The Fermi surface of MoO_2 and WO_2

E. P. Vol'skiĭ and V. M. Teplinskiĭ

Institute of Solid state Physics, USSR Academy of Sciences
(Submitted March 17, 1975)
Zh. Eksp. Teor. Fiz. **69**, 733–752 (August 1975)

Results are reported of an experimental investigation of the quantum oscillations and of the transverse magnetoresistance of MoO_2. It is established that MoO_2 has a Fermi surface of the open type. The obtained data are compared with the previously published results for WO_2 and are discussed jointly.

PACS numbers: 71.30.Hr, 72.20.My

The oxides MoO_2 and WO_2 belong to the large group of transition-metal dioxides.[1] In spite of the appreciable differences between the physical properties of the oxides making up this group, there are grounds for assuming that the electronic energy spectra of all these compounds are similar in nature and structure.[1,2] Among the factual grounds for this assumption we can indicate the common crystal structure, the regular variation of the type of electric conductivity as the cation d-shell is filled (see the table), and finally the results of experimental investigations of the optical spectra[3] and of the soft x-ray spectra.[4]

Thus, the investigation of the properties of any dioxide is not only of independent significance, but can contribute to a better understanding of the nature of the electronic energy spectrum of this group of oxides as a whole. The oxides MoO_2 and WO_2 are furthermore of special interest, since their crystal lattice is distorted in comparison with the ideal tetragonal rutile structure, owing to small displacements of the atoms, and the general character of these displacements and the symmetry of the distortion are the same as in VO_2[5] in the low-temperature dielectric phase. The role of this lattice distortion in the metal-dielectric transition in VO_2 has been discussed many times.[6-8]

The oxides MoO_2 and WO_2 have a distorted structure and metallic conductivity down to liquid-helium temperatures. The metallic conductivity at low temperatures uncovers a possibility of studying certain characteristics of the electronic energy spectrum (dimensions, topology, and shape of the Fermi surface, the effective-mass anisotropy of the conduction electrons) with the aid of the highly perfected experimental methods developed for ordinary metals.[9]

This paper is primarily a continuation of previously initiated[10] investigations of the Fermi surface of MoO_2. Having an MoO_2 crystal of much better quality than used in[10], we decided to attempt to obtain more complete data on that part of the Fermi surface of MoO_2 from which quantum oscillations were observed in[10] only in a narrow interval of the directions of the magnetic field. After obtaining new data by measuring the characteristics of the quantum oscillations, we investigated the transverse magnetoresistance of MoO_2, and this investigation confirmed our assumption of the existence of open trajectories on the Fermi surface of MoO_2.

All our experimental data[10] are compared and discussed jointly.

SAMPLE, PROCEDURE, AND EXPERIMENTAL CONDITIONS

The method of preparing and selecting the sample was the same as before.[10] All measurements whose results are reported here were made on an MoO_2 single crystal with a ratio $\rho(290°K)/\rho(4.2°K) = 650$. (This ratio did not exceed 200 for the MoO_2 samples in[10].) Special pains were taken to select a crystal that had no crystalline domains. The oxide MoO_2 has apparently, like VO_2 in the monoclinic phase,[6] a tendency to form crystalline domains—regions with different orientations of the distortion of the ideal rutile lattice. All possible domains in this crystal should go over into one another under transformations corresponding to those symmetry elements of the initial undistorted lattice which have vanished as a result of the distortion.

We made no special study of the domain structure of MoO_2, but according to our observations crystals in the shape of rods of almost quadratic cross section, elongated along the direction corresponding to the fourfold axis of the assumed undistorted lattice, contained domains as a rule. The crystal chosen by us for the measurements had a different shape and was single-domain.

This crystal was a plane-parallel plate 0.6 mm thick in the form of a rhombus with diagonals 1.9 and 2.1 mm and vertex angles 82 and 98°. The presence of a face with such angles between the edges bounding it is typical of many MoO_2 single crystals.

An x-ray diffraction investigation has shown that such a face, and consequently also the plane of our plate, coincides with the (100) plane of the monoclinic lattice of MoO_2, the diagonals of the rhombus are parallel to the axes [010] and [001], respectively. (In this paper, as in[10], we use the crystallographic indices in the system of the basic vectors of the monoclinic lattice, so that the [010] direction is parallel to the twofold axis and is perpendicular to the symmetry plane (010) of the crystal. The [100] direction is parallel to the fourfold axis of the assumed undistorted structure.)

