THE SHUBNIKOV–DE HAAS EFFECT IN TELLURIUM

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An experimental study of the Shubnikov–de Haas effect has been carried out in tellurium single crystals with concentrations of $(4-10)\times 10^{16}$ cm^{-3}. Analysis of these results indicates that the equal-energy surface for the concentration region investigated corresponds to the four-ellipsoid model with account of spin. Possible types of structures satisfying the experimental results are discussed.

INTRODUCTION

INVESTIGATION of the galvanomagnetic properties of tellurium with a low carrier concentration (10^{14}–10^{15} cm^{-3}) allows us to conclude that in this case we can use the ellipsoid of revolution as a model in first approximation for the equal-energy surface of holes.[1] However, the method of investigation used here cannot solve the problem of the number of such ellipsoids in the valence band. A method which makes it possible to obtain the answer to this question is the study of the quantum oscillations of the electrical resistance in a magnetic field—the Shubnikov–de Haas effect (SdH). The origin of these oscillations is the consequence of the change of positions in the quantum Landau levels $\epsilon_n = \hbar\Omega(n + \frac{1}{2})$ relative to the Fermi level $\zeta(H)$ for a change in the magnetic field (Ω is the cyclotron frequency). For the possibility of observation of the SdH effect, three conditions must be satisfied: 1) a strong degeneracy, $\zeta(H)/kT \gg 1$; 2) a strong magnetic field, $nH/c > 1$; 3) sufficiently low temperature, $kt \ll \hbar\Omega$.

Choice of the range of concentration of current carriers in the samples studied was set in our case by the values of the maximum constant field (38 kG) and the minimum temperature (1.5°K) at our disposal, and also by the condition of the possibility of the observation of oscillations near the first Landau level, where the ratio of the amplitude to the background is a maximum. The range of concentration of holes in tellurium of 4×10^{16}–10^{17} cm^{-3} satisfies these conditions. Choice of this range of concentrations was accomplished for the reason that the anomalous features of the galvanomagnetic properties that are characteristic for tellurium with very low concentration of holes did not appear for such samples.[1]

In the general case of a closed Fermi surface, the period of SdH oscillations in the reciprocal field $\Delta(1/H)$ makes it possible to determine the extremal cross sections of this surface S_φ perpendicular to the magnetic field:

$$\Delta\left(\frac{1}{H}\right)_\varphi = \frac{2\pi e}{\hbar c}\frac{1}{S_\varphi} \qquad (1)$$

(φ is the angle between the direction of the magnetic field and the crystallographic axis C_3). Rotating the magnetic field relative to the crystallographic axes through various angles, one can determine a set of Fermi surface cross sections in different directions and thus establish the complete form of this surface. An investigation was carried out in[2,3] of the SdH effect in tellurium for pulsed magnetic fields for a carrier concentration $p > 10^{17}$ cm^{-3}. In the present research, a study has been carried out in a constant magnetic field, which makes it possible to obtain results with greater accuracy. A comparison of the data of these researches will be given below.

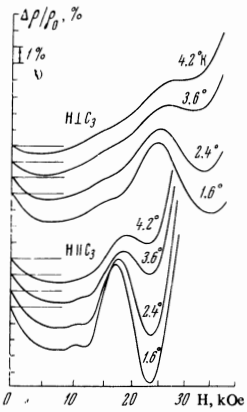

FIG. 1. Dependence of the transverse magnetoresistance ($\mathbf{I}\perp\mathbf{H}$) of a single crystal of tellurium – sample No. 3 – on the intensity of the magnetic field for two directions of the field and various temperatures.

