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Structure of Hexagonal V_3S_4 Determined at Three Different Temperatures

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Abstract

Hexagonal trivanadium tetrasulfide, V_3S_4, is isotypic with Nb_3Se_4 and $Tl_xV_6S_8$. In contrast to $Tl_xV_6S_8$, the hexagonal channels are empty. Quasi-one-dimensional metal zigzag chains lie parallel to the crystallographic c axis with V—V distances of 2.864 (1) Å within the chains and 3.120 (1) Å between the chains. The crystal structure was determined at 295, 170 and 100 K. The contraction of the lattice with falling temperature is isotropic. V_3S_4 is metastable and transforms into the monoclinic V_3S_4 modification at elevated temperatures.

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Comment

Compounds with the hexagonal Nb_3Se_4 structure (Smeggil, 1971) are of great interest because of their quasi-one-dimensional metallic properties (Amberger, Polborn, Grimm, Dietrich & Obst, 1978; Biberacher & Schwenk, 1980; Ishihara & Nakada, 1982, 1983; Ishihara, Nakada, Suzuki & Ichihara, 1984; Bensch, Koy & Biberacher, 1992*a*). During a systematic study of compounds with the Nb_3Se_4 structure with respect to their physical properties, hexagonal V_3S_4 was prepared by a topotactic redox reaction of $K_{0.7}V_6S_8$ with water. $K_{0.2}V_6S_8$ was reported not to be hygroscopic (Bronsema & Wiegers, 1987). In contrast, $K_{0.7}V_6S_8$ is highly air sensitive and reacts immediately with water to give V_3S_4. The preparation of the compound by a topotactic redox reaction using $Tl_xV_6S_8$ ($x = 0.8$) (Vlasse & Fournes, 1976) as starting material leads to products which contain small amounts of Tl ($x \simeq 0.03$) (Bensch, Koy & Wesemann, 1992). $Tl_xV_6S_8$ ($x = 0.8$)

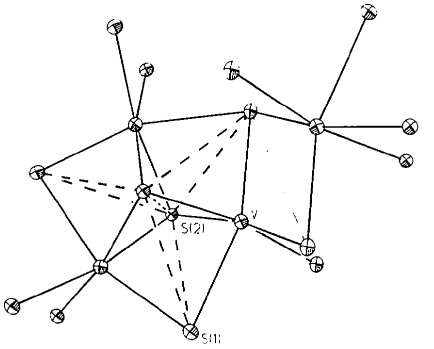

Fig. 1. A triple unit of three face-sharing VS_6 octahedra connected by a common edge to the neighbouring VS_6 octahedron. The common faces are indicated by the broken double lines, the common edge by the broken single line. Probability ellipsoids have been drawn at the 75% probability level ($T = 295$ K).

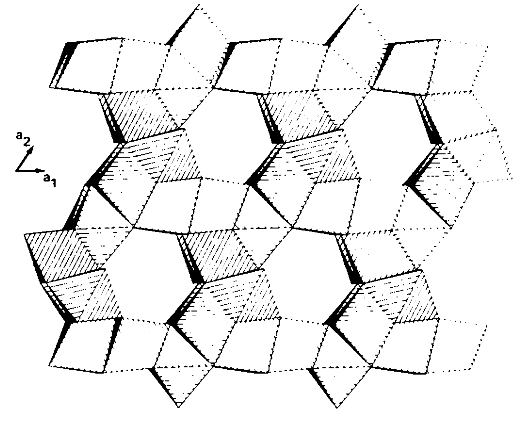

Fig. 2. Polyhedral representation of the structure of hexagonal V_3S_4.

is a superconductor with a transition temperature T_c of about 4.8 K. For $Tl_xV_6S_8$ with $x \simeq 0.1$, a T_c of about 3.8 K is observed (Bensch, Koy & Biberacher, 1992*b*). To monitor changes of the crystal structure as a function of temperature, structure determinations were performed at 295, 170 and 100 K. Even at the lowest temperature no electron-density peak could be detected within the hexagonal channel which may account for O atoms bound to S or 'free' H_3O^+. A view of the triple chains, illustrating the atomic numbering scheme, is given in Fig. 1. Fig. 2 shows a polyhedral representation of the structure.

Experimental

V_3S_4 at 295 K

Crystal data

V_3S_4
$M_r = 281.065$
Hexagonal
$P6_3/m$
$a = 9.118$ (1) Å
$c = 3.3035$ (9) Å
$V = 237.85$ (8) Å^3
$Z = 2$
$D_x = 3.924$ Mg m^{-3}
Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 9$-$13°$
$\mu = 7.11$ mm^{-1}
$T = 295$ K
Needle
0.15 × 0.1 × 0.08 mm
Black
Crystal source: reaction of $K_{0.7}V_6S_8$ with water

Data collection

Stoe AED II diffractometer
ω-2θ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.860$, $T_{\max} = 0.924$
1791 measured reflections
329 independent reflections

316 observed reflections $[F_o > 2\sigma(F_o)]$
$R_{\text{int}} = 0.0254$
$\theta_{\max} = 32.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -5 \rightarrow 5$
3 standard reflections
frequency: 120 min
intensity variation: $< 0.5\%$

Refinement

Refinement on F
Final $R = 0.028$
$wR = 0.0233$
$S = 1.20$
316 reflections
16 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.14$ e Å^{-3}

$\Delta\rho_{\min} = -1.04$ e Å^{-3}
Extinction correction: $F^* = F(1 + 0.002xF^2/\sin 2\theta)^{-1/4}$
Extinction coefficient: $x = 0.0067$ (8)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

