

Chain “Melting” in the Composite Rb-IV Structure

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The Bragg peaks from the structure formed by the guest chains in the incommensurate composite structure of Rb-IV are all found to broaden strongly at pressures below 16.7(1) GPa. This signals a loss of the interchain correlation. At the lowest reachable pressure before the transition to Rb-III, 16.2 GPa, the correlation length is only ~ 30 Å, or 4 times the interchain distance. There is also evidence of a loss of long-range order within each chain. The chains thus exhibit the onset of the characteristics of an ordered 1D liquid.

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The alkali and alkaline-earth metals have long been known to exhibit structural complexity at high pressure associated with changes in the configuration of their valence electrons [1]. Perhaps the most remarkable have been found in Ba-IV, Sr-V, and Rb-IV, which all have a new elemental structure type, comprising two interpenetrating components: a tetragonal “host” framework (space group $I4/mcm$) with channels along the fourfold c axis and 1D chains that lie in the host channels and form “guest” structures that are *incommensurate* with the host along c [2–4]. The same incommensurate composite structures have also been observed in the group V elements As, Sb, and Bi [5]. While Ba, Sr, As, Bi, and Sb have the same 8-atom host structure, the composite structure of Rb-IV has a 16-atom host, as found in an earlier study of ours [4] and shown later in Fig. 3. A structure of this Rb-IV type has also been found for phase III of potassium [6].

Diffraction patterns from these phases contain reflections from the host and guest components. In the case of Bi-III and Sb-II, additional weak satellite reflections have been detected that are attributable to modulations in atomic positions arising from a significant interaction between the host and guest components [5]. The diffraction patterns from single (or quasisingle) crystals of Ba, Sr, and Bi also reveal sheets of diffuse scattering perpendicular to the c axis, arising from a degree of positional disorder of the guest chains along c [2]. However, repeated cycling through the intraphase transition in Ba-IV at 12.5(2) GPa resulted in a marked decrease in this diffuse scattering, leading to the conclusion that the equilibrium state of these phases has the guest chains fully ordered in their relative positions along c [2].

A composite structure of a related kind has long been known to exist in $\text{Hg}_{3-\delta}\text{AsF}_6$ and has been extensively studied [7–10]. The Hg atoms are in 1D chains that run through nonintersecting perpendicular channels in the AsF_6 host structure. Below 120 K, these perpendicular Hg chains form a long-range ordered structure that is incommensurate with the AsF_6 host. However, at room

temperature, the guest chains are almost completely disordered within the AsF_6 framework and produce intense sheets of diffuse scattering perpendicular to the two chain directions with almost uniform intensity. Detailed studies of the shape and widths of these diffuse sheets reveal that the chains can be considered as an ordered 1D liquid [11]. The characteristics of this state are (i) disorder of the chains with respect to one another in their positions along the chain direction and (ii) loss of long-range order within each chain, which causes the fluctuation in the distance between two chain atoms to increase with their separation [11]. This latter effect is manifested in a marked increase in width of the diffuse sheets with the order of the sheet [10–12], and similar behavior is reported in a number of chain-composite structures [13–15].

By contrast, the guest structure of the group I, II, and V elements are all fully ordered at room temperature, some 150 K above the “melting” temperature of the chains in $\text{Hg}_{3-\delta}\text{AsF}_6$, even though the chains in the group II and V elements are ~ 5 – 6 Å apart and those in Rb-IV and K-III are ~ 7 Å apart, compared with only 3.1 Å between the perpendicular chains in $\text{Hg}_{3-\delta}\text{AsF}_6$. And between neighboring *parallel* chains in $\text{Hg}_{3-\delta}\text{AsF}_6$, there is only short range ordering at 120 K, though the separation is ~ 7 Å, similar to Rb-IV and K-III. The difference is striking. Furthermore, we have found that at temperatures as high as 700 K there is still no evidence of any chain melting in Ba-IV (which supports the conclusion, above, that the partial interchain disorder observed in Ba-IV at room temperature is a nonequilibrium state). And there is no loss of order in the chains of Bi-III at ~ 450 K, the maximum temperature to which it can be heated before the transition to Bi-VII [1].

