IUCrJ

Volume 4 (2017)

Supporting information for article:

Incommensurate atomic density waves in the high-pressure IVb phase of barium

Alla Arakcheeva, Maxim Bykov, Elena Bykova, Leonid Dubrovinsky, Phil Pattison, Vladimir Dmitriev and Gervais Chapuis
S1. Selection between the composite (COMP) and the incommensurately modulated structure (IM) models

S1.1. Preliminary analysis

X-ray diffraction experiments and their preliminary analyses are independent of any structure model. For each pressure, each reflection was characterized by its experimental intensity, standard uncertainties and indices, $hklm$, according to the wave vector $\mathbf{H} = ha^* + kb^* + lc^* + mq$, where the reciprocal lattice vectors $a^*$, $b^*$ and $c^*$ correspond to the unit cell parameters $a \approx b \approx 11.5$ and $c \approx 4.6$ Å; $q = \beta b^* + \gamma c^* \approx 0.1 b^* + 1.36 c^*$. The unit cell parameters were refined along with $\beta$ and $\gamma$ over all the reflections of the data collection at each pressure.

S1.2. Description of the experimental data using the COMP and IM structure models

The analysis of the reflection distribution in reciprocal space allows two different interpretations of the experimental data.

*Incommensurately modulated model* (IM). The experimental reflections fit the monoclinic superspace group $P2_1/b(0\beta\gamma)00$ with the indicated unit cell parameters. $hk0$ reflections are the main ones whereas $hklm$ ($m \neq 0$) reflections are satellites.

*Composite model* (COMP). In the frame of the superspace group $P2_1/b(0\beta\gamma)00$, the reflections are considered to originate from two parts, the host and the guest substructures. The superspace group and lattice parameters of the host are identical to those in the IM model. The matrix $(1000 / 0100 / 0001 / 0010)$ transforms the guest lattice to the host. Hence, the guest lattice has the same $a$ and $b$, but has its own lattice parameter $c_G \approx 3.4$ Å and the monoclinic angle $\alpha_G \approx 91^\circ$. Reflections $hkl0$ and $hk0m$ are the main ones for the host and guest parts, respectively. Reflections with $l \neq 0$ and $m \neq 0$ are satellites. If the intensities of the satellites are negligible or zero, then both composite parts are periodic; aperiodicity appears from the irrational value of $c_H/c_G$.

Two different interpretations of the experimental data mainly concern the reflections in terms of "main" and "satellite".

For example, in IM, reflections $hk01$, $hk02$ and $hk03$ are considered as satellites of the 1st, 2nd and 3rd order, respectively, while they are main reflections in COMP. A distribution of the reflections with $I > 1.5\sigma(I)$ is presented in Table S1 for two models, COMP and IM, at room temperature and different pressures.

S1.3. Similarity and difference between structure models COMP and IM

Both IM and COMP models of BaIV-b have been tested and refined for each of the six different pressures. In both models, four sites of Ba atoms describe the structure framework, which is called host in COMP. In both models, these sites correspond to the unit cell with $c \approx 4.6$ Å. Similar average
atomic coordinates and very weak displacive modulations from their positions characterize them. In both models, only one site describes Ba atoms located in the channels formed by the framework. These atoms form a chain in each channel. The chains are called guest in COMP. In COMP, the chain of atoms are slightly modulated along the channels with the average distance Ba - Ba = c_G ≈ 3.4 Å. On the other hand, a strong displacive modulation along the channel with the average distance Ba - Ba = 4.6 Å is observed in the IM model.

**S1.4. Reliability indices confirm the IM model**

Details of the model refinements are listed in Supporting information (Tables 2 - 7) for both COMP and IM models at six different pressures. The quality of the experimental data is not identical for all pressures. This fact affects the absolute value of reliability indices. However, reliability indexes calculated for all main and satellite reflections are systematically lower for the IM model at all pressures. This justifies the high preference of IM in comparison to COMP. The comparison of $R_{\text{all}}$, $R_{\text{main}}$, $R_{\text{1st}}$ and $R_{\text{2nd}}$ are shown in Figure S1.

**Figure S1** Comparison of $R_{\text{all}}$, $R_{\text{main}}$, $R_{\text{1st}}$ and $R_{\text{2nd}}$ for COMP (red) and IM (blue) models.
Table S1  BaIV-b at 16.5 - 21.8 GPa. Distribution of reflections with $I > 1.5\sigma(I)$ in two models, COMP and IM, at room temperature and different pressures

| All reflections | 16.5 GPa | 17.4 GPa | 18.2 GPa | 18.5 GPa | 19.0 GPa | 19.6 GPa |
|-----------------|----------|----------|----------|----------|----------|----------|
| Model:          | IM       | COMP     | IM       | COMP     | IM       | COMP     | IM       | COMP     |
| Main, %; type of reflections |          |          |          |          |          |          |          |          |
| 1st order satellites; type of reflections |          |          |          |          |          |          |          |          |
| 2nd order satellites; type of reflections |          |          |          |          |          |          |          |          |
| 3rd order satellites; type of reflections |          |          |          |          |          |          |          |          |

| All reflections | 16.5 GPa | 17.4 GPa | 18.2 GPa | 18.5 GPa | 19.0 GPa | 19.6 GPa |
|-----------------|----------|----------|----------|----------|----------|----------|
| Model:          | IM       | COMP     | IM       | COMP     | IM       | COMP     | IM       | COMP     |
| Main, %; type of reflections |          |          |          |          |          |          |          |          |
| 1st order satellites; type of reflections |          |          |          |          |          |          |          |          |
| 2nd order satellites; type of reflections |          |          |          |          |          |          |          |          |
| 3rd order satellites; type of reflections |          |          |          |          |          |          |          |          |
S1.5. Details of the structure refinements of BaIV-b at different pressures using two models, composite (COMP) and incommensurately modulated (MI)

