Structural Prediction and Phase Transformation Mechanisms in Calcium at High Pressure

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High-pressure phase transformations of Ca are studied using the metadynamics method to explore the anharmonic free-energy surface, together with a genetic algorithm structural search method to identify lowest enthalpy structures. Disagreement between theory and experiment regarding the structure of Ca in the pressure range 32–119 GPa is partially resolved by the demonstration of different phase transition behavior at 300 K from that at low temperatures. A new lowest enthalpy $I4_1/amd$ structure is obtained with both methods with an estimated superconducting critical temperature in agreement with experiment.

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Ca is one of the most studied elements. There are many reasons for the interest in this element including the understanding of the high-pressure phase transitions [1–4] and its highest observed superconducting critical temperature (T_c) of any element [5]. The high-pressure structures of Ca have been characterized by x-ray diffraction [1,3,4,6] and theoretical methods [2,7–9]. An important and fundamental question remaining unresolved is the structure of Ca in the pressure range 32–119 GPa. Experimental studies have shown that the structure of Ca in this pressure range is simple cubic (sc) [1,3,4,6]. It is reported that Ca transforms from the face centered cubic (fcc) structure to a body centered cubic (bcc) structure at 20 GPa and then to the sc structure at 32 GPa at room temperature. The sc structure is, however, found to be unstable with both linear-response and supercell calculations [9,10]. This apparent discrepancy has led to the questioning of the experimental results and an alternate proposal for the stable structure [9]. The objectives of the present study are to resolve this discrepancy and to determine the lowest enthalpy stable structure through the application of the metadynamics algorithm for phase transitions [11–13] and a genetic algorithm for crystal structure prediction [14–16]. These two techniques are complementary and enable one to explore phase transformations as a function of temperature where contributions such as anharmonicity and entropy are included, as well as to perform direct structural searches at $T = 0$ K. The possible transformation mechanism and pathways to the experimentally confirmed sc phase and a new lowest enthalpy, low temperature phase are also revealed.

The metadynamics algorithm [11,12] for study of structural phase transitions in crystals was employed. This searches for low-free-energy pathways leading from the initial free-energy well to neighboring minima which enables the simulation of structural transformations including transformation pathways that may proceed via several intermediate states. This technique allows investigation of the anharmonic Gibbs free-energy surface that defines the stability regions for a material at finite temperature and pressure. This important feature of the metadynamics technique means that the structures occurring over a wide temperature range at a given pressure may be identified. Successful applications of the method include several examples of reconstructive structural transitions (see, e.g., SiO_2 [17], Si [18], CO_2 [19], and C [20]). In the present study, we apply the metadynamics method employing scaled components of the edge vectors of the simulation supercell as collective variables [12]. The metadynamics method was applied and combined with the projector-augmented plane-wave (PAW) method [21] as implemented in the Vienna *Ab Initio* Simulation (VASP) code [22]. A 2-electron (4*s*) PAW potential with a Perdew-Wang (PW91) exchange-correlation functional [23] was employed. The simulation cells consisted of 32 Ca atoms using a $2 \times 2 \times 4$ Monkhorst-Pack mesh [24] with each metastep consisting of a molecular dynamics run employing a *NVT* ensemble. Structures obtained in selected metasteps in the simulations on supercells are identified using the MATERIALS TOOLKIT [25].

Structural searches were performed using a genetic algorithm for crystal structure prediction [14–16], combined with structural optimizations using the VASP program and PAW potential with a Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [26]. The searches were performed on 80 eight-atom unit cells at 40 and 60 GPa. The *k*-point mesh for each candidate structure was scaled according to the length of the reciprocal lattice vectors with a basic division of 8 and rounded to the nearest higher even integer. Enthalpy calculations were performed using the VASP program and a 10-electron (3*s*3*p*4*s*) PAW-PBE potential. A $16 \times 16 \times 16$ *k*-point mesh was used for all candidate structures. Phonon and electron-phonon coupling (EPC) calculations were performed using program QUANTUM ESPRESSO [27]. A carefully calibrated 10-electron ultrasoft pseudopotential (see the auxiliary material to Ref. [8]) with nonlinear core corrections was used. A $8 \times 8 \times 8$ q-point mesh was used for both phonon and EPC calculations. At each q point, the phonon and EPC matrices were calculated with $16 \times 16 \times 16$ and $32 \times 32 \times 32$ k-point meshes, respectively.

