Structure and Low-Temperature Behaviour of $Tl_{0.82}V_5S_{4.36}Se_{3.64}$

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Abstract. $M_r = 849.51$, $C2/m$, $a = 17.841$ (4), $b = 3.383$ (1), $c = 8.741$ (3) Å, $\beta = 104.88$ (2)°, $V = 509.88$ Å^3, $Z = 2$, $D_x = 5.532$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0.7093$ Å, $\mu = 299.91$ cm^{-1}, $F(000) = 750$, $T = 295$ K, $R = 0.037$ for 842 unique reflections. The structure is built of distorted vanadium chalcogen octahedra connected by face and edge sharing. Owing to the three-dimensional framework large quasi-rectangular channels are built in which the Tl atoms are inserted. Magnetic measurements were performed on a crystalline powder sample in the temperature range 74–290 K. The measured susceptibility obeys a Curie–Weiss law with a term for the temperature-independent paramagnetism (TIP). No ordering of the magnetic moments was observed down to the lowest temperatures. A slight discontinuity appears in the susceptibility *versus* temperature curve around 170 K. This may be due to a phase transition. Differential thermal analysis (DTA) at low temperatures shows an endothermic peak at 168 (2) K.

Introduction. During our investigations of structural and physical properties of three-dimensional channel structures like $Tl_xV_6S_8$ (Polborn, Bensch & Amberger, 1985) and TlV_5S_8 (Bensch, Amberger & Abart, 1984) we have prepared a series $TlV_5S_{8-y}Se_y$, $0 < y < 8$. X-ray investigations were performed on single crystals with the composition $Tl_{0.77}V_6S_8$ (Polborn, Bensch & Amberger, 1985) and $Tl_{0.84}V_5Se_8$ (Bensch, Amberger, Polborn, Steurer & Abart, 1984) and $Tl_{0.82}V_5$-$S_{4.36}Se_{3.64}$. In contradiction to the pure sulfide the two selenides crystallize in the higher symmetric space group $C2/m$. The ratios $c/b = 5.274$ and $c/a = 0.490$

are in good agreement with those found for compounds with the TlV_5S_8 structure (Fournes, Vlasse & Saux, 1977). The magnetic properties are determined by the relatively short metal–metal distances and the different vanadium sites in the structure causing the coexistence of an itinerant magnetic behaviour and a localized magnetic moment.

The binary compounds V_5S_8 and V_5Se_8 are both antiferromagnetic at low temperatures. The magnetism of both compounds is best described by the co-existence of a TIP with temperature-dependent local magnetic moments (Oka, Kosuge & Kachi, 1974; Silbernagel, Levy & Gamble, 1975; Funahashi, Nozaki & Kawada, 1981; Kitaoka & Yasuoka, 1980). The thallium-containing compounds, on the other hand, are paramagnetic down to the lowest temperatures (Bensch, Amberger & Abart, 1984; Vlasse & Fournes, 1976). During our investigations of the ternary compounds we have found that the non-substituted sulfides show discontinuities in the susceptibility and DTA curves at lower temperatures (Bensch, Amberger & Abart, 1984; Bensch, Schlögl & Reller, 1985). The present paper deals with the structure of $Tl_{0.82}V_5S_{4.36}Se_{3.64}$, the magnetic bulk properties and low-temperature DTA investigations.

Experimental. Sample prepared by heating the weighed elements for 24 h in evacuated and sealed silica ampoules to 1243 K. Probe annealed for 12 d at 1073 K. Product slowly cooled to room temperature. Sample consists of black flat needle-like crystals with metallic lustre. Dimensions up to 1 mm in length, 0.2 mm in width and 0.02 mm in thickness. Product is air stable over a long period of time. After a few months the surface is covered with water and/or sulfate/selenate. This was found during our investigations of the binary and ternary vanadium sulfides and selenides.

