

## The Magnetic Susceptibility of Phases with the $\text{Mo}_{17}\text{O}_{47}$ and $\text{Mo}_5\text{O}_{14}$ Types of Structure

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The crystal structures of the two oxides  $\text{Mo}_{17}\text{O}_{47}$ <sup>1</sup> and  $\text{Mo}_5\text{O}_{14}$ <sup>2</sup> are related to each other, but differ markedly from the structures of the other known molybdenum oxides.<sup>3</sup> The basic structure units of the former oxides are  $\text{MoO}_6$  octahedra and  $\text{MoO}_7$  pentagonal bipyramids, which are linked to form a complex pattern of polyhedra. Both oxides have been observed to form within a rather restricted temperature range around 500°C, and the  $\text{Mo}_5\text{O}_{14}$  phase only in an apparently metastable state.<sup>4,5</sup>

Recent investigations performed at this institute have shown that a partial substitution of Ti, V, Nb, and Ta for Mo in  $\text{Mo}_5\text{O}_{14}$  results in a stabilization of the structure. These studies have previously been published in a series of papers,<sup>5-9</sup> as have also data on the metastable  $(\text{Mo}_{1-x}\text{W}_x)_5\text{O}_{14}$  and the stable  $(\text{Mo}_{1-x}\text{W}_x)_{17}\text{O}_{47}$  phase.<sup>10</sup>

A study of the magnetic susceptibility of the various phases with the  $\text{Mo}_{17}\text{O}_{47}$  and  $\text{Mo}_5\text{O}_{14}$  structure types, as measured on polycrystalline specimens, is reported below.

*Experimental.* Appropriate amounts of the starting materials, all of reagent grade, were thoroughly mixed and heated in evacuated, sealed silica tubes at the temperature of phase formation. After the heat-treatment the specimens were quenched to room temperature. All specimens were investigated by recording their X-ray powder patterns in a Guinier-Hägg focusing camera with  $\text{CuK}\alpha_1$  radiation. Further details of the preparation procedure have been given in previous papers.<sup>5,7-10</sup>

It was not possible to prepare monophasic samples of the metastable binary oxide  $\text{Mo}_5\text{O}_{14}$ . The reported  $\chi$  value is obtained from samples contaminated by trace amounts of  $\text{Mo}_4\text{O}_{11}$  or  $\text{Mo}_{17}\text{O}_{47}$ . As both the latter oxides exhibit only a small, temperature-independent paramagnetism<sup>11</sup> it is assumed that the observed susceptibility is not seriously affected by these contaminants.

The measurements of the magnetic susceptibility were performed according to the Faraday principle. The weight of the specimen as well as the force acting on it in the magnetic field were measured by means of a *Cahn RG Electrobalance*. The apparatus permitted almost simultaneous measurements of the force and of the thermocouple emf. Details of the construction will be published elsewhere.<sup>12</sup> Sample amounts of 10–20 mg were normally used, and  $\text{HgCo}(\text{CNS})_4$  was used for calibration.<sup>13,14</sup>

*Results.* The observed gram susceptibilities  $\chi$  at the temperature limits 77 and 295 K are given in Table I. All values are corrected for diamagnetism.<sup>15</sup>

Table I. The magnetic gram susceptibilities  $\chi$  for phases with the  $\text{Mo}_{17}\text{O}_{47}$  and  $\text{Mo}_5\text{O}_{14}$  types of structure. The values are corrected for diamagnetism.

Phase	$\chi \times 10^6/\text{cgs unit}$	
	77 K	295 K
$\text{Mo}_{17}\text{O}_{47}$	+0.80	+0.85
$(\text{Mo}_{0.80}\text{W}_{0.20})_{17}\text{O}_{47}$	+0.71	+0.71
$\text{Mo}_5\text{O}_{14}$	+0.52	+0.60
$(\text{Mo}_{0.96}\text{Ti}_{0.04})_5\text{O}_{14}$	+0.59	+0.60
$(\text{Mo}_{0.92}\text{V}_{0.08})_5\text{O}_{14}$	+0.67	+0.67
$(\text{Mo}_{0.91}\text{Nb}_{0.09})_5\text{O}_{14}$	+0.56	+0.55
$(\text{Mo}_{0.80}\text{Nb}_{0.40})_5\text{O}_{14}$	+0.64	+0.64
$(\text{Mo}_{0.95}\text{Ta}_{0.07})_5\text{O}_{14}$	+0.64	+0.67
$(\text{Mo}_{0.80}\text{W}_{0.20})_5\text{O}_{14}$	+0.53	+0.57

The  $(\text{Mo}_{1-x}\text{V}_x)_5\text{O}_{14}$ ,  $(\text{Mo}_{1-x}\text{W}_x)_5\text{O}_{14}$  and  $(\text{Mo}_{1-x}\text{W}_x)_{17}\text{O}_{47}$  oxides exhibit extended homogeneity ranges, but no significant variation of the susceptibility with vanadium or tungsten content could be observed.

The small, practically temperature-independent susceptibility is thought to be due to Van Vleck paramagnetism.

Any conclusions concerning the valence state of the molybdenum atoms in the binary  $\text{Mo}_{17}\text{O}_{47}$  and  $\text{Mo}_5\text{O}_{14}$  cannot be drawn from this study. The absence of temperature-dependent paramagnetic behaviour excludes only the occurrence of unpaired electrons and thus, *e.g.*, the existence of distinct  $\text{Mo}^{5+}$  ions. The substitution of other transition metals *T* for molybdenum in these phases does not change the magnetic behaviour, and the *T* metal ions are therefore not associated with

unpaired valence electrons. It is, however, not known if the substituents have their highest oxidation numbers and if they prefer specific lattice sites.

A discussion of the electron configuration of these phases is not feasible at the present stage. More knowledge of the physical and structural properties seems necessary; in particular are electrical measurements on single-crystals and single-crystal X-ray data required.

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## The Crystal Structure of $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$

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The crystal structure of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$  has been determined by single crystal methods. Crystals of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$  were prepared from  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]$ , the original method of preparation described by Brauer<sup>1</sup> being slightly modified. X-Ray data were recorded with a single crystal diffractometer (Philips Pailred) using  $\text{MoK}\alpha$ -radiation.

The crystals are orthorhombic with space group  $Pnmm$ , and cell constants of  $a = 6.1 \text{ \AA}$ ,  $b = 11.9 \text{ \AA}$  and  $c = 15.5 \text{ \AA}$ . There are four formula units per unit cell.

It was obvious by inspection of the raw diffraction data that the structure of  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$  was closely related to that of sodium nitroprusside,  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ .<sup>2</sup> This similarity was exploited in the location of the heavy atoms, while subsequent electron density calculations yielded the light atom parameters. After anisotropic least squares refinement, the  $R$ -factor converged to 0.086. The atomic parameters thus obtained are listed in Table I.

Table I. Atomic parameters for  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$ . Space group  $Pnmm$ . The Fe and Na atoms, as well as the  $\text{NH}_3$  group and  $\text{C}_1-\text{N}_1$ , occupy fourfold positions. All other atoms lie in eightfold positions.

Atom	$x$	$y$	$z$
Fe	0.495	0.278	0.500
Na(1)	0.500	0.000	0.247
Na(2)	0.000	0.000	0.378
C(1)	0.251	0.180	0.500
C(2)	0.614	0.183	0.590
C(3)	0.345	0.364	0.412
N(1)	0.100	0.120	0.500
N(2)	0.673	0.125	0.644
N(3)	0.245	0.412	0.361
N(4)	0.768	0.372	0.500
O	0.174	0.125	0.269