Quantum size effect on the paramagnetic critical field in free-standing superconducting nanofilms

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Abstract. The quantum size effect on the in-plane paramagnetic critical field in Pb(111) nanofilms is investigated with the use of the spin-generalized Bogoliubov-de Gennes equations. It is shown that the critical field oscillates as a function of the nanofilm thickness with the period of ~ 2 ML (even-odd oscillations) modulated by the beating effect. The calculated values of the critical field for different nanofilm thicknesses are analyzed in the context of Clogston-Chandrasekhar limit. It is found that the critical field for superconducting nanofilms differs from the Clogston-Chandrasekhar limit. This phenomena is explained in terms of quantization of the electron energy caused by the confinement of the electron motion in the direction perpendicular to the film. The thermal effect and the thickness-dependence of the electron-phonon coupling on the value of the critical magnetic field are also studied.

1. Introduction

The interplay between superconductivity and quantum confinement has attracted growing interest due to the unique phenomena which appear if the electron motion is limited to the size smaller than the coherence length [1, 2, 3, 4, 5, 6, 7, 8]. The huge progress in nanotechnology which has been made in the last decade allows to prepare uniform ultrathin films [9, 10, 11, 12, 10, 11] in which new superconducting properties have been observed. One of them are oscillations of the superconducting energy gap as a function of the nanofilm thickness predicted by Blatt and Thompson [13] in 1963. The authors of Ref. [13] showed that the quantum-well states which are created due to the confinement of the electron motion in the direction perpendicular to the film, greatly modulate the density of states near the Fermi level and thus affect the superconducting energy gap of the nanofilm. As a result, one would expect a significant increase of the energy gap each time when the bottom of a subband passes through the Fermi sphere. Nevertheless, either the experimental studies carried out in these years did not exhibit such an effect or the observed oscillations differed quantitatively from the theoretical predictions [14]. This inconsistency was attributed to the technological difficulties in the preparation of uniform films which were typically polycrystalline and contained a large number of defects. Since then, many technological obstacles were overcame what reopened the issue for the quantum confinement effect on the superconductivity in the nanoscale regime. Recently, Guo at al. [15] have fabricated ultrathin Pb films on Si(111) substrate and observed the oscillations of the critical temperature as a function of the nanofilm thickness. This phenomena has been explained in terms of quantization of the electron energy caused by the confinement of the electron motion in the direction perpendicular to the film. It has been confirmed independently by the measurements of the quantum-well energies by using photoemission spectroscopy. The study of Pb nanofilms has been extended by Eom et al. [16] who have reported T_c oscillations in the epitaxially grown crystalline Pb films in the thickness range $5-18$ ML. In Ref. [16] the critical temperature has been measured using scanning tunneling micoroscopy which

allows to avoid ambiguities associated with the Au layer applied in the transport measurements [15]. A direct correlation between the enhancement of the density of states at the Fermi level and the increase of T_c has been found. It is worth mentioning that all measurements of the critical temperature for Pb nanofilms have reported the same period of oscillations equals to $\sim$ 2 ML. This property called bilayer or even-odd oscillations has been theoretically investigated by Shanenko et al. in Ref. [17] and observed in many other experiments [18, 19, 10].

The new direction of studies devoted to superconductivity in nanoscale regime concerns the effect of quantum confinement on the superconductor to normal metal transition induced by the magnetic field. In the metallic nanowires, it has been shown that a cascade of jumps in the energy gap as a function of the magnetic field occurs [20]. This effect has been explained in terms of depairing in the subsequent bands when the magnetic field increases [20]. Moreover the oscillations of the perpendicular upper critical field in ultrathin lead films have been reported by Bao et al. in Ref. [21]. According to our knowledge, the theoretical study of the superconducting to normal metal transition induced by the in-plane magnetic field and its interplay with the quantum confinement has not been reported until now.

In the present paper we investigate the superconductor-normal metal transition driven by the in-plane magnetic field for **free-standing Pb(111) nanofilms**. It has been found that the critical field oscillates as a function of the nanofilm thickness with the period of $\sim$ 2 ML (even-odd oscillations) modulated by the beating effect with the periodicity of 10 ML. **The calculated values of the critical field for different nanofilm thicknesses are analyzed in the context of Clogston-Chandrasekhar limit. It is found that the Clogston-Chandrasekhar formula can not be used to predict the critical field in the paramagnetic limit for superconducting nanofilms. The new formula for the paramagnetic critical field in the nanoscale regime is proposed.** Finally, we take into account the oscillatory behavior of the electron-phonon coupling and calculate H_c as a function of the nanofilm thickness for the experimental samples for which a good agreement of theory and experiment has been found in the study of the critical temperature [24]. The present paper is organized as follows. In Sec. 2 we introduce the basic concepts of the calculation scheme based on the Bogoliubov-de Gennes equations. In Sec. 3 we analyze the results, while the summary is included in Sec. 4.

