

Crushing Elemental Calcium into a High Temperature Superconductor

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This century has seen remarkable progress in superconducting materials with high critical temperature (T_c), notably in 2001 with the discovery that MgB_2 superconducts at 40 K, and in 2008 the discovery that quasi-two-dimensional iron-based pnictides and chalcogenides superconduct up to 56 K. This progress has overshadowed the equally unexpected increase in T_c in the simplest possible class of materials – elemental simple metals such as lithium and calcium – where $T_c \sim 25$ K has been achieved. This occurs, so far, only at high pressure, where low symmetry, non-close-packed crystal structures are observed. We demonstrate here, using density functional based electronic structure and linear response methods, that calcium contains a large pressure range (32-109 GPa) where *several* such structures compete and coexist at room temperature in what has seemed to be a “simple cubic” structure, and that electron-phonon coupling in these phases is strong enough to account for the observed robust superconductivity.

One of the most unanticipated developments in superconducting critical temperatures (T_c) in the past few years has been achievement of much higher values of T_c in elemental superconductors by the application of high pressure, and that these impressive superconducting states evolve from simple metals (not transition metals) that are non-superconducting at ambient pressure. The first breakthrough arose in Li, with T_c approaching^{1,2} 20 K followed by yttrium^{3,4} at megabar pressure also superconducting up to 20 K and showing no sign of leveling off. Both of these metals have electron-phonon (EP) coupled pairing, according to several linear response calculations⁵⁻⁸ of the phonon spectrum, EP coupling strength, and application of Eliashberg theory. These impressive superconductors have been surpassed by Ca, with T_c as high as 25 K reported⁹ near 160 GPa. Perhaps more unusual is the report, from room temperature x-ray diffraction (XRD), of a simple cubic (hence far from close-packed) structure over a large volume reduction of 90→50% (32-109 GPa). Whether these two unique phenomena are connected, and in what way, raises fundamental new issues in an area long thought to be well understood.

Face-centered cubic (fcc, Ca-I) at ambient pressure, calcium transforms to body-centered cubic (Ca-II) at¹⁰ 20 GPa, is identified as sc (Ca-III) in the very wide 32-109 GPa range, and shows additional phases (Ca-IV, Ca-V) at even higher pressures. A simple cubic (sc) structure for an element is rare, occurring at ambient pressure only in polonium and under pressure only in a handful of elemental metals.^{11,12} This identification of a sc structure for Ca is particularly problematic, since it has been shown by linear response calculations of the phonon spectrum by a few groups¹³⁻¹⁵ that (at least at zero temperature) sc Ca is highly unstable dynamically at *all volumes (pressures)* in the region of interest. Since these calculations are reliable for such metals, there are basic questions about the “sc” structure itself.

So far the higher pressure phases Ca-IV and Ca-V have attracted the most attention, and considerable progress has been made in identifying these phases through a combination of experimental^{9,16} and theoretical work. Ca-IV is identified either as a Pnma space group¹⁷ or $P4_32_12$ symmetry,^{18,19} while Ca-V seems clearly to have a Cmca space group.¹⁷⁻¹⁹ Our focus has been to understand the enigmatic “sc” Ca-III phase that is present from 32-109 GPa, where relatively high T_c emerges and increases with pressure, a phase that XRD at room temperature (T_R) identifies as primitive simple cubic. In this pressure range sc Ca becomes favored over the more closely packed fcc and bcc structures, but the dynamical (in)stability was not calculated by Ahuja *et al.*²⁰

We report here first principles calculations of the enthalpy of five crystal structures, and linear response calculations of electron-phonon coupling, that can provide a resolution to both the structural and superconducting questions. Over most of the 30-150 GPa range, we find at least three crystal phases whose enthalpies indicate they will compete strongly at T_R . The sc phase is badly unstable dynamically (at $T=0$), but the observed “sc” diffraction pattern can be understood as a locally noncrystalline, highly anharmonic material derived from a spatially inhomogeneous and dynamically fluctuating combination of these structures, with most of them being straightforward distortions from the sc structure. The picture that arises is one of high

pressure “crushing” high symmetry crystal structures of Ca into a non-close-packed, highly locally distorted structure which nevertheless is an excellent superconductor in which T_c increases strongly with pressure. This result impacts yet another precept of superconductivity: disorder normally decreases conductivity, and disorder *per se* is never favorable for superconductivity. As mentioned, several groups have calculated that

