GENERIC PROPERTIES OF LAYERED SUPERCONDUCTORS*

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GENERIC PROPERTIES OF LAYERED SUPERCONDUCTORS

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ABSTRACT

A wide variety of layered materials have been found to be superconducting. Among these are graphite intercalation donor compounds, transition metal dichalcogenides, intercalated transition metal dichalcogenides, organic layered superconductors, artificial superlattices, and the cuprates. The normal state properties of all of these compounds are very similar, due to the fact that they all have well-defined Fermi surfaces, and quasi-linear in-plane resistivities at high temperatures. At lower temperatures, charge- or spin-density waves are common in these systems. With the exception of the graphite intercalation compounds, all of the layered superconductors are type-II, and generally highly anisotropic in their superconducting properties. Dimensional crossover from anisotropic bulk to thin film behavior is common to many of these materials.

INTRODUCTION

An important question regarding the mechanism for superconductivity and the resulting superconducting properties of the high T_c cuprates is whether the normal state and superconducting properties of these materials are unique. In order to answer such a question, it is imperative to examine other materials with similar, layered structures which are also superconducting. In fact, many of the normal state and superconducting properties of the high T_c cuprate materials are generic for layered superconductors. The normal state property on which I will focus in this talk is the resistivity. The superconducting properties that will be discussed are the anisotropies of the upper and lower critical fields H_{c2} and H_{c1} , respectively. A detailed presentation of the normal state and superconducting properties, along with many phenomenological theoretical treatments of their superconducting properties will be published in a book¹.

MATERIALS

The first and simplest class of layered superconductors are the electron donor graphite intercalation compounds (GICs). Examples of these materials are C_8Rb and C_4KHg , in which graphite is intercalated with alkali and alkali amalgam. These materials exhibit staging, in which periodic compounds with a fixed number of host graphite layers alternating with an intercalant layer are formed. A number of the stage-1 and stage-2 electron donor GICs are superconducting. C_8Rb is an anisotropic type-I superconductor, with $T_c = 0.025$ K. Others, such as C_8K , are type-I for $H \parallel \hat{c}$, but type-II for $H \perp \hat{c}$. Except for some of these GICs, all other layered superconductors are type-II for all magnetic field directions.

The second class of layered superconductors are the group 5 transition metal dichalcogenides (TMDs), e.g. $2H-NbSe_2$ and $2H-TaS_2$. Since there are generally two configurations of the $T\chi_2$ building blocks from which these materials are constructed, the octahedral and trigonal prismatic configurations, these compounds typically form in a variety of polytypes. One can think of polytypism as a generalization of staging in the GICs, but there are generally multiple structures for each stage. Examples are the $1T$ (stage-1 tetragonal), the $2H_a$ and

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2Hb (stage-2 hexagonal) polytypes the 3R (stage-3 rhombohedral) polytype, and the 4Ha, 4Hb, 4Hc, 4Hd_I, and 4Hd_{II} (stage-4 hexagonal) polytypes. A number of different polytypes are superconducting, with T_c values typically in the range 0.2 K to 7.3 K.

A third class of layered superconductors are intercalated TMDs. The group 5 TMDs intercalated with organic molecules, e.g. 2H-TaS₂(pyridine)_{1/2}, form one subclass. Usually, these materials are highly anisotropic, and can be as anisotropic as any of the high T_c cuprates. Another subclass are groups 4 and 6 TMDs intercalated with inorganic materials, usually alkali or alkali earth elements. Examples are $A_x\text{ZrSe}_2$, $A_x\text{MoS}_2$, and $A_x(\text{H}_2\text{O})_y\text{TaS}_2$. A third subclass are the misfit compounds, in which transition metal monochalcogenides $T\chi$ are effectively intercalated between $T\chi_2$. Since the $T\chi$ layers have different a - and b -axis parameters than do the $T\chi_2$ layers, the resulting overall compounds are incommensurate intercalation compounds. Typical T_c values are 3 – 6K.

The fourth class of layered superconductors are organic layered superconductors. While organic superconductors have been made from a variety of organic donor molecules with inorganic acceptor molecules, those which have layered structures are generally made from bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, or ET, for short). There are two major subclasses of layered organic superconductors, the β -(ET)₂ X and κ -(ET)₂ X subclasses. Examples are β -(ET)₂I₃ and κ -(ET)₂Cu(NCS)₂. These materials form layered structures in which the ET molecules have their long axes perpendicular to the conducting ET layers, with anionic layers between conducting ET layers. The different subclasses have different two-dimensional ET packing configurations within the ET layers, as in the case of polytypism within a given stage number in the TMDs. T_c values ranging from 1 – 12 K have been attained.