Table S2  Crystallographic characteristics and details of the structure refinements of BaIV-b at 19.6 GPa

|                     | Composite model                  | Incommensurately modulated model |
|---------------------|----------------------------------|----------------------------------|
| **Host**            |                                  |                                  |
| \(a\) = 11.439 Å    | \(a\) = 11.439 Å                | \(a\) = 11.439 Å                |
| \(b\) = 11.530 Å    | \(b\) = 11.530 Å                | \(b\) = 11.530 Å                |
| \(c\) = 4.594 Å     | \(c\) = 3.375 Å                 | \(c\) = 4.594 Å                 |
| \(\alpha = 90^\circ\) \(\beta = 90^\circ\) \(\gamma = 90^\circ\) | \(\alpha = 91.794^\circ\) \(\beta = 90^\circ\) \(\gamma = 90^\circ\) | \(\alpha = 90^\circ\) \(\beta = 90^\circ\) \(\gamma = 90^\circ\) |
| \(V = 606 \text{ Å}^3\) | \(V = 445 \text{ Å}^3\)          | \(V = 606 \text{ Å}^3\)          |
| **W-matrix**        | \(W1 = \frac{1000}{0010/0001}\) | \(W2 = \frac{1000}{0010/0001}\) |
| **Superspace group**| \(P2_1/b(0\beta\gamma)00\)       | \(P2_1/b(0\beta\gamma)00\)       |
| **q-vector**        | \(0.107b^* + 1.361c^*\)         | \(-0.0786b^* + 0.735c^*\)        |

No. of reflections:
- Measured: \(I_{\sigma} > 2\sigma(I)\) 15944; 643
- Main refl. 8.8
- 1st order satellites 53.16 (62.14)
- 2nd order satellites 60.67 (66.80)
- 3rd order satellites 44.97 (50.35)

Reliability indices R (Rw),%:
- All refl. 11.20 (7.98) 9.66 (6.73)
- Main refl. 6.73 (6.11) 4.93 (4.57)
- 1st order satellites 53.16 (62.14) 27.20 (23.55)
- 2nd order satellites 60.67 (66.80) 13.41 (12.45)
- 3rd order satellites 44.97 (50.35) 15.76 (15.82)
Table S3  Crystallographic characteristics and details of the structure refinements of BaIV-b at 19.0 GPa

|                                | Composite model | Incommensurately modulated model |
|--------------------------------|-----------------|----------------------------------|
|                                | Host            | Guest                           |
| Unit cell parameters           |                 |                                 |
| $a$ = 11.500 Å                 | $a$ = 11.546 Å  | $a$ = 11.500 Å                  |
| $b$ = 11.553 Å                 | $b$ = 11.588 Å  | $b$ = 11.553 Å                  |
| $c$ = 4.6035 Å                 | $c$ = 3.390 Å   | $c$ = 4.6035 Å                  |
| $\alpha = 90^\circ$           | $\alpha = 92.05^\circ$ | $\alpha = 90^\circ$           |
| $\beta = 90^\circ$            | $\beta = 90^\circ$ | $\beta = 90^\circ$            |
| $\gamma = 90^\circ$           | $\gamma = 90^\circ$ | $\gamma = 90^\circ$           |
| $V = 612 \text{ Å}^3$         | $V = 450 \text{ Å}^3$ | $V = 612 \text{ Å}^3$         |
| W-matrix                      | $W_1 = \begin{pmatrix} 1000 & 0 & 0 & 0 \\ 0 & 100 & 0 & 0 \\ 0 & 0 & 100 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$ | $W_2 = \begin{pmatrix} 1000 & 0 & 0 & 0 \\ 0 & 100 & 0 & 0 \\ 0 & 0 & 100 & 0 \end{pmatrix}$ | - |
| Superspace group               | $P2_1/b(0\beta y)00$ | $P2_1/b(0\beta y)00$ | $P2_2/b(0\beta y)00$ |
| $q$-vector                     | $0.122b^* + 1.358c^*$ | $-0.0898b^* + 0.736c^*$ | $0.122b^* + 1.358c^*$ |

No. of reflections:

- Measured: $I_{\text{w}} > 2\sigma(I)$: 18445; 515
- Main refl.: 7.5
- Reliability indices $R (R_w),\%$:
  - All refl.: 15.18 (9.78) 14.41 (9.63)
  - Main refl.: 7.94 (6.60) 5.46 (5.13)
  - 1st order satellites: 45.83 (49.53) 33.59 (29.54)
  - 2nd order satellites: 59.96 (73.51) 23.25 (22.19)
  - 3rd order satellites: 52.06 (54.03) 22.40 (24.45)
Table S4  Crystallographic characteristics and details of the structure refinements of BaIV-b at 18.5 GPa

