QUANTUM SEEBECK EFFECT

Instituto de Física, Universidade de São Paulo, CP 66.318
05315-970, São Paulo, SP, Brasil

M. Cattani, M. C. Salvadori, F. S. Teixeira

Publicação IF
1674/2012

25/10/2012

UNIVERSIDADE DE SÃO PAULO
Instituto de Física
Cidade Universitária
Caixa Postal 66.318
05315-970 - São Paulo - Brasil

QUANTUM SEEBECK EFFECT

M. Cattani, M. C. Salvadori, F. S. Teixeira
Institute of Physics, University of São Paulo, C.P. 66318, CEP 05315-970, São Paulo, Brasil
mcattani@if.usp.br

Abstract. In this paper, that was written to graduate and post-graduate students of Physics, we study the Quantum Seebeck Effect that we have found when electric currents pass by very thin platinum films with thickness smaller than 15 nm.

I)Introduction.

Since this paper is written to graduate and post-graduate students of Physics it is important to note that the "thermoelectric effects" were analyzed only in earlier textbooks like, for instance, "Physics" of F.W.Sears[1]. They are is not studied in modern textbooks like, for instance, Halliday and Resnick,[2] Tipler,[3] Serway[4] and Sears & Semansky.[5] The "thermoelectric effect" is a direct conversion of temperature differences to electrical voltage and vice-versa.[6] A thermoelectric device creates a voltage when there is a different temperature on each side. Conversely, when a voltage is applied to it, it creates a temperature difference. At the atomic scale, an applied temperature gradient causes charge carriers in the material to diffuse from the hot side to the cold side. This effect can be used to generate electricity, measure temperature or change the temperature of objects. Because the direction of heating and cooling is determined by the polarity of the applied voltage, thermoelectric devices are efficient temperature controllers. This effect can be used to generate electricity, measure temperature or change the temperature of objects. The term "thermoelectric effect" encompasses three separately identified effects: the Seebeck effect, Peltier effect and Thomson effect. Textbooks may refer to it as the Peltier–Seebeck effect.[6] Studies about thermoelectric effects for bulk materials can be found in textbooks, such as, Sears,[1] Sommerfeld,[7] or J.Osada[8] and also in our recent didactical paper.[9]

In Section 1 we make a brief theoretical review of the thermoelectric effects for bulk materials, showing in details only the Seebeck Effect. In Section (2.a) we analyze the Seebeck effect for *thin films* and in Section (2.b) the Quantum Seebeck Effect that we have found for nanometric *very thin platinum* films with dimensions smaller than 15 nm**.**

(1) Thermoelectric effects for bulk materials.

For bulk materials the thermoelectric effect can be understood, from the theoretical point of view, using the Boltzmann transport equation.[8,9] So, let us indicate by ε the electron energy and $f_0(\varepsilon)$ the equilibrium Fermi-Dirac distribution function for the conducting electrons. Submitting the conducting system to an electric field E and to a temperature gradient $\partial T(x)/\partial x$, both along the x-axis, the perturbed electronic distribution function $f(\varepsilon)$ is written as,

$$f(\varepsilon) = f_0(\varepsilon) + p_x\,\chi(\varepsilon),$$

where p_x is the electron momentum along the x-axis, the Boltzmann equation obtained is:

$$-e\,E\frac{\partial f}{\partial p_x} + \frac{p_x}{m}\frac{\partial f}{\partial T}\frac{\partial T}{\partial x} = -\frac{p\,p_z}{m\,\ell}\chi(\varepsilon)$$

where $\ell = \ell(\varepsilon)$ is the electron bulk mean free path.

Solving Boltzmann equations in first order approximation, we have

$$\chi(\varepsilon) = \frac{\ell}{p}\left\{e\,E + \left[\frac{\varepsilon}{T} - \left(\frac{\mu}{T} - \frac{\partial\mu}{\partial T}\right)\right]\frac{\partial T}{\partial x}\right\}\frac{\partial f_0}{\partial\varepsilon}$$

where μ is the chemical potential of the material.

