Pressure Dependent Incommensuration in Rb-IV

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Rb-IV is found to have an incommensurate composite structure, comprising a tetragonal host framework and a simple body-centered tetragonal guest. This does not have the unexpectedly short Rb-Rb distances of the previously reported structure [U. Schwarz *et al.,* Phys. Rev. Lett. **83**, 4085 (1999)]. The ratio of the c-axis lattice parameters is strongly pressure dependent and approaches the commensurate value of $5/3$ at the transition to phase V. A reversible broadening of the guest structure is observed below 16.5(2) GPa.

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The heavy alkali metals undergo an s-to-d electron transfer under pressure, resulting in structural phase transitions from simple high-symmetry cubic phases to complex, lower-symmetry phases [1]. It is only recently, with advances in high-pressure diffraction techniques, that the structures of many of these lower-symmetry phases have been determined, thereby opening up these complex metals to theoretical study [2–4]. In a recent study of Rb-IV, which is stable between ~17 and ~20 GPa [1], Schwarz *et al.* reported the structure as having a composite tetragonal arrangement composed of two interpenetrating substructures [5], as shown in Fig. 3 of Ref. [5] (and also Fig. 3 below). There is a framework of face-sharing antiprisms, and other atoms form chains that lie in channels running along the fourfold c axis of the framework.

This structure bears a striking resemblance to the host-guest composite structures recently reported in the group II and group V elements Ba-IV [6], Sr-V [7], Bi-III [8], Sb-II [8], and As-III [9]. But in all of these, the chains of "guest" atoms form one or more structures that are *incommensurate* with the "host" framework along the c axis. This is an extraordinary new type of structure to find in an element [3]. The host in the II/V elements has the same $I4/mcm$ space group as Schwarz *et al.* reported for the framework structure in Rb-IV, but the latter is more complex, with 16 atoms in the body-centered unit cell rather than the 8 atoms of the host structure in the II/V elements. Furthermore, the diffraction patterns from the II/V elements contain numerous clearly observable diffraction peaks from the crystalline guest component, whereas only one possible nonframework reflection was reported in the diffraction patterns of Rb-IV [5].

There are some difficulties with the commensurate structure for Rb-IV presented by Schwarz *et al.,* as the authors note. Fitting to electron density maxima in Fourier difference maps, and the constraint of a maximum of four chain atoms per unit cell, led to an average chain-atom separation of only 2.59 Å, shorter by 15% than twice the smallest tabulated ionic radius of Rb^+ [5]. It was found that if the occupancies of the chain-atom sites were instead treated as refinable parameters, the values converged to ones giving an average chain-atom separation of 2.97 Å with 3.48 chain atoms per unit cell, but this separation was still notably short [5]. The single nonframework reflection in Rb-IV was attributed to either a partial transformation to phase V or, possibly, some c-axis ordering of incompletely occupied chain sites [5]. But it is surprising that other Rb-V or superstructure reflections are not observed. More recently, it has been suggested that the chains might be incommensurate with the framework structure, as in Ba-IV, but without any interchain ordering in view of the apparent absence of other than the one extra reflection [10]. However, that would be difficult to reconcile with the sharpness of the nonframework reflection in the 18.1 and 19.9 GPa profiles of Fig. 1(a) of Ref. [5].

This is an intriguing problem. The similarities to the Ba-IV structure are clear, and if the true structure is incommensurate, there would be considerable interest in the extension of such structures to the alkali metals and in the differences from the II/V elements shown by the more complex host and by the apparent absence of interchain ordering. We have therefore reinvestigated the Rb-IV structure.

All experiments were done with high-purity samples obtained from the Aldrich Chemical Company, using diamond-anvil pressure cells with tungsten gaskets. The Rb was loaded in a dry oxygen-free atmosphere (<1 ppm O_2 and <1 ppm H_2O) to prevent oxidation. A small ruby sphere was used for pressure measurement. No pressure-transmitting medium was used. Angle-dispersive powder diffraction data were collected on station 9.1 at the Synchrotron Radiation Source (SRS), Daresbury Laboratory, using a wavelength of 0.4654(1) Å [11]. Diffraction patterns of the low-pressure bcc and fcc phases showed no discernible contaminant peaks, confirming that the sample was pure rubidium. The 2D diffraction images were integrated azimuthally [11], and structural information was obtained by Rietveld refinement of the integrated profiles using the program MPROF [12]. The data shown were obtained from a number of different samples, which all exhibited the same behavior, and this behavior is also

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clearly the same as was shown by the samples of Schwarz *et al.* according to the data in Ref. [5].

