QUANTUM LANDAU OSCILLATIONS IN MoO_2 *AND* WO_2

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Quantum Landau oscillations of the 4-MHz surface impedance were observed in MoO_2 and WO_2 single crystals at liquid helium temperatures in magnetic fields up to 53 kOe. The dependence of the oscillation frequency on the direction of the magnetic field was investigated in three crystallographic planes (010), (001), and (011) of the monoclinic lattices of the two compounds. The results obtained were used to determine the shapes and dimensions of the Fermi surfaces of the compounds. The effective electron masses were deduced from the temperature dependences of the oscillation amplitude in a magnetic field directed along the [100] axis.

COMPARATIVE studies of oxides with the same or similar crystal structure are particularly useful in the determination of the electron energy spectra. In this way one can relate the electronic properties of a compound to the distances between the ions in the lattice and to the structure of electron shells of the transition metal atoms.[1] With these considerations in mind we investigated a series of tetravalent transition-metal oxides with the rutile (TiO_2) structure and metallic conduction.[2] These compounds can be prepared as single crystals sufficiently perfect for the observation of such effects as the quantum Landau oscillations and the Azbel'-Kaner cyclotron resonance at liquid helium temperatures. In this way the shape and dimensions of the Fermi surface, the effective masses, and other characteristics of the conduction electrons in such compounds can be investigated.[3]

The preliminary results of our investigation of the quantum Landau oscillations in MoO_2 were published in[4]. We found later that Marcus[5] carried out a similar investigation on MoO_2 and several other oxides of the same series. The present paper is the first report of our study of the quantum Landau oscillations in WO_2 and of additional results obtained for MoO_2.

STRUCTURE AND SOME PHYSICAL PROPERTIES OF MoO_2 AND WO_2

MoO_2 and WO_2 have the same monoclinic structure with the following lattice parameters: a = 5.6109, b = 4.8562, c = 5.6285 Å, $\beta(\angle ac) = 120°57'$, V = 131.52 Å^3 for MoO_2;[6] a = 5.5, b = 4.90, c = 5.66 Å, $\beta(\angle ac) = 120°44'$ for WO_2.[2] The space group of these crystals, C_{2h}^5 ($P2_1/c$), includes a twofold screw axis, parallel to the b axis, and a glide plane, perpendicular to this axis. The unit cells of MoO_2 and WO_2 contain four molecules each.

The lattice of both oxides is the rutile (TiO_2) structure distorted by small displacements of all the atoms. The four metal atoms in the unit cell of MoO_2 are displaced by the following amounts (expressed in units of the a, b, c axes) from the initial positions in the rutile lattice: (−0.018, −0.008; 0.016), (0.018; 0.008; −0.016), (0.018; 0.008; −0.016), (−0.018; 0.008; 0.016).

Figure 1 shows the rutile lattice with arrows indicating the displacements of the metal atoms (the magnitudes of these displacements are greatly exaggerated for clarity). The oxygen-ion octahedra surrounding each metal atom are also distorted.[6] This distortion transforms the line joining metal ions along the C_4 axis to the original rutile lattice (direction a in Fig. 1) into a broken line. The distances between neighboring metal ions along this line are alternately 2.5106 and 3.118 Å for MoO_2 and 2.49 and 3.08 Å for WO_2. Thus, the period of the rutile structure along the fourfold axis is doubled. Moreover, the displacements of the ions reduce the symmetry of the lattice to the monoclinic type (C_{2h}^5).

Figure 1 shows the three fundamental vectors of the lattice of MoO_2 and WO_2. We shall use the system of coordinates formed by these three vectors for the designation of the crystallographic axes and planes in terms of the Miller indices. MoO_2 and WO_2 exhibit metallic conduction right down to liquid helium temperature.[2] Both compounds are diamagnetic.[7] The optical properties of both compounds were investigated in[8] but the results have not yet been interpreted clearly.

