Quantum size effects on the perpendicular upper critical field in ultra-thin lead films

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We report the thickness-dependent (in terms of atomic layers) oscillation behavior of the perpendicular upper critical field $H_{c2\perp}$ in the ultra-thin lead films at the reduced temperature ($t = T/T_c$). Distinct oscillations of the normal-state resistivity as a function of film thickness have also been observed. Compared with the $T_c$ oscillation, the $H_{c2\perp}$ shows a considerable large oscillation amplitude and a $\pi$ phase shift. The oscillatory mean free path caused by quantum size effect plays a role in $H_{c2\perp}$ oscillation.

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There is a long history of scientific research on superconducting thin films. In particular, theoretical and experimental studies have been carried out to understand how the film thickness affects the superconducting properties. It seems that the reported experimental results of thin films can be explained by the existing theories of superconductivity. However, most previously studied superconducting films were still relatively thick, normally over several tens of nanometers, and the film morphology was usually poor. If the film surface is atomically uniform and the thickness is further reduced to several nanometers so that the quantum size effects become apparent, a natural question arises: will some unexpected new phenomena emerge? In particular, does the conventional theory still work?

Previous theoretical works have predicted many possible prominent physical properties modulated by quantum size effects: electronic structure, critical temperature, electron-phonon interaction, resistivity, Hall conductivity, and so on. There are also some related important experimental results. The $T_c$ oscillations in ultra-thin Pb films, which are caused by the density of states oscillations in confined quantum well structures and by the electron-electron interaction mediated by quantized confined phonons. However, the properties of the upper critical field affected by the quantum size effect have not been reported in previous work. In this Letter, we report our experimental observation of the oscillatory $H_{c2\perp}$ through magneto-transport measurement of ultra-thin Pb films. The oscillations are similar to those of $T_c$ but the motivations are more complex. Besides the factors for $T_c$ oscillation, we interpret this unexpected phenomena by the oscillatory mean free path in ultra-thin superconducting films caused by the quantum size effect.

The 3mm×10mm sized Si(111) wafers were used as substrates and prepared by the standard cleaning procedure to obtain the clean Si(111)-7 × 7 surface. The base pressure of the UHV-MBE-STM-ARPES (Angle Resolved Photoemission Spectroscopy) combined system we used was about 5 × 10^{-11} Torr. The Si substrate was cooled down to 145K during the MBE layer-by-layer growth of the Pb films. The growth rate was controlled at 0.2 ML/Min (Monolayer/Minute) and a RHEED (Reflection High Energy Electron Diffraction) was used for real time monitoring of the growth. After deposition, the sample was warmed up slowly to room temperature and transferred to the analysis chamber where the STM and ARPES were used to investigate the surface topography and the electronic structures, respectively.

For ex-situ magneto-transport measurements, all the Pb films were covered with a Au protection layer of 4ML before being taken out of the UHV system.

The $R - H$ measurements were carried out in a very short time after the samples were taken out of the vacuum. The applied field was perpendicular to the sample surface and the temperatures were set near and below $T_c$. To avoid trapping flux in, the magnet was discharged to zero in oscillate mode and the sample was warmed up to 8K before the $R - H$ measurement for each temperature. Then the perpendicular upper critical field $H_{c2\perp}$ at different temperatures was obtained from the $R - H$ measurements at the field where the resistance reached half of the normal state resistance $R_N$. The resistance approaches $R_N$ very gradually because of the magnetoresistance effect. So we took $R_N$ as the resistance where the resistance variation ratio is within 0.1%.

Figure 1 shows the $R - H$ curves of a 21 ML sample at different temperatures. The arrow points out the defined perpendicular upper critical field $H_{c2\perp}$ at 4.7K. The inset of Fig.1 shows $H_{c2\perp}$ vs. temperature for the 21 ML film. It shows a perfect linear dependence on $T$ near $T_c$, which is a typical property of a superconductor with a high value of the Ginzburg-Landau parameter $\kappa$. The inset of Fig.1 can be used to determine the zero field critical temperature $T_c$ by extrapolating the plot to $H_{c2\perp} = 0$. $T_c$ determined in this way is shown as a function of thickness in Fig.4(a). Normally, a direct way of determining critical temperature is through the $R - T$ measurement at zero
The reduced resistances of Pb films as a function of temperature are shown in (a). The resistances are normalized by the normal state resistance at $T = 8K$. The plot is linearly extrapolated with dashed lines to both high and low temperature sides. The measurements were carried out with a Quantum Design Magnetic Property Measurement System (MPMS-5).