|                      | Composite model | Incommensurately modulated model |
|----------------------|-----------------|----------------------------------|
|                      | Host            | Guest                           |                               |
| **Unit cell parameters** |                 |                                 |                               |
| \( a = 11.546 \) Å   | \( a = 11.546 \) Å | \( a = 11.546 \) Å              |                               |
| \( b = 11.588 \) Å   | \( b = 11.588 \) Å | \( b = 11.588 \) Å              |                               |
| \( c = 4.599 \) Å    | \( c = 3.394 \) Å | \( c = 4.599 \) Å              |                               |
| \( \alpha = 90^\circ \) | \( \alpha = 92.08^\circ \) | \( \alpha = 90^\circ \)         |                               |
| \( \beta = 90^\circ \) | \( \beta = 90^\circ \) | \( \beta = 90^\circ \)          |                               |
| \( \gamma = 90^\circ \) | \( \gamma = 90^\circ \) | \( \gamma = 90^\circ \)         |                               |
| \( V = 615 \) Å³     | \( V = 454 \) Å³ | \( V = 615 \) Å³                |                               |
| **W-matrix**         | \( W1 = \)      | \( W2 = \)                      | -                              |
|                      | 1000/0100/0010/0001 | 1000/0100/0001/0010              |                               |
| **Superspace group** | \( P2_1/b(0\beta\gamma)00 \) | \( P2_1/b(0\beta\gamma)00 \) | \( P2_1/b(0\beta\gamma)00 \) |
| **q-vector**         | \( 0.124b^* + 1.355c^* \) | -0.0915b^* + 0.73801c^* | \( 0.124b^* + 1.355c^* \) |
| **No. of reflections:** | 15553; 714 | 15553; 714 | 15553; 714 |
| **No. of refl. / No. of parameters** | 10.3 | 10.3 | 10.3 |
| **Reliability indices R (Rw),%:** |                     |                                 |                               |
| All refl.            | 17.59 (12.29) | 15.31 (10.46) |                               |
| Main refl.           | 10.35 (8.53) | 6.15 (5.41) |                               |
| 1st order satellites  | 44.66 (49.07) | 25.90 (24.13) |                               |
| 2nd order satellites  | 47.06 (52.85) | 23.42 (22.60) |                               |
| 3rd order satellites  | 42.42 (38.30) | 25.08 (27.08) |                               |
Table S5  Crystallographic characteristics and details of the structure refinements of BaIV-b at 18.2 GPa

|                     | Composite model | Incommensurately modulated model |
|---------------------|-----------------|----------------------------------|
|                     | Host            | Guest                           |
| Unit cell parameters| \( a = 11.531 \, \text{Å} \) | \( a = 11.531 \, \text{Å} \) |
|                     | \( b = 11.653 \, \text{Å} \) | \( b = 11.653 \, \text{Å} \) |
|                     | \( c = 4.6109 \, \text{Å} \) | \( c = 3.376 \, \text{Å} \) |
|                     | \( \alpha = 90^\circ \) | \( \alpha = 91.53^\circ \) |
|                     | \( \beta = 90^\circ \) | \( \beta = 90^\circ \) |
|                     | \( \gamma = 90^\circ \) | \( \gamma = 90^\circ \) |
|                     | \( V = 620 \, \text{Å}^3 \) | \( V = 454 \, \text{Å}^3 \) |
| W-matrix            | W1 = \( \frac{1000}{0100/0010/0001} \) | W2 = - |
|                     |                  | \( \frac{1000}{0100/0001/0010} \) |
| Superspace group    | \( P2_1/b(0\beta y/00) \) | \( P2_1/b(0\beta y/00) \) |
|                     | \( P2_1/b(0\beta y/00) \) | \( P2_1/b(0\beta y/00) \) |
| q-vector            | \( 0.092b^* + 1.366c^* \) | \( -0.06735b^* + 0.73206c^* \) |

|                     | \( 0.092b^* + 1.366c^* \) | 9.0 |

No. of reflections:

- Measured: \( I_{\text{av}}>2\sigma(I) \)
  - 18573; 629

- No. of refl. / No. of parameters
  - 9,0

Reliability indices R (Rw),%:

- All refl.
  - 11.33 (7.64)
  - 7.07 (5.77)
  - 47.21 (54.80)
  - 53.48 (64.41)
  - 61.11 (71.39)

- Main refl.
  - 9.28 (6.58)
  - 4.45 (4.33)
  - 23.75 (20.08)
  - 14.40 (13.95)
  - 29.10 (32.27)
Table S6  Crystallographic characteristics and details of the structure refinements of BaIV-b at 17.4 GPa

|                  | Composite model          | Incommensurately modulated model |
|------------------|---------------------------|----------------------------------|
|                  | Host                      | Guest                           |
| Unit cell parameters | \(a = 11.615 \) Å       | \(a = 11.615 \) Å               |
|                  | \(b = 11.626\) Å         | \(b = 11.626\) Å                |
|                  | \(c = 4.634\) Å          | \(c = 3.388\) Å                 |
|                  | \(\alpha = 90^\circ\)    | \(\alpha = 91.04^\circ\)       |
|                  | \(\beta = 90^\circ\)     | \(\beta = 90^\circ\)            |
|                  | \(\gamma = 90^\circ\)    | \(\gamma = 90^\circ\)           |
|                  | \(V = 626 \) Å³          | \(V = 457 \) Å³                 |
| W-matrix         | W1 = 1000/0100/0010/0001  | W2 = 1000/0100/0001/0010         |
| Superspace group | \(P2_1/b(0\beta y)00\)   | \(P2_1/b(0\beta y)00\)          |
| \(q\)-vector     | \(0.062b^* + 1.368c^*\)  | \(-0.06735b^* + 0.73206c^*\)    |
| No. of reflections: |                           |                                 |
| Measured: \(I_\text{ω} > 2\sigma(I)\) | 18897; 557                | 18897; 557                     |
| No. of refl. / No. of parameters | 7.96                      | 7.96                           |
| Reliability indices \(R\) (\(R_w\)),\% |                           |                                 |
| All refl.        | 12.92 (9.68)              | 9.90 (7.97)                    |
| Main refl.       | 10.99 (9.11)              | 5.59 (5.96)                    |
| 1\(^{st}\) order satellites | 49.75 (57.57)            | 31.16 (31.41)                  |
| 2\(^{nd}\) order satellites | 51.56 (66.62)            | 20.22 (21.83)                  |
| 3\(^{rd}\) order satellites | 40.12 (39.07)            | 34.34 (37.94)                  |
Table S7  Crystallographic characteristics and details of the structure refinements of BaIV-b at 16.5 GPa