The structural search results are shown in Fig. 1, where the enthalpies of the most energetically competitive structures are compared over the pressure range up to 100 GPa. Structural searches successfully recovered earlier proposed structures (sc, *Cmcm*, and *Pnma*) and also revealed new energetically competitive structures. A six-coordinated structure with space group $I4_1/amd$ was found to be the lowest enthalpy phase between 34 and 78 GPa. The $I4_1/amd$ structure is isostructural with β-Sn and has also been found in Sr [28]. At 60 GPa, the optimized structural parameters for the $I4_1/amd$ structure are $a = 4.925$ and $c = 2.623$ Å with Ca atoms located at $4b$ symmetry sites $(0, 0, 0.5)$. The bcc structure transforms to the $I4_1/amd$ structure at 34 GPa, which is very close to the measured pressure of 32 GPa at room temperature [1,3,4,6] for the bcc to sc transition. This finding suggests that the $I4_1/amd$ structure is stable and may exist at low temperature. At 78 GPa, the $I4_1/amd$ structure further transforms to the $P4_12_12$ structure [3]. The structural stability of the $I4_1/amd$ structure was established by phonon calculations (see below). The sc structure, on the other hand, yielded imaginary phonon frequencies confirming the previously reported results [9,10]. These phonon calculations do not include anharmonic contributions that are significant at room temperature where the sc structure is observed.

The metadynamics simulations employed Gaussian width and height parameters of 15 $(\text{kbar}\,\text{Å}^3)^{1/2}$ and 200 $\text{kbar}\,\text{Å}^3$, respectively, and starting from the initial bcc structure revealed distinctly different behavior at 5, 50, and 300 K (Fig. 2). At 40 GPa and 300 K, the enthalpy evolution shows a clear drop to a sc structure which remains stable. This finding suggests that, at this pressure range and within the accuracy of the density-functional theory employed, sc is the stable structure at room temperature, which agrees with the experimental x-ray diffraction results. When the same simulation is performed at 50 and 5 K, the phase transition behavior changes, and the structural evolution initially proceeds to the sc structure and then drops to the $I4_1/amd$ structure. At 5 and 50 K an intermediate simple hexagonal (sh) structure appears for several metasteps after the bcc phase, whereas at 300 K it is not formed. The transformation proceeds directly to the sc structure at 300 K. The final structure is the same $I4_1/amd$ structure identified by the genetic algorithm search, reinforcing the prediction for the existence of an $I4_1/amd$ structure at low temperature.

Upper bound estimates of the enthalpy barriers among the bcc, sc, and $I4_1/amd$ phases were obtained using a common maximal method [29] and the 10-electron PAW potential. The bcc to sc pathway at 300 K can proceed via lattice strains alone and continuously through a common R-$3m$ space group [30]. There is a continuous decrease of the rhombohedral angle 109.47° in the primitive bcc structure to the final angle 90° in the sc structure [Fig. 3(a)]. The enthalpies of the intermediate structures are minimized at constant pressure while maintaining each rhombohedral angle. The calculated transition barrier has large pressure dependence consistent with the experimental observation. At 20 GPa, the barrier is ~0.2 eV/atom demonstrating that the bcc structure is favored. At 60 GPa, there is no barrier between bcc and sc. The transition barrier from sc to the $I4_1/amd$ structure has different pressure dependence. Multiple paths requiring small strains, and atomic trans-

