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The Crystal Structure of $Tl_{0.84}V_5Se_8$ and Magnetic Bulk Properties

W. BENSCH,* K. POLBORN, AND E. AMBERGER

Institut für Anorganische Chemie der Universität München, Meiserstrasse 1, D-8000 Munich 2, Federal Republic of Germany

W. STEURER

Institut für Mineralogie und Kristallographie der Universität München, Theresienstrasse 48, D-8000 Munich 2, Federal Republic of Germany

AND J. ABART

Institut für Physikalische Chemie der Universität München, Sophienstrasse 11, D-8000 Munich 2, Federal Republic of Germany

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While the antiferromagnetic binary compound V_5Se_8 (Y. KITAOKA AND H. YASUOKA, *J. Phys. Soc. Jpn.* **48**, 1460, 1980) of which the measured magnetic susceptibility above 27 K cannot be fitted to a Curie–Weiss law and a Curie–Weiss law with a term for the temperature-independent paramagnetism, the ternary compound $Tl_{0.84}V_5Se_8$ exhibits paramagnetism. The measured susceptibility fits the equation $\chi = \chi_0 + C/(T - \theta)$. In comparison to $Tl_{0.96}V_5S_8$ (W. BENSCH, E. AMBERGER, AND J. ABART, in press) with shorter V–V distances than in $Tl_{0.84}V_5Se_8$, the magnetic moment attributed to V(3) in the selenide is markedly higher.

Ternary chalcogenides of thallium and transition elements with the general formulae TlT_5X_8 (T = Ti, V, Cr; X = S, Se) and $Tl_xT_6X_8$ (T = V; X = S; T = Ti, Nb; X = Se) build up channel structures based on an octahedral framework (*1–5, 8*). The TlT_5X_8 compounds crystallize in the TlV_5S_8 structure (*4*). In the course of our investigations of such channel structures, we prepared a compound with the composition $Tl_{0.84}V_5Se_8$. A structural refinement was carried out and the magnetic properties of a powder sample were measured.

The sample was synthesized from the elements. In order to produce single crystals, a slight excess of selenium was used. The mixture was placed in an evacuated and sealed silica tube. After a heat treatment of 14 days at 1273 K, the probe was cooled down to room temperature at a cooling rate of 100 K/hr. The density of the sample was determined by pycnometry. The result is in good agreement with the density derived from X-ray data and has the value 6.353(15) g cm^{-3}. The refined lattice parameters are a = 1830.60(26) pm, b = 345.08(13) pm, c = 887.40(14) pm, β = 104.04(2)°, V = 0.54383 × 10^9 pm^3, Z = 2. The space group is $C2/m$.

The structure refinement of a needle-like

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* Author to whom correspondence should be addressed.

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TABLE I

ATOMIC AND THERMAL PARAMETERS OF $Tl_{0.84}V_5Se_8$

Atom	$C2/m$	x	y	z	Occupation probability	$U11$	$U22$	$U33$	$U23$	$U13$	$U12$
Tl	2(a)	0	0	0	0.2111(9)	0.0259(5)	0.0596(9)	0.0212(5)	0	0.0062(4)	0
V(1)	4(i)	0.2901(1)	0.5	0.1474(2)	0.5	0.0068(6)	0.0169(9)	0.0080(7)	0	0.0025(5)	0
V(2)	2(d)	0.5	0	0.5	0.25	0.0075(9)	0.0202(14)	0.0074(10)	0	0.0016(8)	0
V(3)	4(i)	0.1488(1)	0	0.4956(2)	0.5	0.0082(6)	0.0134(9)	0.0086(7)	0	0.0027(5)	0
Se(1)	4(i)	0.1595(1)	0.5	0.0028(1)	0.5	0.0069(4)	0.0104(5)	0.0096(4)	0	0.0019(3)	0
Se(2)	4(i)	0.2583(1)	0	0.3420(1)	0.5	0.0063(4)	0.0096(5)	0.0083(4)	0	0.0030(3)	0
Se(3)	4(i)	0.0848(1)	0.5	0.3145(1)	0.5	0.0081(4)	0.0109(5)	0.0085(4)	0	0.0034(3)	0
Se(4)	4(i)	0.4277(1)	0.5	0.3172(1)	0.5	0.0064(4)	0.0103(5)	0.0086(4)	0	0.0023(3)	0

