MAGNETOACOUSTIC INVESTIGATION OF THE FERMI SURFACE OF MOLYBDENUM

P. A. BEZUGLYĬ, S. E. ZHEVAGO, and V. I. DENISENKO

Physico-technical Institute for Low Temperatures, Academy of Sciences, Ukr.S.S.R.

Submitted to JETP editor June 24, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 1457-1462 (November, 1965)

The anisotropy of the oscillation periods of the geometrical resonance was investigated in molybdenum single crystals under the conditions of sound propagation along the principal crystallographic directions (ν = 200 Mc; T = 4.2°K; $\mathbf{H} \perp \mathbf{q}$). It is shown that the short-period oscillations, observed for $\mathbf{q} \parallel [100]$, give the dimensions of the electron surface Γ and the long-period oscillations are associated with small hole zones N, in accordance with Lomer's model.[10] The maximum dimensions of the hole regions N are 0.56×10^8 cm^{-1} and the minimum 0.42×10^8 cm^{-1}.

INTRODUCTION

THE success achieved in the preparation of pure transition metals of the chromium group (Cr, W, Mo) has made it possible to undertake in the last few years a number of experiments intended to investigate their electron structure. The measurements of the surface impedance under anomalous skin-effect conditions,[1] and the investigation of the behavior of the resistance of single-crystal samples in a magnetic field,[2,3] established that the electron structure of these transition metals could not be described within the framework of the model of almost-free electrons.

Later, Lomer[4] used the calculations of the electron structure of iron carried out by Wood[5] and suggested a single model for the Fermi surface of the bcc metals in the sixth group (Cr, Mo, W), which was found to be in qualitative agreement with the results of the magnetoacoustic investigations of tungsten[6] and the less complete magnetoacoustic measurements on molybdenum.[7]

However, according to the data on the de Haas–van Alphen effect in weak magnetic fields, obtained by Brandt and Rayne[8] for transition metals of the chromium group, only molybdenum was in very good agreement with Lomer's model.[4] The lack of agreement between the experimental data for chromium and Lomer's model was ascribed by Brandt and Rayne to the fact that the model did not allow for the antiferromagnetism of chromium. The doubling of the oscillation periods of the de Haas–van Alphen effect observed in tungsten, which did not agree with Lomer's model, was associated by Brandt and Rayne with the presence of a sufficiently strong spin-orbit coupling in tungsten, also not allowed for in Lomer's model. It should be mentioned that the presence of a strong spin-orbit coupling in tungsten was confirmed somewhat later by the experiments on the size effect.[9]

It follows that the single model of the Fermi surface proposed by Lomer for all the bcc transition metals of the chromium group can in fact be applied only to molybdenum. Later, Lomer proposed an improved model.[10]

Since the fragmentary experimental data published so far on the magnetoacoustic effects in molybdenum[7] do not make it possible to draw sufficiently reliable conclusions about the adequacy of Lomer's improved model of the Fermi surface,[10] it was of interest to investigate the magnetoacoustic effects in molybdenum in more detail. For this purpose, we studied the anisotropy of the oscillation periods of the geometrical resonance in transverse magnetic fields when the acoustic wave vector $\mathbf{q}$ was oriented along the principal crystallographic directions of a single-crystal sample of molybdenum.

MEASUREMENT TECHNIQUE AND THE PROPERTIES OF THE SAMPLES

To investigate the dependence of the absorption coefficient of ultrasound on the magnetic field, we used the pulse method described earlier.[11] The measurements were carried out using longitudinal ultrasound of 200 Mc frequency at two temperatures: T = 1.8°K in the case $\mathbf{q} \parallel [100]$ and T = 4.2°K in the case $\mathbf{q} \parallel [110]$ and [111].

The molybdenum samples were cut, by means of a thin carborundum disk, from a single-crystal rod which was first subjected to quadruple zone melting

using an electron beam, and which was characterized by R(293°K)/R(4.2°K) ≈ 3000. In the measurements we used cylindrical samples, ≈ 8 mm in diameter and with plane-parallel ends, the normal to which coincided with a principal crystallographic axis within 1°. The ends were ground parallel by hand, using abrasive powders and a grinding plate. The parallelism of the working surfaces was checked by means of a vertical optical lever (type IKV), while the orientation was verified by the x-ray back-reflection method. The thickness of the samples was: 5.48 mm for the [110] direction (sample No. 1); 5.07 mm for the [100] direction (sample No. 2); 3.39 mm for the [111] direction (sample No. 3).

In the case of sample No. 2, the data on the dependence of the absorption coefficient on the magnetic field were obtained by observing the behavior of the second pulse transmitted by the sample.