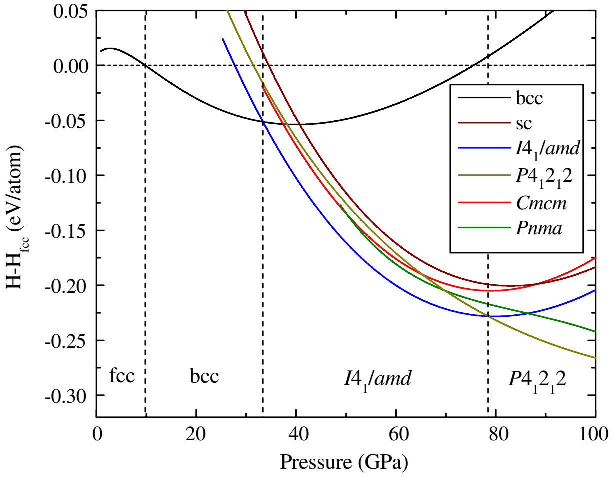

FIG. 1 (color online). Calculated pressure dependence of enthalpies of candidate Ca structures relative to the fcc structure at 0 K. The *Cmcm* structure was proposed in Ref. [9], *Pnma* structure in Refs. [8,9], and the $P2_12_12$ structure in Ref. [3].

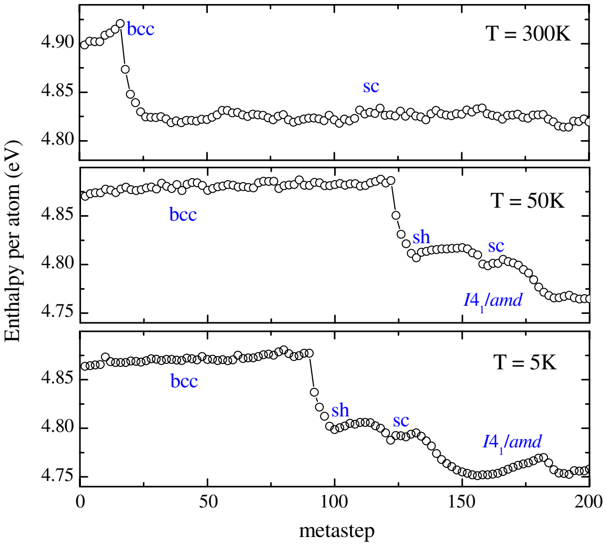

FIG. 2 (color online). Evolution of the enthalpy starting with the initial bcc structure of Ca at 40 GPa at 300, 50, and 5 K.

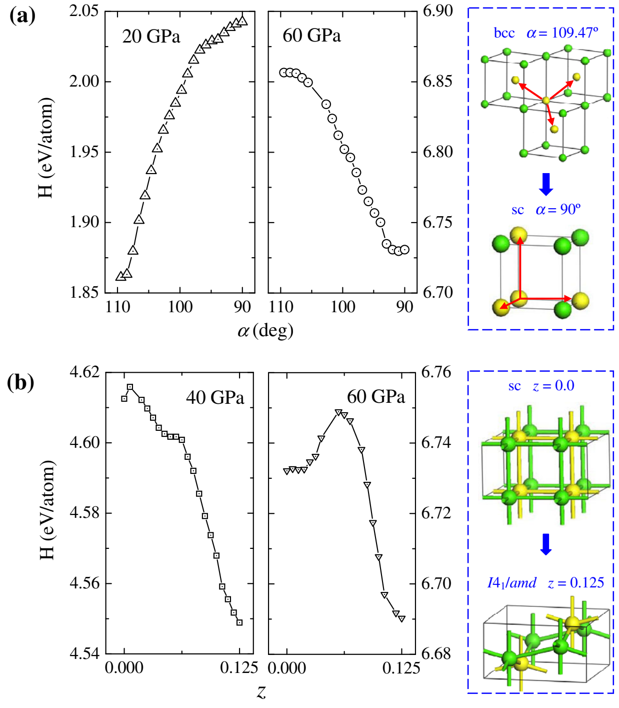

FIG. 3 (color online). (a) Illustration of the bcc → sc transition path through a common maximal subgroup R-$3m$ and calculated enthalpy barriers at 20 and 60 GPa. The atoms in yellow illustrate the rhombohedral angle in the primitive bcc structure. (b) Illustration of the transformation from sc to the $I4_1/amd$ structure following the $Pmma$ maximal subgroup pathway and the calculated enthalpy barriers at 40 and 60 GPa. The Ca atoms are at the $2e$ (0.25, 0.0, $3z$) (green) and $2f$ (0.25, 0.5, z) (yellow) symmetry sites in the $Pmma$ space group, respectively.

