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One-dimensional composite host–guest structure in BaVS_3

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A detailed synchrotron X-ray diffraction (XRD) study performed with a single crystal of BaVS_3 (barium vanadium trisulfide) in the temperature range between 10 and 295 K is reported. Aside from the known tetragonal–orthorhombic (240 K) and orthorhombic–monoclinic (69 K) phase transitions, in the $130 < T \leq 295$ K range the overall structure can be viewed as a host–guest (H–G) composite. The BaS_3 matrix is the host, while the V-chains form the guest. The two subsystems lock in at $T_{\text{LOCK}} = 130 \pm 20$ K. This temperature is marked by a symmetry change from orthorhombic to monoclinic. This results in the formation of twins, implying a structural phase transition identified here for the first time. From the refined structural data, it is possible to follow, starting already at 295 K downwards, the stepwise transformation of VS_6 octahedra into VS_5 tetragonal pyramids as the origin of the structure evolution. The new findings will yield a better understanding of the complex electronic phase diagram of BaVS_3 .

1. Introduction

The crystal structure of BaVS_3 can be described as consisting of hexagonal close packed (hcp) Ba and S atoms with V-chains located in the hexagonal channels formed by S atoms (Fig. 1). The short V–V distances of 2.8 Å along the V-chains, compared to the distance of more than 6 Å between them, was the reason to consider BaVS_3 as an electronically quasi-one-dimensional (quasi-1D) system, expected to exhibit strong on-chain correlations. Indeed, BaVS_3 undergoes a metal–insulator (MI) transition at $T_{\text{MI}} = 69$ K (Gardner *et al.*, 1969; Takano *et al.*, 1977; Massenet *et al.*, 1978; Graf *et al.*, 1995; Kuriyaki *et al.*, 1995; Imada *et al.*, 1998; Forró *et al.*, 2000; Mihály *et al.*, 2000; Inami *et al.*, 2002; Fagot *et al.*, 2005; Sanna *et al.*, 2004; Choi *et al.*, 2009), followed by magnetic ordering below $T_{\text{N}} = 31$ K (Heidemann & Takano, 1980; Leininger *et al.*, 2011; Sugiyama *et al.*, 2020). However, the anisotropy of the conductivity for $T > T_{\text{MI}}$ of $\sigma_c/\sigma_a = 3\text{--}4$ is surprisingly low (Mihály *et al.*, 2000; Barišić, 2004; Kézsmárki *et al.*, 2006). Therefore, its remarkable and intriguing electrical and magnetic properties have been extensively studied starting from 1969 (Gardner *et al.*, 1969) to very recently (Sugiyama *et al.*, 2020). Besides the MI transition and magnetic ordering, numerous measurements of other physical properties are reported in the literature, such as: (i) electrical resistivity (Gardner *et al.*, 1969; Kuriyaki *et al.*, 1995; Graf *et al.*, 1995; Booth *et al.*, 1999; Mihály *et al.*, 2000; Kézsmárki *et al.*, 2006),

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Table 1

Experimental details for the representative structures of BaVS₃.For all structures: $M_r = 284.5$. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Agilent, 2014). A new multipurpose diffractometer PILATUS@SNBL (Dyadkin *et al.*, 2016) was used for the data collections.

