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Abstract

The superconductivity in highly compressed calcium involves the occurrence of closely related low-symmetry structural patterns with an exceptionally low coordination number. Earlier theoretical and experimental results are controversial and some findings are inconsistent with our later observations in the pressure range up to 60GPa. This situation motivated the present concerted computational and experimental re-investigation of the structural arrangement of calcium slightly above the high-pressure limit of the bcc arrangement at low-temperatures. We report here reproducible experimental evidence for a monoclinic distortion (mC4) of the calcium polymorph previously assigned to the tetragonal β-Sn structure type. In accordance, the enthalpies calculated by electronic band structure calculations show the mC4 phase to be more stable than the undistorted β-Sn type by about 100 meV in the entire phase space. The other low-temperature phase of calcium adopts space group Cmcm (oC4) rather than the earlier assigned Cmcm symmetry. These structural alterations substantially effect the density of states at the Fermi level and, thus, the electronic properties.

Keywords: calcium, high pressure, x-ray diffraction, low temperature, total energy, synchrotron radiation, density of states

(Some figures may appear in colour only in the online journal)
1. Introduction

The observation of superconductivity in highly compressed calcium at critical temperatures as high as 29K at 220GPa [1, 2] stimulated a number of theoretical and experimental investigations concerning the underlying atomic arrangement as a basis for reliable calculations on superconducting properties. At ambient temperature, calcium is reported to undergo a transition from fcc (cF4, coordination number (CN) 12) to bcc (cI2, CN 8 + 6) at 20GPa [3, 4] before it transforms into a primitive cubic pattern (cP1, CN 6) at 32GPa [4, 5]. This structure pattern remains essentially stable up to 109GPa [6]. Line-broadening of the so-called primitive cubic phase at low temperatures has been attributed to a rhombohedral distortion [7] or to a superposition of closely related distortion variants [8, 9]. Irrespective of this issue, we will label the phase as pc.

The results concerning the superconducting phase(s) are even more divergent since the structural features of compressed calcium at low temperatures involve the formation of intimately related low-symmetry structural patterns, which are closely related to the primitive cubic arrangement. The formation of these phases with small CNs of the metal atoms is attributed to a pronounced reordering of the valence electrons, i.e. a substantial sd hybridization because of an increasing population of d states upon compression. In earlier experiments, diffraction data recorded at elevated pressure and low temperature indicate the formation of new distorted varieties. The atomic arrangement of the first discovered polymorph was assigned to orthorhombic symmetry with space group Cmcm, although monoclinic symmetry could not be ruled out [7]. The calculated enthalpy of the Cmcm phase was surprisingly high, and the structure has also been shown to be dynamically unstable [10]. In a subsequent investigation, a second low-temperature phase has been discovered and assigned to the tetragonal $\beta$-Sn type [11].

A large number of similar structural motifs was predicted by first principles calculations (an overview is given in table 1 [3, 5, 7, 8, 11–17]; for extensive summaries see [17, 18]).

The present high pressure low-temperature diffraction investigation concentrates on the pressure region neighboring the stability fields of calcium cI2 and pc. At these conditions, the previously assigned orthorhombic and tetragonal low-temperature phases have been observed [7, 8, 11]. Based on full profile refinements, we report evidence for a C2/c distorted cubic primitive arrangement of the so-called $\beta$-Sn calcium polymorph and Cmcm symmetry of the previously reported orthorhombic Cmcm phase.