With the use of sputtering or especially molecular beam epitaxy methods, it has been possible to make a fifth class of layered superconductors, the artificial superconducting superlattices, or multilayers. Such materials are prepared by alternating the deposition of thin layers of a superconducting (S) material such as Nb with thin layers of a different (N , usually non-superconducting) material such as Ge. Subclasses of superlattices are superconducting-superconducting (SS'), superconducting-normal (SN), superconducting-insulating (SI), superconducting-magnetic (SM), and nominally non-superconducting-non-superconducting (NN') superlattices which are superconducting. Normally, periodic superlattices are made, but superconducting superlattices with doubly-periodic, random, and fractal structures have also been made. By varying the thicknesses and compositions of the S and N layers (e.g., in $\text{Mo}_x\text{Ge}_{1-x}/\text{Mo}_y\text{Ge}_{1-y}$ periodic superlattices), it has been possible to control the interlayer couplings and intralayer coherence lengths of the S layers, in order to mimic the properties of known layered superconductors, such as some of the cuprates, albeit with different (i.e., much lower) T_c values.

The cuprates compose a sixth class of layered superconductors. Common to all the members of this class are the conducting CuO₂ layers. There are two subclasses, the electron-doped and hole-doped cuprates. An example of an electron-doped cuprate is Nd_{1.85}Ce_{0.15}CuO_{4-y}. Some of the more important hole-doped cuprates are La_{2-x}Sr_xCuO_{4-y} (LaSr214), YBa₂Cu₃O_{7- δ} (Y123), Bi₂Sr₂CaCu₂O_{8+ δ} (Bi2212), Tl₂Ba₂CuO_{6+ δ} (Tl2201), and the infinite-layer structure ACuO₂, where $A = \text{Ca}_x\text{Sr}_{1-x}$, for example. In addition, there are strong indications that at least one (Bi2212) of these materials can be intercalated with iodine.

Finally, molecular beam epitaxy methods have allowed the synthesis of

cuprate superlattices, or multilayers, which by now comprise a seventh class of layered superconductors. An example is the superconducting-insulating multilayer of Y123/Pr123, which has the overall Y123 structure, but with Y and Pr atoms alternating along $\hat{c}$, forming a superlattice of superconducting Y123 and insulating Pr123 on the scale of a single unit cell. By varying the thickness of the insulating layers, it has been possible to make high T_c , extremely anisotropic layered superconductors.

FERMI SURFACES

All layered superconductors that have been studied have Fermi surfaces, with rather well-defined Fermi edges. This is contrasted with quasi-one-dimensional conductors, as was shown in UPS photoemission experiments² of the quasi-one-dimensional metals $(\text{TaSe}_4)_2\text{I}$ and $\text{K}_{0.3}\text{MoO}_3$, the layered conductor $1T\text{-TaSe}_2$, and bulk Rh. Except for Rh, all three compounds have charge-density wave transitions below T_{CDW} , but the photoemission experiments were performed above T_{CDW} . While the first two materials showed little, if any, sign of a sharp Fermi edge, the layered material $1T\text{-TaSe}_2$ had a very sharp Fermi edge, even at 190 K, the temperature of the measurement. Similar behavior has routinely been seen in other $T\chi_2$ compounds and in a variety of cuprates.

There is a large distinction between the normal state Fermi surface character as observed from photoemission in layered materials that are insulating and those that are superconducting. For example, ARPES measurements³ of oxygen-deficient samples ($\delta \neq 0$) of Y123 have shown that for $\delta < 0.6$, a clear quasiparticle peak can be observed at certain scattering angles, but for $\delta \geq 0.6$, no such peak was observed. This point of behavioral change ($\delta = 0.6$) is precisely the point in stoichiometry at which superconductivity disappears, i.e., for $\delta > 0.6$, Y123 is not superconducting. Neither is its normal state a metal. For $\delta > 0.6$, it is a superconductor, and its normal state is very similar to (although somewhat different from) that of an ordinary metal.