2. Theoretical method

The superconducting properties of the conventional phonon-mediated pairing system can be described with the use of BCS theory which leads to the Bogoliubov-de Gennes

(BdG) equations in the form

$$\begin{pmatrix} H_e^{\uparrow} & \Delta & 0 & 0 \\ \Delta^* & -H_e^{\downarrow *}, & 0 & 0 \\ 0 & 0 & H_e,^{\downarrow} & \Delta \\ 0 & 0 & \Delta^* & -H_e^{\uparrow *} \end{pmatrix} \begin{pmatrix} \mathcal{U}_i^{\uparrow} \\ \mathcal{V}_i^{\downarrow} \\ \mathcal{U}_i^{\downarrow} \\ -\mathcal{V}_i^{\uparrow} \end{pmatrix} = E_i \begin{pmatrix} \mathcal{U}_i^{\uparrow} \\ \mathcal{V}_i^{\downarrow} \\ \mathcal{U}_i^{\downarrow} \\ -\mathcal{V}_i^{\uparrow} \end{pmatrix}, \tag{1}$$

where $\mathcal{U}_i^{\sigma}$ and $\mathcal{V}_i^{\sigma}$ are the spin-dependent electron-like and hole-like wave functions ($\sigma =\uparrow, \downarrow$), Δ is the superconducting energy gap and E_i is the quasi-particle energy. In the presence of the in-plane magnetic field $H_{||}$ the Hamiltonian H_e^{σ} is given by

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

where $s = +1$ corresponds to the spin $\sigma =\uparrow$ and $s = -1$ is related to the spin $\sigma =\downarrow$, m is the electron mass, μ_B is the Bohr magneton, μ_F is the chemical potential and $\mathbf{A}$ is the vector potential related to the parallel magnetic field.

In the present paper we neglect the orbital effects and consider the superconducting nanofilms in the clean paramagnetic limit. This approximation is justified for the nanofilms with the thickness less than the magnetic length $a_H = \sqrt{\hbar/eH_{||}}$. The use of the Clogston-Chandrasekhar paramagnetic field for Pb $H^{CC} = 13.4$ T gives $a_H = 7$ nm which means that the paramagnetic approximation can be used for Pb nanofilms with thickness less than ~ 25 ML (we assume the lattice constant for Pb, $a = 0.286$ nm).

In the paramagnetic limit the Hamiltonian can be further simplified to the form

$$H_e^{\sigma} = -\frac{\hbar^2}{2m}\nabla^2 + s\mu_B H_{||} - \mu_F. \tag{3}$$

In strong Pauli limited superconductors in parallel magnetic field the unconventional superconducting state (FFLO) with non-zero momentum of the Cooper pairs can be created [25, 26]. In the FFLO state the energy gap is not uniform but varies spatially with the period corresponding to the Cooper pair momentum. However, in spite of many theoretical studies [27, 28, 29, 30] experiments indicate the possible existence of the FFLO state only in the heavy fermion system [31] and two dimensional organic superconductors [32]. This is considered to be because the FFLO state is easily destroyed by nonmagnetic impurities [33, 34] (in contrast to the BCS state of s-wave pairing) and it seems to be impossible in ordinary metals considered in the present paper. For this reason we neglected the existence of the FFLO state in the further consideration and assume that the energy gap in the $x-y$ plane is homogeneous. Then the quasi-particle wave functions can be expressed as

$$\begin{pmatrix} \mathcal{U}^{\sigma}_{k_x k_y \nu}(\mathbf{r}) \\ \mathcal{V}^{\bar{\sigma}}_{k_x k_y \nu}(\mathbf{r}) \end{pmatrix} = \frac{e^{ik_x x}}{\sqrt{L_x}} \frac{e^{ik_y y}}{\sqrt{L_y}} \begin{pmatrix} u^{\sigma}_{\nu}(z) \\ v^{\bar{\sigma}}_{\nu}(z) \end{pmatrix} \tag{4}$$

where $\bar{\sigma}$ denotes the opposite spin. In equation (4) the index i has been replaced by k_x, k_y, ν, where k_x, k_y are the electron wave vector components in the x and y direction,

while ν labels the quantum states in the z direction. By substituting the wave function given by (4) into the BdG equations (1) we obtain two independent set of equations

$$\begin{pmatrix} H_e^{\uparrow}(z) & \Delta(z) \\ \Delta(z) & -H_e^{\downarrow *}(z) \end{pmatrix} \begin{pmatrix} u_\nu^{\uparrow}(z) \\ v_\nu^{\downarrow}(z) \end{pmatrix} = E_\nu^{\uparrow} \begin{pmatrix} u_\nu^{\uparrow}(z) \\ v_\nu^{\downarrow}(z) \end{pmatrix}, \tag{5}$$

and

$$\begin{pmatrix} H_e^{\downarrow}(z) & \Delta(z) \\ \Delta(z) & -H_e^{\uparrow *}(z) \end{pmatrix} \begin{pmatrix} u_\nu^{\downarrow}(z) \\ -v_\nu^{\uparrow}(z) \end{pmatrix} = E_\nu^{\downarrow} \begin{pmatrix} u_\nu^{\downarrow}(z) \\ -v_\nu^{\uparrow}(z) \end{pmatrix}, \tag{6}$$