To ensure a specified crystallographic orientation of the sample rotation in the magnetic field of a superconducting solenoid, special holders were made with milled plane-parallel slits in which to insert the sam-

Properties of dioxides of transition metals (nonmagnetic) as a function of the number of d electrons at the cation

Characteristic		Dioxide						
Type of d shell	3d	TiO_2	VO_2	MoO_2	TcO_2	RuO_2	RhO_2	
	4d		NbO_2	WO_2	ReO_2	OsO_2	IrO_2	PtO_2
	5d							
Number of electrons in cation		0	1	2	3	4	5	6
Type of crystal* structure	R	$T>T_t$*** R		DR	DR	R	R	DR
		$T<T_t$, DR						
Type of conductivity**	D	$T>T_t$, M		M	M	M	M	D
		$T<T_t$, D						

*R stands for rotial and DR for distorted rutile.
**M—metal, D—dielectric.
***T_t—temperature of the metal–dielectric transition.

ple, and in the quantum-oscillation experiments also the coils of the high-frequency oscillator tank circuit. In measurements of the magnetoresistance, channels were drilled in the corresponding holder, and gold wires of 0.5 mm diameter were passed through the channels and their ends clamped to the surface of the sample.

The small sample dimensions made possible considerable errors in the sample orientation when mounted in the apparatus. In measurements made in planes perpendicular to the symmetry axis (see Fig. 2) these errors were monitored against the symmetry of the measured quantities, by performing the measurements in a larger angle interval then required if the sample were exactly oriented. In addition, we compared the measured frequencies of the quantum oscillations from magnetic-field directions parallel to the intersection line of the investigated planes. The aggregate of all these checks allows us to state that the inaccuracies in the sample orientation did not exceed 2°.

The quantum oscillations were investigated with the apparatus described in our earlier paper[10] at 1.3°K in magnetic fields up to 57 kG. The magnetoresistance was measured in the same apparatus by a four-contact method in direct current, at 4.2°K. Lowering the temperature to 1.3°K did not affect the magnetoresistance of our sample.

RESULTS

Quantum oscillations. The extremal cross sections of the Fermi surface of MoO_2 were measured as functions of the direction of the magnetic field in the symmetry plane (010) (Fig. 1), and also in a number of planes perpendicular to the symmetry plane and thus passing through the twofold axis [010]. The results for these planes are shown in Fig. 2. The method of constructing the polar diagrams of Figs. 1 and 2 and the designation of the axes are the same as before.[10] The values of the extremal sections are given in gausses, i.e., in the frequencies of the quantum oscillations.

It is convenient to start the description of the results with Fig. 1. The experimental points in this figure break up naturally into a number of groups of branches, a fact emphasized by us with the aid of the curves drawn through these points. The same was done in Fig. 2. For comparison, the dashed lines in Fig. 1 show the dependence of the extremal sections of the Fermi surface of WO_2, from the earlier paper[10], on the field direction.

The similarity between branch g on Fig. 1 and the corresponding branch of the small sections of the Fermi surface of WO_2 was already noted in[10]. We can see now that branches a and d in the same figure trace a contour similar in shape to the large-section contour for WO_2, but in the case of MoO_2, as seen from Fig. 1, this contour is not traced continuously for all magnetic-field directions in the symmetry plane. In addition, new branches b, c, e, and f, have appeared, and no similar branches were observed in WO_2 at all.

In the planes perpendicular to the symmetry plane, the branches of the large sections of the Fermi surface of MoO_2 can be traced only in a certain interval of magnetic-field directions from the symmetry plane (Fig. 2), and take on near the symmetry plane values corresponding to branches a, d, or e in Fig. 1. An analogous correspondence can be established between branch c on Fig. 1 and one of the branches on most

