A Study of Magnetic Properties of $V_xMo_{2-x}O_5$ ($1 \leq x \leq 1.14$)

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Magnetic susceptibility measurements and X-ray powder analysis show that vanadium can substitute for molybdenum in VOMoO$_4$ according to the formula $V_x^{4+}Mo_{3-x}^{4+}O_4$, $1 \leq x \leq 1.14$. All samples studied exhibit antiferromagnetic behaviour with Néel temperatures around 110 K.

Eick and Kihlborg$^1$ determined the crystal structure of VOMoO$_4$ and found it isostructural with MoOPO$_4$. The structure may be described as consisting of strings of cornersharing VO$_4$ octahedra running parallel to the c axis of the tetragonal unit cell. The chains are coupled together by MoO$_4$-tetrahedra so that each tetrahedron joins four different chains of octahedra. The oxygen atoms surrounding a vanadium atom form an almost regular octahedron. The vanadium atom is displaced from the centre of the octahedron, which gives rise to a short vanadium-oxygen distance (1.677 Å).

The existence of a homogeneity range in the system $V_xMo_{2-x}O_5$ was demonstrated by Eick and Kihlborg$^1$ who suggested that $x$ may differ from 1 by a few percent, at most. Later Darriet et al.$^3$ determined the homogeneity range to be $1 \leq x \leq 1.14$.

The present investigation of the magnetic properties of $V_xMo_{2-x}O_5$ has been conducted within a research program intended to elucidate the physical properties of $AOBO_4$ compounds.

**EXPERIMENTAL**

The starting materials were MoO$_3$ (Mal- lineckrodt, Anal. Reag.) and V$_2$O$_5$ (Fisher, p.a.). V$_2$O$_5$ and MoO$_3$ were prepared by hydrogen reduction of V$_2$O$_5$ at 1175 K and of MoO$_3$ at 725 K. The products were characterized by their X-ray powder patterns.

Samples of gross composition $V_xMo_{2-x}O_5$ with $0.95 \leq x \leq 1.20$ were prepared by heating appropriate mixtures of the oxides for six days in evacuated silica tubes at a temperature of 875 K. X-ray powder patterns of the specimens were recorded in a Guinier-Hägg focusing camera with CuK$_{\alpha}$ radiation ($\lambda = 1.54051 \text{ Å}$) and with KCl ($\alpha = 6.2919 \text{ Å}$) as an internal standard.

The magnetic susceptibility measurements were performed according to the Faraday method with a Cahn R. G. electrobalance. H$_2$Co(SCN)$_4$ was used as standard.$^4$ The measurements were made in the temperature range 78 – 700 K with a heating rate of 2 – 4 degrees per minute. One of the samples (VOMoO$_4$) was also studied in the range 4.2 – 120 K. The apparatus used in this experiment also applied

### Table 1. A summary of experimental data.

<table>
<thead>
<tr>
<th>$x$ in $V_xMo_{2-x}O_5$</th>
<th>Cell parameters (Å) at 298 K</th>
<th>$C$</th>
<th>$\theta$</th>
<th>$\mu_{\text{eff}}$ per vanadium(IV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>6.6087(11)</td>
<td>4.2634(8)</td>
<td>0.415</td>
<td>-235</td>
</tr>
<tr>
<td>1.03</td>
<td>6.606(8)</td>
<td>4.2648(5)</td>
<td>0.436</td>
<td>-235</td>
</tr>
<tr>
<td>1.05</td>
<td>6.596(12)</td>
<td>4.2678(10)</td>
<td>0.414</td>
<td>-150</td>
</tr>
<tr>
<td>1.07</td>
<td>6.603(10)</td>
<td>4.2666(8)</td>
<td>0.400</td>
<td>-200</td>
</tr>
<tr>
<td>1.10</td>
<td>6.5917(9)</td>
<td>4.2698(7)</td>
<td>0.371</td>
<td>-200</td>
</tr>
<tr>
<td>1.14</td>
<td>6.5875(7)</td>
<td>4.2709(5)</td>
<td>0.386</td>
<td>-235</td>
</tr>
</tbody>
</table>

the Faraday method but the susceptibility values were obtained from an absolute determination of the field gradient. The two series of measurements yielded susceptibility values in the overlapping temperature region which were in agreement with each other within \( \pm 0.5 \% \).