NORMAL STATE RESISTIVITIES

In-plane resistivities⁴ of the stage-1 alkali GICs fit the simple formula $\rho_{||}(T) = A + BT + CT^2$ quite well in the temperature regime $50 \text{ K} < T < 300 \text{ K}$. Below 50 K, $\rho_{||}(T)$ deviated slightly on the low side from that formula. Such deviations correlate nicely with measurements⁵ of the resistivity $\rho_{\perp}(T)$ along the c -axis direction. In those measurements, $\rho_{\perp}(T)$ decreased monotonically from 300 K to about 50 K, as for a normal metal, but below 50 K, $\rho_{\perp}(T)$ exhibited a minimum around 40-45 K, followed by an increase and a low temperature saturation. While one might naively describe such low temperature behavior as semiconducting or insulating, the saturation at very low T is not characteristic of either of those interpretations. In higher-stage alkali GICs, $\rho_{\perp}(T)$ exhibits hysteretic anomalies⁵, which are indicative of either alkali ordering (a mass-density wave) or charge-density wave formation. Since the alkali atoms are probably nearly completely ionized, mass-density wave formation necessarily implies charge-density wave formation as well.

Such resistive behavior is easier to understand when comparison with the resistive behavior of $2H\text{-TaS}_2$ is made. In accurate measurements⁶ on high-quality single crystals of $2H\text{-TaS}_2$, $\rho_{||}(T) = \rho_0(T + T_0)$ was found to be extremely linear above $T_{CDW} = 75 \text{ K}$, more linear than in any other material of which I am aware (including Bi2212). At T_{CDW} , a small bump in $\rho_{||}(T)$ was observed,

and below T_{CDW} , $\rho_{||}(T)$ was highly non-linear, deviating significantly below the extrapolation of the high- T region. On the other hand, $\rho_{\perp}(T)$ appeared slightly sublinear but metallic in its T -dependence above T_{CDW} , but had a minimum at T_{CDW} , followed by a rise with decreasing T below T_{CDW} , and a low- T saturation. Electron diffraction experiments⁶ confirmed the presence of an incommensurate charge-density wave (CDW) below T_{CDW} . Below $T_c \approx 0.6$ K, $2H$ -TaS₂ is superconducting. Hence, this behavior suggests two things: the linear normal state resistivity is unrelated to magnetism, and occurs above a charge- or spin-density wave transition. Second, the low temperature rise in $\rho_{\perp}(T)$ is not indicative of incoherent tunneling or insulating behavior, but more likely arises from the scattering off the incommensurate lattice distortion present in that temperature regime.

Upon intercalation with pyridine, $\rho_{||}(T)$ remains linear⁷ above 75 K, having increased by a constant factor of 2, reflecting the geometric increase in the sample volume. Below 75 K, however, the bump at 75 K is absent, and below 75 K, $\rho_{||}(T)$ extrapolates smoothly from its high-temperature behavior, approaching a constant at low temperatures, before dropping to zero at $T_c \approx 3.3$ K. In addition, $\rho_{\perp}(T)$ has increased dramatically in magnitude [$\rho_{\perp}(300 \text{ K}) \approx 20 \Omega \text{ cm}$, reflecting the much high anisotropy], and has a metallic-like T -dependence for $T > T_c$. It is likely that the measured resistive anisotropy of about 10^5 is limited by microscopic electrical shorts.

Measurements of $\rho_{||}(T)$ in a variety⁸ of the alkali-intercalated compounds $A_x\text{ZrSe}_2$ and in the misfit compounds⁹ also show nearly linear behavior over a wide temperature regime. In particular, $\text{Na}_{0.52}\text{ZrSe}_2$, while superconducting below 2 K, has a very linear resistivity⁸ for $20 \text{ K} < T < 300 \text{ K}$. Hence, I maintain such linear $\rho_{||}(T)$ behavior is generic for the TMDs and their intercalates.

Of the organic layered superconductors, compounds in the β -(ET)₂ X series generally have¹⁰ $\rho_{||}(T) \propto T^2$. On the other hand, the κ -(ET)₂ X compounds have a different $\rho_{||}(T)$ behavior. Often¹¹, there is a pronounced peak in $\rho_{||}(T)$ in the regime 100-200 K, followed by a metallic-like behavior at lower T . Some (probably better) samples¹² do not show this peak, however. Just above T_c , $\rho_{||}(T)$ is linear¹² in the region $T_c \approx 10 \text{ K} < T < 20 \text{ K}$. In addition, the magnitudes of the measured $\rho_{||}(300 \text{ K})$ values are typically two orders of magnitude higher than in the cuprates.

