Quantum size effect and electric field effect in thin Bi films*

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Calculations are presented for the occurrence of quantum size effects in the electric field effect in thin films of bismuth. The penetration of the applied field is treated in a self-consistent Thomas-Fermi type of approximation. The local value of the conductivity depends on the applied electrostatic potential and is calculated in the relaxation time approximation. The state dependence of the relaxation time is taken to vary inversely as the density of states, similar to earlier calculations for bismuth films. The film conductance shows abrupt changes with applied field for thicknesses which have the Fermi level close to a step in the electronic density of states. The temperature dependence of this quantum size effect is also considered.

I. INTRODUCTION

The term quantum size effect (QSE) refers to the size dependence of the electronic properties of a sample when a state label has a noticeably discrete spectrum rather than a quasicontinuous one (as in bulk material). A simple model[1] of QSE for a thin film of thickness a ($0 \leq x \leq a$) is based on the energy eigenvalue spectrum

$$E_{sk_yk_z} = \epsilon_0 s^2 + \hbar^2(k_y^2 + k_z^2)/2m, \qquad \epsilon_0 = \hbar^2\pi^2/2ma^2, \quad s = 1, 2, 3, \ldots, \tag{1}$$

with k_y, k_z quasicontinuous wave-number labels associated with directions in the plane of the film. In contrast with the bulk band behavior, the energy band for the film consists of subbands[1,2] labeled by the discrete index s and a steplike structure in the density of states (per unit volume) given by

$$N(E) = (m/\pi\hbar^2 a)\left[\left(\frac{E}{\epsilon_0}\right)^{1/2}\right].$$

The square brackets denote the integer part of its content.

Properties of the film which depend in some way on this step structure have QSE behavior. In order to have a significant fractional change in the density of states from one step to the next, those charge carriers involved must have energy E such that $[\sqrt{E/\epsilon_0}]$ is fairly small, less than 10 for example. In addition the effect of thermal smearing must be minimized: $kT \ll \epsilon_0$. The conditions are best fulfilled by a semimetal such as Bi where the Fermi level occurs near the bottom of one band and near the top of another in bulk material.[3] Thus for a 100-nm Bi film, one might estimate that the Fermi energy has a value such that the discrete index s in Eq. (1) has a value of about 3 or 4 for the electron band. The value of ϵ_0 may be about 1.2 meV, somewhat larger than kT at liquid-helium temperatures. For thinner films the s value would tend to small values while ϵ_0 increases.

Calculations of galvanomagnetic properties of semimetal films by Sandomirskii[1] were based on spherical constant energy surfaces for electron and hole bands in the bulk material. The relaxation time was calculated in a Born approximation for randomly distributed δ-function scattering centers. For a state of energy E, the relaxation time so calculated[1] is inversely proportional to $[\sqrt{E/\epsilon_0}] + \frac{1}{2}$. It is this step structure in the energy dependence of the relaxation time that is responsible for most of the QSE oscillations in the calculated quantities. The electric field effect was also treated by Sandomirskii[1] who considered the semimetal film as one plate of a capacitor. By charging the film, one could change the position of the Fermi level relative to the step structure in the density of states. This calculation of the field effect was not, however, done in any sort of self-consistent way. No account was taken of the screening of the film interior by the charge carriers.

Asahi, Humoto, and Kawazu[4] reported calculations of QSE for thin Bi films. In their work, the highly anisotropic constant energy surfaces for bulk Bi were described in an ellipsoidal-parabolic model.[3,5] The electric field effect was not considered by them.

The present work deals with a calculation of the field effect for thin Bi films for which the screening is described in a self-consistent Thomas-Fermi type of approximation. In addition the relaxation time is treated in a more general fashion and the ellipsoidal-parabolic model is assumed to describe constant energy surfaces in the bulk material. All calculations refer to films with the trigonal axis perpendicular to the film. In Sec. II which follows, we develop the theory used in our description. Sec. III reports the results of our calculations.