The transition from Rb-III to Rb-IV on pressure increase was observed at 16.6(3) GPa, but single-phase Rb-IV diffraction patterns were observed only above 17.2 GPa. An integrated diffraction pattern collected at 17.7 GPa on pressure increase is shown in Fig. 1. The additional reflection reported previously [5] and not accounted for by the framework structure of Rb-IV was observed in all samples, as marked at $2\theta = 8.9°$. We found a discontinuity of ~0.02 Å between its position and that of the (101) reflection from Rb-V at the Rb-IV → Rb-V phase transition, observed to begin at 19.6(2) GPa on pressure increase. This discontinuity is directly visible in diffraction patterns obtained on pressure decrease from Rb-V in which the nonframework reflection from Rb-IV and the (101) reflection from Rb-V coexisted as a resolved doublet — as shown in the inset in Fig. 1. We conclude, therefore, that the nonframework peak identified in Ref. [5] arises from Rb-IV and must be accounted for by the Rb-IV structure.

Closer inspection of diffraction profiles collected over a wide range of pressures revealed a number of other nonframework features. The clearest of these is the peak indicated by the arrow at ~13.7° in Fig. 1. We observed this peak in all our samples, but it lies outside the range of data shown in Fig. 1(a) of Ref. [5]. Three other nonframework features were detectable as weak shoulders, two of which are perhaps just visible as faint shoulders on the left of the (002) and (222) reflections in the 18.1 GPa profile in Fig. 1(a) of Ref. [5]. These features were found to be better resolved at lower pressures on pressure decrease. Figure 2 shows an integrated diffraction profile collected at 16.8 GPa from a sample prepared by decreasing the pressure slowly back into Rb-IV from phase V. At this pressure, the additional features are resolved from their neighboring framework peaks, as shown in the inset. A further three weak features not accounted for by the $I4/mcm$ framework structure of Rb-IV were detected at higher 2θ angles.

The resemblance of the previously proposed Rb-IV structure [5] to the host-guest structures observed in the group II and group V elements [6–9] suggested that the additional reflections arose from a guest structure incommensurate with the host framework. *Ab initio* indexing of five of the strongest, along with the $hk0$ reflections from the framework structure, revealed that all the nonframework reflections could be indexed on a body-centered tetragonal lattice with systematic absences consistent with space group $I4/mmm$, and having a c-axis lattice parameter about 1.63 smaller than that of the host framework. This composite structure is shown in Fig. 3, and a Rietveld refinement of it with the data collected at 16.8 GPa, using a pseudo-two-phase technique [7] to fit the host-guest structure, is shown in Fig. 2. The remaining small discrepancies between the observed and calculated profiles arise from the limitations of the single-parameter preferred orientation model used in the refinement.

The refined values of the host-structure atomic coordinates at 16.8 GPa (for the 16k site of space group $I4/mcm$) are $\left(0.7903(1), 0.0851(1), \frac{1}{2}\right)$, very similar to those reported previously [5]. The guest structure has atoms on the 2a site of $I4/mmm$. The refined lattice parameters