The reduced $R$ as a function of $T$ for this sample. The plot is linearly extrapolated with dashed lines to both high and low temperature sides. The measurements were carried out with a Quantum Design Magnetic Property Measurement System (MPMS-5).

$H_{c2 \perp}(T, d) = \sqrt{2} \kappa(T, \infty) H_c(T)(1 + b/d)$, (1)

where $\kappa(T, \infty) \approx 2\sqrt{2} \pi H_c(T) \lambda_L^2(T)/\Phi_0$ and $b = 3\lambda_L^2(T)\xi_c^2(T)/8\lambda_L^2(T)$. Here $H_c(T)$ is the thermodynamic critical field, $\lambda_L$ is the London penetration depth, $\lambda_c$ is the bulk weak field penetration depth, $\Phi_0$ is the flux quantum ($\Phi_0 = hc/2e = 2.07 \times 10^{-15} Wb$), and $d$ is the film thickness. In Fig.3(b), the dashed lines, calculated using Eq.(1) and the related parameters in previous work, with film thicknesses appropriate to our samples, show the same tendency as the experimental curves if the oscillations are ignored. The measured $H_{c2 \perp}$ values of our samples are about three times larger than the calculated values (note the different scales on the two sides of Fig.3(b)), which may be caused by stronger interface or impurity scattering in our films that gives rise to a large resistivity, thus large $H_{c2 \perp}$ (see discussion below). The linear dependence on $t$ shown in Fig.3(a) also gives an information that for a given film thickness, the temperature dependence follows reasonably well with Eq.(1) whether that particular film is at the peak or valley of the $H_{c2 \perp}$ oscillation.

The TGS theory above includes surface scattering effects but does not consider the quantum size effects that occurs in ultra thin films. The absent $H_{c2 \perp}$ oscillation from TGS theory means that the thickness depended quantum size effect is the original source of the $H_{c2 \perp}$ oscillation. According to the G-L (Ginzburg-Landau) theory, $H_{c2 \perp}$ is determined by the in-plane coherence length $\xi_c$. In a three dimensional anisotropic superconductor, the perpendicular upper critical field near $T_c$ is given by $\xi_c$: $H_{c2 \perp} = \Phi_0/\pi \xi_c^2$. Our ultra-thin films are thinner than 10nm which is much smaller than the Pipard coherence length of a bulk Pb superconductor ($\xi_{bulk} = 83nm$),

FIG. 1: R-H curve of the 21 ML sample. The magnetic field is perpendicular to the sample surface. The black arrow indicates the determined upper critical field at 4.70K. The inset shows the $H_{c2 \perp}$ as a function of $T$ for this sample. The plot is linearly extrapolated with dashed lines to both high and low temperature sides. The measurements were carried out with a Quantum Design Magnetic Property Measurement System (MPMS-5).

FIG. 2: The reduced resistances of Pb films as a function of temperature are shown in (a). The resistances are normalized by the normal state resistance at $T = 8K$. (b) shows an oscillation of normal state resistivity at $8K$ as a function of film thickness.

field. We find that the critical temperatures determined by both methods show a consistent oscillation behavior and the values are quite close for every thickness.

The reduced $R - T$ curves of Pb films from 21 ML to 28 ML are shown in Fig.2(a). The normal state resistivity $\rho_n$ oscillation with film thickness at $T = 8K$ is shown in Fig.2(b). The similar resistivity oscillations caused by quantum size effect have been reported in single crystalline Pb and Pb-In thin films at $T = 110K$ [16]. But in polycrystalline films, oscillations of the normal state resistivity have not been observed although $T_c$ has been found to oscillate with film thickness [17]. In our experiment, both $T_c$ and $\rho_n$ oscillations are observed. It indicates that the quantum size effects show up in both superconducting state and normal state but the intensities and mechanisms may vary in different way depending on sample conditions.