II. DESCRIPTION AND THEORY

In the ellipsoidal-parabolic model of bulk Bi, the electron band has six half-ellipsoids for the constant energy surface centered at each of the pseudohexagonal faces of the Brillouin-zone boundary. These are related by inversion through the zone center and by rotations of ±120° about the trigonal direction. The effective masses along the principal axes of one ellipsoid are $m_{1e}=0.0115$, $m_{2e}=0.007\,09$, $m_{3e}=1.71$ all expressed in electron mass units. The principal axis labeled "1" is tilted with respect to the trigonal axis by about 6°. Constant energy surfaces for the hole band are half-ellipsoids of revolution about the trigonal axis centered at each of the two hexagonal faces of the Brillouin zone boundary. In what follows, the trigonal axis will be labeled the x axis while the binary and bisectrix axes are labeled by y and z, respectively. The hole band effective masses are taken to be $m_{xh}=0.758$, $m_{yh}=m_{zh}=0.0676$. The band overlap value is assumed to be 37 meV. Reference 3 may be consulted for further details.

The quantum-size-limited energy spectrum for hole states is then given by

$$E_{nk_yk_z}=n^2\epsilon_{0h}+\frac{\hbar^2}{2}\frac{k_y^2+k_z^2}{m_{yh}},\quad n=1,2,3,\ldots$$

with $\epsilon_{0h}=\pi^2\hbar^2/2m_{xh}a^2$, a being the film thickness. Thus, the bulk hole band becomes a set of subbands in the film, each subband labeled by n. The density of states (per unit volume) for each subband is a constant with value $(m_{yh}m_{zh})^{1/2}/\pi\hbar^2a$. The total density of hole states at energy E then depends on the number of subbands such that $n^2\epsilon_{0h}\leq E$. This number is just $n=[\sqrt{E/\epsilon_{0h}}]$. Therefore, the density of hole states is

$$N_h(E)=[(m_{yh}m_{zh})^{1/2}/\pi\hbar^2a]\,[\sqrt{E/\epsilon_{0h}}\,].$$

The electron states have energy eigenvalues which are also size dependent. However the analysis is somewhat more involved since there are six equivalent half-ellipsoids (which we shall call reference ellipsoids) for the bulk material and the crystal x axis does not coincide with the principal axis because of the 6° tilt angle. One may transform from the principal axis system to the crystal axis system so that for one of the reference ellipsoids,

$$E_{nk_yk_z}=n^2\epsilon_{0e}+\frac{\hbar^2}{2}\left(\frac{k_y^2}{m_{ye}}+\frac{\bar{k}_z^2}{m_{ze}}\right),\quad n=1,2,3,\ldots. \tag{2}$$

In this expression, $\epsilon_{0e}=\pi^2\hbar^2/2m_{xe}a^2$, $\bar{k}_z=k_z-q_n$, q_n having a fixed value for given n, and m_{xe}, m_{ye}, m_{ze} are given by

$$m_{xe}=m_{1e}\cos^2\theta+m_{3e}\sin^2\theta,$$

$$m_{ye}=m_{2e},\quad m_{ze}=m_{1e}m_{3e}/(m_{1e}\cos^2\theta+m_{3e}\sin^2\theta),$$

where θ is the tilt angle of a reference ellipsoid with respect to the trigonal axis. The other two reference ellipsoids may be described from Eq. (2) by rotating in the $k_y,\bar{k}_z$ plane by ±120°. For any one of the three reference ellipsoids, the density of electron states is

$$N_e'(E)=[(m_{ye}m_{ze})^{1/2}/\pi\hbar^2a]\,[\sqrt{E/\epsilon_{0e}}\,]. \tag{3}$$

The total electron density of states is, of course, three times the above, one for each of the three reference ellipsoids (or six half-ellipsoids). Thus $N_e(E)=3N_e'(E)$.