EXPERIMENTAL RESULTS AND THEIR DISCUSSION

Tellurium single crystals, obtained by the Czochralski method with the direction of growth along the principal C_3 axis of the crystal (the "longitudinal orientation," $\mathbf{I}\parallel C_3$) and perpendicular to C_3 (the "transverse" orientation, $\mathbf{I}\perp C_3$), were investigated. The total concentration of current carriers p was determined from the Hall coefficient R in weak and strong (up to 38 kG) magnetic fields: $p = 1/ecR$. The alloying impurity is antimony. The signal, generated by a change in the resistance in the magnetic field, is amplified by a photoelectric amplifier F116/1 and recorded by an x-y plotter. To make weak peaks clear, subtraction of a voltage proportional to the magnetic field was carried out and the resultant difference signal amplified. The resulting $\rho(H)$ curve was found by the graphic averaging of the $\rho(H)$ and $\rho(-H)$ curves.

The cylindrical symmetry of the Fermi surface studied relative to the C_3 axis was first established by rotation of the magnetic field around the principal axis C_3 of the crystal for crystals of longitudinal and transverse orientation.

Figure 1 shows the dependence of the transverse

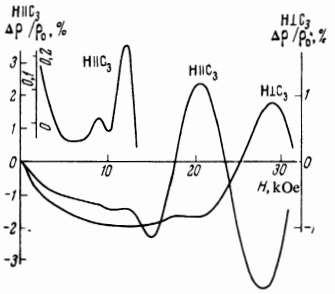

FIG. 2. Dependence of the transverse magnetoresistance of tellurium on the intensity of the field at 1.5°K for one of the samples of transverse orientation. In the upper corner the intitial part of the curve for the case $\mathbf{H} \parallel C_3$ is shown in enlarged form with the linear dependence on the field subtracted out.

magnetoresistance ($\mathbf{H} \perp \mathbf{I}$) for a single crystal of tellurium—sample No. 3 (see Table I)—for the case $\mathbf{I} \perp C_3$ for two orientations of the magnetic field relative to the C_3 axis and at different temperatures. It is seen that the amplitude of the oscillations increases with decrease in the temperature and has a larger value for $\mathbf{H} \parallel C_3$.

Further analysis of the quantum oscillations in tellurium will be given for samples with transverse orientations, making it possible under the condition $\mathbf{H} \perp \mathbf{I}$ to change the angle between $\mathbf{H}$ and C_3 and revealing a very large amplitude of oscillations in comparison with samples with longitudinal orientations. Identifications of the field for which the Fermi level intersects with the Landau level were made from the maxima of the $\rho(H)$ curves[4]. As an example, the result of a study of two other samples of tellurium at $T = 1.5°K$ is shown in Figs. 2 and 3. The period for the reciprocal field $\Delta(1/H)$ was determined from the three clearly discernible maxima on the curve for the magnetoresistance.

For analysis of the experimental data, the ellipsoid of revolution, which has its foundation in the study of galvanomagnetic properties,[1] was taken as a test model of the constant energy surface. For ellipsoid of revolution and for a quadratic dispersion law, the following is obtained from the general expression (1):

$$\Delta\left(\frac{1}{H}\right) = \frac{2e}{\hbar c}\left(3\pi^2 \frac{p}{N/2}\right)^{-2/3}\left(\frac{m_3}{m_1}\right)^{1/3}\left(\cos^2\varphi + \frac{m_1}{m_3}\sin^2\varphi\right)^{1/2} \qquad (2)$$

where m_3 and m_1 are the components of the effective mass tensor in directions parallel and perpendicular to the C_3 axis, N is the total number of equivalent ellipsoids in the band. A formula determining the position of the maximum corresponding to the intersection of the Fermi level with the first Landau level ($1/H_{max}$) differs from (2) only by a constant factor. Inasmuch as complete removal of spin degeneracy can occur in tellurium, it is convenient to consider just the number of equivalent ellipsoids N, keeping it in mind that the degeneracy can be removed both for spin and for the

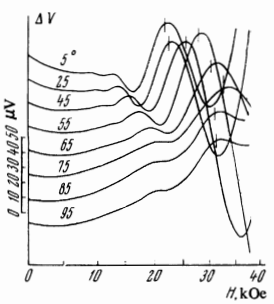

FIG. 3. Dependence of the transverse magnetoresistance of tellurium on the field for different angles between H and C_3, without commutation of the field; the sample No. 5, $T = 1.5°K$. The value of the measured signal ΔV, which is proportional to $\Delta\rho/\Delta\rho\partial$ is plotted along the ordinate. The position of the first maximum of the oscillating component of $\rho(\mathbf{H})$ is indicated by the vertical lines.

