

# Orbital effect on the in-plane critical field in free-standing superconducting nanofilms

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The superconductor to normal metal phase transition induced by the in-plane magnetic field is studied in free-standing Pb(111) nanofilms. In the considered structures the energy quantization induced by the confinement leads to the thickness-dependent oscillations of the critical field (the so-called 'shape resonances'). In this paper we examine the influence of the orbital effect on the in-plane critical magnetic field in nanofilms. We demonstrate that the orbital term suppresses the critical field and reduces the amplitude of the thickness-dependent critical field oscillations. Moreover, due to the orbital effect, the slope  $H_{c,\parallel} - T_c$  at  $T_c(0)$  becomes finite and decreases with increasing film thickness in agreement with recent experiments. The temperature  $t^*$  at which the superconductor to normal metal phase transition becomes of the first order is also analyzed.

## I. INTRODUCTION

The huge progress in nanotechnology which has been made in the last decade reopens the issue of superconducting properties of metallic nanostructures i.e. nanofilms<sup>1-5</sup>, nanowires<sup>6-8</sup> or metallic grains<sup>9-11</sup>. The studies of the quantum size effect and its influence on the paired phase in thin films was initiated by Blatt and Thomson in 1963<sup>12</sup>. The main finding of their work<sup>12</sup> was the appearance of sharp oscillations of the critical temperature as a function of the film thickness. As it was argued<sup>12</sup> this effect results from the confinement of the electron motion in the direction perpendicular to the film. If the size of the system becomes comparable to the electron wave length, the Fermi sphere splits into a set of discrete two-dimensional subbands, energy of which increases with decreasing film thickness. Each time a bottom of a subband passes through the Fermi level, a sharp peak of the critical temperature appears. Due to technological difficulties in the preparation of uniform films, which were typically polycrystalline and contained a large number of defects, the experimental observation of the so-called shape resonances has been reported only recently<sup>13-16</sup>. Measurements of the critical temperature for Pb(111) nanofilms grown on Si substrate<sup>15,16</sup> revealed that the period of the thickness-dependent oscillations is equal to  $\sim 2$  ML. Additionally, the beating effect with the periodicity varying from 7 ML to 14 ML was observed. This feature, called bilayer or even-odd oscillations, was theoretically studied by Shanenko et al. in Ref.<sup>17</sup>. The studies of superconducting properties of the ultra-thin films have been recently extended to the case of high temperature and multiband superconductors. Recently, the enhancement of the superconducting critical temperature with respect to the bulk limit has been reported for interfaces and heterostructures based on cuprates<sup>18</sup>, iron pnictides<sup>19</sup> and  $\text{LaAlO}_3/\text{SrTiO}_3$ <sup>20</sup>. Moreover, the experimental reports on the growth techniques of high quality

$\text{MgB}_2$  films of thicknesses less than 10 nm<sup>21,22</sup> entailed a series of theoretical papers describing the quantum size effect in multiband thin film superconductors<sup>23-27</sup>.

Recent studies devoted to superconductivity in the nanoscale regime concern the effect of the quantum confinement on the superconductor to normal metal phase transition induced by the magnetic field<sup>28</sup>. The thickness-dependent oscillations of the perpendicular and parallel critical field for ultra-thin lead films were reported by Bao et al. in Ref.<sup>29</sup>. Moreover, the study of the superconductor to normal metal transition induced by the parallel magnetic field for Pb monolayer was recently presented by Sekihara et al. in Ref.<sup>30</sup>. In both experiments, the measured parallel critical field was higher than the Pauli paramagnetic limit. This unusual behavior has been explained in our recent papers<sup>31,32</sup> in which we have investigated the quantum size effect on the in-plane critical field in paramagnetic limit. We have shown<sup>31</sup> that the zero-temperature critical field for nanofilms is higher than the Clogston - Chandrasekhar (CC) paramagnetic limit and diverges to the CC (Pauli) limit for sufficiently thick films. This fact has been explained on the basis of the spatially varying energy gap induced by the confinement. In Ref.<sup>31</sup> the new formula for the paramagnetic critical field in nanofilms has been proposed. However, the analysis presented in Ref.<sup>31</sup> has been carried out in the paramagnetic limit. The extension of this study for films thicker than 15 ML requires the inclusion of the orbital effect which significantly affects the superconductor to normal metal transition. According to our knowledge such study has not been reported until now.

In the present paper we consider free-standing Pb(111) metallic nanofilms and investigate the orbital effect on the superconductor-normal metal transition driven by the in-plane magnetic field. Based on the analysis of the spatially dependent energy gap we study the influence of the orbital effect on the critical magnetic field oscillations induced by the confinement. The analysis of the thermal effect in terms of the orbital effect is also included. The

paper is organized as follows: in Sec. II we introduce the basic concepts of the theoretical scheme based on the BCS theory, in Sec. III we present the results while the summary is included in Sec. IV.