Figure 3(a) shows $H_{c2 \perp}$ as a function of the reduced temperature $t = T/T_c$. For every thickness $H_{c2 \perp}$ shows a good linear dependence on $t$ near $t = 1$. $H_{c2 \perp}$ versus film thickness for $t = 0.90$ and 0.95 are shown respectively in Fig.3(b). It is shown that with the film thickness variation, $H_{c2 \perp}$ exhibits an oscillation behavior, which is similar to the reported $T_c$ oscillation [22]. However, the oscillation of $H_{c2 \perp}$ are $\pi$ out of phase to that of $T_c$, i.e., peaks appear in the odd layer samples where dips appear in the even layer samples, which is opposite to the $T_c$ oscillation shown in Fig.4(a).

In the early theories proposed to understand the magnetic properties of thin film superconductors, the TGS (Tinkham, de Gennes and Saint James) theory [18,19] was validated as showing a good agreement with the former experimental results [20,21]. According to TGS theory, the upper critical fields $H_{c2 \perp}$ near $T_c$ should monotonically increase when the film thickness decreases, which can be described in the following form [18]:

$H_{c2 \perp}(T, d) = \sqrt{2} \kappa(T, \infty) H_c(T)(1 + b/d)$, (1)

where $\kappa(T, \infty) \approx 2\sqrt{2} \pi H_c(T) \lambda_L^2(T)/\Phi_0$ and $b = 3\lambda_L^2(T)\xi_c^2(T)/8\lambda_L^2(T)$. Here $H_c(T)$ is the thermodynamic critical field, $\lambda_L$ is the London penetration depth, $\lambda_c$ is the bulk weak field penetration depth, $\Phi_0$ is the flux quantum ($\Phi_0 = hc/2e = 2.07 \times 10^{-15} Wb$), and $d$ is the film thickness. In Fig.3(b), the dashed lines, calculated using Eq.(1) and the related parameters in previous work [18,19] with film thicknesses appropriate to our samples, show the same tendency as the experimental curves if the oscillations are ignored. The measured $H_{c2 \perp}$ values of our samples are about three times larger than the calculated values (note the different scales on the two sides of Fig.3(b)), which may be caused by stronger interface or impurity scattering in our films that gives rise to a large resistivity, thus large $H_{c2 \perp}$ (see discussion below). The linear dependence on $t$ shown in Fig.3(a) also gives an information that for a given film thickness, the temperature dependence follows reasonably well with Eq.(1) whether that particular film is at the peak or valley of the $H_{c2 \perp}$ oscillation.
we can use the quasi two dimensional formula \[25\]:

\[
\left( \frac{dH_{c2\perp}}{dT/T_c} \right)_{T_c} = -\frac{\Phi_0}{2\pi \xi^2_n \xi^2}.
\]  \tag{2}

