THERMODYNAMIC PROPERTIES OF THE PHASE TRANSITION TO SUPERCONDUCTING STATE IN THIN FILMS OF TYPE I SUPERCONDUCTORS

D. V. SHOPOVA*, T. P. TODOROV†, and D. I. UZUNOV‡

CPCM Laboratory, G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, BG-1784 Sofia, Bulgaria.

* Corresponding author: sho@issp.bas.bg
† Permanent address: Joint Technical College at the Technical University of Sofia.
‡ Temporal address: Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, 01187 Dresden, Germany.

Key words: superconductivity, magnetic fluctuations, latent heat, order parameter, phase transition, equation of state.

PACS: 74.20.-z, 64-30+t, 74.20.De

Abstract

The effect of magnetic fluctuations on the free energy, the order parameter profile and the latent heat at the equilibrium point of the first order phase transition to superconducting state in thin films of type I superconductors is considered. The possibility for an experimental observation of the fluctuation change of the order of the superconducting phase transition is briefly discussed. Numerical data for the order parameter jump and the latent heat of Al films are presented for needs of experimental studies.

1. Introduction

The investigation of the fluctuation-induced weakly-first order phase transition in type I superconductors in a zero magnetic field known as Halperin-Lubensky-Ma (HLM) effect [1] has been recently extended to the case of thin superconducting films [2]. It has been shown [2] that the HLM effect in quasi-two-dimensional (quasi-2D) films is much stronger than in bulk (3D) systems [1, 3]. This result opens an opportunity for an experimental observation of the effect in suitably chosen superconducting films.

In this letter we present new and more precise results for the behaviour of the free energy, the order parameter, and the latent heat at the equilibrium phase transition temperature...
for thin films of type I superconductors. The numerical values of physical quantities of experimental interest are calculated for Al films. Our results are compared to those given in Refs. [1][2][3][4]. A detailed information about the HLM effect of a fluctuation change of the order of the superconducting phase transition in a zero mean magnetic field due to persisting magnetic fluctuations and the methods of investigation of this phenomenon are published in Refs. [1][5][6]. We shall follow the notations from Ref. [7] for the parameters of the Ginzburg-Landau (GL) free energy of superconductors.

2. Effective free energy

The starting point of our consideration is the effective free energy density $f(\psi) = F(\psi)/V$ of a type I superconductor with a volume $V$ which is a function of the mean (uniform) superconducting order parameter $\psi = \langle \psi(\vec{x}) \rangle$ of the form (see, e.g., Ref. [2]):

\[ f(\psi) = f_0(\psi) + \delta f(\psi), \]

where

\[ f_0(\psi) = a|\psi|^2 + \frac{b}{2}|\psi|^4, \]  

and

\[ \delta f(\psi) = \frac{1}{2}(D - 1)k_B T \sum_{k}^{\Lambda} \ln \left[ 1 + \frac{\rho(\psi_0)}{k^2} \right]. \]  

In Eqs. (2) - (3), $\rho(\psi_0) = \rho_0|\psi|^2$, where $\rho_0 = (8\pi e^2/me^2)$, $a = \alpha_0(T - T_c)$ and $b > 0$ are the usual Landau parameters. They are related to the zero temperature coherence length $\xi_0 = (\hbar^2/4m\alpha_0 T_c)^{1/2}$, the zero-temperature critical magnetic field $H_{c0} = \alpha_0 T_c (4\pi/b)^{1/2}$, and the initial (unrenormalized) critical temperature $T_{c0}$ [7]. The term $\delta f(\psi)$ in $f(\psi)$ describes the effect of the magnetic fluctuations. In Eq. (3), the sum over the wave vector $\vec{k}$ is truncated by the upper cutoff $\Lambda \geq k \equiv |\vec{k}|$. For films of thickness $L_0$ and volume $V = (L_0 L_1 L_2)$ we shall assume periodic boundary conditions, and $a_0 \ll L_0 \leq \Lambda^{-1} \ll L_\alpha$; $\alpha = 1, 2$. For quasi-2D film, i.e. films obeying the condition $a_0 \ll L_0 \leq \Lambda^{-1}$, the sum in Eq. (1) contains only terms with zero component $k_0 = 2\pi n_0/L_0$ ($n_0 = 0$) of the wave vector $\vec{k} = (k_0, k_1, k_2)$. This means that the thickness $L_0$ should be smaller than the magnetic penetration depth $\lambda(T) = (\lambda_0/t_0)^{1/2}$ which gives the characteristic length of the magnetic fluctuations; $\lambda(0) = \lambda_0 = (b/\rho_0 a_0 T_c)^{1/2}$ is the zero-temperature penetration depth, and $t_0 = (T - T_{c0})/T_{c0}$. We choose the cutoff $\Lambda = (\pi/\xi_0)$, so we shall study films of size $L_0 < \xi_0$. This is consistent with the general requirement $\xi_0 < \lambda(T)$ for the validity of the GL free energy for the type I superconductors (see, e.g., Ref. [7]).

