ESRF	**Experiment title:** Structure of the amorphous and crystalline phases of Cu(II)S at high p, T.	**Experiment number**: HS2100
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Shifts: 18	**Local contact(s)**: Giuliana Aquilanti	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Wilson A. Crichton* ESRF

Giuliana Aquilanti* ESRF

Andrzej Grzechnik* Laboratory of Crystallography, Universität Bayreuth, Bayreuth

Sakura Pascarelli ESRF

Report:

While the initial submission was concerned with GeO_2 we ran the same experiment with covellite as sample because the data we intended to collect had just appeared in PRL.

Background

Our initial interest in this system was based on the report of Peiris *et al.* (1996) who investigated the behaviour of covellite, Cu(II)S, at pressures up to 45 GPa and klockmannite, Cu(II)Se, over a similar range (Peiris *et al.*, 1998). These studies indicated two differing trends:

- *CuS*: loss of all Bragg scattering from covellite by 18 GPa; EoS to 11 GPa indicates -K'; application of pressure above 20 GPa results in increased Bragg scattering from a simple structure.
- *CuSe*: no loss of diffraction, peaks visible up to 52 GPa (no phase transition is implied) and compression is normal with +K'.

These authors conclude that the difference in the behaviour of these two phases is due to CuS being thermodynamically unstable at high P (giving rise to -K' and amorphization) and thus, that a high pressure form of klockmannite may occur at P > 52 GPa. Since these studies, calculations by Milman (2002) have indicated that klockmannite should tend to decompose at moderate pressure to a mixture of umangite (Cu_3Se_2) and kruatite ($CuSe_2$ [pyrite-structure]). This, in addition to recent results that indicate that pressure induced amorphization (PIA) is linked to coordination change warranted a reappraisal of the CuS (+CuSe) data at high pressure to try to establish the mechanism for PIA and the difference in the two chemistries, which are both very similar in structure. This given, we set out to investigate the phase diagram of CuS using XAS, as it would be insensitive to the loss of diffraction signal, using externally heated DACs and followed this up by *in situ* AD-XRD from DACs and large-volume apparatus (at ID30, during IHR).

Results

Room temperature compression of CuS shows, Fig. 1, at least one structural transition (18 GPa) and other electronic transitions (change of Cu valence) that are evident from the shift in the edge and shape of the edge structure (see insert, Fig. 1). Above 18 GPa, there is no change apparent in the XANES or EXAFS region other than p, T evolution. At higher temperature, the nature of these changes is more apparent, Fig. 2. Evidently further analysis must be carried out to assess whether the electronic transitions seen in Figure 1 are associated with structural transitions, however, that there is a link between the pressure of PIA (and loss of covellite peaks) of Peiris *et al.* and structural transition evident from these data is sufficient to warrant further investigation by diffraction methods.

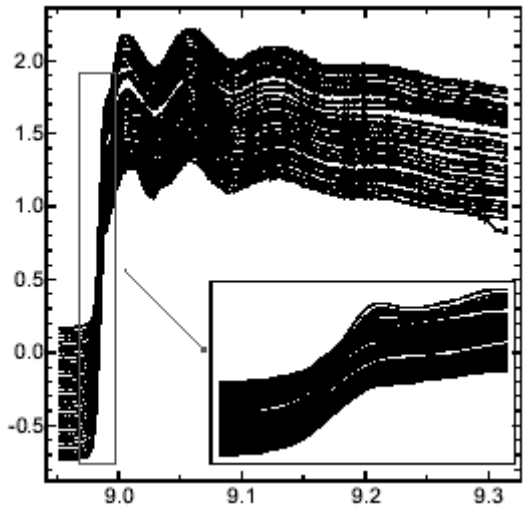

Figure 0. **Cu K-edge spectra of Cu(II)S under pressures to 25 GPa.**

Room temperature diffraction (DAC) shows largely the same trend as described by Peiris *et al.* of extreme loss of intensity and peak broadening (probably, given the structure, due to stacking faults) though at no point do we loose Bragg reflections from the sample; that is, we have no evidence for PIA. Further points that are of note from the room T run (Fig. 3):

- New diffraction peak appears at 3.66 Å between 3 and 5 GPa, though pattern is remains largely covellite-like (green)
- By 9 GPa there are additional peaks present, but again no overall change from a pattern that is still largely covellite-based, still (002) and (004) from covellite
- By 13 GPa, the new peak at 3.66 Å is lost and the complexion of the pattern changes (002 remains) (blue)
- By 16.9 GPa the (002) is no longer visible and the pattern has changed to exclude all high d-spacing reflections >3.5 Å (pink)
- Data at 22 and 25 GPa are distinct from those at pressures before; though the difference is slight. There is, as described by Peiris *et al.*, sharpening in certain regions (pink).

