rotates in the (001) plane.

Oscillations whose period is half as large appear on the experimental curves shown in the figure at definite values of  $\xi$ . We note that under the conditions of these experiments the oscillation period  $\Delta \gamma$  differs from the  $\chi^{\rm OSC}$  period by a negligibly small amount. The causes of so large a relative amplitude of the second harmonic remain unclear to us. A simple calculation of the terms of order  $(\Delta k)^2$  and  $(\Delta \gamma)^2$  in the expansion of  $\Delta Z$  gives a value  $\sim 0.1$ for the ratio of the amplitude of the second harmonic to the first. At the same time, the higher harmonics in the periodic dependence of the susceptibility and of the conductivity on the magnetic field are decreased by a temperature coefficient  $\exp(-\alpha T) \sim 0.03$  at T = 1.4°K. Here α is a certain coefficient, whose value was determined from the temperature dependences of the amplitudes of the oscillations at  $\hat{H} \parallel [100]$  and  $\hat{k} \parallel [100]$ . The value of  $\alpha$  is the same for the oscillations  $\Delta k$  and  $\Delta \gamma$  and corresponds to an effective mass  $m^* = 0.4 m_{\odot}$  (m<sub>o</sub> is the mass of the free electron). Other experimental data [8, 11] give at this orientation a value m\* = 0.27mo. It should be noted that helicon absorption oscillations were observed at T <  $2.5^{\circ}$ K (see Fig. 2), and the amplitude of the oscillations  $\Delta$ k increased more slowly when the temperature was reduced below 2.5°K than would follow from the theoretical relation for the de Haas - van Alphen effect [9]. The reason for the deviations lies apparently in the incomplete allowance for the factors influencing the impedance oscillation amplitude.

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- E. P. Vol'skii and V. T. Petrashev, ZhETF Pis. Red. 7, 427 (1968) [JETP Lett. 7, 335 [1] (1968)].
- V. F. Gantmakher and I. P. Krylov, Zh. Eksp. Teor. Fiz. 49, 1054 (1965) [Sov. Phys.-[2] JETP 22, 734 (1966)].
- I. P. Krylov, ibid. 54, 1738 (1968) [27 (1968)].
  E. A. Kaner and V. G. Skobov, Usp. Fiz. Nauk 89, 367 (1966) [Sov. Phys.-Usp.9,480(1967)]
- V. G. Skobov and E. A. Kaner, Zh. Eksp. Teor. Fiz. 46, 1809 (1964) [Sov. Phys.-JETP [5] <u>19</u>, 1219 (1964)].
- E. A. Kaner and V. G. Skobov, ibid. <u>53</u>, 375 (1967) [26, 251 (1968)]. D. Shoenberg, Phil. Trans. <u>A255</u>, 85 (1962). [6]
- [7]
- [8] G. B. Brandt and J. A. Rayne, Phys. Rev. <u>132</u>, 512 (1967).
- [9] I. M. Lifshitz and A. M. Kosevich, Zh. Eksp. Teor. Fiz. 29, 730 (1955) [Sov. Phys.-JETP 2, 636 (1956)].
- [10] P. B. Miller and P. C. Kwok, Phys. Rev. 161, 629 (1967).
- [11] R. T. Mina and M. S. Khaikin, Zh. Eksp. Teor. Fiz. 48, 111 (1965) [Sov. Phys.-JETP 21, 75 (1965)].

## QUANTUM SIZE EFFECTS IN THIN TIN FILMS

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It is shown in a number of theoretical papers [1-3] dealing with quantum effects in thin films that the thermodynamic and kinetic characteristics of the elementary excitations in the films should oscillate when the thickness is varied, with a period equal to half the de-Broglie wavelength of the excitations. It follows from the latter that these effects can be

