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Temperature-dependent phase reversal of nonresonant microwave and rf absorption in high-T_c superconductors

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The phenomenon of temperature-dependent phase reversal of the nonresonant electromagnetic response of the high-T_c superconductors is studied in the rf and the microwave ranges. Phase reversal is the changeover from a maximum at zero magnetic field and the decrease with the increasing field to a minimum at zero field and the increase with the increasing field. The results are analyzed using an effective-medium theory, treating the sample as a percolating network consisting of the superconducting regions separated by normal metallic regions. The experimental observations are shown to follow naturally from the dependence of the superconducting fraction on the temperature and the magnetic field.

I. INTRODUCTION

The importance of understanding the nature of the response of superconductors to electromagnetic radiation is well recognized. A very convenient method of measuring this response has come into vogue after the advent of high-T_c superconductivity.[1] It is based on the observation that when examined using conventional continuous-wave (CW) electron-paramagnetic-resonance[2,3] (EPR) and nuclear-magnetic-resonance[3] (NMR) spectrometers, the high-T_c superconductors exhibit in the superconducting state intense and narrow absorption signals which sensitively depend upon temperature, magnetic field, the nature (whether ceramic, single crystal, or thin film), and history of the sample, and the oxygen stoichiometry. Over the last four years these signals have been studied in great detail[4–6] and as a result many of their features are understood. However, there still exist many aspects of the phenomenon which are not understood yet. One such feature is the occurrence of the reversal of the phase of the signal as a function of temperature when the sample is cooled below T_c.

In an early report on the phenomenon,[2] it was observed that the signal occurring near zero magnetic field in a ceramic sample of the Y-Ba-Cu-O compound had a complex temperature dependence. Figure 2 of the paper shows how, when warmed from 77 K, the signal shows a reversal of the phase around 80 K before disappearing at the T_c ($\sim$84 K). In the conventional EPR recording of the signals, the magnetic field is modulated, usually at 100 kHz, and a lock-in detection is used giving rise to a derivative of the absorption. Therefore, by a reversal of the phase of the signal, what is implied is a changeover of the field dependence of the signal from a decrease of the absorption with increasing field say, to a situation where the absorption increases with the field, or vice versa. As is to be discussed later, which one of the situations exists in a particular case can be ascertained by simultaneously recording the regular EPR signal from another sample or from an impurity phase, if present, or by recording an NMR signal under the same conditions; the method used depends upon the frequency range in question. Of course, in the case of the resonant signals, the absorption almost always decreases when the magnetic field is swept on either side of the center of the resonance.

The examination of some ceramic samples of the y-Ba-Cu-O compound in the rf range showed[7] a more complex behavior. Just below T_c, a single derivative signal at zero field was observed. When cooled further, the signal broadened and eventually split into what looked like a doublet of derivative signals symmetrically displaced with respect to the position of the zero field. Further cooling led to complex changes in the signal shape resulting finally in a single derivative signal again, but with an opposite phase in comparison with the high-temperature single derivative signal, at about 10 K below T_c. It was also observed that this behavior is frequency dependent in that the sample did not show any phase reversal in the microwave range.

Dulcic *et al.*, in a recent study[8] find similar behavior in single-crystal samples of the Y-Ba-Cu-O compound. As the sample is cooled, first a signal with a maximum at zero field is observed. The intensity of this signal increases over the temperature interval of a degree and then decreases and is replaced by a signal with a minimum at zero field, i.e., again there is a phase reversal. They further find that the signal with the maximum at zero field disappears if the samples are freshly annealed in air at 450 °C, showing that the feature is sensitively dependent on the material properties. A recent paper by Durney *et al.*,[9] reports analogous results observed in thin-film samples of R-Ba-Cu-O (R = Y, Gd, Eu, Nd, Dy,

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and Sm) compounds. Just as in the case of ceramic and single-crystal samples, a phase reversal is observed at a temperature close to T_c.