Taking into account that, along the x-axis, the electrical current density (J) and the thermal current density (Q) are given by

$$J = -e\int 2\frac{d\vec{p}}{(2\pi\hbar)^3}\frac{p_x}{m}f(\vec{p})$$

$$Q = \int 2\frac{d\vec{p}}{(2\pi\hbar)^3}\varepsilon\frac{p_x}{m}f(\vec{p})$$

we can show that J is given by:

$$J = e\left[e\,E - \left(\frac{\mu}{T} - \frac{\partial\mu}{\partial T}\right)\frac{\partial T}{\partial x}\right]D_1 + e\frac{1}{T}\frac{\partial T}{\partial x}D_2 \qquad (1.1)$$

where D_n (n =1,2,…) are given by:

$$D_n = -\frac{16\pi\, m}{3\,(2\pi\hbar)^3}\int d\varepsilon\, \varepsilon^n\ \ell(\varepsilon)\,\frac{\partial f_0}{\partial \varepsilon}$$

where $\ell(\varepsilon) = \ell$ is the *electronic mean free path* of the material.

Using (1.1) we can calculate all thermoelectric effects: Seebeck effect, Peltier effect and Thomson effect. In next Sections only the Seebeck effect will be analyzed.

(1.a) Seebeck Effect for Bulk Materials.

If there is no electric current in the circuit, that is, when $J = 0$ and when $\partial T/\partial x \neq 0$ we can estimate what is known as Seebeck effect. So, putting $J = 0$ in (1.1) we get,

$$E = \frac{1}{e}\left(\frac{\mu}{T} - \frac{\partial \mu}{\partial T}\right)\frac{\partial T}{\partial x} - \frac{1}{eT}\frac{\partial T}{\partial x}\frac{D_2}{D_1}$$

Let us consider a system composed by three materials, 1, 2 and Cu assuming that the junctions between 1 and 2 are maintained at different temperatures T and T´ as is seen in Figure 1. The points P and Q of the Cu are maintained at the same temperature T_o.

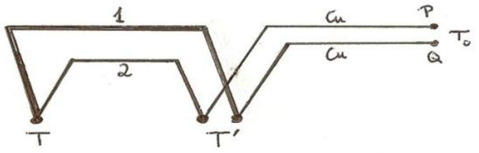

Figure 1: Circuit composed by 3 materials, 1, 2 and Cu. The junctions between 1 and 2 maintained at different temperatures T and T´ and the points P and Q of the Cu are at the same temperature T_o

In this way, the voltage V_{PQ} between P and Q is given by

$$V_{PQ} = \int_P^Q E\,dx = \int_{T_o}^{T'} E_{Cu}\,dx + \int_{T'}^{T} E_1\,dx + \int_{T}^{T'} E_2\,dx + \int_{T}^{T_o} E_{Cu}\,dx =$$

$$= \int_{T'}^{T} (E_1 - E_2)\,dx.$$

That is,

$$V_{PQ} = \int_P^Q E\,dx = \frac{\pi^2 k^2}{3\,e}\int_T^{T'} dT\ T\left[\left(\frac{\Lambda}{\mu}\right)_2 - \left(\frac{\Lambda}{\mu}\right)_1\right] \qquad (1.2),$$

where, $\Lambda = 1 + 2\mu\ell'/\ell$, $\ell(\varepsilon)$ the bulk mean free path and $\ell'(\varepsilon) = d\ell(\varepsilon)/d\varepsilon$. The subscripts 1 and 2 means that the function (Λ/μ) must be calculated for the Fermi energies of the materials 1 and 2, respectively.

