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The structural phase transition in SrV$_6$O$_{11}$

Yoshiaki Hata, Yasushi Kanke and Eiji Kita


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The structural phase transition in SrV$_6$O$_{11}$

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Single-crystal X-ray diffraction and specific heat studies establish that strontium hexavanadium undecaoxide, SrV$_6$O$_{11}$, undergoes a P6$_3$/mmc to inversion twinned P6$_3$mc structural transition as the temperature is lowered through 322 K. The P6$_3$/mmc and P6$_3$mc structures have been determined at 353 K and at room temperature, respectively. For the room-temperature structure, seven of the ten unique atoms lie on special positions, and for the 353 K structure all of the seven unique atoms sit on special positions. The P6$_3$/mmc to P6$_3$mc structural phase transition, accompanied by a magnetic transition, is a common characteristic of AV$_6$O$_{11}$ compounds, independent of the identity of the A cations.

Comment

A series of AV$_6$O$_{11}$ compounds (A = Na, K, Sr, Ba, Pb; de Roy et al., 1987; Kanke, 1999; Kanke et al., 1993; Friese et al., 2006; Mentre et al., 1996) have generated interest because of their structural phase transitions, magnetic and transport properties (Kanke et al., 1990, 1994; Uchida et al., 1991, 2001; Mentre et al., 2001). The crystal structures consist of hexagonal close-packed layers of A and O atoms, and three types of V atoms (Fig. 1). The V1O$_6$ octahedra form a Kagomé lattice by edge sharing. The V2O$_6$ octahedra form face-sharing dimers between the layers of the Kagomé lattice. The coordination of V3O$_5$ is a trigonal bipyramid. While the AV$_6$O$_{11}$ compounds show common characteristics in their paramagnetic states, they exhibit individual characteristics for their magnetically ordered states. In the paramagnetic states, each AV$_6$O$_{11}$ shows one phase transition at a characteristic temperature, $T_v$. Above $T_v$, the compounds crystallize in the centrosymmetric hexagonal space group P6$_3$/mmc, and show Curie–Weiss paramagnetism. Below $T_v$, the compounds lose the centre of symmetry and show second-order transitions to hexagonal P6$_3$mc (Kanke et al., 1994). The V1O$_6$ octahedron forms a regular Kagomé lattice above $T_v$. It distorts to form a V1O$_6$ trimer with a regular triangular shape below $T_v$. Two V2O$_6$ octahedra forming a face-sharing dimer are crystallographically equivalent above $T_v$. Below $T_v$, they become inequivalent. V3 is no longer at the centre of the V3O$_5$ polyhedron below $T_v$. In the P6$_3$mc form of AV$_6$O$_{11}$, V1 exhibits a spin gap behaviour with a spin-singlet ground state, while V2 and V3 possess magnetic moments (Uchida et al., 2001). $T_v$ values for KV$_6$O$_{11}$ (Kanke, 1999), BaV$_6$O$_{11}$ (Friese et al., 2006) and PbV$_6$O$_{11}$ (Kato et al., 2001) are 190, 250 and 560 K, respectively.

As first reported, the room-temperature structure of SrV$_6$O$_{11}$ was assigned to P6$_3$/mmc with a relatively high R factor (Kanke et al., 1992). The $T_v$ = 320 K of SrV$_6$O$_{11}$ exceeds room temperature, which suggests an incorrect assignment of the space group. We have pointed out briefly the existence of the P6$_3$/mmc to P6$_3$mc transition at 320 K (Hata et al., 1999). Kato et al. studied the transition by X-ray powder diffraction. They refined the structures at 100 K in P6$_3$mc and at 623 K in P6$_3$/mmc (Kato et al., 2001). However, we considered a single-crystal diffraction study to be indispensable for an accurate structural characterization of the acentric phase. In the present study, the crystal structure of SrV$_6$O$_{11}$ was determined in detail both above $T_v$ (353 K) and below $T_v$ (room temperature, RT) by single-crystal X-ray diffraction. The transition temperature was determined precisely by a specific heat study.

