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Composite incommensurate K-III and a commensurate form: Study of a high-pressure phase of potassium

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K-III, the high-pressure phase of potassium stable above 20 GPa, is reported to have a host-guest composite structure comprising the same 16-atom host structure as Rb-IV and a *C*-face-centered, rather than a body-centered, tetragonal, guest structure. At 22.0(2) GPa, the incommensurate ratio of the host and guest *c*-axis lattice parameters passes through the commensurate value of 8/5 but, within the experimental resolution of approximately 1 GPa, no lock-in to a commensurate structure is observed.

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I. INTRODUCTION

At ambient conditions, the alkali metals adopt simple atomic arrangements and crystallize in body-centered cubic (bcc) crystal structures.[1] By application of high pressures, they transform first into face-centered cubic (fcc) modifications.[1,2] On further compression, the crystal structures of the alkalis become very complex, and it is only recently, with the advent of high-resolution angle-dispersive powder and single-crystal x-ray diffraction techniques, that the structures of many of these complex phases have been determined.[3–9]

In the case of Rb-IV, stable between 16.6 and 20.0 GPa, the structure has been shown to comprise a 16-atom tetragonal host substructure with *c*-axis channels that contain linear chains of guest atoms[4] forming a body-centered tetragonal guest substructure[7] (see Fig. 1). The host and guest substructures are incommensurate along their common *c* axis.[7] This crystal structure, closely related to the anion sublattice of W_5Si_3-type intermetallic compounds, is so far unique to rubidium, although similar incommensurate composite structures with 8-atom hosts have been observed in Ba and Sr,[10,11] in Bi, Sb, and As,[12–14] and in Sc.[15,16] No composite structure has been reported in Cs at high pressure, but the most recent structural study of K-III (Ref. 17), which is the stable phase between about 22 and at least 50 GPa, reported a 16-atom tetragonal structure with an axial ratio very similar to that of the host substructure of Rb-IV (Refs. 4 and 17). This suggests that K-III might also have an incommensurate host-guest structure.

We have carried out an x-ray powder-diffraction study of K-III to 25 GPa using angle-dispersive techniques. We find that K-III does indeed have a composite structure comprising the same 16-atom host structure as Rb-IV and a *C*-face-centered, rather than body-centered, tetragonal guest structure.

II. EXPERIMENTAL

Experiments were conducted both on a distilled sample and on a commercially purchased sample. Essentially identical results were obtained with each. The samples were loaded in a dry oxygen-free atmosphere in a glovebox. In order to avoid contamination no pressure transmitting medium was used. Diffraction data were collected on station 9.1 at the SRS, Daresbury Laboratory, using a wavelength of 0.4654 Å.[18] The two-dimensional (2D) diffraction patterns were integrated azimuthally[19] and structural information was