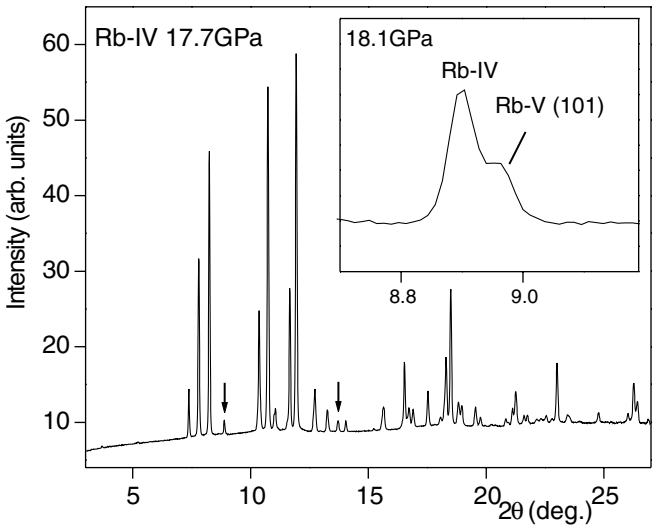

FIG. 1. Integrated 1D diffraction profile collected from a sample of Rb-IV at 17.7 GPa on pressure increase. The two nonframework peaks clearly observable in the profile are indicated with arrows. The inset shows the lower-angle one at 18.1 GPa on pressure decrease. At this pressure the (101) reflection from Rb-V is still clearly visible and has a d spacing ~0.02 Å smaller than the nonframework peak.

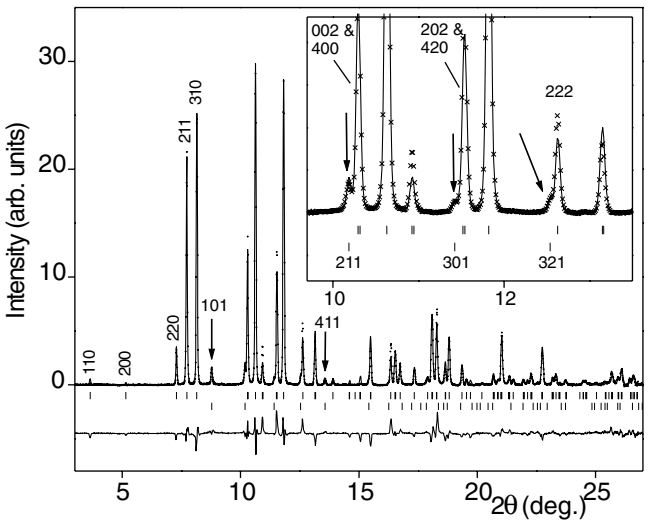

FIG. 2. Integrated 1D profile from Rb-IV at 16.8 GPa (dots) and a Rietveld refinement fit (line). The upper and lower tick marks below the profile show the peak positions of the host and non-$hk0$ guest reflections, respectively. Below the tick marks is the difference between the observed and calculated profiles. In the inset, arrows mark three guest peaks. Their tick marks are indexed, and nearly overlapping host reflections are also indexed. Low-angle host reflections and the two nonoverlapped guest reflections are indexed in the main profile.

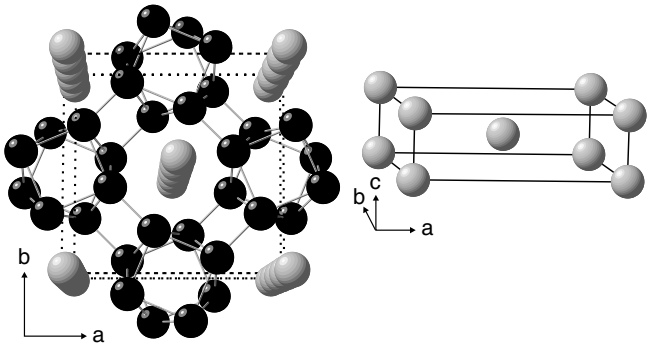

FIG. 3. Host-guest structure of Rb-IV. The host framework is shown in black, and the guest structure in grey.

from the Rietveld fit are $a_H = a_G = 10.3503(1)$ Å, $c_H = 5.1865(2)$ Å, and $c_G = 3.1797(6)$ Å. The spacing of the atoms in the chains is thus $c_G = 3.180$ Å. This is significantly longer than the shortest contact distances of 3.004(2) Å in the host structure at the same pressure, contrary to the problematic short chain-atom separation of 2.59–2.97 Å obtained for a commensurate chain-atom structure [5]. The closest approach between guest and host atoms is 3.131(2) Å. Correlations between the chain-site occupancy and the preferred orientation parameter prevent reliable refinement of the occupancy of the chain-atom sites, but these sites are known to be 100% occupied in Ba-IV [6]. If this is assumed, there are $c_H/c_G = 1.631$ atoms in each of the two channels at 16.8 GPa and hence 19.262 atoms per host unit cell. This is 1.1% lower than the number of atoms per host unit cell determined using the partial occupancy model in Ref. [5] and results in a density for Rb-IV also being 1.1% lower than suggested previously [5]. From a mixed-phase Rb-IV/V profile collected at 20.1 GPa, there is a small volume decrease of 0.9(1)% at the IV → V transition.