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The homogeneity of the product was checked with X-ray powder diffractometry. No second phase could be detected in the powder pattern. Some single crystals were analysed by the microprobe analysis method. The V $K\alpha$ line from vanadium metal, the Tl $M\alpha$ line from $Tl(NO_3)_3$, Se $L\alpha$ from the element and S $K\alpha$ from PbS were used as standards. The margin of error is approximately 4%. The best measurement leads to the composition $Tl_{0.81}V_5S_{4.5}Se_{3.5}$, which is in good agreement with the composition refined during the structure determination. DTA measurements were undertaken with a Mettler 2000 B device. The cooling and heating rate was 5 K min^{-1}. Magnetic measurements were performed with a Faraday balance at various fields up to 0·81 T between 74 and 290 K (Abart & Voitländer, 1981).

Preliminary Weissenberg and precession photographs showed title compound to be monoclinic C. Crystal 0·372 × 0·118 × 0·019 mm; Syntex $P2_1$ diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; cell parameters by least-squares refinement from setting angles of 15 automatically centred reflections in the range $4·7 < \theta < 14·6°$. Max. $\sin\theta/\lambda = 0·705$ Å^{-1}, $\theta/2\theta$ scan mode, $h/k/l$ range: $-24,24/-4,4/-11,11$; 3010 reflections measured, 871 unique. No intensity drop of three standard reflections measured after each block of 97 reflections; numerical absorption correction applied with SHELX76 (Sheldrick, 1976), max. and min. transmission factors: 0·5718 and 0·0679; $R_{int} = 0·028$. $N(z)$ test and E statistics favour centrosymmetric space group $C2/m$. Isotropic refinements on F with SHELX76 started with atomic x and z positions for Tl, V and chalcogen atoms from Bensch, Amberger, Polborn, Steurer & Abart (1984), with site occupation factors (s.o.f.) derived from microprobe analysis. The positions 1, 2, 3 and 4 (Fi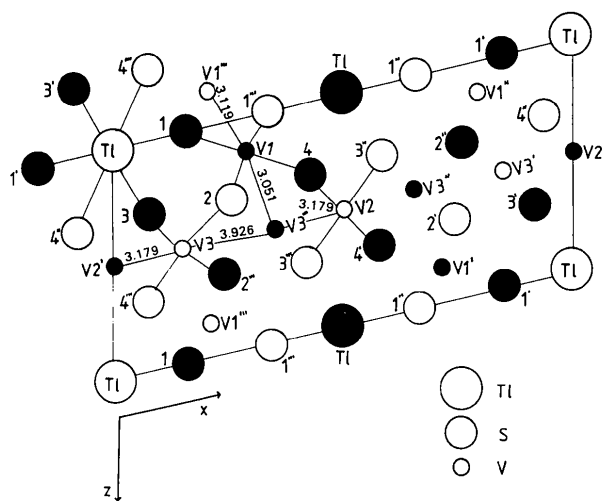g. 1) are occupied with chalcogens in such a way that the sum of the two real s.o.f.'s is fixed at 0·5. Final conventional R factor 0·037 for 842 observed structure factors with $|F| > 3\sigma(|F|)$; 28 reflections unobserved; $wR = 0·035$, $w = 2·8863/\sigma^2(|F|)$, 67 parameters refined. 020 reflection excluded from last cycle of least-squares refinement because secondary extinction suspected. Max. and min. heights in final difference Fourier synthesis 0·690 and $-0·695$ e Å^{-3}; all Δ/σ values $< 0·93$. Scattering factors for S included in SHELX76 program, for Tl, V, Se from Cromer & Mann (1968).

Discussion. Final parameters of all atoms are listed in Table 1.* Fig. 1 shows a projection of the structure along (010). The VX_6 octahedra ($X = $ S,Se) build infinite layers parallel to the (001) plane consisting of V(2) and V(3) octahedra sharing edges. An infinite double chain parallel to the b axis consists of V(1) octahedra sharing edges. These two basic units are connected in sharing common faces. This framework leads to quasi-rectangular channels in which the thallium atoms are inserted (Fig. 2).