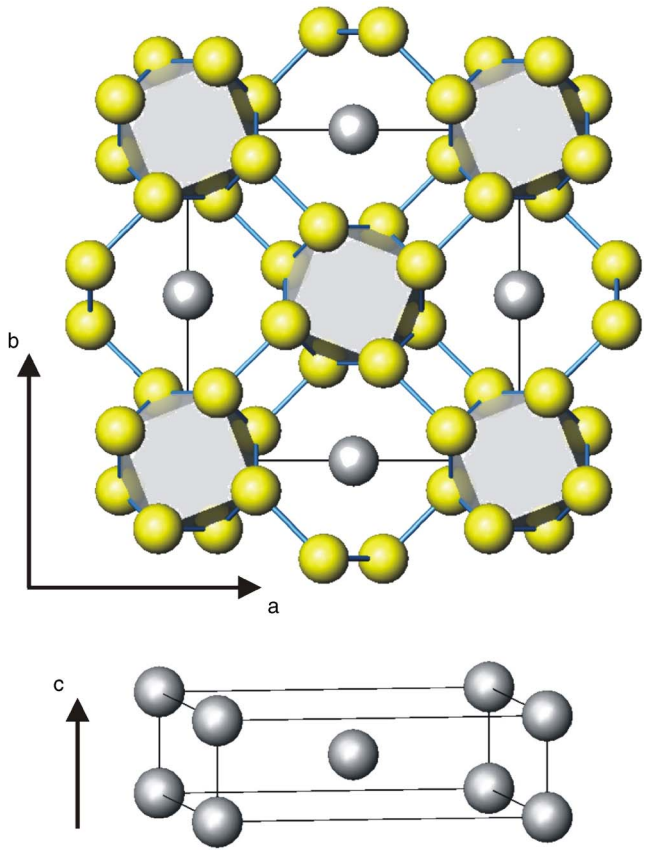

FIG. 1. (Color online) Top: The composite incommensurate structure of Rb-IV, as viewed down the *c* axis. The upper part shows the tetragonal 16-atom host framework (in yellow) and the guest species (in gray) (Refs. 4 and 7). The host atoms form columns of square antiprisms. The perspective lower drawing shows the body-centered tetragonal guest substructure (Ref. 7). Crystallographic axes are labeled.

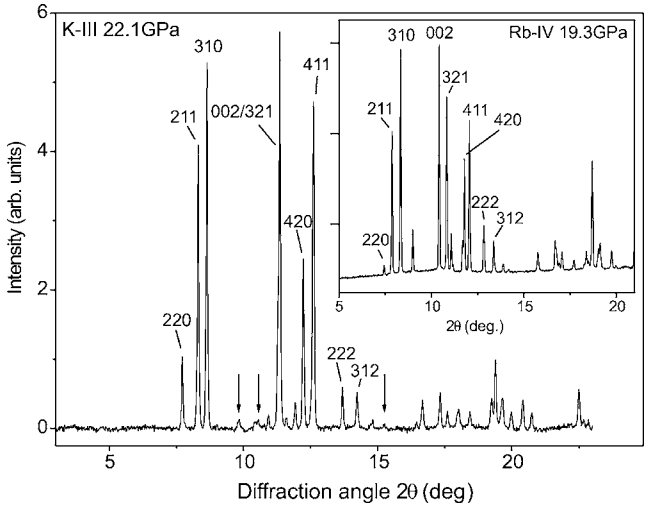

FIG. 2. Integrated 1D diffraction profile from K-III at 22.1 GPa, with the strongest peaks indexed on the tetragonal cell of Winzenick *et al.* (Ref. 17). For comparison, the inset shows a diffraction profile from Rb-IV at 19.3 GPa, with the strongest peaks indexed on the tetragonal host unit cell. The arrows in the K-III profile identify those reflections not accounted for by the tetragonal cell of Winzenick *et al.* (Ref. 17).

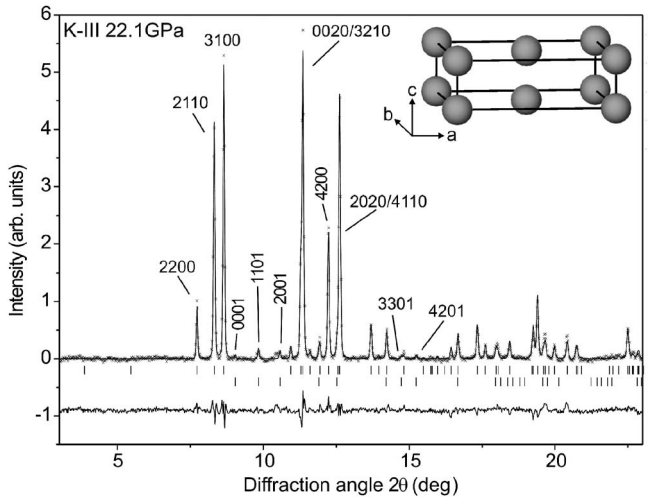

FIG. 3. Rietveld refinement of K-III at 22.1 GPa in superspace group $I4/mcm(00\gamma)0000$. The tick marks below the profile show the peak positions of (upper) the host and host/guest (Ref. 30) reflections, $hkl0$ and $hk00$, respectively, and (lower) the $hk0m$ guest-only reflections. Indices are given for some of the strongest reflections of each type. Below the tick marks is the difference between the observed and calculated profiles. The inset shows a perspective view of the K-III guest structure with crystallographic axes marked.

