Ba-IV-Type Incommensurate Crystal Structure in Group-V Metals

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The long-unknown crystal structure of Bi-III has been solved. It comprises a body-centered-tetragonal (bct) "host" and a bct "guest" component made up of chains that lie in channels in the host; the guest is incommensurate with the host along the tetragonal c axis. Diffraction data for Sb-II reveal that it too can be fitted with the same composite structure. The structures of these two high-pressure phases of Bi and Sb are similar to those reported recently in the alkaline-earth metals Ba and Sr.

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Bismuth is one of the most studied elements at high pressure [1–8]. Nevertheless, there are still several outstanding uncertainties over the Bi phase diagram. The most contentious of these concern the crystal structure of Bi-III, stable between 2.8 and 7.7 GPa, and the possible existence of two other phase transitions at 4.4 and 5.3 GPa *within* the stability field of Bi-III.

The diffraction pattern from Bi-III is known to be very complex [3,5,8] and its crystal structure has been reported previously as tetragonal [4] and orthorhombic [5]. However, in neither case is the fit to the experimental data convincing. Most recently, Chen *et al.* [8], using angle-dispersive x-ray techniques, have reported Bi-III to be tetragonal ($a = 8.659$ Å and $c = 4.238$ Å at 3.8 GPa) with space group $P4/n$ and 10 atoms per unit cell. The same structure had previously been assigned to Sb-II, stable above 8.6 GPa [9]. But though this structure provides a very good fit to the reported Bi-III peak positions and appears to account for all the observed reflections, the calculated density at 3.2 GPa [7] and 3.8 GPa [8] would require a volume *increase* of 2.0(2)% at the Bi-II → Bi-III phase transition.

Here we report a solution for Bi-III that is composed of a tetragonal "host" structure and an interpenetrating "guest" component that is *incommensurate* with the host. We show that this surprisingly complex elemental structure is also that of Sb-II, and possibly occurs in yet another group V metal, As. The structure was found for the first time only recently in the alkaline-earth metals Ba [10] and Sr [11], and has been dubbed "the weirdest known atomic structure of ... any pure element" [12]. Its discovery now in the electronically quite different group V metals is a further surprise that suggests a much wider significance for this strange new type of metallic structure.

Experiments were done with a sample of 99.999% purity (single crystal grade) obtained from the Institute of Rare Metals, Russia. Angle-dispersive powder diffraction data were collected on station 9.1 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory, using an image-plate area detector, with a wavelength of 0.4654(1) Å [13]. Polycrystalline samples were obtained by grinding small pieces of Bi at room temperature. The gasket hole was filled with the resulting very thin flakes, a 4:1 methanol:ethanol mixture as a pressure medium, and a small chip of ruby for pressure measurement. Diffraction patterns collected at ambient pressure revealed the sample to be finely powdered, with little preferred orientation. The 2D images were integrated azimuthally, and structural information was obtained by Rietveld refinement of the integrated profiles using the program MPROF [14].

The diffraction patterns from Bi-I on pressure increase remained smooth, but those obtained from Bi-II and, in particular, Bi-III were highly textured. Analysis of the integrated profiles of Bi-III revealed that although the primitive tetragonal cell of Chen *et al.* [8] fits most of the observed peak positions extremely well, there are 9 reflections not accounted for. In fact, two of the strongest of these reflections — with d-spacings 2.147 Å and 1.244 Å at 3.6 GPa — are discernible (but not mentioned) in the diffraction pattern obtained by Chen *et al.* at 3.8 GPa [8]. Attempts to fit the Bi-III profiles with other previously proposed cells [4,5], or using autoindexing methods, were unsuccessful.

Further increases in pressure resulted in a phase transition to the body-centered-cubic phase, Bi-V, at 8 GPa. On decreasing the pressure back to Bi-III, the diffraction pattern became significantly more textured than that obtained on pressure increase, and contained some strong reflections from sizable crystallites. Samples of Bi-III that were predominantly one single crystallite were obtained by starting with a small cut single crystal of Bi-I, increasing the pressure above 9–10 GPa into phase V, and then decreasing the pressure slowly back into phase III.