## II. THEORETICAL METHOD

The phonon-mediated superconductivity in metallic nanofilms can be described with the use of the BCS theory. The Hamiltonian of the system is given by

$$\begin{aligned}\hat{\mathcal{H}} = & \sum_{\sigma} \int d^3r \hat{\Psi}^{\dagger}(\mathbf{r}, \sigma) \hat{H}_e^{\sigma} \hat{\Psi}(\mathbf{r}, \sigma) \\ & + \int d^3r \left[ \Delta(\mathbf{r}) \hat{\Psi}^{\dagger}(\mathbf{r}, \uparrow) \hat{\Psi}(\mathbf{r}, \downarrow) + H.c. \right] \\ & + \int d^3r \frac{|\Delta(\mathbf{r})|^2}{g},\end{aligned}\quad (1)$$

where  $\sigma$  indexes the spin state ( $\uparrow, \downarrow$ ) and  $g$  is the electron-phonon coupling. In the presence of the in-plane magnetic field  $H_{||}$ , the single-electron Hamiltonian  $\hat{H}_e^{\sigma}$  can be expressed as

$$\hat{H}_e^{\sigma} = \frac{1}{2m} \left( -i\hbar\nabla + \frac{e}{c}\mathbf{A} \right)^2 + s\mu_B H_{||} - \mu_F, \quad (2)$$

where  $s = +1(-1)$  for  $\sigma = \uparrow(\downarrow)$ ,  $m$  is the effective electron mass,  $\mu_F$  is the chemical potential,  $\mathbf{A} = (0, -H_{||}z, 0)$  is the vector potential corresponding to the magnetic field  $\mathbf{H} = (H_{||}, 0, 0)$  applied in-plane and the energy gap  $\Delta(\mathbf{r})$  is defined as

$$\Delta(\mathbf{r}) = -g \left\langle \hat{\Psi}(\mathbf{r}, \downarrow) \hat{\Psi}^{\dagger}(\mathbf{r}, \uparrow) \right\rangle. \quad (3)$$

In ultrathin nanofilms the electron motion is limited in the direction perpendicular to the film ( $z$  axis) resulting in the quantization of the electron energy. We assume that the system is infinite in the  $x - y$  plane. Thus, the field operators in Eq.(1) are expressed as

$$\hat{\Psi}(\mathbf{r}, \sigma) = \sum_{n, \mathbf{k}} \phi_{\mathbf{k}n}(\mathbf{r}) \hat{c}_{\mathbf{k}n\sigma}, \quad (4)$$

$$\hat{\Psi}^{\dagger}(\mathbf{r}, \sigma) = \sum_{\mathbf{k}, n} \phi_{\mathbf{k}n}^*(\mathbf{r}) \hat{c}_{\mathbf{k}n\sigma}^{\dagger}, \quad (5)$$

where  $\hat{c}_{\mathbf{k}n\sigma}(\hat{c}_{\mathbf{k}n\sigma}^{\dagger})$  is the annihilation (creation) operator for an electron with spin  $\sigma$  in a state characterized by the quantum numbers  $(\mathbf{k}, n)$  while  $\phi_{\mathbf{k}n}(\mathbf{r})$  is the single-electron eigenfunction of the Hamiltonian  $\hat{H}_e^{\sigma}$  whose explicit form is given by

$$\phi_{\mathbf{k}n}(\mathbf{r}) = \frac{1}{2\pi} e^{ik_x x} e^{ik_y y} \varphi_{k_y n}(z). \quad (6)$$

where  $\mathbf{k} = (k_x, k_y)$  is the electron wave vector and  $n$  labels the discrete quantum states induced by the confinement along the  $z$  axis.

By using the eigenfunctions given by Eq. (6), one can

reduce the Hamiltonian (2) to the 1D form which corresponds to the  $z$  dependent part -  $\varphi_{k_y n}(z)$ .

$$\begin{aligned}\hat{H}_{e,1D}^{\sigma} = & -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} + \frac{\hbar^2}{2m} (k_x^2 + k_y^2) - \frac{\hbar e H_{||} k_y}{m} z \\ & + \frac{e^2 H_{||}^2}{2m} z^2 + s\mu_B H_{||} - \mu_F,\end{aligned}\quad (7)$$

Note, that in the presence of the magnetic field  $H_{||}$  the eigenfunctions  $\varphi_{k_y n}(z)$  depend on the  $k_y$  component of the wave vector. In our calculations  $\varphi_{k_y n}(z)$  are determined numerically by the diagonalization of the Hamiltonian (7) in the basis of the quantum well states

$$\varphi_{k_y n}(z) = \sqrt{\frac{2}{d}} \sum_l c_{k_y n l} \sin \left[ \frac{\pi(l+1)z}{d} \right], \quad (8)$$

where  $d$  is the film thickness whereby we adopt the hard-wall confinement as the boundary condition in the  $z$  direction.

