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The Signature of Inhomogeneous Superconductivity

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Abstract Superconductivity can be inhomogeneous, having a periodically modulated order parameter, in materials that have long electronic mean free paths and where the effects of vortices are suppressed. One class of materials that has these properties is crystalline organic superconductors. They are stoichiometric compounds and highly anisotropic crystals such that the vortices that form can hide in the least conducting layers. We analyze recent data to look for complexity in the inhomogeneous states, such as changes in the order parameter nodal structure.

Keywords Superconductivity · Inhomogeneous superconductivity · Rf penetration · Organic superconductors

1 Introduction

Inhomogeneous superconductivity, superconductivity with a spatially modulated order parameter, was predicted in 1964 by Fulde and Ferrell [1] and Larkin and Ovchinnokov [2] in superconductors where the effects of vortices could be suppressed. Examples of this exotic superconducting phase are known as the FFLO state. Strong evidence for a realization of an inhomogeneous superconductor was difficult to obtain, first because it was difficult to find a material that had the correct properties to support the creation of an inhomogeneous superconductor, and second because the transition from one superconducting state to another was subtle. Certainly, transport measurements could not be sensitive to changes from a homogeneous to an inhomogeneous superconductor both in the zero resistance state.

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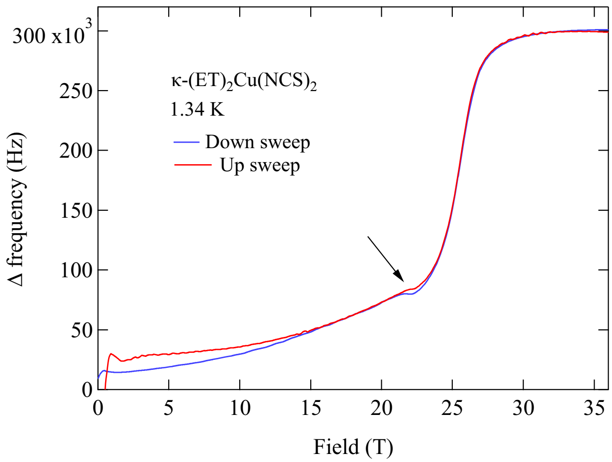

Fig. 1 Field sweeps from the pulsed field at Clark University showing the hysteresis (*arrow*) that develops in the penetration depth just above 21 T below 2.5 K marking H_P, the entrance to the FFLO state. Just above the hysteresis bubble, the London penetration depth begins to diverge marking the end of the superconducting state. Below 12 T, the hysteresis in the up and down sweeps is an instrumental effect due to the dB/dt of the pulsed field (Color figure online)

The first problem was solved by discovering that organic superconductors are electronically clean, the quasiparticles have a long mean free path, and highly anisotropic, such that the vortices could be hidden in the least conducting layers. The second problem was solved by us using rf penetration as a probe. The tunnel diode oscillator (TDO) rf penetration depth system is a particularly good probe because it is responsive to many physical properties of superconductors and conductors. It is also highly sensitive allowing it to respond to very subtle changes in the properties of a sample.

Given that this manuscript is written for JLTP in honor of Prof. Horst Meyer, it is especially noteworthy to point out that the TDO was first used in condensed matter physics in Prof. Meyer's group to measure the density of He-3 in 1966 [3]. An early innovator in electronics, Prof. Meyer's group at the time used home-made lock-in amplifiers and AC impedance bridges to measure capacitance. The TDO brought unprecedented accuracy in density measurement via capacitance cells and the Clausius–Claperon equation.