The Fermi level F is determined by the charge neutrality condition,

$$\int_0^\infty N_e(E)(1+e^{(E-F)/kT})^{-1}\,dE = \int_0^\infty N_h(E)(1+e^{(E-\Delta+F)/kT})^{-1}\,dE$$

with Δ the bulk band overlap and energies are measured relative to the bulk band edges. Because of the step structure and film thickness dependence of the density of states, the Fermi level also depends on film thickness. The step structure of the hole density of states has only a small influence on properties of the film because of the relatively large value of m_{xh}.[6]

We next consider the conductivity tensor components in the plane of the film $\sigma_{\alpha\beta}$ with α and β referring to the y and z directions. We calculate the conductivity in the relaxation time approximation, modified because states are labeled by a discrete index s and two continuous ones k_y,k_z. The expression for the conductivity is easily determined for a single reference ellipsoid to be

$$\sigma_{\alpha\beta}=\frac{-e^2}{\pi\hbar^2a}\left(\frac{m_ym_z}{m_\alpha m_\beta}\right)^{1/2}\sum_n\int_{n^2\epsilon_0}^\infty dE\,\frac{\partial f_0}{\partial E}\,(E-n^2\epsilon_0)\tau_n(E).$$

In this expression the principal axes coincide with the crystal axes, y and z, in some order and $\tau_n(E)$ is the relaxation time angle-averaged over the ellipse labeled by n.

For the hole band, $m_\alpha=m_\beta=m_y=m_z$, and the single expression above gives the contribution of the holes to the conductivity.

It is convenient for the electron band to use $\bar{\sigma}=\frac{1}{2}(\sigma_{yy}+\sigma_{zz})$. Then each of the three reference ellipsoids contribute equally to the orientation-averaged conductivity due to the electrons. The result for the conductivity is given by

$$\sigma=\sigma_e+\sigma_h,$$

$$\sigma_h=-\frac{e^2}{\pi\hbar^2a}\sum_n\int_{n^2\epsilon_{0h}}^\infty dE\,\frac{\partial f_{0h}}{\partial E}\,(E-n^2\epsilon_{0h})\tau_{nh}(E),$$

$$\sigma_e=-\frac{3e^2}{2\pi\hbar^2a}\,\frac{m_y+m_z}{(m_ym_z)^{1/2}}\sum_n\int_{n^2\epsilon_{0e}}^\infty dE\,\frac{\partial f_{0e}}{\partial E}\,(E-n^2\epsilon_{0e})\tau_{ne}(E). \tag{4}$$

The relaxation times have yet to be specified. We consider two possible choices: (a) $\tau_n(E)=\tau_0$, a constant, and (b) $\tau_n(E)$ inversely proportional to the density of such states, $\tau_n(E)\propto a(m_y m_z)^{-1/2}/[\sqrt{E/\epsilon_0}]$. Case (a) obviously simplifies the calculations and in fact leads ultimately to an almost strictly linear field effect; i.e., no quantum size effect. It is the second choice which we believe to be more reasonable in that it is reminiscent of Sandomirskii's model, $\tau_n\propto am^{-1}/(n+\frac{1}{2})$, and is in accord with the expected trend of the dependence of relaxation time on the density of states. Thus for a larger density of states, a carrier in a given state has more states available for scattering and a correspondingly shorter life time.

The conductivity can now be calculated from the above and has thickness and temperature dependence similar to that of Asahi, Humoto, and Kawazu.[4]

We have now developed our description to the point of considering the application of an electric field perpendicular to the film and the consequent change in the conductance of the film. The field is screened by a redistribution of charge in the film.

In order to see the nature of approximations to follow, we wish to set up carefully the description appropriate to a small current in the plane of the film. There will be an arbitrarily small potential drop to which this current is proportional. Initially we describe this relationship by using the conductance Σ of a length of the film rather than the more locally conceived quantity σ, the conductivity. After certain approximations are made, we shall restore the use of σ to the description; although it is the conductance which we ultimately calculate.

For simplicity we consider a square film ($L_y=L_z=L$), a geometry for which averages over crystalline directions are easy to perform. A formal expression for the current associated with carriers moving in the z direction is

$$I=-2e\sum_{\alpha}\langle v_z\rangle_\alpha[f(\alpha)-f_0(\alpha)], \tag{5}$$

where the factor of 2 accounts for spin degeneracy, α labels a single particle state with group velocity component $\langle v_z\rangle_\alpha$. The distribution function $f(\alpha)$ differs from the Fermi distribution function $f_0(\alpha)$ due to the weak current-driving field and to the scattering mechanism which is described in the relaxation time approximation.

