Short Communication

The single crystal structure of V_5S_8 determined at two different temperatures: anisotropic changes of the metal atom network

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Abstract

The crystal structure of V_5S_8 was determined at 295 and 100 K. The thermal expansion of the lattice parameters exhibits a pronounced anisotropy. The contraction of the a-axis is significantly larger than that of the other two axes. The average ⟨V–S⟩ bond lengths as well as the interatomic separation between the V atoms parallel to the *c* axis show no significant changes with temperature. In contrast, a remarkable decrease of the distances between the V atoms in the metal cluster within the *a–b* plane is observed, indicative for stronger bonding interactions. These increased bonding interactions are responsible for the unexpected anisotropic contraction of the lattice parameters with falling temperature.

Introduction

The crystal structure of V_5S_8 was determined from X-ray powder data [1–3]. The single crystal structure was reported in ref. 4. The structure is closely related to the hexagonal NiAs structure. The ordered removal of 3/4 of the V atoms in every second metal layer parallel to the *c* axis results in the vacancy ordered V_5S_8 structure. Within the full metal layers the VS_6 octahedra share common edges. Octahedra of these full layers are connected to octahedra of the partially depleted layers via common faces. This arrangement leads to large nearly rectangular formally empty channels running parallel to the crystallographic *b* axis. Within the fully occupied layers metal clusters composed of four vanadium atoms are formed. The V–V distances are only slightly larger than in the pure metal. The clusters are connected via V atoms of the partially depleted layers.

V_5S_8 has been subjected to numerous investigations concerning magnetic [5–12], electrical and thermodynamical properties [13–19] but no low temperature crystal structure has been reported until now. It was noted that the electrical conductivity changes from p-type conduction at room temperature to n-type at about 150 K [20, 21]. A significant reduction of the crystallographic *c* axis with decreasing temperature was observed in iron substituted V_5S_8 [22].

The aim of the present work was to determine the structure at different temperatures with high accuracy to detect changes of the bonding network which may account for the observed electrical behaviour.

Experimental

Single crystals of V_5S_8 were obtained by a chemical transport reaction using iodine (about 20 mg/cm^3) as transport agent. The mixture of elements was placed in an evacuated and sealed silica tube (length: 18 mm, inner diameter: 10 mm) in the hot zone. The transport proceeds in the temperature gradient 900 to 800 °C. After one week black platelet like tiny crystals up to 2 cm in length were obtained in the cold end of the tube. A single crystal with approximate dimensions $0.06 \times 0.01 \times 0.15$ mm was used for the data collection on a STOE AED II diffractometer (Mo Kα, $\lambda = 0.71073$ Å) at 295 and 100 K. Out to 55° 2θ the whole reciprocal sphere was measured. The data were corrected for Lorentz, polarization effects and a numerical absorption correction was applied. Three reflections were strongly affected by extinction effects and therefore they were omitted. The structure was refined in the non-standard monoclinic space group $F2/m$ which allows an easier comparison with the NiAs structure. The relations between the $F2/m$ setting and the reduced $C2/m$ setting are: (1 0 0) (0 −1 0) (−0.5 0 −0.5). The parameters of the reduced cell are: $a = 11.399$, $b = 6.668$, $c = 7.919$ Å, $\beta = 134.4°$. Further technical details as well as some refinement results are summarized in Table 1. All calculations were performed with the program package SHELX TL Plus. See also 'Supplementary material'.

Results and discussion

The arrangement of the metal atoms within the unit cell is shown in Fig. 1. The lattice parameters obtained at 295 K are larger than those published in ref. 4. The

TABLE 1. Technical details of data collection and some important refinement results. Standard deviations of the last significant digit are given in parentheses

	295 K	100 K	170 K	Ref. 4
a (Å)	11.399(2)	11.356(2)	11.363(3)	11.396(11)
b (Å)	6.668(1)	6.648(1)	6.654(1)	6.645(7)
c (Å)	11.311(2)	11.298(2)	11.302(2)	11.293(4)
β (°)	91.57(3)	91.60(3)	91.55(2)	91.45(6)
V (Å³)	859.4(2)	852.6(2)	854.2(2)	854.9
y^a	0.0007	0.0005		
g^b	0.00079(5)	0.00066(4)		
N_p	38	38		
N_o	540	538		
δF (e/Å³)	0.82	0.84		
	−0.56	−0.54		
R_{int} (%)	2.74	2.09		
R (%)	2.12	1.98		5.7
R_w (%)	1.90	1.74		7.0
GOF	0.82	0.80		
$\alpha_a{}^c \times 10^{-5}$ (K⁻¹)	1.93			
$\alpha_b{}^c \times 10^{-5}$ (K⁻¹)	1.54			
$\alpha_c{}^c \times 10^{-5}$ (K⁻¹)	0.59			

