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Structure and Magnetic Properties of $VOSO_4$†

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The structure of tetragonal α-$VOSO_4$ has been determined from quantitative analysis of X-ray powder intensity data. It is isostructural with $MoOPO_4$ and has chains of corner shared VO_6 octahedra, parallel to the *c* axis, cross linked by corner shared tetrahedra. The vanadium is cooperatively displaced toward an oxygen to give a very short V–O distance (1.63 Å) characteristic of the vanadyl ion. The magnetic properties of α-$VOSO_4$ and β-$VOSO_4$ are different, the former appearing to be ferrimagnetic below about 4°K and the latter antiferromagnetic with $T_N = 25$°K.

Anhydrous $VOSO_4$ exists in two modifications at room temperature. α-$VOSO_4$ is tetragonal (*1*) and is formed by dehydration of its hydrates below 280°C. β-$VOSO_4$ is orthorhombic and may be prepared either from the reaction of H_2SO_4 and V_2O_5 (*2*) or by dehydration above 280°C. The orthorhombic structure has chains of corner-shared VO_6 octahedra connected by corner-shared SO_4 tetrahedra to form a three-dimensional network (*3*). As an extension of the structural work by one of us on orthorhombic β-$VOSO_4$ (*3*) and tetragonal $NbOPO_4$ (*4*), the structure of tetragonal α-$VOSO_4$ has been investigated.

Preliminary analysis of the X-ray powder data presented by Tudo (*1*) indicated that the structure of α-$VOSO_4$ was probably that of $MoOPO_4$ (*5*), $VOMoO_4$ (*6*) and $NbOPO_4$ (*4*). Since α-$VOSO_4$ is only obtained by dehydration, single crystals were not available, and confirmation of the proposed structure by quantitative treatment of the X-ray powder diffraction pattern was undertaken. A preliminary report of this study was given at the Eighth International Congress of Crystallography. Independently, Ladwig (*7*) proposed the same structure for α-$VOSO_4$ based on qualitative interpretation of X-ray powder diagrams, electron diffraction patterns, ir spectra and his knowledge of the structure of other tetragonal $MOXO_4$ compounds.

Experimental

The α-$VOSO_4$ studied was prepared by the dehydration of a commercially available hydrate (Fisher purified) in three steps. After heating this hydrate for many hours in a 130°C drying oven to obtain the monohydrate, it was then transferred to a tube furnace and heated to 260°C in a stream of dry nitrogen for 4 h. Finally the sample, still under flowing nitrogen, was heated to 350°C for ½ h to improve its crystallinity, thus making it less susceptible to rehydration while improving its X-ray pattern. Before this last step, all lines of the X-ray pattern except those of the *hk*0 and *h*00 type were somewhat broadened. However, it was found that heating the α form for long periods of time above 260°C gradually converted it to the orthorhombic β form.

All magnetic measurements were made using a vibrating-sample magnetometer calibrated with nickel metal. Both the α and β forms were studied from 4.2°K to room temperature and in magnetic fields to 17.2 *kOe*. Samples of about 100 mg were placed in teflon containers which, in the case of the hygroscopic α from, were sealed with paraffin.

X-ray intensity data from powder samples were collected either by measuring the area under the peaks on a slow scanned (¼°min) pattern or by accumulating counts while slow scanning through a peak. Where reflections overlapped, they were measured as a single intensity. A Norelco verticle diffractometer with monochromated (LiF crystal) CuK_α radiation was used to collect the data. To

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TABLE I

CRYSTAL STRUCTURE OF α-$VOSO_4$

Space group: $P4/n$ (No. 85)
Unit cell dimensions: $a = 6.261 \pm 0.003$ Å
$c = 4.101 \pm 0.003$ Å
Cell Contents: 2 $VOSO_4$
V in 2(c): $0, \frac{1}{2}, z; \frac{1}{2}, 0, \bar{z}$ $(z = 0.6176 \pm 0.0010)$
O_I in 2(c): $0, \frac{1}{2}, z; \frac{1}{2}, 0, \bar{z}$ $(z = 0.220 \pm 0.004)$
S in 2(b): $0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
O_{II} in 8(g): $x, y, z; \bar{x}, \bar{y}, z; \frac{1}{2}+x, \frac{1}{2}+y, \bar{z}; \frac{1}{2}-x, \frac{1}{2}-y, \bar{z}; \bar{y}, x, \bar{z}; y, \bar{x}, \bar{z}; \frac{1}{2}-y, \frac{1}{2}+x, z; \frac{1}{2}+y, \frac{1}{2}-x, z$
$x = 0.538 \pm 0.003, y = 0.683 \pm 0.003, z = 0.285 \pm 0.003$
Cell temperature factor: $B = 0.4$

prevent rehydration of the sample during data collection, the entire diffractometer was covered with a plastic bag and flooded with dry nitrogen. The intensity data was computer analyzed by the simplex method to refine atomic positional parameters and cell-temperature factor. The same method was used to refine cell dimensions. Crystallographic studies at high temperature were made using a Tem-Pres furnace attachment and a General Electric diffractometer with the sample maintained in a continuous flow of dry nitrogen.