Note. Standard deviations in the last significant digits are given in parenthesis. The anisotropic temperature factor is given by $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

single crystal was based on 1885 unique reflections up to $2\theta = 80°$ ($MoK\alpha_1$ radiation). The scattering factors were taken from (*6*) and corrected for anomalous dispersion (*7*). After absorptional, Lorentzian, polarizational, and isotropic extinctions corrections we obtained a conventional R value of 0.053 for 1557 unique structure factors with $F_0 > 2.5\sigma$ (328 suppressed) and a total of 48 parameters. The weighted R value is 0.043. Lists of the $|F_0|$ values can be obtained from the authors on request. The resultant thermal and position parameters are listed in Table I. During our structure refinement cycles we obtained a relatively high temperature factor component $U22$ for Tl, larger than the $U22$ given by (*1*) for TlV_5Se_8. We found that the $U22$ of all atoms are higher than the $U11$ and $U33$—in agreement with Ref. (*1*). Our lattice constants are somewhat smaller than those given by (*1*), due to the smaller thallium content. The axis ratios a/b and c/a are 5.30 and 0.485, respectively, in excellent agreement with the values of (*1*). Table II shows the interatomic distances. With the V(1) atom in position 4*i* and V(2) in 2*d*, we obtained significantly shorter metal–metal distances in the structure, due to the smaller lattice parameters. The distortions of the octahedral environment of the vanadium atoms are of the same order as in TlV_5Se_8 (*1*).

TABLE II

INTERATOMIC DISTANCES IN $Tl_{0.84}V_5Se_8$ (pm)

Tl–Se(1)	338.7(1)
Tl–Se(3)	332.6(7)
Tl–Se(4)	338.9(7)
V(1)–Se(1)	242.3(3)
V(1)–Se(2)	260.0(9)
V(1)–Se(4)	260.1(3)
V(2)–Se(3)	252.2(2)
V(2)–Se(4)	250.2(4)
V(3)–Se(2)	259.6(2)
V(3)–Se(2)	268.7(3)
V(3)–Se(3)	244.3(4)
V(3)–Se(4)	241.6(3)
V(1)–V(1)	318.0(2)
V(1)–V(1)	345.1(1)
V(1)–V(3)	309.3(1)
V(2)–V(2)	345.1(1)
V(2)–V(3)	323.3(2)
V(3)–V(3)	407.4(3)

Magnetic measurements were carried out with a Faraday balance in the temperature range between 4.2 and 300 K at various fields up to 0.81 *T*. For the calibration of the apparatus we used $CoHg(SCN)_4$ (*9*). A small field dependence, which was due to ferromagnetic impurities,[1] was eliminated

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[1] The chemical analysis with the atomic absorption spectroscopy of the vanadium powder shows that ≤50 ppm iron is present.

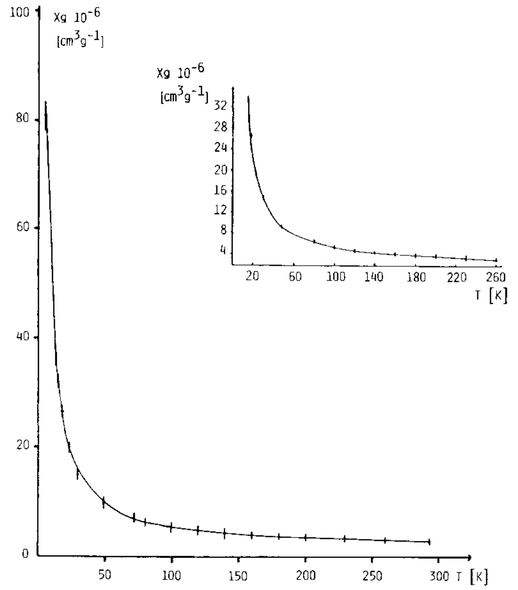

FIG. 1. The temperature dependence of the measured magnetic susceptibility of $Tl_{0.84}V_5Se_8$. The insert shows the temperature dependence in the temperature range 15–260 K.

using a Honda–Owen plot. Figure 1 shows the temperature dependence of the measured susceptibility. The probe shows the coexistence of a temperature-independent paramagnetism and a temperature-dependent paramagnetism, which obeys the Curie–Weiss law. We separated the temperature-independent paramagnetism and Curie–Weiss law susceptibility by fitting the experimental points to the formula $\chi = \chi_0 + C/(T - \theta)$ by a least-square method. The values of the magnetic parameters are listed in Table III. Those of $Tl_{0.96}V_5S_8$, V_5S_8, and V_5Se_8 are included for comparison.