|                      | Composite model |                       | Incommensurately modulated model |
|----------------------|-----------------|-----------------------|----------------------------------|
|                      | Host            | Guest                |                                  |
| Unit cell parameters | $a = 11.608\ \text{Å}$ | $a = 11.615\ \text{Å}$ | $a = 11.608\ \text{Å}$           |
|                      | $b = 11.634\ \text{Å}$ | $b = 11.626\ \text{Å}$ | $b = 11.634\ \text{Å}$           |
|                      | $c = 4.634\ \text{Å}$ | $c = 3.405\ \text{Å}$ | $c = 4.634\ \text{Å}$           |
|                      | $\alpha = 90^\circ$ | $\alpha = 91.02^\circ$ | $\alpha = 90^\circ$              |
|                      | $\beta = 90^\circ$ | $\beta = 90^\circ$   | $\beta = 90^\circ$              |
|                      | $\gamma = 90^\circ$ | $\gamma = 90^\circ$  | $\gamma = 90^\circ$             |
|                      | $V = 626\ \text{Å}^3$ | $V = 460\ \text{Å}^3$ | $V = 626\ \text{Å}^3$            |
| $W$-matrix           | $W1 = \begin{pmatrix} 1000\,0100\,0001 \\ 0001\,0010\,0001 \end{pmatrix}$ | $W2 = \begin{pmatrix} 1000\,0100\,0001 \\ 0001\,0010\,0001 \end{pmatrix}$ | - |
| Superspace group     | $P2_1/b(0\beta\gamma)$ | $P2_1/b(0\beta\gamma)$ | $P2_1/b(0\beta\gamma)$ |
| $q$-vector           | $0.061b^* + 1.361c^*$ | $-0.0448b^* + 0.73475c^*$ | $0.061b^* + 1.361c^*$ |

No. of reflections:

- Measured: $h \omega > 2\sigma(I)$: 20460; 399
- Main refl.: 5.7
- Reliability indices $R, \%(R_w, \%)$
  - All refl.: 15.30 (11.13) 9.09 (6.38)
  - Main refl.: 11.83 (9.87) 4.30 (4.12)
  - 1st order satellites: 49.39 (55.80) 26.72 (24.25)
  - 2nd order satellites: 57.35 (79.74) 26.65 (28.33)
  - 3rd order satellites: 46.76 (50.05) 49.14 (49.11)
S2. Structural information for the refined IM model of BaIV-b phase

Four atomic sites, Ba1, Ba2, Ba3 and Ba4 (Tables 8 - 13) are needed to define the framework in the monoclinic (3+1)D superspace group \(P2_1/b(0\beta\gamma)00\). These four sites are strongly (>99%) correlated among each other, so that only two of them are independent. The correlations appear owing to the pseudo-tetragonal symmetry of the framework. The following constrains have been applied to avoid the correlations:

Ba1 and Ba2 are linked by the local operator \((x1, 0.5-x2, x3, x4)\);

Ba3 and Ba4 are linked by the local operator \((x1+0.5, x2+0.5, x3, x4)\).

Atomic parameters refined for BaIV-b at different pressure are listed in Table 8 - 13.

Table S8  BaIV-b at 19.6 GPa. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x       | y       | z       | Uiso    |
|------|------|---------|---------|---------|---------|
| Ba1  |      | 0.0008(8) | 0.10107(18) | 0.2505 | 0.0217(12) |
|      | s,1  | -0.0043(4) | -0.0003(15) | 0.0004(6) |         |
|      | c,1  | -0.0021(15) | -0.0003(5) | 0.0033(17) |         |
|      | s,2  | -0.0005(6) | -0.0031(19) | 0.0026(9) |         |
|      | c,2  | -0.0016(14) | 0.0008(7) | -0.0297(14) |         |
|      | s,3  | 0.0012(17) | 0.000(3) | -0.0005(8) |         |
|      | c,3  | 0.0110(16) | 0.0005(9) | -0.010(2) |         |
| Ba2  |      | 0.0008(8) | 0.39893(18) | 0.2505 | 0.0217(12) |
|      | s,1  | -0.0043(4) | 0.0003(15) | 0.0004(6) |         |
|      | c,1  | -0.0021(15) | 0.0003(5) | 0.0033(17) |         |
|      | s,2  | -0.0005(6) | 0.0031(19) | 0.0026(9) |         |
|      | c,2  | -0.0016(14) | -0.0008(7) | -0.0297(14) |         |
|      | s,3  | 0.0012(17) | 0.000(3) | -0.0005(8) |         |
|      | c,3  | 0.0110(16) | -0.0005(9) | -0.010(2) |         |
| Ba3  |      | 0.6489(2) | 0.2544(16) | 0.2507 | 0.0278(18) |
|    | s,1   | c,1   | s,2   | c,2   | s,3   | c,3   |
|----|-------|-------|-------|-------|-------|-------|
|    | 0.0016(14) | 0.0003(5) | 0.0004(8) |       |       |       |
|    | -0.0011(6)  | 0.004(2)  | -0.004(3)  |       |       |       |
|    | 0.0071(19)  | 0.0005(10) | 0.0015(12) |       |       |       |
|    | -0.0003(8)  | -0.005(2)  | 0.002(4)   |       |       |       |
|    | -0.0023(19) | -0.0005(7) | -0.0033(9) |       |       |       |
|    | -0.0016(13) | 0.000(2)   | -0.006(5)  |       |       |       |

