

## Self-Hosting Incommensurate Structure of Barium IV

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(Received 11 June 1999)

The structure of phase IV of barium has been solved from single-crystal and powder diffraction x-ray data. It is composed of a tetragonal “host,” with “guest” chains in channels along the  $c$  axis of the host. These chains form two different structures, one well crystallized and the other highly disordered and giving rise to strong diffuse scattering. The guest structures are incommensurate with the host.

PACS numbers: 61.50.Ks, 62.50.+p

At room temperature, barium is known to transform at 5.5 GPa from its ambient-pressure body-centered cubic (bcc) structure to phase II with a hexagonal close-packed (hcp) structure, then to the complex structure of phase IV at 12.6 GPa, and to another hcp phase, V, at 45 GPa [1]. Phase V is stable to at least 90 GPa [1]. A striking feature of phase II is a strong pressure dependence in the  $c/a$  axial ratio, which falls to  $\sim 1.50$  at the II-to-IV transition, well below the value of 1.633 for an ideally close-packed structure; by contrast, the ratio is almost pressure independent at  $\sim 1.58$  in phase V [1]. Barium has long attracted theoretical interest for its pressure-induced  $s \rightarrow d$  electron transfer under pressure [2]. In recent calculations, Zeng *et al.* [3] confirm a strong  $s \rightarrow d$  transfer over the range of phase II, and show that it is the effect of  $d$ -electron repulsion for the range of Ba-Ba distances found in phase II that accounts for the instability of  $c/a$ . However, this effect diminishes as the Ba-Ba distance is reduced further, in accord with the reappearance of a stable hcp structure with a nearly pressure-independent  $c/a$  ratio in phase V. Barium may thus be correctly understood as having a single hcp phase that has a range of instability from 12.6 to 45 GPa. Phase diagram studies have led to the related conclusion that phase V may be a reentrant phase II [4].

Further progress is impeded by the lack of knowledge about the nature of the intervening phase IV. All previous attempts at solving its structure have failed [1,5,6]. Even the unit cell—and hence the equation of state—remains unknown. This phase gives strongly textured, “spotty” powder diffraction patterns. Takemura found that many of the stronger peaks could be indexed on a small body-centered tetragonal (bct) cell, but that this left many weaker features unexplained [1]. We now report a solution that is a complex structure composed of interpenetrating components—a “host” and two different forms of “guest” that are incommensurate with the host.

Most experiments were done with samples of stated purity 99.9 + % purchased from Johnson Matthey. Some comparative data were collected from samples of stated purity 99.994% from Aldrich Chemical Company. 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  $0.4654(1) \text{ \AA}$  [7]. Single-crystal data were collected on 9.1 (using the same setup as for powder diffraction), on a CAD4 4-circle diffractometer on station 9.8 at SRS at wavelength  $0.6891(1) \text{ \AA}$ , and on a laboratory-source CAD4 using the  $\text{MoK}\alpha$  wavelength  $0.71 \text{ \AA}$ . Samples were loaded by cutting small pieces from the purchased material under mineral oil and transferring them, still enveloped in oil, into diamond-anvil cells with chips of ruby for pressure measurement.

Smooth, well-resolved powder patterns were obtained in the bcc and hcp phases, with very low levels of contaminant. We observed no detectable level of the BaO reported by Takemura [1], but did detect a small amount of an unknown hexagonal phase. This was absent in some cases—which thus had no visible contaminant at all—and had no detectable effect on the other behavior of the sample. We found that the highly textured and spotty diffraction pattern of phase IV [1] could be smoothed by cycling the pressure up to  $\sim 25$  GPa and back down to  $\sim 13$  GPa. An integrated profile from such a pattern, collected at 12.9 GPa, is shown in the inset of Fig. 1.

