SOVIET PHYSICS JETP VOLUME 27, NUMBER 1 JULY, 1968

OBSERVATION OF THE QUANTUM AND CLASSICAL SIZE EFFECTS IN POLYCRYSTALLINE THIN BISMUTH FILMS

Yu. F. KOMNIK and E. I. BUKHSHTAB

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

Submitted June 20, 1967

Zh. Eksp. Teor. Fiz. **54**, 63–68 (January, 1968)

The quantum size effect was observed in thin polycrystalline bismuth films having an unbounded texture (trigonal axis in the crystallites oriented normal to the film surface). The Fermi quasimomentum of the electrons in the direction of the trigonal axis was determined from the period of the conductivity oscillations following a thickness change $\Delta d \sim 400$ Å and found to be $(p_z)_F = 4 \times 10^{-22}$ g-cm/sec. It was observed that the monotonic component of the "thickness" dependence of the conductivity decreases with increasing film thickness in the interval 200–2000 Å. Possible causes of this $\sigma(d)$ dependence are discussed. A comparison of the results of the observation of the classical and quantum size effects in polycrystalline bismuth films leads to the conclusion that the electron mean free path in the Bi films is not limited by the crystallite dimensions.

IN thin films it is possible to observe two types of size effects: classical,[1-3] which occurs if the film thickness d is commensurate with the mean-free path l of the electron in the investigated substance, and quantum[4-9], which arises if the film thickness is commensurate with the effective de Broglie wavelength of the electrons λ. The first effect leads to an additional increase of the resistance and to a change of other kinetic characteristics of the film when $d > l$, and can be relatively easily observed[10-14] in those cases when the "critical" thickness $d_c \ll l$. The second effect leads to the appearance of an oscillatory dependence of the thermodynamic properties and of the kinetic coefficients on the thickness of the film and is connected with formation in the energy spectrum of the electrons and holes of subbands whose number changes with changing film thickness. The subbands correspond to different values of the quantum number n, which determines the allowed values of the k_z component of the quasimomentum, $k_z = \pi/d$ (the z axis is normal to the film). The shift of the minimal values of the energy in neighboring subbands is determined by the relation

$$\Delta\varepsilon_{n,n+1} = \frac{\pi^2\hbar^2}{2md^2}(2n+1),$$

and near the Fermi surface it amounts to

$$\Delta\varepsilon_F = 2\pi\hbar\varepsilon_F^{1/2} / (2m)^{1/2}d.$$

To realize the quantum size effect it is necessary that the relaxation time due to the scattering of the electrons in the volume and on the surface be sufficiently large: $\tau \gg \hbar/\Delta\epsilon_F$[5]. From this it follows that it is necessary to carry out the observations at low temperatures, $kT < \Delta\epsilon_F$ under conditions when the carrier scattering in the volume makes a small contribution, and the reflection of the electrons from the surfaces is specular. In addition, it is necessary to have $\Delta\epsilon_{0,1} \sim \epsilon_F$ which occurs only for substances with a small electron effective mass.

1. QUANTUM SIZE EFFECT

Observation of an oscillatory dependence of the conductivity, of the Hall constant, and of the longitudinal magneto-resistance on the thickness of thin single-crystal bismuth films was reported in[15]. The films were prepared by epitaxial growing from a molecular beam on a fresh cleaved surface of heated mica. In[16] are given the results of a structural investigation of such films, indicating that the investigated object is indeed made up of large-block single-crystal films with trigonal-axis orientation along the normal to the surface of the film. The perfection of the structure of such films, together with the inherent high specularity of the surface of bismuth (with respect to scattering of electrons), produces favorable conditions for the observation of the quantum size effect.

At the same time, we were able to observe quantum oscillations of conductivity in thin films of bismuth on a neutral substrate (glass) at room temperature. Such films have relatively small crystallite sizes (on the order of the thickness of the film) and an unbounded texture; the trigonal axis is normal to the surface of the film with a disorientation ~20°, and the azimuthal orientation of the crystallites is arbitrary. These circumstances should make the effect less pronounced. Its observation turned out to be possible as a result of the use of the following procedure: the measurements were made on samples of variable thickness, representing long, narrow strips (1 × 70 mm), with potential leads every 2 mm (see Fig. 1a).