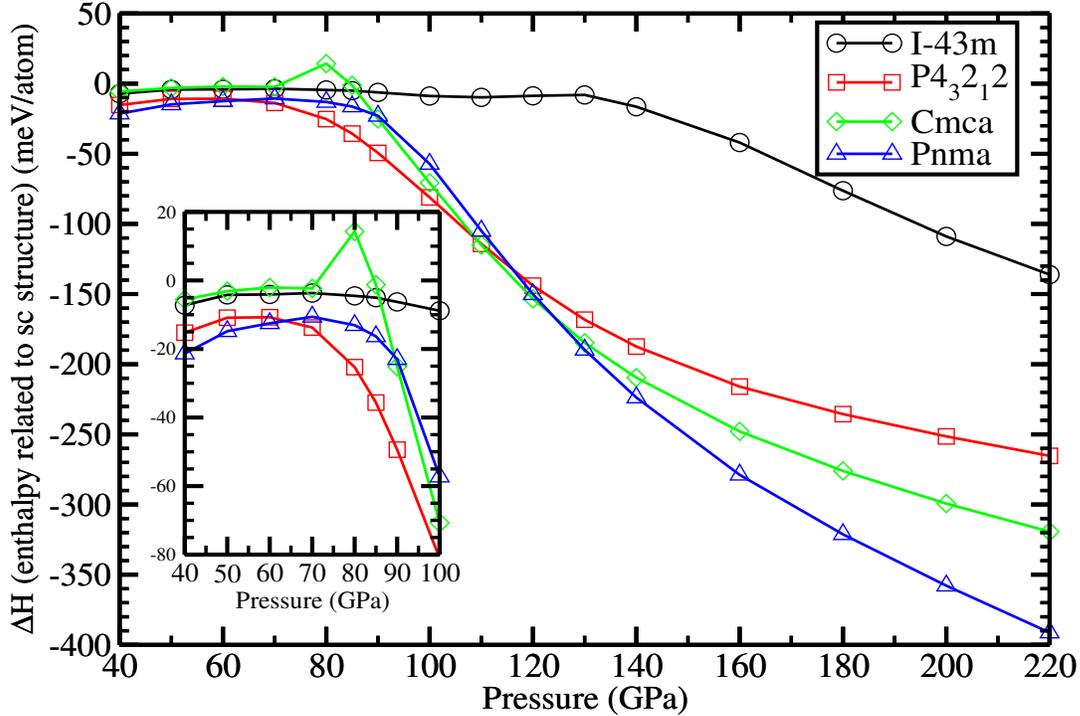


FIG. 1: (color online) Plot of the enthalpy $H(P)$ of the four distorted Ca structures relative to that for Ca in the simple cubic structure. The inset gives an expanded picture of the 40-100 GPa regime.

Ca is dynamically unstable over much of the Brillouin zone in the sc structure.^{13–15} The most unstable modes of sc Ca are transverse [001]-polarized zone boundary modes along the (110) directions. A linear combination of the eigenvectors of this mode at different zone boundary points leads to a body-centered four-atom cell in the space group $I\bar{4}3m$, whose local coordination is shown in the cubic cell in the inset of Fig 2, and has a clear interpretation as a buckled sc lattice. This structure, when relaxed, becomes dynamically stable. We have also included the candidate structures for the high pressure phases with space groups Cmca, Pnma, and P4₃2₁2 in our set of possible sc-derived structures. These are sc-derived structures. For example, a 2×2×2 enlargement of the sc structure, followed by orthorhombic strain $a \neq b \neq c$, with displacements of the atoms from their symmetric sites, results in the Cmca structure. We have calculated enthalpy $H(P)$ curves for each structure in the range 40-220 GPa based on density functional methods.²¹ Using the PWscf code,²² the pressure and space group with initial structural parameters given (lattice constants, internal structural parameters), all structural parameters are varied until a (local) minimum of energy is reached. From the volume $V(P)$ and the total energy $E(P)$ the enthalpy $H(P) = E(P) + PV(P)$ is obtained. Several energy differences and relaxations were checked with the Qbox,²³ FPLO,²⁴ and Wien2k²⁵ codes. The following results are obtained from these studies.