SAMPLES

Single crystals of MoO_2 and WO_2 were prepared by the precipitation from the vapor phase using the method of chemical transport reactions.[9] Typical dimensions of the samples were 1—2 mm. Majority of the crystals had natural faceting, which was used to align sample in the apparatus. The orientations of the faces were determined by x-ray diffraction. Some of the samples were apparently bicrystals or contained slightly disoriented grains. This was why weak large-period beats were observed along certain directions of the magnetic field.

Since the quantum oscillations could be observed only in crystals with a sufficiently long mean free path, which should be large compared with the dimensions of electron orbits in the magnetic field (i.e., larger than 10^{-3} cm in our experiments), it was essential to make a preliminary selection of the samples on the basis of the ratio of their resistances at room and helium temperatures. The ratio of the resistances was measured by the four-probe potentiometric method. We used gold-foil pressure contacts, which improved considerably the reproducibility of the results. The influence of the contact emf's was eliminated by measuring the resistance at a frequency of 20 Hz. We investigated quantum

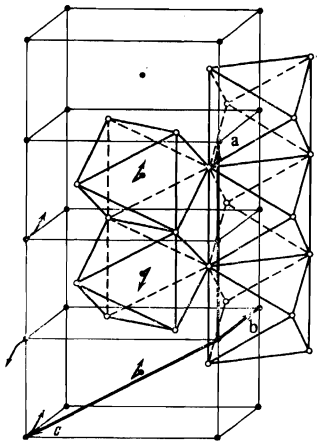

FIG. 1. Relationship between the rutile (TiO_2) structure and the structures of MoO_2 and WO_2: ●—metal; ○—oxygen.

oscillations in MoO_2 and WO_2 samples with resistance ratios in excess of 100.

MEASUREMENT METHOD

As in our earlier investigation,[4] the quantum oscillations of the high-frequency surface impedance were investigated by a method[10] borrowed from the NMR technology. A sample was placed in the field of a coil in the resonance circuit of an oscillator operating close to the point at which oscillations disappeared. The amplitude of the oscillator signal was very sensitive to any change in the Q factor of the circuit. Changes in the surface impedance of the sample resulting from the application of a static magnetic field were manifested as changes in the amplitude of the signal and were measured by the modulation method. All the measurements were carried out keeping the oscillator frequency close to 4 MHz. The magnetic fields ranged up to 53 kG, which was generated by a superconducting solenoid with an aperture of 20 mm size. The temperature was 1.3°K. In the first experiments the magnetic field was modulated at 30 Hz, but later we used 380 Hz, which improved considerably the signal/noise ratio. The sample was rotated relative to the magnetic field of the solenoid by a vernier device mounted on cryostat cover. A system of two pairs of modulation coils with mutually perpendicular axes (these axes were parallel to the plane of rotation of the vernier device) was rotated together with the sample. The angle of rotation was determined from the signal induced by the modulation coils in the solenoid winding.

RESULTS

We investigated the dependence of the oscillation frequency on the direction of the magnetic field in three crystallographic planes of MoO_2 and WO_2: (010), (001), and (011).[1)] The experimental records from which we deduced the oscillation frequency contained from 30 to 100 periods. The magnetic field was measured to within 0.1% of the current through the solenoid, calibrated

[1)]The results for the (011) plane of MoO_2 were reported earlier [4] but the Miller indices of this plane and of several axes were given incorrectly in that paper because of inappropriate selection of the coordinate system.