obtained by least-squares fitting to measured peak positions and by Rietveld refinement of the integrated profiles using JANA2000.[20]

III. RESULTS AND DISCUSSION

In accordance with earlier x-ray diffraction[21] and optical reflectivity data,[22] a bcc (K-I) to fcc (K-II) transformation at 11 GPa precedes the transition from K-II to K-III which was observed at 19.0(5) GPa. Single-phase profiles of K-III were obtained above 21 GPa. A diffraction profile of K-III at 22.1 GPa is shown in Fig. 2. The pattern is very similar to diffraction diagrams obtained from Rb-IV (see inset to Fig. 2). Using the Rb-IV profiles to aid indexing, all the strong peaks in the K-III diffraction profile at 22.1 GPa can be indexed on a body-centered unit cell with dimensions $a=9.767(1)$ Å and $c=4.732(1)$ Å. These dimensions are very close to those reported by Winzenick *et al.*,[17] but this unit cell does not account for a number of additional weak reflections, as identified by arrows in Fig. 2. However, *all* the observed diffraction peaks can be accounted for by a host(H)-guest(G) composite structure with $a=9.767(1)$ Å, $c_H=4.732(1)$ Å, $c_G=2.952(2)$ Å, and $\gamma=c_H/c_G=1.603(2)$ at 22.1 GPa. The weak additional peaks are from the guest component. The systematic absences for the host structure are consistent with space group $I4/mcm$, while the reflections from the guest structure are consistent with a *C*-face centered tetragonal arrangement[23] when the same *a* axis is used for both substructures. Although the host structure is the same as that observed for Rb-IV, the guest structure in Rb-IV is body-centered rather than *C*-face-centered, as shown in Fig. 1.

We have refined the full composite structure of K-III within the formalism of four-dimensional (4D) superspace[24–27] using the superspace group $I4/mcm(00\gamma)0000$.[28,29] The result of a Rietveld refinement to the profile of K-III collected at 22.1 GPa is shown in Fig. 3. Refined atomic coordinates and lattice parameters at selected pressures are given in Table I. At 22.1 GPa, the spacing of the guest atoms along the chains is $c_G=2.952(2)$ Å, somewhat longer than the shortest contact distance in the host structure at the same pressure, where each host atom has five nearest-neighbor host atoms at 2.832(3) Å, 2.887(3) Å(×2), and 2.933(3) Å(×2). The incommensurate nature of the crystal structure causes the host-guest distance to vary from unit cell to unit cell. The closest approach occurs when the chain atoms are located in the center of

TABLE I. Lattice parameters (in Å) and atomic positions of K-III. Host and guest atoms are located at $(x,y,0.5)$ and (0.5,0,0), respectively.

P (GPa)	a_{host}	c_{host}	c_{guest}	x_{host}	y_{host}
19.5	9.937(1)	4.879(1)	3.036(1)	0.7856(6)	0.0881(9)
20.6	9.865(2)	4.810(1)	2.993(2)	0.7941(7)	0.089(1)
21.3	9.819(1)	4.775(1)	2.978(2)	0.7924(6)	0.0914(6)
22.1	9.767(1)	4.732(1)	2.952(2)	0.7897(3)	0.0847(3)
23.1	9.715(1)	4.687(1)	2.935(2)	0.7990(4)	0.0861(6)
22.2[a]	9.770(2)	4.724(1)	2.954(2)	0.7960(4)	0.0845(5)
21.6[a]	9.809(2)	4.762(1)	2.972(3)	0.7947(4)	0.0901(5)
20.5[a]	9.878(1)	4.819(1)	2.996(2)	0.7917(4)	0.0879(4)
19.7[a]	9.9303(2)	4.868(2)	2.880(3)	0.7854(4)	0.0889(4)
18.8[a]	9.979(1)	4.920(2)	3.042(2)	0.7857(4)	0.0871(4)

[a]From data collected on pressure decrease.