In the application of the TDO to rf penetration in superconductors, the advantages and disadvantages are related. The TDO is sensitive to the most minute changes in a sample, an advantage when looking for subtle changes in the properties of a superconductor such as the small paramagnetic signal associated with the FFLO superconducting state. However, it is that same sensitivity that makes the rf penetration measurement a cacophony of signals from different mechanisms. In the superconducting to normal conductor transition, for example, rf penetration is the result of the changing London penetration depth, vortex pinning, vortex motion, and the normal conductor skin depth, which makes it difficult to deconvolute all the effects as described in Ref. [4] and shown in Refs. [5,6] and Fig. 1. One goal in this manuscript is to isolate the changes in the rf penetration depth due to the presence of inhomogeneous superconductivity.

2 Background

Superconductivity is formed when it is energetically favorable for electrons to form Cooper pairs consisting of two electrons with opposite spins. In most cases, superconductivity is destroyed in an external magnetic field due to vortices—non-superconducting regions containing a magnetic field line shielded by circulating electron pairs—which increase in density as the magnetic field is increased and ultimately displace the superconducting phase. Clogston [7] and Chandrasakar [8] were the first to recognize that if the formation of vortices could be suppressed, superconductivity could persist only to a magnetic field limit which arises from the Pauli paramagnetism of the electrons, denoted as H_{P}. At this magnetic field, the energy to flip an electron spin, the Zeeman energy, exceeds the binding energy of the Cooper pairs, destroying the pairs. The FFLO phase was predicted to exist for fields even above H_{P} in electronically clean materials by the authors referred to in the first paragraph and thus labeled with their initials. This spatially inhomogeneous superconducting phase, with paramagnetic spin domains, has since been described theoretically by many others [9–11].

Support for the existence of the FFLO state has come from rf penetration [6,12,13], NMR [14,15], thermal conductivity[16], magnetic torque [17], and specific heat [18]. The agreement between such diverse measurement methods and in particular details of the NMR and caloric measurements make a compelling argument for the existence of inhomogeneous superconductivity. The complexity of the inhomogeneous state is yet to be discovered, and it is worth looking at the measurements in more detail to glean more evidence and determine whether different ground states of the FFLO phase exist as a function of temperature and field.

One of the properties of an inhomogeneous superconductor is that nodes exist in the order parameter in a spatially periodic pattern as defined by one or more q-vectors, which establish the periodicity in one or more dimensions. At the nodes, the density of Cooper pairs goes to zero, and free spins respond to an external magnetic field paramagnetically. The result of placing a paramagnetic material in a magnetic field is that the moments near the surface of the material will orient with the field and lead the magnetic field lines around the material. A consequence of magnetic energy stored in the spins is that the superconducting state can survive to higher externally applied fields than expected. As the external field is increased, it will increase its penetration into the sample until all the spins are oriented, the magnetization is saturated fully, and the superconductivity is destroyed.

The result that the paramagnetism raises the energy needed to break Cooper pairs is one of the remarkable properties of an inhomogeneous superconductor, the ability for the superconducting state to survive above H_{P}. The TDO rf penetration depth measurement is sensitive to the paramagnetism that forms in the zero resistance superconducting state as H_{P} is exceeded. The goal of this study is to analyze any structure found in the TDO signal during the transition to the FFLO state as a function of magnetic field, or in the middle of the FFLO state due to a change in the character of the FFLO state.

Given that the FFLO state is characterized by nodes in the order parameter resulting in paramagnetic spins, it is worth examining the behavior of a paramagnet. A straight forward calculation of the magnetization of a system of non-interacting spin 1/2 particles can be found in many introductory statistical mechanics books [19]. The result for M, the magnetization is,

$$M = (N\mu)\tan h^2(\beta B), \tag{1}$$

where $\beta = 1/kT$, and differentiating by B results in the susceptibility:

$$\chi = N\mu^2(B\beta)^2 \sec^2(\mu B). \tag{2}$$

The TDO is sensitive to both the susceptibility and the penetration depth. These quantities are determined by the complex impedance, L', of the coil containing the sample. For the case of a long rod in a axial coil,

$$L' = L_0\left(1 + 4\pi\eta\{\chi' - \mathrm{j}\chi''\}\right) \tag{3}$$

where L_0 is the empty coil inductance, η is defined as the volume filling factor, and χ' and χ'' are the real and imaginary parts of the sample susceptibility.