Table 1. *Final atomic coordinates and U_{eq} values (Å^2) for $Tl_{0.82}V_5S_{4.36}Se_{3.64}$ with e.s.d.'s in parentheses*

$$U_{eq} = \sum_i \sum_j U_{ik} a_i^* a_k^* (\mathbf{a}_i \cdot \mathbf{a}_k).$$

	x	y	z	s.o.f.	U_{eq}
Tl	0·0000	0·0000	0·0000	0·2048 (7)	0·048
V(1)	0·2910 (1)	0·5000	0·1477 (2)	0·5000	0·020
V(2)	0·5000	0·0000	0·5000	0·2500	0·025
V(3)	0·1498 (1)	0·0000	0·4923 (2)	0·5000	0·022
Se(3)	0·0830 (1)	0·5000	0·3111 (1)	0·2794 (15)	0·016
S(3)	0·0830 (1)	0·5000	0·3111 (1)	0·2206 (15)	0·026
Se(2)	0·2576 (1)	0·0000	0·3396 (1)	0·2590 (16)	0·016
S(2)	0·2576 (1)	0·0000	0·3396 (1)	0·2410 (16)	0·013
Se(1)	0·1584 (1)	0·5000	$-0·0001$ (1)	0·2488 (16)	0·016
S(1)	0·1584 (1)	0·5000	$-0·0001$ (1)	0·2512 (16)	0·022
Se(4)	0·4262 (1)	0·5000	0·3257 (2)	0·1233 (16)	0·020
S(4)	0·4262 (1)	0·5000	0·3257 (2)	0·3767 (16)	0·018

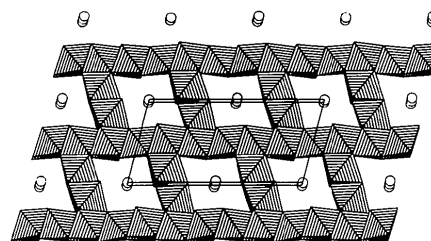Fig. 1. (010) projection of the structure of $Tl_{0.82}V_5S_{4.36}Se_{3.64}$.

Fig. 2. STRUPLO84 drawing (Fischer, 1985) displaying the octahedral framework and the channels occupied by the Tl atoms. The (010) projection is shown after 5° rotation around the a axis.

During our refinement we obtained a relatively high temperature-factor component U_{22} for the Tl atom, which is of the same order as those for Tl in $Tl_{0.84}V_5Se_8$ (Bensch, Amberger, Polborn, Steurer & Abart, 1984). This high value for U_{22} might be due to pronounced vibrations of the Tl atoms parallel to the crystallographic b axis within the channels. The refined site occupation factor for $X(4)$ reaches a ratio of 3:1 for S:Se. All other chalcogen positions are nearly occupied with a ratio 1:1 for S:Se. This slight preference causes a relatively symmetric environment around the V(2) atom. However, the octahedral environments around the vanadium atoms are all more symmetrical than in the pure sulfide.

The interatomic distances are listed in Table 2. It is remarkable that the metal–metal distances vary in an unexpected way going from the pure sulfide to the selenide (Table 2). The distance between V(1) and V(3) is about 4·2% shorter compared with the distance in TlV_5S_8 (Bensch, Amberger, Polborn, Steurer & Abart, 1984).