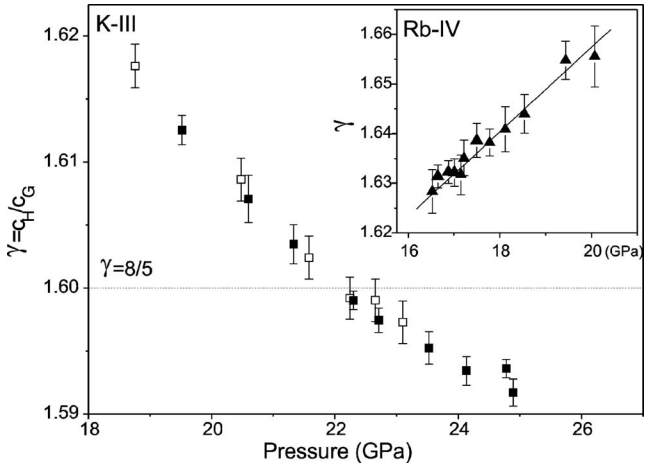

FIG. 4. Pressure dependence of the ratio $\gamma = c_H/c_G$ in K-III to 24.9 GPa. Filled symbols show data collected on pressure increase; unfilled symbols show data from another sample collected on pressure decrease. The commensurate value of 8/5 for c_H/c_G is marked. For comparison, the inset shows the pressure dependence of the c_H/c_G ratio in the composite structure of Rb-IV (from Ref. 7).

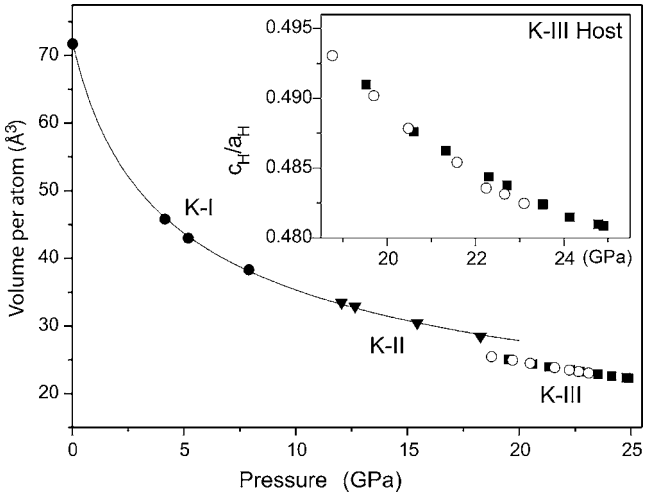

FIG. 5. Pressure dependence of the atomic volume of potassium to 25 GPa. The data for K-I (bcc, filled circles) and K-II (fcc, filled triangles) (Ref. 34) have been fitted to a single equation of state, which is plotted as a solid line. Data for K-III collected on pressure decrease are shown using unfilled symbols. The volume per atom is calculated using the number of atoms in a volume, V_H, corresponding to that of a unit cell of the host substructure, as $V_H/(16+2\times\gamma)$. The inset shows the pressure dependence of the ratio c/a of the K-III host substructure. In both plots, the estimated standard deviations are smaller than the symbols used to plot the points.

squares formed by host framework atoms, and is 2.948(3) Å. The maximum host-guest distance, obtained when the guest atoms are located in the center of square antiprisms of the host framework, is 3.176(4) Å.

The quality of the present data is not sufficient to determine whether, as in Bi-III (Ref. 12) and Sb-II (Refs. 13 and 14), there are additional very weak ($hklm$) reflections resulting from modulations of the host and guest atomic coordinates. As also found in Rb-IV, such reflections may only be visible in data collected from a single-crystal sample.

The incommensurate ratio of the host and guest c-axis lattice parameters of K-III at 22.1 GPa is $\gamma = 1.603(2)$, extremely close to the commensurate value of $8/5 = 1.6$. To confirm that K-III does indeed have an incommensurate host-guest structure, with an irrational value of γ, we have followed the pressure dependence of the lattice parameters over the pressure range 18.8–24.9 GPa. The variation of γ is shown in Fig. 4 and is quite different from that observed previously in Rb-IV, where γ increases with increasing pressure, from 1.628 at 16.5 GPa to 1.655 at 20.1 GPa (Ref. 7) as shown in the inset to Fig. 4.

