

The sign of current carriers in MoO₂

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Variations in the extremal sections of different parts of the Fermi surface (FS) in MoO₂, resulting from a substitution of part of the Mo atoms (~0.1%) by donor (Re) or acceptor (V) impurity atoms, have been detected. For these impurities, the variations in the sections of each part of the FS were opposite in sign and uniform for different orientations of the magnetic field. The signs of the current carriers on different parts of the FS were determined from the signs of the variations in the volume elements bounded by these parts of the FS.

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Previously^{1,2} it was shown that MoO₂ is a compensated metal and the anisotropy of the extremal sections of its Fermi surface (FS) was studied in detail. In order to construct a model of the FS for MoO₂, it is also necessary to have information concerning the sign of the current carriers on different experimentally observed parts of this surface. The present work, which should be viewed as a continuation of Ref. 2, is concerned with this problem.

A well-known^{3,4} method was used in this work in order to determine the sign of the current carriers on different parts of the FS. The essence of this method reduces to the following. When MoO₂ is doped with a small quantity of a donor or acceptor impurity, the electron and hole parts of the FS change their volume in accordance with the type of impurity, and this change can be revealed by the change in the extremal sections of these parts when studying the Landau quantum oscillations^{1,2}.

Monocrystals of pure and doped MoO₂ were grown using the method of transport reactions^{5,6}. Re and V, located in the periodic table to the right and left of Mo, respectively, were chosen as the donor and acceptor impurities due to the close similarity of the crystal structures of the dioxides MoO₂, ReO₂, and VO₂ (Ref. 7). In growing the monocrystals of doped MoO₂, part of the initial batch was replaced by an amount of Re or V₂O₅ that would yield ordered solid solutions of composition Mo_{1-x}(Re or V)_xO₂ (Ref. 8). The growing conditions were the same as when growing monocrystals of pure MoO₂ with the largest resistance ratio γ at room and liquid-helium temperatures (RRR) (Ref. 6).

In order to verify indirectly that Re or V atoms replace Mo atoms, the quantity γ was measured for several specimens from each of the ampules (5 to 10 samples) using the setup described in Ref. 1 and the four-contact method, and the average value $\langle\gamma^{-1}\rangle$ was computed for each ampule. Doped monocrystals were grown in identical ampules and the weights of the initial batches were also equal. Figure 1 displays $\langle\gamma^{-1}\rangle$ as a function of the amount of impurity in the initial batch. The linearity of this dependence indicates, on the average, that the impurity content in the doped monocrystals is proportional to the amount of impurity in the batch. The impurity content of the doped monocrystals in itself was not measured. Typical dimensions of the doped mono-

crystals were 2 × 1 × 0.5 mm. As a rule, both the pure and the doped monocrystals had a well-developed (100) face and one or several (111) faces, which allowed the samples to be easily oriented in the apparatus.

The change in the extremal sections of the FS for doped MoO₂ in comparison with pure MoO₂ was determined from the change in the frequencies of the Landau quantum oscillations of the surface impedance of the sample, as in Refs. 1 and 2, but, in order to increase the sensitivity, the method of recording the oscillations differed from the previous method^{1,2} and consisted of the following. The sample was placed in the field of a coil of a parallel tank circuit tuned to the frequency of a high-frequency oscillator, which was connected with the tank circuit through an active resistance several times greater than the equivalent resistance of the tank circuit at resonance. In such a circuit, the phase of the tank circuit voltage depends on the impedance of the sample. As the constant magnetic field applied to the sample was varied, the derivative of the phase with respect to the magnetic field was recorded by a modulation technique with the help of a Ch7-5 frequency comparator, which functioned as a phase multiplier. The measurements were carried out in a magnetic field up to 75 kOe, created by a superconducting solenoid, at a temperature of 1.4 K, oscillator frequency 1 MHz, and a modulation frequency 380 Hz.