	250 K	220 K	100 K	70 K	150 K
Crystal data					
Crystal system, space group	Hexagonal, $P6_3/mmc$ (for BaS ₃)	Orthorhombic, $Ccm2_1$ (for BaS ₃)	Monoclinic, Cm	Monoclinic, Cm	Monoclinic, Im
a, b, c (Å)	Trigonal, $P\bar{3}m1$ (for V)* 6.7164 (2), 6.7164 (2), 5.6088 (2)	Monoclinic, Cm (for V)* 11.593 (7), 6.708 (5), 5.604 (3)	11.485 (7), 6.751 (5), 5.597 (3)	11.496 (9), 6.742 (7), 5.597 (5)	11.456 (1), 6.764 (1), 11.188 (1)
α, β, γ (°)	90, 90, 120	90, 90.00 (1), 90	90, 90.011 (5), 90	90, 90.012 (6), 90	90, 90.048 (9), 90
V (Å ³)	219.12 (1)	435.8 (5)	434.0 (5)	433.8 (7)	866.94 (9)
Z	2	4	4	4	8
Radiation type, λ (Å)	Synchrotron, 0.70814	Synchrotron, 0.70814	Synchrotron, 0.70000	Synchrotron, 0.70814	Synchrotron, 0.70814
μ (mm ⁻¹)	12.05	12.12	11.79	12.17	12.18
Crystal size (mm)	0.05 × 0.03 × 0.02	0.05 × 0.03 × 0.02	0.05 × 0.03 × 0.02	0.05 × 0.03 × 0.02	0.05 × 0.03 × 0.02
Data collection					
T_{min}, T_{max}	0.649, 1.000	0.606, 1.000	0.628, 1.000	0.529, 1.000	0.671, 1.000
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	2069, 196, 196	3944, 1464, 1464	3199, 1935, 1934	1782, 770, 769	4005, 1187, 1186
R_{int}	0.034	0.014	0.031	0.025	0.030
$(\sin \theta/\lambda)_{max}$ (Å ⁻¹)	0.675	0.676	0.752	0.674	0.673
Refinement					
$R[F > 3\sigma(F)], wR(F), S$	0.034, 0.146, 1.67	0.019, 0.040, 2.83	0.032, 0.045, 3.27	0.048, 0.065, 5.44	0.016, 0.027, 1.16
No. of reflections	196	1464	1935	770	1187
No. of parameters	13	32	59	53	110
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å ⁻³)	1.67, -1.94	0.96, -0.72	1.39, -1.76	2.26, -1.77	0.37, -0.42
Absolute structure		668 of Friedel pairs used in the refinement	806 of Friedel pairs used in the refinement	367 of Friedel pairs used in the refinement	587 of Friedel pairs used in the refinement
Absolute structure parameter		0.28 (2)	0.05 (4)	0.05 (5)	0.097 (19)

Computer programs: *CrysAlis PRO* (Agilent, 2014) and *JANA2006* (Petříček *et al.*, 2014). Note: (*) the structure is considered as a 1D commensurate composite consisting of the BaS₃ matrix and V-chains located in its hexagonal channels (Fig. 1).

(ii) Hall coefficient (Booth *et al.*, 1999), (iii) Raman response with in-chain polarization (Choi *et al.*, 2009), (iv) V L -edge X-ray absorption spectroscopy (Ilakovac *et al.*, 2012), (v) specific heat (Imai *et al.*, 1996), (vi) thermopower (Barišić, 2004). These studies show anomalies at 130 ± 20 K, as do some theoretical models (Jiang & Guo, 2004). This temperature can be associated with an increase of the 1D electronic fluctuations towards the Peierls transition at 69 K (Foury-Leylekan *et al.*, 2012). From the observation of diffuse scattering lines, it appears that the onset of these fluctuations (Fagot *et al.*, 2003) already occurs at 170 K.

Two structural transitions have been well documented in the 5–300 K temperature range (Gardner *et al.*, 1969; Imada *et al.*, 1998; Inami *et al.*, 2002; Fagot *et al.*, 2005; Foury-Leylekan *et al.*, 2012). In the first at $T_S = 240$ K, the higher-temperature hexagonal metallic phase transforms to orthorhombic. The second transition is associated with $T_{MI} = 69$ K, where the orthorhombic phase converts to monoclinic with a doubling of the translation along the c axis. No noticeable structural changes have been detected for the magnetic transitions at $T_N = 31$ K (Fagot *et al.*, 2005). Although the hexagonal and orthorhombic symmetries have commonly been described by the space groups $P6_3/mmc$ and $Ccm2_1$, respectively, observations of a series of extra X-ray diffraction reflections violate both of them (Inami *et al.*, 2002; Girard *et al.*, 2019). Some

doubts with regard to these space-group attributions also arose from neutron diffraction studies (Ghedira *et al.*, 1981). Finally, the interplay between the *structural* and *electronic* phase transformations is still not entirely clear, in particular since the symmetry determination raises some questions for both the hexagonal and orthorhombic phases.

