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On Magnetic Properties of Some Molybdenum Oxides*

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The temperature dependence of the magnetic susceptibility for the microcrystalline compounds MoO_2, η-Mo_4O_{11}, γ-Mo_4O_{11}, $Mo_{17}O_{47}$, Mo_8O_{23}, Mo_9O_{26}, and $Mo_{18}O_{26}$, respectively, has been investigated between 77 and 550 K at various external fields. The susceptibility increases slightly with temperature for all solids. At low temperatures the changes are more pronounced for η-Mo_4O_{11}, γ-Mo_4O_{11}, $Mo_{17}O_{47}$, and $Mo_{18}O_{52}$. The deviations from stoichiometry and the related changes in the concentration of charge carrier have a large influence on the values of the susceptibility. Furthermore, some indications of anistotropy were found.

1. Introduction

The magnetic properties of the various molybdenum oxides are only partially known (*1*, *2*) and it is, therefore, of interest to investigate some of them in more detail. Goodenough (*3*, *4*) has established rules based on the overlap of cation–cation and cation–anion orbitals which establishes a uniform scheme for classifying the magnetic and electrical properties of many inorganic materials. Among these are the simple cubic oxides of the 3*d* transition metals, the mixed oxides of both perovskite and spinel type structures and, the bronze and metal–sulfide structure representatives, respectively. In his model the transfer integral Δ_{cc} depends very sensitively on the interatomic distance R_{cc} between the cations. There is a critical cation–cation distance R_c for a semiconductor–metal transition to occur. This gives rise to the semiconductive or metallic behavior of the individual molybdenum oxide phases.

However, MoO_2, η-Mo_4O_{11} and κ-$Mo_{17}O_{47}$ exhibit metallic behavior whereas their electrical resistivity increases with the cation–cation distances. In previous studies (*5*, *6*) the electrical conduction and the magnetoresistance of some molybdenum oxides, and the magnetic susceptibility of κ-$Mo_{17}O_{47}$ were reported.

2. Experimental

Materials

Both stoichiometric and nonstoichiometric mixtures of Mo metal and MoO_3 powder, pressed at 4 t/cm^2 and room temperature, were placed in evacuated sealed

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quartz tubes and sintered at elevated temperatures. X-ray microprobe analyses showed no significant impurity content.

X-ray fluorescence analyses yielded Fe < 10 ppm, Ni < 4 ppm, and Co < 1ppm as the principal impurities. Details concerning reaction equations, formation temperatures, preparation temperatures, and heating times, respectively, are given elsewhere (*5*, *7*).

Magnetic Measurements

The magnetic susceptibility was determined with the apparatus SUS 10 (manufactured by A. Paar KG, Graz, Austria) that is based on a modified Faraday method, using a sensitive pendulum system. The device permits measurements to be made even in the presence of torques resulting from the magnetic field.

KCL ("suprapur" quality, E. Merck, Darmstadt) was used as the calibration compound because only diamagnetic and/or small paramagnetic effects were relevant in this work. All susceptibility experiments were carried out in a highly purified helium atmosphere (pressure $2.6 \times 10^3\ P_a$) to avoid convections resulting from temperature gradients, while, simultaneously achieving good heat transfer. The data were collected at various external magnetic fields (e.g., 4.1; 7.1; 9.9, and 12.1 kOe) in the temperature range between 77 and 550 K.

Treatment of Data

Gram susceptibility values χ_g at a certain field strength **H** are used throughout this paper. These values were not corrected for diamagnetic atomic contributions. Table I contains the magnetic susceptibility values at 300 K, the temperature-independent diamagnetic corrections, and the accuracy of the measurements, respectively.