For the otherwise isolated film, the state label α coincides with (n,k_y,k_z) and the conductance for a current parallel to the z direction (collinear with the potential gradient) is given by

$$\Sigma_{zz}=\frac{-e^2L}{\pi\hbar^2}\left(\frac{m_y}{m_z}\right)^{1/2}\sum_n\int_{n^2\epsilon_0}^{\infty}dE\,\frac{\partial f_0}{\partial E}(E-n^2\epsilon_0)\tau_n(E).$$

This result is consistent with the earlier one for the conductivity.

Suppose now that we consider a film on which is imposed a static charging field perpendicular to the film. The formal expression for the current in the plane of the film, Eq. (5), is unchanged in form. The states, however, are modified by this field in such a way as to screen the interior of the film. Thus the state label α no longer coincides with (n,k_y,k_z) and the problem must be handled with some kind of self-consistent approach.

The Thomas-Fermi type of approximation has been used over the years to discuss screening in metals and semiconductors with at least semiquantitative success.[7] One may question the validity of the Thomas-Fermi approximation applied to a system which is quantum-size limited. We believe, however, that it is useful in that it is easily applied to the problem, it is a self-consistent approach, and it importantly provides a simple conceptual picture of the screening response.

The Thomas-Fermi approximation is a local one, the effect of the electrostatic potential being described in a band-bending sense. Other quantities, such as the conductivity, are changed according to the local distortion of the energy levels. In using this approximation, we shall return to the use of the local conductivity. It is the conductance which is eventually calculated so that in some sense an average is performed over the local aspects of the approximation.

Corresponding to the relatively weak charging field P which is applied perpendicular to the film, there is an electrostatic potential which locally modifies the energy of a state $E_{nk_yk_z}$ to be

$$E'_{nk_yk_z}(x)=E_{nk_yk_z}-eV(x)$$

with $V(x)$ the self-consistent potential arising from the applied field. $V(x)$ is determined by solving Poisson's equation

$$\frac{d^2V}{dx^2}=-\frac{\Delta\rho(x)}{\epsilon_0} \tag{6}$$

with $\Delta\rho(x)$ the excess charge density induced by the field. This charge density is expressed in terms of the density of electron and hole states as

$$\Delta\rho(x)=-e\left\{\frac{3(m_{ye}m_{ze})^{1/2}}{\pi\hbar^2a}\int_{-eV(x)}^{\infty}dE\left[\left(\frac{E+eV(x)}{\epsilon_{0e}}\right)\right]^{1/2}(1+e^{(E-F)/kT})^{-1}\right.$$
$$\left.-\frac{(m_{yh}m_{zh})^{1/2}}{\pi\hbar^2a}\int_{eV(x)}^{\infty}dE\left[\left(\frac{E-eV(x)}{\epsilon_{0h}}\right)\right]^{1/2}(1+e^{(E-\Delta+F)/kT})^{-1}\right\}. \tag{7}$$

Thus Poisson's equation becomes a nonlinear equation which can be solved numerically for $V(x)$ corresponding to an applied electric field of strength P at $x=0$.

The conductivity can be evaluated locally at each point in the film, the expressions in Eqs. (4) being modified by the now determined potential. They become

$$\sigma_{h(x)} = -\frac{e^2}{\pi\hbar^2 a}\sum_n \int_{n^2\epsilon_{0h}+eV(x)}^{\infty} dE\,\frac{\partial f_{0h}}{\partial E}\,[E-eV(x)-n^2\epsilon_{0h}]\,\tau_{nh}[E-eV(x)],$$

$$\sigma_{e(x)} = -\frac{3e^2}{2\pi\hbar^2 a}\,\frac{m_y+m_z}{(m_y m_z)^{1/2}}\sum_n \int_{n^2\epsilon_{0e}-eV(x)}^{\infty} dE\,\frac{\partial f_{0e}}{\partial E}\,[E+eV(x)-n^2\epsilon_{0e}]\,\tau_{ne}[E+eV(x)]. \tag{8}$$

The conductance of the film is given by ($L_y = L_z$ for simplicity)

$$\Sigma(P) = \int_0^a [\sigma_e(x)+\sigma_h(x)]\,dx. \tag{9}$$

The numerically evaluated integral in the above expression gives the film conductance for applied field P. In a succession of calculations then, the field effect can be investigated for quantum size effects.