In spite of the several reports of this interesting aspect of the nonresonant electromagnetic absorption, no satisfactory explanation of the phenomenon has been put forward so far. In this report we present the results of detailed investigations of the nonresonant rf and microwave absorption, specifically addressing the problem of the phase reversal. Evidence for strong frequency dependence of this behavior is also presented. Finally, we present an analysis of the results in terms of an effective-medium theory for the sample treated as a percolating network of superconducting regions separated by normal, metallic regions. The connectivity of the percolating network and, therefore, its electrical conductivity and diamagnetic susceptibility, are seen to respond sensitively to changes in the static magnetic field and the temperature. A simple effective-medium[10] calculation based on this model shows that the observed phase reversal follows in a natural way from the above parametric dependence.

II. EXPERIMENTAL

For the experiments in the rf range a conventional continuous-wave NMR spectrometer working in the range 5–20 MHz was used. Magnetic-field modulation at 87 Hz and phase-sensitive detection were used. The temperature was varied between 4.2 K and room temperature using an Oxford Instruments continuous-flow cryostat. To determine the absolute field dependence of the absorption signal the ^{1}H NMR signal in a sample of glycerine was recorded under exactly the same conditions.

Experiments were also carried out with a Varian E-109 EPR spectrometer working at a nominal frequency of 9.2 GHz, using a 100-kHz magnetic-field modulation. The lowest temperature available with this instrument was 77 K. In both the frequency (rf and microwave) ranges, magnetic fields of about 100 Oe—in a direction opposite to that of the main magnetic field—were applied by passing dc currents in a pair of Helmholtz coils to enable through-zero sweeps of the magnetic field.

The samples used in this study are of the Bi-Sr-Ca-Cu-O compound, prepared using the conventional ceramic method followed by sintering.

III. RESULTS

The nonresonant rf absorption signals recorded with the magnetic-field modulation and phase-sensitive detection are shown in Fig. 1. The unusual temperature dependence of the signals displayed in the figure is very similar to that reported in Ref. 7, for the Y-Ba-Cu-O samples. A single derivative signal centered at zero Oe is observed at 84.5 K. The absorption is a maximum at zero Oe and it decreases with the increasing magnitude of the field. On cooling, the signal broadens and eventually splits into two signals around 78.5 K. This splitting actually is a result of the displacement of the center of the signal away from zero field. Further cooling the sample leads to the disappearance of the wings and leaves behind a relatively narrow signal again centered at zero field, but now with the opposite phase. The opposite phase of the signal signifies that the absorption has a minimum at zero field and it increases with increasing magnitude of the field as determined by recording the ^{1}H NMR signal under the same conditions (except for the temperature; the latter is recorded at room temperature) as shown in Fig. 2.

We would like to point out that this temperature-dependent phase reversal is different from the phase reversal observed on a reversal of the field sweep for modulation amplitudes below a threshold value, as reported earlier by us[2,3] and other workers,[5] where the effects of the surface currents presumably dominate the loss mechanism.[5] In the present experiments the modulation amplitudes used are always large enough such that the phase is not reversed on a reversal of the direction of the field sweep.

The behavior in the microwave range was different in

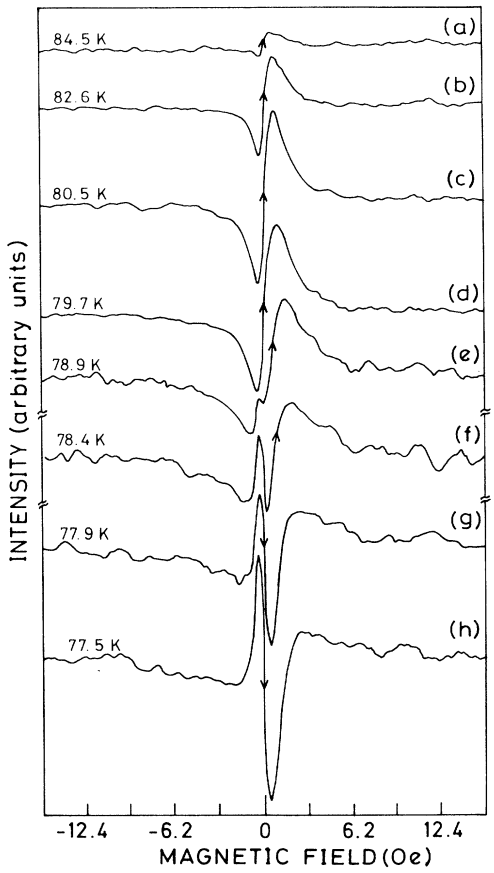

FIG. 1. Nonresonant rf absorption signals as a function of temperature recorded in a ceramic sample of Bi-Sr-Ca-Cu-O compound at 9.5 MHz. The signals marked (a) to (e) are derivatives of absorption maxima whereas those marked (g) and (h) are derivatives of absorption minima. Signal (f) is in the transition region.