2. Materials and methods

2.1. X-ray diffraction

Experiments were conducted on distilled samples of commercially purchased calcium (Alfa Aesar, 99.98% metals basis). The metal was handled and loaded into diamond anvil cells in the dry and oxygen-free atmospheres of gloveboxes. In order to avoid any contamination no pressure medium was used in the first experimental series. Aiming for the best possible hydrostatic conditions in the following measurements, carefully selected small calcium chips were placed in the centre of the gasket before adding helium as pressure transmitting medium (PTM). The diamond anvil cells for the low-temperature measurements were equipped with preindentated gaskets made from rhenium foil. Pressure calibration was performed using small pieces of samarium-doped SrB$_2$O$_3$ (no temperature correction necessary) or tiny ruby spheres which require an empirical correction of the temperature dependent line shift [19]. Temperatures were measured directly on the pressure cell by means of a Si-diode. Several independent experimental series were performed in order to systematically vary temperature as well as pressure protocols as exploratory data evidenced that the low-temperature experiments are seriously affected by kinetic contributions and/or the effect of stress or strain. During the high-pressure low-temperature measurements, the optical emission of ruby was carefully monitored for broadening indicating deviation from hydrostatic conditions. Diffraction data were collected in several runs at ID09A of the ESRF, Grenoble, using wavelengths of 0.415 65, 0.415 17 and 0.414 35 Å and 0.289 55 Å at Petra-III, Hamburg. Absorption effects can be neglected because of the half-spherical shape of the diamonds and the minimal sample thickness of the order 10 µm. The 2D diffraction patterns were integrated azimuthally [20], and structural information was obtained by least-squares fitting to measured peak positions and by refinement of the full integrated profiles (Rietveld method) using JANA2006 [21], WinCSD [22] and GSAS-II [23].

2.2. Band structure calculations

The results for the scalar-relativistic, total energy calculations are obtained from a full-potential local orbital band structure method (FPLO [24, 25]). It should be noted at the outset itself the importance of the all-electron aspect of this code, since even small-core pseudopotentials have been shown to be inept in reproducing all-electron results under volume reduction [26]. Furthermore, considering that the non-spherical aspect of the potential will grow as the volume is reduced, the full-potential aspect of the code can also be important. The calculations were done in the framework of generalized gradient approximation, employing the exchange-correlation potential by Perdew, Burke and Ernzerhof [27].

We have used a single numerical basis set for the core states of calcium (1s 2s 2p) which are treated in a full relativistic way, while the semi core states (3s 3p) are treated as valence states with a single numerical radial function per nl-shell. A triple numerical basis set for the valence sector with three 4s and 3d radial functions and a double numerical basis set with two 4p radial functions are used. The valence states are treated in a scalar relativistic way.

The irreducible part of the first Brillouin zone was sampled with 752 points for both cF4 and cI2; 816 points for cP1; 2496 points for R-3m; 1992 points for the tetragonal $I4_1/amd$; 3736 points for mC4; and 3856 points for both oC4 and Cmcm.

A thorough check of the energy convergence with the number of k-points was performed for all crystal structures.
Table 1. Low-symmetry calcium modifications at pressures up to 100 GPa which were experimentally observed (exp) or predicted by theoretical methods (theo). Experimental work on the cubic phases is included for completeness.

| Modification | Pearson symbol | Lower limit/GPa | Space group | Ref. |
|--------------|----------------|-----------------|-------------|------|
| cF4 (fcc)    | exp            | Ambient         | Fm$ar{3}$m | [3, 5] |
| cF2 (bcc)    | exp            | 19.5 GPa        | I$ar{m}$-3m | [3, 5] |
| cP1 (pc)     | exp            | 32 GPa          | P$ar{m}$-3m | [5]   |
| tI1          | exp            | 32 GPa          | R-3m        | [8]   |
| oC2          | exp            | 44 GPa          | Cm$	ext{mmm}$ | [7, 17]| 4.3 K |
| tI4          | exp            | 35 GPa          | I4$_1$/amd  | [11] |
|              |                | $T < 10$ K      |             |      |
| tP8          | theo           | 77 GPa          | P4$_1$2$_1$2$_2$<sup>a</sup> | [12] |
| oC4          | theo           | 37.5 GPa        | Cn$	ext{cm}$<sup>b</sup> | [13] |
| oP4          | theo           | 45.5 GPa        | P$	ext{n}$n$	ext{ma}$<sup>c</sup> | [13] |
| tI4          | theo           | 33 GPa          | I4$_1$/amd<sup>b</sup> | [14] |
| mC12         | theo           | 71 GPa          | C2/c        | [14] |
| tP8          | theo           | 89 GPa          | P4$_1$2$_1$2$_2$<sup>a</sup> | [14] |
| tI4          | theo           | 32 GPa          | I4$_1$/amd<sup>b</sup> | [15] |
| tP8          | theo           | 74 GPa          | P4$_1$2$_1$2$_2$<sup>a</sup> | [15] |
| tI4          | theo           | 34 GPa          | I4$_1$/amd<sup>b</sup> | [16] |
| cF8 plus 4 other | theo | 40 GPa          | I-43m      | [9]   |

<sup>a</sup> P4$_1$2$_1$2$_2$ and P4$_1$2$_1$2$_2$ form a pair of enantiomorphic space groups (mirror images).

