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OPTICAL ABSORPTION AND INTRABAND TRANSITIONS IN THIN ANTIMONY FILMS

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The optical properties of thin antimony films subject to quantum size conditions have been studied. It is possible to study the discrete energy levels by means of optical absorption in the infrared range. The resonance energy was calculated and it was found that strong absorption lines may appear when the absorptance is close to unity.

1. Introduction

It is known that thin films of semimetals and semiconductors, of thickness comparable with the de Broglie wavelength of the charge carriers, may exibit quantum size effects due to the quantization of the transverse motion of the charge carriers[1,2]. Quantum size effect (QSE) leads to the appearance of an oscillatory dependence of the thermodynamic properties and of the kinetic coefficients on the thickness of the film which is connected with the formation in the energy spectrum of the charge carrier subbands, whose number varies with varying film thickness.

QSE has been observed in thin semimetallic films of bismuth[3,4] and antimony[5,6], where measurements of the electrical resistance display quantum oscillations with thickness in the range 30—40nm, the oscillations period being ~2.5nm.

Measurements of the optical absorption in thin semiconductor films[7-9] show nonmonotonic dependence and a variation of the energy gap with film thickness due to the formation of subbands in the size quantized films.

The aim of the present work is to investigate the optical absorption spectrum of the size quantized antimony films.

We consider a case of a single crystal film of thickness a and the z axis directed normal to the surface where $O \leqslant z \leqslant a$. The electron mean free path is assumed to be larger than a and the surface scattering is at least partly specular. Moreover, we assume that in the crystal film electrons and holes move as independent particles. Production of such films has been reported[4-6]. In this case quantization of the z motion of the particles has observable consequences. We use the free electron model with the free particle wavefunctions $\exp(\mathrm{i}\,\vec{\mathrm{k}}\,\vec{\mathrm{r}})$. If the film has a reflection plane parallel to the surfaces, $|k_z|$ is quantized according to (Fig. 1):

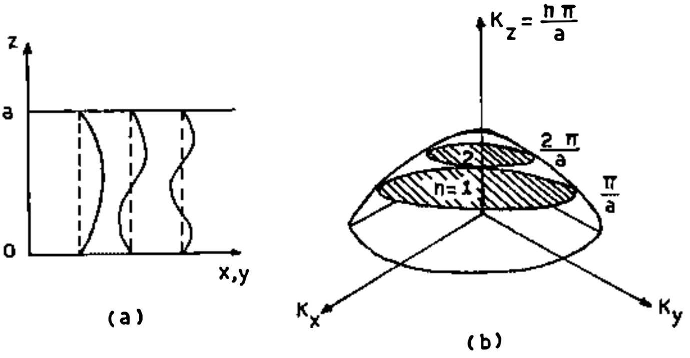


Fig. 1 a) The free electron model wavefunctions.
b) Energy subbands in a semimetal in the $k_x\, k_y\, k_z$ space.

$$|k_z| = n\pi/a. \tag{1}$$

The single particle wavefunction appropriate for this model is given by a complete set of stationary waves normalized per unit area of the film in the form:

$$\Psi(k_x, k_y, n) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\,\pi\,z}{a}\right) \exp\left[\mathrm{i}\,(k_x x + k_y y)\right]. \tag{2}$$

They are the eigensolutions of the Schrödinger equation for a free particle confined to a rectangular potential well with infinite walls and finite width a. The feasibility of this assumption has been recently supported by Kenkre[10].

Band theory effects are introduced into the single particle energy spectrum via the nearly free electron model and an effective mass m^*, which is assumed to be the same as in the bulk system. Therefore, for electrons

$$\xi_e(k_x, k_y, n) = (\hbar^2/2\,m_e^*)\,(k_x^2 + k_y^2) + n^2\,\varepsilon_e \tag{3}$$

where $\varepsilon_e = (\hbar^2 \pi^2 / 2 m_e^* a^2)$ and the hole energy spectrum is

$$\xi_p (k_x, k_y, n) = \Delta - (\hbar^2 / 2 m_p^*) (k_x^2 + k_y^2) + n^2 \varepsilon_p \tag{4}$$

where $\varepsilon_p = (\hbar^2 \pi^2 / 2 m_p^* a^2)$, and Δ is the band overlap parameter of the bulk material. The energy spectrum is consisting of subbands, each subband being determined by a fixed value of n. There may be quite a conspicuous overlap between different subbands when the energy interval $\xi (k_x, k_y, n) - \xi (k_x, k_y, n - 1)$ is small with respect to the width of the subband itself.

Experimental measurements could not resolve QSE hole oscillations in Sb or Bi, because π / k_{Fz} is considerably smaller for holes than for electrons, therefore, we consider only the quantization of electron motion and ignore the holes.