where

$$H_e^{\sigma}(z) = -\frac{\hbar^2}{2m}\frac{d^2}{dz^2} + \frac{\hbar^2 k_\parallel^2}{2m} + s\mu_B H_{||} - \mu_F \tag{7}$$

and $k_\parallel^2 = k_x^2 + k_y^2$. Assuming that the system is infinite in the x and y direction ($L_x, L_y \to \infty$), the order parameter $\Delta(z)$ can be expressed as

$$\begin{aligned} \Delta(z) = \frac{g}{2\pi}\int dk_\parallel \, k_\parallel \sum_\nu \{ & u_\nu^{\uparrow}(z) v_\nu^{\downarrow *}(z) \left[1 - f(E_\nu^{\uparrow})\right] \\ & + u_\nu^{\downarrow}(z) v_\nu^{\uparrow *}(z) f(E_\nu^{\downarrow})\}, \end{aligned} \tag{8}$$

where g is the electron-phonon coupling and $f(E)$ is the Fermi-Dirac distribution. **The summation in Eq. (8) is carried out only over the single-electron states with energy $\xi_{k_x k_y \nu}^{\sigma}$ inside the Debye window $\left|\xi_{k_x k_y \nu}^{\sigma}\right| < \hbar\omega_D$, where ω_D is the Debye frequency and $\xi_{k_x k_y \nu}^{\sigma}$ is given by**

$$\begin{aligned} \xi_{k_x k_y \nu}^{\sigma} = \int_0^d dz \Big\{ & u_\nu^{\sigma *}(z) H_e^{\sigma}(z) u_\nu^{\sigma}(z) \\ & + v_\nu^{\bar{\sigma} *}(z) H_e^{\bar{\sigma}}(z) v_\nu^{\bar{\sigma}}(z) \Big\}, \end{aligned} \tag{9}$$

where d is the nanofilm thickness in the z-direction. The above condition comes from BCS theory and results from the delta-function approximation for the effective electron-electron interaction mediated by phonons [35]. The system of equations (5)-(6) and equation (8) are solved in a self consistent manner. As a result the spatially varying energy gap $\Delta(z)$ is obtained. In the further analysis we often use spatially averaged energy gap defined as

$$\bar{\Delta} = \frac{1}{d}\int_0^d \Delta(z) dz. \tag{10}$$

Since the chemical potential for nanostructures strongly deviates from the bulk value, for each nanofilm thickness we determine the chemical potential by using the formula

$$\begin{aligned} n_e = \frac{1}{\pi d}\int dk_\parallel k_\parallel \sum_\sigma \sum_\nu \int_0^d dz \Big\{ & |u_\nu^{\sigma}(z)|^2 f(E_\nu) \\ & + |v_\nu^{\bar{\sigma}}(z)|^2 [1 - f(E_\nu)] \Big\}. \end{aligned} \tag{11}$$

In our calculations we adopt the the hard-wall potential profile as the boundary conditions in the z direction.

The set of self-consistent equations can lead to solutions with $\Delta \neq 0$ even for the values

of the magnetic field for which the superconducting phase is already not stable - its free energy is greater than the free energy corresponding to the normal metal solution ($\Delta = 0$). That is why in determining the critical field one should calculate and compare the free energy of the normal and superconducting phase, as it is done here.

3. Results

In this section we analyze the superconductor to normal metal transition induced by the parallel magnetic field. The thickness range under consideration is chosen based on the experiments which present measurements for the Pb(111) nanofilms with thickness varying from 5 to 30 ML [16, 15]. The calculations have been carried out for 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 lattice constant $a = 0.286$ nm and the bulk critical temperature $T_{bulk} = 7.2$ K which corresponds to the energy gap $\Delta_{bulk} = 1.1$ meV. **Despite the fact that the phonon dispersion in thin films strongly deviates from that in the bulk, we assume the bulk value of the parameter $\hbar\omega_D$. The reason for that is based on our aditional calculations which show that the results presented in the paper are only slightly affected by the change of this parameter. Much more important effect is related to the change the electron-phonon coupling caused by the interface. This effect in details is considered in the subsection 3.3. Since the diffraction measurements indicate that the in-plane lattice constant a is close to the bulk one, we assume $a = 0.286$ nm corresponding to that measured in the bulk.**

For quantitative description of the quantum size effect in nanofilms the actual band structure from *ab-initio* calculations is needed. The first-principle calculations of the quantized band structure for Pb nanofilms in (111) and (100) direction are presented in Refs. [?, ?] where the oscillations of the work function and the surface energy are studied. It has been found [?] that the properly determination of the oscillation period for Pb(100) films requires consideration of the quantum well states centered at the Γ and M points in the two-dimensional Brillouin zone. On the other hand, the calculations show that the quantum size effect in Pb(111) films can be well described only by the quantum well states centered at the L point [?]. In this direction the energy dispersion is nearly parabolic. Based of these results in the present paper (we consider Pb(111)) we use the parabolic band approximation treating the bulk Fermi level and the electron mass as the fitting parameters. Their values are determined based in such a way as to best reproduce the results of the first-principle calculations for Pb(111) presented in Ref. [?]. We take on $\mu_{bulk} = 3.8$ eV which corresponds to the $n_e = 4.2 \times 10^{21}$ cm^{-3} and $m = 0.25m_0$ where m_0 is the free electron mass.

