Observation of the Quantum and Classical Size Effects in Thin Antimony Films

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The quantum size effect was observed in thin polycrystalline antimony films. The variation of the film resistance with thickness is oscillatory. The oscillation period amounts to ~ 25 Å. The Fermi quasimomentum of the electrons in the direction normal to the film surface was determined. A comparison of the results of the observation of the classical and quantum size effects leads to the conclusion that the electron mean free path in antimony films is not limited by the crystallite dimensions.

The investigation of films is of interest both from the purely scientific point of view and from the practical one, since new specific effects, not observed in bulky samples, can appear in the film state. The increased interest in the physical properties of films is primarily connected with the rapidly developing field of microelectronics.

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 material investigated and leads to an additional increase of resistance and to a change of other kinetic characteristics of the film, and quantum [4–9], which occurs if the film thickness is comparable with the effective de Broglie wavelength of the electrons λ. The quantum size effect (Q S E) leads to an oscillatory dependence of the thermodynamic properties and kinetic coefficients on the thickness of the film (d).

In the case of a semimetal, the Q S E causes the conduction band and the valence band to break up into subbands, whose number changes with changing film thickness. The subbands correspond to different values of the quantum number (n), which determines the allowed discrete values of the quasimomentum vector K_z along the quantizing dimension (Z axis). The shift of the minimal values of the energy in neighboring subbands is determined by

$$\Delta\varepsilon_{n,n+1} = \frac{\pi^2 h^2}{2 m d^2} (2n+1) \qquad (1)$$

and near the Fermi surface it amounts to

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

For semimetals the band overlap Δ decreases by an amount $\Delta\varepsilon_{\text{cond.}} + \Delta\varepsilon_{\text{valence}}$, and if d is sufficiently small a gap is formed and the semimetal turns into a dielectric. This transition should take place at a thickness [7]

$$d_0 = \frac{\pi\hbar}{\sqrt{2\Delta}} \left(\frac{m_e + m_h}{m_e m_h}\right)^{1/2},$$

m_e and m_h are the masses of electrons and holes in the transverse direction.

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

Quantum Size Effect

Semimetal films are at low temperatures the most favorable objects for experimental observation of Q S E: on the one hand, they have a sufficient number of carriers to screen the scattering centers; on the other hand, the effective de Broglie wavelength of the carriers is sufficiently large to permit them to be weakly scattered by these screened centers.

The quantum size effect was observed in bismuth films prepared by epitaxial growing from a molecular beam on a fresh cleaved surface of heated mica [10] and on glass [11, 12] substrates. The period of conductivity oscillations was about 400 Å. However, the subject of these investigations, bismuth films, evidently do not permit agreement between the results obtained and theoretical estimates, since

bismuth films have an anomalous temperature dependence of the resistance which appears even in those cases where the quantum size effect does not occur (for large thicknesses)[13].

Antimony films are a more interesting object of study; they have a pronounced quantum size effect[14, 15]. The oscillations could be observed for thicknesses $\sim 10^{-6}$ cm and the oscillation period of conductivity is small in antimony films and amounts[14] to ~ 25 Å. The splitting of the subbands near the Fermi level is quite large.

In the present work the electrical resistance of thin polycrystalline films of antimony was measured as a function of thickness. The samples were made by vacuum evaporation of highly pure antimony (99.999%) onto quartz substrates at room temperatures in a vacuum of $\sim 10^{-6}$ torr at an evaporation rate of about 30 Å/sec. It is known that such films have a pronounced texture[16]. The 111 direction is perpendicular to the plane of the film. The measurements were made on samples of different thickness (150 to 600 Å). Silver paste contact areas and elastic clamp contacts secured in a frame were used. A small current (10^{-3} A) passed along the film; there were potential contacts along the film, whose potential differences were measured by a potentiometer (Decade PYE potentiometer) and the resistance of the individual sections of the sample were referred to the mean value of the film thickness at the given section. The thicknesses of the films were measured by the Tolansky[17] interference method. The investigated samples were placed in a nitrogen cooled Dewar flask.

To study the thickness dependence of resistivity one must take very precise account of the sample geometry (the width of the sample and the distance between the potential contacts). To eliminate the effect of the geometrical size of the sample, all the calculations were done for the relative quantity $\varrho_T/\varrho_S = R_T/R_S$ (R_T and R_S are the resistances at the experimental temperature and at room temperature 293 °K). Figure 1 shows the dependence of R_T/R_S on thickness d which illustrates the oscillatory character of the change of resistance with thickness. It was observed that the oscillation amplitude of R_T/R_S decreases with increasing temperature T, which corresponds to the thermal quenching of the quantum oscillations of the conductivity. From the period of the oscillations (Δd) one can find the extremal chord $(P_Z)_F^{ext.}$ of the Fermi surface parallel to the normal to the film surface[18]