In keeping with the intrinsic incommensurate nature of the structure, the ratio c_H/c_G is found to vary continuously with pressure, as illustrated in Fig. 4, and it approaches the commensurate value of 5/3 close to the transition to Rb-V. However, single-phase Rb-V patterns are observed above 20.7 GPa while linear extrapolation suggests that a commensurate structure with $c_H/c_G = 5/3$ would not be obtained until 21.2 GPa. The difference in the host structure from the II/V elements leads to a larger c_H/c_G ratio than the range 1.3–1.4 found in Ba [6], Sr [7], Bi [8], Sb [8], and As [9]. The behavior of Rb-IV also differs in that the ratio *increases* with pressure, whereas it decreases in all the II/V elements. The pressure dependence is weak in all but Ba, whose behavior is shown for comparison in Fig. 4. It can be seen that Ba and Rb exhibit a comparably strong pressure dependence.

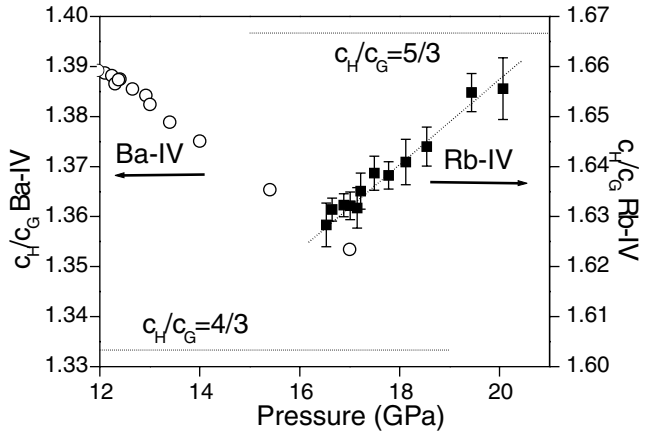

FIG. 4. Pressure dependence of the ratio c_H/c_G in Rb-IV. The dotted line through the points is a guide for the eye. The behavior of Ba-IV is shown for comparison.

The pressure dependence of c_H/c_G and the increased splitting of many partially overlapping host peaks—arising through the change in the c_H/a_H ratio with increasing pressure—account for the elusiveness of the guest reflections. Calculations of the pressure dependence of the d spacings of the three guest peaks indexed as (211), (301), and (321) in the inset in Fig. 2 show that they are all overlapped by reflections from the host structure at 18 GPa and above; it is only below 17 GPa that they become clearly resolved. As single-phase Rb-IV patterns are not observed at such pressures on pressure increase, it is thus only on pressure decrease that guest reflections other than the (101) and (411)—the single reflections identified in Fig. 1—are clearly visible. However, at 16.5(2) GPa, there is a sudden (reversible) change in the guest peaks. Above this pressure they are sharp, with widths similar to those from the host phase, but at 16.5(2) GPa and below they broaden dramatically, as illustrated in Fig. 5 where only the strong (101) reflection remains visible at 16.2 GPa. This is the broad feature marked by an asterisk in the inset in Fig. 5, where it can be seen that the other guest peaks—most clearly (411) and (211)—have apparently disappeared. Thus, the