By using the Bogoliubov - de Gennes transformation  $\hat{c}_{\mathbf{k}n\sigma} = u_{\mathbf{k}n\sigma} \gamma_{\mathbf{k}n} + s v_{\mathbf{k}n\sigma}^* \gamma_{\mathbf{k}n}^{\dagger}$ <sup>33</sup>, the energy gap in the band  $n$  defined as  $\Delta_n = \langle \phi_{\mathbf{k}n} | \Delta(\mathbf{r}) | \phi_{\mathbf{k}n} \rangle$  can be expressed as follows

$$\begin{aligned}\Delta_{n'} = & \frac{g}{4\pi^2} \int dk_x dk_y \times \\ & \times \sum_{n'} C_{k_y n' n} \frac{\Delta_n}{2\sqrt{\xi_{\mathbf{k}n}^2 + \Delta_n^2}} [1 - f(E_{\mathbf{k}n}^+) - f(E_{\mathbf{k}n}^-)],\end{aligned}\quad (9)$$

where  $\xi_{\mathbf{k}n}$  is the single-electron energy,  $E_{\mathbf{k}n}^{\pm} = \pm \sqrt{\xi_{\mathbf{k}n}^2 + |\Delta_n|^2}$  is the quasi-particle energy,  $f(E)$  is the Fermi-Dirac distribution and  $C_{k_y n' n}$  are the interaction-matrix elements given by

$$C_{k_y n' n} = \int dz \varphi_{k_y n'}(z) \varphi_{-k_y n'}(z) \varphi_{k_y n}(z) \varphi_{-k_y n}(z). \quad (10)$$

The summation in Eq. (10) is carried out only over the single-electron states with energy  $\xi_{\mathbf{k}n}$  inside the Debye window  $|\xi_{\mathbf{k}n}| < \hbar\omega_D$ , where  $\omega_D$  is the Debye frequency<sup>33</sup>. The spatially dependent order parameter  $\Delta(z)$  can be expressed as

$$\begin{aligned}\Delta(z) = & \frac{g}{4\pi^2} \int dk_x dk_y \sum_n \varphi_{k_y n}(z) \varphi_{-k_y n}(z) \times \\ & \times \frac{\Delta_n}{2\sqrt{\xi_{\mathbf{k}n}^2 + \Delta_n^2}} [1 - f(E_{\mathbf{k}n}^+) - f(E_{\mathbf{k}n}^-)].\end{aligned}\quad (11)$$

The energy gap  $\Delta(z)$  for given nanofilm thickness  $d$  is calculated in the self-consistent manner using the following procedure. For each value of the wave vector  $k_y$  (note that the range of the wave vector is limited by the condition  $|\xi_{\mathbf{k}n}| < \hbar\omega_D$ ) we calculate the single-electron wave functions  $\varphi_{k_y n}(z)$  and the energies  $\xi_{\mathbf{k}n}$  by the diagonalization of the Hamiltonian (2) in the basis given by Eq. (8). Then, the single-electron wave functions  $\varphi_{k_y n}(z)$  are used to determine the starting value of  $\delta_n$ . The final

value of  $\delta_n$  is calculated by the self-consistent procedure given by Eq. 10. Finally, having  $\delta_n$  and  $\varphi_{k_y n}(z)$ , the spatially dependent order parameter  $\Delta(z)$  is calculated by the use of Eq. 11. The calculations in the paramagnetic limit (with no orbital effect) are carried out by putting  $H_{||} = 0$  in Eq. 7 everywhere except the Zeeman term. In this case the sum (8) reduces to a single term - the situation corresponds to a infinite quantum well with the spin Zeeman splitting.

We should note that aforementioned procedure can lead to solutions with  $\Delta \neq 0$  even for the values of the magnetic field for which the free energy of the superconducting state is greater than the free energy corresponding to the normal metal solution ( $\Delta = 0$ ). Therefore, for each value of the magnetic field we calculate and compare the free energies of the normal and superconducting phase. The theoretical study of the free energy in superconducting nanostructures has been presented in detail in Ref.<sup>34</sup>.

Due to the confinement the chemical potential can strongly deviate from the bulk value. For this reason for each nanofilm thickness we determine the chemical potential from the formula

$$n_e = \frac{1}{d} \int dk_x dk_y \sum_{n\sigma} \int_0^d dz \left\{ |u_{\mathbf{k}n\sigma} \varphi_{k_y n}(z)|^2 f(E_{\mathbf{k}n}) + |v_{\mathbf{k}n\sigma} \varphi_{k_y n}(z)|^2 [1 - f(E_{\mathbf{k}n})] \right\}, \quad (12)$$

where  $n_e$  is the electron density corresponding to the bulk value (corresponding to the chemical potential  $\mu_{bulk}$ ).