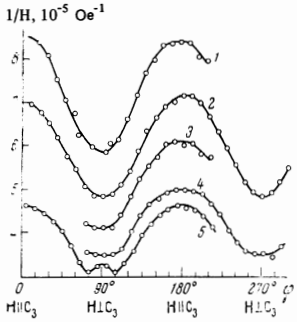

FIG. 4. Angular dependence of the position of the first maximum (n = 1) of the curves of the transverse magnetoresistance ($\varphi = \sphericalangle(C_3, \mathbf{H})$, $T = 1.5°K$). Here and in the following drawings, the numbers on the curves correspond to the number of the samples.

location of the extrema at the equivalent points of the Brillouin zone.

The study of the angular dependence for the period and the first maximum makes it possible to establish whether the model of an ellipsoid of revolution with a quadratic dispersion law corresponds to the experimental data, and also possible to obtain the ratio m_1/m_3. Figures 4—6 show the results of such an analysis for all the single crystals studied. The linearity of the drawings of Figs. 5 and 6 confirm the acceptability of the given model, at least for the first four samples with concentrations up to $p = 8 \times 10^{16}$ cm^{-3}.

The mean value of the ratio obtained with the help of these graphs, $m_3/m_1 = 2.2 \pm 0.1$, and the concentration known from Hall effect measurements were used for the determination of the number of equivalent ellipsoids N from the period of (2). The mean value

$$N/2 = 2.0 \pm 0.15$$

represents the principal result of the present research.

Table I gives the basic characteristics of the samples studied and the results of the calculation of the principal parameters.

The value $m_3/m_1 = 2.2$ obtained in the present work agrees with the results of the study of cyclotron resonance on samples with $p \approx 10^{13}$ cm^{-3}[5,6] and differs strongly from the value of this same ratio obtained in the study of the SdH effect in pulsed fields on samples with $p \sim 10^{18}$ cm^{-3}: $m_3/m_1 = 4.3$—4.8.[2,3] The reason for this divergence must be connected with the difference in the concentrations of holes in the samples studied.

Braun and Landweher,[2] investigating the SdH effect in single crystals of tellurium with concentrations of $1 \times 10^{17} - 6 \times 10^{18}$ cm^{-3}, limit their conclusion to the establishment of rotational symmetry of the Fermi

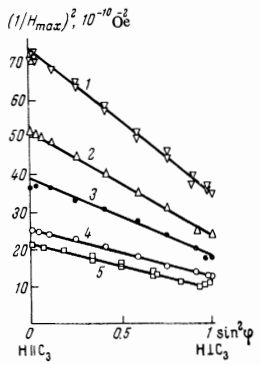

FIG. 5. Dependence of the position of the first maximum of the curves of magnetoresistance on $\sin^2\varphi$. The straight lines correspond to Eq. (2). $T = 1.5°K$.

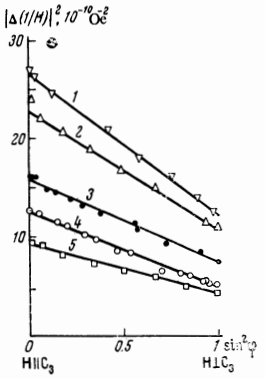

FIG. 6. Dependence of period of oscillation (in the scale of the reciprocal field) on $\sin^2\varphi$. The straight lines correspond to Eq. (2), T = 1.5°K.