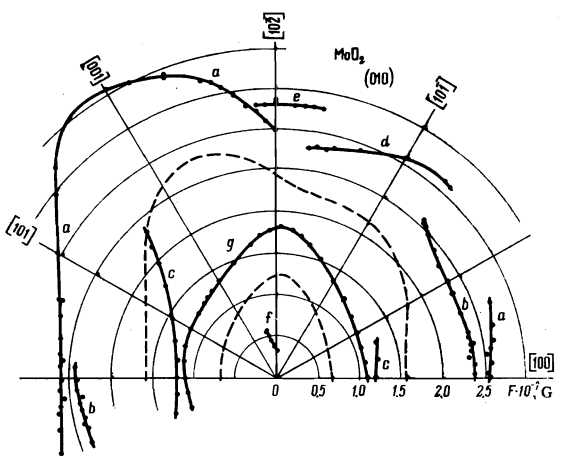

FIG. 1. Frequencies of quantum oscillations in MoO_2. Magnetic field in symmetry plane (010). Indices of crystallographic axes, left to right: [10$\bar{1}$], [001], [102], [101], [100].

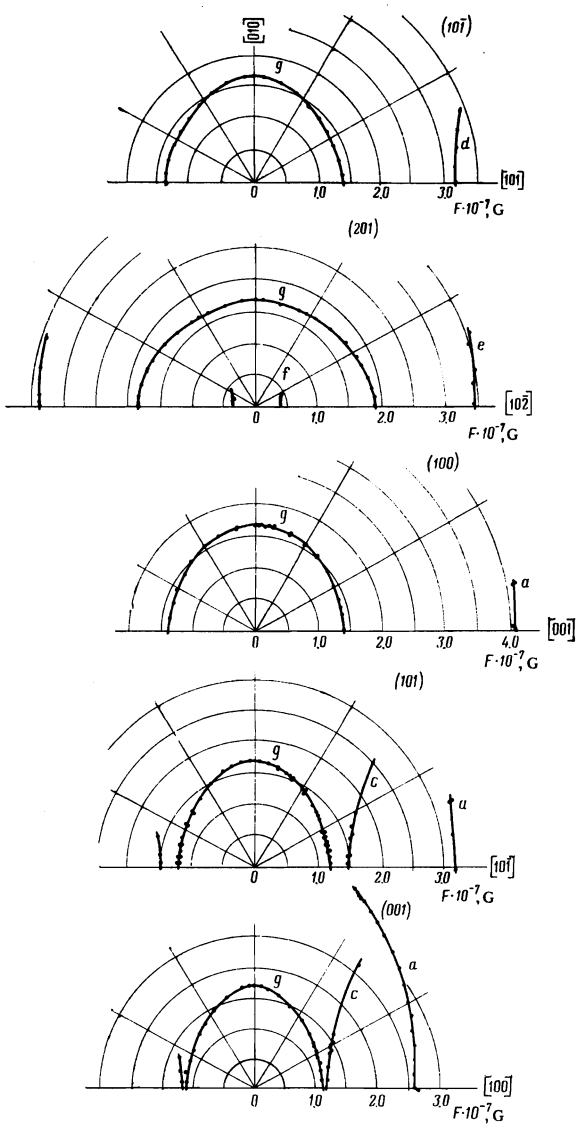

FIG. 2. Frequencies of the quantum oscillations in MoO_2. Magnetic field in various planes perpendicular to the symmetry plane. The axes in the second figure from the top should be marked [20$\bar{1}$] and [102].

diagrams of Fig. 2. A very important result that can be deduced from the data of Fig. 2 is the symmetry of the experimental points of all the observed branches relative to the [010] direction in all the investigated planes containing this direction.

Magnetoresistance. The dependence of the transverse magnetoresistance of MoO_2 on the magnetic field direction in two crystallographic planes, (010) and (10$\bar{2}$), is shown in the polar diagrams of Figs. 3 and 4. The main feature of both diagrams is the presence of a sharp and deep minimum at field directions along the [001] and [010] axes in the planes (010) and (10$\bar{2}$), respectively. The magnetoresistance in these minima was of the order of the electric resistance in the absence of a magnetic field. (In the (10$\bar{2}$) plane the minimum is sharper and the shape of its wings differs somewhat from that observed in the (010) plane.

The field dependence of the magnetoresistance in the interval 1–57 kG was measured for a number of magnetic-field directions, which are marked on the diagrams of Figs. 3 and 4 by the points A, B, C, D, E, F, G, and H. The results are plotted in Figs. 5 and 6,[1)] which show that in fields higher than 35 kG the field dependences can be described by the formula

$$\Delta\rho_H/\rho_0=\alpha+\beta H^2.$$

The accuracy of this approximation in the indicated magnetic-field interval lies within the limits of the measurement error $\Delta\rho H/\rho_0$, i.e., it is not worse than 1%.

