Incommensurate modulations of Bi-III and Sb-II

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Single-crystal diffraction data from the incommensurate host-guest composite structure of Bi-III—stable between 2.8 and 7.7 GPa—are found to contain very weak satellite reflections arising from structural modulations attributed to interactions between the host and guest structures. The principal effects of the modulation are a quasipairing of the guest atoms along their chains and some reduction in the closest approach of the host and guest atoms. It is suggested that these modulations play a key role in the stability of the structure. A similar modulated structure fits powder-diffraction data from Sb-II.

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We have recently shown that Bi-III, the stable phase of bismuth between 2.8 and 7.7 GPa, has a complex elemental structure type,[1] first observed in Ba,[2] and since found also in Sr, Rb, K, Sb, As, and Sc.[3–10] This comprises a tetragonal host structure and an interpenetrating guest structure that is incommensurate with the host along the tetragonal c axis.[1] There is then a noninteger number of atoms in the host unit cell, and this yields a density remarkably close to that measured by Bridgman.[11] The same applies to Sb-II.[1,7,8,11]

An incommensurate composite structure is a remarkably complex arrangement to find in an element; it seems almost a contradiction in terms that a single phase of an element should form two different, interpenetrating and weakly interacting structures. This raises interesting questions as to the role of the incommensuration in the stability of the structure and about possible differences in electronic configuration between the atoms in the host and guest components—which calculations have indicated in the case of Ba.[12] However, no such difference was observed in the computational study of Bi, Sb, and As by Häussermann *et al.*[13] As shown in Fig. 1, the guest atoms form chains lying in channels in the host framework and a particular puzzle is as to how the chains, which are more than 5 Å apart, interact to form a well crystallized three-dimensional (3D) structure.

A similar problem has been examined in the more familiar context of a multicomponent incommensurate composite system, $Hg_{3-\delta}AsF_6$, in which Hg chains lie in nonintersecting perpendicular channels in an AsF_6 host framework, and form an ordered 3D structure only below 120 K.[14] Even though these chains are relatively close together, at a separation of just over 3 Å, modeling indicated that a direct Coulomb interaction between the chains would be too weak to order them,[15] and chain-chain interactions through distortions of the host framework were also concluded to be too weak.[16] Yet we have found that the guest structure in Ba-IV remains stable to at least 700 K, and that in Bi-III to at least 450 K [where it transforms to Bi-VII (Ref. 17)]. The chain-chain or chain-host interactions in these metals are clearly strong enough to order the guest structure to much higher temperatures than in $Hg_{3-\delta}AsF_6$ despite the larger chain separation and screening by the metallic host framework. Only in Rb-IV have we found any evidence for "melting" of the guest component at room temperature, but in this case the chains are even further apart, at some 7 Å.[5,18]

The strength of the host-guest interactions can be probed structurally, as they would be expected to give rise to modulations of both components. No evidence for this has yet been reported in the powder-diffraction studies of alkali and alkaline earth metals or of Sc,[2–6,9,10] but we previously reported that powder profiles of Sb-II contained two very weak additional peaks not predicted by the basic composite structure.[1] The same two peaks, although *extremely* weak, are also evident in powder profiles from Bi-III. A powder-diffraction study of Sb-II by Schwarz *et al.*[7] has found some significant modulations but not in the guest chains. In this paper, we report a complete determination of the modulations in any of these composite systems, using single-crystal diffraction techniques to study Bi-III, and show a strong modulation of the chain atoms such that they form a quasipairing arrangement. We also now find detectable modulation reflections in further data collection from Ba-IV, and we