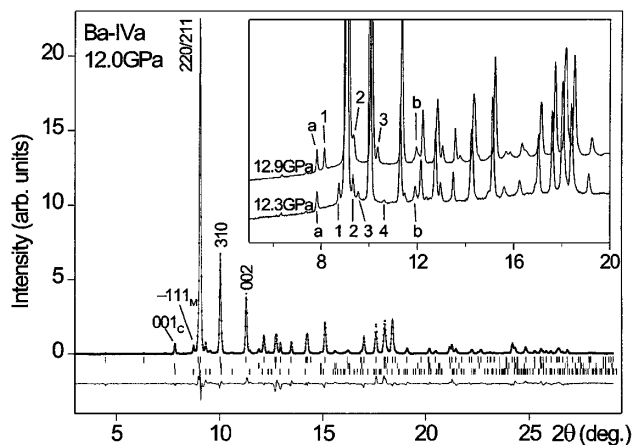


FIG. 1. Integrated 1D profile from Ba phase IVa at 12.0 GPa (dots) and a Rietveld refinement fit (line). The tick marks below the profile show the peak positions of the  $I$ ,  $C$ , and  $M$  components (see text). A few reflections of each are indexed. Below the tick marks is the difference between the observed and calculated profiles. The observed profiles in the inset are for IVa at 12.3 GPa and IVb at 12.9 GPa. The marked peaks are from the  $C$  component (lettered) and from the  $M$  component in IVa and the  $O$  component in IVb (numbered).

All except the labeled weak peaks can be indexed on a bct unit cell with  $a = 8.35 \text{ \AA}$  and  $c = 4.70 \text{ \AA}$ . This cell is related to Takemura's bct cell ( $a' = b'$ ,  $c'$ ) by  $\mathbf{a} = 2\mathbf{a}' + \mathbf{b}'$  and  $\mathbf{c} = \mathbf{c}'$ . No other cell could be found that fit the labeled weak peaks, which were also found to vary in intensity from sample to sample relative to the bct-cell reflections. Furthermore, many of them were observed to change on reducing the pressure—as shown at 12.3 GPa in the inset—while the reflections fitted by the bct cell were unaltered. The peaks labeled “a” and “1” in the 12.9 GPa profile correspond to unindexed peaks 1 and 2 in Takemura's Table II. (The other unindexed peaks in his Table II are all accounted for by our larger cell.) The transition in the weak peaks was found to be reproducible in different samples, with no detectable hysteresis at 12.5(2) GPa. We label the phase below this pressure as IVa and that above it as IVb. On the first pressure increase with a new sample, some transform from phase II to IVa at 12.0(2) GPa and others transform direct to IVb at 12.6(2) GPa. We find a small hysteresis in the II/IVa transition of  $\sim 0.3 \text{ GPa}$  [8]. Identical behavior was found in samples from the 99.994% pure material.

To investigate the origin of the weak unindexed peaks, we collected data as the pressure was increased very gradually through the II/IVa transition. The resulting sample was made up of a small number of relatively large crystallites, and striking diffuse scattering was revealed, in planes with a separation corresponding to a direct-space dimension of  $\sim 3.4 \text{ \AA}$ . (There is evidence for one of these diffuse lines, at the same position in reciprocal space, running from the “top” of line 4 to the “bottom” of line 12 in Takemura's Fig. 5a [1].) No sample showed a plane of diffuse scattering through the origin of reciprocal space.

After many attempts, a sample was transformed to one single crystal of phase IVa at 12.1 GPa. This gave the single set of diffuse lines shown in Fig. 2, each

