Pressure-induced incommensurate-to-incommensurate phase transition in antimony

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An incommensurate composite phase with a monoclinic host-guest structure, designated Sb-IV, is found between the previously known Sb-I and Sb-II phases, and an incommensurate to incommensurate transition between phases II and IV is described. The monoclinic Sb-IV phase is observed on both pressure increase between 8.2 and 9.0 GPa and on pressure decrease between 8.0 and 6.9 GPa. The full structure of Sb-IV, including a determination of the structural modulations of the host and guest components, is reported from x-ray powder diffraction data. The high-pressure phase of arsenic, As-III, is shown to have the same monoclinic composite structure.

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Recent advances in high-pressure powder and single-crystal diffraction techniques have led to the discovery of a new class of elemental incommensurate structures in the alkaline-earth elements Ba and Sr,[1,2] the alkali elements Rb and K,[3,4] and in the group-V elements Bi, Sb, and As.[5] Each of these composite structures comprises a host structure and interpenetrating linear chains of guest atoms that form a crystalline structure incommensurate with the host. Since their discovery, the composite incommensurate structures of Bi-III and Sb-II have attracted further experimental[6–10] and theoretical[9,11] work, aimed at understanding the reasons for their formation and stability and to study various phenomena associated with their incommensurability.

Bi-III, stable between 2.7 and 7.7 GPa, and Sb-II, stable between 8.6 and 28 GPa, are isostructural and comprise a body-centered-tetragonal (bct) host (space group $I4/mcm$) and a bct guest (space group $I4/mmm$).[5] Diffraction profiles of As-III, stable above 48 GPa,[12] are also found to be consistent with a composite structure, but with a bct host and a monoclinic guest.[5] However, while the basic composite structures account correctly for the known densities of Bi -III and Sb-II,[5] and all of the strongest peaks in their diffraction patterns, they do not account for a few very weak diffraction peaks observed in both phases, which arise from modulations of the basic host and guest components.[5,9] And the profiles of As-III contain some weak extra peaks and peak asymmetries that are not accounted for by the basic composite structure.

A recent powder diffraction study of Sb (Ref. 9) confirmed the composite nature of the Sb-II structure and attributed the additional weak reflections to structural modulations. The structure was refined in the four-dimensional (4D) superspace group $I'422(00q_3)0000$ (Ref. 13), where q_3 is the (incommensurate) ratio of the c-axis lattice parameters of the host and guest structures, c_H/c_G, and I' is the centering $(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$ in superspace.

A single-crystal study of Bi-III (Ref. 6) aimed at determining the detailed nature of the structural modulations revealed its true structure to have the superspace group $I'4/mcm(00_{q3})0000$ rather than the lower-symmetry $I'422(00_{q3})0000$.[9,14] In this structure, the guest atoms are not equally spaced within the c-axis chains, but rather their positions are modulated along the chains so as to form quasi-pairs. And, in addition, the host atom positions are modulated in the a-b plane.[6,7] Refinements of powder profiles of Sb-II showed that the same structural model fitted the diffraction data in this case too, with the same amplitude of displacements of the guest atoms, but with host atom displacements that were twice as large as those found in Bi-III.[6] These larger host-atom displacements then account for the larger modulation peaks observed in Sb-II.[5] The quasipairing of the guest atoms along the chains has also been found in a recent computational study of Bi-III and Sb-II, using a commensurate approximant to the true incommensurate structure.[11]

In this paper, we describe further detailed studies of the transition from Sb-I to Sb-II and report the discovery of a monoclinic composite incommensurate structure Sb-IV between Sb-I and Sb-II. This is the first report of a host structure with detectably nontetragonal symmetry in the elemental metals, and we find that this same structure also accounts for the additional peaks and peak asymmetries observed in As-III. The incommensurate to incommensurate Sb-IV $\leftrightarrow$ Sb-II transition is the first phase transition observed in the composite structures of the elements in which both host and guest components are observed to change symmetry.