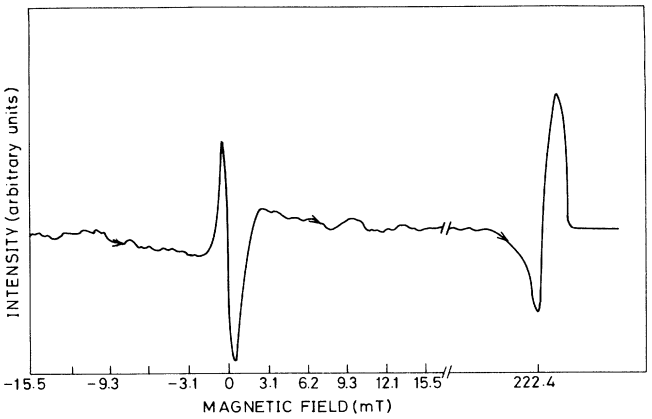

FIG. 2. ^{1}H NMR signal recorded in a sample of glycerine at room temperature, other conditions being exactly the same as for the nonresonant rf absorption signal at 77 K (also shown). To be noted are the opposite phases of the two signals indicating that the nonresonant signal is the derivative of absorption minimum.

that the signal remained a single derivative from 77 K to T_c. Also, over this entire temperature range, the absorption had a minimum at zero field and it increased with increasing field. This behavior was ascertained by recording the Cu^{2+} EPR signal under the same conditions. The results are shown in Fig. 3.

IV. MODEL

We consider a granular model in which the ceramic samples consist of superconducting grains of size of about a few microns ($\gg\xi_0$, the coherence length) and, therefore, with well-defined magnitude of the superconducting order parameter. However, the phase of the order parameter remains random. These superconducting grains are now weakly coupled through normal intergranular regions, giving superconducting-normal-superconducting (S-N-S) junctions. The coupling energy is, however, distributed randomly over a certain range. Two neighboring grains can become phase locked if the intergranular coupling energy ($J_c\phi_0/2\pi$) exceeds the thermal energy, (k_BT), where J_c is the critical current of the intergranular junction. Thus, as we lower the temperature, more and more grains become phase locked and beyond a bond-percolation threshold the bulk superconductivity sets in. This is the familiar bond-percolation model. It is to be noted that the strength of the bond, that is, the coupling energy, is a sensitive function of the magnetic field. In particular J_c gets multiplied by the diffraction factor $\sin(2\pi\phi/\phi_0)$, where ϕ is the flux spanning the junction. There is, however, an additional disorder in the problem coming from the inhomogeneity of the oxygen stoichiometry that results in different grains having different transition temperatures. This distribution of the transition temperatures of the grains is equivalent to a site disorder. This combination of bond dilution as well as site dilution disorder gives a very complex percolation problem for which there does not exist any complete treatment in the literature to the best of authors' knowledge. In the following, we therefore adopt the simplest approach based on an effective-medium theory (EMT) in which we assume that a volume fraction x of the sample is superconducting at a given temperature (T) and applied field (H). The fraction x is a monotonically decreasing function of T and H. The H dependence of x actually comes from the diffraction effect on the intergranular coupling as noted above, whereas the temperature dependence comes from the distribution of the coupling energy, ($J_c\phi_0/2\pi$). The latter decreases with increasing temperature. Now in EMT, the superconducting (S) fraction is characterized by a conductivity $\sigma_S=\infty$ and relative permeability $\mu_{rS}=0$, while the normal(N) region is effectively characterized by the conductivity σ_N and the relative permeability $=\mu_{rN}$. Thus within EMT, parameters σ^* and μ_r^* will be given by

$$x(\sigma_S-\sigma^*)/(\sigma_S+2\sigma^*) + (1-x)(\sigma_N-\sigma^*)/(\sigma_N+2\sigma^*)=0 \quad (1)$$

and

$$x(\mu_S-\mu_r^*)/(\mu_S+2\mu_r^*) + (1-x)(\mu_{rN}-\mu_r^*)/(\mu_{rN}+2\mu_r^*)=0 \; . \quad (2)$$