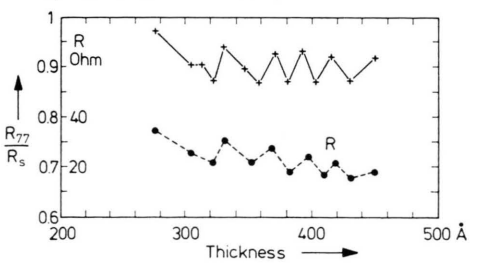

Fig. 1. The oscillatory behaviour of film resistance with thickness.

$$(P_Z)_F^{ext.} = \frac{2\pi\hbar}{\Delta d} \sim 2\sqrt{2\, m^* \varepsilon_F}$$

where m^* is the effective mass corresponding to the motion across the film and ε_F is the Fermi energy. The corresponding value of the quasimomentum obtained in accordance with our data ($\Delta d \sim 25$ Å) is $(P_Z)_F = \frac{1}{2}(P_Z)_F^{ext.} = 1.31 \times 10^{-20}$ g cm/sec.

The thickness of the antimony films studied was such that their carrier spectra contain a substantial (more than 10) number of subbands in the case where a quantum size effect appears, so that the relations obtained in the quasiclassical approximation[18] for $KT > \Delta\varepsilon_F/2\pi^2$ can be used. The resistance of the film is given by

$$\varrho(T,d) = \varrho_0\left[1 + \frac{2\pi KT}{\varepsilon_F}\exp\left\{-\frac{2\pi^2 KT}{\Delta\varepsilon_F}\right\} \cdot \sin\frac{(P_Z)_F^{ext}}{\hbar}\right] d \qquad (2)$$

the amplitude of the quantum oscillations of the resistance by

$$A(T) = \frac{2\pi KT}{\varepsilon_F}\exp\left\{-\frac{2\pi^2 KT}{\Delta\varepsilon_F}\right\}. \qquad (3)$$

The experimentally obtained amplitude value

$$A(T = 77\ ^\circ\mathrm{K}) = \frac{(R_T/R_S)_{max} - (R_T/R_S)_{min}}{(R_T/R_S)_{max} + (R_T/R_S)_{min}} = 2.5 \times 10^{-2}$$

is close to that calculated by formula (3).

If the smearing of the subband edges is taken in account then the amplitude will be[19]

$$A(T) = \frac{2\pi KT}{\varepsilon_F}\exp\left\{-\frac{2\pi^2(KT + \hbar/\tau)}{\Delta\varepsilon_F}\right\}$$

where τ is the electron relaxation time.

It is observable that, no abrupt jumps (Fig. 1), corresponding to the start of the filling of the new

subband, are observed, this could be connected with the smearing of the levels by an amount of the order of $\hbar/\tau$. The fact that a single period of oscillations is manifested in the experiments explicitly indicates that these oscillations are connected with quantization solely of one type of carrier, electrons. This may be connected with the fact that the condition that the distance between the neighboring subbands $\gg h/\tau$ is not satisfied for holes, or else that holes make a small contribution to the conductivity. Since estimates for antimony [20] shows that the number of filled electron subbands is approximately twice that of the hole subbands.

The $\varrho(d)$ plot for sb films Fig. 5 reveals, besides oscillations, one more feature: the specific resistivity of the films decreases with increasing thickness. This feature, observed also at liquid nitrogen temperature, could be attributed to the change of the structure characteristics and the properties of the film surface, since the growth of thickness is accomplished as a rule by an improvement of the structure of the film and elimination of the porosity.

It follows from experimental results that in antimony films up to thicknesses $d \sim 250$ Å the transition into the dielectric state is not observed. Nor was this transition observed for thinner films ($L \sim 150$ Å). However, the structure of the films of such thickness is imperfect and the conclusions become unreliable.

Classical Size Effect

The electrical properties of thin films depends on the film thickness, rate of evaporation and the nature and the temperature of the substrate. Hamburger et al. [21] and Cohen [22] found that films having negative temperature coefficient could in many cases be prepared by deposition on cold substrates (liquid oxygen temperature). Some of these films recovered their metallic properties when heated. This is attributed to the irreversible disappearance of lattice defects [22]. Our measurements of the temperature dependence of the electrical conductivity show that films prepared at room temperature have always positive temperature coefficients and a hysterisis appears when the film is cooled, Figures 2, 3. The difference between the values of the electrical resistance when the sample is heated and then cooled is large for small film thicknesses, Figures 2, 3. This could be attributed to the effect of temperature on the structure of thin films, which induces irreversible changes (partial crystallization and aggregation).

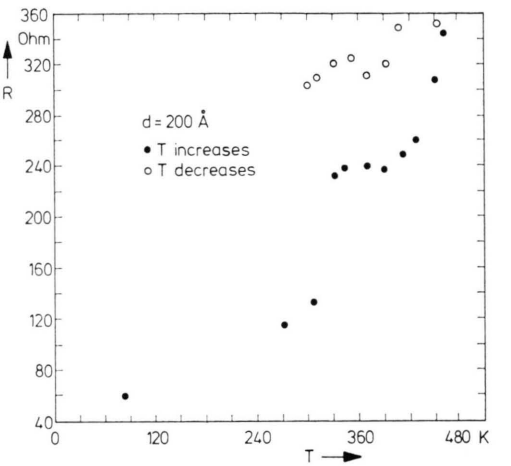

Fig. 2. The dependence of film resistance on temperature ($d = 200$ Å).