|    | s,1   | c,1   | s,2   | c,2   | s,3   | c,3   |
|----|-------|-------|-------|-------|-------|-------|
|    | 0.0016(14) | 0.0003(5) | 0.0004(8) |       |       |       |
|    | -0.0011(6)  | 0.004(2)  | -0.004(3)  |       |       |       |
|    | 0.0071(19)  | 0.0005(10) | 0.0015(12) |       |       |       |
|    | -0.0003(8)  | -0.005(2)  | 0.002(4)   |       |       |       |
|    | -0.0023(19) | -0.0005(7) | -0.0033(9) |       |       |       |
|    | -0.0016(13) | 0.000(2)   | -0.006(5)  |       |       |       |

|    | s,1   | c,1   | s,2   | c,2   | s,3   | c,3   |
|----|-------|-------|-------|-------|-------|-------|
|    | 1.1489(2)  | 0.7544(16) | 0.2507 | 0.0278(18) |       |       |
|    | 0.0016(14) | 0.0003(5) | 0.0004(8) |       |       |       |
|    | -0.0011(6)  | 0.004(2)  | -0.004(3)  |       |       |       |
|    | 0.0071(19)  | 0.0005(10) | 0.0015(12) |       |       |       |
|    | -0.0003(8)  | -0.005(2)  | 0.002(4)   |       |       |       |
|    | -0.0023(19) | -0.0005(7) | -0.0033(9) |       |       |       |
|    | -0.0016(13) | 0.000(2)   | -0.006(5)  |       |       |       |

|    | s,1   | c,1   | s,2   | c,2   | s,3   | c,3   |
|----|-------|-------|-------|-------|-------|-------|
|    | 0.2539(13) | 0.0049(10) | 0.144(2) | 0.0120(17) |       |       |
|    | -0.007(2)  | 0.003(2)  | 0.129(2)  |       |       |       |
|    | 0.0015(19) | 0.0163(16) | 0.193(2)  |       |       |       |
|    | -0.001(3)  | -0.012(2)  | -0.049(2)  |       |       |       |
|    | -0.0010(14) | 0.0044(17) | 0.109(2)  |       |       |       |
|    | -0.0123(18) | 0.0025(15) | -0.093(2) |       |       |       |
|    | -0.0006(2)  | -0.009(2)  | 0.041(3)   |       |       |       |

Ba1g corresponds to channel atoms
**Table S9**  BaIV-b at 19.0 GPa. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x       | y       | z       | Uiso    |
|------|------|---------|---------|---------|---------|
| Ba1  |      | 0.0053(8) | 0.1016(4) | 0.2515(16) | 0.0188(16) |
|      | s,1  | -0.0041(5) | 0.005(2)   | -0.0020(7)  |         |
|      | c,1  | -0.0050(15) | -0.0013(7) | -0.007(3)   |         |
|      | s,2  | -0.0011(8) | 0.003(2)   | 0.0026(11)  |         |
|      | c,2  | 0.0069(16) | 0.0024(9)  | -0.007(2)   |         |
|      | s,3  | 0.0031(14) | -0.0207(13)| -0.0039(11) |         |
|      | c,3  | 0.007(2)   | -0.0004(11)| -0.019(5)   |         |
| Ba2  |      | 0.0053(8) | 0.3984(4)  | 0.2515(16)  | 0.0188(16) |
|      | s,1  | -0.0041(5) | -0.005(2)  | -0.0020(7)  |         |
|      | c,1  | -0.0050(15)| 0.0013(7)  | -0.007(3)   |         |
|      | s,2  | -0.0011(8) | -0.003(2)  | 0.0026(11)  |         |
|      | c,2  | 0.0069(16) | -0.0024(9)| -0.007(2)   |         |
|      | s,3  | 0.0031(14) | 0.0207(13) | -0.0039(11) |         |
|      | c,3  | 0.007(2)   | 0.0004(11) | -0.019(5)   |         |
| Ba3  |      | 0.6481(3) | 0.2458(14)| 0.247(2)   | 0.0230(17) |
|      | s,1  | 0.005(2)   | 0.0018(7)  | 0.0006(9)   |         |
|      | c,1  | -0.0005(6) | -0.0047(17)| 0.002(4)   |         |
|      | s,2  | 0.000(2)   | 0.0018(10)| -0.0004(12) |         |
|      | c,2  | 0.0006(9)  | -0.009(3)  | 0.014(5)    |         |
|      | s,3  | 0.007(2)   | -0.0001(12)| -0.0042(11) |         |
|      | c,3  | 0.0015(10) | 0.017(2)   | 0.009(4)    |         |
| Ba4  |      | 1.1481(3) | 0.7458(14)| 0.247(2)   | 0.0230(17) |
|      | s,1  | 0.005(2)   | 0.0018(7)  | 0.0006(9)   |         |
|      | c,1  | -0.0005(6) | -0.0047(17)| 0.002(4)   |         |
|      | s,2  | 0.000(2)   | 0.0018(10)| -0.0004(12) |         |
|    |     |     |     |     |
|----|-----|-----|-----|-----|
| c,2 | 0.0006(9) | -0.009(3) | 0.014(5) |
| s,3 | 0.007(2) | -0.0001(12) | -0.0042(11) |
| c,3 | 0.0015(10) | 0.17(2) | 0.009(4) |
| Ba1g | 0.2443(14) | 0.0001(7) | 0.136(2) | 0.0134(18) |
| s,1 | -0.00558(18) | 0.0054(18) | 0.139(3) |
| c,1 | 0.0033(18) | 0.0051(18) | 0.201(3) |
| s,2 | -0.0043(18) | -0.0052(18) | -0.051(3) |
| c,2 | 0.0041(18) | 0.0085(18) | 0.125(2) |
| s,3 | -0.0044(18) | 0.0051(18) | -0.089(2) |
| c,3 | -0.0037(18) | -0.0077(18) | 0.035(3) |