The change in the oscillation frequencies as a result of doping turned out to be small (~0.1–1%). For this reason, it was necessary to make highly precise mea-

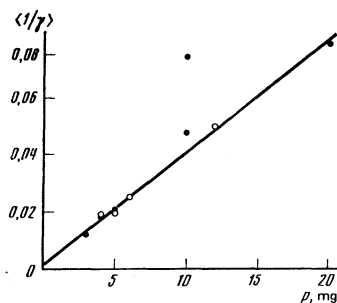


FIG. 1. The average value $\langle\gamma^{-1}\rangle$ for several samples from each ampule of doped MoO₂ as a function of the amount of impurity p in the initial batch: ● — Re, ○ — V₂O₅. The anomalous point, apparently, corresponds to a disruption of the growing regime.

surements of the magnetic field. When determining the field by measuring the current through the solenoid, the appearance of a "frozen-in flux"⁹ destroyed the relationship between the field and the current, which in many cases led to total uncertainty in the measured effect of the doping; the frozen-in flux always arose to one extent or another when the sign of the rate of change of the current through the solenoid changed. In order to avoid this, the field was measured with a low-temperature Hall-sensor, and the oscillations were recorded, as a function of the pickup field. The sensor was placed directly next to the sample.

As is well-known,¹⁰ the calibration of most low-temperature Hall sensors varies from one cooling-heating-cooling cycle to another. While determining the solenoid constant (field to current ratio) with the help of the set-up described in Ref. 11, which allowed NMR measurements of fields that differed by equal amounts, up to the largest field values, it was noticed that the "frozen-in flux" does not occur when the current is fed once slowly (≤ 0.05 kOe/s) to the solenoid after the solenoid is cooled. We calibrated the Hall sensor against the current through the solenoid by this method each time at the beginning of the measurements.

The sample was glued to a special holder. Remounting the sample led to an error in determining the oscillation frequencies not exceeding $\pm 0.02\%$.

The amplitude of the oscillations in the doped samples decreased significantly, so that at first the measurements were performed for several samples doped with Re and V with the magnetic field oriented along the [100] direction, since it was established experimentally that for this field orientation the amplitude of the oscillations was a maximum in all parts of the FS. The oscillation plots that were useful for analysis, i.e., that had a sufficiently high signal-to-noise ratio, were obtained with doped samples having $\gamma \geq 60-70$, for which the order of magnitude of the upper bound of the impurity content was estimated at 0.1% by weight, while at the same time, the amplitude of the oscillations decreased approximately by an order of magnitude in comparison with the amplitude for the pure sample, for which $\gamma = 420$. Table I displays the results of the measurements and the characteristics of the samples. As these measurements have shown, doping with donor and acceptor impurities leads to changes of opposite sign in the oscillation frequencies.

Next, for sample No. 1, measurements were performed with several orientations of the magnetic field in the (010) symmetry plane. The amplitude of the oscillations was greatest for this sample, apparently because of its perfect crystalline structure. The results of these measurements are presented in Table II and in a graphic form in Fig. 2.

In interpreting our results, we did not perform any calculations, so that only a qualitative discussion is given.

As a result of doping, generally speaking, both the FS volume and the FS shape change. For small amounts of impurity, there are basically three reasons for this

TABLE I. Changes (in %) of the oscillation frequencies for different doped samples at $H \parallel [100]$.

Sample number	Impurity in the batch	γ	Branches*		
			g	a	c
1	4 mg V ₂ O ₅	118	0.42±0.03	0.29±0.03	-0.10±0.05
2	5 mg V ₂ O ₅	129	0.46±0.06	0.33±0.08	-0.16±0.06
3	5 mg V ₂ O ₅	68	0.46±0.06	0.36±0.08	-0.10±0.06
4	4 mg Re	65		-0.53±0.06	
5	4 mg Re	95	-0.82±0.03	-0.48±0.05	

*The branches are labelled in the same manner as in Ref. 2.

effect. The first of these is connected with the rigid-band model¹² and consists of a change in the way the bands are filled on doping. In this model it is assumed that doping does not change the electron spectrum. Conversely, the second reason is connected with the change of the spectrum itself upon doping, i.e., with the fact that doped MoO₂ is in a certain sense a substance different from pure MoO₂ (Ref. 13). The third reason follows from the change in the carrier density due to the change in the volume of the unit cell.