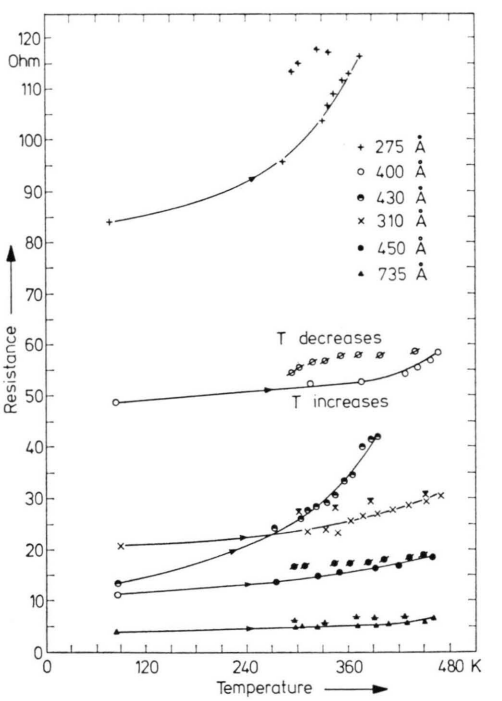

Fig. 3. The dependence of film resistance on temperature ($d = 275$ Å, 310 Å, 400 Å, 450 Å, 735 Å).

The surface of a thin film affects the electronic transport properties of the material by interrupting the transit of carriers along their mean free path. Figure 4 shows that the resistance of antimony films (without considering the oscillatory part) varies with thickness as $R \sim d^{-2}$. Such a dependence

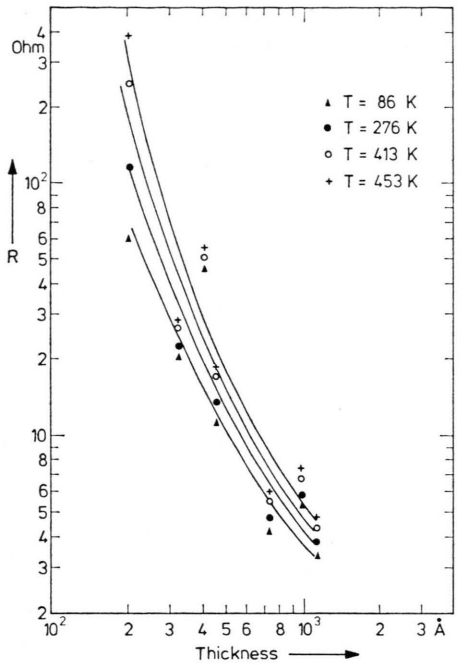

Fig. 4. The dependence of film resistance on the thickness.

is characteristic of the classical size effect [1]. 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]. 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 comparable with the thickness of the film.

Sondheimer [2] studied the case of thin metal films whose surface is not completely specular and obtain the following expression for the electron mobility

$$\frac{\mu_K}{\mu_B} = 1 - \frac{3}{2K}(1-p) \cdot \int_1^\infty \left(\frac{1}{t^3} - \frac{1}{t^5}\right) \frac{1-\exp\{-Kt\}}{1-p\exp\{-Kt\}}\,dt \qquad (4)$$

where $\mu(K)$ and μ_B are the thin film and bulk mobilities, $K = d/L$, d is the film thickness, L the mean free path and $(1-p)$ the fraction of diffuse scattering. The mobility of charge carriers for thin films $[\mu(K)/\mu_B]$ falls off rapidly as the thickness (or the ratio d/L) decreases. Therefore, the increase of resistivity when the film thickness decreases (Fig. 5) could be attributed to the decrease of the mobility as the thickness decreases.

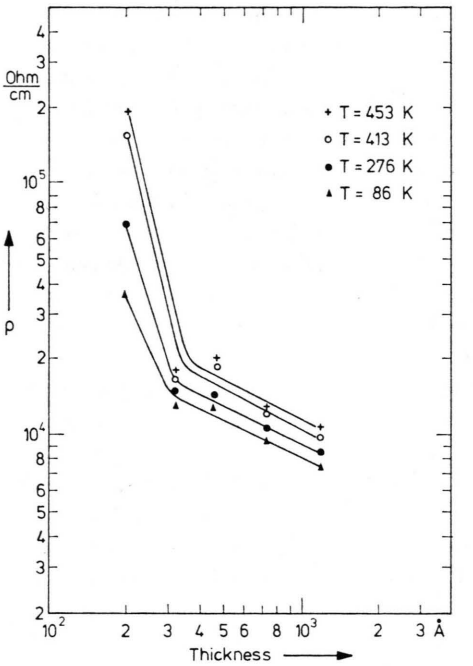

Fig. 5. The variation of the resistivity of the film with thickness.

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