On the Relationship Between the Critical Temperature and the London Penetration Depth in Layered Organic Superconductors

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We present an analysis of previously published measurements of the London penetration depth of layered organic superconductors. The predictions of the BCS theory of superconductivity are shown to disagree with the measured zero temperature, in plane, London penetration depth by up to two orders of magnitude. We find that fluctuations in the phase of the superconducting order parameter do not determine the superconducting critical temperature as the critical temperature predicted for a Kosterlitz-Thouless transition is more than an order of magnitude greater than is found experimentally for some materials. This places constraints on theories of superconductivity in these materials.

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In this paper we considered the layered organic superconductors such as \(\kappa\)-ET\(_2\)X and \(\lambda\)-BETS\(_2\)Y (Ref. 1). Most theories of superconductivity in these materials are based on BCS theory with either phonon or spin fluctuations providing the attractive interaction. However, we will show that simple BCS theory is inconsistent with the measured London penetration depth.\(^2,5,7\) Layered organic superconductors are, in many ways, similar to the cuprates.\(^8\) Both classes of materials are quasi-two dimensional (q2D) and have phase diagrams which include antiferromagnetism, a Mott transition, unconventional metallic states and superconductivity. The superconducting state of the cuprates has d-wave symmetry and, although there is, as yet, no consensus on the pairing symmetry in the organics, several authors have presented evidence for d-wave pairing.\(^9\) NMR experiments on the layered organic superconductors are suggestive of a pseudogap\(^10\) similar to that observed in the cuprates.\(^11\) It has been suggested that the Hubbard model is a minimal model for both of these systems.\(^12,13,14\) The most notable difference between the two classes of materials is that in the cuprates doping changes the charge carrier density. Whereas the organics are, as we will confirm, half filled for all the anions that we consider here.

In general, a state is deemed superconducting if it breaks gauge symmetry and displays a Meissner effect in weak magnetic fields. It follows directly from these very general requirements that a supercurrent, \(J = -D_{\alpha}\delta\mathbf{A}/\hbar \equiv -c^2\mathbf{A}/4\pi\lambda^2\), is induced by a magnetic vector potential \(\mathbf{A}\). \(\lambda\) is the London penetration depth and \(D_{\alpha}\) is the superfluid stiffness. In BCS theory and its extensions one can separate \(D_{s}\), into a superfluid density and an effective mass, \((D_{s} \propto n_{s}/m^*)\). Here \(m^*\) is the effective mass of the quasiparticle excitations and \(n_{s}\) describes the proportion of electrons in the condensate in the terms of the two-fluid model. However, this separation is not a necessary feature of a superconducting state.\(^15\)

In London theory the zero temperature superfluid density is defined as \(n_{s} = m^*c^2/4\pi e^2\lambda_0^2\), where \(\lambda_0\) is the average London penetration depth parallel to the q2D planes at zero temperature. BCS theory\(^16\) predicts that \(n_{s} = n_{e}\) and Eliashberg theory\(^17\) predicts that \(n_{s} \gtrless n_{e}\). It can be shown\(^18\) that, for a charged system, including the Fermi liquid corrections to BCS theory gives

\[
\frac{n_{s}}{n_{e}} = 1 + \frac{\pi}{2} \frac{F_{1}^s}{m^*/m},
\]

where \(F_{1}^s\) is a Landau Fermi liquid parameter. For a Galilean invariant system \(1 + F_{1}^s/3 = m^*/m\) and so \(n_{s} = n_{e}\). But for systems with broken translational symmetry, such as the crystals that we consider here, there is no \textit{a priori} relationship between \(F_{1}^s\) and \(m^*\).

It can be seen from table\(^1\) that the predictions of BCS theory are in disagreement with experiments on the layered organic superconductors by up to two orders of magnitude. It has been suggested that only the q2D pocket of
the Fermi surface of \( \kappa-\text{ET}_2\text{Cu}[\text{N(CN)}_2]\text{Br} \) is involved in superconductivity.\(^{25}\) Such Fermi surface sheet dependent superconductivity can be ruled out as the explanation of the reduced superfluid density because, for example, the Fermi surface of \( \beta-\text{ET}_2\text{IBr}_2 \) \( (n_s/n_e = 0.11) \) has only one sheet.\(^{26}\) Corrections due to the variation in the Fermi velocity around the Fermi surface\(^{33}\) may be able to explain small deviations from \( n_s/n_e = 1 \), but are certainly not large enough to explain the extremely small superfluid density observed in the low \( T_c \) materials.