For the linear dependence on \( t \) near \( t = 1 \) shown in Fig.3(a), \( H_{c2\perp} \) has the same oscillation behavior with thickness as that of \(-\left( \frac{dH_{c2\perp}}{dt} \right)\) at a certain \( t \). The system should be considered as a dirty-limit superconductor because of the strong scattering. For dirty superconductors near \( T_c \), \( \xi^2 \approx \xi_0 l \) where \( \xi_0 \) is the Pipard coherence length and \( l \) is the mean free path for a film \[2, 4\]. According to BCS theory, \( \xi_0 \propto 1/T_c \), therefore we can get \( H_{c2\perp} \propto T_c/l \) at a certain \( t \). In Fig.3(b) and Fig.4(a), it is shown that the oscillation amplitude of \( H_{c2\perp} \) and \( T_c \) are about 40% and 10% respectively. On the other hand, the mean free path \( l \) and the normal state resistivity \( \rho_n \) have the following relation: \( l \propto \rho_n^{-1} \), from which we can derive \( H_{c2\perp} \propto \rho_n T_c \). In Fig.2(b), the \( \rho_n \) oscillation shows a big amplitude about 60% and the same phase as \( H_{c2\perp} \). The rescaled variation of \( \rho_n T_c \) is shown as \( \Delta \rho_n T_c \) in Fig.4(a), which fits well with the oscillation behavior of \( H_{c2\perp} \). It implies \( \rho_n \) oscillation dominates over the \( T_c \) oscillation in \( H_{c2\perp} \) and gives rise to a \( \pi \) phase shift between \( T_c \) and \( H_{c2\perp} \) oscillations. In earlier works, the oscillatory conductivity in quantized thin films has been observed \[10\] and the effects of impurity and surface and interlayer roughness on quantum size effects in thin films have been discussed \[12, 23\]. Though at the moment we do not have a complete answer to the oscillations of \( \rho_n \) with thickness for our films with atomically uniform surfaces, the previous experiments on the layer-spacing oscillation \[24\] provides a strong indication that the modulation of the interface roughness with thickness may play an important role. In that experiment they found that the interlayer spacings oscillate with a period of quasi double layer and even-monolayer samples have shorter interlayer spacings. This is also supported by the binding energy modulation observed \[22, 24\]. It indicates the lattice feels at home with the conduction electrons for the even-monolayer samples while it is not so for the odd-monolayer samples. The unaccommodating lattice and conduction electrons in the odd-layer samples could induce some lattice distortion and therefore enhance the interface roughness. This enhanced interface roughness must induce a higher resistivity.

We believe the experimental findings in our ultra-thin films are due to a variety of combined quantum size effects from ultra-thin film thickness. The quantum size effect can show up either as a modulation of the interface roughness induced by the interlayer spacings as well as the modulation of the phonon modes and the electron-phonon couplings which both affect the normal state transport properties of the samples, of course, also causing the wave vector quantization along the thickness direction. Under the circumstance, only the components of electronic wave vector in the surface plane, i.e., the \( x-y \) plane, have a continuous distribution. Therefore, the electron density distribution is rather inhomogeneous along the \( z \) direction. The modulation of the electron-densities may further feedback to the electron-interface and electron-phonon scattering processes and therefore to the mean free path. Another relevant issue is that the G-L theory is only a mean-field theory in which all the short-distance fluctuations are integrated out. For our ultra-thin films, to give an adequate description of all the electronic states and the scattering processes, we must go back to the microscopic theory of BCS superconductivity within the subband framework and derive the multi-band G-L theory. The G-L order parameter \( \Psi \) perpendicular to the film is limited to quantized values and may also show modulation with the interlayer-spacing modulation. Each subband may have a different value of coherence length \( \xi \) in the \( x-y \) plane, namely \( \xi_{n,d} \).
where \( n \) is the subband index and \( d \) is the number of the monolayers. In general, \( H_{c2\perp} \) is determined by a matrix equation with \( m \) being the size of the matrix in which \( m \) is the number of subbands below the Fermi energy. In the limit that one of the \( \xi_{n,d} \) is much smaller than all the others, \( H_{c2\perp} \) is predominantly determined by this minimum value, which could be much higher than that of the bulk. The story here is similar to that of the newly discovered superconductor \( MgB_2 \), where only two bands are involved \[27\]. If the film becomes thicker, the number of subbands will increase. The interaction of subbands will weaken the quantum size effects and the coherence length will be close to the average one. The oscillation behavior of \( H_{c2\perp} \) will eventually disappear beyond a large thickness.

In conclusion, a large oscillation of \( H_{c2\perp} \) in the ultra thin lead films are observed as a function of film thickness. The \( H_{c2\perp} \) oscillation is opposite to that of \( T_c \) in phase and cannot be simply attributed to the modulation of the density of states and \( T_c \). A large value of \( H_{c2\perp} \) is also observed. Considering the interface and surface scattering and the modulation of coherence length and mean free path induced by the quantum size effect, a possible mechanism is proposed to explain both the anomalous oscillation of \( H_{c2\perp} \) and its large value. We believe that a quantitative description for the findings in our experiments must be based on the combined quantum size induced modulation effects on the interlayer structures, electronic structures, phonons, electron-phonon and electron-interface scattering processes. Further consideration about the flux dynamics is also necessary by including the interface and surface scattering effects and two-dimensional fluctuations in the multi-band G-L theory.