<sup>b</sup> The authors use non-standard settings of the unit cell.

Figure 2. Results of high-pressure low-temperature diffraction experiments on elemental calcium. The Pearson symbols indicate: cF4 (fcc), cF2 (bcc), the phases studied here are mC4 and oC4, respectively; pc indicates primitive cubic and its distorted variants (see introduction).

3. Results

3.1. Overview of measurements

Several experimental series on elemental calcium were performed using different temperature–pressure protocols. Also, experiments involved loadings without pressure medium and measurements using helium as PTM. Typical 2D diffraction images show a smooth intensity distribution despite noticeable texture (figure 1). The integrated patterns allow for the phase assignment (figure 2). The slightly incoherent distribution of the symbols indicates the complex nature of the phase relations especially at low temperatures. Additionally, a number of diffraction patterns evidence extended regions in which two or even three phases coexist. These large differences in the experimentally observed transition pressures, the extended two-phase regions and the observation of three-phase mixtures at low temperatures clearly indicate the significant kinetic contributions to phase formation at these $p$, T conditions. Within these limits, the observed formation range of the phase mC4 is in good agreement with that of the undistorted $\beta$-Sn phase (tI4 in table 1) predicted by theoretical studies [11, 14, 16], but the field in which the phase is experimentally observed in our study is slightly smaller. The range in which diffraction data evidence the oC4 arrangement is in very good agreement with computational prediction (see table 1 and section 3.3). The high-temperature part of the $p$, T phase diagram has been the subject of a recent study [29].

3.2. Monoclinic distortion of the $\beta$-Sn phase

In a first exploratory series without PTM, the transformation from cF2 (bcc) into a phase mixture comprising cF2, pc and the new mC4 arrangement (earlier labelled as $\beta$-Sn, see below) was observed upon simultaneous pressure and temperature increase from 33.8 GPa and 23.2 K to 39 GPa and 52.5 K. Further decrease of pressure and temperature down to 24 K and 34 K produced a mixture of mC4 and cF2 calcium. With helium as PTM, the pressures at which the mC4 phase appeared or vanished exhibited differences as large as 4 GPa, e.g. at 80 and 90 K. Starting with cF2 calcium yielded phase mixtures in which one component can be identified as the mC4 phase. In...
our experiments, pure mC4 calcium only formed upon pressure decrease coming from the orthorhombic oC4 phase.

For structure solution and refinement, we selected patterns comprising the pure modification or well separated contributions of pc and the new phase. The patterns can be indexed and refined using a tetragonal $\beta$-Sn ($tI$4) structure model [11] with $a = 5.297(2)$ and $c = 2.8368(9) \, \text{Å}$, yielding an overall fair agreement (figure 3).

However, closer analysis of the Rietveld refinements results reveals subtle discrepancies, which are only partly eliminated by introducing a correction for the effects of strain. We will illustrate this by example of data taken at 35.5 GPa and 90 K. Most conspicuous is that the half-widths of the two reflections at 2\(\theta\) of 9° and 9.5° differ significantly. Furthermore, the match for the reflections at 12.6° and 18° remains poor. Additionally, weak diffraction intensities are observed at 14.2° and 14.5° which are not accounted for by the tetragonal $\beta$-Sn structure. As the present data bear no significant evidence for extra reflections at low angles, which would indicate a larger unit cell, symmetry breaking of the primitive cubic lattice along series of maximal non-isomorphic subgroups was considered (see figure 4). Refinement results of selected models are listed in table 2.