$^a w = 1/(\sigma^2(F) + yF^2)$. $^b F^* = F[1 + 0.002gF^2/\sin 2\theta]^{-1/4}$. ^{c}Relative thermal expansion coefficient (see text).
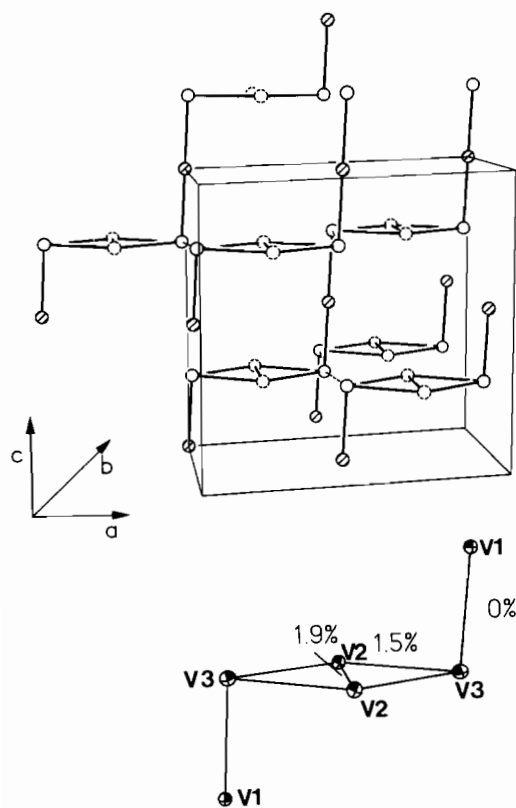

Fig. 1. The arrangement of the V atoms within the unit cell of V_5S_8. The sulfur atoms are omitted for clarity. The inset shows the metal atom cluster composed of four V atoms. The decrease of the bond distances between 295 and 100 K is given as a percentage.

reason for this disagreement may be either a differing composition or different preparation conditions.

The thermal expansion of the lattice shows a pronounced anisotropy. A plot of the lattice parameters versus temperature results in straight lines with different slopes. The slopes are $2.343(8) \times 10^{-4}$, $1.065(3) \times 10^{-4}$ and $0.691(3) \times 10^{-4}$ for the a, b and c axis, respectively. The contraction of the a axis is significantly larger than that of the other two axes. The relative thermal expansion coefficient was calculated according to $\alpha_a = (a_{295} - a_{100})/a_{295} \times (\delta T)$, and analogously for α_b and α_c and are listed in Table 1.

It is noteworthy that the average $\langle V–S \rangle$ bond lengths of the three distinct VS_6 octahedra show no significant changes with temperature (see Table 2). But, whereas the octahedron around V1 is only little affected, the octahedra around V2 and V3 exhibit an increased distortion at 100 K. This is evidenced by the difference δ ($VS_{max} - VS_{min}$) (see Table 2). More pronounced anisotropic changes are observed within the metal network. The V1–V3 separation parallel to the crystallographic c axis remains constant between 295 and 100 K. In contrast, a remarkable decrease of the V–V bond distances in the metal cluster within the a–b plane is observed. The V2–V2 and V2–V3 separations decrease by about 1.9 and 1.5%, respectively indicating stronger bonding interactions between the V atoms (see inset of Fig. 1). These stronger interactions lead to a further displacement of the V2 and V3 atoms from the centers of the octahedra resulting in a larger distortion of the $V2S_6$ and $V3S_6$ octahedra. The separations between

TABLE 2. Important bond distances (Å) and range of angles (°) in V_5S_8 determined at 295 and 100 K. Standard deviations are given in parentheses