**Ba1g corresponds to channel atoms**
Table S10  BaIV-b at 18.5 GPa. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x     | y     | z     | Uiso   |
|------|------|-------|-------|-------|--------|
| Ba1  |      | -0.0003(4) | 0.1011(2) | 0.2553(12) | 0.0099(13) |
|      | s,1  | -0.0044(3) | 0.0172(6) | -0.0034(6)  |        |
|      | c,1  | -0.0030(6) | -0.0009(5) | 0.0135(18)  |        |
|      | s,2  | -0.0022(4) | -0.0001(6) | 0.0014(8)   |        |
|      | c,2  | 0.0051(11) | 0.0066(7)  | 0.013(2)    |        |
|      | s,3  | -0.0153(8) | 0.0071(8)  | -0.0044(8)  |        |
|      | c,3  | -0.0036(10)| 0.0038(7)  | -0.019(3)   |        |
| Ba2  |      | -0.0003(4) | 0.3989(2)  | 0.2553(12)  | 0.0099(13) |
|      | s,1  | -0.0044(3) | -0.0172(6)| -0.0034(6)  |        |
|      | c,1  | -0.0030(6) | 0.0009(5)  | 0.0135(18)  |        |
|      | s,2  | -0.0022(4) | 0.0001(6)  | 0.0014(8)   |        |
|      | c,2  | 0.0051(11) | -0.0066(7)| 0.013(2)    |        |
|      | s,3  | -0.0153(8) | -0.0071(8)| -0.0044(8)  |        |
|      | c,3  | -0.0036(10)| -0.0038(7)| -0.019(3)   |        |
| Ba3  |      | 0.64871(19)| 0.2413(8)  | 0.248(2)    | 0.0203(12) |
|      | s,1  | 0.0024(10) | -0.0013(5)| -0.0005(7)  |        |
|      | c,1  | -0.0005(4) | 0.0063(13)| -0.004(4)   |        |
|      | s,2  | -0.0006(11)| 0.0005(7)  | 0.0009(10)  |        |
|      | c,2  | -0.0012(6) | 0.0064(12)| 0.001(2)    |        |
|      | s,3  | 0.0097(11) | -0.0030(9)| -0.0038(8)  |        |
|      | c,3  | 0.0002(6)  | 0.0042(14)| -0.009(4)   |        |
| Ba4  |      | 1.14871(19)| 0.7413(8)  | 0.248(2)    | 0.0203(12) |
|      | s,1  | 0.0024(10) | -0.0013(5)| -0.0005(7)  |        |
|      | c,1  | -0.0005(4) | 0.0063(13)| -0.004(4)   |        |
|      | s,2  | -0.0006(11)| 0.0005(7)  | 0.0009(10)  |        |
|       |  c,2   |  s,3   |  c,3   |  s,1   |  c,1   |  s,2   |  c,2   |  s,3   |  c,3   |
|-------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Ba1g  | -0.0012(6) | 0.0064(12) | 0.001(2) |        |        |        |        |        |        |
|       | 0.0097(11) | -0.0030(9) | -0.0038(8) |        |        |        |        |        |        |
|       | 0.0002(6) | 0.0042(14) | -0.009(4) |        |        |        |        |        |        |
| Ba1g  | 0.2538(11) | 0.0006(6) | 0.1354(17) | 0.0073(13) |        |        |        |        |        |
|       | -0.0008(18) | 0.0111(10) | 0.1376(18) |        |        |        |        |        |        |
|       | -0.0015(14) | 0.0135(10) | 0.207(2) |        |        |        |        |        |        |
|       | 0.0080(19) | -0.0051(12) | -0.057(2) |        |        |        |        |        |        |
|       | 0.0020(10) | 0.0054(12) | 0.1249(18) |        |        |        |        |        |        |
|       | -0.0030(13) | 0.0069(8) | -0.0965(16) |        |        |        |        |        |        |
|       | -0.0002(17) | -0.0020(14) | 0.034(3) |        |        |        |        |        |        |