TABLE I

MAGNETIC FIELD INDEPENDENT PART OF THE SUSCEPTIBILITY χ_{extr} ($H^{-1} = 0$) WITH CORRECTIONS FOR DIAMAGNETIC CONTRIBUTIONS OF ATOMS FROM SELWOOD (*19*) AT 300 K

Compound	Formal valence status	Diamagnetic correct. χ_{dia} (cm^3/g)	χ_{extr} (cm^3/g) corrected
η-Mo_4O_{11}	$Mo^{IV}Mo_3^{VI}O_{11}$	$-2.84 \cdot 10^{-7}$	$(4.60 \pm 0.004) \cdot 10^{-7}$
γ-Mo_4O_{11}	$Mo^{IV}Mo_3^{VI}O_{11}$	$-2.84 \cdot 10^{-7}$	$(4.45 \pm 0.004) \cdot 10^{-7}$
$Mo_{17}O_{47}$	$Mo_8^{V}Mo_9^{VI}O_{47}$	$-2.84 \cdot 10^{-7}$	$(4.20 \pm 0.005) \cdot 10^{-7}$
Mo_8O_{23}	$Mo_2^{V}Mo_6^{VI}O_{23}$	$-2.81 \cdot 10^{-7}$	$(3.57 \pm 0.007) \cdot 10^{-7}$
Mo_9O_{26}	$Mo_2^{V}Mo_7^{VI}O_{26}$	$-2.81 \cdot 10^{-7}$	$(3.23 \pm 0.007) \cdot 10^{-7}$
$Mo_{18}O_{52}$	$Mo_2^{IV}Mo_{16}^{VI}O_{52}$	$-2.81 \cdot 10^{-7}$	$(3.85 \pm 0.012) \cdot 10^{-7}$

All oxide phases investigated showed a field dependence in their susceptibility. The experimental χ_g values obtained at a certain temperature were plotted against the reciprocal values of the applied magnetic fields and a regression line was computed for each compound. This method, using an inverse proportional magnetic field exceeding the value of the saturation magnetization, was already performed in other cases (*8*, *9*). Figure 1 shows this treatment in the case of Mo_8O_{23} for six field values.

By extrapolation of the regression line to $H^{-1} \rightarrow 0$ the field-dependent part of the susceptibility vanishes and one obtains the field-independent part, χ_{extr}, of the compound investigated. χ_{extr} consists of the paramagnetic contribution typical for the molybdenum oxides in question and, of contributions due to the Pauli paramagnetism of charge carriers and due to the Van Vleck paramagnetism of excited states.

A statistically significant slope of the regression line is a criterion for the field dependence. These values were used for the intercomparison of the oxides with respect to the magnitude of their field dependence at constant temperature.

3. Results

The susceptibility values must be considered in relation to possible magnetic anisotropies due to the lattice structures of the molybdenum oxides. For Mo_8O_{23} and Mo_9O_{26}, where sintered samples with indi-

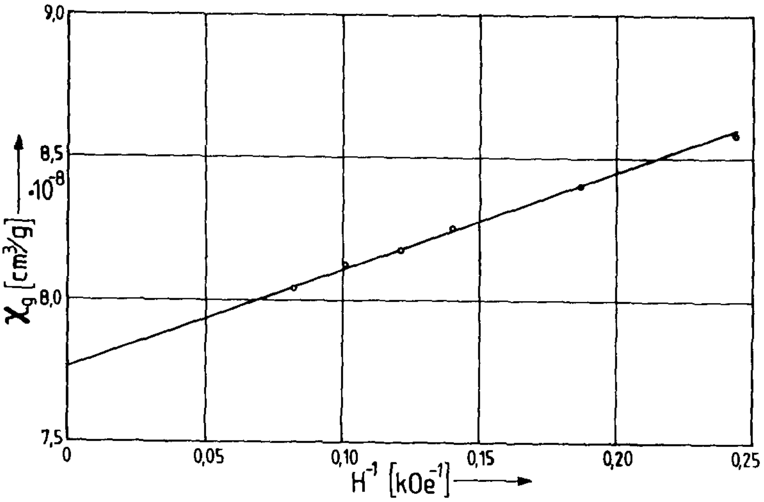

FIG. 1. Magnetic susceptibility χ_g of Mo_8O_{23} as a function of the inverse magnetic field.

vidual crystals (up to 2.0 mm length) were available, a preference of certain crystal directions was detected microscopically. However, no significant anisotropies were found for sintered pellets with crystal sizes below ~0.05 mm. All values given were obtained from both such pellets and powders. Therefore, the data are relevant for a comparison of the various oxide phases. A small paramagnetic increase at low temperature was observed (MoO_2, Fig. 2).

