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Distortions and Stabilization of Simple Primitive Calcium at High Pressure and Low Temperature.
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Ca-III, the first superconducting calcium under pressure, was previously identified as simplecubic (sc) by X-ray diffraction (XRD) experiments, but sc was shown to be unstable by all theoretical calculations. Using our newly developed sub-μm high-pressure single-crystal XRD, cryogenic high-pressure XRD, and theoretical calculations, we demonstrate that Ca-III sustains the sc-like, primitive unit cell that avoids phonon instability by a rhombohedral distortion at 300 K and a monoclinic distortion below 30 K. This surprising discovery reveals a new scenario in which the high-pressure structure of Ca does not reach its zero-temperature global enthalpy minimum, but is dictated by high-temperature anharmonicity and low-temperature metastability.

Keywords: Calcium, high pressure, phase transitions

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Post – *simple cubic* structures in compressed phosphorus and calcium: electronic origin.
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Recent high-pressure x-ray diffraction studies revealed unusual complex structures in phosphorus and calcium that follow the simple cubic structure at pressure above 1 Mbar [1,2]. These post – simple cubic (post-sc) phases P-IV and Ca-IV have close structural relation to the simple cubic via orthorhombic or tetragonal distortion of the basic cell and formation of the superlattice in one direction. For the phase P-IV the basic cell is base-centered orthorhombic, oC2, with a incommensurate modulation defined by a wave vector 0.267. We consider a commensurate approximant with a 11-fold supercell along the c-axis and a modulation wave vector equal 3/11. The phase Ca-IV, tP8, has a tetragonally distorted cubic cell with a commensurate 4-fold supercell along the c-axis. P-IV and Ca-IV have some common structural features in the formation of the post-sc phases that implies some common physical reasons for such complexity. We consider configurations of Brillouin zones and the Fermi sphere within a nearly-free-electron model in order to analyze the importance of these configurations for the crystal structure energy [3] containing two main contributions: electrostatic (Ewald) and electronic (band structure) energies. The latter can be lowered due to a formation of a Brillouin zone plane and an opening of an energy gap at this plane. Under pressure, the band structure energy part becomes more important leading to a formation of complex low-symmetry structures [4]. The stability of the post-sc phases in P and Ca is attributed to the lowering of the electronic band structure energy due to Brillouin zone – Fermi surface interactions.

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Structures of light element solids at extreme pressures.
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A challenge in high pressure research is the dissociation of simple molecules at very high pressures, atomic hydrogen, polymeric nitrogen, symmetric ice…. The reverse, the formation of atomic assemblies resembling molecules under pressure, was discussed in a theoretical study by Neaton and Ashcroft [1]. They predict that for increasing density the common high-coordination structures of simple elements like Lithium (bcc, fcc) will become unstable towards pairing of atoms. Furthermore, the resulting paired structures, similar to those expected for molecular hydrogen at pressures above 150 GPa, will be near-zero-gap semiconductors. We [2] have studied the structural properties of Li to pressures above 100 GPa. To avoid Li diffusion into the diamond anvils resulting in their repeated failure the measurements were performed at low temperature (below 200 K). The bcc to fcc transition was observed near 7.5 GPa in agreement with previous studies. Two structural phase transitions were discovered at ~40 GPa, one to an intermediate rhombohedral phase, which exists only in a narrow pressure range, and the other to a new low-coordination cubic phase different from the structures considered by Neaton and Ashcroft. Three more structural phase transtions were discovered at higher pressures. Measurements have been also performed for the related systems Na (160 GPa) and molecular hydrogen (145 GPa). For Na the same low coordination cubic phase was observed at pressures above 100 GPa, followed by different low coordination phases at higher pressures.

[1] J. B. Neaton J.B., Ashcroft N.W., *Nature*, 1999, 400, 141. [2] work done in collabration with K. Syassen, *MPI-FKF, Suttgart*, E. Gregoryanz and M. McMahon, *CSEC, Edinburgh.*

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