The measured magnetic susceptibility in the temperature range 220 to 74 K is displayed in Fig. 3. No ordering of the magnetic moments is observed down to the lowest temperature. As can be seen a discontinuity occurs at around 165–175 K which might be due to a phase transition. The trend of the temperature dependence of the susceptibility is not changed. A slight hysteresis is observed between cooling and heating. In order to evaluate the magnetic measurements we fitted (1) to the experimental points by a standard least-squares fit:

$$\chi = \chi_0 + C/(T - \theta). \tag{1}$$

χ_0 is the temperature-independent Pauli paramagnetism (TIP), C the Curie constant and θ the Weiss temperature. The fit over the whole temperature range leads to $\chi_0 = 0\cdot00269$ mm^3 g^{-1}, $\theta = -13$ K and $C = 0\cdot107$ mm^3 K g^{-1}. From the Curie constant the effective magnetic moment was calculated using

$$\mu_{\text{eff}} = (3\,R\,C\,M)^{1/2}/N_L\mu_B \tag{2}$$

(C is the Curie constant, M the molecular weight, N_L Avogadro's number and R the gas constant). Using the composition of the title compound we calculate an effective magnetic moment of $\mu_{\text{eff}} = 0\cdot853 \pm 0\cdot014$ μ_B/V atom. The uncertainty of μ_{eff} because of variations in the molecular weight is at maximum $0\cdot004$ μ_B, far smaller than that of the experimental determination. If we assume an additional variation of ± 2 units in the Curie constant the uncertainty of μ_{eff} is at maximum $0\cdot014$ μ_B. This requires no change in the principal interpretations of our results. The effective magnetic moment is distinctly lower than the spin-only value of $2\cdot83$ μ_B for V^{3+}. Such a low value for the magnetic moment is expected from relatively short metal–metal distances in the structure which give rise to an overlap

of d orbitals. Furthermore, the observed effective magnetic moment and χ_0 lie between those found for the pure sulfide $Tl_{0.96}V_5S_8$ and the pure selenide $Tl_{0.84}V_5Se_8$ (see Table 2) (Bensch, Amberger, Polborn, Steurer & Abart, 1984), as is expected from the metal–metal distances (Table 2) of the three compounds.

Table 2. *Interatomic distances* (Å) *for* $Tl_{0.82}V_5S_{4.36}Se_{3.64}$ *with e.s.d.'s in parentheses, vanadium–vanadium distances in* TlV_5S_8, $Tl_{0.82}V_5S_{4.36}Se_{3.64}$ *and* $Tl_{0.84}V_5Se_8$ *and some magnetic data for* TlV_5S_8, $Tl_{0.82}V_5S_{4.36}Se_{3.64}$ *and* $Tl_{0.84}V_5Se_8$

Tl—Se(3)/S(3)	3·222 (1)	V(2)—Se(4)/S(4)	2·426 (1)
Tl—Se(1)/S(1)	3·293 (1)	V(3)—Se(3)/S(3)	2·413 (1)
Tl—Se(4)/S(4)	3·430 (1)	V(3)—Se(2)/S(2)	2·608 (2)
V(1)—Se(2)/S(2)	2·557 (1)	V(3)—Se(4)/S(4)	2·549 (2)
V(1)—Se(4)/S(4)	2·387 (2)	V(3)—Se(4)/S(4)	2·340 (1)
V(2)—Se(3)/S(3)	2·512 (2)		

	TlV_5S_8	$Tl_{0.82}V_5S_{4.36}Se_{3.64}$	$Tl_{0.84}V_5Se_8$
V(1)—V(1)	3·047	3·119	3·180
V(1)—V(3)	3·186	3·051	3·093
V(2)—V(3)	3·201	3·179	3·233
V(3)—V(3)	3·773	3·926	4·074

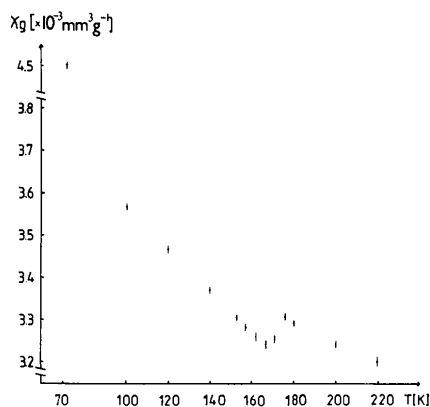|	χ_0 (mm^3 g^{-1})	$\mu_{\text{eff}}(\mu_B)$
TlV_5S_8	0·00287	0·512
$Tl_{0.82}V_5S_{4.36}Se_{3.64}$	0·00269	0·850
$Tl_{0.84}V_5Se_8$	0·00196	1·69