The work was continued with heating, in order to sharpen the pattern into a state that could be investigated by diffraction. It became immediately evident that this had considerable effect on the quality of the data (Fig. 4). The overall shapes of the patterns are very similar (but, it would be extremely difficult to demonstrate that there is no transition between room T and ~ 200 ºC without the XAS data).

In this case the peaks (at 25 GPa and 198ºC) are partly identified as those belonging to the pyrite-structured villamaninite (CuS) and an associated phase(s) that remains unaccounted for at present (not Cu nor any chalcocite or digenite phases). Comparing the sharpened peaks of Peiris *et al.* (at 3.32, 2.67 & 1.67 Å) they are the strongest lines at room T which develop to become [close to the d-spacings of] the (111), (200) and (311) of the villamaninite phase.

Decompression (in 2 steps due to time-constraints) from high p, T conditions (as per the XAS data) shows the back-transformation to an assemblage containing digenite + villamaninite + covellite, later confirmed by large-volume experiments, Fig 5.

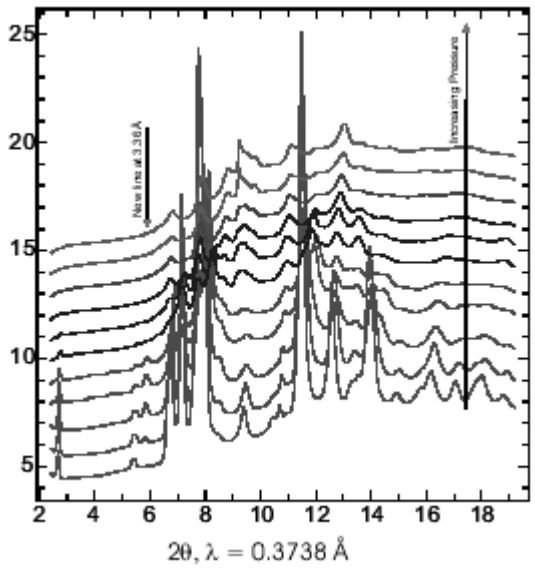

Figure 3. **Room T compression of Cu(II)S, notice there is no loss of diffraction even up to 30 GPa.**

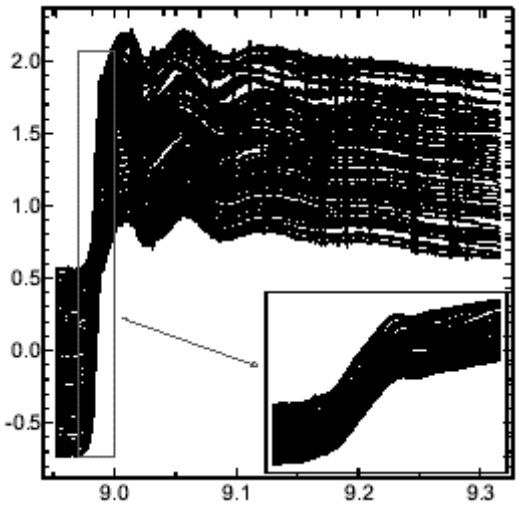

Figure 2. **Complete p cycle at 100 ºC. Structural and electronic transitions are obvious.**

Further experiments were conducted using the Paris-Edinburgh large-volume apparatus to try to define further regions of phase stability. These data shed further light on the assemblage of villamaninite + digenite - at pressures below 15 GPa and temperatures where phases can be reasonably assigned this assemblage is ubiquitous. It was found to be consistent with the DAC data, that, covellite is recoverable through decompression and cooling. Peiris *et al.* also demonstrated that covellite is recoverable at room T. Other interesting features were observed:

- that varying pressure at high T changes the 'liquid-like' background associated with the fast-ion digenite phase; similar to behaviour seen in Ag_2I etc [e.g. Keen *et al.*, 2003]
- as the temperature is increased from the two phase assemblage of digenite + villamaninite, villamaninite melts leaving digenite as the single crystalline phase present.