All samples showed a field dependence of their susceptibility; the reason for this is discussed below for $Mo_{17}O_{47}$. The experi-

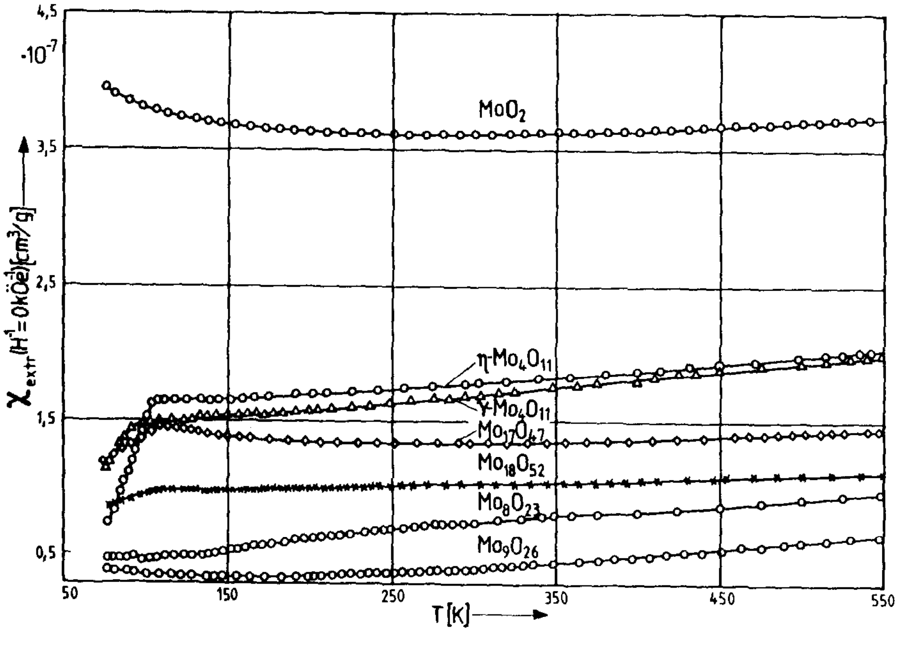

FIG. 2. Magnetic field independent part of the susceptibility $\chi_{\text{extr}}(H^{-1} = 0)$ for some molybdenum oxides as a function of temperature.

mentally determined but uncorrected values of the magnetic susceptibility versus temperature are given in Fig. 3 as an example for the Mo_8O_{23} phase. For further discussion only the field-dependent and extrapolated parts χ_{extr} of the susceptibility are considered (Fig. 2). Figure 2 reveals that the susceptibility of the phases investigated increases with the molybdenum content, except for $Mo_{18}O_{52}$. The metallic phases (MoO_2, η-Mo_4O_{11}, $Mo_{17}O_{47}$) exhibit the highest values. This sequence is also in agreement with the electrical conductivity values of the phases (*5*). Furthermore, the magnetic susceptibility was found to depend on deviations from the stoichiometric composition (Fig. 4). The changes in the susceptibility at low temperatures are caused by a decrease in charge carrier concentration ($Mo_{17}O_{47}$: Fig. 2 (*6*), Mo_4O_{11}: Fig. 6, $Mo_{18}O_{52}$: Fig. 5). It is worth mentioning that the gross behavior of the curves in Fig. 3 does not change under an $1/H$ correction in the presence of an Fe, Ni, Co content up to 30 ppm. The corrected χ values are lower by only 6–8% in these cases.

4. Discussion

Since most of the molybdenum phases have layer structures, measurements on single crystals would be desirable. However, data obtained with microcrystalline material already provide valuable first information on the magnetic behavior. A small impurity content and dislocations have a large influence on both the magnetic susceptibility and the conductivity (*5, 6*), since both the susceptibility values and the activation energy (e.g., for Mo_8O_{23} $E_A \sim$ 0,018 eV calculated from resistivity data) are small.

