<table>
<thead>
<tr>
<th>著者</th>
<th>Hata Yoshiaki, Kanke Yasushi, Kita Eiji</th>
</tr>
</thead>
<tbody>
<tr>
<td>期刊</td>
<td>Acta Crystallographica. Sect. C, Crystal structure communications</td>
</tr>
<tr>
<td>卷</td>
<td>66</td>
</tr>
<tr>
<td>期</td>
<td>12</td>
</tr>
<tr>
<td>页码</td>
<td>i99-i102</td>
</tr>
<tr>
<td>年</td>
<td>2010</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2241/107682">http://hdl.handle.net/2241/107682</a></td>
</tr>
</tbody>
</table>

doi: 10.1107/S0108270110046299
The structural phase transition in $\text{SrV}_6\text{O}_{11}$

Yoshiaki Hata, Yasushi Kanke and Eiji Kita


Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Republication of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see [http://journals.iucr.org/services/authorrights.html](http://journals.iucr.org/services/authorrights.html)

*Acta Crystallographica Section C: Crystal Structure Communications* specializes in the rapid dissemination of high-quality studies of crystal and molecular structures of interest in fields such as chemistry, biochemistry, mineralogy, pharmacology, physics and materials science. The numerical and text descriptions of each structure are submitted to the journal electronically as a Crystallographic Information File (CIF) and are checked and typeset automatically prior to peer review. The journal is well known for its high standards of structural reliability and presentation. *Section C* publishes approximately 1000 structures per year; readers have access to an archive that includes high-quality structural data for over 10000 compounds.

Crystallography Journals Online is available from [journals.iucr.org](http://journals.iucr.org)
The structural phase transition in SrV$_6$O$_{11}$

Yoshiaki Hata,\textsuperscript{a}*, Yasushi Kanke\textsuperscript{b} and Eiji Kita\textsuperscript{c}

\textsuperscript{a}Department of Applied Physics, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan, \textsuperscript{b}Advanced Nano Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044, Japan, and \textsuperscript{c}Department of Applied Physics, University of Tsukuba, Ibaraki 305-8537, Japan

Correspondence e-mail: hata@nda.ac.jp

Received 12 May 2010
Accepted 9 November 2010
Online 19 November 2010

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 $P6_3mc$ structural transition as the temperature is lowered through 322 K. The $P6_3/mmc$ and $P6_3mc$ 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 $P6_3mc$ 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, $T_c$. Above $T_c$, the compounds crystallize in the centrosymmetric hexagonal space group $P6_3/mmc$, and show Curie–Weiss paramagnetism. Below $T_c$, the compounds lose the centre of symmetry and show second-order transitions to hexagonal $P6_3mc$ (Kanke et al., 1994). The V1O$_6$ octahedron forms a regular Kagomé lattice above $T_c$. It distorts to form a V1O$_6$ trimer with a regular triangular shape below $T_c$. Two V2O$_6$ octahedra forming a face-sharing dimer are crystallographically equivalent above $T_c$. Below $T_c$, they become inequivalent. V3 is no longer at the centre of the V3O$_5$ polyhedron below $T_c$. In the $P6_3mc$ 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). $T_c$ 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 $T_c = 320$ 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 $P6_3mc$ 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 $P6_3mc$ 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 $T_c$ (353 K) and below $T_c$ (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 axialymmetry and an extinction rule, $l \neq 2n$ absent for $hhl$, indicating possible space groups $P6_3/mmc$, $P6_3mc$ and $P6_3/cmc$. $P6_3/mmc$ 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 $h \geq 0, k \geq 0, l \geq 0, |h| \leq |k|, 20 < 90^\circ$, and those with $h \leq 0, k \leq 0, l \leq -1, |h| \leq |k|, 20 < 90^\circ$ were collected at both temperatures using a four-circle diffractometer (Enraf–Nonius CAD-4) with Mo Ka 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. As a result, the model examinations give clear results as follows.

The models for room temperature were examined using 1093 Friedel-unaveraged reflections with $I > 1.5 \sigma(I)$, applying the common weighting scheme of $1/\sigma(I)$. As shown in Table 1, the inversion twin $P6_3/mmc$ 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 ($R_1 = 0.0236–0.0242$, $wR_2 = 0.0511–0.0526$, 24–44 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$_6$O$_{11}$ 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 $P6_2c$ and two single-domain models of $P6_3/mc$, using 2031 unaveraged intensities. The $P6_3/mmc$ model, the better $P6_2c$ 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 O2 even in the final refinement. In the present study, in fact only the $P6_3/mc$ model with inversion twinning was 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$_6$O$_{11}$ 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$_6$O$_{11}$ 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$_6$O$_{11}$ (Kanke et al., 1994) and PbV$_6$O$_{11}$ (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 Mo Ka in NaV$_6$O$_{11}$ or may suggest that the volume fraction ratio $(x, y, z) / (x, y, -z)$ is far from 1.0 in PbV$_6$O$_{11}$ and/or in NaV$_6$O$_{11}$.

The $P6_3/mc$ and $P6_3/mmc$ forms of SrV$_6$O$_{11}$ 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$_6$ octaheda 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$_6$O$_{11}$ shows a much smaller change in the V2···V2 distance with the phase transition, as compared to the other AV$_6$O$_{11}$ 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$_6$O$_{11}$ 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 acenitic 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 $T_r$, the V1O$_6$ octahedron no longer forms a regular Kagomé lattice, but distorts to form a V1O$_6$ trimer with a regular triangular shape. A pair of the V2O$_6$ octahedra forming a face-sharing dimer at higher temperatures become 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 $T_r$.

