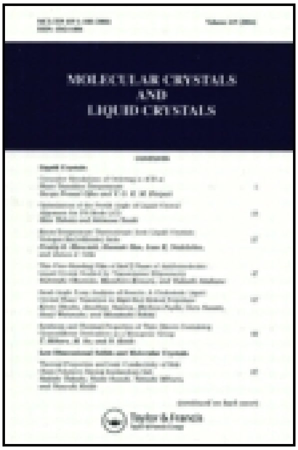

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AC MAGNETIC SUSCEPTIBILITY MEASUREMENTS OF ORGANIC SUPERCONDUCTING MATERIALS

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Abstract Magnetic susceptibility measurements are an indispensable facet of modern solid state characterization. Although AC magnetic measurements have proven invaluable in the development of high temperature superconductors, these techniques have not yet been fully exploited in the characterization of organic superconducting materials. For example, measurements of the real $\chi'(T)$ and imaginary $\chi''(T)$ susceptibility components at constant AC field, and measurement of χ'' as a function of the AC field at constant T can all be used for lower critical field determinations. $\chi''(H_{ac}, T)$ can also be used to estimate the magnetization critical current density J_{cm}. Furthermore, the superconducting transition in organic materials appears to be strongly frequency dependent, indicative of time dependent effects. The AC measurement has also proven extremely useful in the detection of multiple phases within these pivotal materials. This presentation briefly describes the AC measurement technique, and demonstrates its utility in the characterization of organic superconducting materials.

INTRODUCTION

AC and DC magnetic measurements are commonly employed in the investigation of material magnetic properties. For the past two decades and since the discovery of the first organic superconducting materials in 1979, considerable research effort has been expended in the synthesis and characterization of these materials.[1] Although AC susceptibility measurements have been used in the characterization of these materials it has usually only been used to determine transition temperatures, which is not a full exploitation of this measurement. Conversely, the AC technique has been used extensively in, and proven invaluable in the characterization and development of the high temperature superconductors discovered in 1988.[2,3]

This paper will briefly describe this technique, and will present measurement results for organic superconductors elucidating the possibilities for advancement this measurement may provide in this field of study.

AC SUSCEPTIBILITY

In a DC magnetization measurement, a static (DC) applied field H_{dc} magnetizes a sample material, and a value for the sample's magnetic moment **m** is measured. Values for the sample's magnetization M and DC susceptibility, $\chi_{dc} = M/H_{dc}$, are derived quantities. In this measurement, details of the M(H) phase diagram can be determined (e.g., hysteresis loops), and if measurements as a function of temperature are performed details of the sample's H-T phase diagram can be similarly determined. Such measurements are typically performed using Vibrating Sample Magnetometers (VSM), SQUID magnetometers, Extraction magnetometers, and Force (Faraday and Guoy) balances. Since in all of these techniques signal output is intimately related to the sample's moment (or magnetization) which in turn is proportional to the strength of the applied field, then investigating very low field properties (i.e., < 1 Oe) is often not possible, particularly for weak magnetic samples. Further, since this is a static measurement, information concerning magnetic time constants or relaxational processes on short time scales (i.e., < 1 sec.) are unobtainable.

In an AC magnetization measurement, a small amplitude AC field $dH = H_{ac}$ gives rise to a time-varying magnetization $dm = M_{ac}$. The AC susceptibility is then given by $\chi_{ac} = dm/dH$ which is valid in the limit of small H_{ac}. For this reason AC susceptibility is commonly referred to as differential susceptibility. Figure 1 illustrates schematically the AC measurement about a DC operating point.

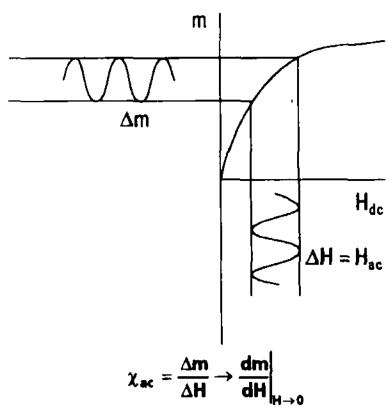

FIGURE 1 A schematic magnetization-field plane M(H) representation of the AC susceptibility.