Experiments were done with a powdered sample of 99.9999% purity obtained from the Aldrich Chemical Company. Angle-dispersive powder diffraction data were collected using an image plate area detector on station 9.1 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory with a wavelength of 0.4654 Å.[15] The 2D diffraction images were integrated azimuthally to obtain 1D profiles,[15] and structural information was obtained by Rietveld refinement of the integrated profiles using JANA2000.[16]

Below 8.0(1) GPa on pressure increase, only peaks from the ambient pressure Sb-I phase are observed (Fig. 1). Above this pressure, peaks from another more complex phase start to appear and the Sb-I peaks are almost completely absent at 8.2(1) GPa (Fig. 1). On further compression to 8.5(1) GPa, the diffraction pattern starts to simplify, and above 9.1(1) GPa the pattern corresponds to that expected from

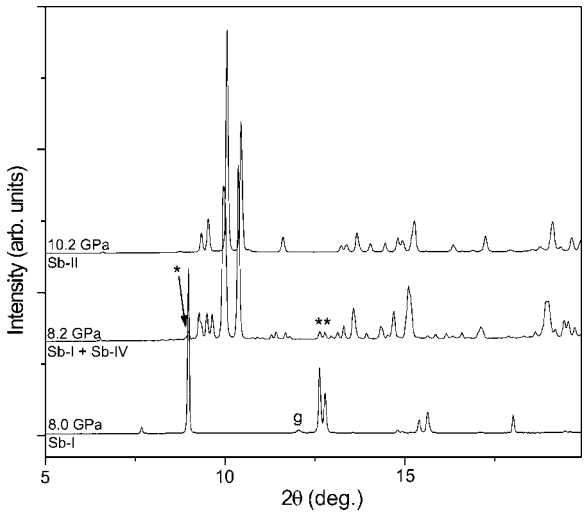

FIG. 1. Diffraction profiles of Sb collected on pressure increase (bottom→top), showing profiles from the Sb-I, Sb-IV, and Sb-II phases. The asterisks in the 8.2 GPa profile denote the remaining reflections from the Sb-I phase. *g* denotes a very weak diffraction peak from the gasket.

Sb-II.[5,6,9] It is evident in Fig. 1 that the phase to which Sb-I first transforms has a more complex diffraction pattern than Sb-II, and we designate this intermediate phase Sb-IV. We note that peaks from Sb-IV are also visible in the 8.7 GPa profile of Fig. 1 in Ref. 9

On pressure decrease, Sb-II starts to transform back to Sb-IV at 8.0(1) GPa (Fig. 2), giving the same complex diffraction pattern observed on pressure increase. Peaks from Sb-I are first observed at 6.9(1) GPa on pressure decrease, and below 6.4(1) GPa only peaks from Sb-I are observed. Sb-IV is thus stable between Sb-I and Sb-II over the range 8.2–9.0 GPa on pressure increase and 8.0–6.9 GPa on pressure decrease.

The incommensurate host-guest structure of Sb-II is described in 4D with the superspace group $I'4/mcm(00q_3)0000$.[6] All the diffraction reflections can then be indexed using four integers (h,k,l_1,l_2), according to $H=ha_H^*+kb_H^*+(l_1+q_3l_2)c_H^*$.[17] The indices of some intense host and guest reflections of the Sb-II phase are given in the 8.9 GPa profile of Fig.2. The indices of the two most intense first order $(min|l_1|,|l_2|=1)$ modulation reflections are given in the inset to Fig. 2.

The similarity of the diffraction patterns of Sb-II and Sb-IV (Fig. 2) suggests that Sb-IV also has a composite structure, but with a symmetry that is lower than that of Sb-II. By using the Sb-II pattern to distinguish host and guest peaks, the Sb-IV pattern obtained at 6.9 GPa on pressure decrease (Fig. 2) was indexed successfully on the basis of two unit cells: a body-centered monoclinic host with $a_H=8.171(1)$ Å, $b_H=8.160(1)$ Å, $c_H=3.951(1)$ Å, and $\beta_H=90.54(1)°$ and a body-centered monoclinic guest with $a_G=8.182(1)$ Å, $b_G=b_H$, $c_G=3.008(1)$ Å, and $\beta_G=92.96(1)°$. The two cells share common *b* and *c* axes, and in both cells, $a_H\times\sin\beta_H=a_G\times\sin\beta_G$, thus ensuring that the host and guest cells have the same dimensions in projection down the *c* axis.