With $\mu_S=0$, $\sigma_S=\infty$, and $\mu_{rN}=1$ we get

$$\sigma^*=\sigma_N/(1-3x) \quad (3)$$

and

$$\mu_r^*=1-\tfrac{3}{2}x \; . \quad (4)$$

For a simple geometry of the sample and the solenoid, e.g., a spherical, or a long cylindrical, or more generally for an ellipsoidal sample placed in a long solenoid carry-

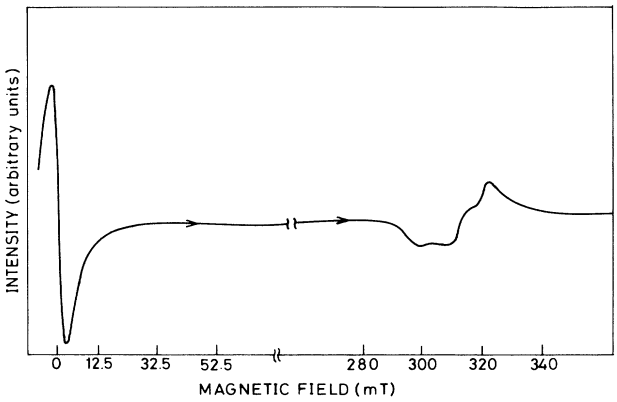

FIG. 3. Nonresonant absorption signal in the microwave range ($\nu=9.2$ GHz) at 77 K along with the Cu^{2+} EPR signal recorded under exactly the same conditions. The latter arises from an impurity phase present in the sample. The opposite phases of the two signals indicate that the nonresonant signal is the derivative of absorption minimum.

ing the rf currents, one can make use of the exact expression for the "eddy-current" complex (ac) magnetic susceptance of the sample in the quasistatic limit (which is valid in the rf and microwave range of frequencies). In our case, however, the sample is roughly characterized by a typical linear dimension of order "a", and acts as a "secondary" to the "primary," the rf coil of the resonant tank circuit of our rf oscillator. The equivalent secondary resistance (R_S) and inductance (L_S) are then approximately given by

$$L_S=\frac{8\pi^2}{3}a\mu_0\mu_r^* \quad \text{and} \quad \frac{L_S}{R_S}=4\pi a^2\sigma^*\mu_0\mu_r^* \tag{5}$$

to within a factor of order unity. If k is the coefficient of mutual coupling between the primary (rf coil) and the secondary (our sample), then there will be a reflected impedance in the primary. Recalling that the rf voltage (V) across the resonant circuit is I_0L_p/R_pC_p where I_0 is the constant rf current and L_p, C_p, and R_p are the inductance, capacitance, and resistance of the resonant rf tank circuit, all that needs to be done is to replace R_p by the sum of the primary resistance and the reflected resistance. This gives us, after some algebra,

$$V/V_0=\alpha/(1-3x)+\frac{1}{\alpha}(1-3x)/(1-\tfrac{3}{2}x)^2 , \tag{6}$$

where

$$V_0=I_0/(k^2\omega C_p) \quad \text{and} \quad \alpha=4\pi a^2\omega\mu_0\sigma_N . \tag{7}$$

In writing this we have assumed a high quality factor Q for the coil and ignored the small change in the resonance frequency due to the reflected impedance.