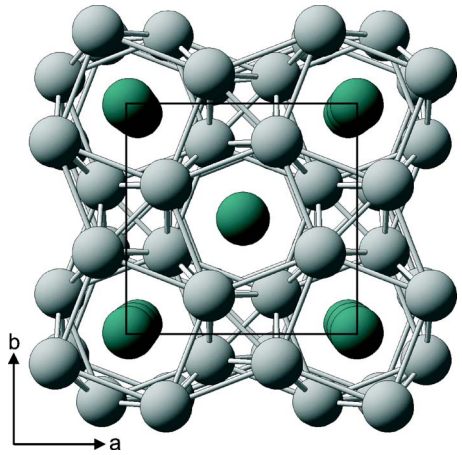

FIG. 1. (Color online) Incommensurate host-guest structure of Bi-III and Sb-II as viewed down the tetragonal c axis. The host atoms are shown as light spheres, and the guest atom chains as dark spheres.

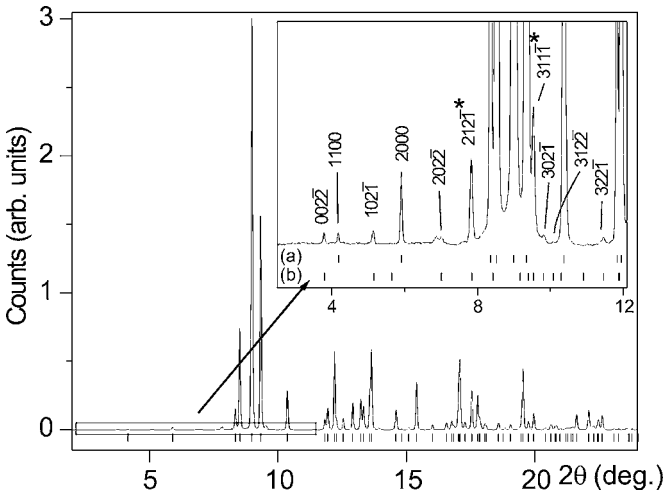

FIG. 2. Powder-diffraction profile from Sb-II at 10.3 GPa. Tick marks beneath the main profile mark the calculated position of reflections from the basic composite structure. The inset shows additional weak satellite reflections, and the tick marks mark the calculated positions of (a) the basic composite and (b) the satellite reflections. Asterisks mark the two satellite reflections detected in the previous study (Ref. 1).

argue that incommensurate modulations play a key role in the stability of this intriguing structure type in the elemental metals.

Experiments were performed with Bi samples of 99.999% purity and Sb samples of 99.9999% purity, obtained from the Institute of Rare Metals, Russia, and the Aldrich Chemical Company, respectively. Initial angle-dispersive powder-diffraction data from Sb-II were collected on ID09 at the European Synchrotron Radiation Source (ESRF) using an image-plate detector and a wavelength of 0.4157 Å. The resulting two-dimensional diffraction images were integrated using FIT2D (Ref. 19) to give standard diffraction profiles. Rietveld analysis of these profiles was performed using the JANA2000 software package.[20]

In our original powder study, we treated the diffraction patterns of Sb-II and Bi-III as a superposition of two 3D reciprocal lattices—one from the host and one from the guest, with common reflections in the $(hk0)$ layer where the two lattices coincide.[1] However, in what follows, it will be advantageous to describe the composite structure in four-dimensional (4D) superspace and index all the diffraction peaks using four integers $(hklm)$, according to $\vec{H}=h\vec{a}^*+k\vec{b}^*+l\vec{c}_H^*+m\vec{c}_G^*$, where $\{\vec{a}^*,\vec{b}^*,\vec{c}_H^*\}$ and $\{\vec{a}^*,\vec{b}^*,\vec{c}_G^*\}$ define the host and guest reciprocal lattices, respectively.[21] Reflections from the host component of the basic composite structure have indices $(hkl0)$, those from the guest have indices $(hk0m)$, and the $(hk00)$ reflections are common to both host and guest. Interactions between the host and guest will result in shifts with respect to the lattice periodic atomic positions, described by modulation functions within the superspace formulism,[21] giving rise to satellite reflections $(hklm)$ with both $l\neq 0$ and $m\neq 0$.