The increase in the susceptibility with the molybdenum content for the individual phases is partly caused by the difference in concentrations of charge carriers and by the resulting Pauli paramagnetism. The rising trend of the susceptibility with increasing temperature also indicates that the charge carriers exert considerable influence (Fig. 3). On the other hand, the lattice expansion must be considered as well, especially for the phases with lower conductivity.

The Magnéli phases Mo_8O_{23} and Mo_9O_{26} show a similar temperature dependence of their magnetic susceptibilities. This is caused by their crystal structures. Both phases are members in the homologous series for Mo_nO_{3n-1}.

Mo_8O_{23}

This compound belongs to the class of Magnéli shear phases (*10*) Mo_nO_{3n-1} with $n = 8$. Its crystallographic shear structure is based upon 8 octahedra connected by common edges. The crystals grow morphologically in a layered structure. Our crystals are probably too small for exact measurements of the anisotropy. The temperature dependence of the susceptibility varies from phase to phase according to the deviations from the stoichiometric composition (compare Fig. 3).

Samples containing <0.1% impurities (with 40 ppm Fe + Ni + Co) exhibit a marked minimum in χ at ca. 140 K, whereas samples with a high resistivity, but a very small content of ferromagnetic impurities (Fe, Co, Ni < 11 ppm), show a smooth change in the susceptibility in this temperature region. A higher content of charge carriers causes an increase in the susceptibility below ~150 K. This is also shown by the temperature dependence of the electrical resistivity (see Fig. 4). The small slope in the magnetic susceptibility is due to an increase of charge carriers above ~160 K.

Mo_9O_{26}

This Magnéli phase with $n = 9$ has a crystallographic shear structure based upon 9 octahedra connected by common edges. It shows a somewhat stronger increase in the

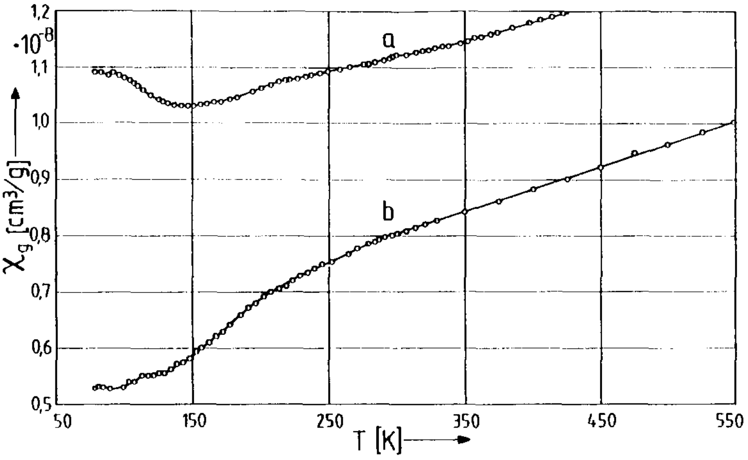

FIG. 3. Temperature dependence of magnetic susceptibility of Mo_8O_{23} at a magnetic field $H = 12.1$ kOe: (a) sintered samples with $\rho \sim 20\ \Omega$cm (~40 ppm Fe + Ni + Co) at 300 K; (b) sintered samples with $\rho \sim 200\ \Omega$cm at 300 K.

magnetic susceptibility versus temperature than does Mo_8O_{23}. The overall behavior (Fig. 2) for the susceptibility of Mo_9O_{26} is similar to that of Mo_8O_{23}. The increase of susceptibility with temperature may be due to both the lattice expansion and the increasing number of charge carriers. This is supported by the low value of the activation energy (~0.018 eV).

$Mo_{18}O_{52}$

Below 1023 K Mo_9O_{26} transforms into $Mo_{18}O_{52}$ which is stable at 300 K (*7*). The high-resistivity phase, however, has a triclinic structure (*7, 11*) and reveals a different temperature dependence of the susceptibility.