2. *Band structure of antimony*

The relevant band structure of antimony is shown in Fig. 2. The surfaces of constant energy of electrons are approximately ellipsoidal [11-13], with the principal axes in the trigonal (z), binary (x) and bisectrix (y) directions. The three electron pockets are located at the L points, while the holes are located near the T point of the Brillouin zone, with the hole sheets having their long axes canted 53° from the trigonal axis[14]. The dispersion relation is nonparabolic, but for a small range of energy around the Fermi energy E_F, the parabolic dispersion relation

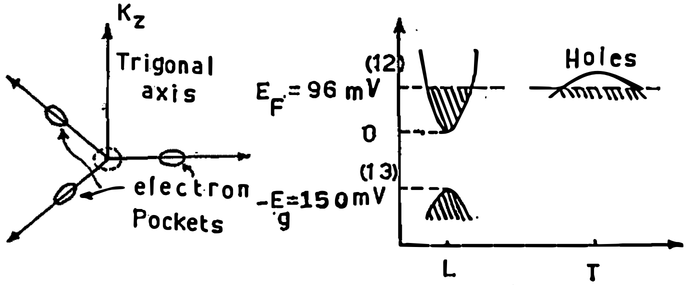
$$\xi = (\hbar^2 / 2 m_0) \vec{k} \cdot a \cdot \vec{k} \tag{5}$$

can be used, where $a = m_0 / m^*$ is the inverse effective mass tensor which depends on the Fermi energy. The components of a at the Fermi energy have been given by Datars and Vanderkooy[15],

$$a_{xx} \approx 10, \qquad a_{yy} \approx 1$$

$$a_{zz} \approx 11, \qquad a_{xy} = a_{xz} = 0.$$

a_{yz} is negligible for the present purpose, therefore, each ellipsoid has a reflection plane parallel to the surfaces.



(a) (b)

Fig. 2 a) Constant energy surfaces in antimony.
b) Energy band structure of antimony.

The characteristic thickness connected with the size quantization of electrons in an antimony film with the trigonal axis normal to the surface is $\pi/k_{Fz} \cong 2.5 + 0.5\,\mathrm{nm} = 47 + 9\,\mathrm{a.u.}$[3,4].

The QSE is pronounced for small quantum numbers $n_F = a\,k_{Fz}/\pi \approx 1$. If p-polarized electromagnetic radiation E_z, $E_z \neq 0$ is shone on the film it will induce optical transitions between occupied and unoccupied electron states. k_x and k_y are conserved in the dipole approximation when the photon momentum is neglected, however $k_z = (n\pi/a)$ can change. Therefore, the transitions are $| k_x, k_y, n_1 > \to | k_x, k_y, n_2 >$ from occupied state to unoccupied final state. The resonance energy of the transition spectral line is given by

$$\xi_{n_1 n_2} = \xi\,(k_x, k_y, n_1\,\pi/a) - \xi\,(k_x, k_y, n_2\,\pi/a) = (\hbar^2/2\,m_0\,a_{zz}\,(\pi/a)^2\,(n_2^2 - n_1^2). \quad (6)$$

For the lowest transition $n_1 = 1$ and $n_2 = 2$ with $a = 25\,\mathrm{nm}$, we obtain $\xi_{12} = 19.8\,\mathrm{meV}$. For antimony the electron plasma frequency ω_p is about $\hbar\,\omega_p \cong 85\,\mathrm{meV}$ (with the electron concentration [15] $5.54 \cdot 10^{19}\,\mathrm{cm}^{-3}$ and the lattice dielectric constant[16] $\varepsilon_l = 85$), therefore, strong resonances may be expected in this range of energies.

3. *The effect of electrons scattering at the surface*

Owing to the scattering of the electrons, the quasidiscrete spectrum is partially smeared out. In order to mantain the quasidiscrete character of the spectrum, it is necessary that the smearing h/τ (where τ is the relaxation time) be smaller than the distance between neighbouring subbands.

For an exact determination of τ it would be necessary to calculate damping of the quasiparticles in the film for different possible scattering mechanisms. Since it is impossible to obtain a sufficiently accurate theoretical estimate, we assume that the electron can cross the film twice on average before being randomized, $\tau \sim 2a/v_z$, where $v_z = a_{zz}\,\hbar\,k_z/m_0$, and k_z is the average value of the initial and final wave vectors, $k_z = (k_{zi} + k_{zf})/2 = (\pi/a + 2\pi/a)/2 = 3\pi/2a$, for $n_1 = 1$ and $n_2 = 2$. Thus

$$\tau = 4\,m_0\,a^2/3\,a_{zz}\,\hbar\,\pi. \quad (7)$$

From Eqs. (6) and (7) we obtain

$$\xi_{12}\,\tau \sim h. \quad (8)$$

Therefore, surface scattering does not obscure the QSE. Long relaxation times have been confirmed[2-6], and QSE oscillations have been observed.