Owing to the rather strong absorption at helium temperature, in samples 1 and 3 we were able to observe only a single transmitted pulse in close proximity to the probing pulse. Therefore, to separate these pulses, we inserted, next to the sample and between the radiator and receiver piezoelectric quartz transducers, a delay unit consisting of a z-cut quartz slab, as was done in the investigation of the magnetoacoustic effects in aluminum. [12]

The values of the velocities of propagation of the longitudinal sound waves along the selected crystallographic directions, necessary for the determination of the dimensions of the Fermi surface in the k-space, were found from the data on the elastic constants at 0°K, which were measured right down to liquid helium temperatures, [13] and were assumed to be as follows

$$v([110]) = 6.53 \cdot 10^5 \text{ cm/sec};$$
$$v([100]) = 6.63 \cdot 10^5 \text{ cm/sec};$$
$$v([111]) = 6.49 \cdot 10^5 \text{ cm/sec}.$$

RESULTS OF MEASUREMENTS

The angular dependence of the oscillation periods of the absorption coefficient, recorded under the conditions $\mathbf{q} \perp \mathbf{H}$ on propagation of a longitudinal ultrasonic wave along the [110] axis, is shown in Fig. 1. It is evident from the polar diagram in Fig. 1 that, in different ranges of angles, three different oscillation periods were reliably recorded: short-period oscillations A and long-period oscillations B and C.

In general, the oscillatory behavior of the absorption coefficient for $\mathbf{q} \parallel [110]$ was observed for

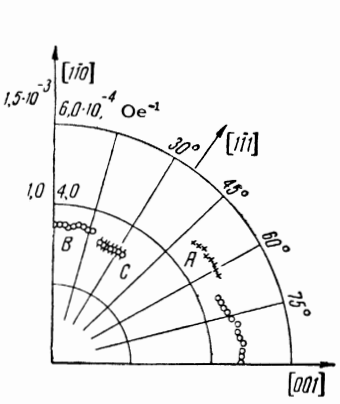

FIG. 1

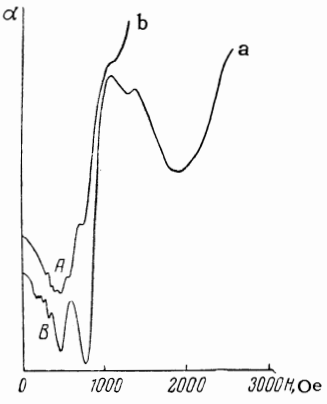

FIG. 2

FIG. 1. Dependence of the oscillation periods of the absorption coefficient on the magnetic field direction for the case $\mathbf{q} \parallel [110]$ and $\mathbf{H} \perp \mathbf{q}$. The direction of the magnetic field is measured from the $[1\bar{1}0]$ axis. The values of the oscillation periods of type A are given by the scale on the right, near the $[1\bar{1}0]$ axis; the values of the oscillations of B and C types are given by the scale on the left.

FIG. 2. Record of the dependences of the absorption coefficient on the magnetic field for $\mathbf{q} \parallel [110]$ and $\mathbf{H}$ directions making angles of ≈6° (curve a) and ≈54° (curve b) with the $[1\bar{1}0]$ axis.

all directions of the magnetic field, but for several directions of $\mathbf{H}$ it was not possible to analyze reliably the records and therefore the data for these directions of the field are not included in the polar diagram.

By way of illustration of the nature of the oscillatory dependence of the absorption coefficient on the magnetic field, Fig. 2 shows the record of $\alpha(H)$ for two cases: $\mathbf{H}$ forming an angle of ≈6° with the $[1\bar{1}0]$ axis (curve a); $\mathbf{H}$ forming an angle of 54° with the same axis (curve b).

Less complete information was obtained from the measurements of the anisotropy of the oscillation periods of the geometrical resonance when sound was propagated along the axes [100] and [111].

In the former case, in spite of the fact that the oscillations were observed for all the directions of the magnetic field and they were particularly clear for the directions of $\mathbf{H}$ close to the twofold axes, the periodicity of the oscillations in the reciprocal of the magnetic field was obtained only in that case when the magnetic field vector made angles not exceeding ≈20° with the fourfold axes. In this range of angles, the period $\Delta(1/H)$ ranged from $(0.90 \pm 0.03) \times 10^{-3}$ Oe^{-1} for $\mathbf{H} \parallel [010]$ to $(0.97 \pm 0.03) \times 10^{-3}$ Oe^{-1} for $\mathbf{H}$, making an angle of ≈20° with the same axis.

For $\mathbf{q} \perp [111]$, the record of the dependences of the absorption coefficient on the magnetic field was quite complex for all the directions of $\mathbf{H}$, indicating

that the observed patterns were due to the superposition of harmonic oscillations of several periods. The most reliably recorded period was $\Delta(1/H) = (0.68 \pm 0.05) \times 10^{-3}$ Oe^{-1}, whose value was practically constant for all the directions of H.