The results evidence that a significantly better fit is obtained with a monoclinic arrangement in space group $C2/c$, $a = 2.84(2)$, $b = 7.472(7)$, $c = 4.05(3) \, \text{Å}$, $\beta = 111.19(5)^{\circ}$ and calcium occupying position 4e ($0,y,1/4$) with $y = 0.6164(8)$. The large standard deviations of the lattice parameters are a consequence of the pronounced pseudosymmetry. The final refinements of the monoclinic mC4 model (figure 3) includes correction for preferred orientation by spherical harmonics.

![Figure 3](image3.png)

**Figure 3.** X-ray diffraction diagram of the mC4 modification of calcium. The upper part shows experimental and calculated intensities as well as the differences $I_{\text{obs}}-I_{\text{calc}}$ for the tetragonal, undistorted $\beta$-tin type ($tI$4, space group $I41/amd$) and the monoclinic model mC4 in space group $C2/c$. Insets visualize regions of special concern. The lower part shows the cumulated development of the difference curves for the tetragonal and the monoclinic model, respectively, as a function of the diffraction angle 2\(\theta\). The selected presentation illustrates the achieved improvement of the profile fit by appropriate symmetry reduction.

| Table 2. Residuals of structure models tested for the so-called $\beta$-Sn high-pressure low-temperature phase of calcium. |
|---------------------------------------------------------------|
| Space group | $R(F^2)$ | $R_{\text{bkg}}^2$ | $wR_e^2$ |
|-----------------|------------|-----------------|------------|
| $I41/amd$      | 0.0496     | 0.0135          | 0.0109     |
| $I41/amd^c$   | 0.046      | 0.0127          | 0.0104     |
| $Imma$         | 0.0785     | 0.0123          | 0.0092     |
| $Fdd2$         | 0.0361     | 0.0099          | 0.0083     |
| $C22m$         | 0.0445     | 0.0104          | 0.0091     |
| $C2/c$         | 0.0336     | 0.0073          | 0.0060     |

$^a$ With uniaxial strain correction.  
$^b$ $R_{\text{bkg}} = \sum (|F_o - F_c| + |F_o - F_b| + |F_c - F_b|)/\sum |F_o|$. 
$^c$ $wR_e = \sqrt{\sum w(\left|F_o - F_c\right|^2 + (F_o - F_b)^2 + (F_c - F_b)^2)/\sum \left|F_o - F_b\right|^2}$. 

![Figure 4](image4.png)

**Figure 4.** X-ray diffraction pattern (line), calculated intensities (grey crosses) and difference curve (light grey line below) of a full-profile refinement of the calcium modification oC4 in space group $Cmcm$. Ticks indicate allowed reflection positions, $R_{\text{obs}} = 0.0289$, $R_P = 0.0055$ and $R_{\text{wp}} = 0.0068$.  

### 3.3. Orthorhombic phase

At temperatures between 62 K and 90 K with helium as PTM, pure diagrams of the second calcium allotrope oC4 are observed. In this temperature range, the pattern directly follows the monoclinic mC4 arrangement at higher pressures. From its diffraction pattern we identify this phase as the orthorhombic oC4 modification, previously reported in space group $Cmcm$ [7, 11, 12]. However, while the diffraction pattern we observe has many similarities to that reported earlier by Mao et al., it contains additional reflections, most notably at 2\(\theta\) of 10° (figure 4), but also at 13.2° and 16.2°. The region of the diffraction pattern where we observe the strongest peak was unfortunately omitted in the earlier investigation (see figure 3 in [7]), but there is clear evidence of the same additional reflections at 11.6° and 14.4° in the older data [7]. Similarly, independent data [11] also has clear evidence of the two strongest additional peaks at 9.8° and 13.4° in the pattern at 39.6 GPa and 6 K, but which the authors labelled as coming from impurities. In combination, the evidence suggests, that the same diffraction pattern, containing the additional peaks, was observed in
these two earlier studies. Unfortunately, the diffraction pattern of the third investigation measured at 40 GPa and 7 K \[12\] was not published, so it is unknown whether they also saw the additional peaks.