The volume of the unit cell of MoO₂ was measured in Refs. 8 and 14 as a function of the concentration of the impurities V and Re, respectively. There was no noticeable change of volume at concentrations ranging from zero to several percent, and since the amount of impurity in the doped MoO₂ in this work did not exceed 0.1% by weight, we will not attribute our results to a change in the unit-cell volume.

In the rigid-band model, all dimensions of each individual part of the FS either increase or decrease upon doping, whereas a change in the form of the spectrum can cause a nonuniform change in these dimensions. In this work, since the impurity concentrations are small, we assume that the FS-dimensions change corresponding to the rigid-band model is greater than that resulting from the change in the spectrum. This assumption proved to be justified in many studies (for example, in Ref. 13) for good metals, while for semimetals of the bismuth type the rigid-band model, in general, turned out to be sufficient for describing the changes in the FS as a result of doping.⁴ The compound MoO₂, in which the carrier concentration constitutes $\sim 10^{-2}$ per molecule,¹ can be more easily regarded as a semimetal than a good metal. In our case, it would have been possible to look for a change in the spectrum by observing a deviation from proportionality in the ratio $\Delta S \propto m^* = (2\pi)^{-1} \partial S / \partial \varepsilon$ under the condition that the anisotropy of the contribution of this effect differs from the aniso-

TABLE II. Changes (in %) in the oscillation frequencies for sample No. 1 at different orientations of H in the (010) symmetry plane.

Branches*	Angle between H and [100]			
	30° (120 $\bar{1}$)	60° (110 $\bar{1}$)	87°	153°
a				0.29±0.03
b	-0.33±0.03			
c		-0.27±0.03		-0.24±0.04
d			0.18±0.02	
e			0.35±0.01	
g	0.20±0.04	1.22±0.02		0.48±0.03

*The branches are labelled in the same manner as in Ref. 2.

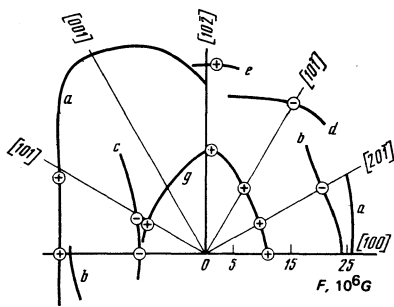


FIG. 2. The signs of the changes of the oscillation frequencies for a MoO_2 sample doped with an acceptor impurity. The magnetic field is oriented along the (010) symmetry plane.

ropy of the effective masses, but, unfortunately, we have no data on the anisotropy of the effective masses in the (010) plane. The values of the masses in this plane were measured only for the direction [100]. For these values, $m_a^* = (0.98 \pm 0.10)m_0$ and $m_g^* = (0.48 \pm 0.05)m_0$, and the ratios $\Delta S/m^*$ agree within the limits of the measurement error.

Thus, the fact that the changes in the oscillation frequencies on the a , g , and c branches in Fig. 2 are of the same sign leads to the conclusion that introduction of an acceptor impurity into MoO_2 increases the volumes of the parts of the FS that correspond to the a and g branches and therefore these are electron parts while the part that corresponds to the c branch decreases in volume and, for this reason, is an electron part. The closeness of the values of the oscillation frequencies for the a and e branches and the equal sign of their change by doping support the assumption, stated previously,² that the e branch belongs to the same part of the FS as the a branch. Branches b and d , apparently, also originate from one part of the FS. The arguments in support of this supposition are as follows. When the magnetic field is oriented at an angle of 47.5° relative to the [100] axis, the oscillation frequency between b and d branches changes jumpwise in a very narrow range of angles, $\sim 0.1^\circ$, and the signs of the changes in frequency in these branches as a result of doping are the same (Fig. 2). This is an electron part and, therefore, the assumption stated in Ref. 2 that the b and d branches stem from the same part of the FS as branch a is not supported. The possibility that the branches c , b , and d are related to the same part of the FS has not been excluded.