Here we report synchrotron XRD experiments performed on a single crystal of BaVS₃ at ten different temperatures in the range 10–295 K. We show that the mismatch between the space groups $P6_3/mmc$ and $Ccm2_1$, and the presence of extra reflections that violate them, can be resolved by a host–guest (H–G) composite model. Accordingly, we consider the BaVS₃ structure as a 1D commensurate composite, which consists of a *host* (H) BaS₃ matrix and *guest* (G) V-chains for $T > 130$ K. H and G change their symmetry individually up to 295 K. The space groups mentioned above are correct, but they relate only to H, while the symmetry of G is systematically lower, which leads to the appearance of the extra reflections. Unlike in the classical approach, this host–guest concept allows us to identify a structural phase transition at $T_{LOCK} = 130 \pm 20$ K. At this temperature, the H and G subsystems lock together, ceasing to behave independently. The low-temperature step-by-step transformation of the VS₆ octahedra into VS₅ pyramids is an essential consequence of the whole set of structural transformations that starts at $T < 295$ K. Finally, our findings

Figure 1

Schematic representation of the BaVS_3 crystal structure. The ab projection (top) and perspective view (bottom) are shown. Ba and S together form a hexagonal close packing (hcp). V-chains are located in the hexagonal channels formed by S atoms. Relationships between the unit-cell parameters are indicated for the hexagonal, orthorhombic and monoclinic settings: $a_{\text{hex}} = b_{\text{hex}} \approx 6.7 \text{ \AA}$, $c_{\text{hex}} \approx c_{\text{orth}} \approx c_{\text{mono}} \approx 5.6 \text{ \AA}$; $a_{\text{orth}} = a_{\text{mono}} \approx \sqrt{3} \times a_{\text{hex}} \approx 11.6 \text{ \AA}$, $b_{\text{orth}} \approx a_{\text{hex}} \approx b_{\text{mono}} \approx 6.7 \text{ \AA}$. V-chains acquire a zigzag configuration (dashed green line) in the orthorhombic and monoclinic phases. The crosses on one of the c axes show the different origins for the BaS_3 -hcp (black) and V-chain (green), which are considered in the present study.

related to structural properties should have a counterpart in the electronic and spin sector, and will thus help the interpretation of the intriguing electronic properties and states observed in BaVS_3 .

2. Experimental

2.1. Synthesis and crystallization

All details of the synthesis and crystallization of high-quality single crystals have been described by Kuriyaki *et al.* (1995).

2.2. Single-crystal synchrotron XRD experiments

Single-crystal XRD data were collected at the Swiss–Norwegian Beamline BM01A (ESRF, Grenoble) at the following temperatures: 10, 40, 70, 100, 110, 150, 200, 220, 250 and 295 K (before and after cooling). The wavelength of $\lambda = 0.7 \text{ \AA}$ was selected for the measurements. The *CrysAlis PRO* software (Agilent, 2014) was used for the systematic investigation of the reciprocal space. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Agilent, 2014). An empirical absorption correction using spherical harmonics was implemented in the SCALE3 ABSPACK scaling algorithm.

Crystal structure studies were performed using the *JANA2006* program package (Petříček *et al.*, 2014). Experimental details are shown in Table 1 for five structures selected from different representative temperature ranges and in Table S1 (see supporting information) for the remaining temperatures.

2.2.1. Reciprocal space observations at different temperatures. Our observations of systematic extra reflections shown in Fig. 2 contradict the generally accepted space group $P6_3/mmc$ for the hexagonal phase and $Ccm2_1$ for the orthorhombic phase, and, in this respect, confirm the observations reported earlier by Imani *et al.* (2002) and Girard *et al.* (2019). The clearly observed hhl reflections with $l = 2n+1$ are incompatible with the c -glide plane of the $P6_3/mmc$ space group, which was expected at $T > T_S = 240 \text{ K}$. Reflections of this type are also clearly visible in the $0kl$ section with $l = 2n+1$ in the 70–220 K temperature range, where the orthorhombic phase is expected. These reflections are not compatible with the c -glide plane of the orthorhombic space group $Ccm2_1$.