Figure 2 shows the powder profile collected from Sb-II at 10.3 GPa. All the strong reflections are accounted for by the basic host-guest structure with $a=8.0676(7)$ Å, $c_H=3.9071(5)$ Å, and $c_G=2.9817(8)$ Å, but the very high intensity of the ESRF reveals 11 additional reflections. Only the two strongest of these, $(212\bar{1})$ and $(311\bar{1})$, were detected in our previous study.[1] All 11 additional reflections can be indexed as first-order satellites (with $n=\min\{|l|,|m|\}=1$) or second-order $(n=2)$ satellites, with the $(hklm)$ indices shown. The two additional reflections observed previously in powder profiles from Bi-III (Ref. 1) can also be indexed as the $(212\bar{1})$ and $(311\bar{1})$ satellites.

The powder-diffraction profiles of Sb-II and Bi-III allowed the nature of the additional peaks to be established, but the weakness of these peaks and their overlap with the (much stronger) main reflections prevented any reliable determination of the details of the modulations beyond that obtained by Schwarz *et al.*[7] Single-crystal data were evidently required for this, but we were unable to grow a single crystal of Sb-II. We thus turned to Bi-III, which has even weaker satellite reflections but which had previously been obtained as quasi-single-crystal samples.[1] Many attempts using the method described previously[1] eventually yielded an acceptable single-crystal sample at 5.5 GPa.

Single-crystal x-ray data were collected on station 9.8 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory, using a Bruker Platform diffractometer equipped with a SMART 1K charge coupled device (CCD) detector.[22] The x-ray wavelength was 0.4815(1) Å, and data were collected in a series of ω scans. Indexing of the main reflections gave lattice parameters of $a=8.5562(4)$ Å, $c_H=4.1817(3)$ Å, $c_G=3.1950(2)$ Å, and $\gamma=1.309(1)$. In addition, first-order satellite reflections with (l,m) indices $(\bar{1},1)$, $(2,\bar{1})$, $(\bar{1},2)$, $(3,\bar{1})$, (1,1), $(4,\bar{1})$, (2,1), and (3,1), and second-order satellites with indices $(3,\bar{2})$, $(\bar{2},2)$, $(4,\bar{2})$, $(\bar{2},4)$, and (2,2) were detected and integrated. A total of 1621 main reflections and 1103 modulation reflections were collected. After removing reflections affected by powder lines from the pressure cell materials or by Bragg reflections from the diamonds anvils, making corrections for sample and pressure cell absorption,[23] and averaging over symmetry-related reflections, the final data set contained 238 main reflections, 111 first-order satellites, and 31 second-order satellites with $I>5\sigma(I)$. There were no detectable third- or higher-order satellites.

We have previously reported the superspace group of Bi-III and Sb-II as $I'4/mcm(00\gamma)0000$, where I' denotes the centering $(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$ in superspace, and $\gamma=c_H/c_G$, where c_H and c_G are the c-axis repeat distances of the basic host and guest structures, respectively.[8,24,25] In their recent powder study of Sb-II, Schwarz *et al.*[7] reported that three superspace groups—$I'4/mcm(00\gamma)0000$, $I'4cm(00\gamma)0000$, and $I'422(00\gamma)0000$—were consistent with the average positions of the host and guest atoms, and they refined their data using $I'422(00\gamma)0000$ as it was the only one of the three space groups that allowed a nonzero amplitude of the first harmonic modulation wave of the guest-atom modulation.