The hole-doped cuprates generally¹³ have a nearly linear $\rho_{||}(T)$ behavior. Recent experiments¹⁴ on untwinned, single crystal Y123 show that $\rho_{\perp}(T)$ is also nearly linear, typical of a metal. It is curious that the measured⁶ $\rho_{||}(300 \text{ K})$ and $\rho_{\perp}(300 \text{ K})$ in $2H$ -TaS₂ are almost identical¹ to those values¹⁴ measured in Y123. Measurements¹⁵ on Bi2212 show a nearly linear $\rho_{||}(T)$, but a rising $\rho_{\perp}(T)$ with decreasing T . Upon intercalation with I₂, $\rho_{||}(T)$ increases by a nearly-constant geometric factor, as occurred in intercalation of TaS₂, but $\rho_{\perp}(T)$ decreased in magnitude, and became linear upon intercalation. While technical problems such as microscopic electrical shorts might be responsible for such behavior, especially considering the large values of $\rho_{\perp}$, it should be noted that the incommensurate crystal distortion¹⁶ vector present in Bi2212 is absent¹⁵ in IBi2212, the CuO₂ layers lying directly on top of one another. Hence, the similarity with the $\rho_{\perp}(T)$ behavior observed in the GICs and in the TMDs suggests that such behavior might indeed be intrinsic, and related to incommensurate mass- or CDW formation. Somewhat different resistive behavior is seen in the electron-

doped cuprates¹⁷. These materials appear metallic both parallel and normal to the layers, with $\rho_{||}(T)$ and $\rho_{\perp}(T)$ that flatten out in the region above T_c .

Perhaps the most unusual behavior of $\rho_{||}(T)$ is seen in the cuprate superlattices¹⁸. With ultrathin superconducting layers separated by much thicker insulating layers, extremely wide superconducting transitions were observed. Such behavior may be related to a Kosterlitz-Thouless transition.

Generally, though, linear normal state $\rho_{||}(T)$ behavior is generic in layered superconductors. As far as I have determined in a wide search of the literature¹, the majority of layered superconductors exhibit such behavior. It occurs above any CDW, spin-density wave, or other periodic lattice distortion. Below such distortions, non-linear $\rho_{||}(T)$ behavior is observed. $\rho_{\perp}(T)$ is dramatically affected by such periodic lattice distortions, often appearing similar to that of an insulator, if one does not examine the low- T regime to low enough T . Removal of such distortions generally removes the increasing $\rho_{\perp}(T)$ with decreasing T behavior.

RELEVANT LENGTHS

The most generic of all features of the superconducting properties of layered superconductors is their anisotropy. Except for some of the GICs, layered superconductors are type-II, and usually extreme type-II, with very large anisotropies. In particular, the critical field H_{c1} at which a single magnetic vortex first enters the superconductor, and H_{c2} , the field at which superconductivity is destroyed, are highly anisotropic.

This anisotropy is usually characterized by the parameter $\gamma = (M/m)^{1/2}$, or as $\epsilon = m/M$, where m and M are the effective masses parallel to and normal to the layers, respectively, and $\gamma = 1/\sqrt{\epsilon}$. Typically, $\gamma \gg 1$ in generic layered superconductors. There are then six lengths which are relevant for the discussion of the generic superconducting properties of layered superconductors. The first two of these are $\lambda_{||}(T)$, $\lambda_{\perp}(T) = \gamma\lambda_{||}(T)$, the magnetic field penetration depths. For a vortex in the superconductor, $\lambda_{||}$ and $\lambda_{\perp}$ characterize the distance over which the magnetic field varies away from the vortex core. For $\mathbf{H}||\hat{c}$, only $\lambda_{||}$ is relevant, but for other field angles, both $\lambda_{||}$ and $\lambda_{\perp}$ are relevant. The next two lengths are the coherence lengths $\xi_{||}(T)$ and $\xi_{\perp}(T) = \xi_{||}(T)/\gamma$. These quantities describe the spatial variation of the superconducting order parameter (in the GL and LD models) away from the vortex core. The last length s , is the c -axis lattice parameter, or the repeat distance along $\hat{c}$, and only enters into the LD model, which is specific for layered superconductors. Note that even for multiple layers per unit cell, the only relevant crystal length parameter is s , due to Bloch's theorem. Generally, we have $\lambda_{||}, \lambda_{\perp} \gg s$, and $\lambda_{\perp}, \lambda_{||} \gg \xi_{||}, \xi_{\perp}$, except for the graphite intercalation compounds.