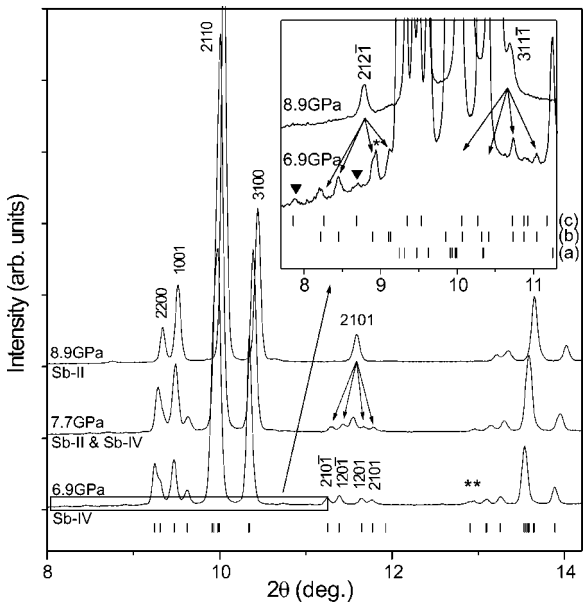

FIG. 2. Powder profiles of Sb collected on pressure decrease (top→bottom). The tick marks below the 6.9 GPa profile indicate the positions of the main host and guest reflections, some of which are indexed. The inset enlarges the low-angle regions of the single-phase Sb-II and Sb-IV patterns obtained at 8.9 and 6.9 GPa, respectively. The tick marks indicate the positions of (a) the main reflections, and (b) first-order and (c) second-order modulation reflections. (The magnification is so great that the modulation reflections are not visible in the main profile.) The filled triangles mark the clearly visible $02\bar{2}2$ and $\bar{2}02\bar{2}$ second-order modulation reflections. Arrows indicate the splitting of some peaks at the transition from Sb-II to Sb-IV. [Two of those derived from the $3\bar{1}11$ peak of Sb-II lie under the (2110) and (3100) main reflections.] The asterisks in the main 6.9 GPa profile and inset mark the appearance of the three strongest peaks from the Sb-I phase.

Analysis of the systematic absences in Sb-IV showed that the host and guest structures have the 3D space groups $I2/c$ and $I2/m$, respectively. The corresponding 4D superspace group is then $I'2/c(q_10q_3)00$, with $I'=(\frac{1}{2},\frac{1}{2},\frac{1}{2},\frac{1}{2})$, $q_1=(a_G\cos\beta_G-a_H\cos\beta_H)/c_G=0.114(1)$ (Ref. 18), and $q_3=c_H/c_G=1.313(1)$. The diffraction peaks of Sb-IV can then be indexed using four integers (h,k,l_1,l_2) according to $H=(h+q_1l_2)a_H^*+kb_H^*+(l_1+q_3l_2)c_H^*$.

But while this composite structure fits the positions of all the *main* host and guest reflections, it does not account for the positions of the modulation reflections. To fit the positions of both the main and modulation reflections it is necessary to use the alternative configuration of host structure with respect to the guest, with $\beta_{H(new)}=180°-\beta_{H(old)}=89.46°$, and hence $q_1\sim0.17$. The final refined lattice parameters from a Rietveld fit at 6.9 GPa are $a_H=8.1710(2)$ Å, $b_H=8.1616(2)$ Å, $c_H=3.9504(1)$ Å, and $\beta_H=89.456(1)°$ and $a_G=8.1815(2)$ Å, $b_G=b_H$, $c_G=3.0083(1)$ Å, $\beta_G=92.959(1)°$, $q_1=0.1662(1)$, and $q_3=1.3132(1)$. A determination of the true unit cell of Sb-IV, the relative arrangement of the host and guest structures, and the magnitude of the incommensurate wave vector, is there-

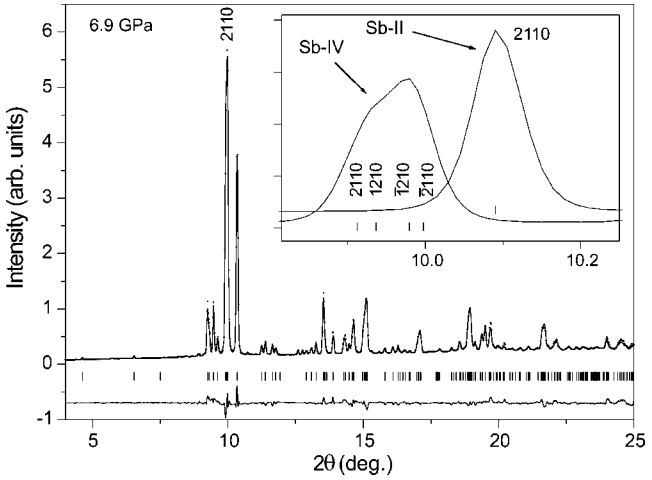

FIG. 3. Rietveld refinement of Sb-IV at 6.9 GPa. The tick marks beneath the profile indicate the positions of the main host and guest reflections. The inset shows the splitting of the strongest host reflection of Sb-II at 8.9 GPa, (2110), into four reflections of Sb-IV at 6.9 GPa.

fore only possible using a combination of both main and modulation reflections.