4. *Optical properties of the non-resonant background*

We calculate now an approximate value of the classical optical absorption rate of an antimony film with $a \sim 25\,\mathrm{nm}$ for optical frequencies near to QSE frequency ω_{12}. Such calculations will allow us to establish some fundamental optical properties of the thin films concerned.

To observe the quantum size effects the electron mean free path should be larger than the film thickness. If the film is sufficiently thin, the attenuation of the incident electromagnetic radiation will be small, and the change of phase of the electromagnetic waves is negligible. Therefore, the electric field is nearly constant along the film. Assuming that the relaxation time τ is isotropic, the electrical conductivity can be approximately represented by the scalar

$$\sigma_e = N e^2 \tau \left[\alpha_{zz} + (\alpha_{xx} + \alpha_{yy})/2 \right] / m_o (1 - \mathrm{i}\, \omega \tau) \tag{9}$$

where N is the concentration of the electrons.

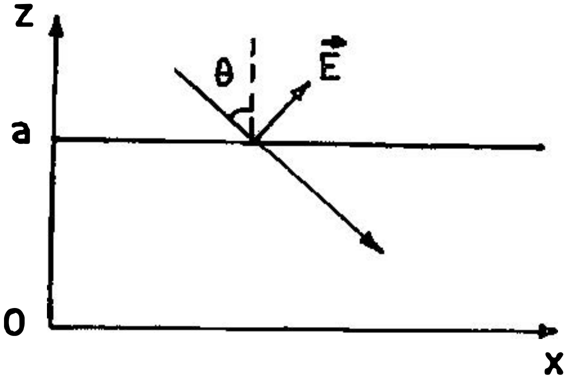


Fig. 3 p-polarized radiation incident on the film.

For thin antimony films in the infrared frequency range, the fraction of energy reflected is small and the fraction of incident energy absorbed A can be calculated from: Absorptance $\cong$ 1 — Transmittance. Following Abeles[17], the classical absorptance of a thin films for p-polarized radiation is given by

$$A_c = \varepsilon_2\, \omega\, a/c \cos \Theta \tag{10}$$

where c is the velocity of light in vacuum, Θ is the angle of incidence and $\varepsilon = \varepsilon_1 + i\, \varepsilon_2$ is the dielectric function. For an isotropic medium and

$$\varepsilon_1 = \varepsilon_l \left\{ 1 - (\omega_p/\omega)^2 \right\} \text{ and } \varepsilon_2 = (\omega_p/\omega)^2/\omega \tau \tag{11}$$

where ε_l is the lattice dielectric constant ($\varepsilon_l = 85$)[16] and ω_p is the plasma frequency. From Eqs. (10) and (11) the value of absorptance A_c for $a = 25$ nm is much smaller than unity. Therefore, this approximate calculation shows that antimony films of thickness subject to the QSE can be nearly transparent outside the interval of the QSE resonance frequencies.

5. Resonant absorption under quantum size effect conditions

Consider a plane electromagnetic wave of a weak p-polarized radiation $\vec{E}_0 \exp(-\mathrm{i}\,\omega\, t)$ with zero scalar potential and a vector potential $\vec{A}_0 = -\mathrm{i}\,(c/\omega)\,\vec{E}_0$, with $\vec{E}_z \neq 0$, the Hamiltonian is $H(\vec{p} - e\,\vec{A}_0/c)$. Since A_0 is small, then:

$$H(\vec{p} - e\,\vec{A}_0/c) = H(\vec{p}) - (e\,\vec{A}_0/c)\,\frac{\partial H}{\partial p} = H(\vec{p}) - (e\,\vec{A}_0/c)\,\frac{\vec{v}}{\hbar}$$

where $\vec{v}$ is the component of velocity along the direction of the field, Therefore, the perturbation in the Hamiltonian is

$$H_1 = -(\mathrm{i}\,e\,\vec{E}_0/\omega)\,\frac{\partial H}{\partial p} = -(\mathrm{i}\,e/\hbar\,\omega)\,\vec{E}_0\,\vec{v}. \tag{12}$$

We consider only transitions in the z direction, therefore, using Eq. (5), the velocity operator is

$$\hat{v}_z = \left(\frac{1}{\hbar}\right)\frac{\partial H}{\partial k} = \frac{\partial H}{\partial p} = \frac{\hbar}{2\,m_0}\,\alpha_{zz}\,(2\hat{k}). \tag{13}$$