A diffraction pattern from such a sample at 4.5 GPa is shown in Fig. 1. There are clear lines of diffuse scattering (from top left to bottom right). We have recently reported the same feature in the high-pressure phases of the alkaline-earth metals Ba (Ba-IV) [10] and Sr (Sr-V) [11], where it arises from positional disorder of one-dimensional chains of atoms in a composite "host-guest" structure. The pattern also contains some 24 single-crystal reflections which can be divided into two classes — those lying on the lines of diffuse scattering (labeled l_G), and those not (labeled l_H). Those on the l_H lines can be accounted for by a

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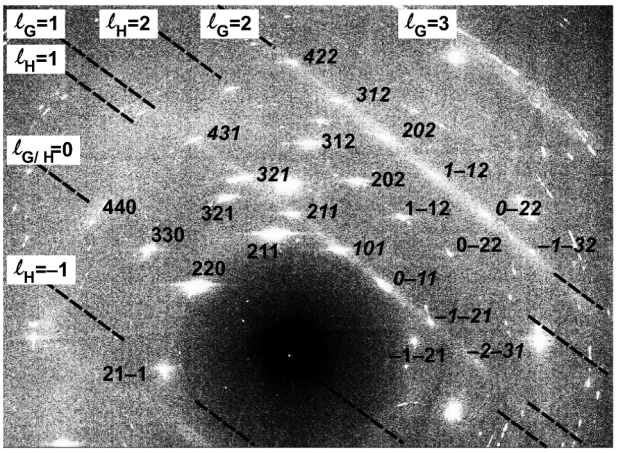

FIG. 1. 2D image from a single crystallite of Bi-III at 4.5 GPa showing $l \neq 0$ lines of diffuse scattering. The location of host (l_H) and guest (l_G) layers of reflections are indicated, and the individual reflections are indexed. Unindexed reflections arise from other crystallites.

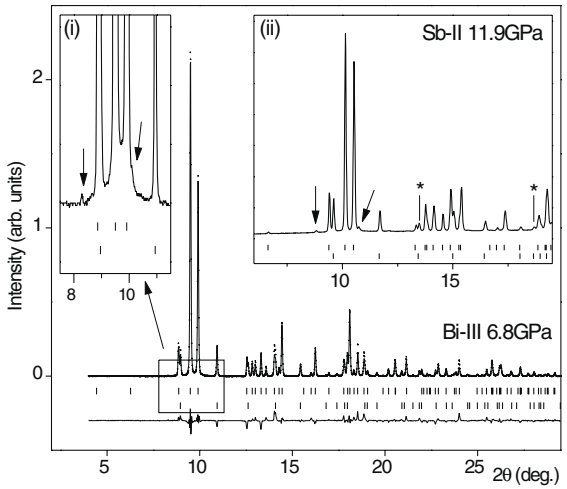

FIG. 2. Integrated 1D profile from Bi-III at 6.8 GPa (dots) and a Rietveld refinement fit (line). The upper and lower tick marks below the profile show the peak positions of the host and non-$hk0$ guest reflections, respectively. Below the tick marks is the difference between the observed and calculated profiles. Inset (i) shows the two weak reflections in Bi-III not accounted for by the basic host-guest structure. Inset (ii) shows the integrated diffraction profile from Sb-II at 11.9 GPa, with tick marks as for Bi-III. The arrows indicate the two most intense extra reflections, located in the same positions as the extra reflection in Bi-III. The asterisks mark two of the five observed reflections not accounted for by the $P4/n$ structure.

body-centered-tetragonal host cell with $a_H = 8.602(1)$ Å and $c_H = 4.207(1)$ Å, while those on the l_G lines index on another body-centered-tetragonal guest cell with $a_G = 8.602(1)$ Å and $c_G = 3.211(1)$ Å. The indices of the 24 reflections are given in Fig. 1 and the systematic absences are consistent with space groups $I4/mcm$ and $I4/mmm$ for the host and guest structures, respectively. Of the 9 reflections not accounted for by the previously proposed primitive tetragonal structure [8], only the weakest two, both of which are much too weak to observe in previously published data [3,5,8], remain unindexed. Some possible explanations for these two peaks—which have d-spacings of 3.254 and 2.671 Å at 4.5 GPa—are given below.