The AC susceptibility can be separated into two components, the real or dispersive component χ' and the imaginary or dissipative component χ'' (i.e., $\chi_{ac} = \chi' - i\chi''$). χ'' is a measure of the energy absorbed by the sample from the applied AC field and is non-zero if either bulk or local magnetic moments are present (e.g., ferromagnets),[4] the sample's M(H) characteristics are hysteretic or non-linear, or if there are any relaxational processes occurring in the sample material under study (e.g., flux dynamics). The AC measurement can be performed in zero DC bias field, thus allowing the determination of very low field magnetic properties, magnetic microstructure, and magnetic ground states. With the addition of a DC bias field, full details of the material's M(H) phase diagram can be determined. Analogous to the DC measurement, the ability to vary temperature provides full details of the H-T phase diagram. Further, by varying the frequency of the applied AC field, determination of magnetic time constants and/or relaxational processes which may be occurring in the material under study are possible.

The measurements illustrated in this paper were recorded on a commercial AC susceptometer — DC magnetometer system (Model 7229) manufactured by Lake Shore Cryotronics. This system is capable of automatically (under full software control) measuring both real χ' and imaginary χ'' components of AC susceptibility through the 10th harmonic as a function of temperature, AC field, and applied DC bias fields to 9 tesla. Additionally, the same system can be used to perform DC Extraction magnetization measurements as a function of DC field and temperature. Measurements from below 1.3 K to above room temperature are possible, with sensitivity approaching 10^{-10} emu.

EXPERIMENTAL RESULTS

Lower Critical Field H_{c1} Determination:

The lower critical field H_{c1} is generally determined from the field dependence of DC magnetization. For $H_{dc} < H_{c1}$ the magnetization is a linear and reversible function of the applied field. For $H_{dc} > H_{c1}$ a change in slope of the magnetization curve is observed. The magnetization becomes irreversible and hysteresis is present. This method suffers from two drawbacks: 1) the transition from below to above H_{c1} usually corresponds to a very gradual change in slope of the magnetization curve which can be difficult to precisely discern, and 2) it can be difficult to perform the measurements at low fields when the superconductor under test has a very low H_{c1} value (e.g., < a few Oe), or when T is close to T_c where H_{c1} is small.

In the AC measurement, for $H_{ac} < H_{c1}$ the real susceptibility component χ' will show perfect diamagnetism (i.e., $\chi'_{Vol} = -1$ SI-units, or it will exhibit diamagnetic properties which are virtually temperature independent until T_c is reached), and the imaginary susceptibility component χ'' will be zero since the magnetization is linear and reversible and hence lossless. For $H_{ac} > H_{c1}$, χ' will depart from "perfect" diamagnetism and since hysteresis loss will now appear in the magnetization-field plane, χ'' will become non-zero.[5] Hence, measurement of $\chi'(T)$ and $\chi''(T)$ at constant AC field, and $\chi''(H_{ac})$ at constant temperature can be used to deduce the lower critical field.

Illustrated schematically in figure 2 (bottom)[6] are χ' (T) and χ'' (T) at different AC field strengths for a typical hysteretic type II superconductor. For decreasing temperature, when $H_{ac} = H_{c2}$ (the upper critical field) χ'' becomes non-zero and χ' becomes diamagnetic. When $H_{ac} = H_{c1}$ χ'' returns to zero, and χ' exhibits complete diamagnetic shielding. The resulting H_{c1} and H_{c2} lines in the H - T phase diagram are shown in the upper portion of figure 2.

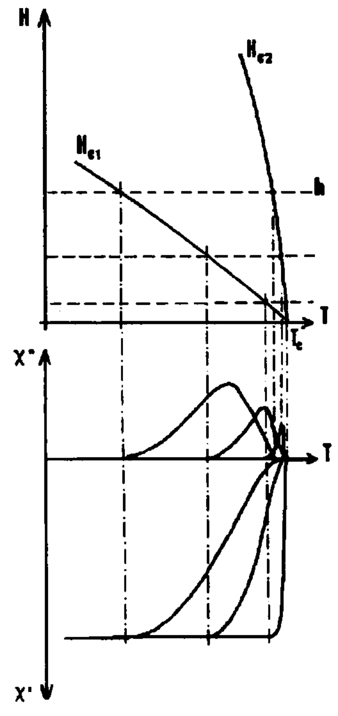

FIGURE 2 H - T phase diagram for type II superconductor (top) as determined from AC response (bottom).