Defining the "Seebeck coefficient" S (or "thermopower" S) by $S = \pi^2k^2\Lambda T/(3\mu e)$, (1.2) becomes

$$V_{PQ} = \int_T^{T'} dT\,(S_2 - S_1) \qquad (1.3).$$

If S is constant for a small temperature difference $T - T' = \delta T$, (1.3) can be written as

$$V_{PQ} \approx (S_2 - S_1)\,\delta T \qquad (1.4),$$

where S_1 and S_2 are calculated at $T = (T+T')/2$.

The voltage created by this effect is on the order of several microvolts per Kelvin difference. The combination, copper-constantan has a Seebeck coefficient of 41 microvolts per Kelvin at room temperature.

The Seebeck effect is used in thermocouple to measure temperature differences. The absolute temperature may be found by setting one end to a known temperature. A metal of unknown composition can be classified by its thermoelectric effect if a metallic probe of known composition, kept at a constant temperature, is held in contact with it.

According to (1.3) the Seebeck Effect depends on the electronic mean free paths, that for bulk materials are given by

$$\ell_{bulk} = m\,v_F\,/(ne^2\rho_{bulk}) \qquad (1.5),$$

where m is the effective electron mass, e the electron charge, v_F the Fermi velocity and ρ_{bulk} is the bulk electrical resistivity.

As will be seen in Section 2, for conductors with nanometric dimensions the total resistivity $\rho(t)$ depends on the film thickness t and is given by $\rho(t) = \rho_{bulk} + \rho_s(t)$, where $\rho_s(t)$ is the resistivity due to the scattering of the electrons by the roughness of the conductor surfaces. In this way, electronic mean free path $\ell_f(t)$ for the film is given by,

$$\ell_f(t) = m\,v_F\,/(ne^2\rho(t)) = \ell_{bulk}\,\rho_{bulk}/\rho(t) \qquad (1.6),$$

that depends on the conductor dimension t.

Since the "thermopower" $S = \pi^2k^2\Lambda T/(3\mu e)$ and $\Lambda = 1 + 2\mu\ell'/\ell$ is a function of ℓ, that is, $\Lambda = \Lambda(\ell)$ we see that the Seebeck voltage V_{PQ}, given by (1.2)-(1.4), will also depend on the mean free path.

2) Seebeck effect for thin and very thin films.

Thin film thermocouples (TFTC) provide a sensitive way of making accurate and fast (down to ~ 1μ s response time) surface temperature measurements. They have the advantages of intimate thermal contact with the surface, low thermal inertia (mass ~10^{-4} g), high spatial resolution, and low cost. Development of TFTCs has been vigorous in recent years,[10] prompted in a large part by the need of the microelectronics industry for TFTCs with ever-smaller dimensions. However, when the film thickness becomes comparable to the mean free path of the charge carriers, all transport processes are expected to exhibit size effects.[11-13] Extensive electric and galvanomagnetic studies of thin films of alkali and noble metals have established the existence of size effects, important from both fundamental and technical points of view.

In the Section 1 we have calculated the electrical and thermal conductivities of metallic bulks using the Boltzmann transport equation. With a similar formalism we can calculate the resistivity of thin nanometric metallic films.[9,11-13] We assume that the films are in a plane (x,y) with lengths L_x and L_y along the axes x and y, respectively, and thickness t along the z-axis. For nanometric dimensions quantum size effects (QSE) play the main role[11] in the electronic conductivity when $t \leq \ell_{bulk}$. In this way a quantum mechanical approach is necessary to describe the conductivity. The coordinates (x,y,z) origin is chosen in the middle point of the film, that is, $-L_x/2 \leq x \leq L_x/2$, $-L_y/2 \leq y \leq L_y/2$ and $-d/2 \leq z \leq d/2$. L_x and L_y are very large, that is, $L_x >> d$ and $L_y >> d$. Due to the very small film thickness t the electronic states are quantized along the z-axis. These quantum states are known as *Fermi subbands*.[11,13] In these conditions the electric resistivity is due to a bulk effect and to the roughness of the film surfaces. The height fluctuations of the film surfaces are located at the planes with z = −t/2 and t/2. The total resistivity $\rho_F(d)$ of a thin film with thickness d is given by