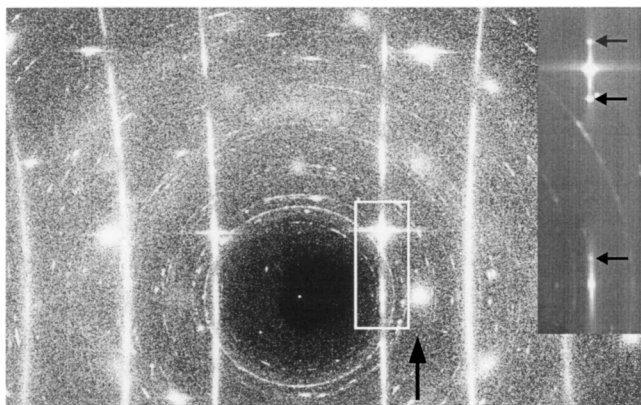


FIG. 2. 2D image from a single crystallite of Ba phase IVa showing  $l \neq 0$  lines of diffuse scattering. The powder rings are from the hcp phase and a weak contaminant (see text). The inset enlarges the marked area, and the arrows indicate  $M$  peaks adjacent to (stronger)  $C$  peaks. The arrow in the 2D image marks a line of  $I$ -lattice reflections.

decorated with a number of sharp reflections, some with “satellite” peaks on either side, as marked by arrows in the inset. Images recorded, as the sample was moved in  $0.5^\circ$  steps around an axis perpendicular to the diffuse planes, revealed the distribution of scattering in reciprocal space shown in Fig. 3. The open circles mark reflections from the main body-centered tetragonal ( $I$ ) unit cell ( $a_I = b_I = 8.42 \text{ \AA}$ ,  $c_I = 4.74 \text{ \AA}$ ). The large crosses mark reflections that can be indexed on another tetragonal unit cell with the same dimensions in the  $a$ - $b$  plane, but with a  $C$ -face-centered lattice and  $c_C = 3.41 \text{ \AA}$ . The filled circles mark reflections that can be indexed on four identical  $C$ -face-centered monoclinic unit cells, related by  $90^\circ$  rotations around the tetragonal  $c$  axis, with  $a_M = 8.46 \text{ \AA}$ ,  $b_M = a_I$ ,  $c_M = 3.43 \text{ \AA}$ , and  $\beta_M = 96.15^\circ$ . As indicated by the different sized circles, the reflections of one of these monoclinic ( $M$ ) lattices are much stronger than those of the other three. The  $I$ ,  $C$ , and  $M$  lattices are all commensurate with each other in the tetragonal  $a$ - $b$  plane. But, the  $C$  and  $M$  lattices—and the planes of diffuse scattering—are incommensurate with the  $I$  lattice along the  $c$  axis.

The same sample was used to collect accurate ( $hkl$ ) reflection intensities on the CAD-4 diffractometers. From these data, the structure solution shown in Fig. 4 was obtained by standard procedures using the program SIR92 [9]. The non- $hk0$   $I$ -lattice reflections give the host structure shown by the dark symbols. There are eight atoms in the unit cell, occupying site  $8h$  of space group  $I4/mcm$ , with coordinates  $x = 0.1486(1)$ ,  $y = x + 0.5$ , and  $z = 0$  at 12.1 GPa. Misfits of this structure to the  $hk0$  intensities revealed that the octagonal channels of the host are occupied by guest chains of atoms running along the tetragonal  $c$  axis. These chains form the structures

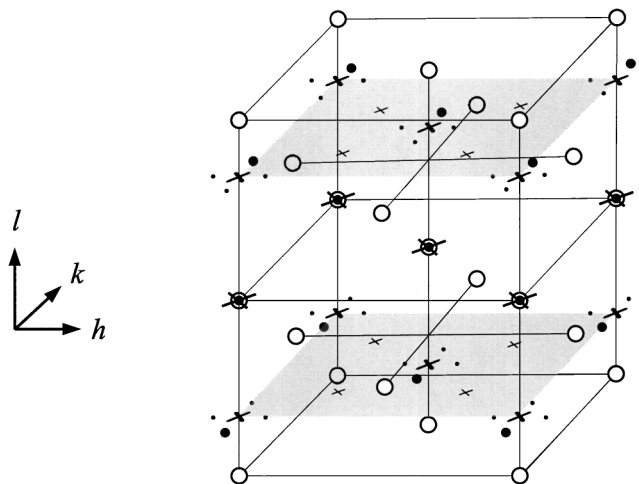


FIG. 3. Composite reciprocal lattice of phase IVa, showing the  $I$  (open circles),  $C$  (large crosses), and  $M$  (small filled circles) reflections, and planes of diffuse scattering. In phase IVb, the  $M$  reflections are replaced by peaks at the positions of the small crosses. The  $hk0$  reflections are from all three components, as indicated.

