WEIRD METALS – MODULATIONS WITHIN GUESTS WITHIN HOSTS

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High-pressure studies on certain elemental metals have unravelled unusual structures such as host-guest complexes. The characteristics of these structures cannot easily be explained and pose quite a challenge for theoretical studies.

It is now more than 40 years since the first high-pressure structures were determined using diamond anvil pressure cells. In that time, great advances have been made in the pressure range accessible with such devices, and in the quality of diffraction data obtainable from them. It is then somewhat surprising that so many significant uncertainties have remained, even in the structures of elements – at quite modest pressures in some cases.

Among the most persistent of the unsolved problems have been those in groups II and V of the periodic table, where the high-pressure phases Ba-IV, Sr-V, Bi-III, Sb-II and As-III have been shown to be complex, but have resisted all previous attempts at full solutions. Recently, using a combination of single-crystal and powder diffraction data collected at the SRS (Daresbury, UK), in-house, and at the ESRF, we have found that in all these cases, the high-pressure structure is very similar and of an entirely new type – described as the 'weirdest known atomic structure of … any pure element' [1].

Figure 1 shows a diffraction pattern collected from a single-crystal of Ba-IV at 12 GPa at the SRS. The diffraction pattern comprises layers of diffuse scattering (seen edge-on in this image), Bragg reflections that lie on the planes of diffuse scattering, "satellite" reflections around these reflections (enlarged in the inset), and Bragg reflections not on the diffuse planes are marked by arrows.

The structure explaining all these features is shown in Figure 2. It is a composite arrangement comprising a tetragonal 'host' structure (which gives rise to the Bragg reflections not on the diffuse planes), and chains of 'guest' atoms lying in channels that run along the c-axis of the host. These chains form C-centred tetragonal and C-centred monoclinic guest structures [2] which give rise, respectively, to the Bragg reflections on the diffuse planes and to the satellite reflections. The diffuse scattering itself can be attributed to a lack of inter-chain ordering in some fraction of the chains. The most surprising thing about this composite structure is that the host and guest structures are *incommensurate* with each other along the c-axis: the ratio of their c-axis lattice parameters, c_H/c_G, is 1.388 at 12 GPa, and varies continuously with pressure.

Further studies of Ba-IV have revealed that at 12.5 GPa, the monoclinic guest structure undergoes a structural phase transition, without any accompanying change in the host [2]. We have termed this an intra-phase transition. Another intriguing aspect of the structure is that the number of atoms in the host unit cell – which is non-integer and equal to $8 + 2x(c_H/c_G) = 10.776$ at 12 GPa – is pressure dependent, through the pressure dependence of c_H/c_G. Some of the chain atoms must then be 'squeezed out' of the channels with increasing pressure.

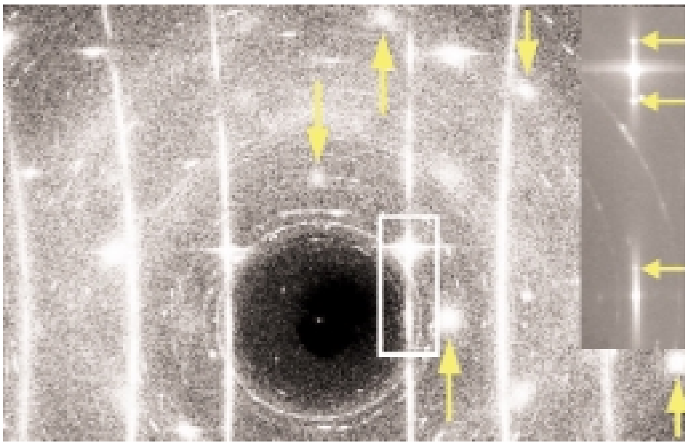

Fig. 1: 2-D diffraction pattern from a single-crystal of Ba-IV at 12 GPa. The inset enlarges the marked area. Vertical arrows mark host reflections, and arrows in the inset mark satellite reflections from the monoclinic guest adjacent to stronger reflections from the tetragonal guest.

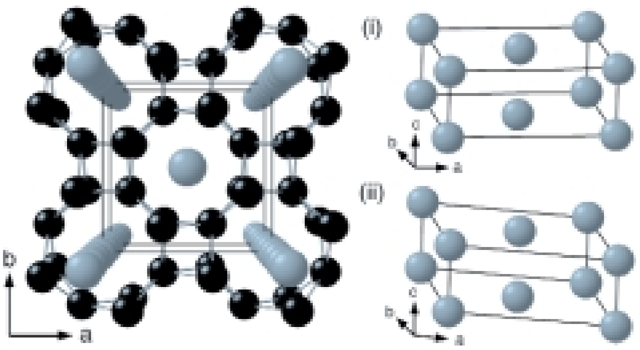

Fig. 2: The composite structure of Ba-IV. The host structure (dark atoms), with guest-atom chains (light atoms), is shown in a c-axis projection. The inset shows the tetragonal and monoclinic guest structures.