Another alternative is to vary pressure, which is known to affect the ordering temperature of $\text{Hg}_{3-\delta}\text{AsF}_6$ strongly, increasing it from 120 K at atmospheric pressure to 240 K at 1 GPa [16]. In our recent study of Rb-IV, we noted that below ~ 16.5 GPa the Bragg peaks from the guest component all broaden strongly, consistent with a reduced

correlation length of the guest structure [4]. Evidence of this broadening can also be seen in the data of Schwarz *et al.* [17]. In this Letter, we report a systematic study of the loss of long-range positional order between the guest-atom chains and also find evidence for a 1D liquidlike loss of long-range order within the chains.

Since the onset of disorder manifests itself as an anisotropic increase in peak widths and the appearance of structured diffuse scattering, single-crystal scattering techniques are clearly preferred. Good-quality single-crystal samples of high-pressure phases are extremely difficult to obtain, particularly at the (high) pressures of 16–20 GPa where Rb-IV is stable. However, after repeated attempts, we found that partial recrystallization of powdered Rb-IV samples on pressure decrease can be exploited to obtain *quasisingle* crystal samples, such as were used for our previous observation of diffuse scattering in Ba-IV, Sr-V, and Bi-III [2,3,5]. Such samples comprise a small number of well crystallized single crystallites that can, as in this case, yield overlapping but separable single-crystal diffraction patterns.

Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source at Daresbury Laboratory using angle-dispersive diffraction techniques and an image plate area detector [18]. The incident x-ray wavelength was 0.4654 Å. The Rb samples were obtained from the Aldrich Chemical Company and were of stated purity 99.99%. To avoid contamination, the samples were loaded into Merrill-Bassett diamond anvils cells in a glove box with an argon atmosphere containing <1 ppm H₂O and O₂. Diffraction patterns showed no evidence of any contaminant peaks. A small ruby sphere was used for pressure measurement and, to avoid contamination, no pressure transmitting medium was used. The 2D diffraction images were integrated azimuthally [18] to give standard powder diffraction profiles. In the formalism of 4D superspace [19], the diffraction peaks are indexed using four indices (hkl_1l_2) with the host and guest reflections having indices (hkl_10) and ($hk0l_2$), respectively.

On pressure increase, the transition from Rb-III to Rb-IV starts at 16.6 GPa, but single-phase Rb-IV patterns are obtained only above 17.2 GPa [4]. A small range of hysteresis allows single-phase Rb-IV patterns to be obtained on subsequent pressure decrease down to 16.2 GPa; just below that pressure the transition back to Rb-III starts [4]. Azimuthally integrated diffraction profiles collected on pressure decrease from 18.5 to 16.2 GPa from a partially recrystallized powder sample of Rb-IV are shown in Fig. 1. The guest peaks, such as (1001) shown, all broaden significantly below 16.7(1) GPa, and their width continues to increase down to 16.2 GPa. At this pressure, only the strongest guest reflection, (1001), remains visible. No increase in the width of the host peaks, such as the (2200), (2110), and (3100) reflections identified in Fig. 1, is observed over the same pressure range. As shown for the (1001) reflection, all of the guest peaks were found to sharpen on pressure increase such

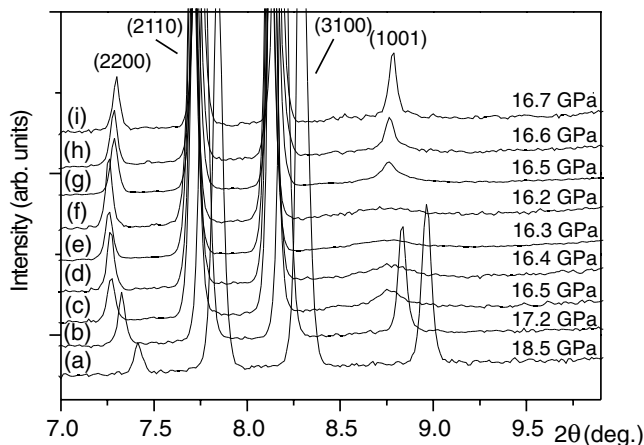


FIG. 1. Part of integrated profiles of Rb-IV on pressure decrease, (a) to (f), and then increase, (f) to (i). (1001) is the strongest reflection from the guest component; other reflections are from the host component.

that their widths were again resolution limited at 16.7 GPa and above.