At both room temperature and 353 K, diffraction data showed hexagonal symmetry and an extinction rule, $l \neq 2n$ absent for hhl, indicating possible space groups P6$_3$/mmc, P6$_2$mc and P6$_3$mc. P6$_3$/mmc is centrosymmetric and gives a unique structural model. But the other two are acentric, and each gives a pair of single-domain models, ($x, y, z$) and ($-x, -y, -z$), and one inversion twin model, [[$x, y, z$] + ($-x, -y, -z$)].

**Figure 1**

The crystal structure of SrV$_6$O$_{11}$ at room temperature, shown with 99% probability displacement ellipsoids.

To examine the possible models, reflections with \( h \geq 0, k \geq 0, l \geq 0, |h| \leq |k|, 2\theta < 90^\circ \), and those with \( h \leq 0, k \leq 0, l \leq -1, |h| \leq |k|, 2\theta < 90^\circ \) were collected at both temperatures using a four-circle diffractometer (Enraf–Nonius CAD-4) with \( K \alpha \) radiation. As the diffractometer is equipped with a scintillation counter, reflections that were too weak were regarded as unobserved. Thus, 185 of a total of 1284 reflections for room temperature, and 349 of 1290 reflections for 353 K were unobserved. Thus, 185 of a total of 1284 reflections for room temperature, and 349 of 1290 reflections for 353 K were unobserved. The data, however, are of high resolution, and 349 of 1290 reflections for 353 K were unobserved. Consequently, they chose the \( P6_3/mmc \) model with inversion twinning is concluded to be insignificant, considering the numbers of parameters. Consequently, they chose the \( P6_3/mmc \) model with the highest symmetry, which was selected.

The models for 353 K were examined using 919 unaveraged reflections with \( I > 1.5\sigma(I) \), applying the common weighting scheme of \( 1/\sigma^2(I) \). As shown in Table 1, the twin model \( P6_3/mmc \) model gave trouble-free convergence and low enough \( R \) factors \( (R_1 = 0.0236–0.0242, wR_2 = 0.0511–0.0526, 26–44 \) parameters). However, all of the remaining models resulted in nonpositive definite atomic displacement parameter(s) and significantly higher \( R \) factors. Consequently, the twinned \( P6_3/mmc \) model was selected. This clear differentiation of the results for the different models also indicates high enough quality of the specimen and high enough resolution of the diffraction data.

The models for 353 K were examined using 919 unaveraged reflections with \( I > 1.5\sigma(I) \), applying the common weighting scheme of \( 1/\sigma(I) \). All seven models gave trouble-free convergence and low enough \( R \) factors \( (R_1 = 0.0236–0.0242, wR_2 = 0.0511–0.0526, 26–44 \) parameters). Consequently, there was no reason to choose any of the acentric space groups, and the \( P6_3/mmc \) model, with the highest symmetry, was selected.

The room-temperature structure of \( SrV_6O_{11} \) had earlier been described by Kanke et al. (1992) using \( P6_3/mmc \). They compared the \( P6_3/mmc \) model, two single-domain models of \( P\bar{6}2c \) and two single-domain models of \( P6_3/mc \), using 2031 unaveraged intensities. The \( P6_3/mmc \) model, the better \( P\bar{6}2c \) model and the better \( P6_3/mc \) model gave \( R = 0.070 \) with 24 parameters, \( R = 0.069 \) with 24 parameters and \( R = 0.064 \) with 35 parameters, respectively. The difference in the \( R \) factors was concluded to be insignificant, considering the numbers of parameters. Consequently, they chose the \( P6_3/mmc \) model with the highest symmetry. However, the study did not examine the twin models for the two acentric space groups. None of the models was free from negative temperature factors, and anisotropic displacement parameters were not applied to \( O_2 \) even in the final refinement. In the present study, in fact only the \( P6_3/mmc \) model with inversion twinning is free of nonpositive definite displacement parameters, and this model clearly gives the best result among the seven models tested. We thus correct the previous report with this determination that \( SrV_6O_{11} \) crystallizes in \( P6_3/mc \) with inversion twinning at room temperature.

