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Neutron Diffraction Study of Molybdenum Dioxide

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The magnetic properties of powdered, crystalline molybdenum dioxide have been studied by neutron diffraction at 293°K and 673°K. The results establish the absence of a permanent magnetic moment on the Mo(IV) ions in this compound and confirm that MoO_2 has a small temperature-independent magnetic susceptibility. This latter is considered to arise from Pauli paramagnetism of the collective electrons.

Introduction

There is some uncertainty in the literature concerning the detailed magnetic properties of molybdenum dioxide and we therefore undertook a neutron diffraction study on powdered MoO_2 over the temperature range 293–673°K to see whether the reported small paramagnetic susceptibility was indeed temperature independent. A further aim was to determine the magnetic form factor of the Mo(IV) ion, if the molybdenum ions were found to have a permanent moment. Our interest in this problem arose from recent work on the magnetically compensated inverse spinel Fe_2MoO_4 in which we showed that the Mo(IV) ion had two unpaired electrons which played a crucial role in the overall magnetic behaviour of the compound (*1*).

Molybdenum dioxide has a deformed rutile-type structure (*2, 3*) in which each molybdenum is coordinated by six oxygen atoms to form MoO_6 octahedra. The octahedra are joined by sharing edges to form strings which are mutually connected into a three-dimensional structure by corner-sharing of the octahedra. In the ideal rutile structure, the metal atoms are equidistant within the strings but in the MoO_2 structure the metal–metal distances are alternately short (2.5106 Å) and long (3.1118 Å) as shown in Fig. 1. This results in the formation of pairs of metal atoms and a consequent distortion of the MoO_6 octahedra which lowers the symmetry from tetragonal for rutile to monoclinic for the MoO_2 structure.

In an isolated Mo(IV) ion there are two 4*d* electrons which could contribute to the paramagnetic moment, but if full double bonds exist between the pairs of Mo(IV) ions, then no contribution to the paramagnetic moments by these *d* electrons would be expected. In 1915 Wedekind and Horst (*4*) reported that MoO_2 was weakly paramagnetic, the value of the moment being $\sim 0.2\ \mu_B$. Later, Selwood (*5*) reported that MoO_2 had almost zero magnetic susceptibility and no antiferromagnetic Néel point up to 1100°C. Tarama *et al.* (*6*), in their study of the electric conductivity and magnetic susceptibility of V_2O_3 catalysts containing small amounts of MoO_2 or α–Al_2O_3 found that the addition of small amounts of MoO_2 increased the effective magnetic moment (μ_{eff}), lowered the Néel temperature, and decreased the activation energy for electric conductivity (E_σ). Røst (*7*), working on alumina-supported MoO_2, found that crystalline MoO_2 showed a temperature independent magnetic susceptibility of $+0.33 \times 10^{-6}$ emu g^{-1} and that dilution of the MoO_2

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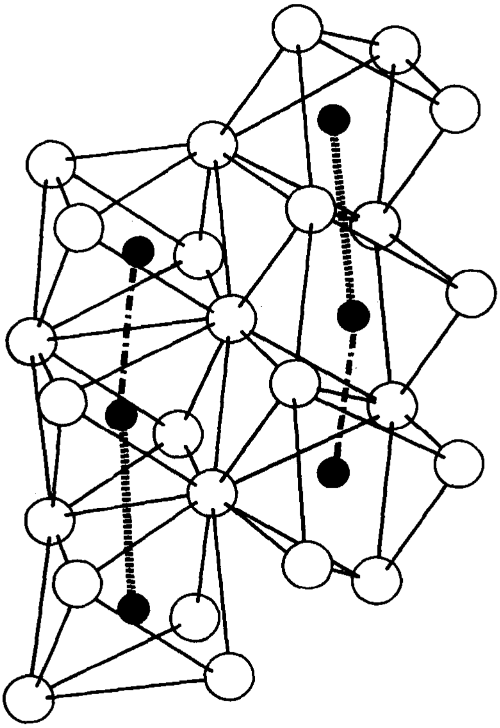

FIG. 1. Structure of molybdenum dioxide showing Mo–Mo pairs and consequent distortions from the ideal rutile structure.

on the alumina increased the susceptibility of the MoO_2 considerably. For the highest dilution with an atomic ratio of Mo/Al = 1/99, the MoO_2 susceptibility was $+27 \times 10^{-6}$ at 78°K, $+9.8 \times 10^{-6}$ at 195°K and $+6.5 \times 10^{-6}$ at 295°K. His results showed that plots of $1/\chi$ versus T obeyed the Curie Law for the most highly diluted MoO_2, whereas plots for the preparations richer in MoO_2 showed a curvature towards the temperature axis. He suggested that the increase in paramagnetism on dilution was probably caused by an increasing number of unpaired electrons due to a decrease in the number of Mo–Mo bonds present in the crystal lattice of MoO_2.

Recently Ben-Dor and Shimony (*8*) reported on the crystal structure, magnetic susceptibility, and electrical conductivity of pure, and NiO-doped molybdenum(IV) oxide and tungsten(IV) oxide single crystals. X-ray diffraction showed the crystal to be monoclinic and doping up to 5% left the crystallographic constants unchanged. The pure compounds were weakly paramagnetic ($\chi_M < 100 \times 10^{-6}$) emu g^{-1}, but doping raised the susceptibility markedly to $\sim 2500 \times 10^{-6}$. Resistance studies showed that these materials were metallic conductors, the room temperature specific resistivity being of the order of (10^{-4}–10^{-3}) ohm cm, decreasing by one order of magnitude at liquid nitrogen temperature. Doping also substantially lowered the conductivity.

The present experiments were designed to obtain a more intimate insight into the magnetic properties of the Mo(IV) atoms in pure molybdenum dioxide.