Let us make the following remark.¹⁾ It is interesting to compare the results of the present work with the data concerning the effect of hydrostatic pressure up to $P = 12$ kbar on the FS of MoO_2 , as obtained in Ref. 15. In the reference indicated, the baric coefficients $S^{-1}dS/dP$ of the changes of the frequencies of the de Haas-van Alphen oscillations were measured for various orientations of the magnetic field, of which two, namely, [100] and [101], coincide with the orientations of the field in the present work. For these orientations, the signs of the baric coefficients coincide exactly with the signs of the changes in the oscillation frequencies as a result of doping with an acceptor impurity, and the ratios of these quantities are equal within the limits of

the measurement error. The exception is the d branch, for which this ratio is four times greater.

The equivalence of the effects of hydrostatic pressure and doping with an acceptor impurity on the electronic properties of the oxides of transition metals was also observed by studying another effect, namely, their influence on the temperature of the metal-insulator V_2O_3 . The curves representing the dependence of this temperature on the pressure and amount of the Ti impurity coincide when an appropriate choice of scale is made.¹⁶ Some reasons for such an equivalence for V_2O_3 were given in Ref. 17 and consist of the following. Since the Ti^{3+} ion has only a single d -electron, while V^{3+} has two such electrons, the addition of Ti to V_2O_3 must lead to some increase in the average positive charge of cations in the lattice, if it is assumed that the d -electrons of the cations are collectivized. An increase in the positive charge of cations should lead to a "compression" of the oxygen octahedrons within which the cations are located, i.e. produce an action equivalent to the action of hydrostatic pressure. From this point of view, the addition of Cr to V_2O_3 must be equivalent to the application of a negative pressure, as is verified experimentally by applying a compensating positive pressure.

Finally, we make one last remark. MoO_2 is a compensated metal, and the compound must retain this property under hydrostatic pressure. For this reason, the signs of the baric coefficients for the g , a , and d branches, corresponding to the hole and electron parts of the FS, respectively, should seemingly also be the same. It is surprising that the d branch has the opposite sign. It is likely that this circumstance could be explained by the large anisotropy of the variation with pressure in the corresponding part of the FS, as a result of which the sections corresponding to the d branch decrease with pressure, although the total volume of all electron parts of the FS increases. The anomalously high ratio of the baric coefficient to the change in the oscillation frequencies as a result of doping for the d branch likewise supports this proposition.

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¹⁾This remark was made by E. P. Vol'skii while discussing the results of the present work.

¹⁾E. P. Vol'skii and V. M. Teplinskii, Zh. Eksp. Teor. Fiz. 63, 1048 (1972) [Sov. Phys. JETP 36, 550 (1973)].

²⁾E. P. Vol'skii and V. M. Teplinskii, Zh. Eksp. Teor. Fiz. 69, 733 (1975) [Sov. Phys. JETP 42, 373 (1976)].

³⁾N. B. Brandt and M. V. Razumenko, Zh. Eksp. Teor. Fiz. 39, 276 (1960) [Sov. Phys. JETP 12, 198 (1961)]; N. B. Brandt and L. G. Lyubutina, Zh. Eksp. Teor. Fiz. 52, 686