### III. RESULTS

In the present paper we consider the free-standing Pb(111) nanofilms. The first-principle calculations of the quantized band structure for Pb nanofilms in (111) and (100) directions are presented in Refs.<sup>35–37</sup>. Authors of these papers have pointed out that in (111) direction the energy dispersion is nearly parabolic and the quantum size effect can be well described by the quantum well states centered at the L-point of a two-dimensional Brillouin zone<sup>35</sup>. Based on these results, in our analysis we use the parabolic band approximation treating the bulk Fermi level  $\mu_{bulk}$  and the electron mass  $m$  as the fitting parameters. Their values are determined based on the results from the first-principle calculations for Pb(111) presented in Refs.<sup>31,35</sup>. We use the following values of the parameters:  $gN_{bulk}(0) = 0.39$  where  $N_{bulk}(0) = mk_F/(2\pi^2\hbar^2)$  is the bulk density of the single-electron states at the Fermi level,  $\hbar\omega_D = 8.27$  meV, the bulk energy gap  $\Delta_{bulk} = 1.3$  meV and  $\mu_{bulk} = 3.8$  eV which corresponds to the electron density  $n_e = 4.2 \times 10^{21} \text{ cm}^{-3}$ .

#### A. Orbital effect on the critical magnetic field.

Figure 1 displays the in-plane critical field  $H_{c,||}$  in units of  $H_{Pb}^{CC}$  as a function of the nanofilm thickness  $d$ , where  $H_{Pb}^{CC}$  is the paramagnetic critical field calculated on the basis of the Clogston-Chandrasekhar limit<sup>38,39</sup> ( $H^{CC} = \Delta_{bulk}/\sqrt{2}\mu_B$ ) which for bulk Pb gives  $H_{Pb}^{CC} = 15.9$  T. The thickness range under consideration is chosen on the basis of the experiments which report the stable Pb(111) nanofilms with the thickness varying from 5 ML to 30 ML<sup>15,16</sup>. Within our analysis the value of  $H_{c,||}$  for each nanofilm thickness is defined as the field for which the spatially averaged energy gap  $\bar{\Delta} = (1/d) \int_0^d \Delta(z) dz$  drops below  $0.01\Delta_{bulk}$ . The physical origin of 'the tooth-

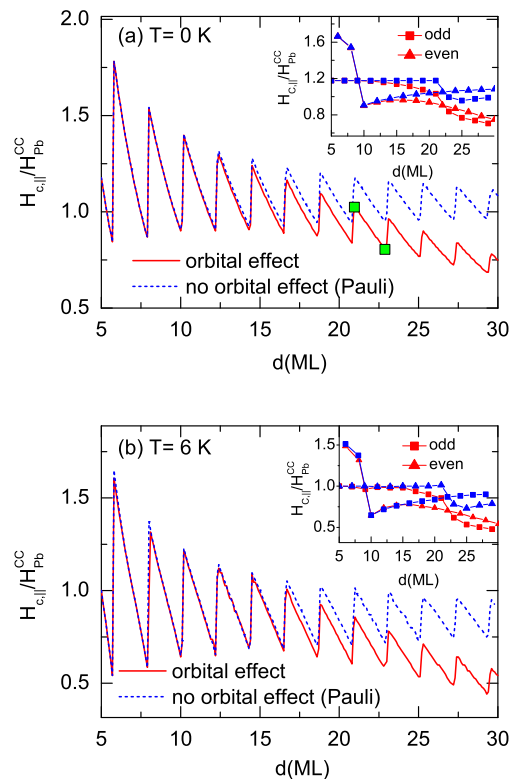


FIG. 1. (Color online) In-plane critical magnetic field  $H_{c,||}$  in units of  $H_{Pb}^{CC}$  as a function of the nanofilm thickness  $d$  calculated with and without (Pauli approximation) the inclusion of the orbital effect. Results for the temperature (a)  $T = 0$  K and (b)  $T = 6$  K. Insets present  $H_{c,||}(d)$  as a functions of number of Pb monolayers assuming the lattice constant  $a_{Pb} = 0.286$  nm. Green squares in panel (a) denote the film thicknesses chosen for presentation in Fig. 5.