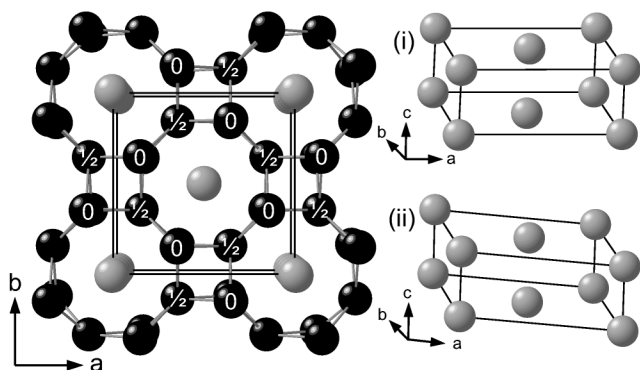


FIG. 4. Structure of Ba phase IVa. The host  $I$  structure (dark symbols) with guest chains (light symbols) is shown in a  $c$ -axis projection. The  $I$ -structure atoms are labeled with their  $z$  coordinates. The insets show (i) the  $C$  and (ii) the  $M$  guest structures.

shown as insets (i) and (ii) in Fig. 4, which give rise to the  $C$  and  $M$  reflections. The  $C$  intensities fall off rapidly with  $l$  index and refine to a structure in which the apparent thermal motion along the  $c$  axis has an rms amplitude  $\sim 0.3$  Å larger than in the  $I$  structure. This corresponds to a random disordering of the chains in position along  $c$  which also accounts for the sheets of diffuse scattering for  $l \neq 0$ . Measurements of reflection widths suggest that the correlation length of this structure in the  $a$ - $b$  plane is of the order of 100 unit cells. By contrast, the intensities of the  $M$  reflections fall off with  $l$  like those of the  $I$  reflections, and the  $M$  reflections show no detectable additional width. In the case of this sample, only  $\sim 10\%$  of the chains are in this well-crystallized  $M$  structure, and 85% of this is in one of the four independent  $M$  domain orientations. (Another sample showed  $\sim 50\%$  in the  $M$  structure with most of this divided approximately equally between two of the domain orientations.) A fit of this composite structure to a powder pattern of IVa at 12.0 GPa is shown in Fig. 1 [10]. The refined unit cell dimensions are  $a_C = b_C = b_M = a_I = 8.4207(13)$  Å,  $c_I = 4.7369(4)$  Å,  $a_M = 8.4623(35)$  Å,  $\beta_M = 96.151(9)^\circ$ ,  $c_C = 3.4117(5)$  Å, and  $c_M = 3.4269(7)$  Å. This indication of a very small ( $\sim 0.4\%$ )  $c$ -axis expansion on crystallizing to the monoclinic form is supported by the 2D images of the single-crystal sample which show the  $M$  reflections to be slightly displaced from the diffuse planes.

A similar study of the IVb phase was carried out on another single-crystal sample at 12.8 GPa. No change was found in the  $C$  or  $I$  structures in passing through the IVa/IVb transition apart from a small decrease in the excess “thermal motion” along  $c$  in the  $C$  form, which might indicate some reduction in the proportion of the disordered  $C$  component. But the four sets of monoclinic reflections in IVa were replaced by reflections at the  $h_C \pm 0.5, k_C + 0.5, l$  positions marked by small crosses in Fig. 3. These can be indexed on an orthorhombic unit cell with  $c = \sim 3.41$  Å and we denote this as the  $O$  com-

ponent of IVb. Refinements of powder data at 12.9 GPa give  $a_C = b_C = a_I = 8.346(3)$  Å,  $c_I = 4.6966(10)$  Å,  $c_C = 3.4095(5)$  Å and  $c_O = 3.4070(27)$  Å. Within error there is no difference between  $c_C$  and  $c_O$ . The single-crystal data quality is poorer in this sample, particularly after passing through the IVa/IVb transition, and the detailed structure of the well-crystallized  $O$  guest component in IVb has yet to be solved. However, it is clearly another arrangement of the  $c$ -axis chains.