The simplest explanation of the penetration depth measurements is that not all of the electrons participate in the superconducting condensate. This would lead to many observable predictions. For example, thermodynamic indications of the superconducting state would be expected to show a ‘mixed’ behaviour, e.g. the specific heat anomaly and the effective Meissner volume should be extremely small in low \( T_c \), low \( n_s \) compounds. Thus the observation of a clear anomaly in the heat capacity\(^{28}\) and a complete Meissner effect\(^{28}\) in \( \alpha-(\text{ET})_2\text{NH}_4\text{Hg(NCS)}_4 \) \( (n_s/n_e = 0.05) \) appear to rule out scenarios in which only a fraction of the conduction electrons enter the condensate. Another possibility that retains the independent concepts of the effective mass and the superfluid density is to allow the Cooper pair to have an effective mass that is not simply \( 2m_e \). This has been discussed elsewhere and we will not dwell on this idea here as it was shown\(^{27}\) that even in these scenarios it is still necessary to set \( n_s/n_e \neq 1 \) to explain the observed behaviour of the layered organic superconductors.

Note that for the organics the superfluid density is smallest for those materials with the lowest \( T_c \),'s and the smallest effective masses, i.e., those materials that are the least strongly correlated. This is in direct contradiction with the predictions of the simple interpretations of the BCS and Eliashberg\(^{28}\) theories where as the electron-phonon (or indeed electron-electron) coupling increase so do \( m^* \) and \( T_c \). In the underdoped cuprates the pseudogap is associated with low critical temperatures and small superfluid densities, whereas in the organics the pseudogap like features are associated with high critical temperatures and large superfluid densities. However, in both classes of materials the pseudogap is found close to the Mott transition.

It has been suggested\(^{19}\) that in the cuprates \( F^*_1 \) increases as \( m^* \) increases, rather than in the decreasing as is the case for a Galilean invariant Fermi liquid. Could a similar, albeit significantly stronger, effect be at play here? If \( n_s \to 0 \) as \( T_c \to 0 \) (while at the same time \( m^* \) decreases) then \( \Box \) requires that \( F^*_1 \to -3 \) as \( T_c \to 0 \). For a momentum independent self energy \( F^*_1 = 0 \) (Ref. \( 34 \)); therefore for either the BCS or Eliashberg theories to be consistent with the data would require a strong momentum dependence in the self energy. Electron phonon coupling can only generate a momentum dependent self energy if Migdal’s theorem is strongly violated.\(^{48}\) However, a strong momentum dependent self energy may be a more natural feature of spin fluctuation mediated superconductivity.\(^{34}\)

In the case of very strong electron-electron interactions equation \( \Box \) may not be valid. However, importantly, unlike underdoped cuprates, in the organics the normal state at temperatures only slightly above \( T_c \) appears to be a good Fermi liquid.\(^{48}\) Hence, there is a need to calculate \( D_s \) for the models and approximations that have been proposed for the organic superconductors\(^{23,34}\) to see if they predict the observed variation in \( D_s \) with \( T_c \).

A possible explanation of the measured penetration depths is that the microscopic theory of superconductivity in the layered organics, whatever it may be, does not admit the separation of the superfluid stiffness into parts that correspond naturally to a superfluid density and an effective mass. This has the advantage of allowing the observation of a small superfluid stiffness to be reconciled with evidence that all of the electrons participate in the condensate.

To explain the Uemura relation\(^{38}\) namely that in the underdoped cuprates \( T_c \propto 1/\lambda^2_0 \), Emery and Kivelson\(^{45}\)
proposed that phase fluctuations can limit the transition temperature of a 2D superconductor. The limit on $T_c$ due to phase fluctuations, $T^{\text{max}}_\theta$, is given by

$$k_B T^{\text{max}}_\theta = A \frac{h^2 e^2 a}{16 \pi^2 \lambda^2_0}.$$  

(2)

where $a$ is the larger of $d$, the average spacing between the q2D planes, and $\sqrt{\pi \xi_\perp}$, where $\xi_\perp$ is the coherence length perpendicular to the planes. $A$ is a constant of order 1. In the case of vanishingly small coupling between the planes we have a genuinely two dimensional system and therefore the superconducting transition is a Kosterlitz–Thouless phase transition. In the underdoped cuprates further support for these ideas comes from measurements of the optical conductivity of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ for $T > T_c$ which are consistent with the predictions of Kosterlitz–Thouless theory and the observation of vortex like excitations above $T_c$ in La$_{2-x}$Sr$_x$CuO$_4$. However, we should note that the evidence of phase fluctuations in these experiments did not extend to temperatures as high as those at which the onset of the pseudogap is observed.

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suggested that the data of Uemura et al.

implies that the critical temperatures of the layered organic superconductors in general and of $\kappa$-ET$_2$Cu(NCS)$_2$ in particular are also limited by phase fluctuations. In figure 1 we plot $T_c$ as a function of $\lambda_0$ for a variety of layered superconductors. It can clearly be seen that $T^{\text{max}}_\theta$ is more than an order of magnitude larger than $T_c$ for some of the materials considered (c.f., Ref. 15).