This compound exhibits only a small temperature dependence of its susceptibility down to lower temperatures of ca. 115 K (see Fig. 5). The triclinic structure of $Mo_{18}O_{52}$ has a marked substructure similar to a MoO_3 structure with distorted MoO_6 octahedra connected by common edges. Each octahedron has an unoccupied corner which extends into the empty space be-

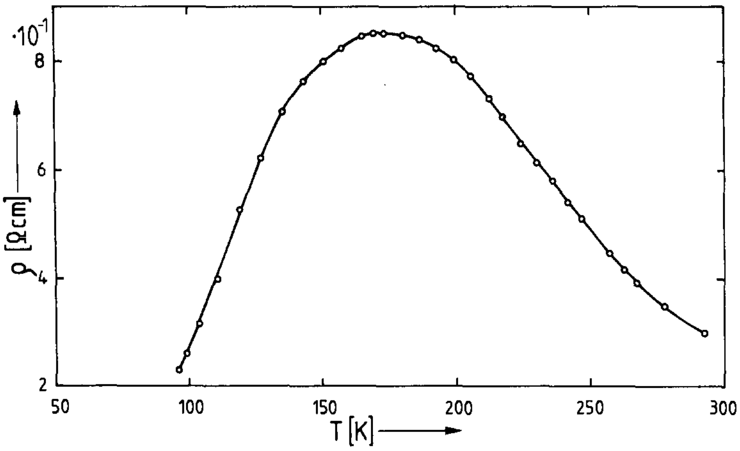

FIG. 4. Variation of resistivity of Mo_8O_{23} crystals (~40 ppm Fe+Ni+Co) with the temperature measured with four point technique.

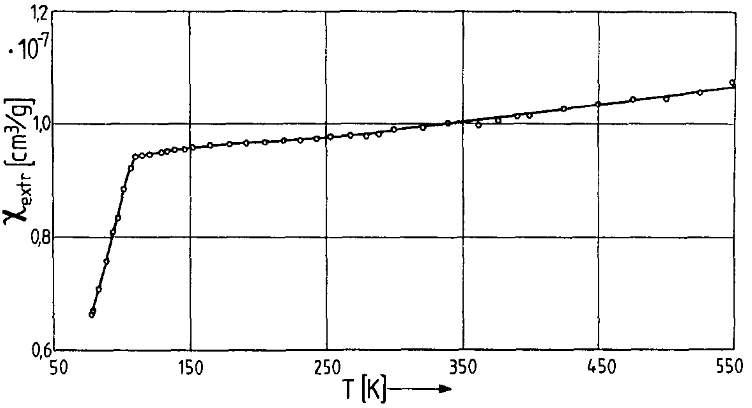

FIG. 5. Magnetic susceptibility of $Mo_{18}O_{52}$ between 77 and 550 K.

tween the neighboring layers. This produces a "zigzag stripe" pattern which extends in the 010 direction. Its width corresponds to 18 MoO_6 octahedra. Some Mo atoms along this zigzag stripe, however, occupy tetrahedral sites in the MoO_4 groups. This may be the reason for the "trapping" effect of the charge carriers below 115 k (Fig. 5). The larger increase in resistivity below 115 K confirms this view (*5*).

Mo_4O_{11}

This compound has a monoclinic structure of its η phase like the metallic MoO_2, whereas the γ phase has an orthorhombic structure (*11*, *12*). Both phases differ in the relative orientation of the layers consisting of regions with MoO_6 octahedra (ReO_3 structure) and MoO_4 tetrahedra that connect the octahedral part. In the metallic η-Mo_4O_{11} phase the layers with the ReO_3-type are ordered parallel to each other, whereas in γ-Mo_4O_{11} they are arranged like the mirror image of the former ones.

The large slope in the susceptibility curves (Fig. 6) below 110 K agree with a large rise of the electrical resistivity (*5*). This may be caused either by a "trapping" of charge carriers or by a negative electronic exchange.

