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Microwave observation of magnetic field penetration of high-T_c superconducting oxides

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Microwave methods, using a conventional EPR spectrometer, have been applied to a study of magnetic field penetration of the high-T_c superconducting oxides $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_7$, and $EuBa_2Cu_3O_7$. Signals over 10^5 times the sensitivity limit of the EPR spectrometer were obtained. Huge low-field peaks were observed in the superconducting phase for magnetic fields below 10 G. The peak signal decreased exponentially with temperature just below T_c. These observations are taken as evidence of the spin-glass features of these materials and of fluxoid penetration of intrinsic Josephson junctions.

INTRODUCTION

The recently discovered[1] high-T_c superconducting oxides exhibit unusual magnetic properties. The diamagnetism measured when the samples are cooled in a small magnetic field (Meissner effect) is a fraction of that observed when the samples are cooled in zero field[2] (shielding), indicating strong flux trapping.[3] In addition, the ac and dc magnetic susceptibilities are not the same.[4] Small fields have a large effect on the diamagnetic susceptibility[5,6] and the resistivity.[5] Also, there is a slow relaxation of the magnetic moment to an equilibrium value after the magnetic field is changed suddenly.[7] Most of these properties can be understood in terms of clusters of superconducting grains,[8–10] weakly coupled through intrinsic Josephson junctions. Exposure to magnetic fields decouples the grains,[6] so that the magnetic susceptibility of the sample is that of isolated superconducting grains rather than coupled clusters of grains. When the magnetic field is removed, flux remains trapped in intergranular Josephson junctions.

Superconductive glass properties[10] and grain decoupling by magnetic fields[6] can be usefully studied at microwave frequencies using an EPR spectrometer, an extremely sensitive tool for the detection of microwave absorption or dispersion. The outputs of the EPR spectrometer, nominally the field derivative of microwave absorption and the field derivative of microwave dispersion, provide information on the magnetic and thermal response of the superconducting oxides. In this paper, we report a study of the superconducting properties of $La_{1.85}Sr_{0.15}CuO_4$, $YBa_2Cu_3O_7$, and $EuBa_2Cu_3O_7$ using an EPR spectrometer.

EXPERIMENT

A Bruker EPR ER-200D spectrometer, working in the X band (around 9.4 GHz) and up to 100 kHz field modulation frequency, was used for these studies. Temperature variation was obtained with a He gas-flow cryostat allowing the stabilization of sample temperatures between 8 and 300 K with ± 0.2 K precision.

$La_{1.85}Sr_{0.15}CuO_4$ was prepared by coprecipitation of the metals as oxalates. Stoichiometric ratios of La_2O_3, $SrCO_3$, and CuO were dissolved in concentrated nitric acid and then precipitated by addition of oxalic acid. The mixture was evaporated to dryness and subsequently fired in air for 14 h at 800 °C, 12 h at 900 °C, 2 h at 1100 °C, 6 h at 900 °C, and finally, slowly cooled to room temperature over 8 h. $YBa_2Cu_3O_7$ and $EuBa_2Cu_3O_7$ were prepared using a modification of a published procedure[11] by reacting stoichiometric quantities of $BaCO_3$, CuO, and either Y_2O_3 or Eu_2O_3. After dissolving the starting materials in concentrated nitric acid and evaporating the solution to dryness, the resulting nitrates were decomposed in air at 800 °C for 4 h. The black powders obtained were then ground in a mortar and pressed into pellets. $YBa_2Cu_3O_7$ was sintered at 950 °C for 12 h in flowing oxygen and the pellets were subsequently slow cooled to room temperature over 5 h in flowing oxygen. $EuBa_2Cu_3O_7$ was sintered for 15 h at 950 °C in flowing oxygen, cooled to 650 °C in 2 h, annealed at this temperature for 7 h in flowing oxygen, cooled to 200 °C in 10 h in flowing oxygen, and finally quenched to room temperature. X-ray diffraction showed that the products consisted of single-phase material.

Between 5 and 10 mg of superconducting oxide powder was placed in a quartz tube sealed at the other end. A Au(Fe)-chromel thermocouple was introduced into the open end and the quartz tube was then sealed at the other end. The tube was inserted in the TE_{102} cavity of the EPR spectrometer. In this cavity the microwave electric field has a node at the position of the quartz tube with the sample at the maximum of the microwave magnetic field. It is presumably the response to the magnetic component of the microwave field that determines the EPR spectrometer output. To reach zero and slightly negative fields, the magnet was biased by an external constant-current source connected to the rapid scan coils of the EPR spectrometer. The field of the current source was 39 G.