It is a comparison of the lengths $\xi_{\perp}$ and s which can give rise to dimensional crossover. Since $\xi_{\perp}(T) \propto |T - T_c|^{-1/2}$, above T_c , a region fluctuating from the normal into the superconducting state extends over many layers near to T_c , and over only one layer far above T_c . This gives rise to dimensional crossover at the temperature $T_0 > T_c$ can occur in the fluctuations of the measurable quantities, where $\xi_{\perp}(T_0) = s/2$. Below T_c , normal regions (introduced by a vortex parallel to the layers, or by thermodynamic fluctuations) extend over many layers near to T_c , but are localized between the superconducting layers at low T . Hence, dimensional crossover can also occur at the temperature $T^* < T_c$ given by $\xi_{\perp}(T^*) = s/\sqrt{2}$ below T_c .

PHENOMENOLOGICAL MODELS

One might think that it is then only necessary to calculate the critical field quantities along each of the crystal axis directions, and all of the important features of the critical fields would be known. While there is some truth to this in the case of H_{c2} , provided that one uses the correct model, it is not true of H_{c1} , for which the angular dependence itself is very important. To illustrate these differences, I shall briefly discuss three phenomenological models of increasing complexity and accuracy, which have been widely used to study layered superconductors: the anisotropic London model, the anisotropic Ginzburg-Landau (GL) model, and the Lawrence-Doniach (LD) model.

The first model I shall discuss is the anisotropic London model. This model has the advantage of its simplicity, but the disadvantage in that it neglects the vortex cores as well as the explicit layered structures. Hence, there is no dimensional crossover in this model. Since it neglects the vortex cores, it essentially sets $\xi_{||}, \xi_{\perp} \rightarrow \infty$, or the Ginzburg-Landau parameters $\kappa_{\perp} = \lambda_{||}/\xi_{||} \rightarrow \infty$ and $\kappa_{||} = \gamma\kappa_{\perp} \rightarrow \infty$. Nevertheless, even for the magnetic field at an arbitrary direction, it is possible to patch up the model, introducing a core cutoff obtained from the anisotropic GL model, in such a way as to extend the validity of the anisotropic London model to $H_{c1}(\theta) \leq H \ll H_{c2}(\theta)$, where θ is the angle $\mathbf{H}$ makes with the c -axis.

The Helmholtz free energy difference between the superconducting and normal states in the anisotropic London model is given by

$$\mathcal{F} = \frac{1}{8\pi} \int d^3\mathbf{r} (\mathbf{b}^2 + \lambda_L^2 \text{curl } \mathbf{b} \cdot \overleftrightarrow{\mathbf{m}} \cdot \text{curl } \mathbf{b}), \quad (1)$$

where $\mathbf{b}(\mathbf{r})$ is the local magnetic induction, $\lambda_L = [m_g c^2 / (4\pi n_s e^2)]^{1/2}$ is the geometric-mean London penetration depth, where n_s is the superfluid density, and $m_g = (m_1 m_2 m_3)^{1/3}$ is the geometric mean effective mass. For uniaxial anisotropy, we set $m_1 = m_2 = m < m_3 = M$. The effective mass tensor $\overleftrightarrow{\mathbf{m}}$ is diagonal, with (11) and (22) elements $\overline{m} = m/m_g$, and (33) element $\overline{M} = M/m_g$.