The final Rietveld fit to the diffraction pattern of Sb-IV at 6.9 GPa is shown in Fig. 3 and is excellent (R_p=4.5%, R_{wp} =5.9%, χ^2=0.99). Sb-IV has eight host atoms in the general (x,y,z) position and two guest atoms at $(0,0,0)$ of the superspace group $I'2/c(q_1 0 q_3)00$. The refinement of Sb-IV was performed using both the main (host and guest) reflections and modulation reflections of both first and second order. The modulation was fitted with two different models: (1) a simple harmonic function and (2) a harmonic function for the host atoms and a combination of a harmonic function and a sawtooth function for the guest atoms. This second model, which is equivalent to that used in powder refinements of Bi-III and Sb-II gives a better fit for Sb-IV and is used to obtain the final atomic coordinates.[6] The atomic coordinates of Sb-IV at 6.9 GPa obtained from the final Rietveld fit are $(0.1611(4),0.6569(3),0.004(1))$ and $(0,0,0)$ for the host and guest atoms, respectively. This compares with the refined structure of Sb-II at 10.2 GPa, where the host and guest atoms are at $(0.1572(1),0.6572(1),0)$ and $(0,0,0)$, respectively, in superspace group $I'4/mcm(00q_3)0000$.

The similarity of the atomic coordinates of the host atoms in both structures and the very small departure ($\sim$0.5°) of β_H from 90° suggest that there is only a very small distortion of the host structure at the II-IV transition. However, the drop in symmetry from tetragonal to monoclinic is clearly evident in the splitting of *both* the main host and guest peaks of Sb-II: in particular, the greater departure of the guest β angle from 90° leads to asignificant splitting of the $(hk0l_2)$ guest peaks (Fig. 2). A monoclinic guest structure has previously been reported in Ba-IVa, although the β angle is a little larger in that case (96.15°), and the guest structure is C face centred rather than body centered.[1] However, in Ba-IVa *only* the guest structure was observed to have monoclinic symmetry—no splitting or asymmetry of the main host reflections was observed. However, a description of the composite Ba-IVa structure in 4D superspace necessarily requires a monoclinic superspace group, and the host structure of Ba-IVa must also therefore have monoclinic symmetry, but with a β angle that is, as yet, indistinguishable from 90°.

The transition from tetragonal to monoclinic symmetry also leads to a splitting of the modulation peaks, as illustrated for the $21\bar{2}1$ and $31\bar{1}1$ reflections in the inset to Fig. 2. Although two similarly split second-order modulation peaks—$0\bar{2}2\bar{2}$ and $\bar{2}0\bar{2}2$—are also visible in the Sb-IV profile (as marked by the solid triangles in the inset to Fig. 2), the corresponding (unsplit) second-order 0222 peak in the Sb-II pattern is too weak to observe. This suggests a change in the magnitude and/or the form of the modulation at the Sb-II $\rightarrow$ Sb-IV transition.

The extreme weakness of the modulation reflections and the fact that the great majority of them are overlapped by the much stronger main reflections makes a detailed study of the modulations using powder techniques very difficult. However, the pressure dependence of the modulation in Sb-II could be estimated by extracting the intensity of the first-order $(2\bar{1}2\bar{1})$ modulation reflection (see the inset to Fig. 2) and normalizing this to the intensity of the (3100) reflection, which, because $l_1=l_2=0$, does not depend on the modulation. As the pressure is increased from 8.9 to 25.6 GPa, just below the transition to Sb-III, the relative intensity of the $2\bar{1}2\bar{1}$ reflection decreases from 1.4(3)% to 0.6(2)%. Assuming that only the amplitude, and not the form, of the guest-atom modulation changes over this pressure range, the closest approach distance between the guest atoms in the quasipairs decreases by only 1.4% from 2.831 to 2.792 Å between 8.9 and 25.6 GPa, while over the same range the average guest-guest intrachain distance ($=c_G$) decreases by 3.5% from 2.991 to 2.887 Å. A similar effect of relative pressure independence of the closest approach between the modulated atoms has been recently reported for a modulated high-pressure structure of Te-III.[19]

