

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

B. BLOM and M. NYGREN

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

Magnetic susceptibility measurements and X-ray powder analysis show that vanadium can substitute for molybdenum in $VOMoO_4$ according to the formula $V_{1-x}^{4+}V_{2(x-1)}^{5+}Mo_{2-x}^{6+}O_5$, $1 \leq x \leq 1.14$. All samples studied exhibit anti-ferromagnetic behaviour with Néel temperatures around 110 K.

Eick and Kihlberg¹ determined the crystal structure of $VOMoO_4$ and found it isostructural with $MoOPO_4$.² The structure may be described as consisting of strings of cornersharing VO_6 -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 Kihlberg¹ 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 (Malinkrodt, Anal. Reag.) and V_2O_5 (Fisher, *p.a.*). V_2O_5 and MoO_3 were prepared by hydrogen reduction of V_2O_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 $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) and with KCl ($a = 6.2919$ Å) as an internal standard.

The magnetic susceptibility measurements were performed according to the Faraday method with a Cahn R. G. electrobalance. $HgCo(SCN)_4$ was used as standard.^{4,5} 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.

x in $V_xMo_{2-x}O_5$	Cell parameters (Å) at 298 K		C	θ	μ_{eff} per vanadium(IV)
	a	c			
1.00	6.6087(11)	4.2634(8)	0.415	–235	1.82
1.03	6.6060(8)	4.2648(5)	0.436	–235	1.90
1.05	6.5962(12)	4.2675(10)	0.414	–150	1.87
1.07	6.6033(10)	4.2666(8)	0.400	–220	1.85
1.10	6.5917(9)	4.2698(7)	0.371	–200	1.82
1.14	6.5875(7)	4.2709(5)	0.386	–235	1.90

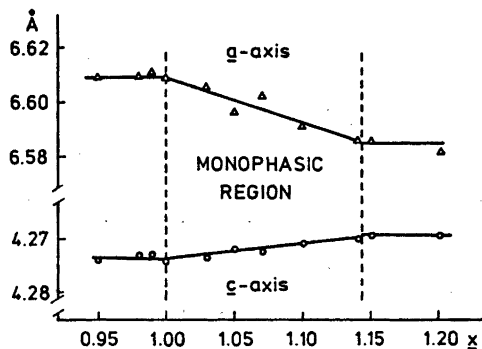


Fig. 1. Cell parameters for $V_xMo_{2-x}O_5$.

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

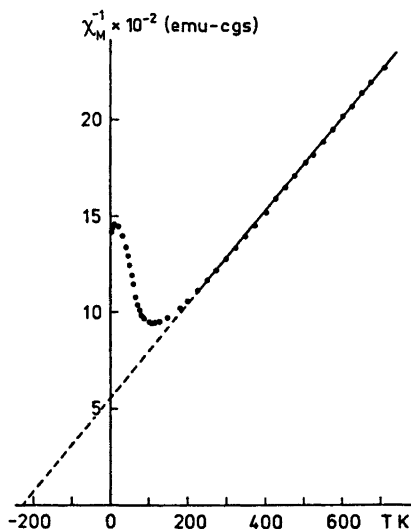


Fig. 2. The inverse molar susceptibility plotted versus the temperature for $V_xMo_{2-x}O_5$ with $x=1.00$ ($VOMoO_5$).

are in good agreement with previously reported data for $VOMoO_5$ and $V_{1.10}Mo_{0.90}O_5$.³

A representative plot of the inverse susceptibility versus the temperature is given in Fig. 2 for the composition $VOMoO_5$. 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 $\mu_{V^{4+}} = 2.83[C/(2-x)]^{\frac{1}{2}}$ yielded a Bohr magneton number of 1.82 for $VOMoO_5$; 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.*⁶ have reported the molar susceptibility of $VOMoO_5$ at 293 K to be 7.67×10^{-4} emu per mol which compares favourably with our value 7.94×10^{-4} . (The conversion factor to SI units is $4\pi \times 10^{-6}$.)

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

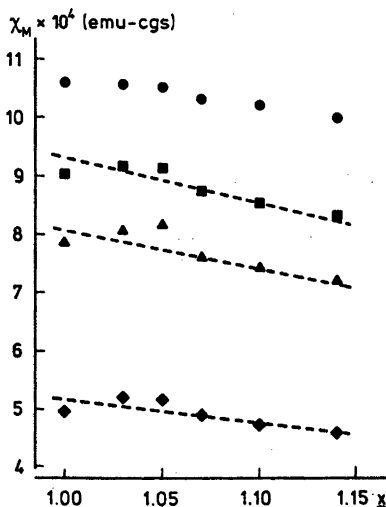


Fig. 3. The molar susceptibility plotted versus x in $V_xMo_{2-x}O_5$ at the Néel temperature (\bullet), 225 K (\blacksquare), 298 K (\blacktriangle) and 600 K (\blacklozenge). The dotted lines are calculated values with $\theta = -215$ K and $\mu_{V^{4+}} = 1.73$ in eqn. 1.

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 tetravalent 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

$$\chi_M = \frac{2\mu_{V^{4+}}(1-x)}{2.83^2(T-\theta)} \quad (1)$$

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

All samples showed antiferromagnetic behaviour with Néel temperatures around 110 K. The susceptibility at the Néel temperature varied between 1.06×10^{-3} and 1.00×10^{-3} 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 $V_{1-x}^{4+}V_x^{5+}Mo_{1-x}^{6+}O_8$ over the compositional region $1 \leq x \leq 1.14$.

This result evidently confirms the mechanism of substitution put forward by Eick and Kihlborg¹ 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.

Acknowledgements. The authors wish to thank Professor Arne Magnéli and Dr. Lars Kihlborg for their advice in connection with this work. Drs. S. Humble and K. Svensson of the Department of Solid State Physics, Royal Institute of Technology in Stockholm, are gratefully thanked for their kind assistance with the susceptibility measurements in the temperature region 4.2–90 K. This investigation has been supported by the Swedish Natural Science Research Council.

REFERENCES

1. Eick, H. and Kihlborg, L. *Acta Chem. Scand.* 20 (1966) 722.
2. Kierkegaard, P. and Westerlund, M. *Acta Chem. Scand.* 18 (1964) 2217.
3. Darriet, J., Galy, J. and Hagenmuller, P. *J. Solid State Chem.* 3 (1971) 596.
4. Kizhaev, S. A., Usachev, P. V. and Yudin, V. M. *Fiz. Tverd. Tela (Leningrad)* 13 (1971) 2829.
5. Råde, H.-St. *J. Phys. Chem.* 77 (1973) 424.
6. Doyle, W. P., McGuire, G. and Clark, G. M. *J. Inorg. Nucl. Chem.* 28 (1966) 1185.

Received December 19, 1975.