As noted by Schwarz *et al.*[7] the average host-atom structure of Sb-II and Bi-III can be well described using the $8h$ $(x,x+\frac{1}{2},\frac{1}{2})$ positions of space group $I4/mcm$, the $8j$ $(x,x+\frac{1}{2},\frac{3}{4})$ positions of space group $I422$, or the $8c$ $(x,x+\frac{1}{2},z$

$\sim\frac{1}{4}$) positions of space group $I4cm$. The 8h positions of $I4/mcm$ and the 8j positions of $I422$ describe an identical arrangement of atoms, while if $z=\frac{1}{4}$ in the 8c positions of $I4cm$, then this too describes the same atomic arrangement. Refinements of the ($hkl0$) host reflections with $l\neq 0$ in space group $I4cm$ revealed that the refined value for the z coordinate was 0.272(12), within 2σ of $\frac{1}{4}$. The spacial arrangement of the host atoms is thus the same when refined in all three space groups, and we have thus chosen the highest-symmetry description, the 8h positions of space group $I4/mcm$. Furthermore, a distinction between the (3+1)D superspace groups, $I'4/mcm(00\gamma)0000$ and $I'422(00\gamma)0000$, can be made from the systematic absences of the modulation reflections, where the superspace c-glide condition in $I'4/mcm(00\gamma)0000$ leads to the reflection condition ($0klm$), $k+m,l=2n$. Close analysis of the ($0klm$) reflections in both the powder and single-crystal data shows that this condition is satisfied, and therefore that the superspace group of Bi-III can be uniquely determined as $I'4/mcm(00\gamma)0000$. In this superspace group, symmetry restricts the modulation of the guest atoms to even orders of harmonic waves.

Refinement of the basic structure against the main reflections gave atomic coordinates $\left(0.1532(2),x+\frac{1}{2},0\right)$ for the host atom (Bi1) and (0,0,0) for the guest atoms (Bi2)—very similar to those we reported previously[1]—with an R factor of $R_{main}=9.0\%$. All refinements were performed with JANA2000. Initial refinements of the modulated structure using Fourier series to describe the modulation function were unsatisfactory: the fit to the second-order satellites was poor, and the introduction of further Fourier components resulted in unstable refinements. Further analysis was, instead, conducted using the BAYMEM program recently developed for a maximum entropy method (MEM) analysis of electron density in superspace.[26] Optimization of the electron density by BAYMEM converged to $R=4.1\%$ using all 380 reflections.

The superspace group of Bi-III puts symmetry restrictions on the possible modulations: the host atoms can be displaced along x, y, or z, with shifts in x and y related by symmetry, while the guest atoms can be displaced only along z. Modulation functions were obtained from the 4D electron density produced by the BAYMEM analysis by determining the position of the center of charge as a function of superspace coordinates x_{14} and x_{24},[21] as defined and shown in Fig. 3. For the host atom, the principal modulation has a block-wave-like form in the xy plane [Fig. 3(a)], and the displacements of the guest atom follow a distorted sawtooth function of period $\frac{1}{2}$ in x_{24} [Fig. 3(b)]. These two principal modulations have maximum displacements that are similar in magnitude (within a factor of $\sim$2), while those of the host atom along z are approximately an order of magnitude smaller and will be neglected. It was possible to model the modulation of the guest atom for subsequent structure refinements in JANA2000 using idealized functions, but such functions were unable to model the complex block-wave form of the host-atom modulation, and so harmonic functions were retained. Using these models, and including anharmonic temperature factors for both atoms, the final fit to the single-crystal data gave $R_{main}=6.4\%$, $R_{sat}^{1st}=9.3\%$, and $R_{sat}^{2nd}=16.1\%$. We note that the fit to the main reflections improves from $R_{main}=9.0\%$ to 6.4% on introduction of the modulation. The relatively high R values for the satellites are explained by their low intensities and the remaining imperfections in the model for the modulation functions.