The Fermi level in a schematic energy band for the ReO_3 structure (*13*) with d^6 configuration lies between the lower $\pi^*(t_2g)$ band and the higher $\sigma^*(e_g)$ band. The presence of the MoO_4 tetrahedra can give rise to additional energy levels with electrons in the $\sigma^*(e_g)$ band, thus pushing the Fermi level into the $\sigma^*(e_g)$ band. For η-Mo_4O_{11} the transport mechanism of charge carriers is not completely clear, but by comparison with $Mo_{17}O_{47}$ the polarization effect of the carriers is less pronounced. The conductivity behavior seems to be similar to the Magnéli phases Ti_nO_{2n-1} (*14–16*). The polarization effects, however, are not so pronounced for η-Mo_4O_{11}, thus causing its metallic behavior which is crystallographically less disturbed. Considering the larger concentration of electrons (Pauli paramagnetism), the susceptibility of η-Mo_4O_{11} is higher than that of γ-Mo_4O_{11}. The extrapolated susceptibility curves intersect at 888 K in correspondence with the phase transition (Fig. 2) from the monoclinic η-Mo_4O_{11} to the triclinic γ-Mo_4O_{11}-structure.

A formal determination of the Mo valences provides an indication for the presence of unpaired spins for this compound ($Mo_8^{V}Mo_9^{VI}047$). The Mo atoms of the bridged octahedra in the clusters have a smaller distance than in the metal (2.725 Å). Therefore, a direct overlap of the orbitals is

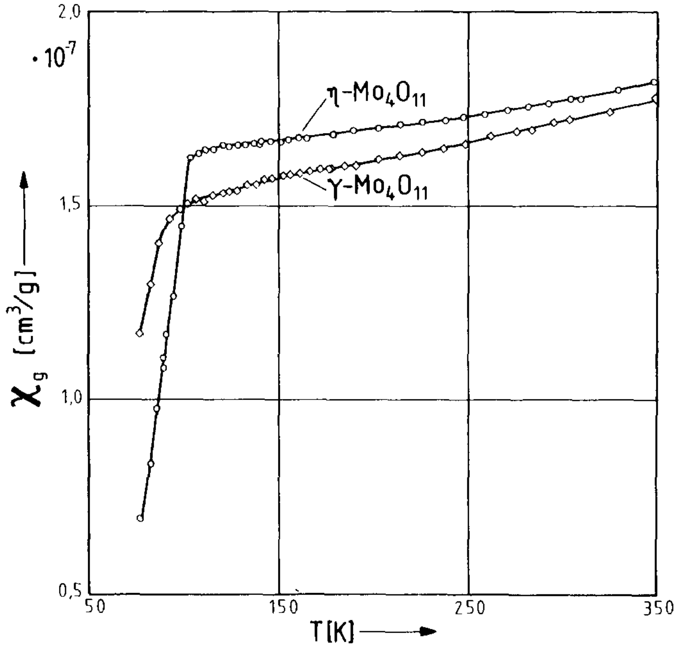

FIG. 6. Magnetic susceptibility of η- and γ-Mo_4O_{11} between 77 and 350 K at a magnetic field $H = 12.1$ kOe.

expected that leads to a stronger antiferromagnetic interaction.

Viswanathan *et al.* (*17*) encountered metallic conductivity ($2.75 \cdot 10^{-3}$ Ωcm at 300 K) for $W_{18}O_{49}$ which has a structure similar to that of $Mo_{17}O_{47}$. From optical and resistivity data they concluded that $W_{18}O_{49}$ shows polaronic conductivity such as WO_3 and H_xWO_3 ($x < 0.1$). From our measurements of the specific resistivity, magnetoresistivity, and diffuse reflectance spectra (with a reflectance minimum at 600 nm), respectively, it is probable that $Mo_{17}O_{47}$ also has polaronic properties but more detailed studies are necessary to support this supposition. The presence of only ~0.5 at% W in this compound completely changes both the reflectivity and the magnetic susceptibility, as preliminary measurements have shown (*18*).

For all compounds the magnetic field behavior of the susceptibility depends sensitively on the presence of Fe, Co, and Ni. On samples with nearly stoichiometric composition we have found that the field dependence changes with the crystallographic directions, since the sintered compounds grow in a preferred direction (*18*).

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