The calculation above is for a simple homogeneous paramagnetic system. In the case of an inhomogeneous superconductor, changes in the FFLO state could come about because of the changing topology of the nodes in the order parameter affecting either η or χ'. In general for a conductor or superconductor, the penetration depth and hence η from Eq. (3) tends to dominate the change in inductance [20], but deep in the superconducting state η could be changing slower than χ' and χ' could dominate the signal. The nodal structure of the order parameter is sensitive to the boundary conditions of the superconducting wave function, which depends on such things as the symmetry of the superconducting energy gap, the shape of the Fermi surface, the vortex structure, and the unit cell. In the simplest case, the nodes could be one-dimensional [9], but two- and three-dimensional patterns are likely [10,21], and the complexity could be temperature or magnetic field dependent.

3 Data

The data examined in this manuscript come from experiments that have been reported on previously [6,12,13]. All of the data were collected using the same technique of placing the sample in the coil of a self-resonating TDO and measuring the frequency shift. Most was taken in pulsed magnetic fields at Clark University, although one experiment was done in the DC fields and dilution refrigerator of the National High Magnetic Field Laboratory (NHMFL) in Tallahassee Florida. The FFLO state is very sensitive to angle of the applied magnetic field to the plane of the conducting layers, and the FFLO state is not stable if the sample is more than 0.3°–2° away from parallel,

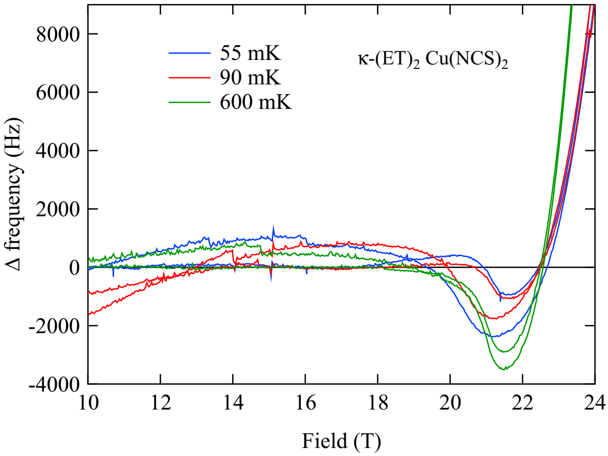

Fig. 2 Up and down magnetic field sweeps near the entrance to the FFLO phase showing the dip in the penetration depth after a background was subtracted. These are DC field sweeps from the NHMFL. At the lowest temperatures, the hysteresis becomes more complex with a shift between the minima of the up and down sweeps, reminiscent of the specific heat data [18] (Color figure online)

depending on the particular sample. Therefore, in many cases an off angle field sweep was used as background data.

A typical field sweep is shown in Fig. 1. These data are from the pulsed magnetic field at Clark University. The dip in the rf penetration near 21 T in Fig. 1 and in more detail from the DC field experiment in Fig. 2 is just before the beginning of the increase in the London penetration depth and shows the signature of entering the FFLO state. The dip is the paramagnetic signal generated by the appearance of spins at the nodes in the order parameter and marks H_P phase line, which is flat, in that it has no field dependence as a function of temperature. The relatively flat low-temperature part of the phase line is predicted by the WHH formula [22] and experimentally shown in a weaker Pauli paramagnetically limited organic superconductor [23]. Together with the determination of H_{c2}, where the rf penetration levels out at high field, the Clark data plus the data from the portable dilution refrigerator at the NHMFL produced the phase diagram shown in Fig. 3. A similar phase diagram for the same material was first proposed based on a related measurement technique by Singleton et al. in 2000 [24]. In contrast to the TDO measurements presented here, the measurements by Singleton et al. did not show a sharp transition at H_P, and consequently the position of the phase line between the traditional vortex state and the FFLO state was not correct. Without the obvious delineation between the two superconducting phases, it was not yet clear that the FFLO state existed.