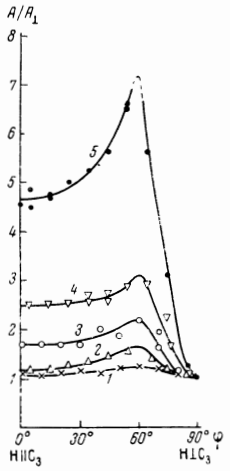

FIG. 7. Angular dependence of the amplitude of the first maximum, T = 1.5°K.

surface, which resembles a barrel in shape. Guthman and Thuilier[3] studied samples with concentrations of 10^{17}—10^{18} cm^{-3}. In their brief note,[3] these authors remark that their results correspond to the ellipsoidal model. But in this case, from their measurements of the period of oscillations and the ratio $m_3/m_1 \approx 4$, a value is obtained for the number of ellipsoids N that is close to two. And in the present work, for concentrations of 1×10^{17} cm^{-3}, the angular dependence of the position of the first maximum was distorted, indicating the absence of the assumed model (Figs. 3—5). The reasons for such complications can be either the topological features of the Fermi surface for filling of the zone above 10^{17} cm^{-3} or anisotropies of a nonquadratic dispersion law, which is found only for $p \gtrsim 10^{17}$ cm^{-3}.

Another peculiarity, whose origin is unknown to date, appears in the study of the dependence of the amplitude of the first maximum on the angle φ, which is shown in Fig. 7. It is seen that a change in the amplitude of this maximum has a nonmonotonic character. The dependence shown in Fig. 7 of the reduced value of the amplitude on the angle φ for different samples has a maximum for $\varphi = 60°$, and is the sharper the higher the concentration of holes in the sample.

CONCLUSIONS

Let us consider what conclusions can be drawn on the band structure of tellurium, starting out from the total number of equivalent extrema N = 4 that was determined above.

The cylindrical symmetry of the equal-energy surfaces in tellurium, which is confirmed both by the present measurements and by other data,[1,2,5,6] shows that the extremum of the valence band is found either on the Δ axis or on the lateral edges of the Brillouin zone, W, shown in Fig. 8. The presence of direct optical transitions[7] shows that the extrema are evidently found at points of zero slope, i.e., in the notation of[8] (Fig. 8), at the points $\Gamma(k_Z = 0)$ or $Z(k_Z = b/2)$ on the Δ axis, or the points B(D) $(k_Z = 0)$ or M(P) $(k_Z = b/2)$ on the W axis. The points on the Δ axis, particularly Γ and Z, are points of zero slope only for the doubly degenerate double valued representations $\overline{\Gamma}_3$ or $\overline{Z}_3$, and are not such for the nondegenerate representations $\overline{\Gamma}_1$ and $\overline{\Gamma}_2$ or $\overline{Z}_1$ and $\overline{Z}_2$, which combine under time inversion. At the points on the W axis, for example, B and M, the corresponding representations $\overline{B}_1$ and $\overline{B}_2$ or $\overline{M}_1$ and $\overline{M}_2$ do not join together. These representations appear as the result of spin-orbital splitting of the fourfold degenerate representation $B_3 \rightarrow \overline{B}_1 + \overline{B}_2 + \overline{B}_3$, for which the point B, as also M, Γ, and Z, is not a point of zero slope. However, if the spin splitting is comparable with the distance to the nearest terms, then the representations $\overline{B}_1$ and $\overline{B}_2$, as also $\overline{B}_3$ (or $\overline{M}_1$, $\overline{M}_2$, $\overline{M}_3$) can correspond to the extremum of the bands. Here the points B and D, as also M, and P are connected by virtue of time reversal, if at the point M the extremum corresponds to the representation M_1 and at the point B the same energy corresponds to B_2 and conversely.

The value N = 4 generally eliminates the location of the extrema at the points Γ and Z, where N = 2. If the extrema are located at the points B or M or at an arbitrary point on the Δ axis, then for N = 4 the doubly degenerate (in the spin) representations $\overline{B}_3$, $\overline{M}_3$ or $\overline{\Delta}_3$ correspond to the top of the valence band. In this case, the surfaces of constant energy near the extremum are non-ellipsoidal and can have the shape of a torus.[9] However, this should not be known from measurements of the SdH oscillations, since the non-

Table I. Fundamental characteristics of the single crystals of tellurium studied. Transverse orientation ($I \perp C_3$); T = 1.5°K