Experimental

Measurements were carried out on MoO_2 powder of 99.999% purity. Magnetization was measured from liquid helium temperature to 400°K in Foner vibrating magnetometer. Neutron diffraction was done at 293°K and 673°K on 'Curran' at AERE Harwell.

Results and Discussion

The neutron diffraction pattern at 293°K is shown in Fig. 2, and Table I gives the values of calculated and experimental integrated intensities at 293°K and 673°K. In addition to the reflections indexed from X-ray data, three weak peaks were observed at low angles in the neutron diffraction data both at 293°K and 673°K. The peaks at $2\theta \sim 22.9°$ and 21.4° are probably the $\lambda/2$ reflections for $(31\bar{1}, 220)$ and $(201, 22\bar{1})$, respectively. However, the reflection at $2\theta = 20.20°$ could not be identified. The data at 673°K indicate a very small thermal expansion of the lattice without actually causing any deformation.

The small, positive, temperature-independent magnetic susceptibility of 0.33×10^{-6} emu g^{-1} reported by Røst (7) is consistent with our own measurements, and demonstrates the absence of any permanent moment on the molybdenum atoms in MoO_2. On the other hand, the moment per molybdenum atom in MoO_2 diluted with Al_2O_3 (as measured by Røst) extrapolates at infinite dilution to $\mu_{eff} = 2.76\ \mu_B$ indicating a spin of $S = 0.98$ for the isolated Mo atom, on the assumption of

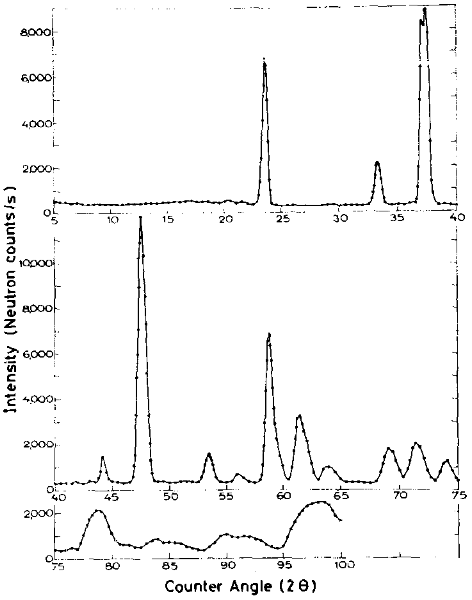

FIG. 2. Neutron diffraction pattern at 293°K.

complete orbital quenching, consistent with two aligned 4*d*-electrons.

In MoO_2 the two molybdenum 4*d* electrons are in the t_{2g} orbitals. These overlap along the *c*-axis, i.e. d_{xy} and d_{yz}, forming metal–metal double bonds. The energy levels of these bonds fall in the same range as the span of the Mo–O π^* band and the overlap of these bonds with the π^* band gives rise to metallic conductivity, as first proposed by Goodenough (*9*). Røst and others indicated that by diluting MoO_2 with a magnetically inert matrix these bonds are broken and the two 4*d* electrons of Mo become free to contribute to the magnetic susceptibility. However, the distorted rutile structure of MoO_2 is due to the presence of these double bonds, so when they are broken the structure should change. Røst has given no information regarding the change in structure, although he has mentioned that molydenum compounds were not detected by X-rays in the mixtures with small amounts of MoO_2. Experiments by Ben-Dor and Shimony (*8*) are not very helpful in this context as they have used nickel, a paramagnetic ion, as a dopant. It would, however, be interesting to study the influence of a nonmagnetic dopant on the crystallographic and magnetic properties of MnO_2.

TABLE I

POWDER NEUTRON DIFFRACTION INTENSITIES OF MoO_2 AT 293°K AND 673°K

h k l	I_{calc}	I_{obs}	
		293°K	673°K
1 0 0	1	0	0
0 1 1	100	100	100
1 1 0			
1 0 $\bar{2}$	1	0	0
2 0 $\bar{2}$	7.7	38	36.4
2 1 1	90.5		
0 2 0	46.8		
0 0 2	7.6		
2 0 0	8.9		
1 1 1	0.18		
2 1 $\bar{2}$	89.9	103	94.8
0 2 1	28.8	117	111
2 1 0	93.4		
3 0 $\bar{2}$	8.3	18.4	16.7
1 2 $\bar{2}$	21.8		
1 2 1	0.47		
2 1 $\bar{3}$	36.7	291	267
2 2 $\bar{2}$	30.5		
1 1 $\bar{3}$	6.2		
3 1 $\bar{1}$	4.2		
0 2 2	119.8		
2 2 0	35.1		
2 2 2	7.4		
3 0 0	1.1	0	0
3 1 $\bar{3}$	10.4	35	32
1 3 $\bar{1}$	3.0		
0 3 1	10.0		
0 1 $\bar{3}$	8.7		
3 2 $\bar{2}$	1.9	8.45	7.2

From Røst's results it might have been supposed that the two 4*d* electrons of molybdenum do not contribute wholly towards the $\sigma + \pi$ bond formation and a very small contribution is responsible for the small moment. If this were so it should show in the neutron diffraction studies. However, comparison of the neutron diffraction peak intensities at 293°K and 673°K show no magnetic contributions in the reflections at smaller angles. Also, the absence of a strongly sloping background probably indicates the absence of paramagnetic diffuse scattering. This confirms the temperature-independent nature of the magnetic susceptibility of MoO_2.

We conclude that the very small magnetic moment of Mo(IV) in MoO_2 is due to Pauli paramagnetism arising from the collective electrons in the overlapping Mo–O π^* band which itself is similar in energy to the Mo–Mo σ and π bonds.

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