We used sputtered silver contact areas and elastic clamp contacts secured in a frame. The variable thickness of the sample was ensured by the natural distribution of the density of the molecular beam in the condensation plane. The resistances of the individual sections of the sample, measure with a potentiometer circuit, were referred to the mean value of the film thickness at the given section. Thus, the entire sample spanned a definite interval of thicknesses, within which

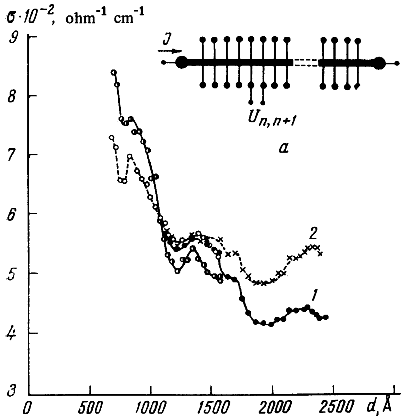

FIG. 1. Dependence of the specific conductivity on the thickness of thin films of bismuth. The measurements were performed at a temperature 4.2°K on samples of variable thickness obtained at 350°K: 1 – prior to annealing, 2 – after annealing at 420°K. The differently marked experimental points pertain to different samples; a – configuration of sample, the circles denote the contact areas.

there can occur one, two, or several periods of oscillation. The distribution of the thicknesses in the sample was investigated by us in the case of thick films (2000–3000 Å) with the aid of an interference method, and in thin films (<200 Å) by measurements of the optical density S and using a previously prepared plot of S against the thickness d (see [17]). The use of cylindrical evaporators [18] has made it possible to retain the distribution of the molecular beam unchanged during the entire time of sample production. The initial bismuth was 99.9999% pure and the condensation was in a vacuum of 10^{-6} mm Hg.

Figure 1 shows the specific conductivity of thin bismuth films as functions of the thickness (the results are given for two samples); the plots reveal quite clearly oscillations with a period of $\sim$400 Å. From the period of the oscillations, in accordance with [19],

$$\Delta d = 2\pi\hbar/(P_z)_F^{ext}$$

it is possible to obtain the extremal chord $(P_z)_F^{ext}$ of the Fermi surface in the direction of the z axis. The corresponding value of the quasi-momentum obtained in accordance with our data, is $(p_z)_F = (\frac{1}{2})(P_z)_F^{ext} = 4.1 \times 10^{-21}$ g-cm/sec, and agrees well with the known values of this quantity for the electron ellipsoids in the band structure of bulky bismuth [19-22]. Contributing to the appearance of the size effect in non-single-crystal films of bismuth is the circumstance that the band structure of Bi has axial symmetry relative to the trigonal axis. Thus, in all the crystallites, the orientation of the trigonal axis relative to the normal to the surface of the film (the observed type of texture) is the necessary condition for the appearance of conductivity oscillations.

The $\sigma(d)$ plot for Bi reveals, besides oscillations, one more feature: the conductivity of the films decreases with increasing thickness. This feature, observed also at nitrogen temperature, cannot be attributed to the change of the structure characteristics and the properties of the film surface, since the growth of the thickness is accompanied as a rule by an improvement rather than deterioration of the structure of the film.

It is precisely the improvement of the film structure and the elimination of the porosity that causes the conductivity of films obtained on mica [15,16,23] to increase with increasing thickness up to 1000 Å, since the critical thickness for Bi is much larger on mica ($\gtrsim$200 Å) than on glass ($\sim$ 30 Å). Annealing of the films (at 150°C) leads to a natural increase of their conductivity. However, for films of thickness less than 1000 Å the annealing has an opposite effect, connected apparently with the increase of the porosity of very thin films as a result of the recrystallization that takes place in them.

From the observed nontrivial thickness dependence of the monotonic component of the conductivity of Bi films it follows that a decrease of the film thickness is accompanied by an increase of the relaxation times of the electrons and the holes, due to the scattering of the latter predominantly by the film defects (assuming that the effective masses of the carriers do not depend on the film thickness). We point out two possible causes of this fact.

1. A change of the electron energy and the Fermi level as a result of redistribution of the density of states when the size quantization is turned on. In this case, from the condition for the conservation of the number of states per unit volume, it follows that the Fermi energy should increase with decreasing film thickness. The latter can lead to an increase of the relaxation time ($\tau \propto \epsilon_F^{3/2}$), as a result of a decrease of the effective cross section for the scattering of the electrons by the defects. Yet a major increase of the Fermi energy would lead to noticeable decrease of the period of the oscillations with decreasing thickness ($\Delta d \propto \epsilon_F^{-1/2}$), something which we did not observe (see also [16,24]). Apparently, in bismuth, as a result of the possibility of the spilling of the quasiparticles from the electron into the hole band, the expected change of the Fermi energy is not realized.

2. Another possible cause is the decrease of the electron scattering probability in thin films that exhibit a quantum size effect, as a result of the decrease in a number of allowed states; this imposes an additional limitation on the conditions for the conservation of the total angular momentum. Under these conditions, the electron gas should become less sensitive to the scattering centers as the number of subbands decreases.