For quasi-2D systems, the continuum limit applied to the sum in Eq. (3) yields a simple integral over $\vec{k} = (0, k_1, k_2)$. Solving this integral we obtain

\[ \delta f(\psi) = \frac{k_B T}{4\pi L_0} \Lambda^2 \left[ \left( 1 + \frac{\rho_0 |\psi|^2}{\Lambda^2} \right) \ln \left( 1 + \frac{\rho_0 |\psi|^2}{\Lambda^2} \right) - \frac{\rho_0 |\psi|^2}{\Lambda^2} \ln \left( \frac{\rho_0 |\psi|^2}{\Lambda^2} \right) \right]. \]  

The second term in the r.h.s. of Eq. (4) is nonanalytical and cannot be expanded in powers of $\psi$. An incomplete Landau expansion of this free energy in positive powers of
can be performed, provided

\[(\rho_0|\psi|^2/\Lambda^2) \ll 1.\]  

(5)

This inequality should be satisfied in the stable (Meissner) phase \(\psi(T) > 0\), i.e., at the absolute minimum \(f[\psi(T)]\) of the function \(f(\psi)\) below the phase transition temperature.

Hereafter we shall denote by \(\psi(T)\) the equilibrium value of \(\psi\), which describes a stable (or metastable) phase and is a solution of the equation of state \((\partial f/\partial \psi) = 0\). The condition (5) and the problems included in the reminder of this article can be considered in terms of auxiliary parameters corresponding to the theory, in which the \(\delta f(\psi)\)-part of the free energy is neglected, i.e., corresponding to the free energy \(f_0(\psi)\) given by Eq. (2). Within this simplified theory the modulus of the equilibrium zero-temperature order parameter is given by

\[|\psi_0| = |\psi(T = 0)| = (\alpha_0 T_0/b)^{1/2}.\]

This quantity can be used to define the reduced order parameter \(\varphi = (|\psi|/|\psi_0|) \geq 0\) of the general theory represented by the complete free energy \(f(\psi)\). At equilibrium, i.e., \(\psi = \psi(T)\), the condition (5) can be written in the form \[\varphi(T)/\lambda_0 \Lambda < 1.\] If we suppose that the difference between the values of \(\varphi(T)\) for the simplified and complete theories can be ignored, we shall obtain that \(\lambda(T)\Lambda > 1\), which is consistent within the superconductivity theory; see our discussion below Eq. (3). We have recently investigated Eq. (4) with the help of the Landau expansion in Ref. [2]. Here we shall consider the free energy \(f(\psi)\) given by Eqs. (1), (2), and (4) without such an expansion.

Using the reduced order parameter \(\varphi\) the free energy \(f(\psi)\) can be represented in the form

\[f(\varphi) = \frac{H_0^2}{8\pi} \left\{2t_0 \varphi^2 + \varphi^4 + C(1 + t_0) \left[\left(1 + \mu \varphi^2\right) \ln \left(1 + \mu \varphi^2\right) - \mu \varphi^2 \ln (\mu \varphi^2)\right]\right\},\]

(6)

where

\[C = \frac{2\pi^2 k_B T_0}{L_0 \xi_0^2 H_0^2},\]

(7)

and \(\mu = (\xi_0/\pi \lambda_0)^2\).