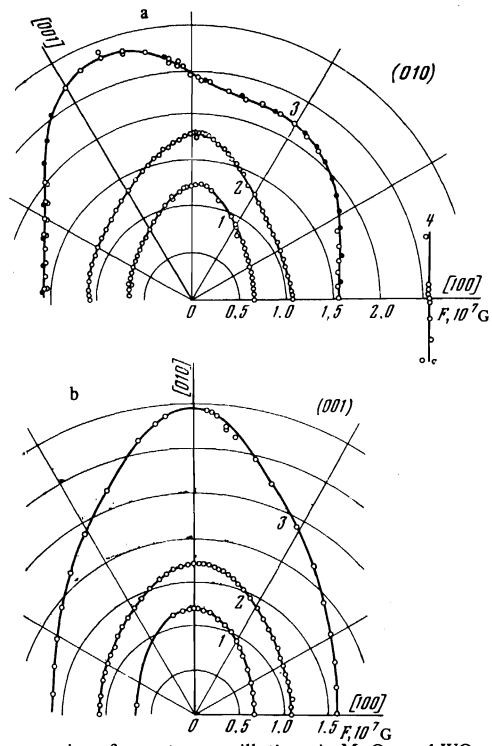

FIG. 2. Frequencies of quantum oscillations in MoO_2 and WO_2: a—magnetic field in the (010) symmetry plane; b—magnetic field in the (001) plane, perpendicular to a symmetry plane; 1, 3—WO_2; 2, 4—MoO_2.

relative to nuclear resonance. In this way we were able to measure the oscillation frequency with an error not exceeding 1%.

The results of measurements are plotted in polar coordinates in Fig. 2 and are also listed in Table I. The frequency of the quantum Landau oscillations, expressed in terms of the reciprocal of the magnetic field, is proportional to the area of the section of the Fermi surface which is extremal in p_z and perpendicular to the magnetic field:

$$F = 10^{16}\frac{ch}{4\pi^2 e}S_{ext}$$

(S_{ext} is in $Å^{-2}$). Thus, the curves plotted in Fig. 2 are evidence of anisotropy of the extremal sections formed by cutting the Fermi surfaces of MoO_2 and WO_2 with

Table I. Frequencies quantum oscillations in MoO_2 and WO_2 in a field of 10^7 G (average values derived from points in Fig. 2)

θ от [100], deg	MoO_2				WO_2					
	(010)		(001)	(011)	(010)		(001)		(011)	
0	1.08	2.55	1.08	1.08	0.67	1.57	0.67	1.59	0.67	1.56
10	1.06	2.59	1.09	1.10	0.67	1.60	0.67	1.62	0.67	1.58
20	1.06	—	1.11	1.12	0.68	1.68	0.69	1.67	0.68	1.64
30	1.08	—	1.14	1.15	0.71	1.82	0.73	1.77	0.70	1.76
40	1.13	—	1.20	1.18	0.76	1.98	0.77	1.91	0.75	1.94
50	1.21	—	1.28	1.24	0.83	2.11	0.85	2.12	0.82	2.19
60	1.35	—	1.40	1.32	0.93	2.22	0.94	2.38	0.91	2.52
70	1.52	—	1.54	1.43	1.06	2.27	1.05	2.71	1.03	2.84
80	1.73	—	1.66	1.56	1.22	2.31	1.15	3.15	1.14	3.04
90	1.82	—	1.69	1.66	1.25	2.49	1.20	3.45	1.20	3.15
100	1.64	—	—	1.68	1.15	2.76	—	—	1.15	3.12
110	1.51	—	—	1.59	1.01	2.84	—	—	1.03	2.95
120	1.37	—	—	1.47	0.91	2.70	—	—	0.93	2.66
130	1.27	—	—	1.35	0.83	2.41	—	—	0.85	2.29
140	1.20	—	—	1.26	0.77	2.06	—	—	0.78	2.00
150	1.15	—	—	1.18	0.73	1.82	—	—	0.73	1.80
160	1.12	—	—	1.13	0.70	1.68	—	—	0.70	1.65
170	1.10	2.59	—	1.10	0.67	1.60	—	—	0.68	1.58

planes perpendicular to that in which the magnetic field is rotated. All the three investigated planes have one common axis [100] from which the angles defining the direction of the magnetic field are measured. The direction of measurement of the angles from the [100] axis was chosen arbitrarily and, therefore, the curves plotted in Fig. 2a might possibly have to be rotated by 180° relative to the line perpendicular to the [100] axis in the figure.