3.1. Paramagnetic critical field oscillations

In Fig. 1 the in-plane critical field $H_{c,||}$ as a function of the nanofilm thickness is presented for different temperatures T. The value of $H_{c,||}$ is determined based on calculations of the energy gap versus the magnetic field and is defined as the field for which the spatially averaged energy gap $\bar{\Delta}$ drops below $0.01\Delta_{bulk}$. Fig. 1(a) shows that the paramagnetic

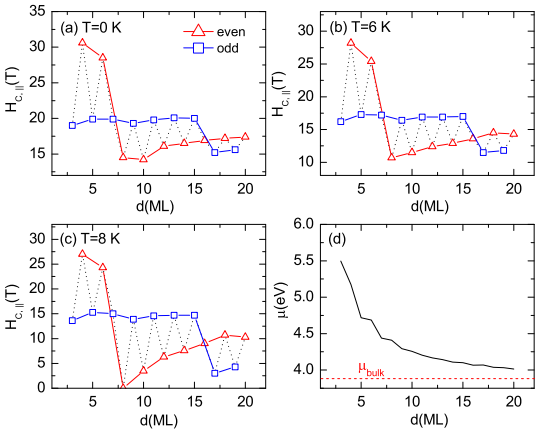

Figure 1. (Color online) In-plane critical magnetic field $H_{c,||}$ as a function of the nanofilm thickness d calculated for the temperature (a) $T = 0$ K (b) $T = 6$ K and (c) $T = 8$ K. Results for even-layered nanofilms are marked by triangular red points while for odd-layered nanofilms by square blue points. (d) Chemical potential μ as a function of the nanofilm thickness d.

critical field oscillates with the period of 2 ML. The difference between 2 ML and the real period of the quantum well states which pass through the Fermi surface results in the beating effect with the periodicity of 10 ML. The even-odd (bilayer) oscillations with the beating effect have been observed in recent measurements of the critical temperature [16, 15] and the electron-phonon coupling in Pb thin nanofilms [10]. In these experiments the modulation periodicity varies from 7 ML [16] to 9 ML [36] indicating that this quantity depends on the quality of the nanofilm and might vary from one experiment to another. The oscillations of $H_{c,||}$ in Fig. 1 result from the confinement of the electron motion in the direction perpendicular to the film. The confinement of the electron motion leads to the quantization of its energy. The Fermi sphere transforms into the series of parabolic subbands, positions of which on the energy scale decreases with increasing nanofilm thickness. Since the Cooper-pairing in the phonon-mediated superconductor is determined by the number of the electron states in the energy window $[\mu - \hbar\omega_D, \mu + \hbar\omega_D]$ ($\hbar\omega_D$ is Debye energy), the superconducting energy gap increases each time, the subsequent subband passes through the Fermi surface. The presented mechanism, predicted theoretically in 1963 by Blatt and Thomson [13], results in the tooth-like oscillations of the spatially averaged energy gap $\bar{\Delta}$ as a function of the nanofilm thickness. The tooth-shape of the energy gap oscillations is directly related to

the changes of the electron density of states in the vicinity of the Fermi level. It abruptly increases when the subband minima reach the Fermi level and then exponentially decreases with increasing nanofilm thickness [13]. The zero temperature energy gap $\bar{\Delta}$ as a function of the number of monolayers is presented in Fig. 2. **We see that the**

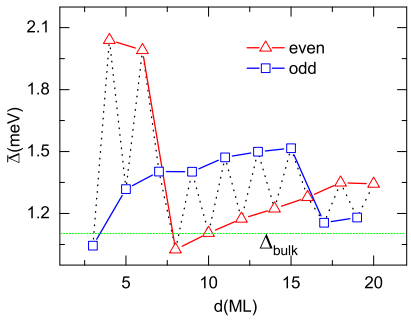

Figure 2. (Color online) Zero temperature spatially averaged energy gap $\bar{\Delta}$ as a function of the nanofilm thickness d. Results for even-layered nanofilms are marked by triangular red points while for odd-layered nanofilms by square blue points. Green horizontal line denotes the value of the energy gap in the bulk.