Figures 3 and 4 show $\chi'(T)$ and $\chi''(T)$, respectively, at different AC field strengths for a deuterated crystal sample of κ - $(ET)_2Cu(NCS)_2$ ("ET" = bis(ethylenedithio tetrathiafulvalene). Nominal sample dimensions were 1 mm x 1 mm x 0.5 mm, and the applied AC field was oriented perpendicular to the crystal face with the largest area, which corresponds to the *bc*-plane. On warming, the temperatures at which χ' deviates from (nearly) "perfect" diamagnetic behavior are determined from figure 3, and the temperatures at which χ'' becomes positively valued are determined from figure 4. The temperature at which these transitions occurs for each AC field strength corresponds to $H_{c1}(T)$.

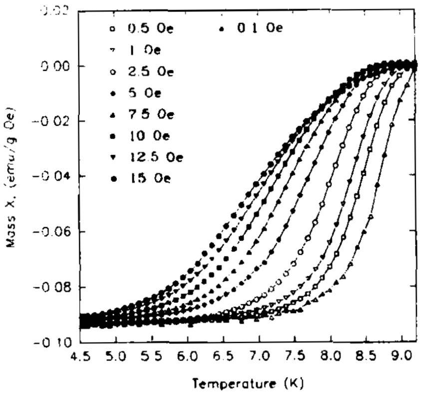

FIGURE 3 $\chi'(T)$ as a function of AC field strength for deuterated κ - $(ET)_2Cu(NCS)_2$.

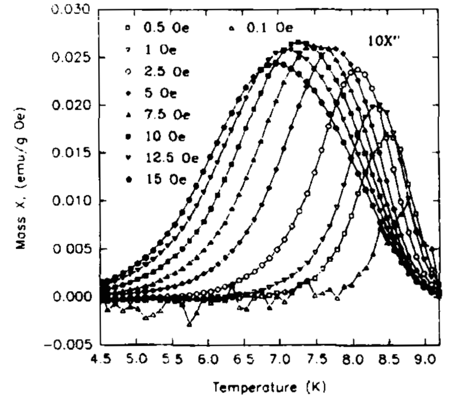

FIGURE 4 $10\chi''(T)$ as a function of AC field strength for deuterated κ - $(ET)_2Cu(NCS)_2$.

Figure 5 shows the imaginary component χ'' as a function of AC field strength at a number of fixed temperatures for the same sample. Analogous to above, for each temperature, the AC field at which χ'' becomes non-zero on warming corresponds to H_{c1}.

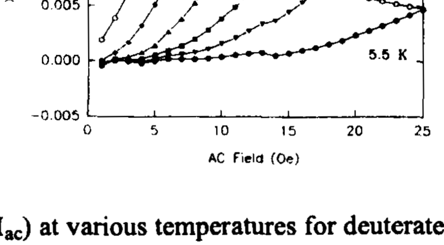

FIGURE 5 $\chi''(H_{ac})$ at various temperatures for deuterated κ - $(ET)_2Cu(NCS)_2$.

Investigation of the harmonic generation, χ_n, $n > 1$ in the alternating magnetic response of organic superconductors can also be used to estimate H_{c1}. χ' and χ'' are referred to as the fundamental susceptibility components. Hysteresis loops that are symmetrical with respect to the origin cause the generation of odd harmonics. The transition to the mixed state at H_{c1} is again accompanied by the onset of hysteresis losses, and thus H_{c1} is indicated by the appearance of $\chi_n > 0$, n odd.[7] Figure 6 shows the third harmonic susceptibility χ_3 as a function of temperature for various AC field strengths. The temperatures at which χ_3 becomes non-zero on warming corresponds to H_{c1} (note: The disappearance of the harmonic components indicates linear behavior and hence flux motion without pinning, thus the temperature at which χ_3 returns to zero for $T > T(\chi_{3max})$ in figure 6 has been associated with the irreversibility temperature T_{irr} in high T_c superconductors[7,8]).