observed with sufficiently high probability in perfect films of semimetals and semiconductors. Indeed, the first objects of the experimental investigations were films of semimetals [4-6], in which oscillations of the conductivity and of the galvanomagnetic properties were observed upon variation of the film thickness. With respect to normal metals, it seems at first glance that these effects are only of theoretical interest, since the electrons in them have not only a small de-Broglie wavelength but also a small coefficient of specular reflection from the surface. Yet it is just in normal metals possessing superconductivity (unfortunately, superconducting semiconductor films have not yet been investigated) that we can expect to observe, besides the already known effects, also the new effect predicted by Blatt and Thompson [7] and considered also in later theoretical papers [8, 9], namely: the superconducting gap and the critical temperature should oscillate, with an attenuating amplitude, when the film thickness is varied. The effect is due to the nonmonotonic dependence of the state density on the film thickness. The period of the oscillations, just as in the preceding cases, is equal to half the de-Broglie wavelength.

We attempted to observe the Blatt-Thompson effect in tin films by using samples of variable thickness. The use of this method has made it possible to observe conductivity oscillations in antimony films [5], with a period  $\sim 28$  Å. This is not the limit of the capabilities of the method. Each measurement run was performed on one sample of variable thickness (70 mm long) with the aid of potential contacts spaced at constant intervals (2 mm). A shortcoming of the method is that the film thickness is not strictly constant in the section between two contacts. In addition, the surface of sample, naturally, has microscopic irregularities. On the whole, however, each section can be characterized by a certain effective average thickness that differs from the thickness of the neighboring section by a finite amount  $\delta d$  corresponding to the interval between the points on the experimental curves. Thus, the method ensures a steadily increasing thickness from any given section of the sample to the next one. The absolute value of the thickness was determined from the optical density S, a plot of S(d) being prepared beforehand by means of the independent method described in [10]. The error in the determination of the thicknesses amounts to 10%, and the sensitivity of the method reaches 1 Å.

The films were condensed in vacuum ( $\sim 10^{-6}$  Torr) on a glass substrate at 200°K. The substrate was cooled in order to decrease the critical thickness  $d_c$  ( $d_c = 200 - 250$  Å at room temperature), at the expense of a certain deterioration of the film structure. Electron-microscopic and electronographic investigations of control samples obtained on acetate lacquer under the same conditions has shown that the films have a clearly pronounced texture: the [100] direction is oriented normal to the film surface. The disorientation angle of the texture axis is  $\sim 10^{\circ}$ . The crystal dimension in the film plane exceeds the film thickness; the films are monocrystalline in thickness. Films having a thickness close to critical are not continuous, but are cut up by channels (labyrinths) with practically vertical walls.

Figure 1 shows the distribution of the relative resistance  $R/R_N$  of the individual sections of a sample of variable thickness at different temperatures. It is clearly seen that the distribution of  $R/R_N$  is an oscillating function of the film thickness. Similar

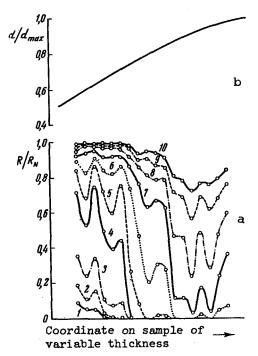


Fig. 1. a) Distribution of relative resistance  $R/R_N$  along a sample of variable thickness at temperatures (°K) 3.828 (1), 3.831 (2), 3.836 (3), 3.850 (4), 3.860 (5), 3.875 (6), 3.889 (7), 3.902 (8), 3.913 (9), and 3.920 (10); b) distribution of thickness along the sample.

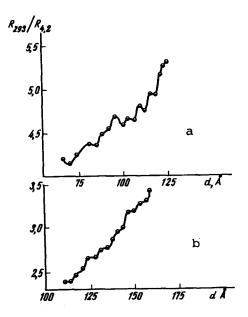


Fig. 3. Conductivity  $\sigma_{42}/\sigma_{293} = R_{293}/R_{42}$  vs. thickness of thin tin film.