		T (K) 295	100
V1–S1	2×	2.411(1)	2.410(1)
V1–S3	4×	2.399(1)	2.395(1)
⟨V1–S⟩		2.403	2.400
δ(V1–S$_{max-min}$)		0.012	0.015
V1–V3	2×	2.918(1)	2.920(1)
V2–S1	2×	2.457(1)	2.462(1)
V2–S2	2×	2.317(1)	2.311(1)
V2–S3	2×	2.390(1)	2.384(1)
⟨V2–S⟩		2.388	2.386
δ(V2–S$_{max-min}$)		0.140	0.151
V2–V2		2.880(1)	2.826(1)
V2–V3	2×	3.047(1)	3.001(1)
V3–S3	2×	2.423(1)	2.429(1)
V3–S1		2.442(1)	2.441(1)
V3–S2		2.320(1)	2.311(1)
V3–S3	2×	2.379(1)	2.368(1)
⟨V3–S⟩		2.3943	2.391
δ(V3–S$_{max-min}$)		0.122	0.130
V3–V1		2.918(1)	2.920(1)
V3–V2	2×	3.047(1)	3.001(1)
V3–V3	2×	3.354(1)	3.351(1)
⟨S–V1–S⟩		86.5(1)–180.0(1)	86.1(1)–180.0(1)
⟨S–V2–S⟩		79.1(1)–169.4(1)	78.2(1)–168.3(1)
⟨S–V3–S⟩		85.1(1)–172.7(2)	84.1(1)–171.3(1)

the clusters exhibit no significant changes with temperature.

In summary, the unexpected anisotropic contraction of the lattice parameters with decreasing temperature is mainly caused by stronger bonding interactions between vanadium atoms of the clusters within the full metal layers, i.e. within the a–b plane. The changes of the interactions between V and S atoms play only a minor role. The anisotropic variations of the V–V bonding network as a function of temperature may be responsible for the observed electrical properties.

Supplementary material

Lists of F_o-F_c, positional parameters, bond angles and tables of anisotropic displacement parameters U_{ij} are available from the authors on request.

References

1 S. Brunie and M. Chevreton, C. R., 258 (1964) 5847–50.
2 F. Gronvold, H. Haraldsen, B. Pedersen and T. Tufte, Rev. Chim. Miner., 6 (1969) 251.
3 A. B. deVries and F. Jellinek, Rev. Chim. Miner., 11 (1974) 624.
4 I. Kawada, M. Nakano-Onoda, M. Ishii, M. Saeki and M. Nakahira, J. Solid State Chem., 15 (1975) 246.
5 Y. Kitaoka and H. Yasuoka, J. Phys. Soc. Jpn., 48 (1980) 1949.
6 B. G. Silbernagel, R. B. Levy and F. R. Gamble, Phys. Rev. B, 11 (1975) 4563.
7 B. G. Silbernagel and A. H. Thompson, Physica B + C, 86–88 (1977) 1003.
8 A. B. deVries and C. Haas, J. Phys. Chem. Solids, 34 (1973) 651.
9 M. Nishihara, Y. Yasuoka, Y. Oka, K. Kosuge and S. Kachi, J. Phys. Soc. Jpn., 42 (1977) 787.
10 J. B. Forsyth, P. J. Brown, I. Kawada, H. Nozaki and M. Saeki, J. Phys. C, 12 (1979) 4261.
11 Y. Oka, K. Kosuge and S. Kachi, Phys. Lett. A, 50 (1974) 311.
12 H. Nozaki, M. Umehara, Y. Ishizawa, M. Saeki, T. Mizoguchi and M. Nakahira, J. Phys. Chem. Solids., 39 (1978) 851.
13 H. Nakazawa, M. Saeki and M. Nakahira, J. Less-Common Met., 40 (1975) 57.
14 Y. Oka, K. Kosuge and S. Kachi, J. Solid State Chem., 23 (1978) 11.
15 Y. Oka, K. Kosuge and S. Kachi, J. Solid State Chem., 24 (1978) 41.
16 A. Fujimori, Physica B, 163 (1990) 736.
17 K. Basu, M. Wakihara and M. Taniguchi, Thermochim. Acta, 92 (1985) 223.
18 K. Basu and M. Taniguchi, J. Thermal. Anal., 30 (1985) 1129.
19 M. Yokoyama, M. Yoshimura, M. Wakihara, S. Somiyo and M. Taniguchi, J. Solid State Chem., 60 (1985) 182.
20 M. Taniguchi, M. Wakihara and Y. Shirai, Z. Anorg. Allgem. Chem., 461 (1980) 234.
21 H. Nozaki, Y. Ishizawa, M. Saeki and M. Nakahira, Phys. Lett. A, 54 (1975) 29.
22 W. Bensch, R. Schlögl and E. Amberger, Helv. Chim. Acta, 69 (1986) 35.