To obtain better peak intensities for detailed structure refinement, we attempted to minimize recrystallization by increasing the pressure at 200 K, much further from the melting curve. The resulting diffraction patterns were considerably smoother powders than those obtained on pressure increase at room temperature. A Rietveld fit to the integrated profile obtained from such a sample at 6.8 GPa, using a pseudo-two-phase technique to fit the host-guest structure [10,11], is shown in Fig. 2. The remaining small discrepancies between observed and calculated profiles arise from the inadequacies of the single-parameter preferred orientation model. The refined value of the host-structure x coordinate (for the $8h$ sites of $I4/mcm$) at 6.8 GPa was 0.1536(3), compared with 0.1484(3) in Ba-IV at 12.9 GPa [10], and 0.1460(2) in Sr-V at 56 GPa [11]. Refinements of two further Bi-III samples obtained at low temperature gave x coordinates of 0.1531(3) and 0.1544(3), at 6.7 and 5.0 GPa, respectively. The refined lattice parameters at 6.8 GPa are $a_H = a_G = 8.5182(2)$ Å, $c_H = 4.1642(2)$ Å, and $c_G = 3.1800(3)$ Å, giving a c_H/c_G ratio of 1.309(1). This is somewhat smaller than the value of 1.404(1) found in Sr-V at 56 GPa [11] and 1.378(1) in Ba-IV at 12.9 GPa [10].

As said, this basic composite structure cannot account for two weak peaks observed reproducibly in the Bi-III diffraction profiles. These peaks are *extremely* weak [see inset (i) and the main profile in Fig. 2]. They exist only in the Bi-III phase, and they compress at the same rate as the host and guest peaks. One possibility is that they arise from another (minority) guest structure: we found two different guest structures coexisting in Ba [10]. These peaks might also indicate some modulation of the host or guest structure. The weakness and limited number of the extra reflections prevents a unique solution being found at this stage.

The refined structure is shown in projection down the c axis in Fig. 3. The inset shows the guest structure on the same scale. The host structure, which is the same as that found in Ba [10] and Sr [11], can be regarded as being built from two-dimensional nets containing square and triangular arrangements of atoms. In the notation of Pearson [15], these are 3^2434 nets since each atom forms part of three triangles (3) and two squares (4), arranged in the sequence "33434" around the atom. The host structure comprises such 3^2434 nets stacked along the z axis, at $z = 0$ and $z = \frac{1}{2}$ with those at $z = \frac{1}{2}$ offset by $[\frac{1}{2}, \frac{1}{2}, 0]$. The squares of these nets are centered above one another, forming channels running along the z axis which are occupied by the atoms of the guest structure. The guest atoms also form planar nets, which, as they consist only of squares, are termed 4^4. This body-centered guest structure is different from those so far found in Ba and Sr [10,11], but can be regarded as a special case of the C-face-centered monoclinic

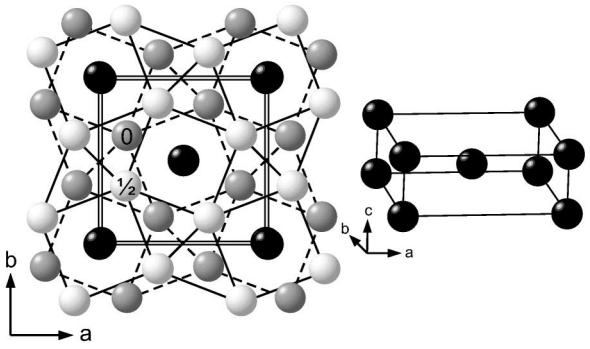

FIG. 3. Structure of Bi-III shown in projection down the c axis. The 3^2434 nets of the host structure located at $z = 0$ (dark grey symbols) and $z = \frac{1}{2}$ (light grey symbols) are outlined using solid and dashed lines, respectively. The guest atoms are shown using black symbols. The inset shows a perspective view of the guest structure on the same scale.