Ba1g corresponds to channel atoms
Table S11  BaIV-b at 18.2 GPa. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x     | y     | z     | Uiso   |
|------|------|-------|-------|-------|--------|
| Ba1  |      | -0.0029(13) | 0.10109(19) | 0.2545(14) | 0.0173(8) |
|      | s,1  | -0.0034(3)  | 0.0018(15)  | -0.0002(8) |        |
|      | c,1  | -0.0018(17) | 0.0000(4)   | 0.009(2)   |        |
|      | s,2  | -0.0001(5)  | 0.0008(15)  | 0.0027(11) |        |
|      | c,2  | -0.0010(12) | -0.0002(7)  | 0.000(3)   |        |
|      | s,3  | 0.005(3)    | -0.0131(8)  | -0.0012(10)|        |
|      | c,3  | 0.009(2)    | 0.0001(9)   | -0.001(3)  |        |
| Ba2  |      | -0.0029(13) | 0.39891(19) | 0.2545(14) | 0.0173(8) |
|      | s,1  | -0.0034(3)  | -0.0018(15) | -0.0002(8) |        |
|      | c,1  | -0.0018(17) | 0.0000(4)   | 0.009(2)   |        |
|      | s,2  | -0.0001(5)  | -0.0008(15) | 0.0027(11) |        |
|      | c,2  | -0.0010(12) | 0.0002(7)   | 0.000(3)   |        |
|      | s,3  | 0.005(3)    | 0.0131(8)   | -0.0012(10)|        |
|      | c,3  | 0.009(2)    | -0.0001(9)  | -0.001(3)  |        |
| Ba3  |      | 0.64874(15) | 0.2524(16)  | 0.2503(14) | 0.0203(8) |
|      | s,1  | 0.0003(17)  | -0.0014(8)  | 0.0010(8)  |        |
|      | c,1  | -0.0002(4)  | 0.001(2)    | -0.002(2)  |        |
|      | s,2  | 0.000(2)    | 0.0001(7)   | -0.0003(10)|        |
|      | c,2  | -0.0008(6)  | -0.0001(15) | -0.005(3)  |        |
|      | s,3  | 0.0040(17)  | 0.0012(9)   | -0.0045(10)|        |
|      | c,3  | 0.0003(9)   | 0.0157(10)  | -0.009(2)  |        |
| Ba4  |      | 1.14874(15) | 0.7524(16)  | 0.2503(14) | 0.0203(8) |
|      | s,1  | 0.0003(17)  | -0.0014(8)  | 0.0010(8)  |        |
|      | c,1  | -0.0002(4)  | 0.001(2)    | -0.002(2)  |        |
|      | s,2  | 0.000(2)    | 0.0001(7)   | -0.0003(10)|        |
|    | s,3 | c,3 | c,2 |
|----|-----|-----|-----|
| s,3 | 0.0012(9) | 0.0157(10) | -0.0001(15) |
| c,3 | 0.0003(9) | -0.0008(6) | -0.005(3) |

**Ba**

|    | s,1 | c,1 | c,2 |
|----|-----|-----|-----|
| s,1 | 0.008(3) | 0.015(2) | 0.135(3) |
| c,1 | 0.0008(17) | 0.015(2) | 0.135(3) |
| c,2 | 0.012(2) | 0.007(3) | -0.0045(10) |

**Ba**

|    | s,2 | c,3 | c,3 |
|----|-----|-----|-----|
| s,2 | 0.0054(19) | 0.0123(14) | -0.093(2) |
| c,3 | 0.0081(18) | 0.003(2) | 0.035(3) |

**Ba** corresponds to channel atoms
Table S12  BaIV-b at 17.4 GPa. Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x     | y     | z     | Uiso   |
|------|------|-------|-------|-------|--------|
| Ba1  |      | 0.0025(8) | 0.1014(2) | 0.2502 | 0.0115(11) |
|      | s,1  | 0.0005(4)  | -0.0075(15) | -0.0006(13) |       |
|      | c,1  | -0.0043(11) | -0.0001(8)  | -0.007(3)   |       |
|      | s,2  | -0.0017(8)  | 0.0131(16)  | -0.006(2)   |       |
|      | c,2  | 0.0001(13)  | -0.0014(15) | 0.014(2)    |       |
|      | s,3  | 0.0019(19)  | 0.007(2)    | -0.0004(15) |       |
|      | c,3  | -0.0145(8)  | -0.0029(9)  | 0.006(5)    |       |
| Ba2  |      | 0.0025(8) | 0.3986(2) | 0.2502 | 0.0115(11) |
|      | s,1  | 0.0005(4) | 0.0075(15) | -0.0006(13) |       |
|      | c,1  | -0.0043(11) | 0.0001(8)  | -0.007(3)   |       |
|      | s,2  | -0.0017(8) | -0.0131(16) | -0.006(2)   |       |
|      | c,2  | 0.0001(13) | 0.0014(15)  | 0.014(2)    |       |
|      | s,3  | 0.0019(19) | -0.007(2)  | -0.0004(15) |       |
|      | c,3  | -0.0145(8) | 0.0029(9)  | 0.006(5)    |       |
| Ba3  |      | 0.6486(2) | 0.2530(18) | 0.2506 | 0.0142(12) |
|      | s,1  | 0.002(2) | 0.0017(14) | -0.0008(13) |       |
|      | c,1  | 0.0003(6) | -0.009(3)  | 0.001(3)    |       |
|      | s,2  | 0.0062(19) | -0.001(2)  | 0.0025(19)  |       |
|      | c,2  | 0.0007(14) | 0.0164(17) | 0.015(3)    |       |
|      | s,3  | -0.008(2) | -0.0030(10) | -0.0033(16) |       |
|      | c,3  | 0.0012(10) | 0.001(3) | 0.008(6)    |       |
| Ba4  |      | 1.1486(2) | 0.7530(18) | 0.2506 | 0.0142(12) |
|      | s,1  | 0.002(2) | 0.0017(14) | -0.0008(13) |       |
|      | c,1  | 0.0003(6) | -0.009(3)  | 0.001(3)    |       |
|      | s,2  | 0.0062(19) | -0.001(2)  | 0.0025(19)  |       |
|   |   |   |   |   |
|---|---|---|---|---|
| c,2 | 0.0007(14) | -0.0164(17) | -0.015(3) |   |
| s,3 | -0.008(2) | -0.0030(10) | -0.0033(16) |   |
| c,3 | 0.0012(10) | 0.001(3) | 0.008(6) |   |
| Ba1g | 0.25 | -0.0169(11) | 0.254(5) | 0.026(2) |
| s,1 | 0.0000(14) | -0.0037(18) | 0.148(5) |   |
| c,1 | 0.0000(14) | -0.0077(18) | -0.151(3) |   |
| s,2 | 0.0000(14) | 0.0054(12) | 0.006(3) |   |
| c,2 | 0.0000(14) | -0.0137(15) | -0.037(6) |   |
| s,3 | 0.0054(19) | 0.0123(14) | -0.093(2) |   |
| c,3 | 0.0081(18) | 0.003(2) | 0.035(3) |   |