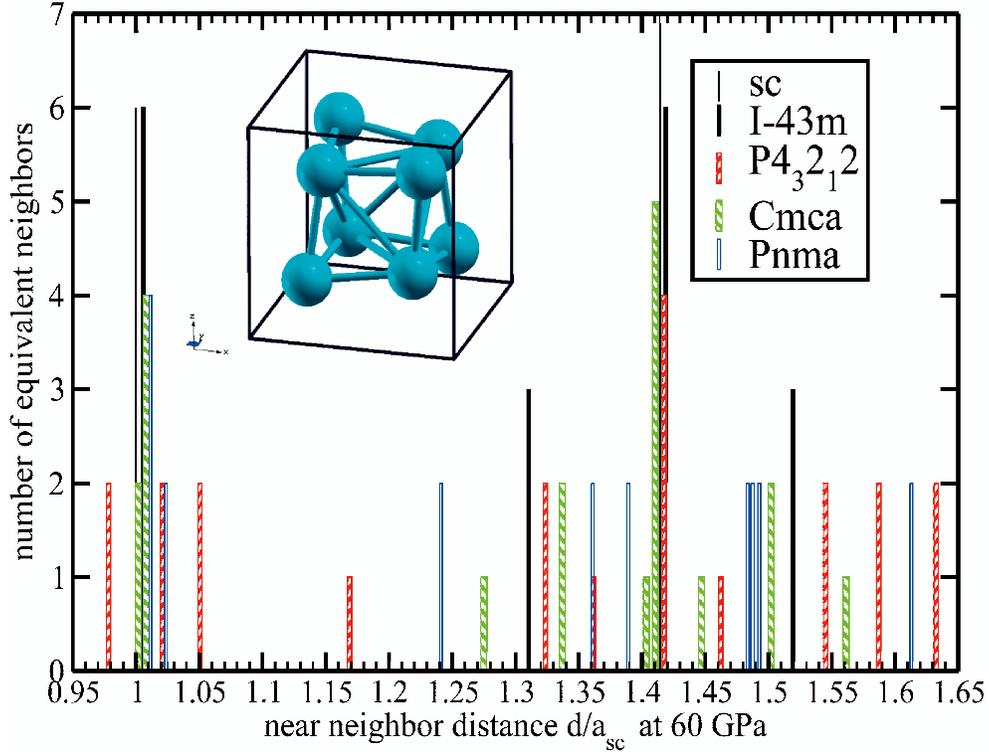


FIG. 2: (color online) Local coordination of the five structures of Ca, plotted as number of neighbors versus the distance d relative to the cubic lattice constant a_{sc} with the same density. The inset shows the unit cube of the $I\bar{4}3m$ structure (which contains two primitive cells); this structure retains six near neighbors at equal distances but three different second neighbor distances. The $P4_32_12$ and $Pnma$ structures can be regarded to be seven-coordinated, albeit with one distance that is substantially larger than the other six.

1. *Several crystal structures become quasi-degenerate.* In the 40-70 GPa range, all five of the structures we have studied have enthalpies that differ by less than 20 meV/Ca (230 K/Ca), as shown in Fig. 1. In the 80-100 GPa range, the $P4_32_12$ phase is marginally the more stable phase. Three phases are degenerate, again within 20 meV/Ca, in the 100-130 GPa region and are almost exactly degenerate around 110-115 GPa. Thus at room temperature all five phases, including the sc one, are thermodynamically accessible up to 80-90 GPa, above which the sc and $I\bar{4}3m$ structures become inaccessible. The other three phases remain thermally accessible to 130 GPa. Above 140 GPa, the $Pnma$ phase becomes increasingly more stable than the others. These highest pressure results were reported recently by Yao *et al.*¹⁷ Although equally dense, quasi-degenerate, and related to the sc structure, these structures differ in important ways from the sc structure and each other. In Fig. 2 the distribution of (first and second) neighbor distances d , relative to the sc lattice constant a_{sc} , are pictured. The collection of distances cluster around $d/a_{sc} \sim 1$ and, more broadly, around $\sqrt{2}$. In an ensemble of nanocrystallites of these phases, the radial distribution function in the simplest picture should look like a broadened version of the sc one. For Ca the actual microscopic configuration at room temperature, where fluctuations (spacial and temporal) can occur among these phases (whose enthalpies differ by less than $k_B T_R$ per atom), will no doubt be much more complex. However, this simplistic radial distribution plot makes it plausible that the resulting thermal and spatial distribution of Ca atoms will produce an XRD pattern more like simple cubic than any other simple possibility. Teweldeberhan and Bonev have noted the near degeneracy of some of these phases in the 40-80 GPa region, and suggest that the $T=0$ structure in $Pnma$ in the 45-90 GPa range.¹⁵