$$\rho_f(t) = \rho_S(t) + \rho(\infty) = 1/\sigma_S(t) + \rho_{bulk} \qquad (2.1),$$

where $\rho_S(t)$ and $\sigma_S(t)$ are, respectively, the surface resistivity and conductivity of the thin film and $\rho(\infty) = \rho_{bulk}$ is the bulk conductor resistivity (or the resistivity of the film when $t \to \infty$). From the $\rho_f(t)$ resistivity measurements[10,11] of we can determine the surface conductivity using (2.1): $\sigma_S(t) = 1/ [\rho_f(t) - \rho_{bulk}]$.

The *quantum size effects* are small[11-13] when $t >> \ell$; they become significant only for $t \leq \ell$.

(2.a) The Seebeck effect for *thin* metallic films.

We say that a film is *thin* when $t >> \ell$. The *bulk* limit is obtained making $t\to\infty$. A large number of experimental works[14-17] on the electrical conductivity of *thin films*, that is, when $t >> \ell$, has shown that the ratio σ_f/σ_{bulk} is well described by $\sigma_f/\sigma_{bulk} = 1 - c/t$, where σ_{bulk} is the bulk conductivity and *c* is a constant. With the same precision the resistivity ratio ρ_f/ρ_{bulk} is given by $\rho_f/\rho_{bulk} = 1 + c/t$. The 1/t variation is in good agreement with the **semiclassical predictions** of Fuchs[18] (see Appendix):

$$\sigma_f/\sigma_{bulk} \approx 1 - (3/8)(1 - p)\ell/t\,, \qquad (2.2),$$

where *p* is the fraction of energy lost by the charge carriers when reflected by the film surface. Since $\rho = 1/\sigma$, Eq. (2.2) can be written in terms of the resistivity ratio,

$$\rho_f/\rho_{bulk} \approx 1 + (3/8)(1 - p)\ell/t \qquad (2.3).$$

As shown in Appendix the semiclassical theory predicts that the resistivity would obey a law

$$\rho_f/\rho_{bulk} = 1 + \Sigma_n\, a_n(\ell/t)^n \qquad (2.4).$$

where n=1,2,…

According to Justi et al.[19] and Mayer,[20] when Eq. (2.2) is obeyed the thermoelectric power S_F of pure metal thin films with thickness $t >> \ell$ is given by

$$S_f = S_{bulk}[(1 - (3/8)\ell/t)(1 - p)U/(1 + U)]\,, \quad (t >> \ell) \qquad (2.5),$$

where $U = (\partial \ln\ell(\varepsilon)/\partial \ln\varepsilon)_{\varepsilon=\xi}$, ε is the electron energy, $\xi = \varepsilon_F$ is the Fermi energy and the bulk thermoelectric power S_{bulk} is given by

$$S_{bulk} = -(\pi^2/3e)(k^2T/\xi)(U + 1), \qquad (2.6),$$

From (2.5) and (2.6) we obtain

$$\begin{aligned}\Delta S &= S_{bulk} - S_f = S_{bulk}(3/8)[(\ell/t)(1 - p)U/(1 + U)] \qquad (t >> \ell)\\ &= -(\pi^2/8e)(k^2T/\xi)\,[\ell U(1 - p)/t]\\ &= -9.2 \times 10^{-3}(T/\xi)\,[\ell U(1 - p)/t] \quad (\mu V/deg) \qquad (2.7).\end{aligned}$$

Thus, for *thin films* ($t >> \ell$), according (2.7), the Seebeck factor ΔS obey a 1/t law. This is seen in Figure 2 that will be analyzed in next Section.

(2.b) The Seebeck effect for *very thin* metallic films.