lations were examined [29]. The candidate path with the lowest barrier went through a $Pmma$ subgroup with Ca atoms in symmetry sites $2e$ (0.25, 0.0, $3z$) and $2f$ (0.25, 0.5, z). Along this pathway, the fractional coordinate z continuously increases from 0.0 to 0.125. These atomic shifts along the z axis result in a slight increase in the c/a ratio by ~6%. The calculated barrier with this path has distinct pressure dependence and increases from less than 0.003 eV/atom at 40 GPa to about 0.02 eV/atom at 60 GPa [Fig. 3(b)]. This suggests that the observation of the $I4_1/amd$ structure will proceed more easily in experiment at pressures just above the transition pressure from the bcc to sc structure. The small calculated enthalpy barrier at 40 GPa corresponds to a temperature of <100 K and indicates that the transition from bcc to the $I4_1/amd$ structure may be observable.

The calculated band structure and projected densities of states (DOS) to s, p, and d orbitals of the $I4_1/amd$ structure at 60 GPa is shown in Fig. 4(a). The DOS of the $I4_1/amd$ structure are dominated by d-orbital character. The increasing of d-band occupancy under compression was suggested [2] as the reason for the bcc to sc structural transition for Ca, but a more detailed investigation of ion-ion interactions may be required for the bcc to $I4_1/amd$ phase transition. The phonon dispersion curves and EPC of the $I4_1/amd$ structure were evaluated at 60 GPa [Fig. 4(b)]. The $I4_1/amd$ structure is stable as indicated by the lack of imaginary frequencies. The Eliashberg phonon spectral function $\alpha^2F(\omega)$ [31] shows that the EPC distributes evenly over the entire vibrational range and the integrated EPC parameter λ is 0.59. The calculated average and logarithmic average of phonon frequency, $\bar{\omega}_2$ and $\omega_{\log}$, are 247 and 191 K, respectively. A Coulomb pseudopotential μ^* of 0.1 was found appropriate to reproduce the experimental T_c for other high-pressure phases of Ca [8]. By using values of μ^* from 0.05 to 0.15, the T_c values for the $I4_1/amd$ structure at 60 GPa estimated using the Allen-Dynes modified McMillan equation [31] are from 6.8 to 2.2 K, in agreement with the measured T_c of 2.5 and 5 K at same pressure [5].

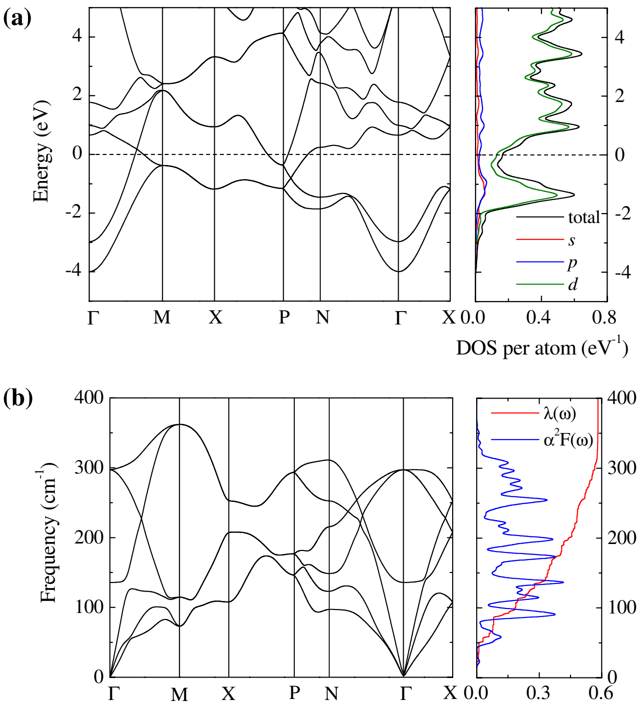

FIG. 4 (color online). (a) Band structure, total DOS, and projected DOS to s, p, and d orbitals of the $I4_1/amd$ structure near the Fermi level at 60 GPa. (b) Phonon dispersion curves, Eliashberg phonon spectral function $\alpha^2F(\omega)$, and the integrated EPC parameter $\lambda(\omega)$ of the $I4_1/amd$ structure at 60 GPa.