Since the  $C$ ,  $M$ , and  $O$  guest structures are all identical in a  $c$ -axis projection, the relative occupancies of the host and guest parts can be obtained from a simultaneous fit to the  $hk0$  reflections and the non- $hk0$   $I$ -lattice reflections. In phase IVa at 12.1 GPa, the guest sites refine to a 100% occupancy within a 1% error. There are then  $c_I/c_{C,M} = 1.388$  guest atoms in each of the two channels in the  $I$  unit cell, and hence a total of 10.776 atoms in the  $I$  cell. The guest occupancy also refines to 100% within error in phase IVb at 12.8 GPa, but, because of the decrease in  $c_I/c_C$  with pressure shown in the inset to Fig. 5, there are 10.756 atoms in the  $I$  cell at this pressure [11]. On the assumption of 100% occupancy at all pressures, the measured  $c_I/c_C$  ratio can thus be used to derive  $V/V_0$  values, as plotted in Fig. 5 [12,13]. A value derived from Takemura’s data at 16.5 GPa is also shown and falls on our curve well within error. Since there is no discernible  $V/V_0$  discontinuity at the II/IV transition, something close to 100% occupancy of the guest sites is in fact required. The curve shown as a guide to the eye suggests that the density may also be continuous with phase V but, because the calculation of  $V/V_0$  depends on the  $c_I/c_C$  ratio, values have not been obtained above  $\sim 18$  GPa, the limit so far

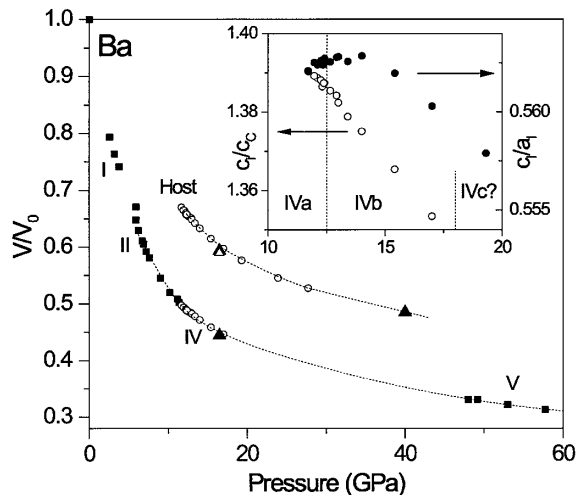


FIG. 5.  $V/V_0$  for the full phase IV structure of Ba, and for the host component (open circles). The host values have been offset for clarity. The curves are guides to the eye. Values for phases I, II, and V (solid squares) are from Ref. [1]. Values plotted as large solid triangles are from Ref. [1] at 16.5 GPa and Ref. [14] at 40 GPa. The one plotted as a small open triangle is from Ref. [6] at 16.5 GPa. The inset shows the pressure dependence of  $c_I/c_C$  and  $c_I/a_I$ .

of guest-structure data quality good enough to measure  $c_C$ . However, lattice parameters have been obtained for the host structure to 24 GPa and its  $V/V_0$  is plotted in Fig. 5, along with values taken from two previous studies at 16.5 GPa [1,6] and another at 40 GPa [14].