The dip in rf penetration shown in detail in Figs. 1 and 2 corresponds to an increase in paramagnetism and screening, which is expected if entering a FFLO state, and should have the same effect as making the London penetration depth smaller. These changes are seen clearly as the FFLO state is entered, although the signal from the diverging London penetration depth as the superconductor is turned into the normal state is much more dramatic. Deconvoluting the diverging London penetration depth

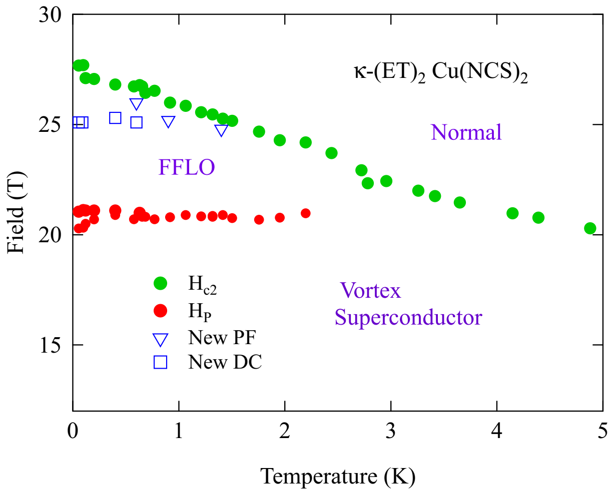

Fig. 3 The low-temperature high magnetic field part of the phase diagram from rf penetration in *red* and *green filled symbols*. The Pauli paramagnetic limit is shown as *filled red circles*. Hysteresis from up a down field sweeps produces the two sets of points below 0.4 K. The additional proposed phase line separating two possible ground states of the FFLO phase is shown with *open symbols*. The electronic phases are labeled in *purple* (Color figure online)

with the development of the FFLO state is difficult. Indeed in other systems, such as λ-(BETS)$_2$GaCl$_4$, the FFLO state is formed in the middle of the divergence of the London penetration depth and it is usually necessary to analyze the data by looking at the first or second derivatives to find phase transitions [13]. What is still not clear is how the FFLO state evolves as a function of magnetic field and whether the penetration depth is sensitive to changes in the nature of the FFLO state.

4 Analysis

As mentioned, the dip in penetration depth is a measure of paramagnetism and indirectly a measure of the density of nodes—the more nodes, the more free spins, and consequently, the more paramagnetism. The magnitude and arrangement of the q-vectors associated with the nodes should affect the depth of the rf penetration. Higher temperatures that broaden the nodes [25] will also effect the penetration depth. In general, the order parameter periodicity wavelength diminishes in length (length $= 2\pi/q$, thus the q-vector is growing) as the magnetic field increases, increasing the number of nodes [21]. Other mechanisms can change the topology of the nodes such as shifts in the vortex structure or pairing symmetry, which in turn will affect the pair breaking. More sensitive TDO measurements in a superconducting magnet may make some of these details clear.

As mentioned earlier, one useful way to analyze the data is to use an off angle field sweep as a background (superconductivity but no FFLO state) and subtract it from a zero angle field sweep (superconductivity and a FFLO state). The difference