LOW-FIELD PEAK

All high-T_c superconducting oxides that we investigated exhibited huge (compared to the strength of EPR signals) signal peaks at very low fields with similar absorption and dispersion modes (Fig. 1). In the discussion, we suggest that the low-field peak is associated with intergranular Josephson coupling. For $La_{1.85}Sr_{0.15}CuO_4$ the peak is at 2.6 G, for $YBa_2Cu_3O_7$ at approximately 8 G, and for $EuBa_2Cu_3O_7$ at 110 G. (For the third material the structure of the signal is more complex with minor peaks at lower fields.) For comparison, polycrystalline V_3Si, synthesized from powders of vanadium and silicon and having the $A15$ structure, was studied. No peaks were observed although the signals for positive and negative directions of the field scan appeared to be of opposite sign at temperatures below $T_c \approx 16.5$ K.

The position of the peak is temperature independent but its height decreases with increasing temperature (Fig. 2). Decrease in peak height is slow at low temperatures. Near the transition to the normal state the decrease is exponential. In the normal state the peak has disappeared completely.

Absorption and dispersion signals are of comparable magnitude and exhibit large hysteresis. In $La_{1.85}Sr_{0.15}CuO_4$, for example, the component in phase with the modulation field is opposite in sign for positive and negative directions of magnetic field scan at modulation amplitudes (MA) smaller than 0.1 G. The hysteresis decreases when the modulation amplitude is increased (Fig. 1). Dependence of the peak height on MA in $La_{1.85}Sr_{0.15}CuO_4$ (Fig. 3) and $EuBa_2Cu_3O_7$ is nonlinear.

Magnetic memory effects produced by flux-trapping are also observed. The sample was first exposed to a magnetic field H. The field was next reduced to zero and then scanned through the low-field peak. In all samples (measurements were made at temperatures below the transition) the peak started to decrease for $H > 150$ G for $La_{1.85}Sr_{0.15}CuO_4$, 100 G for $YBa_2Cu_3O_7$, and 500 G for $EuBa_2Cu_3O_7$ (Figs. 4 and 5). For H greater than 300 G for $La_{1.85}Sr_{0.15}CuO_4$, 600 G for $YBa_2Cu_3O_7$, and 7000 G for $EuBa_2Cu_3O_7$, the decrease of the peak height saturated. In addition, the maximum of the peak shifts to higher fields after sample exposure to a magnetic field. However, if the sample is heated above T_c and then cooled to the original temperature, the memory of prior magnetic fields is lost.

TRANSIENTS AND BASE-LINE SHIFTS FOLLOWING FIELD OR TEMPERATURE CHANGE

When the magnetic field or the temperature is abruptly changed, the signal from the superconducting oxide immediately undergoes a change in the base line and then slowly relaxes to a new equilibrium value. Both transient and base-line shift decrease with increasing temperature and completely disappear above T_c. For the same magnitude of magnetic field change, transients and base-line shifts are greater the lower the initial magnetic field. The magnitudes and signs of transient or base-line shifts are not always reproducible, which can be attributed to the nonequilibrium nature of the superconducting glass state of high-T_c superconducting oxides.[3,10]

TEMPERATURE DEPENDENCE OF MICROWAVE CAVITY FREQUENCY

The EPR spectrometer is equipped with automatic frequency control (AFC). The AFC controls the frequency of the generated microwaves so that resonance with the