On cooling (quench) covellite is formed - though the reaction is not complete, Fig 6. In no run was an assemblage similar to the very high pressure DAC data seen [i.e. villamaninite + post-digenite phase(s)]. This was probably as 15 GPa (and therefore the P at which Peiris *et al.* noted PIA and we observed no covellite) was not exceeded.

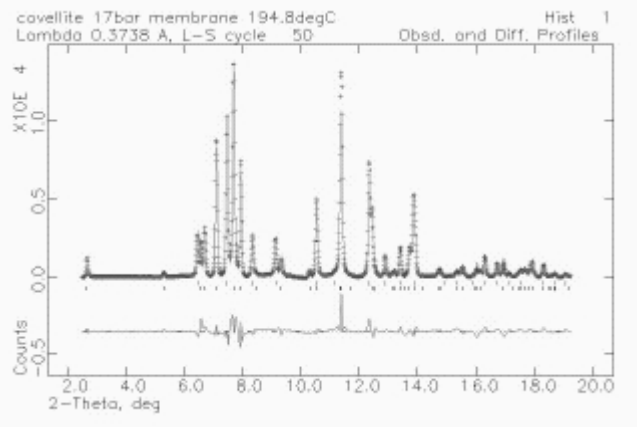

Figure 5. In situ **Rietveld refined covellite + villamaninite (+ digenite confirmed by LVP).**

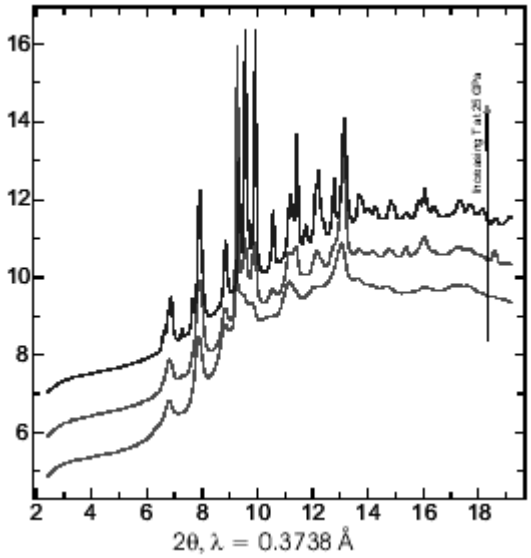

Figure 4. **Heating at 25 GPa,villamaninite + post-digenite phase.**

Figure 6. **Recovered sample capsule, shows incomplete back-reaction to form covellite, with its characteristic blue-black colour.**

Conclusions

- We observe transitions that are electronic in nature, which can be associated with the development of new peaks in the sub-10 GPa range. Identification of the origin of these peaks will remain difficult (for XRD) due to the signal from the sample itself.
- At 18 GPa, there is no PIA, but also, no covellite and the transformation(s) above 18 GPa yield villamaninite + and as yet unidentified post-digenite phase.
- The assemblage villamaninite + digenite is the ubiquitous low-moderate pressure (<15 GPa) at temperature. This is a result that is consistent with previous work on the synthesis of covellite by Munson (1966) and Bither *et al.* (1969).
- Pyrite-structured villamaninite is formed in this system at high pressure, in association with other phases. If we extend this further, to include other chacogen chemistries, we can say pyrite will tend to be formed - in addition to another phase that is dependent on initial chemistry, pyrite formation is independent of chemistry [see Bither *et al.*, 1969 - Mn, Fe, Co, Ni, Cu, S, Se, Te for pyrite and pyrite + digenite; Munson (1966) for pyrite + S; Hinze and Neuhaus (1969) for pyrite + Cu (S, Se and Te); Murray and Heyring (1975) for CuSe decomposition to kruatite (pyrite) + umangite with grinding.]
- From these data, which are in agreement with all early data and recent calculations; we conclude that Cu(II)S and Cu(II)Se are indeed rather similar in behaviour and by extension, as are other chalcogens like these. Independent of chemistry, they will all tend to form pyrite-type phases at high p(, T). Possible reasons for which are discussed in Takeuchi *et al.* (1985) and Gotsis *et al.* (1992).