shape of $H_{c,||}$ oscillations at $T = 0$ K [Fig. 1(a)] is strongly correlated to the shape of $\bar{\Delta}$ oscillations in Fig. 2. The reason for this results from the fact that in the ultra thin nanofilms with in-plane magnetic field, the pair-breaking mechanism is mainly governed by the paramagnetic (Pauli) limit which is given by Clogston-Chandrasekhar (CC) [22, 23] formula, $H^{CC} = \Delta_{bulk}/(\sqrt{2}\mu_B)$. Therefore, the bilayer oscillations of the in-plane critical field presented in Fig. 1(a) are caused by the contribution of the subsequent subbands which increase the density of state at the Fermi level. In Fig. 3 the quasi-particle energy E versus the wave vector k is presented for the film thickness $d = 5, 6$ ML (a,b) and $d = 8, 9$ ML (c,d). The first pair of thicknesses correspond to the range in which $H_{c,||}$ is higher for the even-layered films while the second pair is related to the range for which a reversed situation is observed. We see that for the film thickness $d = 5$ ML two lowest subbands participate in the creation of the superconducting state [Fig. 3(a)]. Increasing the thickness by one monolayer causes that the third subband begins to contribute to the superconducting phase which leads to the enhancement of the critical field depicted in Fig. 1(a). In the thickness range $3-7$ ML the subsequent subbands pass through the Fermi level only if the number of monolayers is even. The period of the passages can be well estimated by the single-electron energy level in the form $E \approx \hbar^2\pi^2\nu^2/(2md^2)$, where the hard-wall potential is assumed in the z direction. The difference between 2 ML and the real period of the quantum well states which pass through the Fermi surface ($\Delta d = 2.2$ ML) results in the beating effect observed in Fig. 1(a). This is the reason for which in Fig. 3(c,d) the new subband ($\nu = 4$) appears for the odd-layered film ($d = 9$ ML), in contradiction to the pair $d = 5, 6$ ML [see Fig. 3(a)(b)]. The source

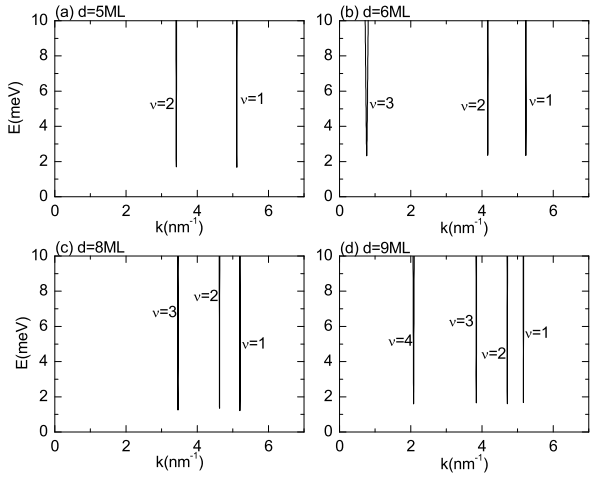

Figure 3. Quasi-particle energy E as a function of the wave vector k for the film thickness (a) $d = 5$ ML, (b) $d = 6$ ML, (c) $d = 8$ ML, (d) $d = 9$ ML.

of the beating effect is clearly visible in Fig. 4 in which the energy of the quantum well states as a function of the nanofilm thickness is presented. In Fig. 4 only the states

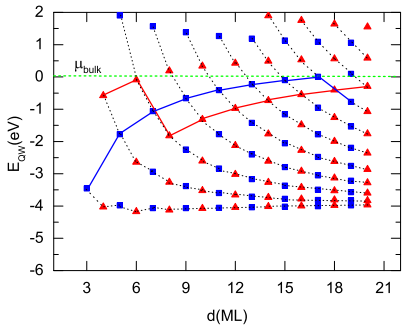

Figure 4. (Color online) Energy of the quantum well states E_{QW} as a function of the film thickness d. Results for even-layered nanofilms are marked by triangular red points while for odd-layered nanofilms by square blue points. The Fermi level μ is set to zero. The energy closest to the Fermi level are joined by the blue(red) line for the even(odd) number of monolayers.

with the energy below Fermi level (set as zero energy) are occupied and contribute to the Coooper pair condensation. The closer to the Fermi energy they are located the larger is their contribution to the density of states at the Fermi level and consequently Cooper pairing. In Fig. 4 the energies closest to the Fermi level are joined by the blue (red) line for the even (odd) number of monolayers. Note that such procedure leads to the "structure" (in the sense of the shape) exactly the same as depicted in Fig. 1(a).

Let us now discuss the value of the paramagnetic critical field obtained from our calculations in the context of Clogston-Chandrasekhar limit. It is well-known that in

the ultra thin films with the in-plane magnetic field, the orbital-magnetic interaction is strongly reduced and the upper limit of the critical field is determined by the paramagnetic breakdown of the Cooper pairs. For the bulk energy gap $\Delta_{bulk}^{Pb} = 1.1$ meV the CC formula gives $H^{CC} = 13.4$ T. This value strongly differs from the critical field obtained in our calculations which vary from 15 T to 30 T. Such deviation for the Pb nanofilms has been recently reported in Ref. [37] in which the experimentally measured critical field $H_{C,||}$, has been much higher than the paramagnetic limit H^{CC}. It seems that such discrepancy results from the enhancement of the energy gap presented Fig. 2. Nevertheless, the use of the CC formula with the spatially averaged energy gap calculated for each nanofilm thickness $H_d^{CC} = \bar{\Delta}(d)/(\sqrt{2}\mu_B)$ still produces the value of the critical field which is lower than the results from numerical solution of the spin-generalized BdG equations, i.e. for $d = 6$ ML, $H_d^{CC} = 24.5$ T while calculated $H_{C,||} = 28.5$ T. This fact can be easily understood if we realize that the superconducting energy gap depends on the z coordinate and is not uniform as in the expression for CC critical field. Taking into account the correction which results from the averaging of the energy gap over the z coordinate we introduce the thickness-dependent parameter $\alpha(d)$ and propose the expression for the critical field in the form