like' oscillations in Fig. 1 can be explained in terms of the electron energy quantization related to the confinement of the electron motion in the direction perpendicular to the film<sup>5,28</sup>. If the thickness of the nanofilm becomes comparable with the electrons wave length the Fermi sphere splits into the set of discrete subbands. Increase

of the film thickness results in a decrease of the discrete subband energies. Each time a subband passes through the Fermi level the density of states in the energy window  $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ , in which the phonon-mediated pairing occurs, abruptly increases. This phenomenon leads to the thickness-dependent oscillations of the energy gap and the critical field presented in Fig. 1. As we can see, in the thickness range between two subsequent resonances, the critical magnetic field almost linearly decreases with increasing nanofilm thickness<sup>12,28</sup>. The predicted enhancement of the critical field reaches almost twice the value of the paramagnetic limit in the bulk Pb. Similar behavior was recently reported for Pb nanofilms in Ref.<sup>30</sup> where it is shown that experimentally measured critical field  $H_{c,\parallel}$  was much higher than the paramagnetic limit  $H_{Pb}^{CC}$ . The increase of the paramagnetic in-plane critical field in nanofilms has been explained in our recent paper<sup>31</sup>. In the insets of Fig. 1 we show the value of  $H_{c,\parallel}$  as a function of monolayer number (we assume the lattice constant  $a_{Pb} = 0.286$  nm corresponding to the bulk value). Results presented in such manner reveal the bilayer (even-odd) oscillations with the beating effect observed in experiments with Pb nanofilms<sup>15,16</sup> and explained in Refs.<sup>17,31</sup>.

In order to analyze the influence of the orbital effect on the in-plane critical field, in Fig. 1 we present the results of the calculations carried out with the inclusion of the orbital effect (solid, red line) and in the Pauli approximation (dashed, blue line). From Fig. 1 one can see that the orbital effect leads to a decrease of the critical field what is clearly visible for thick nanofilms. In comparison with the Pauli approximation the amplitude of the critical field oscillations is also reduced with increasing nanofilm thickness. One should note (see Fig.2) that the orbital effect significantly affects the value of  $H_{c,\parallel}(d)$  for nanofilms with the thickness greater than 15 ML. The up-

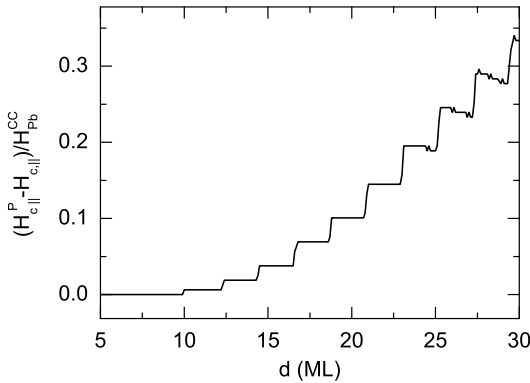


FIG. 2. (Color online) Difference between the critical magnetic field calculated in the Pauli approximation ( $H_{c,\parallel}^P$ ) and with the inclusion of the orbital effect ( $H_{c,\parallel}$ ) in units of  $H_{Pb}^{CC}$ . Results for  $T = 0$  K.

per limit of the thickness above which the Pauli approximation is no longer satisfied can be approximated by the magnetic length  $a_H = \sqrt{\hbar/eH_{\parallel}^P}$ , where  $H_{\parallel}^P$  is the paramagnetic (Pauli) critical field. Nevertheless, the use of the Clogston-Chandrasekhar paramagnetic field for the bulk  $H_{Pb}^{CC} = 15.9$  T gives  $a_H \approx 22$  ML which is greater than the thickness limit 15 ML determined from the numerical calculations. This discrepancy results from the different values of the paramagnetic critical field  $H_{\parallel}^P$  in nanofilms in comparison with the bulk value<sup>31</sup>.

The suppression of the critical field induced by the orbital effect can be explained on the basis of the classical Lorentz force acting on electrons in the magnetic field. The parallel magnetic field applied along the  $x$  axis (for

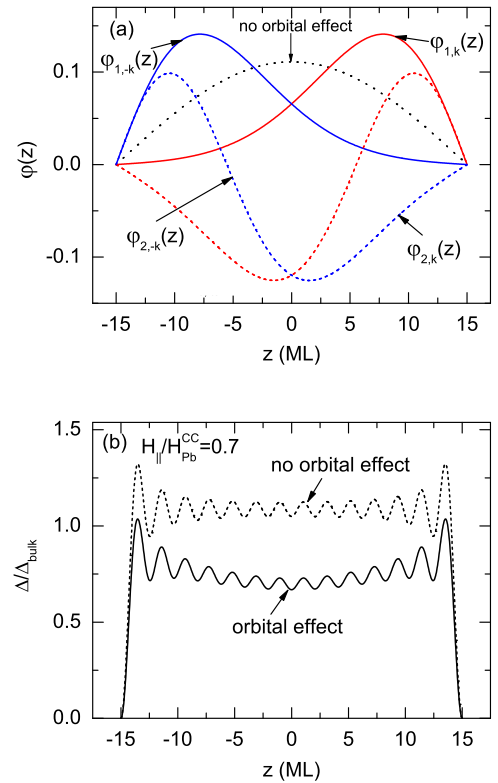


FIG. 3. (Color online) (a) Wave functions for the first  $\varphi_{1,\pm k}(z)$  and the second  $\varphi_{2,\pm k}(z)$  quantum well states calculated for opposite  $\mathbf{k}$  vectors. States with opposite  $\mathbf{k}$  are shifted towards the opposite edges of the sample. The wave function  $\varphi_{1,+k}(z) = \varphi_{1,-k}(z)$  obtained for the case with no orbital effect is marked by the black, dotted line. (b) Spatial dependent energy gap  $\Delta(z)$  in units of  $\Delta_{bulk}$  calculated for the magnetic field  $H_{\parallel}/H_{Pb}^{CC} = 0.7$  with (solid line) and without (dashed line) orbital effect. Results for  $d = 30$  ML.