Equation(6) is our main result, which gives the change in the rf voltage (the signal) as the volume fraction x is changed by varying T and H. In Fig. 4, we have plotted V/V_0 as a function of x for a chosen value of the parameter $\alpha=0.3$, which for $\sigma=10^6$ $(\Omega\ \text{cm})^{-1}$ and $\omega=10$ MHz would correspond to a sample diameter of about 3 mm. The important feature to note is that there is a minimum in the graph. As will be shown, this minimum is responsible for the reversal of the phase of the signal as we reduce the temperature. Further, the minimum disap-

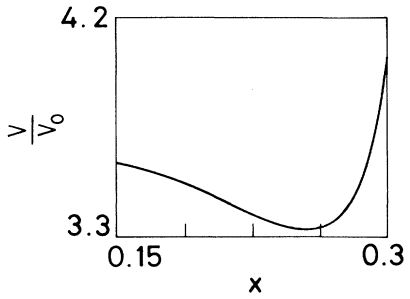

FIG. 4. The normalized voltage V/V_0 across the rf coil as a function of the superconducting fraction x calculated for $\alpha=4\pi a^2\omega\mu_0\sigma_N=0.3$.

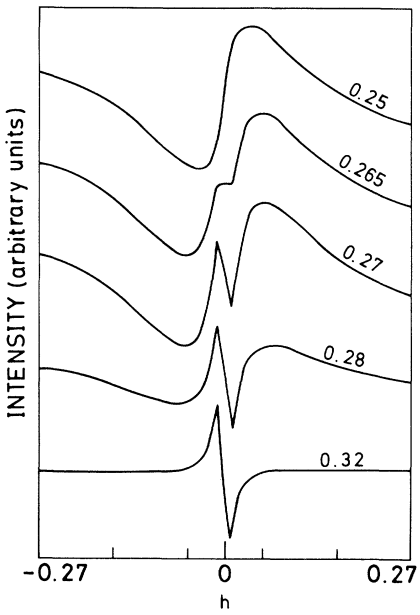

FIG. 5. Field derivatives of the normalized rf voltage V/V_0 for $\alpha=0.3$ and for varying values of $x(0,T)$. For $x\leq 0.27$ (see Fig. 4), the signals are derivatives of absorption maxima and the remaining are those of absorption minima.

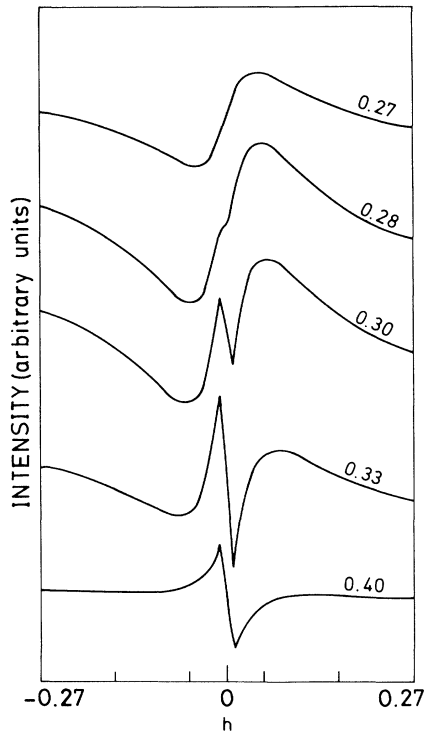

FIG. 6. Field derivatives of the normalized rf voltage V/V_0 for $x(0,T)=0.27$ and for different values of α. For $\alpha\leq 0.30$, the signals are derivatives of absorption maxima and the remaining are those of absorption minima.

pears at frequencies greater than a critical value that depends on the sample-specific parameters a and σ_N.

In order to study the effect of the field we need the explicit form of the field dependence of $x(T,H)$. As we have noted earlier, x is a monotonically decreasing function of field and, of course, it has to be an even function. Ideally, diffraction effects of the field on the intergranular coupling together with a specification of the distribution of these coupling strengths will in principle determine x. For the purpose of a qualitative analysis we have chosen the simplest form

$$x(H,T)=x(0,T)-|h|\ , \tag{8}$$

where h is normalized with respect to some characteristic field. The qualitative feature, namely the phase reversal, depends only on the fact that x is a monotonically decreasing function of $|h|$ and T.

In Fig. 5, we have plotted the field derivative of the normalized signal V/V_0 obtained from expression (6), for varying values of $x(0,T)$ and fixed α. In Fig. 6, we have made an analogous plot but with different values of α, keeping $x(0,T)$ fixed. Thus Fig. 5 simulates the dependence of the signal on temperature [through $x(0,T)$], for fixed frequency (through α) and Fig. 6 simulates the dependence on frequency (through α) for fixed temperature [through $x(0,T)$].