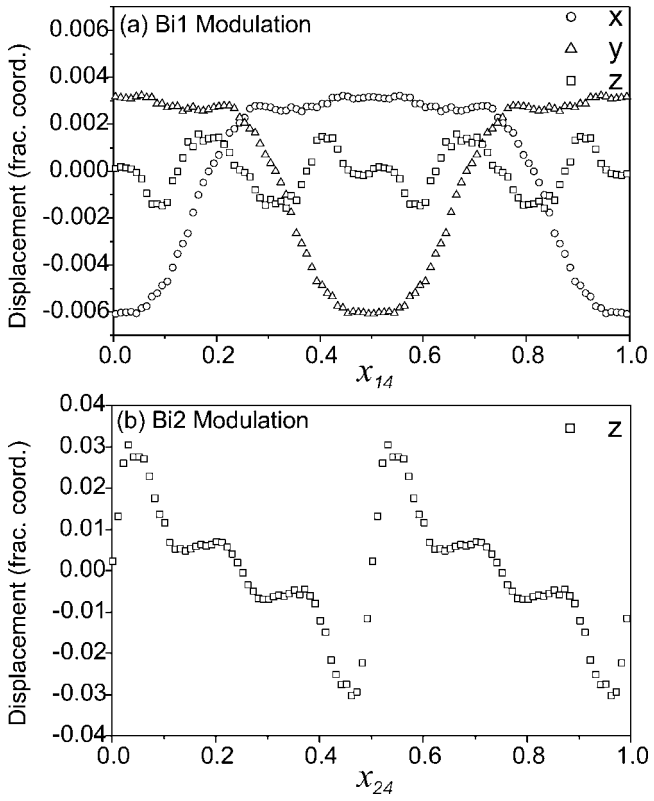

FIG. 3. Displacements (in fractional units) of the Bi1 host atoms and Bi2 guest atoms away from their unmodulated positions, as determined from the MEM refinement, as a function of x_{14} and x_{24} (Ref. 21), respectively. x_{14} can be considered as the fractional coordinate of the host atoms in the guest unit cell, given by $x_{14}=z(\mathrm{Bi1})c_H/c_G$, and x_{24} as the fractional coordinate of the guest atoms in the host unit cell, given by $x_{24}=z(\mathrm{Bi2})c_G/c_H$. The displacements shown apply (a) to the host atoms at (0.1532, −0.3468, $z=0,1,2,\ldots$) and, with the sign of the x and y deviations reversed, to the host atoms at (−0.1532, −0.3468, $z=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$), and (b) to the guest atoms at (0,0, $z=0,1,2,\ldots$) and at ($\frac{1}{2},\frac{1}{2}$, $z=\frac{1}{2},\frac{3}{2},\frac{5}{2},\ldots$). (The x_{14} values for the seven layers of Bi1 atoms shown in Fig. 4 are 0.000, 0.654, 0.309, 0.964, 0.618, 0.273, and 0.927 from bottom to top. The x_{24} values for the five guest atoms in Fig. 4 can be read directly as 0.000, 0.764, 0.528, 0.292, and 0.056.)

We thus believe that the most accurate determination of the modulation functions is given by the results of the MEM analysis, but the limited diffraction data measurable along the c^* axis leaves some uncertainty about the exact details of the fine structure of the sawtooth-shaped guest-atom modulation, particularly the magnitude of the departures from a simple sawtooth shape. Although the MEM analysis suggests that the guest-atom modulation is continuous in x_{24} and passes through zero at $x_{24}=0$ and $\frac{1}{2}$, it seems physically more probable that this modulation is actually *discontinuous* at $x_{24}=0$ and $\frac{1}{2}$, and that the limited c^*-axis resolution of the data smears the discontinuities out in the MEM analysis. In analyzing the effects of the modulation on the Bi-Bi dis-