the  $s$ -wave superconductors the direction of  $H_{\parallel}$  is not relevant) results in the Lorentz force directed perpendicular to the plane (along the  $z$  axis). For electrons with opposite  $\mathbf{k}$  vector (which form the Cooper pair) the Lorentz

forces have opposite orientations. As a consequence, for nanofilms with the thickness reduced to several monolayers, the electron density in the  $z$ -direction is shifted from the center to the edges (in accordance with the Lorentz force orientation). The shift of the density for electrons with opposite  $\mathbf{k}$  towards opposite edges of the sample is clearly visible in Fig. 3(a) which presents the single-electron wave functions for the first  $\varphi_{1,\pm k}(z)$  and the second  $\varphi_{2,\pm k}(z)$  quantum well state. This effect does not take place for the case with no orbital term included for which  $\varphi_{1,+k}(z) = \varphi_{1,-k}(z)$ . According to Eq. (10) the energy gap depends on the overlap between the wave functions of electrons with opposite momenta, which from the Cooper pairs. As presented in Fig. 3(a) the orbital effect results in the reduction of this overlap and consequently leads to the suppression of the energy gap and the critical magnetic field. We should mention that the presented explanation is correct only for nanofilms which are too thin for the formation of the vortex state, which is the case considered here. The Lorentz force manifest itself also in the spatial distribution of the energy gap presented in Fig. 3(b). It is well known that in superconducting nanostructures the energy gap is not uniform, as in the bulk, but it depends on the position. The spatially dependent energy gap for the nanofilm thickness  $d = 30$  ML and the magnetic field  $H_{||}/H_{Pb}^{CC} = 0.7$  is presented in Fig. 3(b). The comparison of the results calculated with and without the inclusion of the orbital effect allows to conclude that the reduction of the gap parameter caused by the orbital effect is most significant at the center of the film.

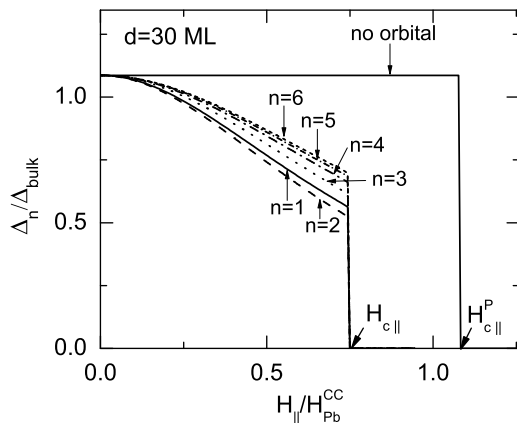


FIG. 4. Energy gap  $\Delta_n$  in units of  $\Delta_{bulk}$  as a function of the magnetic field  $H_{||}$  in units of  $H_{Pb}^{CC}$  for the nanofilm thickness  $d = 30$  ML.

Let us now explain the 'step-like' dependence of the difference  $H_{c,||}^P - H_{c,||}$  as a function of the film thickness presented in Fig. 2. The thicknesses  $d$  for which the steps appear correspond to peaks of the critical field seen in Fig. 1. This indicates that the presented behavior

is directly related to the discrete energy spectrum induced by the confinement. Therefore a subband passing through the Fermi level (with increasing  $d$ ) not only contributes to the increase of the density of state at the Fermi level but also to the orbital effect. This orbital contribution from subsequent subbands manifests as the steps in Fig. 2. Since the orbital effect corresponding to each subband is different, the heights of the steps also differ. The different importance of the orbital term in different subbands is clearly visible in Fig. 4 in which we present the subband energy gap  $\Delta_n$  as a function of the magnetic field  $H_{||}$ . For comparison  $\Delta_n(H_{||})$  in the Pauli limit is also shown. The slow decrease of the energy gap with increasing magnetic field seen in Fig. 4 results from the orbital effect. Note that in the Pauli limit  $\Delta_n$  is the same for all subbands and does not depend on the magnetic field in the superconducting state. This clearly shows that the orbital effect coming from different subbands  $n$  is different resulting in the steps with unequal height in Fig. 2.