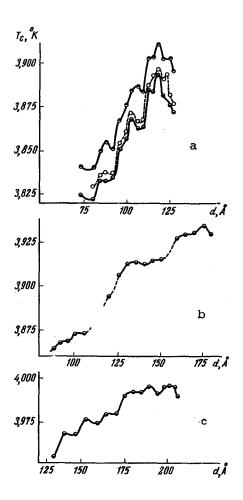


Fig. 2. Critical temperature vs. thickness of thin superconducting tin films. The critical temperature was determined by the following criteria:  $\bullet$  - R/R<sub>N</sub> = 0.5; O - R/R<sub>N</sub> = 0.1;  $\bullet$  - extrapolation of linear section of the transition.

measurements were made on a number of samples with a temperature interval (5 - 8) x  $10^{-3}$  oK. These data were used to plot  $R/R_N(T)$  for all sections of each of the investigated samples. The temperature of the superconducting transition was taken to be either the temperature corresponding to  $R/R_N = 0.5$  or  $R/R_N = 0.1$ , or else the value obtained by extrapolating the linear section of the transition to its intersection with the temperature axis.

It is seen from Fig. 2a that T<sub>C</sub> determined in accordance with any of the foregoing criteria is not a smooth function of the film thickness, but exhibits periodic oscillations. Figure 2a shows two types of oscillations of T<sub>C</sub>: a "coarse" structure with a period 15 Å, and oscillations having a small amplitude and half this period. The oscillations with period 15 Å were observed by us in all the investigated samples, and occurred in the region of larger thicknesses, where the thickness "pitch" did not make it possible to resolve the singularities having a smaller period (Fig. 2c). The amplitude of the oscillations of T<sub>C</sub> changes from sample to sample and is apparently determined by the quality of the film with respect to its structural characteristics and its surface quality. On the other hand, the positions of the extrema for different samples agrees very well in the overlapping regions of thickness, viz., maxima are observed as a rule at thicknesses that are multiples of 15 Å.

Besides the oscillations of  $T_c$ , the same samples revealed weak oscillations of conductivity when the thickness was varied; the more perfect the film, i.e., the larger the value of  $R_{293}/R_{4.2}$ , the more noticeable the oscillations (Figs. 3a and b). In those cases when the "pitch" of the points was sufficiently small, an oscillation period 7 - 8 Å was observed. The corresponding value of the Fermi quasimomentum in the [100] direction is

$$P_{\rm m} = h/2\Delta d = 4.7 \times 10^{-20} \text{ g cm/sec},$$

which agrees very well with the values obtained for tin by M. Khaikin [11], A. Korolyuk [12], and T. Olsen [13].

The values of the effective-mass-tensor component corresponding to the [100] direction are respectively  $0.5m_0$  and  $0.13m_0$  for the oscillation periods 7 and 15 Å (for a Fermi velocity  $v_F = 1 \times 10^8$  cm/sec [11, 14]). These values of m\* agree satisfactorily with some of the values given in [15].

These facts offer evidence that the observed oscillations of the critical temperature agree with the assumptions that follow from the work of Blatt and Thompson [7] with respect to the period of the oscillations. On the other hand, the small amplitude of the observed oscillations is apparently due to structural imperfections of the films and to the small fraction of the specularly reflected electrons in tin. It should be noted that the presence of size quantization can not explain in this case the course of the monotonic component of the thickness dependence of  $T_c$ , since its behavior turned out, unexpectedly to be the opposite in a number of samples of that expected from theoretical considerations [16]. The decrease of  $T_c$  with decreasing thickness of the film was observed earlier for uneven films obtained by low-temperature condensation [17]. In our measurements this decrease is negligible, and in one case we observed the usual behavior (an increase of  $T_c$  with decreasing thickness) as well as oscillations of  $T_c$  with a period 7 - 8 Å. Thus, the course of the monotonic component of  $T_c$  (d) is strongly affected by factors other than the quantum size effect.