Ba1g corresponds to channel atoms
**Table S13  BaIV-b at 16.5 GPa.** Final coordinates, isotropic displacement parameters and Fourier amplitudes of the displacive modulation function. The waves are sorted by the term s for sine, c for cosines and order n.

| Atom | Wave | x       | y       | z       | Uiso    |
|------|------|---------|---------|---------|---------|
| Ba1  | s,1  | -0.0011(7) | 0.1014(2) | 0.2506  | 0.0174(12) |
|      | c,1  | -0.0003(4) | -0.0056(16) | 0.0033(11) |
|      | s,2  | 0.0012(8) | 0.0076(16) | 0.0000(12) |
|      | c,2  | 0.0011(15) | -0.0016(12) | 0.018(2) |
|      | s,3  | -0.0021(17) | -0.007(2) | -0.0031(12) |
|      | c,3  | -0.0132(11) | 0.0018(7) | -0.004(3) |
| Ba2  | s,1  | -0.0011(7) | 0.3986(2) | 0.2506  | 0.0174(12) |
|      | c,1  | -0.0003(4) | 0.0056(16) | 0.0033(11) |
|      | s,2  | 0.0012(8) | -0.0076(16) | 0.0000(12) |
|      | c,2  | 0.0011(15) | 0.0016(12) | 0.018(2) |
|      | s,3  | -0.0021(17) | 0.007(2) | -0.0031(12) |
|      | c,3  | -0.0132(11) | -0.0018(7) | -0.004(3) |
| Ba3  | s,1  | 0.6488(2) | 0.2532(11) | 0.2504  | 0.0191(16) |
|      | c,1  | -0.002(2) | -0.0002(9) | -0.0011(11) |
|      | s,2  | -0.0018(6) | -0.009(3) | 0.000(3) |
|      | c,2  | -0.0056(15) | 0.0016(13) | -0.0012(15) |
|      | s,3  | 0.0012(12) | -0.011(3) | -0.005(4) |
|      | c,3  | -0.0061(17) | 0.0019(13) | 0.001(3) |
|      | s,4  | -0.0002(9) | 0.0078(16) | 0.022(4) |
| Ba4  | s,1  | 1.1488(2) | 0.7532(11) | 0.2504  | 0.0191(16) |
|      | c,1  | -0.002(2) | -0.0002(9) | -0.0011(11) |
|      | s,2  | -0.0018(6) | -0.009(3) | 0.000(3) |
|      | s,3  | -0.0056(15) | 0.0016(13) | -0.0012(15) |
Ba\(_{1g}\) corresponds to channel atoms

### S3. Details on the interatomic distance distribution

The magnitudes of the modulations are three orders smaller for all the Ba\(_{Fr}\) comparing to the magnitude of Ba\(_{Ch}\) along the \(c\) axis (Table S8 - S13). The magnitude of the Ba\(_{Ch}\) atom modulation is also negligible along the \(a\) and \(b\) axes (Table S8 - S13). Consequently the structure modulation essentially affects the Ba\(_{Ch}\)–Ba\(_{Ch}\) distances along the channels. In general, they vary from 2.90 to 6.91–7.25 Å between the nearest atoms (Fig. 4 in the main text) with an average value corresponding to the lattice parameter \(c \approx 4.6\) Å. The variation of 70-85% of the Ba\(_{Ch}\)–Ba\(_{Ch}\) distances in the 2.9 - 3.8 Å range (Fig. 4, a and b in the main text) lead to their grouping in dumbbells and triplets (Fig. 4, c in the main text). The extreme values of the range are closely related to Ba-Ba distances at higher and lower pressure, respectively: 3.0 Å in the hcp Ba\(_V\) at \(P > 45\) GPa and 3.8 Å in the hcp Ba\(_{II}\) at \(P < 12\) GPa (Kinichi, 1994). More than 80% of the host atoms have Ba\(_{Fr}\)-Ba\(_{Fr}\) contacts within the narrow range of 3.2 – 3.4 Å. Hence, the appearance of the incommensurately modulated state of Ba\(_{IV}\) is directly linked to the formation of short Ba - Ba contacts in the range 2.8 - 3.0 Å. The shortest Ba\(_{Ch}\)-Ba\(_{Fr}\) contact is also approximately 2.8 Å.

The atomic density in the channels is about 4/3 smaller than what was assumed before using the composite model for Ba\(_{IV}\)-a (Kenichi, 1994). Indeed, in the Ba\(_{Ch}\)-chain, the average length of the Ba\(_{Ch}\)–Ba\(_{Ch}\) contact is about 4.6 Å given by the lattice constant \(c\), while this length is about \(c_G \approx 3.4\) Å in all publications. In particular, assuming a hypothetical composite model for Ba\(_{IV}\)-b, the density could be overestimated by about 7%.