### 1. Orbital effect on $H_{c,||}(T_c)$

In this subsection we discuss the influence of the orbital effect on the superconductor to normal metal phase transition induced by the magnetic field in non-zero temperature. In Fig. 5 we present the spatially averaged energy gap as a function of magnetic field and temperature for the nanofilm thickness (a)  $d = 21$  ML and (b) 23 ML. The chosen thicknesses correspond to the maximum and the minimum of the zero-temperature critical field presented in Fig. 1(a). As one can see the range of magnetic field and temperature in which the film remains in the superconducting state varies with its thickness. Since the significant impact of the orbital effect can be observed in the vicinity of  $T = T_c(0)$ , we restrict our analysis to this range. Fig. 6 presents the  $h - t$  phase diagram for different nanofilm thicknesses, where  $h$  and  $t$  are the normalized critical magnetic field  $h = H_{c,||}/H_{c,||}(0)$  and the normalized temperature  $t = T/T_c(0)$ , respectively.  $H_{c,||}(0)$  and  $T_c(0)$  are the critical field at  $T = 0$  and the critical temperature for  $H_{||} = 0$ . As presented in Fig. 6, for the nanofilm thickness  $d = 10$  ML for which the orbital effect is negligibly small, the slope of  $h(t)$  at  $t = 1$  is infinite and can be approximated by the formula  $dh/dt \approx \sqrt{1/(1-t)^4}$ . Due to the orbital effect the slope  $h(t)$  at  $t = 1$  becomes finite for thicker nanofilms ( $d = 20, 30$  ML) and gradually decreases with increasing thickness. Similar behavior has been recently reported in the experiments with Pb nanofilms<sup>13,41</sup>. The authors of Refs.<sup>13,41</sup> have argued that such dependence is caused by the boundary scattering, and therefore results from the roughness of the sample. As we have shown here the same behavior can be also induced by the orbital effect in the ultra clean film.

The orbital effect in nanofilms influences also the or-

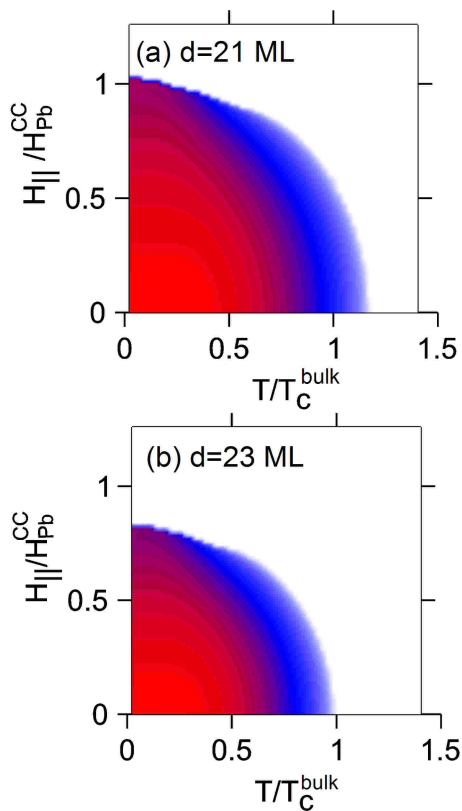


FIG. 5. (Color online) Spatially averaged energy gap  $\bar{\Delta}$  as a function of magnetic field  $H_{||}$  and temperature  $T$  for the nanofilm thickness (a)  $d = 21$  ML and (b)  $d = 23$  ML. The value of the energy gap in each figure is normalized with respect to its maximum.

der of the superconductor to normal metal phase transition. It is well known that for the orbital limiting case, with no Pauli effect, the superconductor to normal metal transition induced by the magnetic field is of the second order. In contrast, in the Pauli limit the second order transition is suppressed with decreasing temperature and below  $t^* = 0.56$  it becomes of the first order<sup>42,43</sup>. The superconducting nanofilms are systems in which the orbital and the paramagnetic effects are comparable while their relative importance can be controlled by changing the film thickness. By analyzing the free energy of the superconducting and the normal state we have determined the temperature  $t^*$  at which the superconductor to normal metal phase transition becomes of the first order for different nanofilm thickness. In Fig. 7 one can see that for ultrathin nanofilms, for which the paramagnetic effect is dominant,  $t^*$  diverges to the value 0.56 predicted by Kazumi Maki in Refs.<sup>42,43</sup>. If we increase the thickness, the temperature  $t^*$  decreases which is directly related to the enhancement of the orbital effect. The extrapolation of  $t^*(d)$  for  $t^* = 0$  gives  $d = 39$  ML which is the limit above which the transition of the second order occurs in

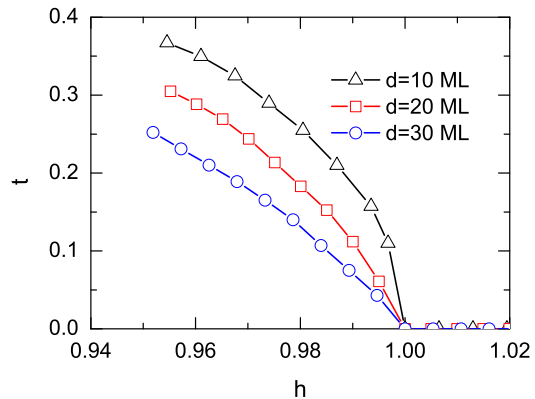


FIG. 6. (Color online) Normalized critical magnetic field  $h = H_{c,||}/H_{c,||}(0)$  as a function of normalized temperature  $t = T/T_c(0)$  for different nanofilm thicknesses  $d$ .