While the symmetry of the Sb-II structure requires that the guest atoms are modulated only along the *c*-axis chains, which therefore remain linear, the monoclinic symmetry of Sb-IV allows additional modulations of the guest atoms in the $a-b$ plane. As a result of these additional displacements, the intensities of the Sb-IV modulation reflections are somewhat larger than those observed in Sb-II. For example, the sum of the normalized intensities of the four modulation reflections that comprise the $2\bar{1}2\bar{1}$ reflection of Sb-II (see the inset to Fig. 2) at 6.9 GPa is some 3 times larger than the intensity of the $2\bar{1}2\bar{1}$ reflection in Sb-II at 8.9 GPa. Rietveld refinement of the Sb-IV profile at 6.9 GPa reveals that the modulation of the guest atoms in the $a-b$ plane is significant, with a maximum displacement [0.88(30) Å] along the *y* axis that is considerably larger than the maximum displacement of the atoms along the chains [0.28(1) Å]. As a result, the guest atoms of Sb-IV again form quasipairs, but these are tilted with respect to the *c* axis, resulting in zigzag chains running along the host structure channels. This is the first example of nonlinear guest atom chains among the host-guest structures of elements. Sb-IV is then the most strongly

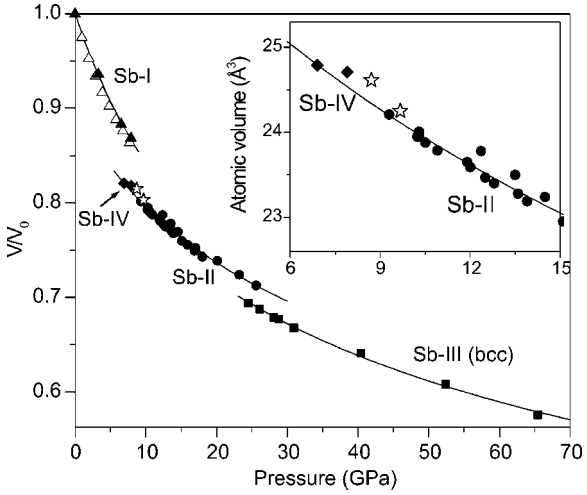

FIG. 4. The equation of state of Sb to 65 GPa. Data from the present study are plotted using solid symbols, while the compression data of Bridgman (Ref. 21) are plotted with open symbols. The inset shows an enlarged view of the compression of Sb-IV and Sb-II in the region of the transition. The solid curves through the data points represent the equations of state fitted using the second-order Birch-Murnaghan equation with the resulting values of K_0 =39.7(5) GPa and V/V_0=1 for Sb-I, K_0=71(2) GPa and V/V_0 =0.891(5) for Sb-IV and Sb-II, and K_0=74(3) GPa and V/V_0 =0.861(5) for Sb-III, with V_0=30.20(2) Å^3 and K_0'=4 for all phases.

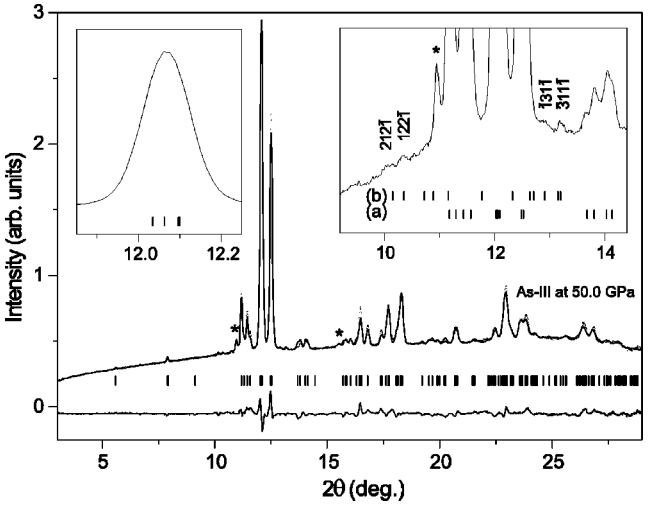

FIG. 5. Rietveld refinement of As-III at 50.0 GPa. The tick marks beneath the profile indicate the positions of the main reflections. The left-hand inset shows the group of the strongest host reflections and the right-hand inset shows the first order modulation reflections with their hkl_1l_2 indices. The tick marks indicate the positions of (a) the main reflections and (b) the first-order modulation reflections. Asterisks indicate reflections from the As-II phase with simple cubic structure.

modulated composite structure yet observed in the elements.