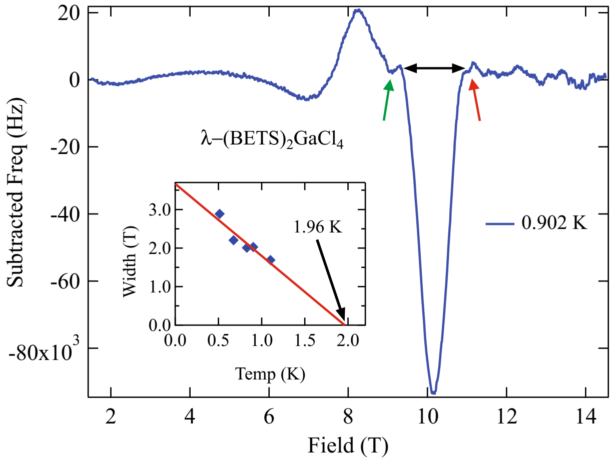

Fig. 4 By subtracting an off angle sweep from an exactly parallel sweep, the difference should be the signal produced by the presence of the FFLO state, which does not form if the angle is more than about 1.5° from parallel. In this case, the more robust part of the signal is a large dip over the field range of the FFLO phase. We mark our selection of H_P with a *green arrow* and H_{c2} with a *red arrow*. H_P in this material is at about 9.4 T. Following the width of that dip, shown by the *double-ended black arrow*, we extrapolate the width to the disappearance of the FFLO state at 1.96 K (Color figure online)

should be only features related the FFLO state. An example subtracted trace from the pulsed field λ-$(BETS)_2GaCl_4$ experiment is shown in Fig. 4. The large feature in these data is a measure of the width of the FFLO state in field, the distance from H_P to H_{c2}. An extrapolation of this width to zero is an estimation of the position of the tricritical point in the phase diagram and that value, 1.96 K, is slightly larger than the value from the phase diagram in Fig. 5. With the limits of the FFLO state determined, the next detail we attempted to locate was any possible phase transitions within the FFLO state. Figure 6 shows a bend in the penetration depth signal in the sample κ-$(ET)_2Cu(NCS)_2$ that can be traced from the pulsed field to the DC measurements and can be used to create the new phase line shown in Fig. 3. Whether this corresponds to a phase change such as predicted in some calculations [10] will require more careful measurements. A similar transition was suggested in another organic conductor using NMR as a probe [26].

Some details are extractable from the TDO data as the applied field sweeps through H_P. These details are the amount of hysteresis between the up and down field sweeps, and the depth of the dip in penetration. Figure 7 shows the evolution of these measures as a function of temperature. The hysteresis is complex because it has two aspects: a shift in the position (in magnetic field) of the minimum and the amplitude (frequency difference) of the up and down sweep minimum. The measures behave differently as a function of temperature. The difference in the position of the minima, seen qualitatively in Fig. 2, converges rapidly to zero by 600 mK, similar to the hysteresis of the up and down sweeps of the specific heat[18]. In contrast, the amplitude drops as it approaches 600 mK and then gets larger before abruptly disappearing at about 2.5 K. This trend is inconsistent with the hysteresis seen in the specific heat. Switching to the strength of

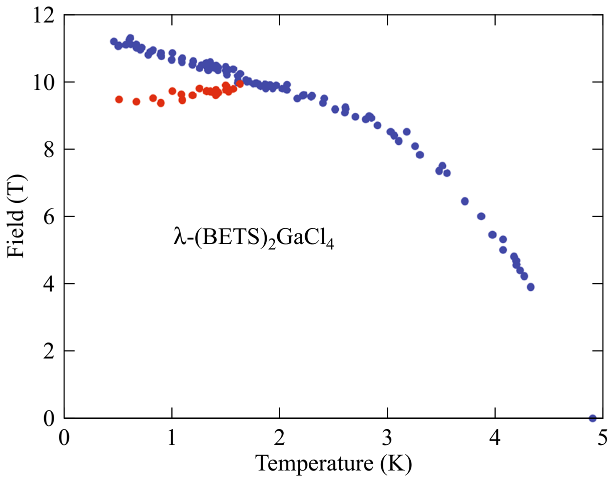

Fig. 5 Using the transitions identified in field sweeps such as in Fig. 4, this is the phase diagram that results, first presented in Ref. [13]. H_{c2} is shown in *blue* and H_P in *red*. H_P is almost temperature independent, in this case between about 9.4 and 9.8 T (Color figure online)