Figure 2 compares half of the 2D diffraction pattern collected from the Rb-IV sample at 18.5 GPa (left) with half of that collected at 16.3 GPa (right) on pressure decrease. Below 16.7 GPa, sheets of diffuse scattering (seen edge on as lines in the 16.3 GPa pattern) start to develop and become more intense as the pressure is reduced further to 16.2 GPa. (The differently oriented lines of diffuse scattering in the 16.3 GPa pattern originate from differently oriented quasisingle crystallites within the sample.) On increasing pressure again from 16.2 GPa, the diffuse scattering decreases in intensity and is no longer discernible above 16.7 GPa.

The insets enlarge the marked region in Fig. 2 (right) and are centered on the two strongest spots on the (1001)

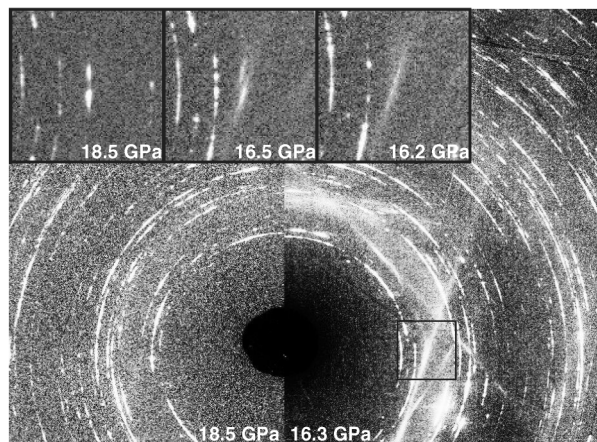


FIG. 2. 2D images collected from Rb-IV on pressure decrease at 18.5 GPa (left) and 16.3 GPa (right). Insets show enlarged views of the marked region in the 16.3 GPa data, centered on two reflections on the (1001) Debye-Scherrer ring from the guest component.

Debye-Scherrer (DS) ring. Above 16.7 GPa, both spots are compact and elongated only slightly around the DS ring. They each appear to be made up of reflections from a small number of very similarly aligned crystallites. As can be seen in the inset at 16.5 GPa, both spots elongate below 16.7 GPa in a direction that is not around the DS ring but lies in the plane of diffuse scattering—thus confirming that the broadening is in the ab plane, perpendicular to the chain direction. Their width becomes resolution limited again on raising the pressure back above 16.7 GPa. The lower of the two spots is by far the more intense, and it can be seen by comparing the insets at 16.5 and 16.2 GPa that it is only this lower spot that gives detectable diffuse scattering in the pressure range of strong broadening. All measurements were thus taken from this one spot. As the guest reflections broaden in the ab plane, tails of adjacent broadened peaks start to overlap to form the sheets of diffuse scattering seen as lines at 16.3 GPa in the main part of the figure. But, even at 16.2 GPa, the sheets remain quite structured, with most of the scattering peaked around the positions of the guest reflections such as (1001), as shown in the insets. (The contrast in the main figure has been adjusted to enhance the much weaker scattering between the peaks, and the lines thus appear more uniform than they are.) Loss of all interchain ordering would leave *only* sheets of more or less uniform diffuse scattering from the guest atoms, as observed in HgAsF_6 at ambient temperature [8].