New and surprising observations occur in the temperature range between $T_S = 240 \text{ K}$ and $T_{MI} = 69 \text{ K}$. The splitting of reflections, which is expected below $T_S = 240 \text{ K}$ due to the hexagonal–orthorhombic symmetry reduction, changes

Figure 2

Selected sections of the experimental reciprocal space for BaVS_3 in the 70–295 K temperature range. (a) In the $hk3$ and $0kl$ sections taken for the hexagonal phase at 295 K, the red circles highlight $00l$ and hhl reflections with $l = 2n+1$, which violate the hexagonal space group $P6_3/mmc$. The symmetry of the patterns indicates the $6/mmm$ Laue class. (b) In the $0kl$ section taken at different temperatures between 70 and 220 K, the red arrows point to rows of $0kl$ reflections with $l = 2n+1$, which violate the orthorhombic space group $Ccm2_1$.

Figure 3

The $hk0$ sections of the reciprocal space showing a correlation between the splitting of reflections and the published electrical properties of BaVS_3 . In the insets, framed with red squares, one of the reflections is enlarged for each temperature.

sharply between 150 and 110 K (Fig. 3). The predicted maximum reflection splitting is determined by the order relationship between the hexagonal and orthorhombic Laue classes, *i.e.* $24/8 = 3$. This is what is indeed observed in the temperature range from 150 to 220 K. However, the observed splitting is of a much higher order at 110 K and below (Fig. 3), and it is similar to the monoclinic splitting that is typical for temperatures below $T_{\text{MI}} = 69$ K. The observed splitting evolution is completely reversible with respect to temperature. This new observation is corroborated by observations of anomalies in the above-mentioned physical properties, which indicate a remarkable electronic transition at about 130 K. It should be emphasized that in parallel, starting around 170 K, diffuse scattering lines were observed by Fagot *et al.* (2003). Their intensity and sharpness increase upon cooling, being a signature of 1D structural fluctuations. They are accompanied by a change in electrical resistivity which increases strongly from about 130 K down to T_{MI} (Gardner *et al.*, 1969; Kuriyaki *et al.*, 1995; Kézsmárki *et al.*, 2006; Barišić, 2004; see also Fig. S2 in the supporting information).

Figure 4

The group-subgroup relationships for BaVS_3 between 10 and 295 K. The bold black arrows indicate the relationships within the host (H) and the guest (G) components of the structure. Below T_{LOCK} , both components acquire the same (equilibrium) monoclinic symmetry. The lowering to monoclinic symmetry at T_{MI} is due to a doubling of the unit-cell c parameter.

It is worth mentioning one more observation related to the structure below $T_{\text{S}} = 69$ K. Some systematic reflections could possibly but mistakenly be indexed with the new modulation vector $\mathbf{q}' = 0.5\mathbf{a} + 0.5\mathbf{b} + 0.5\mathbf{c}_{\text{hex}}$. However, these reflections originate from three twin components related by the threefold axis, as illustrated in Fig. S1 (see supporting information).

Summarizing the analysis of the reciprocal space at different temperatures, we establish with certainty that the symmetry of BaVS_3 needs to be revised in the temperature range 69–295 K.