2. *Volume collapse occurs in some phases.* Figure 3 shows the behavior of $V(P)$ relative to the smooth behavior in the sc phase. Around 75 GPa the $Cmca$ structure suffers a rapid decrease in volume by 4-5%;

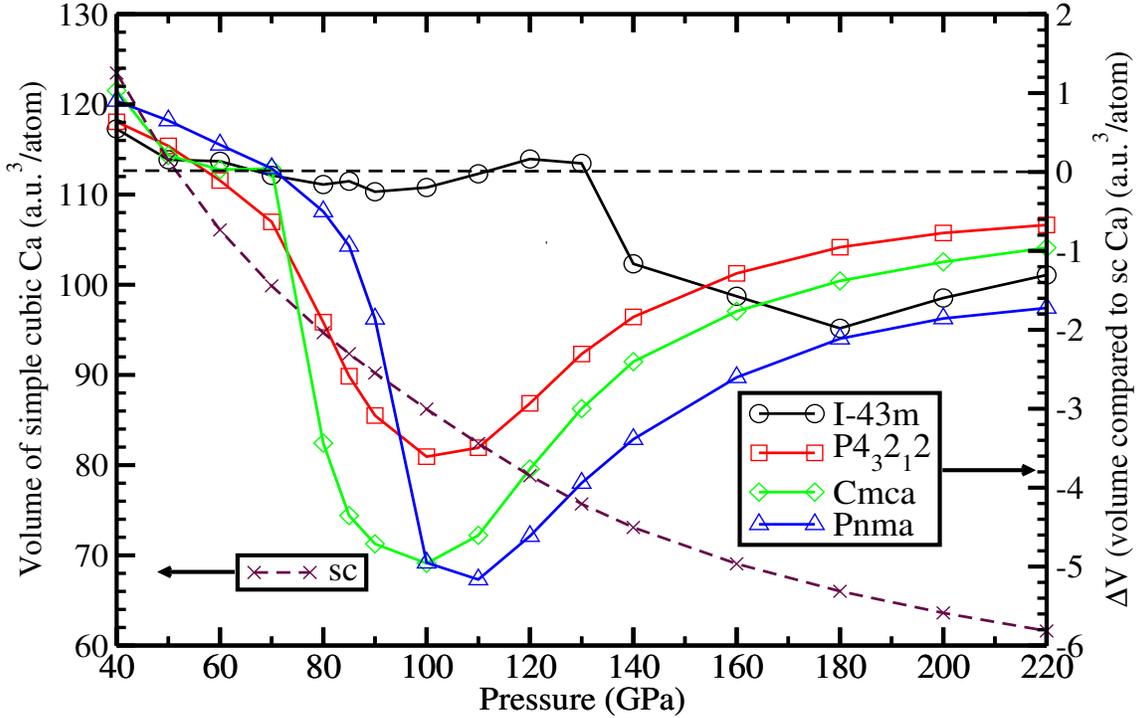


FIG. 3: (color online) Plot (right hand axis) of the volume-pressure $V(P) - V_{sc}(P)$ behavior for each of the four distorted structures, relative to the behavior of sc Ca (shown as the dashed line and the left hand axis). The dips in the curves (70 GPa for Cmca, 80-100 GPa for $P4_32_12$, 90 GPa for Pnma, 140 GPa for I43m) reflect volume collapse regions.

whether actually discontinuous or not (see below) is probably not relevant to Ca at room temperature. Around 100 GPa, the Pnma phase undergoes a somewhat smaller but still very clear and rapid volume collapse (again, $\sim 5\%$). The $P4_32_12$ system undergoes a somewhat milder (3%) collapse in the 80-100 GPa range. No collapse occurs for I43m until beyond 130 GPa, where the volume does decrease relative to the sc volume.