3. Results and discussion

It is known [1] that the HLM effect is stronger in type I superconductors with relatively small GL parameter \(\kappa = (\lambda_0/\xi_0)\). This is obvious from Eq. (6). That is why we can choose as adequate examples the aluminium (AL, \(\kappa \sim 0.01, \xi_0 = 1.6 \mu m, T_c \approx 1.19 K, H_c(0) \approx 99 Oe\)) and tungsten (W, \(\kappa \sim 0.001, \xi_0 = 37 \mu m, T_c \approx 5 mK, H_c(0) \approx 1.15 Oe\)).

One cannot be certain about the best choice of the substance for an experimental check of the HLM effect before a comprehensive consideration of the experimental problem.

Our concrete aim is to establish the size of the effect and we shall do the calculations for Al, which is probably one of the best candidates for experiments. The numerical values of the parameters \(\tilde{C} = CL_0\) and \(\mu\), where \(\lambda_0 = (hc/2\sqrt{2}eH_0\xi_0)\), can be calculated from the experimental data for \(T_c, H_c(0), \) and \(\xi_0\) of Al, given above. Note, that the available
Figure 1: Curves representing the free energy (6) for five values of $t_0$: $t_0 = -0.001$ (see □-line), $t_0 = -0.00127$ (+), $t_0 = -0.00137$ (◦), $t_0 = -0.001473$ (⋄), $t_0 = -0.0018$ (—).

Experimental data vary depending on the way of preparation of samples and the type of measurement. Besides, the experimental values used here are for bulk monocrystals of Al and differ within 10 - 20% from those for thin Al films of thickness much smaller than the value $L_0 = 0.1 \mu m$ considered below. However, the variation of the experimental data, used here does not essentially influence our numerical results.

The free energy density $f(\varphi)$ for Al films of thickness $L_0 = 0.1 \mu m$ and several values of the parameter $t_0$ is calculated from Eq. (4). The result is shown in Fig. 1. The reduced order parameter corresponding to metastable and stable superconducting states is calculated with the help of the equations $f(\varphi) = 0$, $(\partial f/\partial \varphi) = 0$, and the stability condition $\partial^2 f/\partial \varphi^2 > 0$ (see Fig. 2).

Fig. 1 exhibits a well established phase transition of first order. This confirms the preceding results [2] obtained with the help of Landau expansion; note that in Ref. [2] another normalization of the effective free energy has been used, which seems to be less convenient than the present one. The positive minima of the free energy describe metastable superconducting states (overheated superconductivity). The respective metastable values of the reduced order parameter $\varphi$ are shown by the dashed curve in Fig. 2. The metastability states are closed in the temperature interval from $T^* = 0.9990 T_{c0}$ to $T_{eq} \approx 0.9985 T_{c0}$ – the equilibrium temperature of the first order phase transition. The curve marked by squares (□) in Fig. 1 corresponds to $T = T^*$, i.e., this is the curve, at which the minimum of the free energy for a nonzero value of $\varphi$ appears for the first time when the temperature is lowered from the side of the normal phase. The curve drawn by ”diamonds” (⋄)
corresponds to the equilibrium transition temperature $T_{eq}$, at which the minimum of the free energy for nonzero value of the order parameter $\varphi$ is equal to zero. There the energies of the superconducting and the normal phases are equal. The superconducting phase is stable for all temperatures below $T_{eq}$. The stable superconducting states are shown by the solid curve in Fig. 2 for several values of $t_0$ below $t_{0eq} = t_0(T_{eq}) \approx -0.0015$.