Results and Discussion

At room temperature the tetragonal cell dimensions of our sample of α-$VOSO_4$ were $a = 6.261 \pm 0.003$ Å, $c = 4.101 \pm 0.003$ Å, $c/a = 0.655$. This is to be compared to Tudo's (*1*) values of $a = 6.267$ Å, $c = 4.119$ Å, $c/a = 0.657$. Tudo's larger c axis suggests that his sample retained a trace of water.

Our most reliable set of data, containing nineteen observed intensities, shows good agreement with the proposed $MoOPO_4$ structure type having the atomic positions listed in Table I. Refinement of the atomic parameters based on minimization of a discrepancy factor

$$R = \sum |I_0 - I_c| / \sum I_0$$

indicated that the strongest reflection (200) had too much influence on the structure determination. Refinement of the data with this reflection removed resulted in a much better over-all fit of intensities and an R factor of 0.094. The final atomic parameters and cell temperature factor are also listed in Table I. A comparison of observed and calculated intensities is given in Table II. Near-neighbor interatomic distances and selected bond angles calculated from the above parameters are shown in Table III. They are all consistent with the known structural chemistry of the vanadyl and sulfate ions.

TABLE II

OBSERVED AND CALCULATED INTENSITIES FOR α-$VOSO_4$

I_{obs}	I_{calc}	hkl	d_{calc}
2	1	110	4.427
51	51	001	4.101
20	20	101	3.431
100[a]	87	200	3.130
	2	111	3.009
35	35	201	2.488
6	10	211	2.312
	0.1	121	
10	9	220	2.214
3	2	002	2.050
15	10	310	1.980
	2	130	
26	14	102	1.949
	12	221	1.948
16	15	112	1.861
	1	301	1.860
0	0.2	131	1.783
	0.1	311	
1	1	202	1.715
5	5	212	1.654
	3	122	
2	3	321	1.599
	1	231	
16	11	400	1.565
5	5	222	1.504
19	3	330	1.476
	8	302	1.463
	7	401	1.462
8	7	312	1.424
	2	132	
	1	411	1.424
	0.1	141	
10	2	420	1.400
	8	240	

[a] Not used in refinement.

TABLE III

SOME INTERATOMIC DISTANCES (Å) AND ANGLES IN α-$VOSO_4$

V–O (±0.03)

$V–2O_I\ (O_I–2V) = 1.63, 2.47$

$V–4O_{II}\ (O_{II}–V) = 2.04$

$O_I–V–O_{II} = 101°, 79°$

$O_{II}–V–O_{II} = 88°$

S–O (±0.02)

$S–4O_{II}\ (O_{II}–S) = 1.46$

$O_{II}–S–O_{II} = 111°, 106°$

O–O (±0.04)

$O_I–4O_{II} = 2.85^a$

$4O_{II} = 2.88^a$

$4O_{II} = 3.12$

$(O_{II}–3O_I) = (2.85, 2.88, 3.12)$

$O_{II}–2O_{II} = 2.83^a$

$2O_{II} = 2.42^b$

$2O_{II} = 2.86$

$O_{II} = 2.34^b$

$O_{II} = 3.29$

$O_{II} = 3.63$

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[a] Interatomic distances within VO_6 octahedra.

[b] Interatomic distance within SO_4 tetrahedra.

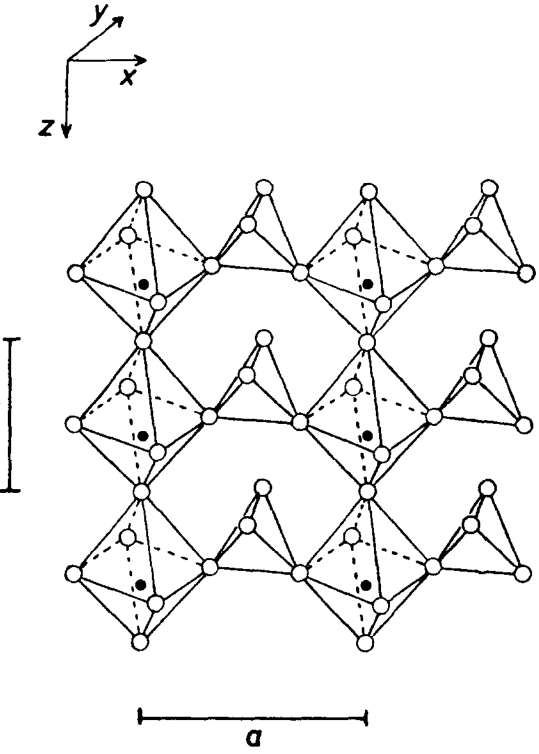

FIG. 1. 010 view of α-$VOSO_4$ showing chains of VO_6 octahedra cross-linked by SO_4 tetrahedra.