Further evidence that $T_c$ is limited by the temperature at which pairing occurs and not by the energy scale of phase fluctuations comes from the ratio of the zero temperature superconducting order parameter, $\Delta(0)$, to $T_c$. For $\kappa$-ET$_2$Cu[N(CN)$_2$]Br and $\kappa$-ET$_2$Cu(NCS)$_2$ it has been found that $\Delta(0)/k_B T_c = 2.5 - 2.8$. These values of $\Delta(0)/k_B T_c$ seem more consistent with strong coupling superconductivity than with the expectation that, if $T_c$ is limited by phase fluctuations, $\Delta(0)/k_B T_c \gg 2$, which is indeed found for the underdoped cuprates. Measurements of $\Delta(0)/k_B T_c$ in low $T_c$ materials may be expected provide a more stringent test of this criterion, however, we are not aware of any such measurements.

The destruction of superconductivity by phase fluctuations is strongly linked with the idea that preformed pairs are responsible for the pseudogap in the cuprates. Therefore the observation that $T_c$ is not limited by phase fluctuations in the layered organics makes it unlikely that preformed pairs are responsible for the pseudogap like features observed by NMR.

For the cuprates several theories have been proposed that may admit an increase in the superfluid stiffness as one moves away from the Mott insulating phase by increasing the doping from half filling. Examples of these include the RVB states and its generalisation gossamer superconductivity, the SU(2) slave-Boson model and the two-species treatment of the $t$-$J$ model. Thus the observation that the superfluid stiffness varies as one moves away from the Mott insulating phase in the layered organic superconductors may indicate that one of these theories provides the correct microscopic description of these materials. Clearly detailed calculations are required to discover whether any of these models agree with the experimentally measured penetration depth.

It appears then that the key to understanding the microscopic details of the superconducting state in the organic superconductors is the low $T_c$ materials. In addition to the need for a detailed systematic, study of the thermodynamics of the low $T_c$ materials discussed here there are several other materials with low abient pressure $T_c$'s that should be investigated such as $\beta$-ET$_2$AuI$_2$ ($T_c = 4.9 K$), $\kappa$-ET$_2$I$_3$ ($T_c = 3.6 K$), $\lambda$-BETS$_2$GaCl$_3$F ($T_c = 3.5 K$), $\kappa$-DMET$_2$AuBr$_2$ ($T_c = 1.9 K$), BO$_2$Re$_2$H$_2$O ($T_c = 1.5 K$) and $\beta$-BO$_3$Cu(NCS)$_3$ ($T_c = 1.1 K$).

![FIG. 1: Variation of the superconducting critical temperature, $T_c$, with the zero temperature penetration depth, $\lambda_0$. The experimental data is taken from Pratt et al. and Lang et al. and Larkin et al. and shows data for $\kappa$-ET$_2$Cu[N(CN)$_2$]Br (open diamond), $\kappa$-ET$_2$Cu(NCS)$_2$ both at ambient pressure (circle) and under pressure (open squares), $\lambda$-BETS$_2$GaCl$_4$ (square), $\beta$-ET$_2$IBr$_2$ (diamond) $\kappa$-ET$_2$NH$_4$Hg(NCS)$_4$ (triangle) and $\kappa$-BETS$_2$GaCl$_4$ (empty circle). The empirical fit, $T_c \lambda^2 = 2.0 \text{ K} \mu\text{m}^2$, to the data from Pratt et al. is also reproduced (dotted dashed line). Note that the data of Larkin et al. (open squares) is actually for the penetration depth at $T = 0.35 T_c$. This means the data should be shifted somewhat to the left. However, even given this caveat the pressure dependence data of Larkin et al. is in broad agreement with the ambient pressure data of Pratt et al. The upper limit imposed on $T_c$ by phase fluctuations, $T^{\text{max}}_\theta$, is shown for both the three dimensional (dashed line, $A = 2.2$) and two dimensional (solid line, $A = 0.9$) cases. Although it is possible that the details of the short-range interactions of the layered organic superconductors change the exact numerical values of $A$ (c.f., Ref. 14), it is difficult to imagine that this effect is large enough to account for the order of magnitude difference between the predictions of the phase fluctuation model and the observed variation of $T_c$ with $\lambda_0$. For the phase fluctuation curves (solid and dashed lines) we take $a = d = 18 \text{ Å}$, where $a$ is the length parameter in equation (2) and $d$ is the interlayer spacing which approximately 18 Å for all of these materials.]
We have shown that the zero temperature superfluid stiffness of the layered organic superconductors is up to two orders of magnitude smaller than is predicted by simple BCS theory. We have also shown that phase fluctuations do not limit $T_c$ in these materials as the transition temperature is more than an order of magnitude smaller than is predicted for a Kosterlitz–Thouless phase transition. This places constraints on theories of superconductivity in layered organic superconductors. It is therefore clear that the unusual behaviour of the penetration depth is a key experimental result which any theory of the layered organic superconductors must explain.

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1 ET is bis(ethylenedithio)tetraselenafulvalene, X and Y are anions, e.g., X=Cu(NCS)$_2$ or Y=GaCl$_3$ and the Greek indices indicate crystal structure; see Refs. 13 for a recent review.

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Note that none of the phonon mechanism that have been discussed in the context of the organics have proposed that Migdal’s theorem is broken.