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Names and affiliations of applicants (* indicates experimentalists):

Dr. M.I. McMahon*****
Dr. D.R. Allan
Dr. S.A. Belmonte
Mr. T. Bovornratanaraks
Prof R.J. Nelmes
Dr. Ca. Vanpeteghem
Dr. S. Rekhi*****

School of Physics
The University of Edinburgh
Kings Buildings
Edinburgh EH9 3JZ
U.K.

Report:

The electronic structure of the elements at ambient conditions is well known and understood. However, under pressure, the relative movement of electron levels can result in electronic structures that are completely different to those found at ambient pressure. This can lead to structural transitions from high-symmetry close-packed structures to complex, open-packed structures.

Recently, we have reported an entirely new elemental structure type at high pressure [1]. This structure, first observed in the group-II element barium [1], comprises a body-centred tetragonal 'host' structure that has channels along the c axis. Contained in these channels are chains of atoms from one or more 'guest' structures that are *incommensurate* with the host along *c*. Since its discovery in Ba, we have found the same incommensurate structure type to be stable in another group-II element Sr [2], and in the group-V elements Bi, Sb and As [3]. While the host structure is the same in each element, a number of different guest structures are observed: face-centred tetragonal, face-centred monoclinic, body-centred tetragonal, and body-centred monoclinic. In addition, in Ba, we have observed structural phase transitions *within* the guest structure without any accompanying transition in the host structure [1]. We have termed these intra-phase transitions.

The observation of incommensurate host-guest structures in all of the heavier group-II and group-V elements begs the important question as to whether the structural similarities observed both within and between these groups extend to their lighter members – that is, Ca and P. At lower pressure, both of these elements have a simple-cubic (SC) structure that is stable over a remarkably wide pressure range, despite the low packing fraction of the atoms. In Ca, the SC phase is stable to the highest pressure to which Ca has so far been studied is ~85 GPa. In the present study to 125GPa, we observed a structural phase transition at 113(5)GPa to a phase giving a complex diffraction pattern. Unfortunately, the data were not of sufficient quality to determine the nature of the high-pressure structure.

Ca was loaded into two diamond anvil cells with mineral oil as a pressure transmitting medium and silver as a pressure marker. Diffraction data were collected on ID30 in ~5GPa steps, through the fcc (0 to 19.5GPa), bcc (19.5 to 32GPa) and simple cubic (32 to 113GPa) phases. The compressibility of Ca to 113GPa, obtained from measurement of individual peak positions, is shown in Figure 1. Fitting the compressibility data to Birch-Murnaghan equation of state gave the following bulk moduli.

Phase	Atomic Volume ($Å^3$)	Bulk Modulus (GPa)	Pressure Derivative
I (fcc)	44.64(55)	15(1)	3.38(13)
	46(1)	9.9(8)	4.0 (fixed)
II (bcc)	25.08(13)	75(11)	1.6(1.3)
	25.24(16)	58(4)	4.0 (fixed)
III (sc)	19.76(6)	83(2)	3.37(7)
	20.23(10)	65(2)	4.0 (fixed)

The simple cubic phase was found to be stable until 113(5)GPa, when it underwent a structural phase transition. The same transition pressure was observed in both samples. The diffraction pattern from Ca-IV is considerably more complex than that of the simple cubic phase, but, unfortunately, the peaks from the silver pressure marker obscured the crucial sample peaks that would make structure solution possible. Attempts to fit the data from the new phase with the hcp structure suggested that Ca-IV does not have this structure. Attempts to fit host-guest structures of the types found previously in Ba, Sr and Rb [1,2,4], were less definitive – Ca-IV may well have a composite structure type. However, further data are urgently required for a definitive answer.

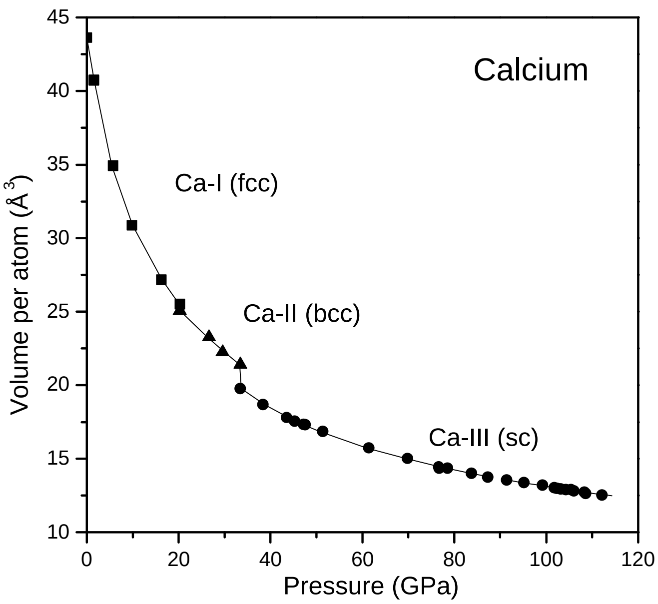

Figure 1: The compressibility of Calcium to 113GPa. The line throught the data is the fitted equation of state of each phase

[1] R.J. Nelmes, D.R. Allan, M.I. McMahon and S.A. Belmonte, Phys. Rev. Lett. **83**, 4081-4084 (1999).

[2] M.I. McMahon, T. Bovornratanaraks, D.R. Allan, S.A. Belmonte and R.J. Nelmes, Phys. Rev. B **61**, 3135-3138 (2000).

[3] M.I. McMahon, O. Degtyareva and R.J. Nelmes, Phys. Rev. Lett. **85**, 4896-4899 (2000).

[4] M. I. McMahon, S. Rekhi and R. J. Nelmes, Phys. Rev. Lett. **87**, 055501-055504 (2001).