3. *A first-order isostructural collapse occurs in this system.* At 80 GPa the Cmca phase undergoes a discontinuous change that is not evident from the calculated $V(P)$ results. However, by looking at all the structural parameters presented in Fig. 4, it is clear that the lattice constants change (especially one internal coordinate changes, by nearly 0.1) discontinuously at the volume collapse. This discontinuity signals some microscopic change in the electronic state, perhaps of the type proposed for high pressure lithium.^{26,27}

The overall picture that arises from these results is that, in most or all of the range 40-130 GPa, there are 3-5 crystal structures that are quasi-degenerate, and which can be expected to be competing thermodynamically at room temperature in most of that range. While one might anticipate an instability of the simple cubic phase to a higher packing fraction phase, that interpretation is not supported in this system. For low symmetry phases “packing fraction” begins to lose its clarity, and in fact these structures have essentially equal densities in the 60-70 GPa range. The $P4_32_12$ and Pnma phases can be viewed as 7-fold coordinated; one of the sc second-neighbors moves inward to a distance $d=1.17-1.25 a_{sc}$. However, the volume does change

(rapidly or discontinuously) for three of the phases, which might be interpreted as attaining a somewhat larger packing fraction within each structural motif. This collection of information elaborates on the initial,

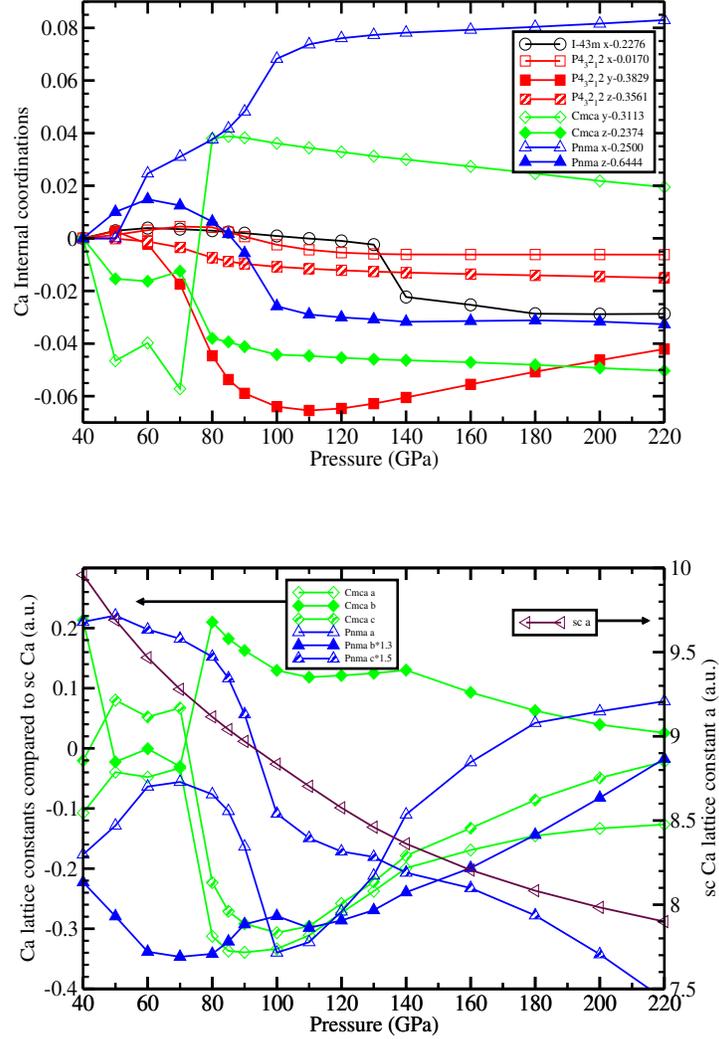


FIG. 4: (color online) Top: Pressure variation of the internal structural parameters of the four distorted Ca structures. Bottom: Pressure variation of the lattice constants of the Cmca and Pnma structures (the corresponding behavior for P4₃2₁2 is smooth). Note the first-order change in the Cmca quantities near 75 GPa.