The interchain correlation length can be quantified from the broadening of the guest reflections. The width of one of these (1001) spots perpendicular to the chain direction was obtained by integrating it to a 1D profile along the direction of the line of diffuse scattering. The additional width over that measured at 18.5 GPa, Δ_{FWHM} , is plotted against the interchain spacing in Fig. 3(a), and subtraction of the unbroadened width affords an approximate deconvolution of the intrinsic spot size. The corresponding estimated correlation length, $2\pi/\Delta_{\text{FWHM}}$, is shown in Fig. 3(b). The dimension of the spot along the relevant direction at 18.5 GPa corresponds to a $2\pi/\Delta_{\text{FWHM}}$ value of ~ 500 Å, which is thus the effective resolution limit of these measurements. Below 16.7 GPa, the (1001) peak broadens rapidly [Fig. 3(a)] such that at 16.2 GPa the interchain correlation length falls to 30 Å, or 4 times the interchain spacing of 7.350 Å at this pressure. A reasonable extrapolation of the (steep) dependence of the correlation length on interchain spacing suggests that long-range order on the scale of the crystallite size is reached at a spacing of ≥ 7.27 Å, and extrapolation to greater interchain spacing suggests that the chains would fully melt with a small further expansion of the spacing to ~ 7.38 Å, which corresponds to a pressure of ~ 15.8 GPa.

It is noteworthy in Fig. 2 that only the first-order sheets of diffuse scattering are detectable. This is significant in indicating that there is also a loss of long-range order within each chain [10–12], as found in other chain-

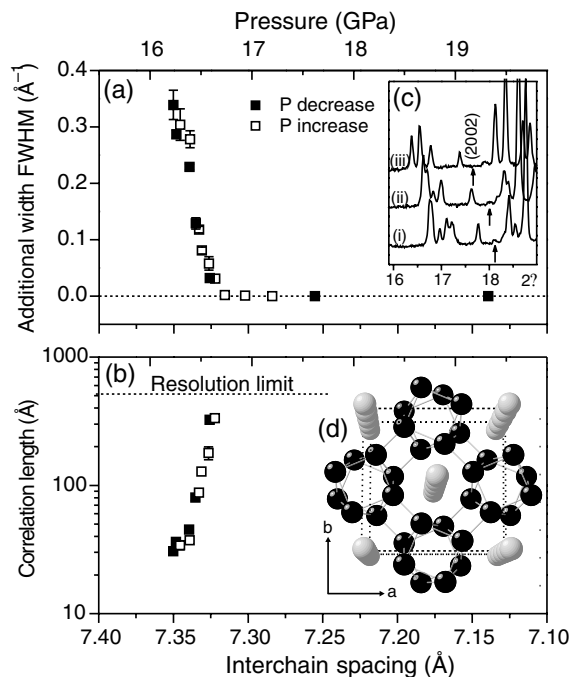


FIG. 3. (a) Additional width in excess of the intrinsic full width at half maximum height of the (1001) spot in the ab plane, and (b) the corresponding correlation length of the guest structure in Rb-IV. Dotted lines are guides to the eye. Inset (c): reduction in the intensity of the (2002) modulation reflection, at the positions marked by arrows, as pressure is decreased from (i) 19.8 GPa to (ii) 18.5 GPa to (iii) 16.9 GPa. Inset (d): the host-guest structure of Rb-IV. The host framework is shown in black, and the chains of guest atoms in gray.

composite structures [13–15]. We thus show that the guest chains in Rb-IV exhibit both of the principal characteristics of an ordered 1D liquid [11]: disorder in the relative positions of chains along the chain direction and (intra-chain) disorder within individual chains. It is interesting that a precursor of the along-chain disorder develops as an anisotropy of atomic thermal motion above 16.7 GPa: as shown for (2002) in inset (c) of Fig. 3(a), guest reflections with $l > 1$ weaken and become undetectable as the pressure falls from 19.8 to 16.9 GPa. The observed intensities indicate approximately isotropic thermal motion in the chains at 19.8 GPa and an additional along-chain root-mean square amplitude of ~ 0.30 Å at 16.9 GPa.