It is clear that γ of K-III decreases smoothly through the commensurate value of 8/5, with no evidence of any discontinuity. K-III is thus intrinsically incommensurate, and within the experimental resolution of approximately 1 GPa we do not observe any evidence for a lock-in when the axial ratio passes through the commensurate value. Nevertheless, at a pressure of 22.0(2) GPa, K-III has an axial ratio of 8/5. We have recently shown that the host-guest structure with an eight-atom host in Sc-II passes through a 4/3 commensurate form,[16] and that opened up the first possibility for exact calculations in any of the host-guest systems, specifically for those with eight-atom host structures. This result for K-III now presents the opportunity for an exact band structure calculation of an elemental composite host-guest structure with a 16-atom host.

Recently, the guest component of the Rb-IV composite structure was found to become disordered at pressures below 16.7 GPa, such that the chains of guest atoms become partially melted to a one-dimensional (1D) liquidlike state.[31,32] To investigate whether a similar melted-chain state might exist in potassium at room temperature, we have made careful studies of the guest peaks in K-III on pressure decrease down to 18.4(3) GPa, where the sample transformed back to K-II. We observed no peak broadening of the guest peaks, and the guest-atom chains remain ordered down to the lowest pressure of the K-III stability range.

Finally, Fig. 5 shows the compressibility of potassium up to 25 GPa. No discontinuous volume decrease is observed at the K-I→K-II transition at 11 GPa, and these two phases have therefore been fitted with a single Vinet equation of state,[33] giving values for the bulk modulus and its pressure derivative of $B_0 = 4.21(5)$ GPa and $B' = 3.68(3)$, with the ambient-pressure volume V_0 fixed at 72.23 Å.[3] The relative volume change $\Delta V/V_0$ at the K-II→K-III transition amounts to −4.1(1)%.

The c/a ratio of the K-III host (inset of Fig. 5) adopts values below 0.5 and decreases with pressure. By contrast, this ratio increases from 0.500 at 17 GPa to 0.506 at 20 GPa in Rb-IV.[4] Thus both the c_H/a_H and c_H/c_G ratios decrease with pressure in K-III but increase with pressure in Rb-IV, suggesting that c_H is relatively more compressible in K-III. It remains to be investigated if this behavior can be related to the difference in the arrangement of the guest atoms.

In conclusion, we find K-III to have an incommensurate host-guest composite structure, with the same 16-atom host

as Rb-IV but with a *C*-centered, rather than body-centered, guest structure. K-III presents an opportunity to make an exact computational study of band structure and chemical bonding of an elemental host-guest composite structure that is pressure driven through a commensurate axial ratio. At pressures exceeding those of the present investigation, discontinuous changes in the diffraction peaks attributed to the guest species indicate a different ordering of the guest atoms in K-III above 31 GPa.[34] New phases of K observed at pressures above 60 GPa will be reported elsewhere.[35]