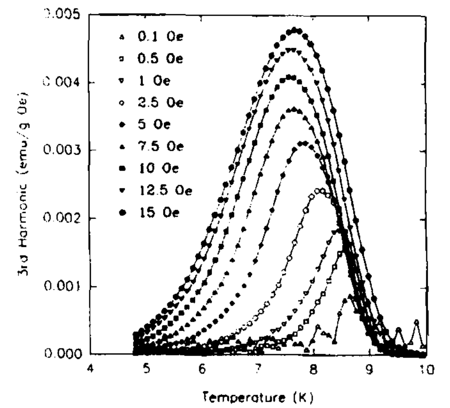

FIGURE 6 $\chi_3(T)$ as a function of AC field strength for deuterated κ - $(ET)_2Cu(NCS)_2$.

The following criteria were used to determine the H_{c1} values in table 1 and shown in figure 7. From figure 3, a 2 % deviation from the value of χ' at 4.5 K was used as an indicator of deviation from "perfect" diamagnetism. From figures 4, 5, and 6 H_{c1} was determined by extrapolating the roughly linear rise in $\chi''(T)$, $\chi''(H_{ac})$, and $\chi_3(T)$, respectively, downward to where they intersect the low temperature (nearly) linear portions of these respective curves.

Figure 7 shows the lower critical field $H_{c1}(T)$ as determined from each of these techniques. The curves are only intended to be guides for the eye. Extrapolating (linearly) these curves to 0 K yields the $H_{c1}(0\ K)$ values presented in table 1.

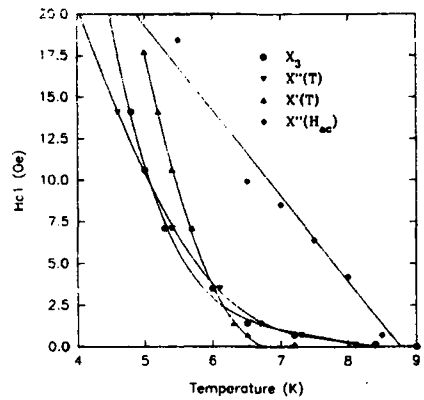

FIGURE 7 The temperature dependence of the lower critical field $H_{c1}(T)$ for deuterated κ - $(ET)_2Cu(NCS)_2$.

TABLE 1 0 K lower critical field values for deuterated κ - $(ET)_2Cu(NCS)_2$.

H_{c1} (0 K)	Technique	Fig. Ref.
50 Oe	$\chi'(T)$	Figure 3
45 Oe	$\chi''(H_{ac})$	Figure 5
30 Oe	$\chi''(T)$	Figure 4
25 Oe	$\chi_3(T)$	Figure 6

Although published values for H_{c1} for κ - $(ET)_2Cu(NCS)_2$ [9,10,11,12,13] vary dramatically, these values agree quite well with those tabulated by Nozawa et al.[10], and Sugano et al.[11] There are currently no published values of H_{c1} for deuterated κ - $(ET)_2Cu(NCS)_2$.

CRITICAL CURRENT DETERMINATIONS

Under the assumption that the critical state of the κ - $(ET)_2Cu(NCS)_2$ superconductor can be described by the Bean critical state model[14], then the magnetization critical current density J_{cm} is given by:

$$J_{cm} = H_p/a$$

where H_p is the full penetration field, i.e., the field which penetrates to the sample center, and (a) is a sample dimension. The equation stated above is valid for slab-like samples of thickness (2a) which are (infinitely) long, and for applied fields parallel to the long axis. Equations can be derived for other sample geometries and field orientations. By employing this model it is found that J_{cm} is proportional to the width of the hysteresis loop obtained in the DC measurement, and in the AC measurement, H_p is equal to the amplitude of the measuring field H_{ac} at the peak in χ'' (i.e., for cylinders $H_p = H_{ac}$, and for slabs $H_p = 4H_{ac}/3$).[4,15] Therefore,