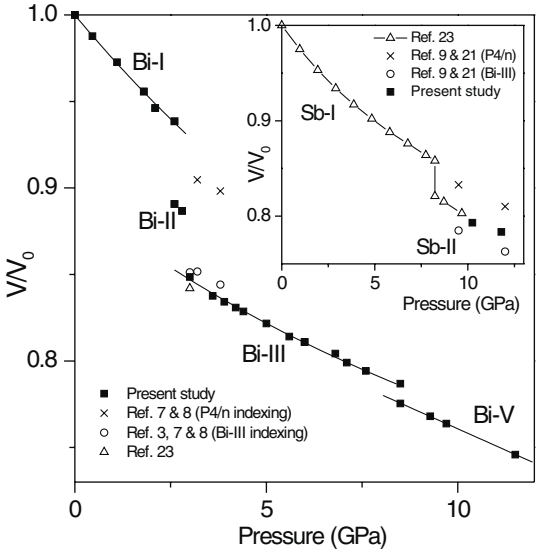

FIG. 4. V/V_0 for Bi to 12 GPa. Data from the present study are shown using solid symbols; other symbols are identified in the figure. The inset shows compression data for Sb to 10 GPa. The solid lines are guides to the eye.

guest found in Ba-IVa [10] with a monoclinic angle given by $\pi/2 + \arctan(c_G/a_G) = 110.47°$.

The Bi-III structure appears to be closely related to that of the compound In_5Bi_3 [16]. The In_5Bi_3 structure comprises six almost equally spaced 3^2434 nets stacked as in Bi-III to make three unit cells of the Bi-III host structure. Arranged within these layers are four equispaced planar 4^4 nets which resemble four unit cells of the Bi-III guest structure, except that the atoms are in a C-face-centered rather than body-centered arrangement. With that one exception, the monatomic equivalent of the In_5Bi_3 structure is strikingly similar to a Bi-III structure with a commensurate c_H/c_G ratio of $4/3 = 1.333$. However, the c_H/c_G ratio of 1.309(1) in Bi-III is very significantly different from $\frac{4}{3}$, and, being only very slightly pressure dependent, does not approach any commensurate value over the stability range of the phase.

Two special features of an incommensurate host-guest structure are that the host cell contains a noninteger number of atoms, and the density of the structure cannot be determined without a knowledge of the occupancy of the guest sites. The quality of the present powder diffraction data does not allow us to obtain an accurate value for this occupancy: refinements showed a strong correlation between the refined occupancy and the variable parameter of the preferred orientation model. However, the guest sites are known to be 100% occupied in Ba-IV [10]. If the same is assumed for Bi-III, there are then $c_H/c_G = 1.310$ guest atoms in each channel, and hence a total of 10.620 atoms in the host cell at 6.8 GPa. The compression of Bi-III assuming 100% guest-site occupancy is plotted in Fig. 4. The previously reported Bi-III data of Chen *et al.* [7,8] plotted according to their proposed structure (×) show the unphysical density decrease from Bi-II referred to. When these data and the other previously reported data of Brugger [3] are plotted as the host-guest structure [17,18], as shown (∘), the agreement with our present results is very good. Our results give the volume changes ($\Delta V/V_0$) at the II → III and III → V phase transitions as 3.5(1)% and 1.1(1)%, respectively. These values agree extremely well with the previous directly measured values of ~3.3(3)% [2] and ~1.2(3)% [2], respectively, thus supporting strongly the assumed 100% guest-site occupancy.