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[1] R. D. Parks, *Superconductivity* (Marcel Dekker, Inc., New York, 1969).

[2] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley Publishing Co., Inc., California, 1987).

[3] M. Tinkham, Phys. Rev. **129**, 2413 (1963).

[4] M. Tinkham, *Introduction to Superconductivity* (2nd Edition, McGraw-Hill, Inc. New York, 1996).

[5] D. Saint James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).

[6] G. D. Cody and R. E. Miller, Phys. Rev. Lett. **16**, 697 (1966); Phys. Rev. **173**, 481 (1968); Phys. Rev. B **5**, 1834 (1972).

[7] Y. Bruynseraede, K. Temst, E. Osquiguil, C. Van Haesendonck, A. Gilabert, and K. Schuller, Physica Scripta **T42**: 37-45 (1992).

[8] J. M. Blatt and C. J. Thompson, Phys. Rev. Lett. **10**, 332 (1963).

[9] Ming Yu and Myron Strongin, Phys. Rev. B **14**, 996 (1976).

[10] Peter Saalfrank, Surface Science **274**, 449 (1992); Giuliana Materzanini, Peter Saalfrank, and Philip J. D. Lindan, Phys. Rev. B **63**, 235405 (2001).

[11] E. H. Hwang, S. Das Sarma, and M.A. Stroscio, Phys. Rev. B **61**, 8659 (2000).

[12] Nandini Trivedi and N. W. Ashcroft, Phys. Rev. B **38**, 12298 (1988); D. Calecki, Phys. Rev. B **42**, 6906 (1990).

[13] C. M. Wei and M. Y. Chou, Phys. Rev. B **66**, 233408 (2002).

[14] Yu. F. Komnik, E. I. Bukshatab, and K. M. Kankovskii, Zh. Eksp. Teor. Fiz. **57**, 1495 (1970) [Sov. Phys. JETP **30**, 807 (1970)]; Yu. F. Komnik, E. I. Bukshatab, Yu. V. Nikitin, F. I. Chuprinin, and C. Sulkowski, Thin Solid Films **11**, 43 (1972).

[15] B. G. Orr, H. M. Jaeger, and A. M. Goldman, Phys. Rev. Lett. **53**, 2046 (1984).

[16] M. Jalochowski and E. Bauer, Phys. Rev. B **38**, 5272 (1988); M. Jalochowski, E. Bauer, H. Knoppe, and G. Lilienkamp, Phys. Rev. B **45**, 13607 (1992).

[17] P. M. Echternach, M. E. Gershenson, and H. M. Bozler, Phys. Rev. B **47**, 13659 (1993).

[18] M. H. Upton, C. M. Wei, M. Y. Chou, and T.-C. Chiang, Phys. Rev. B **65**, 241306(R) (2002).

[19] P. Czoschke, Hawoong Hong, L. Basile, and T.-C. Chiang, Phys. Rev. Lett. **92**, 226801 (2003).

[20] J. J. Paggel, D.-A. Luh, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **92**, 186803 (2004); M. H. Upton, C. M. Wei, M. Y. Chou, T. Miller, and T.-C. Chiang, Phys. Rev. Lett. **93**, 026802 (2004).

[21] Yang Guo, Yan-Feng Zhang, Xin-Yu Bao et al., Science **306**, 1915 (2004).

[22] Tai-Chang Chiang, Science **306**, 1900 (2004).

[23] Yan-Feng Zhang, Jin-Feng Jia, Tie-Zhu Han et al., Phys. Rev. Lett. **95**, 096802 (2005).

[24] V. M. Sadovskii, *Superconductivity and Localization* (World Scientific Publishing, Singapore, 2000).

[25] A. E. Meyerovich and I. V. Ponomarev, Phys. Rev. B **65**, 155413 (2002); Phys. Rev. B **67**, 165411 (2003).

[26] A. E. Koshelev and A. A. Golubov, Phys. Rev. Lett. **90**, 177002 (2003); A. Gurevich, Phys. Rev. B **67**, 184515 (2003).