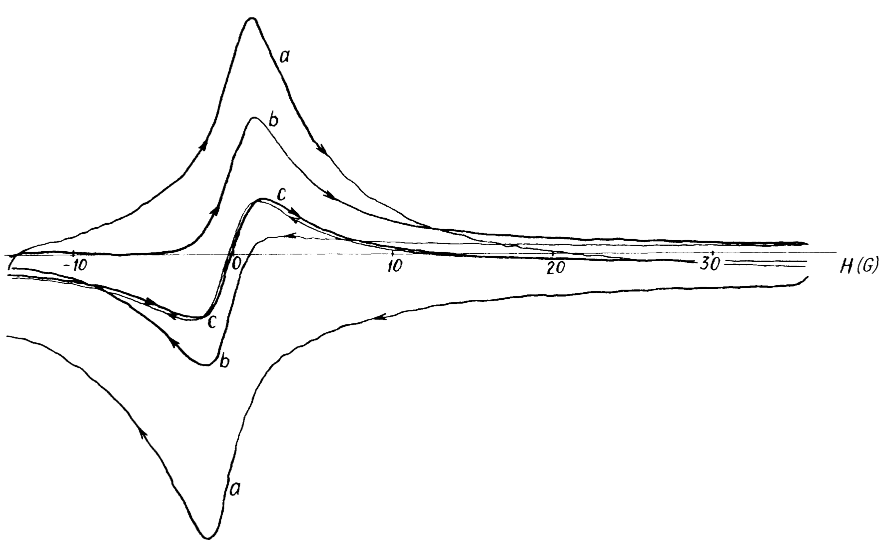

FIG. 1. Absorption signal from $La_{1.85}Sr_{0.15}CuO_4$ for different modulation amplitudes ($T = 15$ K). (a) $A_M = 0.01$ G and receiver gain $G_R = 2500$. (b) $A_M = 0.1$ G and $G_R = 250$. (c) $A_M = 1$ G and $G_R = 25$. Microwave power here and for all figures in 20 dB, unless specified otherwise.

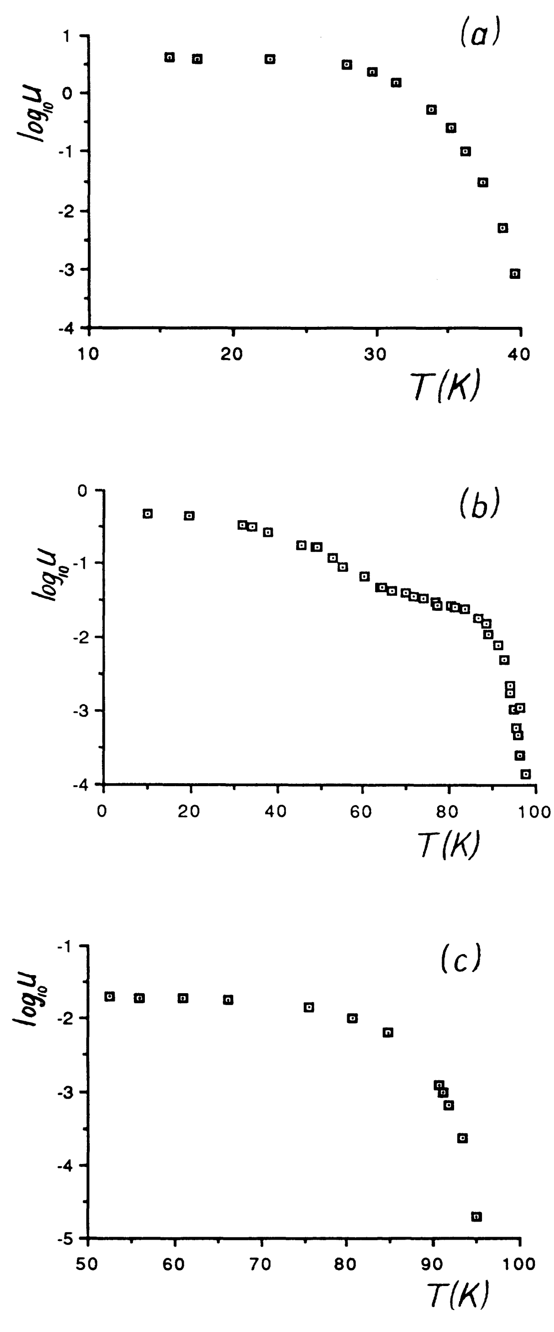

FIG. 2. Temperature dependence of logarithm of huge low-field peak-height $\log u$ (u in this and other figures is in arbitrary units) in (a) $La_{1.85}Sr_{0.15}CuO_4$, (b) $YBa_2Cu_3O_7$, (c) $EuBa_2Cu_3O_7$.

cavity is maintained. When supplemented by a microwave frequency counter, AFC makes possible a study of the temperature dependence of the loaded-cavity resonance frequency.