For the field along a crystal symmetry (or axis) direction, one may use Eq. (1) to calculate $\mathcal{F}(\mathbf{B})$, where $\mathbf{B}$ is the macroscopic magnetic direction, or spatial average of $\mathbf{b}$. Such cases are rather simple, as the only tensor ($\overleftrightarrow{\mathbf{m}}$) in the problem is diagonal. For other field directions, it is not so simple. Let us assume

$$\hat{\mathbf{B}} = \hat{\mathbf{x}} \cos \theta \cos \phi + \hat{\mathbf{y}} \cos \theta \sin \phi + \hat{\mathbf{z}} \sin \theta. \quad (2)$$

In order to find the spatial distribution of $\mathbf{b}$, it is useful¹⁹ to rotate the axes so that one of the rotated axes ($\hat{\mathbf{z}}'$) is parallel to $\hat{\mathbf{B}}$. This leads to a transformed Helmholtz free energy difference of the form

$$\mathcal{F}' = \frac{1}{8\pi} \int d^3\mathbf{r}' [\mathbf{b}'^2 + (\overrightarrow{\nabla}' \times \mathbf{b}') \cdot \overleftrightarrow{\mathbf{M}} \cdot (\overrightarrow{\nabla}' \times \mathbf{b}')], \quad (3)$$

where

$$\overleftrightarrow{\mathbf{M}} = \overleftrightarrow{\lambda} \cdot \overleftrightarrow{\mathbf{m}} \cdot \overleftrightarrow{\lambda}^{-1} \quad (4)$$

is the rotated effective mass matrix, and $\overleftrightarrow{\lambda}$ is the rotation matrix. In this rotated frame, $\overleftrightarrow{\mathbf{M}}$ is not diagonal, and has the non-vanishing elements $(\overleftrightarrow{\mathbf{M}}')_{11} =$

$\bar{m}$, $(\vec{M})_{22} = \bar{m} \cos^2 \theta + \bar{M} \sin^2 \theta$, $(\vec{M})_{33} = \bar{m} \sin^2 \theta + \bar{M} \cos^2 \theta$, and $(\vec{M})_{23} = (\vec{M})_{32} = (\bar{m} - \bar{M}) \sin \theta \cos \theta$. The two off-diagonal elements cause the lines of constant supercurrent to lie in a plane which is not normal¹⁹ to $\hat{\mathbf{B}}$, and give rise to a torque on the superconductor, since $\mathbf{B}$ is not parallel to $\mathbf{H}$.

In order to introduce a vortex, one first assumes the vortices are straight (and directed parallel to $\hat{\mathbf{B}}$), minimizes the rotated London free energy with respect to variations in $\mathbf{b}$, and adds a δ -function source term with the weight of a singly-quantized vortex at the origin in the plane normal to $\hat{\mathbf{z}}'$,

$$\mathbf{b}' + \lambda_L^2 \vec{\nabla}' \times [\vec{M} \cdot (\vec{\nabla}' \times \mathbf{b}')] = \hat{\mathbf{z}}' \Phi_0 \delta^{(2)}(\mathbf{r}'), \quad (5)$$

where $\Phi_0 = hc/(2e)$ is the flux quantum. Since this equation is linear, it can be solved by Fourier transformation, giving $\mathbf{b}'(k_x, k_y)$. In order to calculate the line energy of a vortex at an arbitrary direction, one then uses Eq. (5) in Eq. (3), and integrates by parts, leading to²⁰

$$\mathcal{F}'/V' = \frac{B'}{8\pi} \int \frac{d^2 k}{(2\pi)^2} b'_3(k_x, k_y). \quad (6)$$

The question then arises as to what to use for the cutoff. In my book¹, it is shown explicitly that the correct form for the vortex core cutoff is

$$k_x^2 + \mathcal{A}^2(\theta) k_y^2 \leq \xi_{||}^{-2}, \quad (7)$$

where $\xi_{||}$ is the GL coherence length parallel to the layers, and

$$\mathcal{A}^2(\theta) = \cos^2 \theta + \gamma^{-2} \sin^2 \theta. \quad (8)$$

Note that this cutoff has an elliptical cross-section in Fourier space. Using this elliptical cutoff, the vortex line energy can be calculated, and one finds¹,

$$\mathcal{F}'/V' = \frac{\Phi_0 B'}{(4\pi \lambda_{L,||})^2} f_L(\theta), \quad (9)$$

where

$$f_L(\theta) = \mathcal{A}(\theta) [\ln \kappa_{||} + C_L] - |\cos \theta| \ln \left(\frac{\gamma [|\cos \theta| + \mathcal{A}(\theta)]}{1 + |\cos \theta|} \right), \quad (10)$$

in the limit $\kappa_{\perp} \gg 1$, where $\kappa_{||} = \gamma \kappa_{\perp}$, $C_L = 0$, and we have set $\kappa = \lambda_L/\xi$, where ξ is the geometric mean coherence length. This line energy of a single vortex can be used to calculate H_{c1} , from

$$\mathbf{H}_{c1} = \hat{\mathbf{B}} H_{c1,||\mathbf{B}} + \hat{\theta} H_{c1,\perp\mathbf{B}}, \quad (11)$$

where

$$H_{c1,||\mathbf{B}} = \frac{\Phi_0}{4\pi \lambda_{L,||}^2} f_L(\theta), \quad (12)$$