RESULTS AND DISCUSSION

The X-ray photographs showed monophasic powder patterns for \( 1 \leq x \leq 1.14 \). The cell parameters are given in Table 1 and Fig. 1. The \( c \) axis exhibits a small increase while the \( a \) axis decreases for increasing \( x \) values. Our findings are in good agreement with previously reported data for VOMoO\(_4\) and \( V_{1.13}Mo_{0.87}O_4 \).

A representative plot of the inverse susceptibility versus the temperature is given in Fig. 2 for the composition VOMoO\(_4\). The susceptibility exhibits a maximum value at 110 K (viz. a Néel point) and obeys the Curie-Weiss law \( [\chi_M = C/(T - \theta)] \) for temperatures above 225 K. The Curie constant, \( C \), was calculated from the slope of the straight line shown in Fig. 2. The relation \( \mu_{\text{B}} = 2.83[C / (2 - x)]^{\frac{1}{2}} \) yielded a Bohr magneton number of 1.82 for VOMoO\(_4\); compared with the spin only value of 1.73 for \( V^{4+} \) this confirms that the vanadium atoms are tetravalent and, consequently, the molybdenum atoms hexavalent. The increase of the susceptibility below 10 K is probably due to impurities. A summary of the magnetic susceptibility data is given in Table 1.

Doyle et al.\(^4\) have reported the molar susceptibility of VOMoO\(_4\) at 293 K to be \( 7.67 \times 10^{-4} \) emu per mol which compares favourably with our value \( 7.94 \times 10^{-4} \). (The conversion factor to SI units is \( 4\pi \times 10^{-4} \)).

When \( x \) becomes greater than 1 an amount of \( x-1 \) pentavalent vanadium atoms per formula unit will replace hexavalent molybdenum atoms in the tetrahedra. To keep the crystal electrically neutral \( x-1 \) vanadium

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**Fig. 1.** Cell parameters for \( V_xMo_{1-x}O_4 \).

**Fig. 2.** The inverse molar susceptibility plotted versus the temperature for \( V_xMo_{1-x}O_4 \) with \( x = 1.00 \) (VOMoO\(_4\)).

**Fig. 3.** The molar susceptibility plotted versus \( x \) in \( V_xMo_{1-x}O_4 \) at the Néel temperature \( (\bigcirc) \), 225 K \( (\square) \), 298 K \( (\triangle) \) and 600 K \( (\blacklozenge) \). The dotted lines are calculated values with \( \theta = -215 \) K and \( \mu_{\text{B}} = 1.73 \) in eqn. 1.
atoms within the octahedra will increase their oxidation number to plus five. This substitution mechanism would cause a decrease in the Curie constant with increasing $x$ values while the number of Bohr magnetons per mol tetra-valent vanadium atom should be constant. This is in satisfactory agreement with our observations (cf. Table 1).

The susceptibility should decrease with increasing $x$ for a fixed temperature according to the formula

$$\chi_M = \frac{2\mu_{V^+} (1-x)}{2.83^2 (T - \theta)}$$

(1)

In Fig. 3 $\chi_M$ is plotted versus $x$ for three temperatures. It is evident that a fairly linear relationship exists between $\chi_M$ and $x$. The dotted lines are obtained from equation 1 with $\theta$ equal to the mean value of those given in Table 1 and $\mu_{V^+}$ equal to the spin only value for V$^{4+}$ (1.73).

All samples showed antiferromagnetic behaviour with Neél temperatures around 110 K. The susceptibility at the Neél temperature varied between $1.06 \times 10^{-4}$ and $1.00 \times 10^{-4}$ emu per mol within the homogeneity range as shown in Fig. 3.

The magnetic susceptibility data thus show that vanadium substitutes for molybdenum in VOMoO$_4$ according to the formula V$_{x-z}$Mo$_x$O$_{4z}$ over the compositional region $1 \leq x \leq 1.14$.

This result evidently confirms the mechanism of substitution put forward by Eick and Kihlberg from considerations of the variation of the cell parameters. Our findings, however, do not support the possibility that $x$ might assume values below 1, i.e. that molybdenum might substitute for vanadium in the octahedra.

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REFERENCES


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