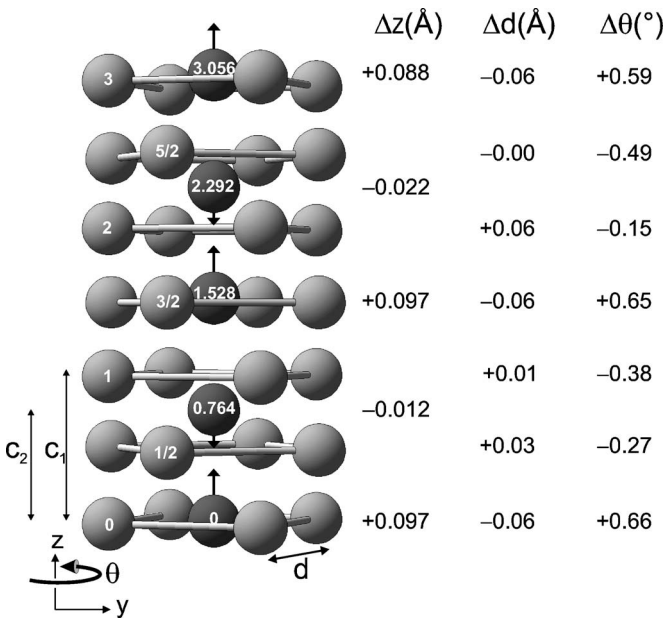

FIG. 4. Part of the Bi-III structure plotted over the range $-0.5<x<0.5$, $-0.5<y<0.5$, and $0\leqslant z<3.2$, where z is referred to the host unit cell. Host atoms (light spheres) and guest atoms (dark spheres) are all shown in their unmodulated positions. Some atoms are labeled with their z coordinates relative to the host unit cell. The host atoms referred to in Fig. 3 are those furthest to the left in each layer. The host atoms form squares in the x-y plane of side d, oriented at angle θ around z. Arrows on the guest atoms show (much exaggerated) the relative magnitudes and directions of the modulation displacements derived from Fig. 3. The values of these displacements Δz (Å) are tabulated, with also the modulations Δd (Å) in d and $\Delta\theta$ (°) in θ for the host atoms.

tances, we have therefore assumed a guest-atom modulation that has maximum and minimum values, rather than zeros, at $x_{24}=0$ and $\frac{1}{2}$. The marginal uncertainty in this matter has little consequence as $<1\%$ of the atoms in the structure are affected.

The structure determined for Bi-III also gives a good fit to the powder data from Sb-II shown in Fig. 1. In particular, a sawtooth-shaped modulation function for the guest atom again gives a better fit to the data than a purely harmonic model.[24] While the modulation of the guest atoms in Sb-II is very similar to that observed in Bi-III, the modulation of the host atoms is twice as large, resulting in the significantly stronger satellite peaks observed in Sb-II. Further detailed comparison between the two structures will require a single-crystal study of Sb-II.

Figure 4 illustrates the nature of the structural modulation over three unit cells of the host structure. A chain of guest atoms is shown passing through the origin of the structure, with the square arrangements of host atoms around the chain. All atoms are in their unmodulated positions, and the incommensurate nature of the basic composite structure is evident. The directions and magnitudes of the modulation displacements superimposed on this basic structure are indicated as described in the figure. These displacements can be derived directly from Fig. 3: for example, the guest atom at $z=1.528$ in the host cell is at $x_{24}=0.528$, which yields a deviation of +0.0305 in Fig. 3 and hence the displacement of +0.097 Å shown in Fig. 4. Figure 3 shows that guest atoms with unmodulated positions nearly coplanar with a host-atom square are relatively strongly displaced away from the plane of the square, whereas those with positions between the host-atom squares are (less strongly) displaced toward the midpoint. (We have assumed above that guest atoms coplanar with the squares are also strongly displaced.) The net effect on the guest chains can be seen to produce a quasipairing of atoms. This is a quite marked effect: the paired separations range from 3.16 down to 3.08 Å, with an interpair distance up to more than 0.2 Å larger at 3.23 and 3.31 Å compared with a constant guest-guest spacing of 3.195 Å in the unmodulated structure. The closest guest-guest approach is smaller than the closest approach distance of 3.118 Å in Bi-II at 2.7 GPa (Ref. 24), and is very comparable with the closest approach distance of 3.071 Å in Bi-I at atmospheric pressure.[27]

