pressures. Specifically, elemental Ca adopts the *fcc* [34,35], *bcc* [34,35], *β*-tin [36,37], *C*2/*c*-12 [35], $P4_32_12$-8 [38], *Pnma*-4 [39], and *C*2/*m*-32 [36] structure in the stable pressure ranges considered, 0—200 GPa, whereas elemental Li undergoes a series of phase transitions of *bcc* [40], *fcc* [40], *R*-3*m* [40], *I*-43*d* [40], *Aba*2-40 [20], *Pbca* [41], and *Cmca*-56 [20] in this pressure range. Thermodynamically, a compound located on the convex hull is stable against the decomposition into any other compositions if its enthalpy of formation is negative.

Stability. As depicted in Fig. 1(a), all the Ca_xLi_{1-x} systems which have positive enthalpy of formation are not stable except $CaLi_2$. This is consistent with the previous knowledge that $CaLi_2$ is the only binary compound formed by elemental species of Ca and Li at
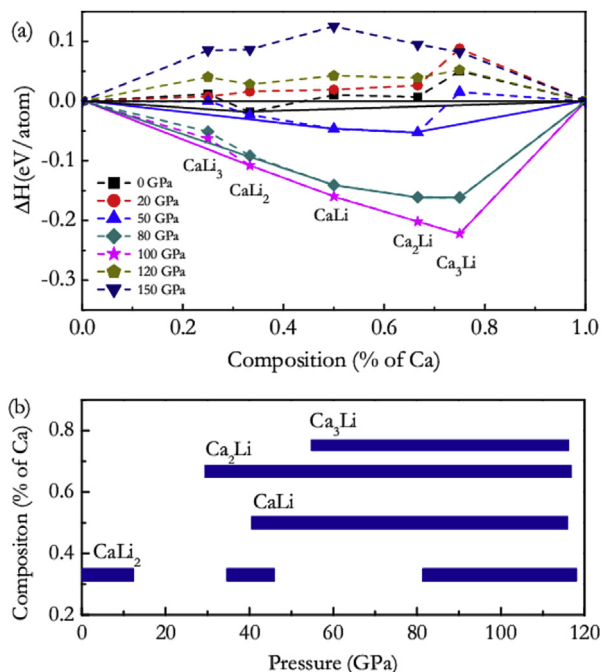
Fig. 1. Stability of Ca_xLi_{1-x} compounds under pressure. a, Enthalpies of formation of Ca_xLi_{1-x} under a series of pressures from 0 to 200 GPa. The dotted lines connect the data points, and the solid lines denote the convex hull. b, Predicted stable pressure ranges for Ca_xLi_{1-x} compounds. The purple segment represents the pressure range. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)