Between the two temperatures, viz. room temperature and 353 K, the specific heat of \( SrV_6O_{11} \) shows only one anomaly, at 322 K. Consequently, we conclude that the structural phase transition takes place at 322 K and coincides with the magnetic transition.

The structural refinements of the \( P6_3/mc \) forms of \( NaV_6O_{11} \) (Kanke et al., 1994) and \( PbV_6O_{11} \) (Mentre et al., 1996) converged promptly without applying twinning. Kanke (1999) suggested that this may be due to the small anomalous dispersion term for Na for \( K\alpha \) in \( NaV_6O_{11} \), or may suggest that the volume fraction ratio \( (x, y, z)\) is far from 1.0 in \( PbV_6O_{11} \) and/or in \( NaV_6O_{11} \).

The \( P6_3/mc \) and \( P6_3/mmc \) forms of \( SrV_6O_{11} \) are illustrated in Figs. 1 and 2, respectively. In both forms, the \( V1 \) ellipsoid is elongated towards the centre of the \( V1 \) trimer. \( V2 \) is nearly isotropic in the \( P6_3/mmc \) form. In the \( P6_3/mc \) form, though, \( V21 \) is oblate, compressed into (001) and \( V22 \) is prolate along [001]. \( V3 \) shows extended displacement along [001] in the \( P6_3/mmc \) form, but is rather isotropic in the \( P6_3/mc \) form.

For the \( P6_3/mc \) form, seven of the ten unique atoms lie on special positions, and for the \( P6_3/mmc \) form, all of the seven unique atoms sit on special positions. In the centric structure, the \( V1O_6 \) octahedra form a regular Kagomé lattice with a uniform \( V1 \)–\( V1 \) distance of 2.8887 (1) Å (Table 2). In the \( P6_3/mc \) phase, though, the Kagomé lattice distorts, with the \( V1O_6 \) octahedra forming a trimer with a regular triangular shape; and the \( V1 \)–\( V1 \) distance separates into two types, viz. inter-trimer [2.9736 (6) Å] and intra-trimer [2.7966 (6) Å] (Table 3).

It is noteworthy that \( SrV_6O_{11} \) shows a much smaller change in the \( V2 \)–\( V2 \) distance with the phase transition, as compared to the other \( AV_6O_{11} \) compounds. In both the \( P6_3/mmc \) and \( P6_3/mc \) forms, analogous \( V1–O \) distances show similar values, independent of the nature of \( A \). On the other hand, in both forms the \( V2–O \) and the \( V3–O2 \) distances tend to be longer for divalent \( A \) cations and shorter for monovalent \( A \).

Figure 2
The crystal structure of \( SrV_6O_{11} \) at 353 K, shown with 99% probability displacement ellipsoids.
The \( P6_3/mmc \) to \( P6_3/mc \) structural phase transition, accompanied by a magnetic transition, is a common characteristic of \( AV_6O_{11} \) compounds, independent of the \( A \) cations. The acentric form of \( SrV_6O_{11} \) shows features in common with the corresponding \( P6_3/mmc \) forms of \( AV_6O_{11} \) (\( A = Na, K, Sr, Ba, Pb \)). Below \( T_c \), the \( V_1O_8 \) octahedron no longer forms a regular Kagomé lattice, but distorts to form a \( V1O_8 \) trimer with a regular triangular shape. A pair of the \( V2O_6 \) octahedra forming a face-sharing dimer at higher temperatures becomes inequivalent. \( V3 \) moves away from the centre of the \( V3O_5 \) polyhedron. The \( V1 \) trimer formation accompanying the structural transition is considered to be the factor that suppresses the paramagnetism below \( T_c \).