Many experimental work[11]shown that for *very thin* films that is, when $t \leq \ell$ the resistivity ratios $(\rho_f/\rho_{bulk})_{Pt}$ obey a law completely different from (2.3) predicted by the semiclassical approach. For instance, in a previous work[21-24] we have shown that the ratio ρ_f/ρ_{bulk} for Pt films with thickness in the range $1.31 \leq t \leq 11.66$ nm is given by

$$(\rho_f/\rho_{bulk})_{Pt} = 1 + 6.5/t + 140/t^9 \qquad (2.8).$$

For these films **quantum size effects** become relevant because $t \leq \ell$, noting that for Pt we have $\ell_{bulk} \approx 10.0$ nm.

To verify the deviation of the ΔS factor from the 1/t law our Seebeck device[12] (see Fig.2) was composed by *very thin films* of Pt (film 1) and a thick film of Au (film 2). The Pt films had thickness in the range $1.31 \leq t \leq 11.66$ nm and the gold film had a constant thickness equal to $t_{Au} = 141$ nm.

In our experiment $\Delta S = (S_{bulk})_{Au} - (S_{film}(t))_{Pt}$ represented in Fig.2 by $\Delta S = S_B - S_F$, where $S_B = (S_{bulk})_{Au}$ and $S_F = (S_{film}(t))_{Pt}$.

In Figure 2 is shown details of our thermocouples that have been used[12] to measure the Seebeck effect. In Figure 3 are shown the measured ΔS values as a function of 1/t where t are the thickness of the Pt films.

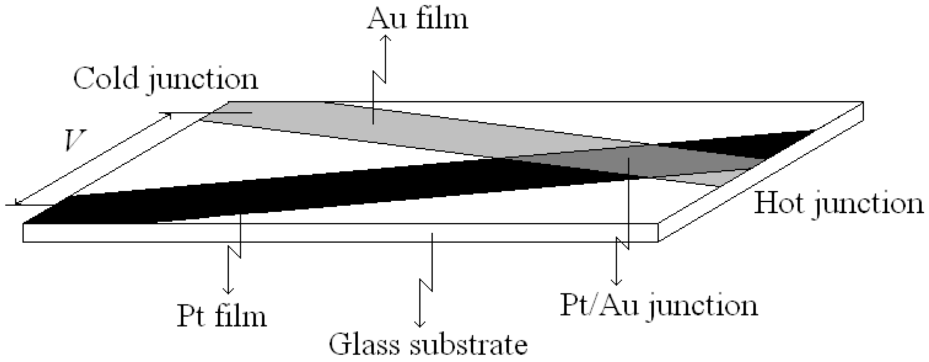

Figure 2. Our thermocouples[12] were formed of and Pt and Au strips, 6 mm wide, on glass microscope slides. The thermoelectric voltage *V* is measured as indicated.