To obtain the number of transitions $W(\omega)$ per unit time per unit area of the film and for unit area of the incident beam (i.e. for area $1/\cos\Theta$ of the film), induced by radiation of frequency ω, we make use of the Golden rule 18,19). The required matrix element for the transition is

$$M_{n_1n_2} = -\frac{\mathrm{i}\,e\,E\,\hbar}{\omega\, m_0}\cdot\alpha_{zz}\sin\Theta\int_{-\infty}^{\infty} dz\,\Psi^*(k_x, k_y, n_1)\,\hat{k}\cdot\Psi(k_x, k_y, n_2).$$

The selection rules for the transitions between such states are

$\Delta n = \text{odd}$ (intraband transitions)

$\Delta n = \text{even}$ (interband transitions)

$$M_{n_1n_2} = \left(\frac{e\,E_0\,\hbar}{\omega\, m_0}\,\alpha_{zz}\sin\Theta\right)\frac{4}{a}\left(\frac{n_1\,n_2}{(n_2^2 - n_1^2)}\right). \tag{14}$$

Therefore, the transition probability per unit time is

$$P_{n_1n_2} = \frac{2\pi}{\hbar}\,|\,M_{n_1n_2}\,|^2\left[\frac{1/\pi\,\tau}{\hbar^2\,(\omega_{n_1n_2}-\omega)^2 + (\hbar/\tau)^2}\right]. \tag{15}$$

The factor in the square bracket on the right hand side of Eq. (15) is the Lorentz line shape normalized so that it tends to $\delta\,[\hbar\,(\omega_{n_1 n_2} - \omega)]$ as τ tends to infinity. Performing the summation over k, the spin variable, and over the three ellipsoids, the number of transitions $W(\omega)$ will be

$$W(\omega) = \frac{2\pi}{\hbar}\left(\frac{a_{zz}\hbar\, e\, A_0}{m_0\, c}\right)^2 \sin^2\Theta \iint \left(\frac{3\cdot 2\, dk_x\, dk_y}{(2\pi)^2 \cos\Theta}\right)\cdot$$

$$\cdot\left(\frac{4}{a}\right)^2 \left(\frac{n_1^2\, n_2^2}{n_2^2 - n_1^2}\right)\left[\frac{1/\pi\tau}{\hbar^2\,(\omega_{n_1 n_2} - \omega)^2 + (\hbar/\tau)^2}\right]. \tag{16}$$

The absorptance of the film is equal to the absorption cross section (for one photon flux absorption by one electron) per unit area, therefore

$$A_{n_1 n_2}(\omega) = \frac{\hbar\,\omega\, W(\omega)}{u\,(c/\eta)} \tag{17}$$

where u is the average energy density of the radiation field, η is the refractive index. From Eqs. (16) and (17)

$$A_{n_1 n_2}(\omega) = \left(\frac{4\pi^2 e^2}{\eta\, c\, m_0}\, a_{zz}^2\, \hbar^2\right)\left(\frac{\sin^2\Theta}{\cos\Theta}\right)\frac{6}{(2\pi)^2}\left(\frac{4}{a}\right)^2\cdot$$

$$\cdot\iint \left(\frac{n_1^2\, n_2^2}{n_2^2 - n_1^2}\right)\left(\frac{1/\pi\tau}{\hbar^2\,(\omega_{n_1 n_2} - \omega)^2 + (\hbar/\tau)^2}\right) dk_x\, dk_y. \tag{18}$$

For the transition $n_1 = 1$ and $n_2 = 2$ with $\omega\tau \sim 2\pi$ and $\omega \sim \omega_{12}$, the absorptance reduces to

$$A_{12}(\omega) \sim (\sin^2\Theta/\cos\Theta)/[1 + (\omega_{12} - \omega)^2\,\tau^2]. \tag{19}$$

The absorptance will reach its maximum near QSE resonant frequency ω_{12}, ($\omega_{12} = 3\cdot 10^{13}$ for $a = 25$ nm), and away from ω_{12} the absorptance decreases and is given by expression (10), while the reflectance becomes appreciable. Higher transitions will occur at higher frequencies and lower wavelengths, and thinner films have higher transmission.

The above analysis reveals that the detection of QSE in thin antimony films and similar materials by infrared absorption spectroscopy measurements is possible. Experimental measurements have confirmed the feasibility of infrared spectroscopy in the case of In Sb[7,8] and Pb Te[9] films.

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OPTIČKA APSORPCIJA I ELEKTRONSKI PRELAZI UNUTAR VRPCI TANKIH ANTIMONSKIH FILMOVA

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Proučavana su optička svojstva tankih antimonskih filmova u uvjetima pri kojim dimenzije sistema mogu utjecati na njihova kvantna svojstva. Uspostavlja se da je moguće proučavati diskretna energetska stanja sistema pomoću optičke apsorpcije u infracrvenom području. Izračunata je rezonantna energija i predviđena je jaka apsorpciona linija kada koeficijent apsorpcije teži jedinici.