obvious observation that the “sc” phase Ca III cannot be simple cubic. Ca-III must be (at room temperature) a locally inhomogeneous and dynamically anharmonic structure for which a snapshot of the local structure will reveal some combination of, or interpolation between, these five crystal structures. Although Ca-III is not simple cubic and not even crystalline, it has one similarity to sc, in that each of these phases and presumably the actual, very complex, structure is *not* close-packed. Fujihisa *et al.*¹⁹ have analyzed some of these structures around 150 GPa, where the 7-fold coordination becomes clearer. This case of high pressure “sc” Ca at room temperature may constitute yet another facet of the “weird structures” that occur in alkali

and alkaline-earth metals under pressure.²⁸

One interpretation of these structural results is that it is not enthalpically very important how the Ca ion cores are arranged, except that low coordination environments are preferred over the intuitively expected high coordination phases. Since dimerization (bond formation) is not a characteristic of any of these structures, the important feature may be that these relatively open structures allow the electrons to use the interstitial regions to reduce their kinetic energy. If so, an atom-based picture (s, p, d orbitals etc.) becomes less useful, and a picture of free electrons perturbed by Ca ion core pseudopotentials may become a more useful viewpoint.

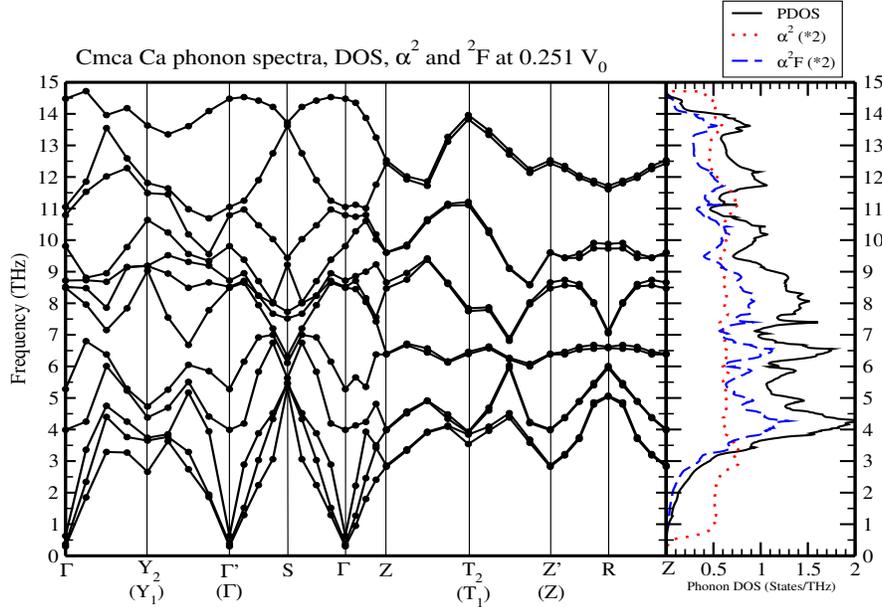


FIG. 5: Phonon spectrum, phonon DOS, α^2 and α^2F of Cmca Ca at 0.251 V_0 (~ 130 GPa from PwSCF). The high symmetry points are $\Gamma(0, 0, 0)$, $Y_1(1, 0, 0)$, $Y_2(0, 1, 0)$, $\Gamma'(1, 1, 0)$, $S(0.5, 0.5, 0)$, $Z(0, 0, 0.5)$, $T_1(1, 0, 0.5)$, $T_2(0, 1, 0.5)$, $Z'(1, 1, 0.5)$ and $R(0.5, 0.5, 0.5)$ in the units of $(2\pi/a, 2\pi/b, 2\pi/c)$.

4. *Strong electron-phonon coupling.* The unprecedentedly high $T_c \approx 25$ K in Ca for an element must be addressed. In the microscopically inhomogeneous Ca-III (“sc”) phase there is no realistic yet computationally viable method to do this. Shi *et al.* reported calculations of T_c for Ca in the sc structure, using the rigid muffin-tin approximation for electron-phonon coupling and modeling the lattice frequencies in terms of the calculated bulk modulus.²⁹ This procedure produced relatively high values of T_c , but the dynamic instability of the sc phase means this is not a viable picture of calcium. Since T_c is highest in the Ca-IV and Ca-V phases and the lattice becomes stable there, we focus here on one of them, the Cmca structure at 130 GPa, where the volume is reduced by a factor of four from ambient volume. We have obtained similar strong coupling for other structures and pressures.