_{Ab initio}_ indexing of the diffraction profile showed that all of the peaks can be fitted with a C-centred orthorhombic unit cell with dimensions \(a = 3.846(1)\), \(b = 3.684(1)\), and \(c = 5.296(1)\) Å with four atoms in the unit cell and systematic absences corresponding to space group \(Cmcm\). A full Rietveld refinement of the \(oC4\) (\(Cmcm\)) structure to diffraction data collected at 33.2 GPa and 62 K (figure 5) revealed that the four atoms in the cell are located on the \(4c\) Wyckoff sites at \((0, y, 1/4)\) with \(y = 0.045(2)\). This \(Cmcm\) structure is the same as one of the previously proposed arrangements ([13], see table 1), and is closely related to the \(Cmmm\) structure [7], but with the \(c\)-axis doubled. The \(Cmcm\) and \(Cmmm\) structures are the same when \(y = 0\), and the \(Cmcm\) becomes the \(pc\) structure (\(cP1\)) when \(y = 0, a = b\) and \(c/b = \sqrt{2}\).

The principle structural difference between the \(Cmcm\) and \(Cmmm\) structures is that the former features alternative displacements of layers of atoms by \(\pm 0.17\) Å along the \(y\) axis. These displacements can greatly reduce the enthalpy of the \(Cmcm\) structure relative to that of the undistorted \(Cmmm\) structure, which is claimed to have a significantly higher enthalpy than the tetragonal \(\beta\)-Sn structure [7]. The crystal structures of these newly identified calcium modifications \(mC4\) and \(oC4\) both comprise calcium atoms adopting a CN of six (figure 6).

Figure 5. Graphical representation of group-subgroup relations of crystal structures related to the bcc (\(cI2\), space group \(Im-3m\)) and the primitive cubic (\(cP1\), space group \(Pm-3m\)) arrangement. The new modifications \(oC4\) (\(Cmcm\)) and \(mC4\) (\(C2/c\)) are located in the lower part. Relevant structure models are indicated in grey.

Figure 6. Atomic arrangement in the \(mC4\) (left) and \(oC4\) (right) modification of elemental calcium. Both crystal structures represent distorted variants of a cubic primitive pattern in which the atoms adopt CN six. For \(mC4\), the calculated bond length correspond to 2.67(1), 2.83(1) and 2.84(2) Å (all with multiplicity 2), for \(oC4\) to 2.663(5) (multiplicity 4) and 2.669(5) Å (multiplicity 2).
3.4. Computational results

As an independent check of the stability of the revised high-pressure phases, we performed density functional theory (DFT) based total energy calculations using the full-potential code FPLO [24, 25] to investigate the energetics of the various structural phases as a function of pressure. An appropriate DFT-based phase diagram would be the pressure ($p$)–enthalpy ($H$) plot, wherein both pressure and enthalpy are calculated using the Murnaghan [28] equation of state fit to the total energies as a function of volume. The resulting data for the various phases (figure 7) evidence that, consistent with many previous experimental and theoretical observations, the $cF_4$ (fcc) phase is the stable structure at ambient pressure and transforms around 6 GPa to the $cI_2$ (bcc) phase.

A plethora of competing or contradicting phases in both high-pressure experiments and calculations manifest in the pressure range above 30 GPa (see table 2). In the current calculations, we have for the first time considered the energetics of the monoclinic $mC_4$ phase and observe evidence that around 35 GPa, calcium transforms from $cI_2$ to this $mC_4$ phase. The transition is consistent with our experiments and strengthens the correctness of the diffraction pattern refinement with the $mC_4$ model. The enthalpy of the tetragonal variant in space group $I4_1/amd$ ($\beta$-Sn aristotype) is higher by about 100 meV in the entire phase diagram and therefore clearly less stable than the $mC_4$ phase.

Next, considering the enthalpies of the two orthorhombic phases, $Cmmm$ and $oC_4$ ($Cmcm$), the latter is energetically more preferable and becomes more stable than $cI_2$ (bcc) above 45 GPa. This result is also conforming our above described

![Figure 7](image.png)

**Figure 7.** The calculated value of enthalpy $H$ as a function of pressure for the various phases of calcium. All the enthalpy values have been scaled with respect to the $cF_4$ (fcc) phase. For most structure patterns, the Pearson Symbols are given ($cF_4$, $cI_2$, $cP_1$, $mC_4$, $oC_4$). For clarity, three structure models are labelled by their space groups (rhombohedral distortion of primitive cubic: $R\bar{3}m$, undistorted $\beta$-tin type: $I4_1/amd$, and the previously assigned orthorhombic low-temperature modification of calcium [7]: $Cmmm$).