The equilibrium entropy jump $\delta s = -df[T, \varphi(T)]/dT$ at $T_{eq}$ per unit volume (the total entropy jump is $\delta S = V\delta s$) is obtained in the form

$$\delta s = -\frac{H_{co}^2}{4\pi T_{c0}} \left\{ \frac{C}{2} \left[ (1 + \mu \varphi_{eq}^2) \ln (1 + \mu \varphi_{eq}^2) - \mu \varphi_{eq}^2 \ln (\mu \varphi_{eq}^2) \right] \right\}. \quad (8)$$

For the Al film of thickness $L_0 = 0.1 \mu m$, the $C$–term in the curly brackets of Eq. (8) is of order $10^{-3} \varphi_{eq}^2$ and can be neglected. Taking the value of the order parameter jump $\varphi_{eq} \sim 0.033$ from Fig. 2, we obtain

$$\delta s = -\frac{H_{co}^2}{4\pi T_{c0}} \varphi_{eq}^2 \approx -0.7 \text{ erg K.cm}^{-3}. \quad (9)$$

In order to show the significance of this result we compare it with the specific heat capacity jump at the second order phase transition point, $T_{c0}$, described by the free energy $f_0(\varphi)$:

$$\delta C(T_{c0}) = \frac{H_{co}^2}{4\pi T_{c0}} \approx 660 \text{ erg K.cm}^{-3}. \quad (10)$$
The ratio \( \frac{\delta s/\delta C}{\delta s/\delta C} \sim 0.001 \) is \( 10^3 \) times bigger than the respective quantity for bulk Al [1]. Comparing with the results [3] for bulk Al one can see that the metastability domain \( (T^*-T_{eq}) \) for the film under consideration is also \( 10^3 \) times larger than for bulk Al. The calculated value \( (\varphi_{eq} \approx 0.0032) \) of the order parameter jump in bulk Al is about 0.1 of that shown in Fig. 2. While the overheated and stable superconducting states in quasi-2D Al films appear only for \( t_0 < 0 \), i.e. below \( T_{co} \), in 3D Al these states occur also slightly above \( T_{co} \).

The present results are consistent with those obtained by Landau expansion [2] of the free energy (6). However, there is a difference in the numerical values of some parameters considered in the present investigation and those in Ref. [2]. Obviously, the Landau expansion has some limitations when applied to free energies of the type (6).

4. Conclusion

The results show that Al films of thickness below 0.1\( \mu \)m can be used for an experimental test of the HLM effect. Calculations for thinner Al films or for W, where the GL parameter is 10 times smaller, will give much stronger effect and, hence, better opportunity for an experimental test. The thickness of the film may be lowered up to the nm scale, below which the superconductivity is destroyed.

Acknowledgements. Useful discussions with Profs. P. Fulde, R. Klem, K. Maki, A. C. Mota, and Yu. N. Ovchinnikov, are gratefully acknowledged. One of us (D.I.U.) thanks the hospitality of MPI-PKS (Dresden).

References

[1] B. I. Halperin, T. C. Lubensky, and S. K. Ma, *Phys. Rev. Lett.* **32**, 292 (1974).

[2] R. Folk, D. V. Shopova and D. I. Uzunov, *Phys. Lett.* A **281**, 197 (2001).

[3] D. V. Shopova, T. P. Todorov, T. E. Tsvetkov and D. I. Uzunov, *Mod. Phys. Lett.* B (2002), in press; T. E. Tsvetkov, MS Thesis, Sofia University (June, 2002).

[4] J-H. Chen, T. C. Lubensky, and D. R. Nelson, *Phys. Rev.* B**17**, 4274 (1978).

[5] R. Folk and Yu. Holovatch, in: *Correlations, Coherence, and Order*, ed. by D. V. Shopova and D. I. Uzunov (Kluwer Academic/Plenum Publishers, New York-London, 1999), p. 83.

[6] D. I. Uzunov, *Introduction to the Theory of Critical Phenomena* (World Scientific, Singapore, 1993).

[7] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, Part 2, [Landau and Lifshitz Course of Theoretical Physics, vol. 9] (Pergamon Press, Oxford, 1980).