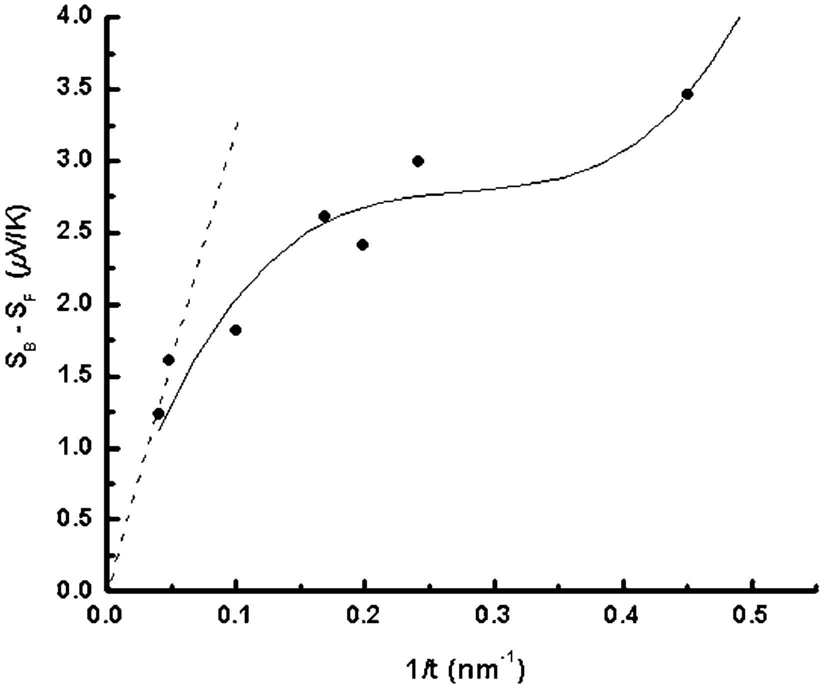

Figure 3. The measured[12] Seebeck power $\Delta S = S_B - S_F$, where $S_B = (S_{bulk})_{Au}$ and $S_F = (S_{film}(t))_{Pt}$,as a function of 1/t where t are the thickeness of the Pt films.

In Figure 3 the experimental results[12] are represented by solid circles, and the continuous line is a best-fit to the experimental results, given by the function

$$\Delta S_F = 0.194 + 26.7(1/t) - 93.6(1/t)^2 + 112.0(1/t)^3. \qquad (2.9).$$

The straight dashed line shows the linear behavior of ΔS as a function of 1/t as expected for films thick compared to about 20 nm, when $t >> \ell$. This figure clearly shows that the thermopower ΔS_F varies linearly with 1/t only for Pt films with thickness less than about 20 nm. This behavior is in accord with the theoretical predictions described above: a linear relationship is expected for $t >> \ell$. On the other hand, for *very thin films*, that is, with $t < \ell$ the factor ΔS_F obeys a clearly non-linear law given by (2.9). This behavior is due to quantum size effects that become relevant when $\ell \geq t$. Note that Eqs. (2.2)-(2.7) were derived using a semiclassical approach[18-20] that is applicable only when quantum size effects are negligible, i.e., when $t >> \ell$, resulting in ΔS varying linearly with 1/t. To explain theoretically (2.9), that is, the *quantum Seebeck effect*, it would be necessary perform a quantum mechanical calculation of the thermoelectric power of very thin films. This calculation is still lacking.

Appendix. Semiclassical approach for thin films.

As can be seen, for instance, in the paper of Justi et al.,[19] the thermoelectric power S_F of a film with thickness t is calculated using the Boltzmann transport equation. It is assumed that the charge carriers are free electrons obeying the Fermi-Dirac statistics and that the relaxation time τ is given by $\tau = \ell/v_F$, where v_F is the Fermi velocity. According to their approach S is given by

$$S_F = -(\pi^2 k^2 T/3e)[d\ln\sigma(E)/dE]_{E=\xi} \; . \qquad (A.1)$$

Defining $\psi(E) = \sigma(E)/\sigma_{bulk}$ they have shown that S_F is written as

$$S_F = -(\pi^2 k^2 T/3e)\{1 + U\,[1 + \chi(d\,\ln\psi(\chi)/d\chi)]\} \qquad (A.2)$$

where $\chi = t/\ell$ and $U = (\partial\ln\ell(E)/\partial\ln E)_{E=\xi}$.

According to Fuchs,[18] taking into account semiclassical size effects, $\psi(\chi) = \sigma(\chi)/\sigma_{bulk}$ is given by

$$\sigma(\chi)/\sigma_{bulk} = 1 - [3(1-p)/8\chi](1 - e^{-\chi}) + [3(1-p)^2/4\chi]F(\chi,p), \qquad (A.3)$$

where p (*scattering coefficient*) is the fraction of the energy lost by electrons when reflected by the film surfaces,

$$F(\chi,p) = \sum_{\nu=1}^{\infty} p^{\nu-1}\{B(y)(\,y^2 - y^4/12) + e^{-y}(1/2 - 5y/6 - y^2/12 + y^3/12),$$

$y = \nu\,\chi$ and $B(y) = -\,\mathrm{Ei}(-\,y)$.