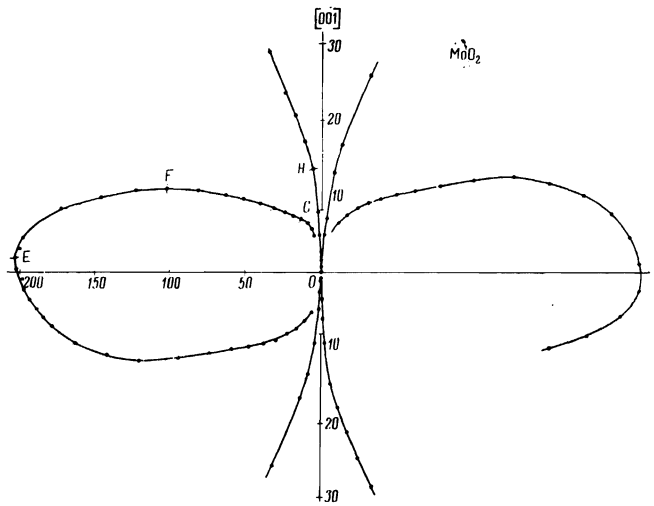

FIG. 3. Anisotropy of the transverse magnetoresistance MoO_2 in the (010) plane. The region of the sharp minimum is shown in enlarged scale, as marked on the vertical axis of the polar diagram.

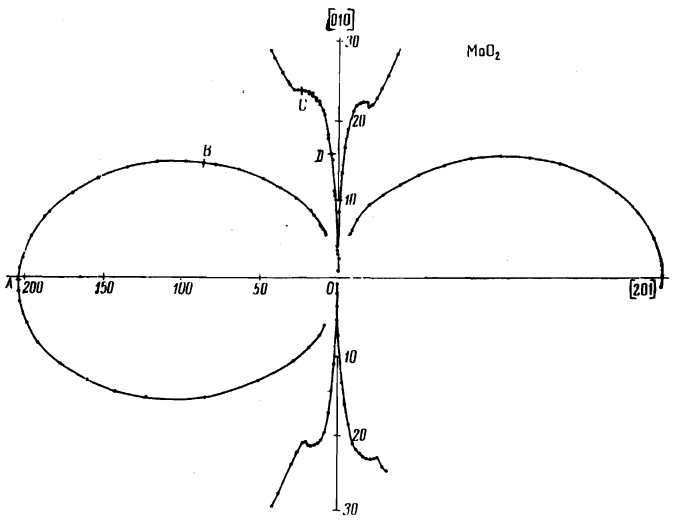

FIG. 4. Anisotropy of transverse magnetoresistance of MoO_2 in the (102) plane. The reion of the sharp minimum is shown in enlarged scale as marked on the vertical axis of the polar diagram.

DISCUSSION OF RESULTS

On the basis of the experimental results of the present and preceding[10] investigation we can attempt to describe some characteristic features of the Fermi surfaces of MoO_2 and WO_2, such as the topology, shape, dimensions, and position within the Brillouin zone.

For convenience in the subsequent discussion, we introduce the following notation:

α_1-WO_2—small-section surface of WO_2, branch 1 on Fig. 2.[10]

α_1-WO_2—large-section surface of WO_2, branch 3 on Fig. 2.[10]

α_1-MoO_2—surface corresponding to branch 2 of Fig. 2,[10] branch g on Figs. 1 and 2 of the present paper.

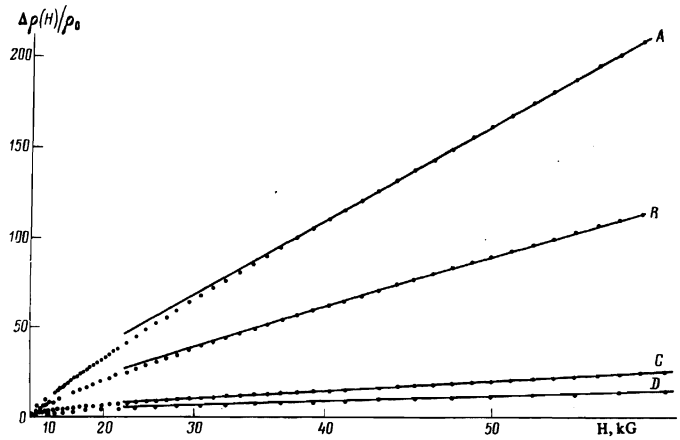

FIG. 5. Field dependences of the transverse magnetoresistance at the magnetic field directions marked on Fig. 4.