Unlike the behavior shown in Fig. 2 for Rb-IV, higher order sheets are readily visible in Ba-IV, Bi-III, and Sr-V, as shown in Fig. 2 of Ref. [2], Fig. 1 of Ref. [5], and Fig. 4 of Ref. [3], respectively. This throws further light on the nature of the disorder in these other different systems. It is evident that, although the chains in part of the Ba-IV, Bi-III, and Sr-V samples are positionally disordered, there is no detectable lack of intrachain long-range order—a conclusion in keeping with the other evidence already cited that in these cases the disorder arises from incomplete formation of the equilibrium (crystalline) state rather than the melting seen in Rb-IV. It is remarkable that, although the chains in Ba-IV, Bi-III, and Sr-V are

incommensurate with the host and thus weakly interacting with it, they still lack the intrachain disorder of Rb-IV, even when in a positionally disordered configuration with respect to one another. It may be significant that Rb has the largest interchain spacing yet found—and that no such structure has been found in Cs where the spacing would be expected to be larger still.

The apparent difficulty of disordering the chains in the elemental metals despite the large interchain distances raises questions about the nature of the chain-chain interaction. Emery and Axe [11] concluded that the interaction between parallel chains in $\text{Hg}_{3-\delta}\text{AsF}_6$ —which are $>7 \text{ \AA}$ apart as in Rb-IV—was of very short range and could not arise from a direct Coulomb interaction. They suggested, rather, that the host structure, or some form of modulation of the electron density in the Hg chains, must play a role in the coupling. A direct Coulomb interaction between the chains would be expected to be ineffective in Rb-IV due to the screening of the metallic host lattice, quite apart from the large ($>7 \text{ \AA}$) interchain spacing. Brown *et al.* [20] discuss the possibility of indirect interactions between the chains of $\text{Hg}_{3-\delta}\text{AsF}_6$ transmitted by small distortions of the host structure, but conclude that interactions of this kind will also be very weak because of the incommensurability between the chains and the host. However, we have found in the case of Bi-III that the chain-atom positions are modulated along the chain direction in such a way as to form approximately into pairs [21]. Such modulations give rise to additional satellite reflections and signal a significant interaction between the chains and the host. We do not observe any satellite reflections in Rb-IV, but calculations show that significant modulations could be present without giving rise to satellites with detectable intensity in quasi-single-crystal data. And, in further data collection stimulated by this work on Rb-IV, we have now found readily measurable modulation reflections in Ba-IV also. By contrast, there is no evidence in the high-quality single-crystal data from $\text{Hg}_{3-\delta}\text{AsF}_6$ of any similar modulations [9,22].

Strong host-chain interactions may thus provide a plausible origin for chain ordering in the composite elemental metals at much higher temperatures than in systems such as $\text{Hg}_{3-\delta}\text{AsF}_6$. The transition to the disordered state below 16.7 GPa in Rb-IV may then arise from a reduction in such interactions as the channels in the host structure expand beyond a certain critical size or their separation exceeds a critical value, and it seems reasonable to speculate that modulation reflections may develop in $\text{Hg}_{3-\delta}\text{AsF}_6$ as the chain ordering temperature increases under pressure. Another recent suggestion [23] is that the stability of the guest structure in the metals may be enhanced by an intrinsically metallic pseudogap mechanism such as has been proposed to account for complex stacking structures in alkali metals [24], and that the chain melting in Rb-IV arises because this mechanism is less effective in Rb-IV than in Ba-IV.

It would clearly be of particular interest to obtain yet higher quality data to look for modulation satellites in Rb-IV and to look for changes in them approaching the melting transition. In the meantime, this remains a puzzling, unique, and novel state in an element that merits a range of further study, including of the chain dynamics.

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Note added in proof.—In the preliminary stage of a full single-crystal study of Rb-IV at 19.3 GPa, we have found that the modulation reflections are indeed present, and that the strongest of them have intensities $\sim 1\%$ of the strongest (1001) guest reflection.

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