The effective masses were deduced from the temperature dependence of the oscillation amplitude only for the [100] direction of the magnetic field for both oxides. We shall now describe separately the results obtained for each compound.

MoO_2. We observed oscillations of two frequencies differing approximately by a factor of 2. Oscillations at the lower frequency were observed for all the directions of the magnetic field in the investigated planes and the frequency varied continuously. The part of the Fermi surface corresponding to these oscillations is evidently closed, as concluded in our earlier paper.[4] The new measurements of the anisotropy of the extremal sections of this surface in the (010) and (001) planes (Fig. 2) show that the symmetry of the Fermi surface corresponds to the C_{2h} group, i.e., it is identical with the point symmetry of the crystal. In fact, if we consider the (010) plane, which is a symmetry plane of the crystal and is therefore perpendicular to the twofold axis, we find that the curve joining the experimental points in Fig. 2a has only an inversion center. For the (001) plane, which is perpendicular to a plane of symmetry of the crystal, the anisotropy curve of the extremal sections has—as expected—two mutually perpendicular lines of symmetry. According to our experimental data (Fig. 2) the volume of this part of the Fermi surface of MoO_2 corresponds to 1.1×10^{-2} electrons (or holes) per MoO_2 molecule.[2)]

Oscillations at the higher frequency were observed only in a small range of angles near the [100] axis (Fig. 2a) and the results obtained were insufficient to judge the shape and dimensions of the corresponding part of the Fermi surface of MoO_2. The effective mass deduced from the temperature dependence of the amplitude of the oscillations of the lower frequency excited in a magnetic field directed along the [100] axis was $(0.97 \pm 0.2)m_0$, as reported in our earlier paper.[4]

WO_2. As in the case of MoO_2, we observed oscillations of two frequencies but we were unable to study both frequencies for all the directions of the magnetic field in the investigated planes (Fig. 2). The results obtained suggest the existence of two closed parts of the Fermi surface of the WO_2. The volume of the smaller part corresponds to 0.6×10^{-2} electrons (or holes) per WO_2 molecule. The volume of the second part is approximately 4 times as large. As in the case of MoO_2, the symmetry of both parts of the Fermi surface corresponds to the point group C_{2h}. The effective masses deduced from oscillations in a magnetic field directed along the [100] axis were $(0.47 \pm 0.05)m_0$ for the smaller part of the Fermi surface and $(0.67 \pm 0.07)m_0$ for the larger part. The Dingle temperature (0.6°K) was deduced from the low-frequency branch of the oscillations excited in a magnetic field of the same direction.

DISCUSSION OF RESULTS

Unfortunately, theoretical calculations of the electron structure of MoO_2 and WO_2 have not yet been made. Therefore, we can discuss our results only in general terms. Since a unit cell in both oxides contains an even number of molecules, it follows that if the Fermi surfaces of both compounds are closed, the volumes of the electron and hole parts should be equal. In particular, if we assume that there are no other parts of the Fermi surface of WO_2 apart from those revealed in our study, we may conclude that the two types (parts) of the Fermi surface considered above are present in the ratio 1/4 in the Brillouin zone, i.e., in the ratio proportional to their volumes. It is not yet possible to say which of these surfaces contain holes and which electrons. Since the star of any point in the Brillouin zone of a crystal of symmetry C_{2h} comprises one, two, or four (but no more) points, it follows from our considerations that the Fermi surface of WO_2 consists of one closed electron (or hole) part and four closed hole (or electron) parts.

The almost complete identity of the crystal structures of both oxides and the similarity of the atomic structure of Mo and W suggest that the Fermi surfaces of MoO_2 and WO_2 should be similar. Therefore, the closed part of the Fermi surface of MoO_2 should correspond to the smaller of the two surfaces of WO_2. Further experimental results are needed before we can fully accept or reject the suggestions made above.

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[2)] The quoted values of the electron density in MoO_2 and WO_2 are only estimates. More precise calculations of the Fermi surface volumes and of the electron densities are being made at present with the aid of a computer.