In Fig. 5 the phonon dispersion calculated from linear response code LMTART^{30,31} is presented. The maximum frequency is three times its $P=0$ value.³² Not only are all phonons stable, in fact there are not even any soft branches. The maximum phonon frequency is triple its zero pressure value. The mean phonon energy is 25.6 meV (300 K), the maximum is 28.3 meV (330 K). The frequency-dependent coupling $\alpha^2(\omega)$ is the ratio of electron-phonon coupling spectral function $\alpha^2F(\omega)$ and the phonon density of states $F(\omega)$. In this case that $\alpha^2(\omega)$ is constant across the entire spectrum (below 1 THz the computational precision degrades, but since $F(\omega)$ is nearly vanishing, this region of vibrations becomes irrelevant for superconductivity). This constancy of coupling strength is unusual but perhaps of no great significance; note that $\alpha^2(\omega)$ varies

considerably in high pressure Li with $T_c \sim 20$ K, and also in high pressure yttrium with $T_c \sim 20$ K.

The calculated electron-phonon coupling strength is $\lambda = 1.2$. The only additional quantity needed to obtain the theoretical value of T_c is the screened Coulomb ‘pseudopotential’ μ^* . Using the conventional range $0.10 \leq \mu^* \leq 0.15$ and the strong-coupling Allen-Dynes equation, we find T_c lies in the range 20-25 K, in very satisfying agreement with the observed values of T_c in this pressure range. Calculation for a few other structures and pressures also give strong electron-phonon coupling $\lambda \sim 1.2$ -1.45, and similarly high values of T_c .

Now we summarize. First, calculations of enthalpy versus pressure for five crystalline phases of Ca (simple cubic and four distortions from it) indicate quasi-degeneracy that implies a locally disordered, anharmonically fluctuating structure at room temperature or above that can account for the XRD observations of a ‘‘sc’’ structure, whereas the actual sc structure itself is badly unstable (at $T=0$). Secondly, linear response calculation of the the electron-phonon coupling strength and superconducting T_c at very high pressure accounts for its impressive superconductivity in that regime. These results resolve some of the outstanding questions on the structure and record high T_c for an element, and should help in obtaining a more complete understanding of the rich phenomena that arise in simple metals at high pressure.

I. METHODS

For electronic structure and energies we have used three codes, the full potential local-orbital (FPLO) code,²⁴ the FPLAPW method as implemented in Wien2K,²⁵ and the Qbox code²³ to do various structural optimizations and electronic structure calculations, checking for consistency among the results. For the enthalpy calculations we used the PWscf code.²² Both Qbox and pwSCF use norm-conserving pseudopotentials, while the FPLO and Wien2k codes are all-electron and full potential. The linear-response calculations of phonon spectra and electron-phonon spectral function $\alpha^2F(\omega)$ were done using the all-electron, full potential LMTART code.³⁰

The parameters used in PWscf for the enthalpy calculations were: wavefunction planewave cutoff of 60 Ry, density plane-wave cutoff of 360 Ry, k mesh samplings (respectively, number of irreducible k points) $24*24*24$ (455), $32*32*32$ (897), $24*24*8$ (455), $24*24*24$ (3614), $24*32*32$ (6562) for sc, $I\bar{4}3m$, $P4_32_12$, $Cmca$, and $Pnma$ structure, respectively. Increasing the number of k points lowers the enthalpy by only 1-2 meV/ Ca almost uniformly for all structures, resulting in negligible change in volume, lattice constants, and internal coordinates.

Structure Optimization. The dynamic instability of the sc phase of Ca suggested relaxation of the structure using molecule dynamics (MD) methods. Our MD calculations with the Qbox code resulted in a four-atom bcc cell with space group $I\bar{4}3m$ (#217) that is dynamically stable at least from 40 GPa to 110 GPa. In this structure, Ca occupies the $8c$ wyckoff position with atomic coordinate (x, x, x) , with $x \approx 0.22$. Since $x=0.25$ will restore the sc structure, this $I\bar{4}3m$ structure is easily seen to be a straightforward distortion from the simple cubic structure.

Ishikawa *et al.*¹⁸ suggested that Ca forms an orthorhombic structure at 120 GPa. Our MD calculations confirmed the stability of this structure, which has space group $Cmca$, which is a base-centered orthorhombic structure with Ca at Wyckoff position $8f$ $(0, y, z)$, where $x \sim 0.34$ and $y \sim 0.19$. Since $x=0.25$ and $y=0.25$ and appropriate lattice constants will restore the simple cubic structure, this $Cmca$ is also a readily recognized as a distortion from the sc structure. Linear response calculations also show that this structure is dynamically stable over a wide pressure range.

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