It should be mentioned that in order to establish the reproducibility of the oscillation patterns, the dependence $\alpha(H)$ was, in all cases, recorded twice for each direction of the sound and magnetic field, and the oscillatory behavior of $\alpha(H)$ was always found to have good reproducibility.

DISCUSSION OF RESULTS

The principal features of the electron structure of molybdenum, given by the initial[4] and improved[10] models of Lomer, are identical: all the constant-energy surfaces are closed and the number of holes is equal to the number of electrons. Moreover, the distribution, with respect to the center of the Brillouin zone, of the main electron and hole regions and of small hole regions is similar in both models.

In these circumstances, it is not surprising that the magnetoacoustic investigation of molybdenum carried out earlier[7] and the investigations of the de Haas–van Alphen effect in weak magnetic fields[8] were found to be in qualitative agreement with the initial Lomer model. However, the authors of the second paper[8] pointed out a discrepancy between the experimental data and the initial Lomer model, mainly in the form of the small electron packets located along the directions ⟨100⟩ and the incorrect dimensions of the hole regions in the direction ⟨110⟩. Obviously, these experimental data were used as the basis of Lomer's modification of his initial model.

Since the principal features of the initial and improved Lomer models are similar, and the difference between them reduces to the form and dimensions of the Fermi surface, on the one hand, and the positions of the small electron regions in the Brillouin zone, on the other, an experimental investigation should give a less ambiguous answer both in respect to the dimensions and in respect to the topology.

Figures 3a and 3b show the central Brillouin zone which includes the constant-energy surfaces of the electron zones (with the centers at Γ and X) and hole zones (with the centers at H and N). We note that the distance $\Gamma H = K_0 = 2\pi/a_0 = 199 \times 10^8$ cm^{-1}, where a_0 is the lattice constant.

We shall compare the obtained experimental data with Lomer's model, bearing in mind the fact that the oscillation period of the absorption coefficient of sound is related to the extremal radial dimensions of the Fermi surface along the $[\mathbf{q} \times \mathbf{H}]$ direction by the following expression

$$K = eS / 2\nu c\hbar\Delta(1/H),$$

where S is the velocity of propagation of the acoustic wave, e is the electronic charge, and ν is the frequency of sound.

Figure 4 shows, in accordance with the latest Lomer model, a part of the central section of the electron surfaces Γ and X by a plane perpendicular to the [110] axis, where points represent the values of the extremal dimensions of the Fermi surface found from the periods of the type A oscillations. As is evident from Fig. 4, the experimen-

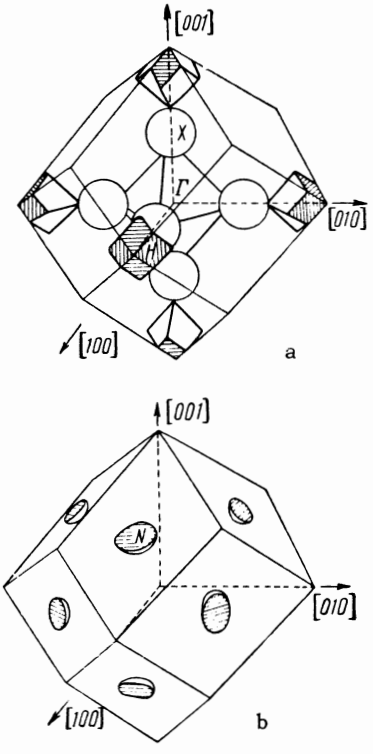

FIG. 3. Fermi surface of molybdenum according to Lomer's model.[10] a) Γ, X are the electron zones: H are the hole zones; b) N are the small hole zones.

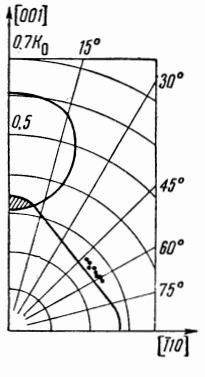

FIG. 4. Section of the surfaces of the electron zones X and Γ made by the plane K[110] = 0. The points indicate the data obtained from the values of the type A oscillation periods (cf. Fig. 1).

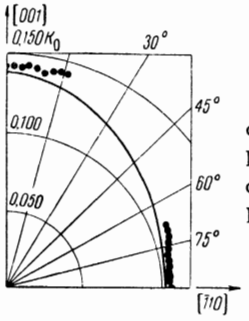

FIG. 5. Section of the Fermi surface of a hole zone N made by the plane K[110] = 0. The points show the data obtained from the values of the type B oscillation periods (cf. Fig. 1).