Experimental
Sr$_2$V$_6$O$_{12}$ and V$_2$O$_3$ 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 Sr$_2$V$_6$O$_{11}$ were hexagonal plates with principal faces [001]. 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 chromalumel thermocouple with a water-ice standard. The specific heat of single-crystal Sr$_2$V$_6$O$_{11}$ 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$_6$O$_{11}$ at 353 K

**Crystal data**
Sr$_2$V$_6$O$_{11}$  
$M_r = 569.26$  
Hexagonal, $P6_3/mmc$  
a = 5.7773 (1) Å  
$c = 13.0852 (3)$ Å  
$V = 378.234 (13)$ Å$^3$

**Data collection**
Enraf-Nonius CAD-4 diffractometer  
Absorption correction: Gaussian (SDP; B. A. Frenz & Associates Inc., 1985)  
$T$$_{min} = 0.413$, $T$$_{max} = 0.532$  
447 measured reflections  
645 independent reflections

**Refinement**
$R(F^2) = 2\sigma(F^2) = 0.022$  
$\Delta \rho_{max} = 0.84 e \AA^{-3}$  
$\Delta \rho_{min} = -0.74 e \AA^{-3}$  
$R_{int} = 0.016$  
$S = 1.37$  
26 parameters

**Selected bond lengths (Å)**

**SrV$_6$O$_{11}$ at room temperature**

**Crystal data**
Sr$_2$V$_6$O$_{11}$  
$M_r = 569.26$  
Hexagonal, $P6_3/mmc$  
a = 5.7702 (1) Å  
$c = 13.0784 (3)$ Å  
$V = 377.109 (13)$ Å$^3$

**Data collection**
Enraf-Nonius CAD-4 diffractometer  
Absorption correction: Gaussian (SDP; B. A. Frenz & Associates Inc., 1985)  
$T$$_{min} = 0.318$, $T$$_{max} = 0.529$  
1284 measured reflections

**Refinement**
$R(F^2) = 2\sigma(F^2) = 0.055$  
$S = 1.21$  
$R_{int} = 0.016$  
$\Delta \rho_{max} = 0.97 e \AA^{-3}$  
3 standard reflections every 240 min

**Selected bond lengths (Å)**

Structural parameters including one single-domain model or two inversion twin models, scale factors and one free parameter for extinction correction were refined with SHELXL97 (Sheldrick, 2008).

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Results for refinement of different models for Sr$_2$V$<em>6$O$</em>{11}$ at room temperature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Model</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>Unique</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>(x, y, z)$^f$</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>($-x$, $-y$, $-z$)$^f$</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>(x, y, z)$^f$</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>($-x$, $-y$, $-z$)$^f$</td>
</tr>
<tr>
<td>$P6_3/mmc$</td>
<td>($-x$, $-y$, $-z$)$^{(0)}$</td>
</tr>
</tbody>
</table>

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 (7) 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) = 0.5199(481) (72).

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Selected bond lengths (Å) for Sr$_2$V$<em>6$O$</em>{11}$ at 353 K.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1−O1</td>
<td>2.7232 (13) V2−O2 2.0423 (16)</td>
</tr>
<tr>
<td>Sr1−O2</td>
<td>2.892 (2)  V3−O2$^a$ 1.810 (2)</td>
</tr>
<tr>
<td>V1−O1</td>
<td>1.9522 (9)  V3−O3 2.090 (2)</td>
</tr>
<tr>
<td>V1−O3</td>
<td>2.0438 (12)  V1−V1$^f$ 2.8887 (1)</td>
</tr>
<tr>
<td>V2−O1</td>
<td>1.9312 (14)  V2−V2$^{(0)}$ 2.7186 (9)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $-x$, $-y$, $-z$+1/2; (ii) $-x$, $-y$, $-z$+1; (iii) $x$, $y$, $z$; (iv) $-x$, $y$, $z$+1/2.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Selected bond lengths (Å) for Sr$_2$V$<em>6$O$</em>{11}$ at room temperature.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr1−O11</td>
<td>2.738 (2)  V22−O12 1.951 (2)</td>
</tr>
<tr>
<td>Sr1−O12</td>
<td>2.700 (2)  V22−O2 2.025 (3)</td>
</tr>
<tr>
<td>Sr1−O2</td>
<td>2.8887 (9)  V3−O2$^{(0)}$ 1.8057 (15)</td>
</tr>
<tr>
<td>V1−O11$^f$</td>
<td>1.9422 (18)  V3−O3 2.038 (4)</td>
</tr>
<tr>
<td>V1−O12</td>
<td>1.9595 (16)  V3−O3$^{(0)}$ 2.136 (3)</td>
</tr>
<tr>
<td>V1−O31</td>
<td>2.069 (2)  V1−V1$^{(0)}$ 2.7966 (6)</td>
</tr>
<tr>
<td>V1−O32</td>
<td>2.018 (2)  V1−V1$^f$ 2.9736 (6)</td>
</tr>
<tr>
<td>V21−O11</td>
<td>1.911 (2)  V21−V22 2.7151 (8)</td>
</tr>
<tr>
<td>V21−O2</td>
<td>2.063 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) $y$, $-x$, $y$, $z$+1/2; (ii) $x$, $y$, $z$, $z$+1; (iii) $-x$, $y$, $z$+1/2; (iv) $-x$, $x$, $z$, $z$+1; (v) $x$, $-y$, $x$, $z$; (vi) $-x$, $y$, $x$, $z$; (vii) $x$, $x$, $z$, $z$; (viii) $-x$, $x$, $z$, $z$;}
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