$$H_{C,||} = \alpha(d)\frac{\bar{\Delta}(d)}{\mu_B}. \tag{12}$$

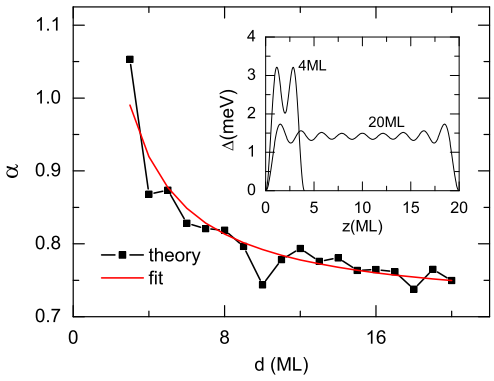

Figure 5. (Color online) α as a function of the film thickness d. The red line is the fitting curve in the form $\alpha = A/d + 1/\sqrt{2}$; $A = 1.17$. The inset: the spatially varying energy gap $\Delta(z)$ calculated for the nanofilm thickness $d = 6$ ML and $d = 30$ ML.

Fig. 5 shows that the parameter α is the decreasing function of the thickness d and for sufficiently large thickness reaches the value $\alpha = 1/\sqrt{2}$). The asymptotic behavior of $\alpha(d)$ for $d \to \infty$ results from the fact that for the large thickness the spatially varying energy gap diverges to the uniform one - compare $\Delta(z)$ for the thicknesses $d = 6$ and 30 ML presented in the inset of Fig. 5. The dependence $\alpha(d)$ can be well fitted using the formula $\alpha = A/d + 1/\sqrt{2}$ where the thickness d denotes the number of monolayers - see Fig. 5. It should be noted that the smallest difference between the quasiparticle

energy in the superconducting state and the Fermi energy is the same for each band created due to the confinement of electrons in the direction perpendicular to the sample (c.f. Fig. 3). Using this energy gap, instead of the averaged energy gap $\bar{\Delta}$ in the CC formula, one obtains the same values of critical fields as the ones resulting from the BdG equations.

3.2. Thermal effect

In the present subsection we discuss in detail the effect of temperature on the superconductor to normal metal transition induced by the in-plane magnetic field. The critical field $H_{c,||}(d)$ presented in Fig. 1 for different temperatures T shows that its value gradually decreases with increasing temperature. Since the critical temperature oscillates as a function of the nanofilm thickness (similarly to the energy gap depicted in Fig. 2), at the temperature $T = 10$ K, the nanofilms with the thickness $d = 7, 8$ ML are superconducting while the film with the thickness therebetween transits to metallic state.

In Fig. 6 we present the spatially averaged energy gap as a function of the magnetic field and temperature. The results in Fig. 6 have been calculated for the nanofilm thicknesses $d = 7, 8, 10$ and 11 ML. To make it more transparent, the value of the energy gap in each of the figures is normalized with respect to its maximum. In Fig. 6

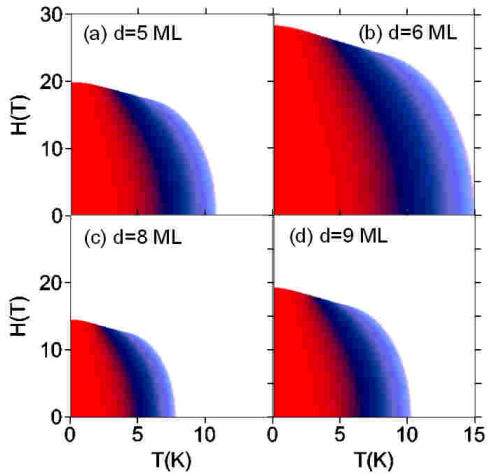

Figure 6. (Color online) Spatially averaged energy gap $\bar{\Delta}$ as a function of the magnetic field H and temperature T for the nanofilm thickness (a) $d = 7$ ML, (b) $d = 8$ ML, (c) $d = 10$ ML and (d) $d = 11$ ML. The value of energy gap in each figure is normalized with respect to its maximum.

we can see that the range of the magnetic field and temperature for which the sample is superconducting is larger for the thickness for which the enhancement of the energy gap (see Fig. 2) is found. Nevertheless the thickness-dependence is not visible in the normalized critical magnetic field $h = H_{c,||}/H_{c,||}(0)$ as a function of $t = T/T_c(0)$, where