Figure 2 shows plots of the change of the specific conductivity of films with thickness at different temperatures, obtained from a continuous recording of the changes of the conductivity of films during the course of their condensation. It is seen from Fig. 2 that at low temperatures, within the thickness range for which

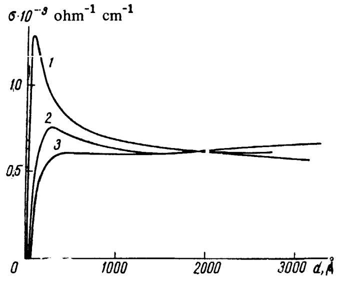

FIG. 2. Specific conductivity vs. thickness of thin films of bismuth. The measurements were performed during the course of condensation of bismuth at temperatures 210 (1) 230 (2) and 250°K (3).

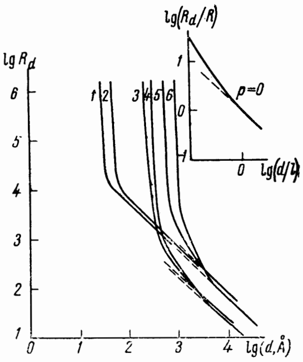

FIG. 3. Resistance vs. thickness of thin bismuth films, obtained during the course of condensation of the metal at the following substrate temperatures (in degrees K); 1–300, 2–340, 3 and 4–380, 5–390, 6–400. $T < T_l$ for curves 1 and 2 and $T > T_l$ for curves 3 - 6.

the relation $\Delta\epsilon_F > kT$ is satisfied, one observes, just as Fig. 1, a growth of the conductivity with decreasing film thickness[1)]. Yet no oscillations of the conductivity are observed in this case. This is probably connected with the deterioration of the structural characteristics of the films deposited at temperatures much lower than room temperatures; thus, an electron diffraction investigation of Bi films has shown that the degree of disorientation of the texture increases with decreasing condensation temperature (to ~60° at 180°K), and no texture is observed at all at temperatures close to the characteristic temperature $T_m \approx 180$°K[25]. As a result of the increase of the disorientation of the crystallites, the spectrum of the states for the film as a whole turns out to be strongly smeared out, as a result of which no oscillations are observed; yet in individual crystallites the states are strictly quantized with respect to the p_z component, as before, so that the limitations on the conservation of the quasimomentum continue to remain in force.

2. CLASSICAL SIZE EFFECT

Continuous plotting of the conductivity of bismuth films during the course of condensation has revealed a classical size effect[26]. In the upper right of Fig. 3 are shown curves plotted in accordance with the relations of Fuchs[1] for the classical size effect in coordinates log (R_d/R) and log (d/l). A similar characteristic kink at thicknesses 2000 – 4000 Å is observed on the experimental log R_d vs. log d curves for Bi films condensed at temperatures above the characteristic condensation point T_l[25], which equals ~ 370°K for bismuth. At the temperature T_l a change occurs in the condensation mechanism. Above this temperature, the condensation is realized in the initial ("precritical") period not in the crystal but in the liquid phase, as a result of which the condensate formed after the crystallization has a coarse uneven surface and has no texture. We note that for the classical size effect to appear it is very important to have a non-specular (diffuse) character of reflection of the electrons from the external boundaries of the film[1,2]. Apparently the increase of the condensation temperature above T_l is in the case of bismuth the only possible method of producing a "non-specular" surface. It is precisely this circumstance, and not so much the structural differences between the Bi films obtained at $T < T_l$ and $T > T_l$[26], which determines the fact that the classical size effect is observed only in films obtained at temperatures higher than T_l.

We show below the conditions for the appearance of the quantum and classical size effects as functions of the temperature at which the films were produced on a neutral substrate and as functions of their structural characteristics:

	$T \sim T_m$	$T_m \ll T < T_l$	$T > T_l$
Quantum size effect:	–	+	–
Classical size effect:	–	–	+
Perfect structure:	–	+	–
Specular electron reflection:	+	+	–

For the appearance of a quantum size effect it is necessary to have simultaneously a texture and specular film surfaces; for the classical size effect it is necessary that the external boundaries not be specular. The requirement that the film be single-crystal is not essential. The results offer evidence that in the investigated polycrystalline Bi films the electron mean free path l is relatively large. Thus, the quantity $l \sim 2000-4000$ Å at 400°K, determined from the classical size effect, is in reasonable agreement with the data for the electron mean free path in bulky bismuth (at room temperature $l \sim 1-2\ \mu$[10,23]). The distinct manifestation of the classical size effect makes it possible to assume that in films of smaller thickness the mean free path of the electrons moving at small angles to the outer surfaces of the film remains sufficiently large and is not limited by the dimensions of the crystallites, which are commensurate with the thickness of the film. In the opposite case, besides the absence of a kink on the curves of Fig. 2, the quantum size effect would also vanish, since the condition $\Delta\epsilon_F\tau \gg \hbar$ would not be satisfied. Indeed, in the case when the mean free path is limited by the thickness of the film, it turns out that