$$J_{cm} \approx H_{ac}/a$$

where the approximation is given because most samples are to some extent irregular in geometry. And, in this particular case not only is the sample not a "slab", but the field in these experiments was not oriented parallel to the crystal "long" axis (but rather perpendicular to the *bc* crystal plane). Nevertheless, for demonstrative purposes, the data in figure 4 (i.e., $\chi''(T)$) can be used to estimate the temperature dependence of the magnetization critical current density (note: For high T_C superconductors, the superconducting grains are coupled for the small amplitude fields typical of the AC measurement and hence J_{cm} is the *intergranular* component. Conversely, for the high fields typical of the DC measurement the grains are decoupled and hence J_{cm} is the *intragranular* component.). These results are illustrated in figure 8. Extrapolating this curve to 0 K yields a J_{cm}(0 K) value of ~ 10^4 A cm^{-2} (H perpendicular to *bc*), which is in quite good agreement with those values reported by Kuznetsov[9] et al. for hydrogenated κ -$(ET)_2Cu(NCS)_2$.

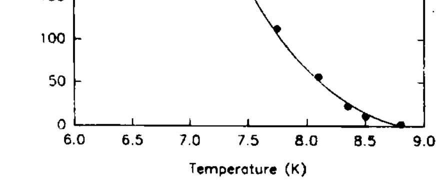

FIGURE 8 The temperature dependence of the magnetization critical current density $J_{cm}(T)$ for deuterated κ - $(ET)_2Cu(NCS)_2$.

DYNAMICS

In a conventional DC magnetometer, one is limited to acquiring information concerning dynamic processes in a time window of > 1 second (typically to 10^4 sec.). Although this is certainly useful for studying magnetization relaxation processes on this time scale, it cannot yield information on shorter time scales. The AC susceptibility technique provides the capability to acquire information concerning for example, flux dynamics, in a time window of 1 to 10^{-4} seconds. This has evolved into a very powerful method in characterizing high T_c superconductors. It has been used to study flux pinning, thermally activated flux motion, and has led to a better understanding of the vortex-glass phase or flux-creep mechanism in these materials since it provides a mechanism for studying the dynamics of the glassy phase.[16,17,18]

Figures 9 and 10 show $\chi'(T)$ and $\chi''(T)$, respectively, for a deuterated sample of κ - $(ET)_2Cu(NCS)_2$ as a function of frequency. There are clear indications of frequency- or time-dependent effects occurring in this material. These results, i.e., a shift in the curves toward higher temperatures as exemplified by both χ' and χ'' for increasing frequency are consistent with similar measurements performed on high T_c superconductors. Additional studies are necessary to determine the utility of this technique in achieving a better understanding of flux-dynamics in the organic superconductors.

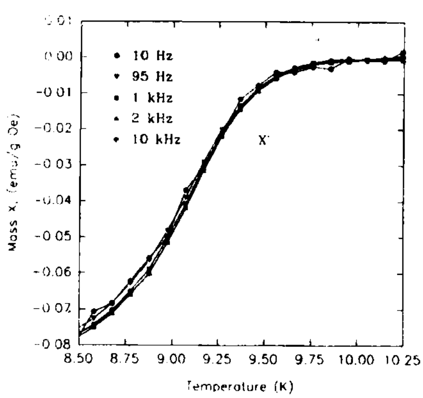

FIGURE 9 $\chi'(T)$ as a function of frequency for deuterated κ - $(ET)_2Cu(NCS)_2$.

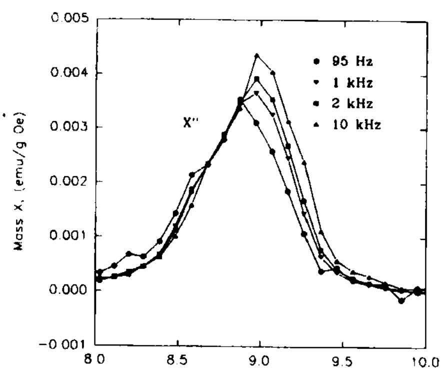

FIGURE 10 $\chi''(T)$ as a function of frequency for deuterated κ - $(ET)_2Cu(NCS)_2$.