The crystal structure of α-$VOSO_4$ may be described as continuous chains of corner shared VO_6 octahedra running parallel to the *c* axis. Each chain is connected to four other chains by corner sharing with sulfate tetrahedra, as shown in Fig. 1. Alternatively, the structure may be described as a distortion of a cubic-close-packed oxygen lattice in which one-fifth of the octahedral sites are occupied by vanadium and one-tenth of the tetrahedral sites are occupied by sulfur (*6*). An undistorted cubic-close-packed arrangement of this type would have a c/a ratio of 0.632 and an oxygen volume of 15.5 $Å^3$ ($r = 1.40$ Å). In α-$VOSO_4$ we find $c/a = 0.655$ and an oxygen volume of 16.08 $Å^3$, indicating that the distortion of the oxygen lattice from a close-packed arrangement is small.

Although the oxygens surrounding a vanadium ion form almost perfect octahedra, the vanadium ions are cooperatively displaced from the centers of the octahedra to form one very short (1.63 Å) vanadium–oxygen bond characteristic of the vanadyl ion, as illustrated in Fig. 2(a). This short vanadyl bond is also present in similar compounds such as $VOMoO_4$ (1.677 Å) (*6*), β-$VOSO_4$ (1.594 Å) (*3*) and $VOSO_4{\cdot}5H_2O$ (1.591 Å) (*8*). Vanadium is bonded to four other oxygens at 2.04 Å giving it a five-fold coordination. The last oxygen of the octahedra is 2.47 Å from the vanadium and must be only weakly bonded. This very large V-O distance has the effect of breaking the chains of octahedra and gives the structure a layered character. This is supported by our observation that all lines, except the *hk*0 type, gradually broadened and weakened on absorption of water. Ladwig (*7*) has discussed the mechanism of hydration to $VOSO_4{\cdot}H_2O$ in terms of this layer structure.

The SO_4 tetrahedra are only slightly elongated along the *c* axis, as shown in Fig. 2b. The sulfur-oxygen distance of 1.46 Å in α-$VOSO_4$ is very similar to the average S–O distance of 1.430 Å found in β-$VOSO_4$ (*3*) and is within the range 1.44–1.53 Å given in the International Tables (*9*).

A study of the crystallographic properties of α-$VOSO_4$ up to 400°C showed that the α phase, once formed, converts only slowly to the β phase. The cell dimensions increase regularly with temperature and at 400°C are $a = 6.283 \pm 0.010$, $c = 4.185 \pm 0.010$, $c/a = 0.666$. The thermal expansion coefficients based on this data, $\alpha_a = 8 \times 10^{-6}$ and $\alpha_c = 50 \times 10^{-6}$, show that the distances in the *c* direction increase with temperature about six times

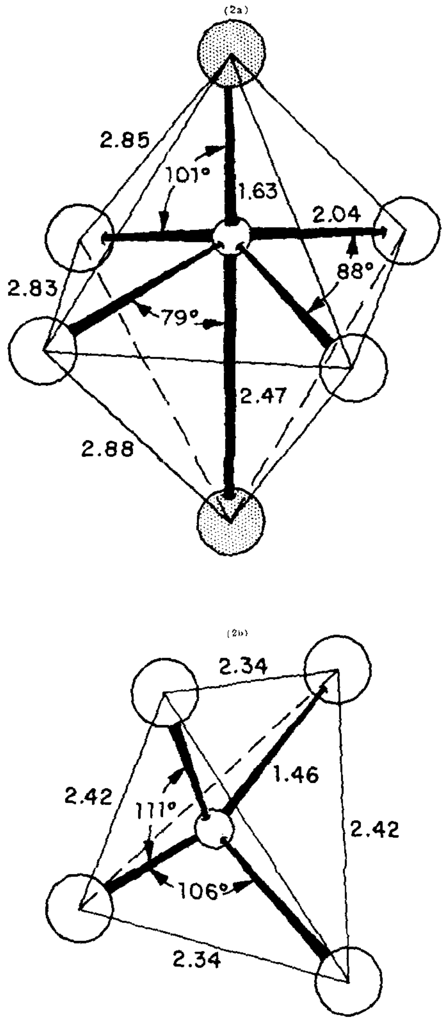

FIG. 2. (a) Oxygen coordination with vanadium (small circle), O_I is shaded. (b) Oxygen coordination with sulfur (small circle).

as fast as the distances in the *a* direction, strongly reflecting the layered nature of this structure. Intensity data collected at 400°C, while not as reliable as the room temperature data, gave essentially the same structure, the increase in the *c* axis being largely confined to an increase in the long $V-O_1$ distance.