When $\chi = t/\ell >> 1$, since $\psi(\chi) = \sigma(\chi)/\sigma_{bulk} \approx 1 - [3(1-p)/8\chi]$, one can verify, taking into account Eq.(A.2), that

$$S_F = -(\pi^2 k^2 T/3e)\,[1 + U(1 - 3(1-p)\ell/8t)]. \qquad (\,t >> \ell)\ldots..(A.4)$$

In the limit $\chi \to \infty$ we obtain from Eq.(A.4) the bulk thermopower $S_B = S_{bulk}$:

$$S_B = S_{bulk} = \lim_{\chi\to\infty} S = -(\pi^2 k^2 T/3e)\,(U + 1)\,,$$

according to (2.6).

REFERENCES

(1)F. W. Sears. "Física 2". Ao Livro Técnico. RJ(1956).
(2)R.Resnick e D.Halliday. "Física". LTC. RJ(1976).
(3)P.A.Tipler. "Física". Editora Guanabara. RJ(1985).
(4)R.A.Serway. "Física". LTC. RJ(1992).
(5)F.W.Sears e R.A.Freedman."Física". Addison Wesley. SP(2004).
(6)"Thermoelectric Effect. http://en.wikipedia.org/wiki/Thermoelectric_effect
(7)A.Sommmerfeld."Thermodynamics and Statistical Mechanics. Academic Press (1964).
(8)J.Osada. "Mecânica Estatística". Notas de Aulas. IFUSP(1970).
(9)M.Cattani."Boltzmann Transport Equation and the Electrical and Thermal Conductivities of Metallic Bulks" http://publica-sbi.if.usp.br/PDFs/pd1671.pdf (09maio12).
(10)L. Scarioni and E.M. Castro, J. Appl. Phys. 87, 4337 (2000).
(11)G.Fishman and D.Calecki. PRL 62,1302 (1989); PRB 43,11581(1991).
(12)M.C.Salvadori, A.R. Vaz, F.S.Teixeira and M.Cattani.Appl.Phys. Lett. 88,133106 (2006) and many references there in.
(13)M.Cattani. "Electrical Conductivity of Very Thin Metallic Films" http://publica-sbi.if.usp.br/PDFs/pd1672.pdf (18maio12).
(14) C.R. Tellier and A.J. Tosser. "Size Effects in Thin Films". Elsevier Scientific Publishing Company (1982) and many references therein.
(15)M. Jalochowski, E. Bauer, H. Knoppe and G. Lilienkamp. Phys. Rev. B 45, 13607 (1992).
(16)E.V. Barnat, D. Nagakura, P.I. Wang and T.M. Lu, J. Appl. Phys.91, 1667 (2002).
(17)S.M. Rossnagel and T.S. Kuan, J. Vac. Sci. Technol. A20,1911 (2002).
(18)K.Fuchs. Proc.Cambridge.Phil.Soc.34,100 (1938).
(19)E. Justi, K. Kohler and G. Lautz, Z. Naturforsch. 6A, 456; 544 (1951).
(20)H. Mayer, Physik dünne Schichten, (Wissenschaftlische-Verlagsgesellschaft MBH, Stuttgart) vol. 2, p. 232 (1955).
(21)M.C. Salvadori, A.R. Vaz, J.C. Farias and M. Cattani. Surf. Rev. Lett. 11, 223 (2004).
(22)M. Cattani and M. C. Salvadori, *Surf. Rev. Lett.* **11**, 283 (2004).
(23)M. Cattani and M. C. Salvadori, *Surf. Rev. Lett.* **11,** 463 (2004).
(24)M.Cattani, M.C.Salvadori, F.S.teixeira and R.S.Wiederkehr. Surf. Rev. Lett. 14, 345(2007).