Although the structure of Bi-III has long been uncertain, more contentious still has been the possible existence of two further transitions within the Bi-III stability field at 4.3 and 5.3 GPa. Since the first report in 1935 [1], a large number of studies using a wide variety of experimental techniques have been unable to agree whether these transitions are real or not [6]. The host-guest nature of the structure opens up the intriguing new possibility of transitions occurring only within the guest component without affecting the host, such as we have already found in Ba and Sr [10,11]. We have looked for this in Bi-III, but so far our data show no changes in either the guest reflections or in the two additional reflections marked in Fig. 2. However, our work on Ba suggests that these subtle transitions may be dependent on sample conditions, and hence sometimes appear and sometimes not. This would be an elegant solution to an elusive problem, but further studies are needed.

Prior to Bi-III, the $P4/n$ structure was proposed for the structure of Sb-II, stable above 8.6 GPa [9], and subsequently As-III, stable above 48 GPa [19,20]. We find that the reported d-spacings for Sb-II at 9.5 GPa [21] and 12 GPa [9] can be fitted by the same host-guest structure as we report here for Bi-III [22], with $a_H = 8.032(6)$ Å, $c_H = 3.899(4)$ Å, and $c_G = 2.988(6)$ Å at 9.5 GPa, and $a_H = 7.965(5)$ Å, $c_H = 3.858(4)$ Å, and $c_G = 2.945(5)$ Å at 12 GPa. The c_H/a_H and c_H/c_G ratios of ~0.485 and ~1.307 are very close to those found in Bi-III. The resulting calculated volume change ($\Delta V/V_0$) at the Sb-I → Sb-II transition is 6.4%, significantly larger than the value of 1.6% obtained assuming the $P4/n$

structure. However, *neither* of these values agrees with the 3.7% change reported by Bridgman from volumetric studies [23]. We have now made our own diffraction study of Sb-II. We observed 14 non-$hk0$ guest reflections in Sb-II, five of which (not reported in Ref. [9]) cannot be accounted for by the $P4/n$ structure. And the atomic volume of Sb-II obtained from our data lies very close to the compression data of Bridgman [23], as shown in the inset of Fig. 4. As in Bi-III, the profiles from Sb-II contain some very weak reflections not accounted for by the host and guest unit cells. The two most intense of these reflections are in the same positions as the extra peaks observed in Bi [see inset (ii) of Fig. 1], suggesting that they are a reproducible feature of these phases.

The limited number of reflections reported for As-III by Greene *et al.* [19] can all be accounted for by the $P4/n$ unit cell alone, and the host-guest structure thus provides no better a fit. The reported densities of As-II and As-IV [19] also offer no distinction between the two structures. However, in the light of the present results on Bi and Sb, it is not improbable that As-III too has the Ba-IV-type incommensurate structure. New high-quality diffraction data from As-III are now required (see note added).

The Ba-IV structure is thus emerging as a significant new type of atomic arrangement in metals. Furthermore, Schwarz *et al.* have recently reported a related structure for phase IV of Rb [24]. It has chains running through a (more complex) host structure, but the chains were found to be *commensurate* with the host [25]. The remarkable similarity of the Bi-III (and Ba-IV, Sr-V, and Sb-II) structure to the monatomic equivalent of the In_5Bi_3 structure is intriguing. There are many other related 3^2434 structures [16], and Schwarz *et al.* [24] note that the Rb-IV structure resembles the metal-atom sublattice in another alloy structure, Si_3W_5, which is based on 3^2634 nets in the same notation [15,16]. All these relationships merit further investigation, and the origins of the entirely unexpected incommensuration need to be understood. First theoretical insights into the stability of the Ba-IV structure has now been obtained from calculations using a commensurate approximation [26], and Heine has suggested possible critical factors for the incommensuration such as charge density waves and the strength and form of the host-guest interaction [12]. Further work is also needed to determine the true structure of As-III (see note added), and to look for similar and related structures in other elemental systems.

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Note added.—Preliminary recent data are consistent with a tetragonal host and a monoclinic guest for As-III.

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