- (1967) [Sov. Phys. JETP 25, 450 (1967)].
- ⁴N. B. Brandt, R. Muller, and Ya. G. Ponomarev, *Zh. Eksp. Teor. Fiz.* 71, 2268 (1976) [Sov. Phys. JETP 44, 1196 (1976)]; Z. Altounian and W. R. Datars, *Can. J. Phys.* 53, 459 (1975).
- ⁵L. A. Klinkova and E. D. Skrebkova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 13, 463 (1977).
- ⁶L. A. Klinkova and E. D. Skrebkova, *Izv. Akad. Nauk SSSR, Neorg. Mater.* 13, 2180 (1977).
- ⁷B. G. Brandt and A. C. Skapski, *Acta Chem. Scand.* 21, 661 (1967); A. Magnelli and G. Andersson, *Acta Chem. Scand.* 9, 1378 (1955); D. Colaitis, C. Lecaille, and D. Lebas, *Rev. de Chim. Min.* 9, 709 (1972); John M. Longo and Peder Kierkegaard, *Acta Chem. Scand.* 24, 420 (1970).
- ⁸L. A. Klinkova and E. D. Skrebkova, *Zh. Neorg. Khim.* 23, 180 (1978).
- ⁹E. N. Lysenko, *Príb. Tekh. Eksp.* 1, 168 (1978); Maxfield and Merrill, *Review of Scientific Instruments* 36, No. 8 (1965).
- ¹⁰H. H. Sample and L. G. Rubin, *Cryogenics* 17, 597 (1977); L. G. Rubin, D. R. Nelson, and H. H. Sample, *Review of Scientific Instruments* 46, 1624 (1975).
- ¹¹V. M. Teplinskii, *Inventor's Certificate SSSR*, N. 468203, kl. G-01R33/08, 1973, published in *Otkrytiya, izobriteniya, promyshlennye obraztsy, tovarnye znaki, byulleten'* No. 15, 1975.
- ¹²R. C. Young, *Rep. Prog. Phys.* 40, 1123 (1977); A. P. Cracknell and K. C. Wang, *The Fermi Surface*, Oxford U. Press, 1973.
- ¹³P. M. Holtham and D. Parsons, *J. Phys. F* 6, 1481 (1976); I. M. Templeton and P. T. Coleridge, *J. Phys. F* 5, 1307 (1975).
- ¹⁴O. Sävborg, *Mater. Res. Bull.* 11, 275 (1976).
- ¹⁵E. P. Vol'skii, A. G. Gapotchenko, E. S. Itskevich, and V. M. Teplinskii, *Zh. Eksp. Teor. Fiz.* 76, 1670 (1979) [Sov. Phys. JETP 49, 848 (1979)].
- ¹⁶McWhan and J. P. Remeika, *Phys. Rev. B* 2, 3734 (1970).
- ¹⁷E. P. Vol'skii, "Metal-Insulator phase transitions in transition metal oxides," Preprint, Institute of the Physics of Metals of the Academy of Sciences of the USSR, Sverdlovsk, 1974.

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Phase diagram of superfluid He³

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The thermodynamics of liquid He³ is investigated in the vicinity of the line of the phase transitions into the superfluid state. Neglecting the weak dipole-dipole interaction, renormalization-group equations that describe the evolution of the effective coupling constants in the critical region are derived. It is shown that these equations have no stable fixed points, so that the superfluid phase transitions in liquid He³ should in principle be of first order. Computer solution of the renormalization group equations has established that allowance for the interaction of the critical fluctuations can lead in a number of cases to a reversal of the sign of the difference of the free energies of the phases *A* and *B*, i.e., to expansion of the region of thermodynamic stability of one of the two superfluid states. Specifically, fluctuation stabilization of the Anderson-Morel phase should be observed in He³.

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1. INTRODUCTION

In the present paper we investigate the influence of the critical fluctuations of the order parameter, which correspond to superfluid phase transitions in superfluid He³, on the structure of the phase diagram of this Fermi liquid. It is known that below 2.6 mK and in the absence of an external magnetic field liquid He³ can exist in one of two superfluid modifications (see, e.g., Ref. 1). Both modifications were described theoretically back in the early sixties, i.e., long before they were experimentally observed. The first to attract the attention of the theoreticians was a phase characterized by an anisotropic gap in the spectrum of the elementary excitations;² it is presently known as the *A* phase. This was followed by the development of a theory of the superfluid state with isotropic gap, the *B* phase,³ and the basis for the observation of the structure of this phase

was the fact that in the weak-coupling approximation the *B* phase has a lower free energy than the *A* phase.

The discovery, after ten years, and identification of the anisotropic superfluid state of liquid He³ (Ref. 4) have cast doubts on the applicability of a theory of the BCS type in this case.⁵ To explain the experimentally observed thermodynamic stability of the *A* phase in a definite range of temperatures and pressures, Anderson and Brinkman went beyond the framework of the weak-coupling approximation and took into account the renormalization of the vertex due to the exchange of the spin (noncritical) fluctuations.⁵ It turned out that paramagnon exchange does indeed stabilize the phase *A*, and allowance for the sixth-order invariants in the expansion of the free energy explains, at least qualitatively, the structure of the phase diagram of liquid He³ as a whole.⁶ We recall that this diagram contains two superfluid sec-