2.2.2. Revising the BaVS_3 space-group symmetry down to $T_{\text{MI}} = 69$ K. The $6/mmm$ Laue class of the hexagonal phase (Fig. 2a) and the presence of the extra reflections in the hexagonal and orthorhombic phases leads to the space group $P\bar{6}m2$ (instead of $P6_3/mmc$) for the hexagonal phase and its subgroup $Cmm2$ (instead of $Ccm2_1$) for the orthorhombic phase, in agreement with the reported symmetries by Inami *et al.* (2002). However, down to 130 K, structure refinements based on about 3000 experimental single-crystal reflections (which includes about 200 extra reflections) show that Ba and S atoms can only be correctly fitted within the commonly used space groups: $P6_3/mmc$ for the hexagonal phase and $Ccm2_1$ for the orthorhombic phase. This implies that the BaS_3 substructure does not contribute to the intensity of the extra reflections. These weak reflections arise from a small difference in two V–V distances along the c axis. The difference can only be achieved with lower V-chain symmetry: the space group $P\bar{3}m1$ (instead of $P6_3/mmc$ for BaS_3) and its monoclinic subgroup $C2/m$ (instead of the orthorhombic $Ccm2_1$ for BaS_3), with a shift of about (but not identical to) $0.25c$ between origins (inversion centers in the hexagonal phase) characterizing the BaS_3 hcp matrix and the V-chain (Fig. 1). Here we face a discrepancy in the description of the symmetry of the two parts of the same structure.

This controversy could be resolved by applying an approach called the host–guest commensurate composite structure (Arakcheeva *et al.*, 2002; Höhn *et al.*, 2006; McMahon & Nemes, 2006). This type of crystal structure assumes different symmetries for the *host* (usually a 3D matrix) and the *guest*

(usually a chain inside a 3D matrix) with the same lattice parameters. Similarly, we consider the BaS_3 hcp matrix as the host (H) and V-chains as the guest (G). Consequently, to refine the hexagonal phase (at 295 and 250 K), we use the space group $P3m1$, which is common for H and G, and additional pairwise restrictions for Ba, S and V sites according to their true symmetry. For the orthorhombic phase (at 220, 200 and 150 K), the $C1m1$ space group, which is common for H and G, was used with the corresponding pairwise restrictions for Ba, V and two S sites. Examples of atomic sites and the applied restrictions are available in the supporting information. The host–guest approach perfectly fits our diffraction experiments down to 150 K. It should be mentioned that the contribution of quasi-elastic scattering to the intensities of the extra reflections (Girard *et al.*, 2019) cannot be excluded since

their calculated intensities are systematically somewhat lower than those observed.

Starting from 110 K and down to $T_{\text{MI}} = 69$ K, both H and G adopt the common monoclinic symmetry $C1m1$ in agreement with the above-described observations of the monoclinic splitting for diffraction reflections below 130 K (Fig. 3).

Our study confirms the space group $I1m1$ with a double unit-cell c parameter, which has been reported numerous times for the structure below T_{MI} after the initial publication by Fagot *et al.* (2005).

The summary of the structure symmetry reconsideration is presented in Fig. 4, which shows a scheme of the group–subgroup relationships found for BaVS_3 in the 10–295 K temperature range.

Figure 5

Structural characteristics of BaVS_3 between 10 and 295 K. (a) The VS_6 chain represents ranges separated by the transformation temperatures. VS_5 tetragonal pyramids (green) and VS_6 octahedra (blue), highlighted according to (b) V–S distances and (c) the bond valence sum of V. For each V polyhedron, the equatorial (orange) and apical (brown) V–S contacts are shown; dashed brown lines specify the longest apical contacts. (b) Geometry characteristics: V–V–V angles and V–V and V–S distances. The markers indicate experimental values; the lines are guides for the eyes. (c) Bond valence sums (BVSs) calculated for each V atom in its octahedral (V^{4+}S_6 , blue rhombuses) and pyramidal (V^{4+}S_5 , green triangles) environment. The choice of polyhedron (dashed blue and green lines) is confirmed by the calculations, which are very close to the nominal BVS = 4. The colour coding is identical in all panels.

3. Results and discussion

3.1. Structural phase transition at T_{LOC} at 130 ± 20 K

The first important result of the present study follows directly from the symmetry revision of BaVS_3 at different temperatures above T_{MI} (Figs. 3 and 4). It appears that the structural phase transition observed at 130 ± 20 K correlates remarkably well with the change in the slope of the electrical resistivity from negative to positive at about 130 K (Kézsmárki *et al.*, 2006; see also Fig. S2 in the supporting information). As already mentioned in the *Introduction*, other properties also show changes/anomalies in the behaviour at this temperature. This structural transition consists of a monoclinic transformation of the entire BaVS_3 structure and the loss of the inversion centre in the V-chains. This leads to a locking of the two structural subsystems, H and G, so that we denote the transition temperature as $T_{\text{LOCK}} = 130 \pm 20$ K. It is

important to emphasize that, at this temperature, instead of one V site, two independent crystallographic V sites appear with monoclinic (m) local symmetry. This novel insight should be carefully considered theoretically with respect to the 1D electronic instability which is clearly visible below T_{LOCK} .