$H_{c1,\perp\mathbf{B}} = \partial H_{c1,\parallel\mathbf{B}}/\partial\theta$, and $\hat{\theta} = \partial\hat{\mathbf{B}}/\partial\theta$ is the appropriate unit vector normal to $\hat{\mathbf{B}}$. It should be noted that the above anisotropic cutoff should be used in all anisotropic London calculations, especially those with the vortex lattice at an arbitrary direction. This has not yet been done, but will appear in my book¹.

Let us now consider the anisotropic GL model. In this model, the order parameter ψ appears in an important way. The Helmholtz free energy difference between the superconducting and normal states is

$$\mathcal{F} = \int d^3\mathbf{r} \left[\alpha(T)|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \sum_{i=1}^3 \frac{1}{m_i} \left| \left(-i\hbar \frac{\partial}{\partial x_i} - 2eA_i/c \right) \psi \right|^2 + \mathbf{b}^2 \right], \quad (13)$$

where $\alpha(t) \approx \alpha_0(T - T_c)$, β is essentially constant, and the A_i are the vector potential components, $\mathbf{b} = \text{curl } \mathbf{A}$. The GL geometric mean coherence length $\xi = \hbar^2/(2m|\alpha|)$, and the geometric mean penetration depth $\lambda = mc^2/(16\pi e^2|\psi_0|^2)$, where $|\psi_0| = (|\alpha|/\beta)^{1/2}$ is the maximum magnitude of ψ , far from a vortex or a surface. The geometric mean GL parameter $\kappa = \lambda/\xi$. For simplicity of notation, it is customary to scale lengths relative to λ , magnetic fields relative to $\sqrt{2}H_2 = \Phi_0/(2\pi\xi\lambda)$, where H_c is the bulk thermodynamic critical field, vector potential components in units of $\Phi_0/(2\pi\xi)$, and magnetic energy density in units of $H_c^2/(4\pi)$. Letting $\psi = |\psi_0|f \exp(i\phi)$ and making the appropriate gauge transformation on the A_i , we obtain the standard form for the anisotropic GL Helmholtz free energy density,

$$\frac{\mathcal{F}}{V} = \int d^3\mathbf{r} \left(-f^2 + f^4/2 + \mathbf{b}^2 + \sum_{i=1}^3 \frac{1}{\bar{m}_i} \left[\frac{1}{\kappa^2} \left(\frac{\partial f}{\partial x_i} \right)^2 + a_i^2 f^2 \right] \right), \quad (14)$$

where a is the gauge-transformed vector potential.

We note that the effective masses appear in the denominators of the gradient and vector potential component terms, unlike the anisotropic London model, in which they appear in the numerators of the current energy density term. To transform this free energy density²¹, we therefore first make the appropriate anisotropic scale transformation, in which $x_i \rightarrow (\bar{m}_i)^{-1/2} x'_i$, and Maxwell's equations are preserved²¹. This transformation changes the direction of $\hat{\mathbf{B}}$ to $\hat{\mathbf{B}}'$, and diagonalizes the gradient and vector potential terms. However, it modifies the magnetic energy density term, leaving it diagonal, but with the inverse effective masses multiplying each component b_i^2 . By analogy with the anisotropic London model, it is then necessary to rotate the axes so the rotated $\hat{\mathbf{z}}'' = \hat{\mathbf{B}}'$. This is accomplished with a rotation matrix²¹ $\overleftrightarrow{\lambda}'$. One then makes an isotropic scale transformation, scaling lengths by $\alpha(\theta, \phi) = (\hat{\mathbf{B}} \cdot \overleftrightarrow{m} \cdot \hat{\mathbf{B}})^{1/2} = \gamma^{2/3} \mathcal{A}(\theta)$ for uniaxial anisotropy. One obtains¹