- I. M. Lifshitz and A. M. Kosevich, Izv. AN SSSR, ser. fiz. 19, 395 (1955). [1]
- V. B. Sandomirskii, Zh. Eksp. Teor. Fiz. 52, 158 (1967) [Sov. Phys.-JETP 25, 101 (1967)] I. O. Kulik, ZhETF Pis. Red. 5, 423 (1967) and 6, 652 (1967) [JETP Lett. 5, 345 (1967)] [2]
- [3] and 6, 143 (1967)].
- [4] Yu. F. Ogrin, V. N. Lutskii, and M. I. Elinson, ibid. 3, 114 (1966) [3, 71 (1966)].
- [5]
- Yu. F. Komnik and E. I. Bukhshtab, ibid. 6, 536 (1967) [6, 58 (1967)]. Yu. F. Komnik and E. I. Bukhshtab, Zh. Eksp. Teor. Fiz. 54, 63 (1968) [Sov. Phys.-JETP [6] 27 (1968)].
- [7] I. M. Blatt and C.J. Thompson, Phys. Rev. Lett. 10, 332 (1963).
- V. Ya. Demikhovskii, Fiz. Tverd. Tela 7, 3600 (1965) [Sov. Phys. Sol. State 7, 2903 [8]. (1966)].
- [9] H. Raufuss, Z. Naturforsch. 22a, 985 (1967).
- L. S. Palatnik and G. V. Fedorov, Dokl. Akad. Nauk SSSR 113, 100 (1957). [10]
- [11] M. S. Khaikin, Zh. Eksp. Teor. Fiz. 41, 1773 (1961) [Sov. Phys.-JETP 14, 1260 (1962)].
- [12] A. P. Korolyuk, Dissertation, Khar'kov State University, 1961.
- [13] T. Olsen, The Fermi Surface (Proc. Int. Conf.), A. Harrison and W. B. Webb, ed. p. 237, 1960.
- [14] W. I. Tomash, Trans. Tenth Intern. Conf. on Low Temp. Physics, IIA, p. 266, 1967.
- [15] M. S. Khaikin, Zh. Eksp. Teor. Fiz. 42, 27 (1962) [Sov. Phys.-JETP 15, 18 (1962)].
- [16] B. Z. Kresin and B. A. Tavger, ibid. 50, 1689 (1966) [23, 1124 (1966)].
- [17] N. V. Zavaritskii, Dokl. Akad. Nauk SSSR 82, 229 (1952).

## ROLE OF EXCITON STATES IN THE PROCESS OF PHOTOCURRENT FORMATION IN GERMANIUM

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Germanium is one of the few semiconducting crystals in which the impurity content can be controlled with a high degree of accuracy. Particular interest attaches in this connection to research on exciton absorption of light in this crystal. The first to observe and to study exciton absorption in germanium, in indirect and direct transitions, were Macfarlane and his co-workers [1]. Recently Asnin, Rogachev, and Ryvkin [2] used exciton states to explain peculiar phenomena observed in the photoconductivity of germanium at low temperatures. We believe, however, that a direct proof of the part played by excitons in the production of free carriers can be obtained only by spectral investigations. This precisely was how Apker and Taft [3] demonstrated experimentally for the first time the role of excitons in the external photoeffect. We know of only one similar investigation of indirect exciton transitions in germanium [1]. Continuing a cycle of research initiated by us in 1956 on the role of excitons in photoelectric phenomena, we undertook a spectral investigation of the photoconductivity of pure germanium single crystals at 77°K, using an instrument with sufficiently large dispersion.

Free standing germanium single crystals measuring 5 x 2 x 2 mm, with ohmic contacts, were placed directly in a dewar with liquid nitrogen. The polished surfaces of the crystals were polished prior to the experiment in hydrogen peroxide or in CP-4. An MDR-2 monochromator with dispersion 80 A/mm was used. The photocurrent was recorded at 600 Hz with an amplifier (28 IM) and was continuously plotted with an EPP-09 automatic recorder. The rate scanning the spectrum ranged in different experiments from 10 to 1 A/sec.

The results are shown in the figure. Curve a is the spectrum of the photocurrent in the germanium immediately after etching the sample in H<sub>2</sub>O<sub>2</sub>. Similar curves were obtained