The presence of a quantum size effect may be qualitatively understood as follows: For a judiciously chosen film thickness and $T=0$, the Fermi level occurs very close to a step in the electronic density of states. (The effect of the hole band is negligible.) Now an external field is applied and close to the exposed surface, the step in the density of states moves in energy below the Fermi level. The relaxation time

$$\tau_n \propto 1\Big/\left[\left(\frac{F-eV(x)}{\epsilon_{0e}}\right)^{1/2}\right]$$

is reduced significantly and the conductivity in this region of the film is lowered. Further increasing the applied field causes the size of this region of the film to increase, further lowering the film conductance. One should then expect an abrupt decrease in the conductance with the usual linear field effect superimposed. This picture is confirmed by our calculations which we next present.

III. RESULTS AND DISCUSSION

Our numerical results follow from the solution of Eqs. (6)-(9) and the determination of the Fermi level from the charge neutrality condition for the overlapping bands. At temperatures of 4.2 K and higher, considerably more time is required for the numerical work. Most calculations then refer to $T=0$ K.

The quantum size effect on the electric field effect should only be discernible for film thickness

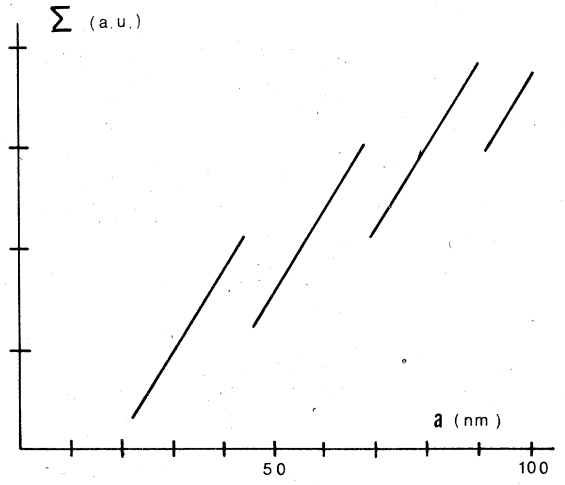

FIG. 1. Film conductance in arbitrary units is shown as a function of film thickness at $T=0$ K. Discontinuities occur at thickness values for which the Fermi level coincides with a step in the electron density of states.

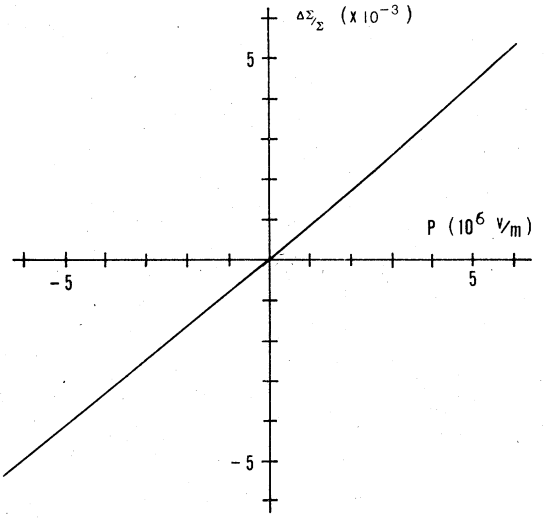

FIG. 2. Fractional change in film conductance with applied electric field is shown. Calculations at $T=0$ K and at $T=4.2$ K give virtually identical results. The film thickness $a=60$ nm is such that the Fermi level is far from a step in the density of states