In summary, the metadynamics and genetic algorithm structural searches revealed a new stable $I4_1/amd$ structure of Ca in the pressure range 34–78 GPa. Exploration of the anharmonic Gibbs free-energy surface of Ca at high pressures and finite temperature indicated that, at 40 GPa, the sc structure is obtained as the stable structure for Ca at 300 K, whereas a new stable $I4_1/amd$ structure appears when the temperature is lowered to 50 K. The calculated T_c of the predicted $I4_1/amd$ structure is in good agreement with experiment. Metadynamics and genetic algorithm structural searches therefore have provided initial insight into the role of anharmonic and entropic contributions in the structural stability of sc Ca and led to the prediction of a new stable Ca structure at low temperature.

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[1] H. Olijnyk and W. B. Holzapfel, Phys. Lett. **100A**, 191 (1984).
[2] R. Ahuja *et al.*, Phys. Rev. Lett. **75**, 3473 (1995).
[3] H. Fujihisa *et al.*, Phys. Rev. Lett. **101**, 095503 (2008).
[4] T. Yabuuchi *et al.*, J. Phys. Soc. Jpn. **74**, 2391 (2005).
[5] T. Yabuuchi *et al.*, J. Phys. Soc. Jpn. **75**, 083703 (2006).
[6] Q. F. Gu *et al.*, Phys. Rev. B **79**, 134121 (2009).
[7] T. Ishikawa *et al.*, Phys. Rev. B **77**, 020101(R) (2008).
[8] Y. Yao *et al.*, Phys. Rev. B **78**, 054506 (2008).
[9] A. M. Teweldeberhan and S. A. Bonev, Phys. Rev. B **78**, 140101(R) (2008).
[10] G. Gao *et al.*, Solid State Commun. **146**, 181 (2008).
[11] R. Martoňák, A. Laio, and M. Parrinello, Phys. Rev. Lett. **90**, 075503 (2003).
[12] R. Martoňák *et al.*, Nature Mater. **5**, 623 (2006).
[13] A. Laio and M. Parrinello, Proc. Natl. Acad. Sci. U.S.A. **99**, 12 562 (2002).
[14] A. R. Oganov and C. W. Glass, J. Chem. Phys. **124**, 244704 (2006).
[15] C. W. Glass, *et al.*, Comput. Phys. Commun. **175**, 713 (2006).
[16] Y. Yao, J. S. Tse, and K. Tanaka, Phys. Rev. B **77**, 052103 (2008).
[17] D. Donadio *et al.*, Phys. Rev. Lett. **100**, 165502 (2008).
[18] J. Behler *et al.*, Phys. Rev. Lett. **100**, 185501 (2008).
[19] J. Sun *et al.*, Proc. Natl. Acad. Sci. U.S.A. **106**, 6077 (2009).
[20] J. Sun, D. D. Klug, and R. Martoňák, J. Chem. Phys. **130**, 194512 (2009).
[21] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[22] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).
[23] J. P. Perdew *et al.*, Phys. Rev. B **46**, 6671 (1992).
[24] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[25] Y. Le Page and J. R. Rodgers, J. Appl. Crystallogr. **38**, 697 (2005).
[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[27] S. Baroni *et al.*, Rev. Mod. Phys. **73**, 515 (2001); P. Giannozzi *et al.*, http://www.quantum-espresso.org.
[28] T. Bovornratanaraks *et al.*, Phys. Rev. B **73**, 144112 (2006).
[29] H. T. Stokes and D. M. Hatch, Phys. Rev. B **65**, 144114 (2002).
[30] H. Katzke and P. Tolédano, Phys. Rev. B **75**, 174103 (2007).
[31] P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).