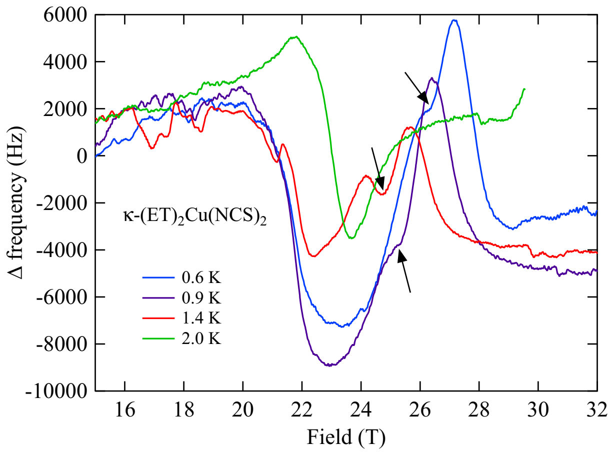

Fig. 6 Pulsed field sweeps near the entrance to the FFLO phase showing the dip in the penetration depth after a background is subtracted. The large feature develops for all temperatures at about 21 T. A second feature found in all the the sweeps below 2.0 K may be a change in the nature of the FFLO phase and is plotted in the phase diagram in Fig. 3 (Color figure online)

the dip in penetration depth at the transition, it grows in amplitude as the temperature rises reaching a peak at 600 mK. The data here overlap between the DC and pulsed field experiments and the amplitude of the dip begin to reduce in size above 600 mK. There is no analog to this dip in the specific heat, somewhat surprising given that the magnetization and specific heat are both thermodynamic variables. More interesting is the fact that the hysteresis disappears in the specific heat for most of the phase line, and many theorists claim the whole phase line should be first order[10,27].

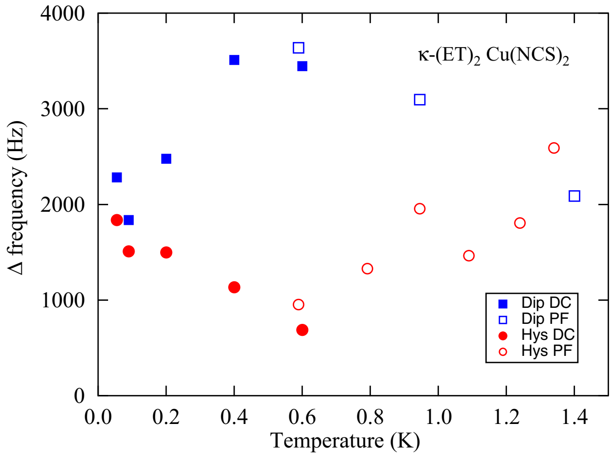

Fig. 7 The amplitude of the hysteresis is in *red*, *solid circles* for DC field sweeps and *open circles* for pulsed fields. Although the hysteresis drops systematically in at low temperature, it becomes larger again at higher temperature. Although the DC and pulsed field data overlap at 0.6 K suggesting that the pulsed field results are correct, there could be an artifact in the pulsed field data due to the asymmetrical $\mathrm{d}B/\mathrm{d}t$ between the up and down sweeps. The dip in the penetration depth is shown in *blue squares*, again solid for DC fields and open for pulsed. This signal should be a measure of the density of nodes in the sample due to the FFLO phase. It grows as a function of temperature but starts to drop at 0.6 K as it is seen in the pulsed field data. A corresponding signal is curiously not present in the specific heat data (Color figure online)

5 Conclusion

A brief introduction was given for the role of rf penetration depth measurements for determining the existence of the FFLO state. Some evidence was shown for possible changes in the configuration for the FFLO state as a function of magnetic field. A possible disagreement between rf penetration and specific heat measurements was found. Many of these issues will be investigated in future experiments with higher signal-to-noise ratio measurements made possible by recent improvements of the TDO, and DC field measurements at the NHMFL.

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