No. of sample	$p \times 10^{-16}$, cm^{-3}	$R\sigma$ cm^2/V-sec	$\frac{uH_{max}}{c}$	$\Delta\left(\frac{1}{H}\right)_{\parallel} \times 10^5$, Oe^{-1}	$\Delta\left(\frac{1}{H}\right)_{\perp} \times 10^5$, Oe^{-1}	$\frac{m_3}{m_1}$	$\frac{N}{2}$	$\frac{\zeta}{KT}$
1	4.3	2250	0.26	5.2	3.48	2.2	1.9	13.8
2	5.7	3550	0.5	4.76	3.26	2.1	2.2	16.5
3	6.3	3700	0.6	3.98	2.72	2.1	1.9	18.0
4	8.0	5500	1.1	3.55	2.24	2.5	1.9	21.0
5	11	4300	0.9	3.04	2.1	2.1	2.2	26.0

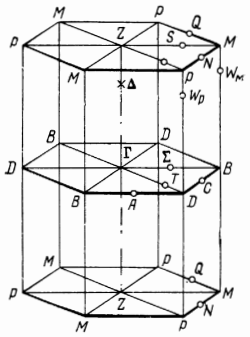

FIG. 8. Brillouin zone for tellurium

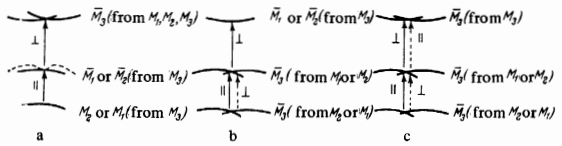

FIG. 9. Possible schemes of distribution of zones satisfying the selection rules established in [7,11].

ellipsoidal character appears only up to energies $\lesssim 10^{-4}$ eV,[10] since the Fermi energy for our samples exceeded 2×10^{-3} eV, as is seen from Table I.

In this case, if the extrema were situated at an arbitrary point of the W axis, the non-degenerate double-valued representations $\overline{W}_1$ or $\overline{W}_2$ would correspond to the value N = 4. Here, if the representation W_1 corresponds at the point k_0 to the minimum energy of the hole, then the representation at the point $-k_0$ is W_2.

Optical measurements[7,11] show that in tellurium, direct optical transitions are permitted between the valence band and the conduction band for polarization perpendicular to the C_3 axis and are forbidden for polarization that is parallel to that axis. Transitions between neighboring valence bands, on the other hand, are permitted for parallel polarization and are forbidden for the perpendicular case. If it is assumed that the transitions which are possible only with account of spin-orbit interaction have approximately the same intensity as those permitted for the ordinary representations, then it follows from the selection rules given in Table II that the only possible scheme that is in accord with these experimental data is the scheme shown in Fig. 9a, which was proposed by Hulin,[8] and the corresponding location of the extrema at the points B or M. However, this scheme corresponds to the value N = 2. If the intensity of the half-forbidden transitions, i.e., transitions which are permitted only because of relativistic effects, indicated in Fig. 9 by the dots, is small, then the optical data permit schemes 9b and 9c, which correspond to N = 4.

We note that the scheme 9c could be important also for location of the extrema at the points Γ and Z, but in this case, as is shown above, N = 2. Evidently, variant 9c is less probable, since the "half-forbidden" interband transitions ought to appear, since they appear, for example, in materials of the PbTe group.[12] However, the less intense intraband "half-forbidden" transitions, which correspond to the scheme of 9b, could also be unnoticed. Thus, if the extrema of the both bands are actually found in one of the points of zero slope, then the value N = 4 shows that the points B or M appear at these points, and the distribution of levels at these points corresponds to schemes 9b and 9c.