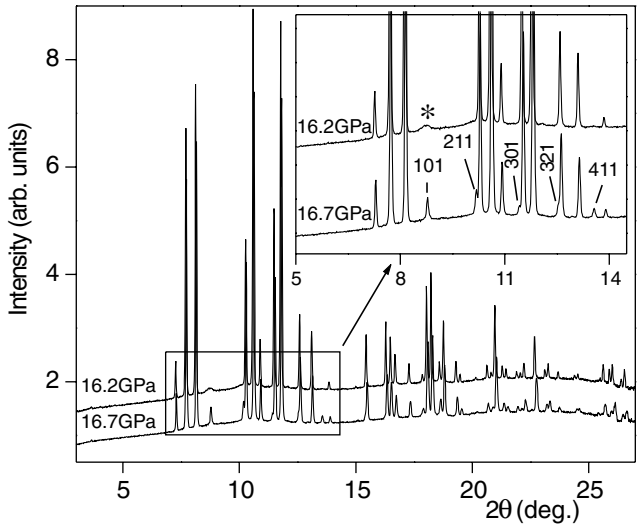

FIG. 5. Integrated 1D profiles from Rb-IV at 16.7 and 16.2 GPa. The inset shows an enlarged view of the region of the (101), (211), (301), (321), and (411) guest reflections. The asterisk marks the broad feature at the (101) position in the 16.2 GPa profile.

presence of the crystalline guest phase is obvious only on pressure decrease *and* in the narrow range of 17.0–16.5 GPa. We note that the pattern obtained at 16.2 GPa (Fig. 5) is strikingly similar to that in Fig. 1(b) of Ref. [5]. (The pressure for the latter data is reported as 16.9 GPa by Schwarz *et al.,* but the measured pressures in Ref. [5] all appear to be systematically 0.4 GPa higher than ours for the same lattice parameters [13].) On further pressure decrease, the broadened (101) guest peak remained visible to 16.0 GPa, where the sample began to transform back to Rb-III.

The much increased width of the guest peaks below 16.5 GPa is consistent with a reduced correlation length of the guest structure in the *ab* plane. Further, preferably single-crystal, diffraction data will be required to characterize the nature of the guest phase below 16.5 GPa completely. We note that the pressure at which the guest reflections broaden is very similar to the equilibrium transition pressure for Rb-III ↔ Rb-IV. It is intriguing that something akin to melting of the guest structure may be occurring at this pressure. Another possibility is that the chain separation—which at 7.3 Å is significantly larger than in the II/V systems—passes through a critical value for long range ordering of the chains.

The observation of an incommensurate host-guest structure in Rb-IV shows that this new type of elemental structure exists in an increasing number of electronically different systems. And our results show that these incommensurate structures are not limited to the host structure common to all the II/V systems, albeit the Rb-IV host has the same $I4/mcm$ space group. Schwarz *et al.* noted the close similarity of the Rb-IV structure to that of the metal-atom sublattice in W_5Si_3 [5], and we have noted an even closer relationship between the incommensurate structures observed in Ba-IV, Sr-V, Bi-III, Sb-II, and As-III and the (commensurate) structures of other binary alloys, such as Al_2Cu [6] and In_5Bi_3 [8]. This might suggest that the elements themselves are behaving as binarylike systems—with the host and guest atoms perhaps having different electronic configurations. Further detailed computational and experimental studies are required to address this interesting possibility. Some first theoretical insights have been obtained for Ba-IV [4], but present computational techniques for *ab initio* calculations are limited to commensurate structures and hence can yield only approximate results. Now Rb-IV is the first of this new class of incommensurate elements to offer the exciting possibility of comparing the stability of a known commensurate phase (Rb-V) directly with the (extrapolated) commensurate form expected for Rb-IV at ~21 GPa [14], and investigating why Rb-V is the more stable. Such a comparison should yield the electron density of Rb-IV, and also give insight into the stabilization of Rb-IV with respect to Rb-V when c_H/c_G deviates from 5/3.

The reduction of the *ab* plane correlation length observed in Rb-IV raises a further interesting possibility of obtaining a system with *no* interchain ordering. Though the transition back to Rb-III intervenes at room temperature, it may be possible to "melt" the guest chains at high temperatures such that there is no correlation in the *ab* plane. This phenomenon has been observed previously in the (incommensurate) Hg chains in $Hg_{3-\delta}AsF_6$ [15], and it would be of great interest to study such effects in an element.

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