The two structural forms of anhydrous $VOSO_4$ exhibit very different magnetic properties. Above 10°K, the α-form obeys the Curie–Weiss law $\chi_m = C_m/(T-\theta)$ with $C_m = 0.355$ ($\mu_{eff} = 1.69$ μ_B) and $\theta = -12$°K (Fig. 3). The theoretical spin-only value of μ_{eff} for V^{4+} ($3d^1$) is 1.73 μ_B. Recently, Edge (*10*) has reported that at room temperature the susceptibility of α-$VOSO_4$ "corresponded to one unpaired electron per vanadium." Doyle et al. (*11*) have reported an effective magnetic moment of 1.34 μ_B for $VOMoO_4$ based on a single temperature measurement (20°C) and the assumption $\theta = 0$°K. Their low μ_{eff} is compatible with a $\theta < 0$°K.

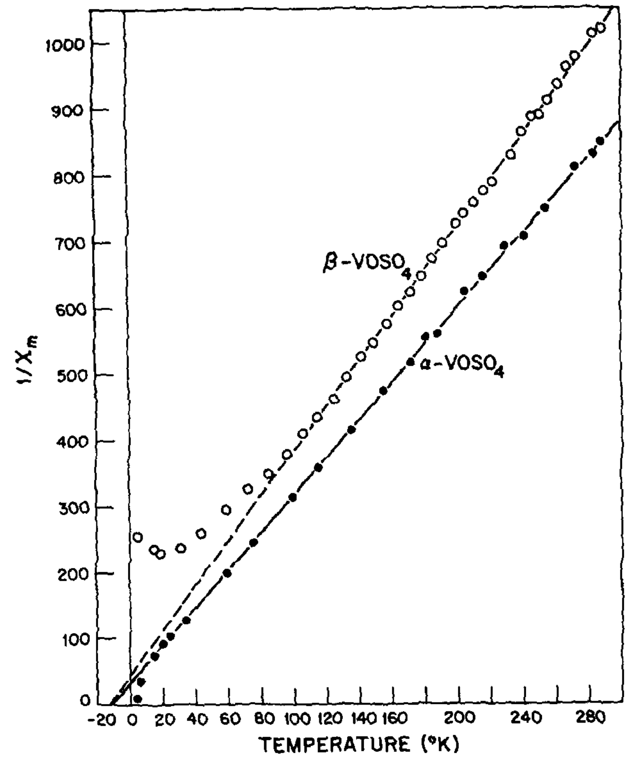

FIG. 3. Plot of reciprocal molar magnetic susceptibility versus temperature for α-$VOSO_4$ (filled circles) and β-$VOSO_4$ (open circles).

Below 10°K, the suceptibility of α-$VOSO_4$ increases sharply and continuously to 4.2°K where it reaches about $\frac{1}{3}\mu_B/V^{4+}$. Field studies to 17.2 *k*O*e* at 4.2°K showed the nonlinear effects of saturation that are characteristic of ferro- or ferrimagnetism while field studies at 77°K and room temperature were linear and characteristic of paramagnetism. Such a large moment per V^{4+} ion is difficult to attribute to impurities since X-ray patterns of samples studied never showed detectable second phases. The negative value for θ points to a ferrimagnetic order of vanadium, and inspection of the structure indicates that the order is probably complex. A Curie temperature close to 4.2°K is indicated, since the magnetization is still increasing sharply with decreasing temperature.

For β-$VOSO_4$ prepared from solution, the susceptibility obeys the Curie–Weiss law above 100°K with $C_m = 0.296$ ($\mu_{eff} = 1.54$ μ_B) and $\theta =$

−12°K (Fig. 3). The effective moment per V^{4+} ion in its paramagnetic temperature region is lower than the theoretical spin-only value or the experimental value found in α-$VOSO_4$. Both forms of $VOSO_4$ have the same value for θ indicating that the predominant V–SO_4–V antiferromagnetic superexchange interaction is unchanged.

At lower temperatures, β-$VOSO_4$ shows a maximum in its magnetic susceptibility, which is interpreted as a Néel point $T_N = 25$°K. Field studies at 4.2°K, 77°K and room temperature all show a linear dependence to 17.2 *k*O*e*.

Acknowledgments

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