ESRF	**Experiment title:** Search for Composite Structures in Ca above 110GPa	**Experiment number**: HS-2303
Beamline: ID09	**Date of experiment**: from: 17/09/03 to: 20/09/03	**Date of report**: 24/02/04
Shifts: 9	**Local contact(s)**: Dr. Michael Hanfland	*Received at ESRF:*

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Report:

Changes in the internal electronic structure of atoms under high pressure can lead to dramatic changes in crystal structure, resistivity and superconductivity. Recently, we have reported a new complex structure type in elemental metals at high pressure. This composite structure, first observed in the group-II element barium, comprises a body-centred tetragonal (bct) "host" structure that has channels along the *c* axis. Contained in these channels are 1-dimensional chains of atoms from one or more "guest" structures that are *incommensurate* with the host along *c*. Since its discovery in Ba [1], we have found the same structure type to be stable in another group-II element Sr [2], in the group V elements Bi, Sb and As [3], in the group-I element Rb [4]. Most recently, using a combination of powder diffraction data from the ESRF, and single-crystal data collected at SRS, we have observed that in Bi and Sb, interaction between the host and guest components leads to additional structural modulations of their structures and the appearance of very weak satellite reflections [5].

The observation of incommensurate host-guest composite structures in all the heavier group-II elements raises the question as to whether the same structure also exists in the lighter members of this group – that is, Ca and P. The sequence of transitions in Ca with increasing pressure is fcc → bcc → simple cubic, showing a puzzling progression of *decreasing* coordination with increasing density. In experiment HS-1392, we followed the structural dependence of Ca to 120GPa – well above the limit reached in earlier studies of 80GPa – and observed a previously unknown phase transition to Ca-IV at 113GPa. However, the sample quality was insufficient to identify the structure of the new phase. In experiment HS-2303 we wished (i) to determine the structure of Ca-IV above 113GPa, and (ii) if it is indeed a host-guest structure, to determine whether or not it has any additional satellite reflections that would indicate modulations of the host and guest components.

Ca was loaded into two diamond anvil cells prior to arrival at ESRF. Data were collected in steps up to 120GPa, and we again found the phase transition to Ca-IV at 115(5)GPa. A diffraction profile obtained at 120GPa is shown in Figure 1. Unfortunately, the sample had become slightly contaminated during loading process, and the diffraction profile in Fig. 1 thus contains some additional weak reflections. Attempts to index the profile shown in Figure 1 have so far proved unsuccessful, and analysis is still on-going. However, the diffraction profile bears little resemblance to those obtained from host-guest structures in other group II elements, suggesting that Ca-IV has a different structure. Repeated attempts to obtain Ca-IV in other samples were also unsuccessful: a further 5 Ca samples were loaded at the ESRF, and in each case the pressure cell failed to reach the required pressures before either the gasket hole or the diamonds failed.

While the further Ca samples were being prepared and the pressure cells reloaded, diffraction data were collected from two backup samples of the group V element Se. Recently we have reported that the long-known phase of Te stable above 5GPa, Te-III, has an incommensurate structure previously unknown in the elements [6]. Trial data collected at SRS suggested that Se-IV, the phase of Se stable above 28GPa, has the same incommensurate structure as Te-III. The high-quality data collected at ESRF shows that Se-IV does indeed have the same incommensurate structure, and the extremely high intensity available on ID09 meant that the pressure dependence of this structure, including the modulation parameters, could be determined to very high pressures. A Reitveld refinement to a Se-IV profile at 42GPa is shown in Figure 2. The analysis and interpretation of this data is almost complete, and a paper describing the results is soon to be submitted.

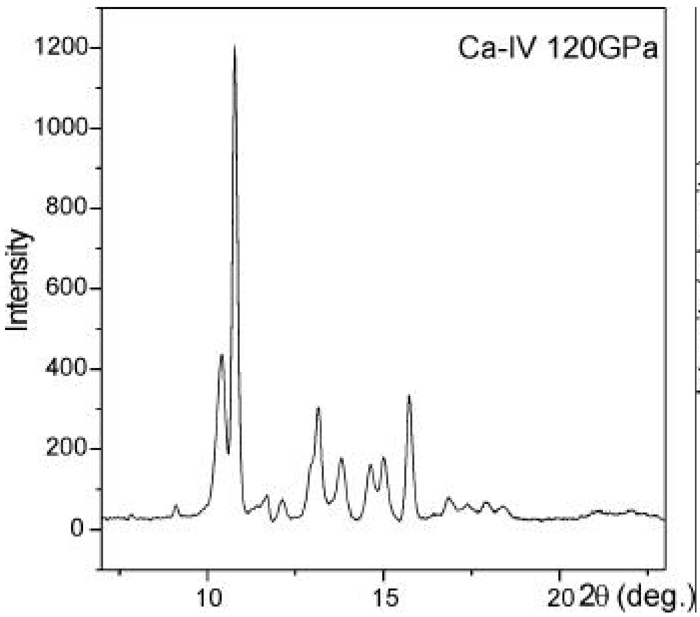

Figure 1

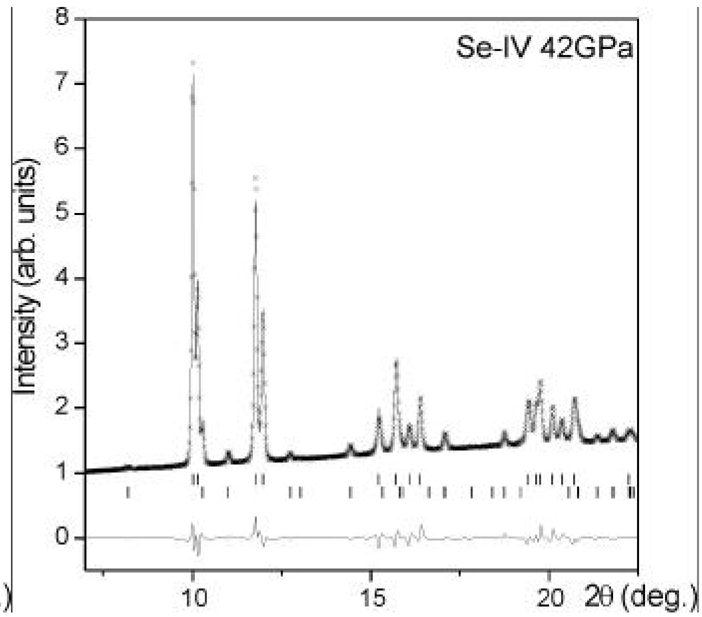

Figure 2

References

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