MULTIPLE PHASE DETECTION

Multiple phases, structural and magnetic, are inherent to both high T_c and organic superconducting materials. In a DC measurement one phase may be "favored" over another (i.e., one may be screened by the other) because of the relatively large field amplitudes which are often used. With the small amplitude fields which are typical of the AC measurement, multiple magnetic phases are generally differentiable. As an illustration, four different single crystal organic superconductors were measured simultaneously. They were: β-$(ET)_2IBr_2$, β-$(ET)_2AuI_2$, κ - $(ET)_2Cu(NCS)_2$, and κ - $(ET)_2Cu[N(CN)_2Br]$. Each of these superconductors is characterized by it's own T_c. Figure 11 shows both χ' and χ'' as a function of temperature for this "multiple-phase" sample. Clearly, both χ' and χ'' show clear indications of each superconducting phase.

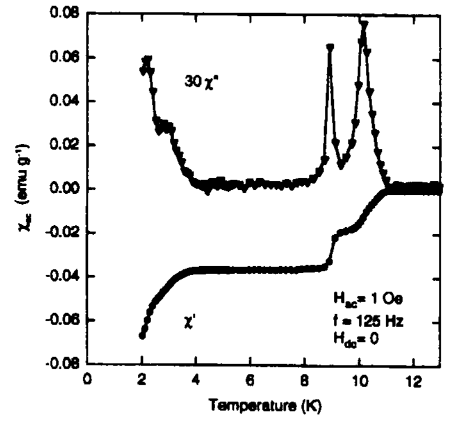

FIGURE 11 $\chi'(T)$ and $30\chi''(T)$ for a "multi-phase" sample composed of β-$(ET)_2IBr_2$, β-$(ET)_2AuI_2$, κ - $(ET)_2Cu(NCS)_2$, and κ - $(ET)_2Cu[N(CN)_2Br]$.

Further, for a single superconducting sample, the Bean model predicts a response in the third harmonic χ_3 near T_c. For a sample consisting of two superconducting phases, two peaks are predicted near the transition points, provided that one phase is not screened by the other. Thus in a multiphase sample, each phase is expected to reveal itself in χ_3.[7,8] This is illustrated in figure 12 where $\chi_3(T)$ is shown for the same "four-phase" sample. Again, each phase is clearly indicated in the harmonic response, providing yet another means for investigating multiphase materials.

CONCLUSIONS

The AC susceptibility technique is a remarkably powerful tool for the characterization of superconducting materials. This paper has attempted to outline the utility of this technique in the characterization of organic superconducting and other magnetic materials. It has been demonstrated that the measurement can be used to determine: transition temperatures, lower critical fields, magnetization critical current density, and to investigate flux dynamics and the multiphase nature of these materials. Other determinations are also possible using the AC technique, for example estimates of the upper critical field H_{c2}.

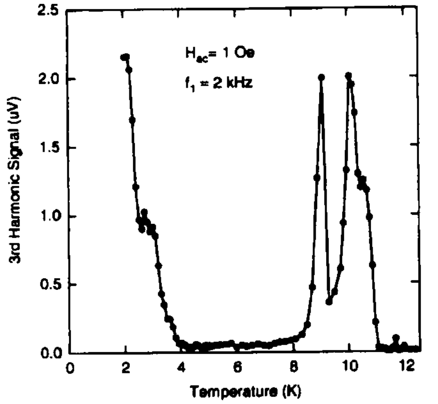

FIGURE 12 $\chi_3(T)$ for a "multi-phase" sample composed of β-$(ET)_2IBr_2$, β-$(ET)_2AuI_2$, κ - $(ET)_2Cu(NCS)_2$, and κ-$(ET)_2Cu[N(CN)_2Br]$.

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4. In the absence of net magnetic moments (e.g., as in uncanted anti-ferromagnetic substances with perfectly matched anti-parallel alignment of opposing sublattices) χ" is zero. Hence, the AC measurement can be used to distinguish between transitions to 3-D antiferromagnetic versus ferro- or ferri-magnetic ground states.

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