V. DISCUSSION AND CONCLUSION

Figure 5 clearly shows the phase reversal of the signal as we reduce the temperature [increase $x(0,T)$] below the nominal T_c; that is, at higher temperatures the absorption decreases with increasing field, while at lower temperatures the opposite holds. This is precisely what we observe in our samples at rf frequencies. Figure 6 shows a similar reversal as a function of frequency. This reconfirms the earlier observation of the absence of the phase reversal in microwave absorption though it was observed in the rf range.[7]

It should be noted that the nonresonant microwave absorption in high-temperature superconductor (HTSC) samples has been attributed to fluxon dynamics.[6] However, since the fluxon density is proportional to the applied field, the nonresonant absorption must always increase as the field is increased from zero. Thus the phase reversal observed experimentally cannot be understood in terms of this picture. Much below T_c when the sample is almost completely superconducting (i.e., very high Meissner fraction), the loss must entirely be due to the fluxons. However, in the percolating regime close to T_c, the dominant mechanism of loss seems to involve the conductivity of the normal fraction, which also gives phase reversal in a natural way as discussed in the above effective-medium treatment.

As has been mentioned earlier similar phase reversals have been observed in single crystals[8] of HTSC's with sharper transitions which, however, disappear on annealing. This again implies inhomogeneity and weak links as assumed in our macroscopic treatment.

However, one cannot rule out an intrinsic mechanism for phase reversal even in perfect single crystals as originating in the superconducting fluctuations (fluctuating conductivity and diamagnetism), in the critically-slowed-down region around T_c, that may simulate a percolative behavior if the time scale of the probe is shorter than the time scale of the critical fluctuations. This must be formally similar to our present model in the narrow critical range of temperatures. Here, the magnetic-field dependence arises from the suppression (enhancement) of diamagnetism above (below) the T_c by the applied field. This is expected to be a much weaker effect confined to a very narrow range of temperature.

In conclusion, therefore, we have proposed an explanation for the phase reversal of the nonresonant microwave and rf absorption signals observed in inhomogeneous high-T_c superconductors based on a percolative model treated in an effective-medium approximation. The calculated temperature as well as the frequency dependence of absorption signal is in qualitative accord with experimental observations.

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[1]J. G. Bednorz and K. A. Muller, Z. Phys. B **64**, 189 (1986).

[2]S. V. Bhat, P. Ganguly, and C. N. R. Rao, Pramana J. Phys. **28**, L425 (1987).

[3]S. V. Bhat, P. Ganguly, T. V. Ramakrishnan, and C. N. R. Rao, J. Phys. C **20**, L539 (1987).

[4]K. W. Blazey, K. A. Muller, J. G. Bednorz, W. Berlinger, G. Amoretti, E. Buluggiu, A. Vera, and F. C. Matacotta, Phys. Rev. B **36**, 7241 (1987).

[5]A. M. Portis, K. W. Blazey, K. A. Muller, and J. G. Bednorz, Europhys. Lett. **5**, 467 (1988); M. Pozek, A. Dulcic, and B. Rakvin, Solid State Commun. **70**, 889 (1989).

[6]K. W. Blazey, A. M. Portis, K. A. Muller, and F. Holtzberg, Europhys. Lett. **6**, 457 (1988).

[7]S. V. Bhat, V. V. Srinivasu, and C. N. R. Rao, Physica C **162-164**, 1571 (1989).

[8]A. Dulcic, R. H. Crepeau, J. H. Freed, L. F. Schneemeyer, and J. V. Waszczak, Phys. Rev. B **42**, 2155 (1990).

[9]R. Durney, A. Dulcic, R. H. Crepeau, J. H. Freed, and P. Kuss, Physica C **171**, 401 (1990).

[10]R. Landauer, in *Electrical Transport and Optical Properties of Inhomogeneous Media, (Ohio State University, 1977)*, Proceedings of the First Conference on the Electrical Transport and Optical Properties of Inhomogeneous Media, edited by J. C. Garland and D. B. Tanner, AIP Conf. Proc. No. 40 (AIP, New York, 1978).