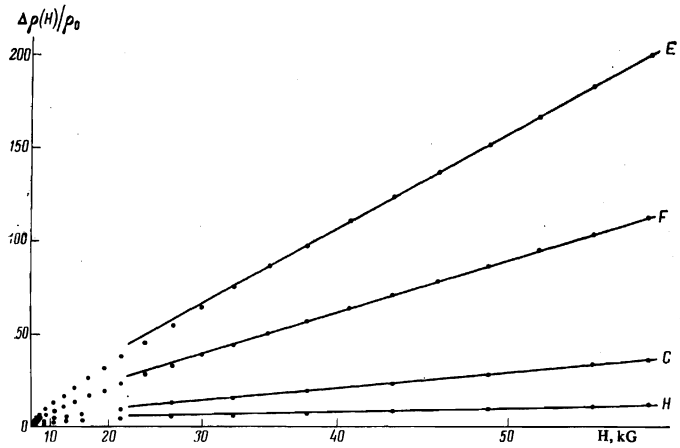

FIG. 6. Field dependences of the transverse magnetoresistance for the magnetic field directions marked in Fig. 3.

α_2-MoO_2—surface corresponding to branches a and d on Figs. 1 and 2 of this paper.

α_3-MoO_2—surface corresponding to branch c on Figs. 1 and 2 of this paper.

Branches b and e can be tentatively assigned to the surface α_2-MoO_2, assuming that they stem from additional extremal sections of this surface, shifted along p_z.

It is convenient to start the discussion with the most general characteristics of the Fermi surfaces of MoO_2 and WO_2. As already noted,[10] these oxides should be compensated metals. This follows from a simple calculation of the number of valence electron in the cell. The quadratic field dependence of the magnetoresistance of MoO_2 in strong fields (Figs. 5 and 6) can be regarded as an experimental confirmation of this assumption. Thus, the Fermi surface and the metallic conductivity of MoO_2 and WO_2 are the result of the intersection of two or more electron bands. This intersection is larger for MoO_2 than for WO_2, since the volumes of all the Fermi-surface parts seen by us for the two oxides differ by almost a factor of 2.

The open character of the Fermi surface of MoO_2 is apparently the result of the increase of its volume in comparison with WO_2, although it should be noted that we have not proved rigorously that there exist open parts of the Fermi surface of WO_2 not observed by us. The existence of open trajectories on the Fermi surface of MoO_2 is convincingly proved by the data of Figs. 3 and 4. The sharp minima in the anisotropy of the magnetoresistance, seen in these figures, are characteristics of compensated metals with open trajectories.[11] Singularities of this type were observed in RuO_2.[12]

On the basis of the data of Figs. 3 and 4 we can conclude that the open trajectories in MoO_2 are stretched out along a direction parallel to the symmetry plane and perpendicular to the [001] axis. It is quite possible that the corresponding equal-energy surface is made up of surfaces of the type α_2 and α_3.

The parts of the Fermi surfaces of both oxides investigated by us constitute only a negligible fraction of the volume of the Brillouin zone, less than 10%. It can be assumed that each of the surfaces listed above corresponds to an extremum of one of the intersecting zones. This raises naturally the question of the location of the points of these extrema in the Brillouin zone.

Our experimental data are insufficient to answer this question fully, but they limit strongly the possible regions where these points may be located.

As already noted, all the branches on all the diagrams of Fig. 2 are symmetrical about the [010] direction. Since this fact is observed not in one plane, as before,[10] but in several, this indicates unequivocally that the extremum points of the corresponding surfaces lie either on a symmetry plane drawn through the center of the Brillouin zone, or on faces of the zone parallel to this plane (Fig. 7). In either case this means that the multiplicity of any extremum, i.e., the number of nonequivalent points into which it goes over under transformations of the crystal point group C_{2h}, can be equal either to unity or to two. Unity is obtained if the extremum point coincides with one of the inversion points Γ, A, B, E, D, C, or Y on Fig. 7 (the points in the Brillouin zone are designated as in[13] before).