![Figure 8](image.png)

**Figure 8.** Comparison of the calculated electronic total DOS (grey shaded) and partial d-DOS (dashed lines) for Ca under pressure. For the DOS values at the Fermi level (states per eV and atom; the contribution of $d$-like states and their percentage of the total DOS are given in parenthesis), we obtain at 40GPa for $mC_4$ ($C2/c$) 0.374 (0.266 $d$-states, 71%) and for $I4_1/amd$ 0.239 (0.182, 76%); at 50GPa for $oC_4$ ($Cmcm$) 0.311 (0.261, 84%) and for $Cmmm$ 0.450 (0.421, 94%), respectively.

x-ray diffraction pattern fitting and provides an independent check towards the validity of the selected structure models.

It should now be noted that the differences in the enthalpies between $cI_2$, $mC_4$ and $oC_4$ differ by less than $k_B T$ in the 30–40 GPa range and therefore can be co-existing below room temperature. This finding is in accord with the observation that slightly different stability fields arise in response to the experimental pressure-temperature pathway (i.e. changing pressure at constant temperature or vice versa). Similarly, in the 40–60 GPa range, enthalpies of $mC_4$, $cP_1$ and $R\bar{3}m$ differ by less than $k_B T$ and therefore the experimentally observed co-existence of the three phases is compatible with the present computational results.

The detailed knowledge of the pressure-temperature phase diagram is especially relevant with respect to the emergence of superconductivity in calcium around 50 GPa. For a quantitative microscopic understanding of the superconductivity under pressure, the precise knowledge of the electronic structure is an indispensable prerequisite. The calculated band structures clearly demonstrate that the electronic structures of the different phases are markedly distinctive (figure 8). In particular, the value of the electronic density of states (DOS) at the Fermi
level, which is directly related to the superconducting critical temperature \( T_c \), differs by more than 30% between the monoclinically distorted variant \( mC4 \) (\( C2/c \)) and the tetragonal aristotype \( f4I/amd \) at 40 GPa. A similar variance is found for the orthorhombic phases \( Cmcm \) and \( oC4 \) (\( Cmcm \)) at 50 GPa (figure 8). Most notably, the character of the contributing states varies considerably. With increasing pressure, the contribution of \( d \)-like states increases from about 70% at 40 GPa in the \( mC4 \) phase to 84% at 50 GPa in the \( oC4 \) (\( Cmcm \)) phase. Thus, a theoretical investigation of the superconductivity in \( \text{Ca} \) under pressure (which is beyond the aim of the present study) necessarily needs to be based on precise experimental structural data.

4. Conclusions

In conclusion, our study provides both experimental and computational evidence that the low-temperature structures of calcium crystallize in the atomic arrangements \( mC4 \) and \( oC4 \) adopting space groups \( C2/c \) and \( Cmcm \), respectively. The atomic arrangements may be viewed as variants of a cubic primitive arrangement with specific symmetry-breaking distortions. The computations reveal that the enthalpy of the monoclinic phase is lower by about 100 meV than that of the earlier suggested tetragonal variant, the undistorted \( \beta \text{-Sn} \) aristotype. In equal measure, the enthalpy of the orthorhombic phase \( oC4 \) (space group \( Cmcm \)) is significantly lower than that of the previously suggested \( Cmcm \) arrangement. The calculated differences in the enthalpies between \( cI2 \) (bcc), \( mC4 \) (distorted \( \beta \text{-Sn} \)) and \( oC4 \) differ by less than \( k_B T \) between 30 and 40 GPa providing a natural explanation for the experimentally observed coexistence of phases. The accurate phase diagram and the respective crystal structures have impact on the understanding of the superconductivity of calcium under pressure since the calculated band structures evidence not only different DOS values for the involved phases at the Fermi level, but also pronouncedly different contributions of \( d \)-like atomic states.

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