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[1] D. A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).
[2] M. Hanfland, I. Loa, and K. Syassen, Phys. Rev. B **65**, 184109 (2002).
[3] U. Schwarz, K. Takemura, M. Hanfland, and K. Syassen, Phys. Rev. Lett. **81**, 2711 (1998).
[4] U. Schwarz, A. Grzechnik, K. Syassen, I. Loa, and M. Hanfland, Phys. Rev. Lett. **83**, 4085 (1999).
[5] U. Schwarz, K. Syassen, A. Grzechnik, and M. Hanfland, Solid State Commun. **112**, 319 (1999).
[6] M. Hanfland, K. Syassen, N. E. Christensen, and D. L. Novikov, Nature (London) **408**, 174 (2000).
[7] M. I. McMahon, S. Rekhi, and R. J. Nelmes, Phys. Rev. Lett. **87**, 055501 (2001).
[8] M. I. McMahon, R. J. Nelmes, and S. Rekhi, Phys. Rev. Lett. **87**, 255502 (2001).
[9] R. J. Nelmes, M. I. McMahon, J. S. Loveday, and S. Rekhi, Phys. Rev. Lett. **88**, 155503 (2002).
[10] R. J. Nelmes, D. R. Allan, M. I. McMahon, and S. A. Belmonte, Phys. Rev. Lett. **83**, 4081 (1999).
[11] M. I. McMahon, T. Bovornratanaraks, D. R. Allan, S. A. Belmonte, and R. J. Nelmes, Phys. Rev. B **61**, 3135 (2000).
[12] M. I. McMahon, O. Degtyareva, and R. J. Nelmes, Phys. Rev. Lett. **85**, 4896 (2000).
[13] U. Schwarz, L. Akselrud, H. Rosner, A. Ormeci, Y. Grin, and M. Hanfland, Phys. Rev. B **67**, 214101 (2003).
[14] O. Degtyareva, Ph.D. thesis, The University of Edinburgh, Edinburgh, 2003.
[15] H. Fujihisa, Y. Akahama, H. Kawamura, Y. Gotoh, H. Yamawaki, M. Sakashita, S. Takeya, and K. Honda, Phys. Rev. B **72**, 132103 (2005).
[16] M. I. McMahon, L. F. Lundegaard, C. Hejny, S. Falconi, and R. J. Nelmes, Phys. Rev. B **73**, 134102 (2006).
[17] M. Winzenick, V. Vijayakumar, and W. B. Holzapfel, Phys. Rev. B **50**, 12381 (1994).
[18] R. J. Nelmes and M. I. McMahon, J. Synchrotron Radiat. **1**, 69 (1994).
[19] R. O. Piltz, M. I. McMahon, J. Crain, P. D. Hatton, R. J. Nelmes, R. J. Cernik, and G. Bushnell-Wye, Rev. Sci. Instrum. **63**, 700 (1992).
[20] V. Petricek, M. Dusek, and L. Palatinus, *The Crystallographic Computing System* JANA2000 (Institute of Physics, Praha, Czech Republic, 2000).
[21] H. Olijnyk and W. B. Holzapfel, Phys. Lett. **99A**, 381 (1983).
[22] K. Takemura and K. Syassen, Phys. Rev. B **28**, 1193 (1983).
[23] The nonstandard space group setting used for the guest structure is $C4/mmm$, with a single atom at (0,0,0). This nonstandard setting is chosen so that the *a* and *b* lattice parameters of the host and guest components are identical.
[24] P. M. deWolf, Acta Crystallogr. **30**, 777 (1974).
[25] P. M. deWolf, Acta Crystallogr. **33**, 493 (1977).
[26] A. Janner and T. Janssen, Phys. Rev. B **15**, 643 (1977).
[27] A. Janner and T. Janssen, Physica A **99**, 47 (1979).
[28] S. van Smaalen, Crystallogr. Rev. **4**, 79 (1995).
[29] In an alternative nomenclature the superspace group is labeled as $L^{I4/mcm}_{-111}:C^{C4/mmm}_{-111}$, see P. M. deWolf, A. Janner, and T. Janssen, Acta Crystallogr. **37**, 625 (1981) and A. Yamamoto, *ibid.* **49**, 831 (1993).
[30] The *hk*00 reflections are insensitive to the incommensuration since it is along the common *c* axes of the host and guest components. These reflections thus derive from the whole structure, host and guest together.
[31] M. I. McMahon and R. J. Nelmes, Phys. Rev. Lett. **93**, 055501 (2004).
[32] S. Falconi, M. I. McMahon, L. F. Lundegaard, C. Hejny, R. J. Nelmes, and M. Hanfland, Phys. Rev. B **73**, 214102 (2006).
[33] P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, J. Phys. C **19**, L467 (1986).
[34] U. Schwarz, I. Loa, M. Hanfland, and K. Syassen (unpublished).
[35] I. Loa, M. Hanfland, N. E. Christensen, and K. Syassen (unpublished).