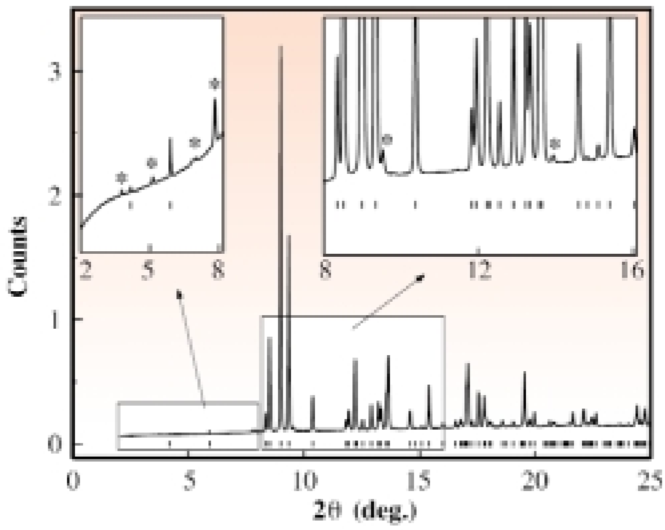

Fig. 3: Integrated profile from Sb-II at 10.3 GPa [7]. The tick marks show the positions of reflections from the host-guest composite structure. The strongest of the additional reflections are marked by asterisks.

Sr-V is stable above 46 GPa and known to have a similar diffraction pattern to Ba-IV. Studies at the SRS and on ID9 at the ESRF have revealed that it too has a composite host-guest incommensurate structure of the Ba-IV type, with c_H/c_G = 1.404 at 56 GPa [3]. We have also found that Sr-V undergoes an intra-phase transition at 71(1) GPa [3]. However, the structure of the guest phase above this pressure remains unknown.

The structure shown in Figure 2 bears a striking resemblance to the (commensurate) structure proposed previously for Bi-III and Sb-II [4], but which cannot be correct on density considerations. Powder and single-crystal studies of Bi-III and Sb-II have shown that in both cases, the true structure is a composite incommensurate structure with the same tetragonal host as Ba-IV and Sr-V, but with a different, body-centred tetragonal, guest [5]. The calculated densities of these incommensurate phases agree extremely well with those determined directly over 40 years ago by Bridgman and others. Recent studies of As-III at the ESRF and the SRS have shown that while it also has the same tetragonal host as Ba, Sr, Bi and Sb, the guest is monoclinic.

While the composite host-guest structures fit all the main features in the observed Bi-III and Sb-II diffraction profiles, there are a number of extremely weak reflections in profiles collected at the ESRF (see Figure 3) that are not accounted for. These peaks are from a furthur modulation of the structure [7]. It is clear that there are further levels of complexity yet to be uncovered in these strange phases!

It is a challenge for theoretical study to understand why such complex structures are stable over pressure ranges as large as 5 - 30 GPa and more. This challenge is made more difficult by the incommensurate nature of the structures. Heine has suggested possible critical factors for incommensuration such as charge density waves and the strength of the host-guest interaction [1]. First insight into the stability of Ba-IV has been obtained from calculations of a commensurate approximation [6]. Some other insight might come from an intriguing similarity with commensurate analogues found in binary alloys such as Al_2Cu and In_5Bi_3, which raises the interesting possibility that the Ba-IV-type phase might also be considered as an 'alloy' – comprising atoms with, perhaps, two different electronic arrangements. There is much yet to do, including further diffraction work to search for more of these 'weird metals' in other elements. ■

References

*[1] V. Heine, Nature **403**, 836-837 (2000).*
*[2] R.J. Nelmes, D.R. Allan, M.I. McMahon and S.A. Belmonte, Phys. Rev. Lett. **83**, 491-494 (1999).*
*[3] M.I. McMahon, T. Bovornratanaraks, D.R. Allan, S.A. Belmonte and R.J. Nelmes, Phys. Rev. B. **61**, 3135-3138 (2000).*
[4] J.H. Chen, H. Iwasaki and T. Kikegawa, High Press. Res. 15, 143-158 (1996).
*[5] M.I. McMahon, O. Degtyareva and R.J. Nelmes, Phys. Rev. Lett. **85**, 4896-4899 (2000).*
*[6] S.K. Reed and G.J. Ackland, Phys. Rev. Lett. **84**, 5580 (2000).*
[7] O. Degtyareva, M.I. McMahon and R.J. Nelmes, to be submitted (2001).

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