A determination of the exact volume change at the Sb-IV→Sb-II transition via a refinement of a mixed-phase profile is complicated by the overlap of many of the reflections in each phase. However, the discontinuity of the host and guest lattice parameters at the transition clearly identifies the transition as being first order, while extrapolation of the volumes of Sb-II and Sb-IV to a pressure of 8.0 GPa suggests that the volume change at the transition $\Delta V/V_{tr}$, where V_{tr} is the atomic volume of Sb-IV at the transition, is no larger than 0.5(1)%. Sb-II is stable to 28 GPa, where it transforms to body-centered-cubic Sb-III.[20] The volume change at the Sb-II→Sb-III transition is $\Delta V/V_{tr}$=3.3(1)%, where V_{tr} is the atomic volume of Sb-II at the transition. Sb-III is then stable up to at least 65 GPa, the highest pressure reached in the present study. The volume change at the Sb-I→Sb-IV transition is V/V_{tr}=5.0(1)%, where V_{tr} is the atomic volume of S-I at the transition. A revised phase transition sequence of Sb under pressure at room temperature is thus: Sb-I (As-type)→Sb-IV (incommensurate monoclinic composite) →Sb-II (incommensurate tetragonal composite) →Sb-III (bcc). The equation of state of Sb to 65 GPa is shown in Fig. 4.

Previously, we reported that a preliminary study of As showed that As-III, stable above 42(1) GPa, has a composite incommensurate structure similar to that in Sb-II and Bi-III, but with a tetragonal host structure and monoclinic guest.[5] However, the fit to the As-III data was less satisfactory than for either Sb-II and Bi-III, and the proposed composite structure left a number of extremely weak additional peaks unaccounted for. More detailed refinements now reveal that As-III has the same monoclinic structure as Sb-IV, with the same $I'2/c(q_1 0 q_3)00$ space group, and that the four additional peaks arise from modulations of the structure. At 50.0 GPa, the refined cell parameters are a_H=6.7673(2) Å, b_H=6.7464(2) Å, c_H=3.2491(1) Å, and β_H=89.654(2)° and a_G=6.7719(2) Å, $b_G=b_H$, c_G=2.4903(1) Å and β_G =92.099(2)° and the modulation vector has q_1=0.1162(3) and q_3=1.3047(1) and the host and guest atoms are at **(**0.1612(5),0.6521(5),−0.004(2)**)** and (0,0,0), respectively. A Rietveld refinement of a diffraction profile obtained at 50.0 GPa is shown in Fig. 5. Attempts to determine the nature of the structural modulations in As-III were unsuccessful—although four first-order modulation reflections are visible (as highlighted in the inset to Fig. 5), the quality of the diffraction data is insufficient for quantitative analysis of the modulation parameters. Single-crystal data are thus required. We have followed the composite structure of As-III up to a maximum pressure of 52 GPa and have observed no subsequent phase transitions. Further studies are thus required to determine whether As-III undergoes a transition to a Sb-II-like tetragonal composite structure at higher pressures, before the transformation to a bcc phase, reported at 97 GPa.[12]

In summary, a high-pressure phase of Sb, Sb-IV, with a monoclinic composite structure has been found between the previously known Sb-I and Sb-II phases; the lower symmetry of Sb-IV results in larger structural modulations and nonlinear guest atom chains, and As-III also has the Sb-IV structure. An understanding of why Sb-II becomes unstable with respect to Sb-IV and indeed why such complex structures are stable at all is now required. Although constrained to using commensurate approximations to the true incommensurate

structures, conventional computation methods have recently been used to investigate the host-guest composite structures of Bi, Sb, and their alloys (Refs. 11 and 22). Similar techniques might therefore be used to provide insight into the energetics of the present incommensurate-to-incommensurate transition by a suitable choice of approximant structures.

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[14] In the powder study of Sb-II reported in Ref. 9 it was not possible to distinguish between three different spacegroups for the host and guest structures. The 4D space group of $I'422(00q_3)0000$ was then chosen as the other two possibilities require that the first-order modulation waves for the guest atoms have zero amplitude. In the present powder study of Sb-II, we can also make no definite distinction between the same three spacegroups, but we have assumed that Sb-II is isostructural with Bi-III and have therefore made our refinements in superspace group $I'4/mcm(00q_3)0000$. This makes no difference to our conclusions.

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