Because of the uncertainty in determining the exact θ value, we do not attribute the slight positive value to a ferromagnetic behavior. The fit suggests that $Tl_{0.84}V_5Se_8$ is paramagnetic down to the lowest temperatures. In contrast to the selenide V_5Se_8 (*10*), the measured susceptibility of $Tl_{0.84}V_5Se_8$ can be fitted to the formula given above. In V_5Se_8 the magnetic moments are in ordered antiferromagnetic state at 27 K. Above the Néel temperature T_N the measured susceptibility of this vanadium selenide cannot be fitted either to a Curie–Weiss law or to a Curie–Weiss law with a term for the temperature-independent paramagnetism (*10*).

Proceeding from the sulfide $Tl_{0.96}V_5S_8$ to the selenide $Tl_{0.84}V_5Se_8$ a decrease in the temperature-independent paramagnetism is observed, together with an increase of the Curie constant. If we assume that the whole magnetic moment of $Tl_{0.84}V_5Se_8$ is localized at only one vanadium atom an effective local moment of 1.69 ± 0.03 μ_B is derived from the Curie constant. The most probable carrier of the local moment in the selenide is the V(3) atom in 4*i*, with the nearest vanadium neighbors at 309.3, 323.3, and 407.4 pm. These distances are clearly longer than in the sulfide compounds, where they amount to 301.1, 314.4, and 381.1 pm, respectively (*4*). We attribute the significant decrease of χ_0, together with the increase of the magnetic moment, to the greater metal–

TABLE III

MAGNETIC DATA OF $Tl_{0.96}V_5S_8$, $Tl_{0.84}V_5Se_8$, V_5S_8, AND V_5Se_8

Compound	$\chi_0 \times 10^6$ ($cm^3\ g^{-1}$)	$C \times 10^6$ ($cm^3\ K\ g^{-1}$)	θ (K)	T_N (K)	$\mu_{eff}(\mu_B)$	Ref.
$Tl_{0.96}V_5S_8$	2.87	46.3	−40	—	0.57	*11*
$Tl_{0.84}V_5Se_8$	1.96 ± 0.03	337 ± 15	2.5 ± 2	—	1.69 ± 0.03	This work
V_5S_8	4.0	1560	−10	35	2.5	*12*
V_5Se_8	—	—	−10	27	2.5	*10*

metal distances in the selenide, resulting in a markedly decreased V–V *d*-orbital overlap.

In addition, the effective magnetic moments for V(3) in the Tl compound are smaller than in the binary vanadium selenide and sulfide ((*10–12*); see Table III). V_5S_8 and V_5Se_8 crystallize in a partially depleted layer structure, with metal clusters in the *a–b* plane and short metal–metal distances between these clusters parallel to the crystallographic *c* axis—which gives rise to an antiferromagnetic ordering at about 30 K in both compounds. Progressing from V_5S_8 to V_5Se_8, the lattice parameters are distinct greater in the selenide. Due to this greater crystallographic axis, the distances between the metal atoms in the clusters and between these clusters are somewhat greater in V_5Se_8. The effective magnetic moment per vanadium atom in the partially depleted layers and the Néel temperature is not affected by these greater metal–metal distances—as can be seen from Table III. In first approximation, we can conclude that in antiferromagnetically ordered compounds the metal distances are not the most important factors which determine the ordering of the magnetic moments. This is not the case in paramagnetic compounds such as $Tl_{0.96}V_5S_8$ and $Tl_{0.84}V_5Se_8$—as can be seen from Table III. This observation—the increase of the Curie constant and a decrease of the temperature-independent paramagnetism with greater lattice parameters—is supported by our investigations on the compound $Tl_{0.83}V_5S_{4.4}Se_{3.6}$ (*13*). If all vanadium atoms in TlV_5S_8 or $Tl_{0.84}V_5Se_8$ were magnetic, the effective magnetic moments would decrease to values of 0.254 and 0.755 ± 0.017 μ_B, respectively. Additional investigations are necessary in order to determine whether only one type or all crystallographically inequivalent vanadium atoms carry the local magnetic moment.

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