V_3S_4 at 170 K

Crystal data

V_3S_4
$M_r = 281.065$
Hexagonal
$P6_3/m$
$a = 9.104$ (2) Å
$c = 3.2973$ (8) Å
$V = 236.68$ (8) Å^3
$Z = 2$
$D_x = 3.944$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 9$-$13°$
$\mu = 7.145$ mm^{-1}
$T = 170$ K
Needle
0.15 × 0.1 × 0.08 mm
Black

Data collection

Stoe AED II diffractometer
ω-2θ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.860$, $T_{\max} = 0.924$
1797 measured reflections
329 independent reflections

321 observed reflections $[F_o > 2\sigma(F_o)]$
$R_{\text{int}} = 0.0297$
$\theta_{\max} = 32.5°$
$h = -14 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -5 \rightarrow 5$
3 standard reflections
frequency: 120 min
intensity variation: $< 0.5\%$

Refinement

Refinement on F
Final $R = 0.0294$
$wR = 0.0237$
$S = 1.19$
321 reflections
16 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.16$ e Å^{-3}

$\Delta\rho_{\min} = -1.24$ e Å^{-3}
Extinction correction: $F^* = F(1 + 0.002xF^2/\sin 2\theta)^{-1/4}$
Extinction coefficient: $x = 0.0048$ (7)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

V_3S_4 at 100 K

Crystal data

V_3S_4
$M_r = 281.065$
Hexagonal
$P6_3/m$
$a = 9.099$ (1) Å
$c = 3.2970$ (8) Å
$V = 236.39$ (8) Å^3
$Z = 2$
$D_x = 3.949$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 26 reflections
$\theta = 9$-$13°$
$\mu = 7.153$ mm^{-1}
$T = 100$ K
Needle
0.15 × 0.1 × 0.08 mm
Black

Data collection

Stoe AED II diffractometer
ω-2θ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.861$, $T_{\max} = 0.924$
1799 measured reflections
329 independent reflections

316 observed reflections $[F_o > 2\sigma(F_o)]$
$R_{\text{int}} = 0.0289$
$\theta_{\max} = 32.5°$
$h = 14 \rightarrow 14$
$k = 0 \rightarrow 14$
$l = -5 \rightarrow 5$
3 standard reflections
frequency: 120 min
intensity variation: $< 0.5\%$

Refinement

Refinement on F
Final $R = 0.0298$
$wR = 0.0213$
$S = 1.21$
316 reflections
16 parameters
$w = 1/[\sigma^2(F) + 0.0001F^2]$
$(\Delta/\sigma)_{\max} \leq 0.001$
$\Delta\rho_{\max} = 1.33$ e Å^{-3}
$\Delta\rho_{\min} = -1.52$ e Å^{-3}
Extinction correction: $F^* = F(1 + 0.002xF^2/\sin 2\theta)^{-1/4}$
Extinction coefficient: $x = 0.0028$ (6)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement coefficients* (Å^2)

$U_{\rm eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic displacement exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$.

	x	y	z	$U_{\rm eq}$
295 K				
V	0.4874 (1)	0.1216 (1)	0.2500	0.06 (1)
S(1)	0.3474 (1)	0.2971 (1)	0.2500	0.06 (1)
S(2)	0.3333	0.6666	0.2500	0.05 (1)
170 K				
V	0.4874 (1)	0.1215 (1)	0.2500	0.04 (1)
S(1)	0.3472 (1)	0.2969 (1)	0.2500	0.04 (1)
S(2)	0.3333	0.6666	0.2500	0.04 (1)
100 K				
V	0.4875 (1)	0.1214 (1)	0.2500	0.03 (1)
S(1)	0.3473 (1)	0.2967 (1)	0.2500	0.03 (1)
S(2)	0.3333	0.6666	0.2500	0.03 (1)

Table 2. *Selected bond lengths* (Å) *for* V_3S_4 *determined at different temperatures*

	295 K	170 K	100 K
V—2V	2.864(1)	2.859(1)	2.856(1)
V—2V	3.120(1)	3.115(1)	3.114(1)
V—2S(2)	2.444(1)	2.440(1)	2.440(1)
V—S(1)	2.358(1)	2.355(1)	2.354(1)
V—S(1)	2.497(1)	2.493(1)	2.490(1)
V—2S(1)	2.340(1)	2.337(1)	2.338(1)
V—S(av.)	2.404	2.400	2.400

Lists of structure factors, anisotropic displacement parameters and selected bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55842 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1019]

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A New Type of One-Dimensional Compound: Structure of $Nb_4(Te_2)_4Te_4I$

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Abstract

The new infinite-chain niobium telluride iodide has been prepared by reaction of the elements at 893 K. $Nb_4(Te_2)_4Te_4I$ represents a new one-dimensional structure type. The structure consists of $[Nb_4(Te_2)_4Te_4I]_\infty$ chains which are formed by the four-nuclear butterfly cluster units '$Nb_4(Te_2)_4Te_4$' with the I atoms bridging between different cluster units.

Comment

Low-dimensional niobium and tantalum chalcogenide compounds have received much attention in the last few years (Rouxel, 1986*a*; Badding & Disalvo, 1990; Liimatta & Ibers, 1987, 1988, 1989). The main interests lie in the synthesis, structure and especially the unusual properties such as superconductivity (Shenoy, Dunlap & Fradin, 1981), charge-density waves (Rouxel, 1986*b*; Mihaly, Chen, Kim & Gruner, 1988), anisotropic electrical conductivity and optical behaviour (Wilson, Disalvo & Mahajan, 1975). Although numerous investigations have been conducted on niobium/tantalum chalcogenides, examples of low-dimensional niobium/tantalum telluride compounds are still very limited. Here we report on the structure determination of a new one-dimensional compound $Nb_4(Te_2)_4Te_4I$. The compound was obtained by solid-state reactions of the approximate stoichiometric elements at about 893 K. Single crystals used in the structure determination