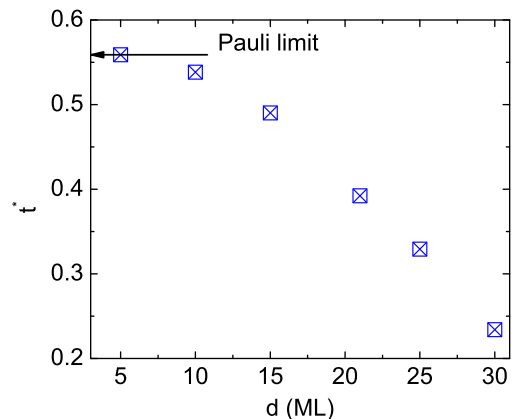


FIG. 7. (Color online) Temperature  $t^*$  at which the superconductor to normal metal transition becomes of the first order as a function of the nanofilm thickness  $d$ .

the whole range of temperatures which corresponds to the orbital limiting case.

#### IV. SUMMARY

The superconductor to normal metal phase transition driven by the in-plane magnetic field for Pb(111) nanofilms has been investigated in the framework of the BCS theory. We have shown that the orbital effect suppresses the critical field as well as the amplitude of the critical field oscillations induced by the quantum confinement (shape-resonances). The analysis of the  $H_{c,||} - T_c$  diagram allows to demonstrate that due to the orbital effect the slope  $H_{c,||} - T_c$  at  $T_c(0)$  becomes finite and systematically decreases with increasing film thick-

ness. This result agrees with recent experiments for Pb nanofilms<sup>13,41</sup>. We have also analyzed the thermal effect and shown that the temperature  $t^*$  at which the superconductor to normal metal transition becomes of the first order reduces with increasing film thickness. For the ultrathin nanofilms, in which the Pauli pair-breaking mechanism is dominant,  $t^*$  approaches to 0.56 in agreement with the theoretical prediction by Kazumi Maki<sup>42,43</sup>.

It is worth mentioning that our study take into account only the electronic structure. However, in the nanoscale regime, the confinement affects not only the electronic spectrum but also the phononic degrees of freedom which for nanofilms strongly deviates from that in the bulk<sup>44</sup>. The quantization of the phononic spectra in nanofilms and its influence on superconducting properties have been considered in many papers<sup>45–47</sup>. Moreover, the effect of the confinement on the electron-phonon coupling strength has been recently studied by Saniz et al. in Ref.<sup>48</sup>. In this paper<sup>48</sup> attractive electron-electron interaction has been derived with the use of the Green function approach beyond the contact potential approximation. It has been found that the increase of the critical temperature observed in superconducting nanofilms is due to the increase of the number of phonon modes what results in the enhancement of the electron-phonon coupling. Since the modification of the phononic dispersion due to the confinement only slightly changes the superconducting properties of nanofilms, the general results of the present paper remain valid.

Nevertheless, there is another factor which can considerably affects the shape resonances in experiments. Note that in our study we assume the hard wall potential profile in the direction perpendicular to the film what refers to the case of the so-called free-standing nanofilms. How-

ever, in experiments a thin film is never isolated but grows on a substrate (for Pb nanofilms usually on Si). Due to the interface effect the substrate layers strongly affect both the electronic structure and the phononic dispersion of the nanofilm. The role of the substrate on the shape resonances has been recently studied in Ref.<sup>27</sup>. Taking into account a finite lifetime of the quantized states and modeling the substrate/thin-film interface by a more realistic finite step potential, the authors of Ref.<sup>27</sup> showed that for the case of strong-coupling to the substrate the shape resonances are significantly suppressed in reference to the free-standing limit. However, for metallic superconductors (with long coherence length) the enhancement of the energy gap is so strong that the shape resonances should be experimentally observed despite the destructive influence of the substrate.

Finally, we would like to point out that one should be careful when using the BCS theory in the description of the strongly-coupled superconductors such as Pb, as in some cases it can lead to overestimation of the size effect with respect to the behavior reported in the experiments<sup>9</sup>. The more appropriate description of the strongly-coupled superconductors requires the use of the Eliashberg theory. Nevertheless, the results from recent experiments<sup>2,4,9,15,16</sup> for Pb nanostructures are qualitatively well described by the BCS model.

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