The modulation displacements of the host atoms are principally in the xy plane [Fig. 3(a)] and involve variations in both the size of the host-atom squares around the guest atoms (Δd in Fig. 4) and their orientation ($\Delta\theta$). The displacements reduce the closest approach distance of the host and guest atoms to 3.20 Å, a little below the closest-contact distance of 3.24 Å found in the unmodulated structure, and cause the shortest host-host atom distance to vary between 3.12 and 3.16 Å about the 3.14 Å of the unmodulated structure. It can be seen in Fig. 4 that the host-atom squares contract around the points of strongest displacement of the chain atoms.

An *ab initio* calculation of the high-pressure behavior of As, Sb, and Bi has treated the incommensurate phases by approximating them with a commensurate supercell that has $c=3c_H$ and $\gamma=\frac{4}{3}=1.333$.[13] This approximation reproduces the stability ranges of the composite structures of all three elements very well (when extrapolated to 0 K). The relaxed structure has symmetry $P4/ncc$, and in Bi-III, the guest atoms form pairs—reminiscent of the true structure—with intra- and interpair distances of 3.05 and 3.32 Å, respectively, interpolated to 5.5 GPa ($V/V_0=0.815$).[13] A similar pairing of guest atoms is calculated in Sb and As. But, in contrast to the pairing predicted to occur in Li at high pressure,[28] there is significant electron density between the paired atoms and they are covalently bonded. Also, unlike the similar calculations performed earlier on Ba-IV,[12] no difference in the electronic configurations of the host and guest atoms is observed. Further information has come from results obtained from studies of alloys of Bi and Sb (75:25, 50:50, and 25:75) in the host-guest structure, conducted to look for experimental evidence of preferential occupancy of the host and guest sites.[29] No such evidence was found: it seems that the intermediate compositions are random alloys—even for the compositions (75:25 and 25:75) that would allow complete host-guest ordering.

These calculations and our structural results taken together offer a key insight into the puzzle of the stability of the guest structure, showing that if the chain atoms form pairs, then they are likely to be bonded—thus bringing about a strong modulation of the electron density along the guest chains. The conclusions discussed above about the expected

weakness of possible interactions in the case of $Hg_{3-\delta}AsF_6$ are based on the host and guest structures being unmodulated or only very weakly modulated, in which case their mutual incommensuration makes them essentially noninteracting.[14] However, Emery and Axe[15] noted that the range of direct chain-chain interaction would be increased by along-chain modulation of the electron density. Significant mutual modulations would also enhance indirect chain-chain interactions via distortions of the host. For example, where in Fig. 4 a host square contracts (negative Δd), the adjacent squares—of which the atoms shown in Fig. 4 are also part—must expand, and this is likely to constrain the relative positioning of the adjacent chains. These conclusions are evidently inconsistent with our previous finding that there are no detectable modulations in Ba-IV,[2] given the strength of interactions shown by the stability of the Ba-IV guest structure to at least 700 K. We have therefore collected further diffraction data from the single-crystal sample used in the previous study,[2] with the increased sensitivity to weak reflections afforded by the 9.8 station at SRS and its CCD detector. This has revealed numerous weak but readily detectable modulation reflections, with relative intensities that indicate modulations of a similar order of magnitude to those in Bi-III. We thus conclude that modulations play a key role in the structural stability. This can only be checked directly where we have single-crystal data (Bi-III and Ba-IV) or the modulation reflections are strong enough to be detectable in powder data [Sb-II and As-III (Ref. 24)]. But it is plausible that the chain melting in Rb-IV at the lowest extreme of its pressure range[5,18] arises from the significantly greater chain-chain separation. And it is plausible too that the rapid increase in ordering temperature with pressure observed[30] in $Hg_{3-\delta}AsF_6$ arises from increasing pressure-induced modulations as host-guest distances are reduced.

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