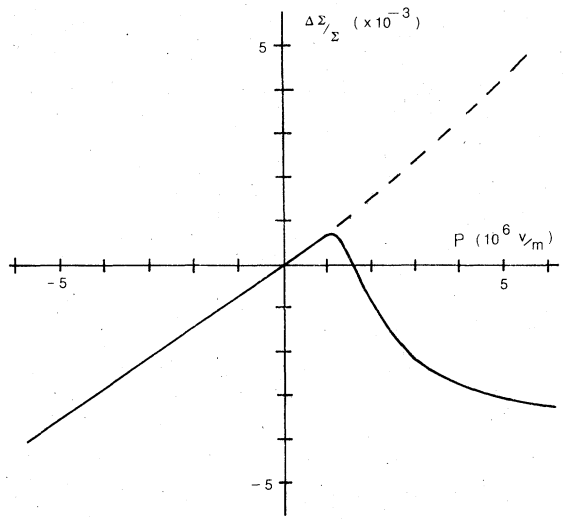

FIG. 3. Fractional change in film conductance is shown for two types of assumptions for the relaxation time. The broken line has τ a constant; the solid line is for τ inversely proportional to the density of states. The calculation is for a 66-nm film at $T=0$ K.

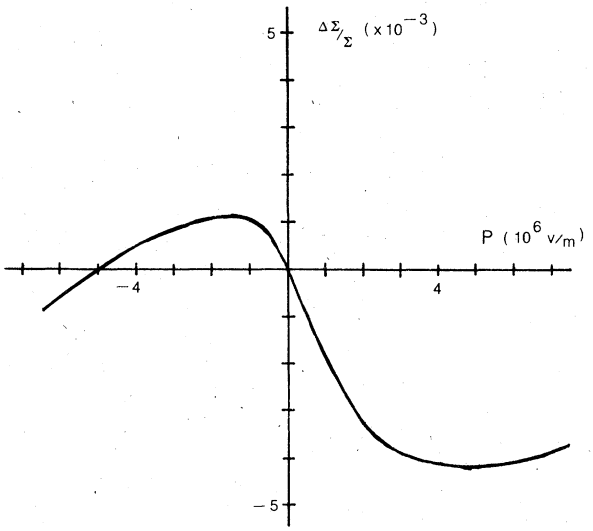

FIG. 4. Fractional change in conductance with electric field for a 67-nm film at $T=4.2$ K.

such that the Fermi level is close to a step in the electronic density of states. One may locate these regions from a knowledge of the thickness dependence of the conductance at $T=0$ K with no externally applied transverse field. That dependence Σ_0 vs a is shown in Fig. 1. These results were obtained with the relaxation time being inversely proportional to the density of states. At those values of film thickness for which the conductance is discontinuous, the Fermi level coincides with a step in the electronic density of states. These values are at about 44, 67, and 90 nm for the range of our calculations. No significance should be attached to their precise values since they depend on effective mass and band overlap parameters.

For a film whose thickness is not close to a step value, one expects a linear field effect. Such a case is shown in Fig. 2 for a 60-nm film. The fractional change in conductance $\Delta\Sigma/\Sigma_0$ is linear in the applied field. The calculations give the same result at $T=0$ K and at $T=4.2$ K.

The quantum size effect is present in the calculations for $a=66$ nm illustrated in Fig. 3. In one set, for the broken line, the constant relaxation time assumption was used; the field effect is almost linear. The only indication of a quantum size effect is a slight upturning of the curve. The solid curve shows the second set of calculations for the inverse density-of-states–dependent relaxation time. There is an abrupt departure from linearity in accord with the qualitative discussion given above. All calculations subsequently discussed were done in the inverse density-of-states approximation for the relaxation time dependence.

We note that the zero-field slope $\Sigma_0^{-1}\, d\Sigma/dP$ at $P=0$ is positive for this value of film thickness, $a=66$ nm. The value of the zero-field slope can change with a small change in temperature or thickness. Thus in Fig. 4, for a film thickness of 67 nm at $T=4.2$ K, the zero-field slope is negative. The slope is negative at $T=0$ K with a further increase of a to a value between 67 and 68 nm.