Fig. 3. The measured magnetic susceptibility in the temperature range 220 to 74 K.
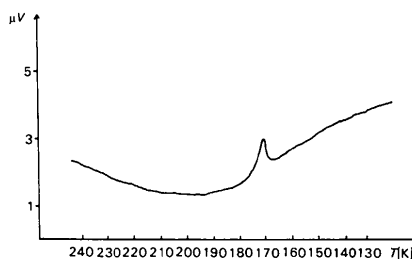
Fig. 4. The DTA curve recorded between 240 and 130 K.

Fig. 4 shows the DTA curve recorded between 240 and 130 K. A small endothermic peak occurs at 168 (2) K. The peak is completely reversible with a slight hysteresis of about 5 K. Because the base line is not completely linear an exact value for the change in free enthalpy and consequently in the entropy should not be estimated. The peak in the DTA curve lies in the same temperature range as observed in the magnetic susceptibility curve (Fig. 3).

The structure of the title compound shows an unusual connection scheme with edge- and face-sharing octahedra. This leads to distorted $V(S,Se)_6$ octahedra with short metal–metal bonds in the structure. The partial itinerant character of this compound is supported by the magnetic measurements. The discontinuity in the magnetic-susceptibility curve and the endothermic peak in the DTA curve are a clear indication for a phase transition at around 170 K. Further investigations are in progress to clarify the nature of this phase transition.

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Structure of Kamiokite

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Abstract. $Fe_2Mo_3O_8$, $M_r = 527.51$, hexagonal, $P6_3mc$, $a = 5.781$ (1), $c = 10.060$ (1) Å, $V = 291.2$ (1) Å^3, $Z = 2$, $D_m = 5.96$, $D_x = 6.02$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71069$ Å, $\mu(Mo\ K\alpha) = 11.14$ mm^{-1}, $F(000) = 484$, $T = 298$ K, $R = 0.027$ for 656 independent reflections. In the structure, the layer composed of MoO_6 octahedra alternates with the layer composed of FeO_6 octahedra and FeO_4 tetrahedra along c. These polyhedra are linked together by edges and corners to form a three-dimensional network. The very short Mo–Mo bond length of 2.533 (1) Å confirms the presence of triangular clusters of bonded Mo atoms.

Introduction. Kamiokite, $Fe_2Mo_3O_8$, was first described as a new mineral by Sasaki, Yui & Yamaguchi (1975) from the Kamioka mine, Gifu Prefecture, central Japan. It was also reported from the Mohawk and Ahmeek mines, Michigan (Picot & Johan, 1977). We here present the result of a crystal structure analysis of the type mineral specimen from Kamioka. The chemical composition of the specimen was reported as $(Fe_{2.01}Mn_{0.03})_{2.04}Mo_{2.98}O_8$ (Sasaki et al., 1975), which was very close to the ideal composition.

The mineral belongs to the ternary oxide group with the formula $M_2^{II}Mo_3^{IV}O_8$ (where $M = $ Mg, Mn, Fe, Co, Ni, Zn and Cd). The members of this group were prepared and examined systematically by McCarroll, Katz & Ward (1957) who reported that the compounds were isostructural because of the similar characteristics of their X-ray powder diffraction patterns; they presented the results of structure determinations on $Zn_2Mo_3O_8$ and $Mg_2Mo_3O_8$. Later a refinement of the structure was accomplished by Ansell & Katz (1966) on $Zn_2Mo_3O_8$, confirming the previously reported structural features. The result is used as the basis for the present work on $Fe_2Mo_3O_8$ (kamiokite).