**Experimental**

\( Sr_2V_2O_5 \) and \( V_2O_3 \) were mixed in a 1:5 molar ratio. The mixture was sealed in a platinum capsule and heated at 1073 K for 1 d and at 1473 K for 2 weeks, successively. Crystals of \( SrV_6O_{11} \) were hexagonal plates with principal faces \([010]\). Sizes were typically 0.2 mm across the plate and 0.1 mm in thickness.

Data collection at 353 K was achieved by blowing hot nitrogen gas onto the specimen. The temperature was calibrated by a chromel-alumel thermocouple with a water-ice standard. The specific heat of single-crystal \( SrV_6O_{11} \) was measured using a Quantum Design Physical Property Measurement System (PPMS). The temperature range of the measurements was from 2.4 to 350 K.

**\( SrV_6O_{11} \) at 353 K**

**Crystal data**

\( SrV_6O_{11} \)

\( M_r = 569.26 \)

Hexagonal, \( P6_3/mmc \)

\( a = 5.7773 (1) \AA \)

\( c = 13.0852 (3) \AA \)

\( V = 378.234 (13) \AA^3 \)

**Data collection**

Enraf-Nonius CAD-4 diffractometer

Absorption correction: Gaussian (\( SDP; B. A. Frenz & Associates Inc., 1985 \))

\( T_{\text{min}} = 0.413, T_{\text{max}} = 0.532 \)

1294 measured reflections

**Refinement**

\[ R(F^2 > 2\sigma(F^2)) = 0.022 \]

\[ wR(F^2) = 0.054 \]

\( S = 1.37 \)

447 reflections

**Selected bond lengths (\( \AA \)) for \( SrV_6O_{11} \) at room temperature.**

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<th>Length (( \AA ))</th>
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<td>( Sr1-O1 )</td>
<td>2.723 (13)</td>
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<tr>
<td>( V1-O1 )</td>
<td>2.892 (1)</td>
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**Structure analysis of \( SrV_6O_{11} \) at room temperature.**

**Symmetry codes:**

1. \( x, y, z + \frac{1}{2} \)
2. \( -x, y, -z + \frac{1}{2} \)
3. \( x + 1, y, -z \)
4. \( -x + 1, y, -z \)
5. \( x, y, z + \frac{1}{2} \)
6. \( -x + 1, y, -\frac{1}{2} \)
7. \( x + 1, y, -\frac{1}{2} \)
8. \( -x, y, -z + \frac{1}{2} \)
9. \( x + 1, y, -z \)
10. \( -x + 1, y, -z \)

**Notes:**

- (a) number of reflections; (b) number of parameters; (c) displacement parameters of \( V1 \) are negative; (d) displacement parameters of \( O2 \) are negative; (e) the volume fraction (\( x, y, z \)) (\( -x, y, -z \)) = 0.434 (0.566) (7); (f) displacement parameters of \( V1 \) and \( O2 \) are negative; (g) displacement parameters of \( V1, O1 \) and \( O2 \) are negative; (h) the volume fraction (\( x, y, z \)) (\( -x, y, -z \)) = 0.519 (0.481) (72).

**Table 1**

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**Table 2**

Selected bond lengths (\( \AA \)) for \( SrV_6O_{11} \) at room temperature.

**Symmetry codes:**

1. \( x, y, z + \frac{1}{2} \)
2. \( -x + y, -z + \frac{1}{2} \)
3. \( y, x, z + \frac{1}{2} \)
4. \( -x + y, -z + \frac{1}{2} \)

**Table 3**

Selected bond lengths (\( \AA \)) for \( SrV_6O_{11} \) at room temperature.

**Symmetry codes:**

1. \( y, x, z + \frac{1}{2} \)
2. \( -y + x, -z + \frac{1}{2} \)
3. \( y, x, z - \frac{1}{2} \)
4. \( -y + x, -z - \frac{1}{2} \)
For both temperatures, data collection: CAD-4 (Enraf–Nonius, 1981); cell refinement: CAD-4; data reduction: SDP (B. A. Frenz & Associates Inc., 1985); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: VESTA (Momma & Izumi, 2008); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3226). Services for accessing these data are described at the back of the journal.

References