3.2. Analysis of the temperature-dependent geometric characteristics

Another set of important information is obtained from the analysis of the T -dependent geometric characteristics of the BaVS_3 structure (Fig. 5). Namely, we analyze here the evolution of: (i) intra-chain V–V–V angles; (ii) V–V and V–S interatomic distances, which are then related to (iii) the bond valence sum (BVS) of V^{4+} . BVS is calculated for each V site in its octahedral (VS_6) and pyramidal (VS_5) environment and compared to the nominal BVS = 4 for V^{4+} .

Figure 6

Illustration of the transformation of VS_6 octahedra into VS_5 pyramids as a general underlying principle for changes in the BaVS_3 structure as a function of temperature. The interatomic distances are given in Å. Arched arrows point to the transformation of short apical V–S contacts in VS_6 octahedra. The numerical values of the distances are highlighted in red, which change as a result of the corresponding structural phase transitions. Straight red arrows show displacements of V atoms, which initiate the transformation of the structure. (a) Compression of the apical V–S contacts in the hexagonal phase results in a too-short V–V contact, indicated in brown. During the T_s transition, this contact relaxes due to its increase as a result of the V-atom displacement, which leads to a zigzag deformation of the V-chain. (b) At the T_{LOCK} phase transition, further compression of the apical V–S contact for one V atom occurs due to its predominant displacement, which leads to the loss of the inversion centre (black crosses) in the V-chain. This results in two sites, V1 and V2, for the V atom instead of one. (c) During the T_{MI} structural transition, the uniformly compressed apical V–S contact for each V atom is realized due to different displacements of the V atoms along the c axis. As a consequence, the number of V sites increases from two to four (V1, V2, V3 and V4). A side effect is a significant difference of the intra-chain V–V distances, indicated in brown.

In agreement with the previously published studies, the essential change of the V–V–V angle (from 180 to 165.4°) is observed at T_S , and the difference in the V–V distances varies within the range of about 0.2 Å below T_{MI} .

The new experimental data characterize the host–guest structure at temperatures above T_{LOCK} and the monoclinic structure between T_{MI} and T_{LOCK} . Unlike in all previously published studies, the difference between the intra-chain V–V distances is observed even in the hexagonal phase, *i.e.* above the temperature of the structural transition at T_S . This difference, of about 0.1 Å at 295 K, increases to about 0.2 Å at 250 K. The zigzag deformation of the V-chain arising at T_S reduces the difference to 0.07 Å at 220 K and then to 0.04 Å at 150 K. This small difference is maintained almost down to T_{MI} . The small increase of this value up to 0.07 Å is observed at 70 K, *i.e.* immediately before the MI transition.

The analysis of the V–S distances points to a remarkable difference between the equatorial (yellow dots/lines in Fig. 5) and apical (brown dots/lines in Fig. 5) interatomic contacts in the temperature-dependent VS_6 octahedra. The equatorial V–S distances are more or less stable within 2.35 ± 0.05 Å at any temperature, while the apical contacts are strongly temperature dependent. At temperatures above T_S (295 and 250 K), there are no differences between them. However, below T_S , the difference appears and increases systematically to about 0.6 Å at 10 K. This is the main tendency of the $BaVS_3$ structure evolution between 295 and 10 K (Fig. 5). This observation leads us to consider an optimal number of S^{2-} ions, *i.e.* six in a $V^{4+}S_6$ octahedron or five in a $V^{4+}S_5$ pyramid, which can exactly fit the expecting oxidation state of V^{4+} . The BVS presented in Fig. 5(c) indicates that the $V^{4+}S_6$ octahedron is preferable down to T_{LOCK} . Two different polyhedra, *i.e.* a $V^{4+}S_6$ octahedron and a $V^{4+}S_5$ pyramid, can be recognized between T_{LOCK} and T_{MI} , and only the $V^{4+}S_5$ pyramid has the exact characteristics of the structure below T_{MI} .