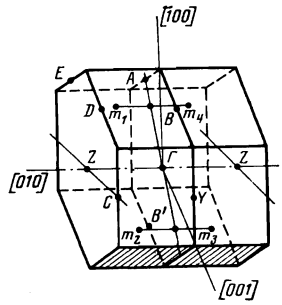

FIG. 7. Brillouin zone of MoO_2 or WO_2 (the principal direction of the direct lattice are indicated).

The similarity of the anisotropy of the extremal sections of surfaces α_1 and α_2 of MoO_2 and WO_2 respectively allows us to assume that the corresponding extrema of $\epsilon(p)$ are also equally arranged. In this case everything stated above concerning MoO_2 applies equally well to WO_2. But this means that the model proposed earlier[10] for the Fermi surface of WO_2 and indirectly for MoO_2 does not appear to correspond to reality. The main premise of the indicated model was that the ratio of the volumes bounded by the surfaces α_1 and α_2 of WO_2 and calculated approximately from the extremal sections is 1:4. According to this model, the extrema of $\epsilon(p)$ corresponding to the surfaces α_1 should be located in some four common points of the Brillouin zone, connected by symmetry transformation, e.g., m_1—m_4 in Fig. 7. In light of the foregoing, this contradicts our new results.

It should be noted that if an extremum point does not coincide with one of the inversion points of the Brillouin zone, then the volume of the corresponding equal-energy surface cannot be determined uniquely at all from the extremal sections of this surface.

Thus, if we reject the model proposed in[10], then we must assume the existence of some still-unobserved part of the Fermi surface of MoO_2 or WO_2, in which the electronic states are characterized by large effective masses, and the amplitude of the quantum oscillations is small. (The effective mass determined by us from measurements of the temperature dependence of the quantum-oscillation amplitude for branch a of Fig. 1, at a field direction along [100], turned out to be $0.95m_0$. An increase of this mass to $2m_0$ in a 52-kG field would decrease the oscillation amplitude by a factor 50 and would make the oscillations unobservable at our sensitivity.)

The foregoing discussion shows that in spite of the appreciable volume and accuracy of the experimental data obtained by us, it is still impossible to construct an unambiguous empirical model of the Fermi surfaces of MoO_2 and WO_2. It may be, however, that these data are sufficient to correct uniquely the calculations of the electronic energy spectrum of these oxides, of the type given earlier[13] for VO_2.

In conclusion, the authors thank L. A. Klinkov for much work on the growing of the MoO_2 crystal, V. Sh. Shekhtman, B. A. Abdikamalov, and V. I. Kozlov for an x-ray diffraction investigation of our samples, and M. G. Lazarev for help with the measurements.

[1)]The scale on the abscissa axes in these figures is quadratic.

[1] D. B. Rogers, R. D. Schannon, A. W. Sleight, and J. L. Gillson, Inorg. Chem. 8, 841 (1969).

[2] J. B. Goodenough, Prog. Solid State Chem. 5, 145 (1971).
[3] L. L. Chase, Phys. Rev. B10, 2226 (1974).
[4] D. W. Fischer, J. Appl. Phys. 40, 4151 (1969).
[5] A. Magneli and G. Andersson, Acta Chem. Scand. 9, 1378 (1955).
[6] J. R. Brews, Phys. Rev. B1, 2557 (1970).
[7] C. J. Hearn, J. of Phys. C5, 1317 (1972).
[8] J. W. Pierce and J. B. Goodenough, Phys. Rev. B5, 4104 (1972).
[9] D. Shoenberg, in: Physics of Metals, J. Ziman, ed., Cambridge, 1969.
[10] E. P. Vol'skiĭ and V. M. Teplinskiĭ, Zh. Eksp. Teor. Fiz. 63, 1048 (1972) [Sov. Phys.-JETP 36, 550 (1973)].
[11] R. Bass and P. A. Schroeder, J. Phys. Chem. Solids 35, 967 (1974).
[12] S. M. Marcus, Phys. Lett. 28A, 191 (1968).
[13] E. Caruthers and L. Kleinman, Phys. Rev. B7, 3760 (1973).

Translated by J. G. Adashko
78