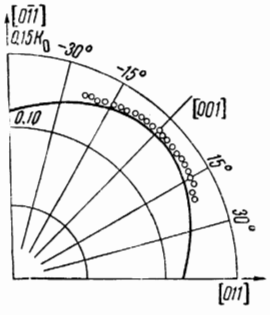

FIG. 6. Section of the Fermi surface of a hole zone N made by the plane K[100] = 0.5 K_0. The points give the experimental data.

tal data are in good agreement with the dimensions of the electron surface with its center at Γ. Unfortunately, the short-period type A oscillations could be observed reliably only for magnetic field directions within a limited range of angles and therefore it was not possible to establish the complete form of the central section of the main electron zone Γ.

The long-period type B oscillations, recorded for the same direction of the acoustic wave vector, fit quite satisfactorily (Fig. 5) the form and theoretical dimensions of the small hole regions N, elongated along the directions parallel to the [001] axis, intersected centrally by planes parallel to the (110) plane. It should be noted that the dimensions and form of the central section of the same hole regions N by planes parallel to the (100) plane are also in good agreement with the periods of oscillations measured under the conditions $\mathbf{q} \parallel [100]$ (cf. Fig. 6) with the directions of **H** making angles up to 20° with the direction [010]. Thus, the measurements carried out for $\mathbf{q} \parallel [110]$ and $\mathbf{q} \parallel [100]$ establish quite reliably the maximum and minimum dimensions of the hole regions N, which amount to

$$d_{max} = 0.56 \cdot 10^8 \text{ cm}^{-1}, \qquad d_{min} = 0.42 \cdot 10^8 \text{ cm}^{-1}.$$

Unfortunately, the experimental points referring to the small hole regions do not cover the whole quadrant and, therefore, we cannot establish completely the shape of these regions. However, from the fact that the shape and dimensions of the central section of a region N are identical for $\mathbf{q} \parallel [110]$ and $\mathbf{q} \parallel [100]$, it follows that this hole surface N is probably a surface of revolution. The maximum cross sectional area of such surfaces is, according to our data, 0.20 Å^{-2}. The same extremal area, found from the de Haas–van Alphen effect investigations,[8] is 0.23–0.25 Å^{-2}.

The oscillations of type C, observed under the conditions $\mathbf{q} \parallel [110]$, and the oscillations recorded under the condition $\mathbf{q} \parallel [111]$, are evidently due to the electron surfaces X, lying along the ⟨100⟩ axis and intersecting, in accordance with Lomer's model, the Γ surface. This is supported by the fact that the diameter of these surfaces, estimated from the oscillation period, is $(0.60–0.72) \times 10^8$ cm^{-1}, which is therefore greater than the actual maximum dimension of the hole regions N.

The results of the investigation of the de Haas–van Alphen effect[8] also support indirectly the existence of the electron surfaces X. In fact, the main result of this investigation, as far as molybdenum was concerned, was to establish the existence of small regions flattened along the directions ⟨100⟩, whose shape and dimensions could be explained by assuming the presence of the electron surfaces X along the ⟨100⟩ axis, the latter surfaces intersecting the surface Γ whose diameter was in agreement with the results of the present work.

Thus, our investigation is in good agreement with the data of earlier experimental studies[7,8] and gives additional information on the electron structure of molybdenum, indicating that the later Lomer model is more correct.

[1] E. Fawcett and D. Griffiths, J. Phys. Chem. Solids **23**, 1631 (1962).
[2] E. Fawcett, Phys. Rev. Letters **7**, 370 (1961).
[3] E. Fawcett, Phys. Rev. **128**, 154 (1962).
[4] W. M. Lomer, Proc. Phys. Soc. (London) **80**, 489 (1962).
[5] J. H. Wood, Phys. Rev. **126**, 517 (1962).
[6] J. A. Rayne, Phys. Rev. **133**, A1104 (1964).
[7] C. K. Jones and J. A. Rayne, Phys. Letters **8**, 155 (1964).
[8] G. B. Brandt and J. A. Rayne, Phys. Rev. **132**, 1945 (1963).
[9] W. M. Walsh, Jr. and C. C. Grimes, Phys. Rev. Letters **13**, 523 (1964).
[10] W. M. Lomer, Proc. Phys. Soc. (London) **84**, 327 (1964).
[11] A. A. Galkin and A. P. Korolyuk, PTÉ, No. 6, 199 (1960).
[12] Bezuglyĭ, Galkin, and Pushkin, JETP **44**, 71 (1963), Soviet Phys. JETP **17**, 50 (1963).
[13] F. H. Featherston and J. R. Neighbours, Bull. Am. Phys. Soc. **8**, 194 (1963).

Translated by A. Tybulewicz
186