This analysis allows us to propose a scenario for the temperature-dependent structure transformations of $BaVS_3$.

3.3. A possible scenario for the temperature-dependent structure transformations of $BaVS_3$ below 295 K

The analysis described above indicates the existence of a unique mechanism causing the evolution of the $BaVS_3$ structure with decreasing temperature. This mechanism manifests itself as a successive deformation of regular $V^{4+}S_6$ octahedra stable at room temperature, towards the stabilization of the $V^{4+}S_5$ pyramids, which is completed at temperatures below T_{LOCK} . This deformation of the octahedra is realized by successive contraction of one of the apical V–S contacts and the corresponding increase of the other one, while maintaining the equatorial V–S contacts in the VS_6 octahedra, as illustrated in Figs. 5 and 6. In the hexagonal phase, the contraction of the apical V–S contact is possible only if the V atoms move closer together along the V-chain. Even a slight compression of this contact (*e.g.* 0.03 Å at 250 K) leads to the formation of an unstable short V–V contact (*e.g.* 2.70 Å at 250 K), which causes the first structural phase transition at T_S (Fig. 6a). As a

result of this transition, the apical V–S contacts decrease essentially due to the appearance of a V–V–V angle of about 165°, which in turn recovers the stable V–V distances. The structure remains practically unchanged down to 150 K with short apical contacts of about 2.23 Å and a $V^{4+}S_6$ octahedron for two V atoms connected by a centre of inversion within the V-chain. An additional temperature decrease induces further contraction of the V–S apical contacts. A significant shortening of one of them occurs at T_{LOCK} , stabilizing its $V^{4+}S_5$ pyramid, while the $V^{4+}S_6$ octahedron is still stable for the second V atom (Figs. 5c and 6b). The loss of the inversion centre in the V-chain leads to a significant distortion in the short V–S apical contacts (2.19 *versus* 2.26 Å) and the corresponding polyhedra characteristic of two V atoms. The distortions are completely eliminated at T_{MI} due to the doubling of the unit-cell *c* parameters (Figs. 5c and 6c). At $T < T_{MI}$, the structure becomes stable with respect to charge compensation within the $V^{4+}S_5$ pyramids for the whole set of V atoms. However, this is accompanied by a significant difference (2.94 *versus* 2.78 Å) in V–V distances in the V-chain, in agreement with most of the previous studies. It is important to note that each described structural transition can be considered as initiated by the displacement of V atoms, as shown in Fig. 6. This indicates the electronic instability of V as the main cause of structural transformations, which already manifest themselves as diffusion scattering at temperatures below 170 K (Fagot *et al.*, 2003).

4. Summary

Using single-crystal X-ray synchrotron diffraction experiments, we reveal that, upon decreasing the temperature, the series of structural phase transitions in the complex quasi-1D metallic system $BaVS_3$ satisfies the group–subgroup symmetry relationships only if its structure is considered as a 1D commensurate composite, which consists of the host (H), the BaS_3 hcp matrix and the guest (G) V-chains. The host–guest structure model reveals a structural phase transition at $T_{LOCK} = 130 \pm 20$ K, which was not previously observed and which can be considered as a prerequisite for the metal–insulator transformation. The refined structural characteristics obtained in the 10–295 K temperature range indicate the presence of a unique ingredient required for the correct description of the structural evolution with temperature. It is associated with the VS_6 octahedra that characterize the structure at room temperature, which successively transform upon decreasing the temperature into VS_5 tetragonal pyramids, characteristic of the structure below $T_{MI} = 69$ K. We are convinced that our findings will yield a better understanding of the low-temperature driven electronic transformations of the $BaVS_3$ quasi-1D electronic system.

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