However, the results of the most recent calculations of Picard and Hulin[13] reveal still another possibility of interpretation of these data. According to their calculations, the terms $\overline{M}_1$ or $\overline{M}_2$ correspond to the top of the valence band, but the extrema are found not at the point M itself, but close to it and displaced in comparison with the energy at this point by the amount Δ of the order of hundredths of electron volts. For such a structure of the bands (shown in Fig. 9a by a dotted curve), the value N = 4 although their Fermi energy does not exceed Δ; for higher energies, N should approach 2, which can explain the result of the research of Guthman and Thuilier mentioned above.[3] Inasmuch as this transition takes place in the concentration range from 10^{17}–10^{18} cm^{-3}, the depth of the minimum Δ should lie in the range $(0.3–1.5) \times 10^{-2}$ eV.

If the valence band actually has extrema close to the point M, then, first, indirect optical transitions should be observed and, second, the longitudinal effective mass should depend strongly on the energy. Although a strong increase in the mass of the holes in observed in the experiment with increase in their concentration and temperature (P. Grosse, M. Lutz, private communication), just the transverse mass changes very rapidly and not the longitudinal. The magneto-optical measurements also do not reveal any noticeable non-parabolic character of the valence band (K. Winzer and P. Grosse, private communication). Therefore, for the final solution of the problem of the structure of the valence band, more careful investigations of the optical properties of tellurium near the absorption edge are necessary.

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Table II. Selection Rule for representations at the points Γ, Z, B, M, Δ, and W

	Single-valued				Double-valued		
	M_1	M_2	M_3		$\overline{M}_1$	$\overline{M}_2$	$\overline{M}_3$
M_1	—	∥	⊥	$\overline{M}_1$	—	∥	⊥
M_2	∥	—	⊥	$\overline{M}_2$	∥	—	⊥
M_3	⊥	⊥	⊥, ∥	$\overline{M}_3$	⊥	⊥	⊥, ∥

⊥ – transitions allowed for $E \perp C_3$; ∥ – transitions allowed for $E \parallel C_3$.

[1] R. B. Parfen'ev, A. M. Pogarskiĭ, I. I. Farbshteĭn and S. S. Shalyt, Fiz. Tverd. Tela 4, 3596 (1962) [Soviet Phys.-Solid State 4, 2630 (1963)]; A. M. Pogarskiĭ, I. I, Farbshteĭn and S. S. Shalyt, Fiz. Tverd. Tela 7, 2383 (1965) [Soviet Phys.- Solid State 7, 1925 (1966)].

[2] E. Braun and J. Landweher, J. Phys. Soc. Japan 21, Suppl. 380 (1966).

[3] C. Guthman and J. M. Thulier, Comp. rend. (Paris) **263**, 303B (1966).
[4] S. S. Shalyt and A. L. Éfros, Fiz. Tverd. Telo. **4**, 1233 (1962) [Soviet Phys.-Solid State **4**, 903 (1962)].
[5] J. M. Mendum and R. N. Dexter, Bull. Amer. Phys. Soc. 9, 632 (1964).
[6] J. C. Picard and D. L. Carter, J. Phys. Soc. Japan **21**, Suppl. 202 (1966).
[7] C. Rigaux and G. Drilhon, J. Phys. Soc. Japan **21**, Suppl., 193 (1966).
[8] M. Hulin, J. Phys. Chem. Solids **27**, 441 (1966).
[9] G. E. Pikus, Fiz. Tverd. Tela **3**, 2809 (1961) [Soviet Phys. Solid State **3**, 2050 (1962)].
[10] V. A. Noskin, I. I. Farbshteĭn, and S. S. Shalyt, Fiz. Tverd. Telo (in press).
[11] R. S. Caldmell and H. J. Fan, Phys. Rev. **114**, 664 (1959), P. Grosse and M. Selders, Phys. Kondens, Materie **6**, 126 (1967), V. M. Korsunskiĭ and M. L. Lisitsa, Fiz. Tverd. Tela **2**, 1619 (1960) [Sov. Phys.-Solid State **2**, 1466 (1960)].
[12] S. L. Mitchell and E. D. Palik, Proc. Phys. Conf. of Semicond. Paris, 1964, p. 325.
[13] M. Picard and M. Hulin, Phys. Stat. Solidi **23**, 563 (1967).

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