The excellent fit of the 40 GPa data [14] to the host  $V/V_0$  curve strongly suggests that phase IV is characterized across its whole range by the same host structure. It appears that the equilibrium form of the guest in the IVa region would be a single domain of the monoclinic structure. It is this monoclinic form that undergoes the transition to the  $O$  guest of IVb, without any apparent change in the host or the highly disordered  $C$  component—apart from a change in the slope of  $c_I/c_C$  versus pressure, and in the behavior of  $c/a$  of the  $I$  structure, as shown in the inset to Fig. 5. There is evidence in diffraction patterns for a further change in the guest structure at  $\sim 18$  GPa: phase IV appears to be a sequence of complex forms—IVa, IVb, IVc, etc. The fractional coordinates obtained for the host structure from the single-crystal data are the same within error in both IVa and IVb. From the values given above for IVa, each Ba atom in the host structure at 12.0 GPa has two nearest neighbors at 3.381(1) Å, four at 3.447(1) Å, and one at 3.541(1) Å. These, and the separation of 3.41–3.43 Å in the guest chains [15], are similar to the closest approach of atomic centers in the hcp phase [1] extrapolated to the same pressure, 3.445(3) Å. However, the incommensurate chains have a much shorter minimum distance from the host atoms of 3.212(1) Å and a maximum distance of 3.423(1) Å. The incommensuration between the chains and the host suggests a weak interaction and a segregation into two electronically distinct species [16], to which this close approach may be related. The monoclinic distortion possibly avoids the local stress of this close approach occurring in common  $a$ - $b$  planes throughout the structure. Neighboring chains are displaced  $\sim 0.47$  Å along  $c$  in the  $M$  structure, and the  $\sim 0.3$  Å magnitude of the excess “thermal motion” in the  $C$  phase suggests that its chains may adopt the monoclinic distortion over nearest-neighbor distances. The crystallization of the guest components must otherwise be primarily mediated by guest-guest interactions over the large interchain distance of  $\sim 6$  Å.

A structure of a related kind is known in  $\text{Hg}_{3-\delta}\text{AsF}_6$  [17]. The Hg atoms are in chains that run through two, nonintersecting, perpendicular sets of channels in the  $\text{AsF}_6$  host structure and are incommensurate with it, and form an ordered 3D structure below 120 K only [18]. Structures with remarkably similar phenomenology to Ba-IV are known in organic inclusion compounds—for example, as formed by  $\alpha$ ,  $\omega$ -dibromoalkane guest molecules in the channels of urea as a host [19]. And there is a commensurate prototype of the Ba-IV structure formed by  $\text{Al}_2\text{Cu}$  and other intermetallics. The Al atoms have the same structure as the Ba-IV host, and the Cu atoms form the chains [20]. But these are all 2-component

structures. We know of nothing yet discovered to compare with an incommensurate host-guest structure in an element. This structure—with its remarkable stability over more than 30 GPa, incomplete order, incommensuration, mixed symmetry, and sequence of partial phase transitions—presents a challenge to computational studies and invites substantial further experimental characterisation.

We thank R. A. Cowley and G. J. Ackland for helpful discussions and drawing our attention to the  $\text{Hg}_{3-\delta}\text{AsF}_6$  and  $\text{Al}_2\text{Cu}$  structures, and T. Bovornratanaraks, C. Vanpeteghem, and S. J. Teat for some assistance with data collection. We acknowledge technical support from H. Vass, M. A. Roberts, and A. A. Neild. This work is supported by grants from the EPSRC, funding from the CCLRC, and facilities provided by Daresbury Laboratory. M. I. M. acknowledges support from the Royal Society.

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  - [9] A. Altomare *et al.*, *Acta Crystallogr. Sect. A* **47**, 744 (1991).
  - [10] Scattering from all three components adds as amplitudes in the  $hk0$  reflections, which were thus calculated separately in the fit.
  - [11] The  $P$  dependence of  $c_I/c_C$  implies that chain atoms are expelled from the host structure with increasing pressure.
  - [12] This ignores the small effect of the possible  $\sim 0.4\%$  difference between  $c_C$  and  $c_M$ . There is no evidence for a significant difference between  $c_C$  and  $c_O$  in IVb.
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