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Effect of pressure on the Fermi surfaces of the dioxides of molybdenum and tungsten

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For the study of the properties of transition-metal dioxides it is important to know their electronic structure and the dependence of the latter on the lattice parameters. An investigation of the de Haas-van Alphen effect under pressure can yield these data. We measured the change of the size of the sections of some parts of the Fermi surfaces of single crystals of MoO₂ and WO₂, whose Fermi surfaces are similar.

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The electric and magnetic properties of the oxides of transition metals¹ are governed by a complicated system of relatively narrow (less than 1 eV) closely lying and partially overlapping electron bands connected with the *d*-levels of the metallic ions and preserving a rather distinctly pronounced *d* character in the crystalline state.² This leads to a definite similarity of their electronic spectra.

The structure of the *d* band in transition-metal oxides should be quite sensitive to the change of the interatomic distances and of the lattice symmetry. This manifests itself in a tendency to formation of distorted crystal structure, and in the role that small displacements of the atoms and the formation of the distorted structure play in the mechanism of the metal-insulator transition in a number of oxides (V₂O₃, VO₂, NbO₂).¹ For the same reasons one should expect the properties of

the oxides to be sensitive to the lattice deformation that is produced, in particular, by hydrostatic pressure. In fact, a rather strong influence of pressure on the metal-insulator transition temperature in V₂O₃ was observed in Ref. 3. However, analogous experiments⁴ on VO₂ have shown that the influence of pressure on the metal-insulator transition in this oxide is much weaker.

In oxides that retain metallic conductivity at liquid-helium temperature, the influence of pressure on the electronic characteristics can be investigated in considerable detail by measuring the shape and dimensions of the Fermi surface (FS). So far, however, no such experiments were performed on any oxides. We report here the results of such an investigation on the metallic oxides MoO₂ and WO₂, whose FS at zero pressure was investigated quite in detail before.^{5,6} Since MoO₂ and WO₂ have the same distorted rutile crystal structure as

VO₂ in the dielectric phase, the results can be compared with the above-mentioned data for VO₂.

MEASUREMENT PROCEDURE AND SAMPLES

We investigated the influence of hydrostatic pressure up to 12 kbar on the oscillation frequency in the de Haas-van Alphen (dHvA) effect. We used for this purpose the modulation method of observing the dHvA effect,⁷ and a low-temperature chamber of the type described in Ref. 8 to obtain hydrostatic pressure, using an oil-kerosene mixture as the pressure-transmitting medium. The modulating and receiving coils were located inside the high-pressure chamber. The unbalance signal of the receiving coils was transmitted through a matching transformer (to increase the signal/noise ratio), and through a filter that suppressed the fundamental-frequency signal at 185 Hz, to a second-harmonic detection circuit.

The chamber was made of heat-treated beryllium bronze with outside and inside diameters 18 and ~4.5 mm, respectively. The pressure in the chamber was produced by a press at room temperature, and prior to pouring in the helium the chamber was cooled slowly (~12 hours) in the cryostat to nitrogen temperature. The pressure in the chamber was determined at helium temperatures from the temperature of the superconducting transition in indium, recorded by a magnetic method. The pressure measurement accuracy was ±0.1 kbar.

The measurements were performed in a field up to 80 kOe, produced by a superconducting solenoid, at a temperature 1.5 K. The solenoid was calibrated by the NMR method, and the field was next determined by measuring the current through the solenoid. The dHvA oscillations for each value of the pressure were recorded in a single passage in one and the same field interval and at the same field scanning rate. Despite the presence of a "frozen-in flux," the calibration of the solenoid has shown that this procedure yielded field values from 15 to 80 kOe reproducible within better than 10⁻³.

The MoO₂ and WO₂ single crystals were irregular polyhedra measuring ~2 mm with natural faceting in which, as a rule, the (100) plane was very well pronounced, so that the samples could be set accurate to ±3° relative to the field direction.

The measurements were made on three MoO₂ samples with resistivity ratios $\rho(290\text{K})/\rho(4.2\text{K})=1000, 480$ and 400 and on two WO₂ samples with $\rho(290\text{K})/\rho(4.2\text{K})=500$ and 110, such that in certain orientations the measurements were repeated with different samples. The results for the different sample agreed within the limits of errors.

MEASUREMENT RESULTS AND DISCUSSION

The dependence of the dHvA oscillations on the pressure was measured with the magnetic-field direction in the symmetry plane (010) in MoO₂ for the three directions [100], [101], and [001], and in WO₂ for the two directions [100] and [101]; in addition, measurements

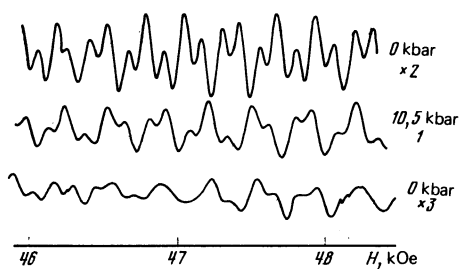


FIG. 1. Typical plots of MoO₂ oscillations at H|| [100] and at various pressures. Upper—prior to application of the pressure, middle— $P=10.5$ kbar, lower—after removal of pressure. The numbers on the right indicate the pressures and the factors that reduce the oscillation amplitudes to a single scale.

on MoO₂ were made in the direction [21 $\bar{1}$] outside the symmetry plane. Oscillations with sufficiently high signal/noise ratio were observed in the field interval 15–80 kOe, the number of oscillations in this interval being 100–300. The error in the measurements of the oscillation frequency was ~0.1%. At zero pressure, our results agree with the data of Refs. 5 and 6.