$H_{c,||}(0)$ and $T_c(0)$ is the critical field at $T = 0$ and the critical temperature for $H = 0$, respectively. In other words the phase diagram $h - t$ presented in Fig. 7 looks the same for each film thickness which is understandable if we recall our restriction to the Pauli limit with no orbital effect. The initial behavior of h at the temperature close to T_c

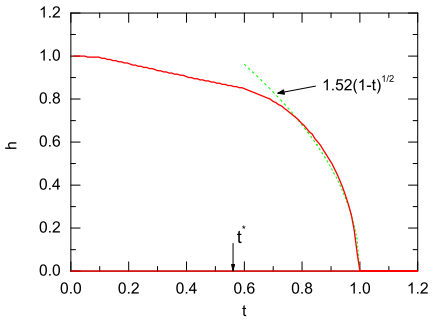

Figure 7. (Color online) Critical field $h = H_{c,||}/H_{c,||}(0)$ as a function of $t = T/T_c(0)$ obtained from the solution of BdG equations. Here the dashed green line corresponds to $h = 1.52(1-t)^{1/2}$. The first to second order transition, t^*, is marked by arrow.

$(t = 1)$ can be well estimated by the formula $h = A(1-t)^{1/2}$. Note that, in contrast to the orbital limit with no Pauli effect, the slope of h at critical temperature $t = 1$ is infinite and in the vicinity of $t = 1$ is expressed by $dh/dt \propto \sqrt{1/(1-t)}$. In this range the transition at $H_{c,||}$ is of second order. In the Pauli limit the second order transition is suppressed with decreasing temperature and below $t^* = 0.56$ it becomes the first order [38, 39]. The first to second order transition is clearly presented in Fig. 8 in which the energy gap versus magnetic field is presented for different temperatures. Note that the critical field $H_{c,||}$ at $T = 0$ is not equal to the paramagnetic limit H^{CC}

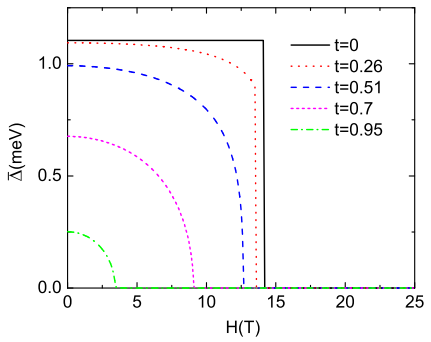

Figure 8. (Color online) Spatially averaged energy gap $\bar{\Delta}$ as a function of magnetic field H for different temperatures. The first to second order transition emergences at $t = t^* = 0.56$. Calculations performed for the film thickness $d = 10$ ML.

but is further enhanced. A detailed discussion of the deviation of the critical field from H^{CC} is presented in sec. 3.A.

3.3. Thickness dependent electron-phonon coupling

The microscopic model based on the spin-generalized BdG equations allows to analyze superconductor to normal metal transition in the nanofilms when its thickness is reduced to few nanometers. However, in the nanoscale regime, the confinement affects not only the electronic spectrum, but also the phononic degrees of freedom. The phonon dispersion in thin films strongly deviates from that in the bulk [40]. The quantization of the phononic spectra in the nanofilms and its influence on T_c and energy gap oscillations have been considered in Ref. [41]. However, the effect of the confinement on the electron-phonon coupling strength has not been included. This lack has been recently supplemented by Saniz et al. in Ref. [42]. In this paper [42] the authors have investigated the effect of confinement on the strength of the electron-phonon coupling as well as the electronic spectrum and its influence on the oscillations of the critical temperature. The formula for the phonon-mediated 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. In contradiction to previous models [7, 17], this study predicts the suppression of the critical temperature with increasing density of states at the Fermi level. Such conclusion seems not to be confirmed by recent experiments in which the direct correlation between the T_c oscillations and the energy distribution of the quantum well states in nanofilms is observed [16]. In

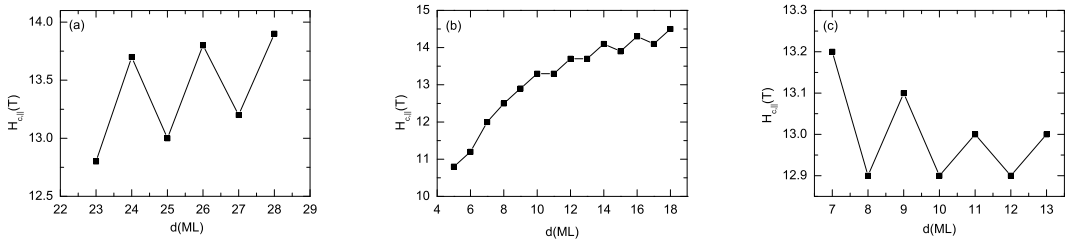

Figure 9. Zero temperature critical field as a function of the nanofilm thickness. Results calculated for the parameters determined from the fitting of T_c with experimental measurements from (a) Ref. [43], (b) Ref. [18] and (c) Ref. [16] (see table 1).