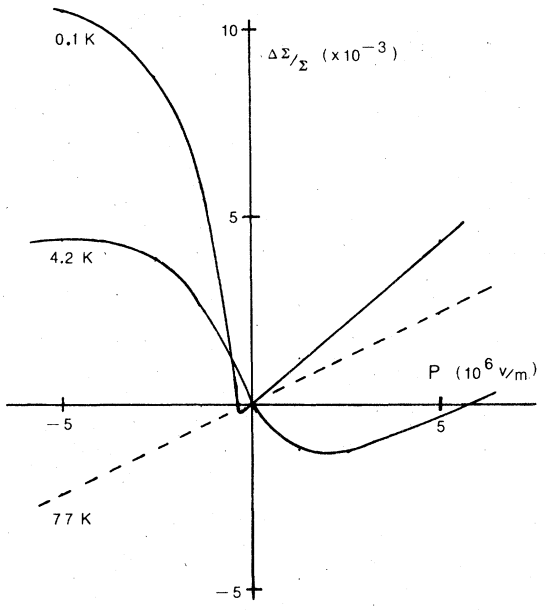

FIG. 5. Fractional change in conductance for a 68-nm film is shown for three temperatures, $T=0.1$, 4.2, 77 K. The quantum size effect has disappeared at the highest temperature.

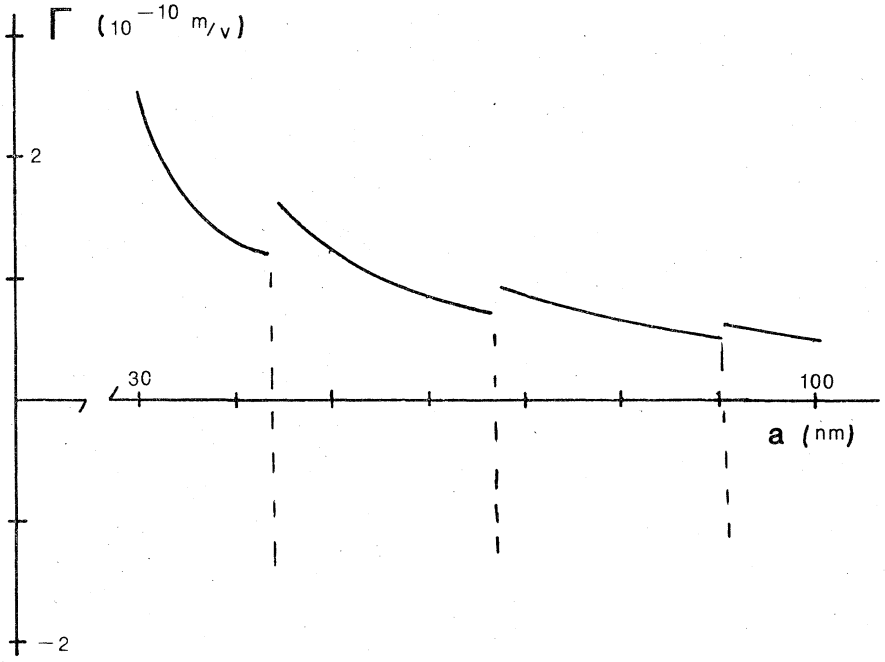

FIG. 6. Values of the zero-field slope, $\Gamma = \Sigma_0^{-1}\,(d\Sigma/dP)$ at $P=0$, are shown vs the film thickness at $T=0$ K. Quantum size effects occur in the vicinity of discontinuities.

The temperature dependence of the field effect is dramatic at a film thickness of 68 nm as shown in Fig. 5 for values of T equal to 0.1 K, 4.2 K, and 77 K. The zero-field slope is positive at $T=0.1$ K, negative at $T=4.2$ K, and positive again at $T=77$ K. In addition, the structure or quantum size effect has disappeared at 77 K.

We see then that quantum size effects in the electric field occur over a very narrow range of thickness and at low temperatures. As described above, the field effect alternates its behavior over a 2-nm thickness variation from 66 to 68 nm. With temperature, it has washed out at $T=77$ K. Its experimental observation would require the use of films of exceedingly uniform thickness. Efforts to observe experimentally in this laboratory[8] size effects of the above type have not been successful to date.

We summarize in Fig. 6 the field effect over a wide range of film thicknesses by giving the value of the zero-field slope, $\Gamma = \Sigma_0^{-1}(d\Sigma/dP)$ at $P=0$, all for $T=0$ K. Quantum size effects occur in the regions where the slope has discontinuities. One should expect these discontinuities to moderate at higher temperatures, for films of nonuniform thickness, or both.

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