$$\Delta\varepsilon_F\tau = \frac{2\pi\hbar\varepsilon_F^{1/2}}{(2m)^{1/2}d}\,\frac{md}{(2m\varepsilon_F)^{1/2}} = \pi\hbar,$$

that is, the inequality indicated above is not strong. The absence of obligatory scattering of the electrons from the boundaries of the crystallites, as applied to bismuth, could be explained as being due to the fact that the de Broglie wavelength of the electrons in Bi is large (from the obtained results, $\lambda \approx 2\Delta d \approx 800$ Å) compared with the thickness of the intercrystallite boundaries. Yet this statement is apparently more general in character, since the classical size effect was observed also on small-crystal thin films of normal metals[11-14].

[1)] The sharp decrease of the conductivity at very small "critical" thicknesses is due to the discrete structure of the thin films in the initial period of condensation.

[1] K. Fuchs, Proc. Camb. Phil. Soc. 34, 100 (1938).

[2] E. H. Sondheimer, Adv. Phys. 1, 1 (1952).

[3] M. I. Kaganov and M. Ya. Azbel', Zh. Eksp. Teor. Fiz. 27, 762 (1954).

[4] I. M. Lifshitz and A. M. Kosevich, Izv. AN SSSR ser. fiz. 19, 395 (1955).

[5] V. B. Sandomirskiĭ, Zh. Eksp. Teor. Fiz. 43, 2309 (1962) [Sov. Phys.-JETP 16, 1630 (1963)]; Radiotekhnika i élektronika 7, 19671 (1962).

[6] V. Bezak, J. Phys. Chem. Sol. **27**, 821 (1966).

[7] V. B. Sandomirskiĭ, Zh. Eksp. Teor. Fiz. **52**, 158 (1967) [Sov. Phys.-JETP **25**, 101 (1967)].

[8] I. O. Kulik, ZhETF Pis. Red. 5, (1967) [JETP Lett. 5, (1967)].

[9] I. O. Kulik ibid. 6, (1967) [6, (1967)].

[10] V. I. Kaidanov and A. R. Regel'. Zh. Tekhn. Fiz. **28**, 402 (1958) [Sov. Phys. Tech. Phys. **3**, 378 (1958)].

[11] F. W. Reynolds and G. R. Stilwell, Phys. Rev. 88, 418 (1952).

[12] A. M. Toxen, ibid. **123**, 442 (1961).

[13] R. Grigorovich, A. Devenyl and T. Botila, J. Phys. Chem. Sol. **23**, 428 (1962).

[14] G. Wedler and M. Fouad, Z. Phys. Chem. **40**, 1 (1964).

[15] Yu. F. Ogrin, V. N. Lutskiĭ, and M. I. Elinson, ZhETF Pis. Red. **3**, 114 (1966) [JETP Lett. **3**, 71 (1966)].

[16] Yu. F. Ogrin, V. N. Lutskii, et al. Radiotekhnika i élektronika **12**, 748 (1967).

[17] L. S. Palatnik, and G. V. Fedorov, Dokl. AN SSSR 113, 100 (1957).

[18] Yu. F. Komnik, L. S. Palatnik, and G. V. Fedorov, Izv. AN SSSR OTN No. 11, 193 (1957).

[19] M. S. Khaikin and V. S. Édel'man, Zh. Eksp. Teor. Fiz. **47**, 878 (1964) [Sov. Phys.-JETP **20**, 587 (1965)].

[20] V. S. Édel'man and M. S. Khaikin, ibid. **49**, 107 (1965) [**22**, 77 (1966)].

[21] G. E. Smith, G. A.Baraff, and J. M. Rowell, Phys. Rev. **135**, A1118 (1964).

[22] L. A. Fal'kovskiĭ and G. S. Razina, Zh. Eksp. Teor. Fiz. **49**, 265 (1965) [Sov. Phys.-JETP **22**, 187 (1966)].

[23] V. P. Duggal, R. Rup, and P. Tripathi, Appl. Phys. Lett. 9, 293 (1966).

[24] V. N. Lutskiĭ, D. N. Korneev, and M. I. Elinson, ZhETF Pis. Red. **4**, 267 (1966). [JETP Lett. **4**, 179 (1966)].

[25] Yu. F. Komnik, Fiz. Tverd. Tela 6, 2897 (1964) [Sov. Phys.-Sol. State 6, 2309 (1965)].

[26] Yu. F. Komnik and L. S. Palatnik, ibid. **7**, 539 (1965) [**7**, 429 (1965)].

Translated by J. G. Adashko
10