Figure 1 shows by way of example oscillation trains for an MoO₂ sample at H|| [100] and at various pressures. Following a complete measurement cycle (pressure increase followed by a decrease) the amplitude of the low-frequency oscillations changes little, while that of the high-frequency oscillation decreases somewhat.

Figures 2a and 2b show the measured frequencies $F(P)$ as functions of the pressure at H|| [101] for two sections of the FS of MoO₂—small and large, designated in accord with Ref. 5 as α_1 -MoO₂ and α_2 -MoO₂. Figures 2c and 2d show similar results for WO₂. Notice must be taken of the nonlinearity of some of the $F(P)$ curves, beyond the error limits. The initial slopes were used to determine the values of $d \ln S/dP$, which are listed in the table for all the FS sections measured by us. Figure 3 shows in an easily visualized form all the results obtained in the (010) plane.

From the presented data (see the table and Figs. 2

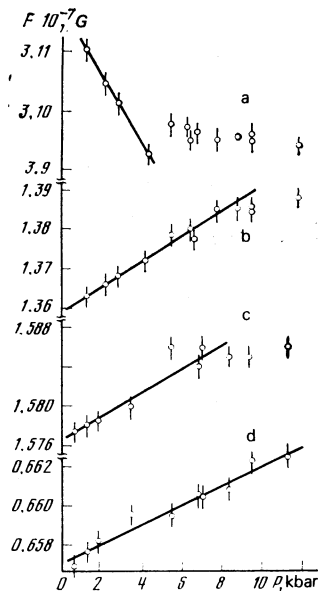


FIG. 2. Plots of $F(P)$ for sections α_2 and α_1 respectively of MoO₂ (a, b) at H|| [101] and WO₂ at H|| [100] (c, d).

TABLE I. Baric coefficients of the extremal sections ($d\ln S/dP$) $\cdot 10^4$, kbar $^{-1}$.

Field orientation	Sections*			
	MoO ₂		WO ₂	
	α_1	α_2	α_1	α_2
[100]	5±1.5	2.4±2	8.5±2.5	7.5±2.5
[001]	7.6±2	—	—	—
[101]	24±5	-18±4	11±3	—
[211]	7.8±2	—	—	—

*The symbols for the sections are the same as in Ref. 5.

and 3) it follows quite definitely that the volumes of the small closed parts of the Fermi surfaces of α_1 -MoO₂ and α_1 -WO₂ increase with increasing pressure. Unfortunately, the data obtained by us for the α_2 -MoO₂ and α_2 -WO₂ surfaces do not give any indications of the signs of the volume changes. We note also that, from among the investigated magnetic field direction, a noticeably large value of $d\ln S/dP$ is observed for [101]. This anisotropy may be due to the effect of the pressure on the atom displacement that determines the distorted rutile structure of the two investigated oxides.

A direct comparison of our results with those of the investigation of VO₂ under pressure is, of course, impossible. However, the increase observed by us in the volumes of the Fermi surfaces of type α_1 in MoO₂ and WO₂ can be set in correspondence with the conclusion that the band overlap in VO₂ increases under pressure.⁴ The weak pressure dependence of the metal-insulator transition temperature in VO₂ can also be set in correspondence with the small changes of the extremal sections of the Fermi surfaces of MoO₂ and WO₂ (~0.1% per kbar) in our experiments.

The following arguments can also be advanced concerning the values of $d\ln S/dP$: the unit cell of MoO₂ is more stretched along the a axis and more compressed along the body diagonal than that of WO₂. The FS of WO₂ has a smaller volume than MoO₂, and under pressure it approached, so to speak, the volume of the FS of MoO₂. It can therefore be assumed that the principal role in the formation of the conduction bands is played by the overlap of the diagonal orbitals. The same result was obtained also in the calculations⁹ of the electronic structures of MoO₂ and WO₂.

It should be noted finally that the substantial difference between $d\ln S[001]/dP$ and $d\ln S[101]/dP$ for the small part of the FS of MoO₂ shows that its shape can differ substantially from an ellipsoid.

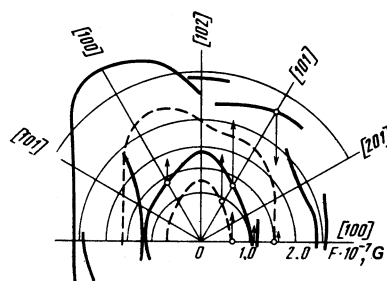


FIG. 3. The frequencies in the (010) plane are presented in polar coordinates in units of 10^7 G. The solid and dashed lines correspond to the dHvA frequencies of MoO₂ and WO₂, respectively. The length and direction of the arrows show the relative value and sign of the baric coefficient of the section in the given direction.

In connection with the metallic properties of WO₂ and MoO₂, the question arises of the possible superconductivity of the two oxides under pressure. In addition, polymorphism is possible. We have therefore measured the electric resistance of WO₂ and MoO₂ as a function of pressure up to 80 kbar at room temperature, as well as the temperature dependence of this resistance at $P = 80$ kbar in the helium-temperature region.¹⁾ A monotonic decrease of the resistance in the isotherms was observed, in accord with the assumption that the band overlap increases. In the isobars at $T \geq 1.8$ K, we observed no resistance jump to indicate superconductivity in these oxides.

¹⁾The electric resistance of MoO₂ and WO₂ under pressure was measured together with M. A. Il'ina, to whom the authors are deeply grateful.

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