order to determine the realistic value of the electron-phonon coupling which occurs in experiments, there is one more aspect which should be taken into consideration. Note that the results presented in this paper regard the so-called freestanding nanofilms. In fact, Pb films are grown on Si(111) substrate and, for the purpose of the transport measurements, are covered by the layer of Au. Both these layers strongly affect the electron-phonon coupling in the nanofilm due to the interface effect. It has been recently observed [36] that the electron-phonon coupling for Pb nanofilms on Si substrate is lower than in the bulk and diverges to the bulk value with increasing film thickness. The

Reference	$g_0N(0)$	$g_1(\pi)$	$g_1(2\pi)$
Ref. [16]	0.36	$-0.12g_0$	$0.84g_0$
Ref. [18]	0.39	$0.64g_0$	$1.46g_0$
Ref. [43]	0.39	$1.67g_0$	$2.13g_0$

Table 1. The value of parameters used in Ref. [24] to reproduce the oscillations of T_c observed in experiments - see Reference column.

results presented in Ref. [36] indicate that the interface effect has a strong impact on the electron-phonon coupling and should be taken into account in the presented model in order to reproduce the experimental data. The simple approximation which allows to take this effect into account has been recently proposed by Chen et al. in Ref. [24]. It has been assumed [24] that in the first approximation the spatially-dependent electron-phonon coupling can be well estimated by the formula

$$g(z) = \begin{cases} g_{if} & 0 < z < d_{if} \\ g_0 & d_{if} < z < d \end{cases}, \tag{13}$$

where d_{if} is the interface thickness with the electron-phonon coupling g_{if} and g_0 is the electron-phonon coupling in the bulk. Averaging over the z coordinate and including the oscillatory behavior of g coefficient reported in experiments [36] leads to the formula (for details see Ref. [24])

$$\bar{g} = g_0 - \frac{g_1\left(\frac{4\pi aN}{\lambda_F}\right)}{N}, \tag{14}$$

where $g_1(x)$ is a periodic function, N is the number of monolayers, λ_F is the Fermi wavelength and a is the lattice constant. Since the period of T_c oscillations in Pb nanofilms is measured to be ~ 2 ML, the authors of Ref. [24] have reduced the function $g_1(x)$ to only two parameters: $g_1(\pi)$ for an odd number of monolayers and $g_1(2\pi)$ for an even number of monolayers. By appropriate choice of these parameters and by setting the Fermi level to the value corresponding to the period of the quantum-size oscillations (2 ML) one can well reproduce the experimental data of $T_c(d)$ coming form Ref. [18, 16, 43]. The values of the parameters used for each of the mentioned references is presented in table 1. In the present subsection we use these parameters to predict the zero temperature in-plane critical field as a function of the nanofilm thickness. We believe that such procedure allows to determine the realistic value of the critical field comparable with recent experimental measurements [37]. The thickness-dependent oscillations of the zero temperature critical field are presented in Fig. 9. Although the periodicity of the $H_{c,||}$ oscillations for each of the considered references is the same and equal 2 ML, the characteristics of these oscillations are different and vary form one experiment to another. This difference regards the overall trend of $H_{c,||}$ which is an increasing function of the thickness in case of Refs. [43, 18] but decreasing in the case of Ref. [16]. Note that the values of the critical field in Fig. 9 are suppressed as compared

to the critical field calculated with the electron-phonon coupling for the bulk [compare with Fig. 1(a)].

4. Summary

The superconductor to normal metal phase transition driven by the magnetic field for Pb nanofilms is investigated with the use of the BdG equations. Only the Pauli pair-breaking mechanism is included as it is assumed that the external magnetic field is parallel to the surface of the nanofilm. It is shown that the even-odd oscillations of the critical magnetic field appear as the thickness of the sample is increased. The shape of the $H_{c,||}$ oscillations is directly related to the shape of the thickness dependence of the superconducting gap. The beating effect visible in the oscillations is discussed in the context of the energy of the quantum well states which appears due to the confinement of the electron motion in the direction perpendicular to the sample. As it has been shown the period in the nanofilm thickness between two neighbouring peaks in the critical field is equal to 2.14 ML. As the number of the monolayers has to be an integer the beating effect appears in the oscillatory behavior of $H_{c,||}$ and $\bar{\Delta}$. We also show that the zero-temperature critical field in the nanofilms is higher than the Clogston - Chandrasekhar paramagnetic limit and it diverges to the CC value for sufficiently thick films. This fact is explained in term of the spatially varying energy gap induced by the confinement. The phase diagrams in the (H, T) plane are presented for different values of d. According to the obtained results the thickness-dependence is not visible in the phase diagrams when both the field and the temperature are normalized $h = H_{c||}/H_{c||}(0)$ and $t = T/T_c(0)$. Moreover, the interface effect on the electron-phonon coupling is included by using a simple approximation proposed in Ref. [24]. This leads to a spatially dependent g factor and its oscillatory behavior with increasing nanofilm thickness. As it is shown this effect leads to a suppression of the critical field values in comparison to the ones corresponding to the bulk. We believe that such approach allows for comparison of the calculated $H_{c,||}$ oscillations with the experimental results.

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