$$\frac{\tilde{\mathcal{F}}}{\tilde{V}} = \alpha^{-3} \int d^3\tilde{\mathbf{r}} \left(-f^2 + f^4/2 + \frac{1}{\tilde{\kappa}^2} (\overleftrightarrow{\nabla} f)^2 + \tilde{a}^2 f^2 + \tilde{\mathbf{b}} \cdot \overleftrightarrow{K} \cdot \tilde{\mathbf{b}} \right), \quad (15)$$

where $\tilde{\kappa} = \kappa/\alpha$, and the non-vanishing elements of $\overleftrightarrow{K} = \overleftrightarrow{\lambda}' \cdot \overleftrightarrow{m}^{-1} \cdot \overleftrightarrow{\lambda}'^{-1}$ are $K_{11} = \gamma^2 \cos^2 \theta + \sin^2 \theta$, $K_{22} = \gamma^2 \cos^2 \theta + \gamma^{-2} \sin^2 \theta$, $K_{33} = 1$, and $K_{23} =$

$K_{32} = (\gamma - \gamma^{-1}) \sin \theta \cos \theta$. By a procedure analogous to that of the anisotropic London model, but without the necessity of introducing an anisotropic cutoff, one obtains the single vortex line energy, and $H_{c1,||B}$. The result does not differ much from the anisotropic London results for $\kappa_{\perp} \gg 1$, the only difference being in the constant C in Eq. (10), where $C_{GL} = 0.497$, whereas $C_L = 0$. However, it is possible to solve for the line energy for arbitrary $\kappa_{\perp}$, using a variational approach¹, and the models give significantly different results for much smaller $\kappa_{\perp}$ values.

The best model for layered superconductors is the Lawrence-Doniach model. Unfortunately, it is also the hardest to solve, except at H_{c2} . In this model, we consider very thin layers discretely indexed by j . The difference in Helmholtz free energy between the superconducting and normal states is^{22,23}

$$\mathcal{F} = \sum_j \int d^2 \mathbf{r} \left(\alpha(T) |\psi_j|^2 + \frac{\beta}{2} |\psi_j|^4 + \frac{1}{2m} |(-i\hbar \vec{\nabla} - 2e\mathbf{A}/c) \psi_j|^2 \right. \\ \left. + \zeta \left| \psi_j - \psi_{j+1} \exp \left[(2\pi i / \Phi_0) \int_{j_s}^{(j+1)s} A_z(\mathbf{r}) d\mathbf{z} \right] \right|^2 + \frac{1}{8\pi} \int_{j_s}^{(j+1)s} d\mathbf{z} b^2 \right), \quad (16)$$

where ζ is the Josephson coupling parameter. In terms of the effective mass M normal to the layers, $\zeta = \hbar^2 / (2Ms^2)$. This model explicitly contains all of the relevant lengths inherent in a layered superconductor, and hence allows for dimensional crossover^{22,23}. At H_{c2} , $\mathbf{B} = \mathbf{H}$, so we can choose the vector potential $\vec{A} = (A_x, A_z)$ to be $\vec{A} = Hy(\hat{x} \cos \theta - \hat{z} \sin \theta)$. Since at H_{c2} , $\psi_j \rightarrow 0$, one may linearize the LD order parameter equation, leading to

$$\left[\frac{\hbar^2}{2m} \left(-\frac{d^2}{dy^2} + \left[\frac{2\pi Hy \cos \theta}{\Phi_0} \right]^2 \right) + 2\zeta \left[1 - \cos \left(\frac{2\pi s Hy \sin \theta}{\Phi_0} \right) \right] + \alpha(T) \right] \psi(y) = 0 \quad (17)$$

This is a one-dimensional Schrödinger equation with both harmonic and periodic potentials, and has been solved in detail^{1,24} for arbitrary θ . Dimensional crossover is found at $\xi_{\perp}(T^*) = s/\sqrt{2}$, as anticipated for $H_{c2,||}(T)$, with $H_{c2,||}$ diverging at T^* , provided that $\xi_{\perp}(0) < s/\sqrt{2}$. Hence, it only occurs for sufficiently anisotropic layered superconductors. Such behavior is not present in the anisotropic London and GL models, since they do not take account of the discrete layered structure.

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