Since the microwave frequency used in the EPR spectrometer is much less than the energy gap of $La_{1.85}Sr_{0.15}CuO_4$, the microwave reflectance is higher for

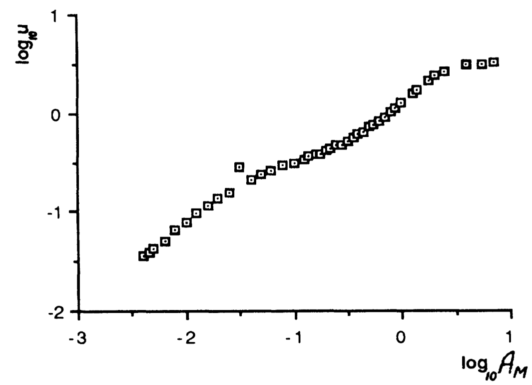

FIG. 3. Dependence of peak height in $La_{1.85}Sr_{0.15}CuO_4$ on modulation amplitude. Logarithm of peak height is plotted vs logarithm of modulation amplitude ($T = 10$ K).

the material in the superconducting state.[12,13] Also, because the magnetic component of the microwave field is excluded from the superconductor by the Meissner effect, the microwave frequency should be greater when the sample is in the superconducting state. Thus, the temperature dependence of the frequency should be s shaped, its inflection point (≈ 35 K) corresponding to the midpoint of the superconducting transition as observed experimentally (Fig. 6). The observed relative frequency shift $\Delta\omega/\omega$ is of order 10^{-4}.

DISCUSSION

Whereas conventional resistivity measurements detect a superconducting transition only when the contacts to the sample are connected by superconducting material, the microwave method does not require continuity through the sample. The method is extremely sensitive since the signal obtained is five orders of magnitude greater than the sensitivity limit of the EPR spectrometer. Indeed, the receiver gain used to detect the signal for temperatures around 10 K was only 20, whereas the spectrometer operates at receiver gains up to five orders of magnitude higher.

One of the most unusual properties of new high-T_c superconducting oxides is the suppression of the magnetic susceptibility by very low magnetic fields. Fields as low as 10 G (well below H_{c1}) suppress the diamagnetic susceptibility and increase the resistivity of $YBa_2Cu_3O_7$.[5,6] For example, a $YBa_2Cu_3O_7$ sample exhibited 97% diamagnetism in magnetic fields below 5 G and 61% diamagnetism in magnetic fields above 15 G.[6]

Such large changes in diamagnetism over such a narrow field range can be expected to give large absorption and dispersion signals. Indeed, grain decoupling by low magnetic fields decreases the volume from which magnetic flux is excluded and thus increases the effective volume that microwaves penetrate. This should decrease the frequency of the loaded cavity and increase the absorption of microwaves by the superconductor. Therefore, both absorption and dispersion signals should be observed at very

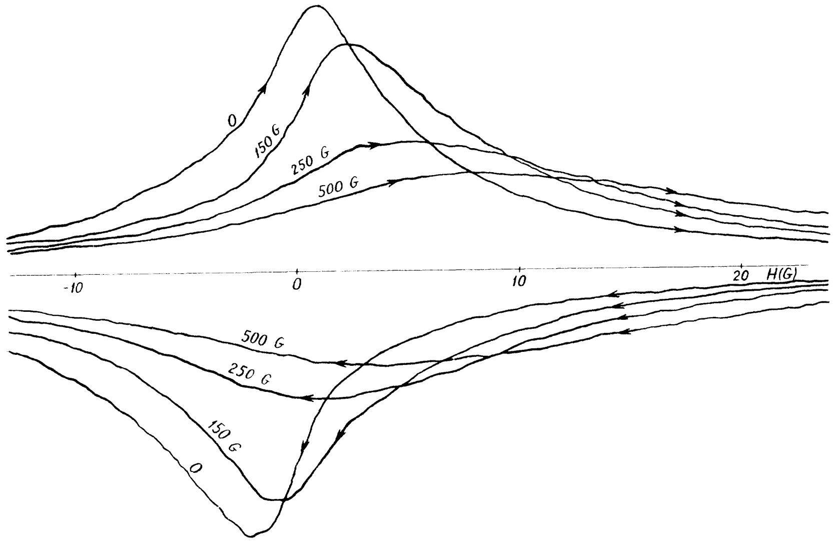

FIG. 4. Absorption signal from $La_{1.85}Sr_{0.15}CuO_4$ after brief exposure to magnetic fields. Signals for no previous exposure to magnetic field, for brief exposure to the fields 150 G, 250 G, and 500 G are shown. $A_M = 0.01$ G, $G_R = 1600$, $T = 14$ K.

low fields.

The drastic change in diamagnetism in a very narrow magnetic field range as well as our microwave observations can be understood from the behavior of Josephson junctions in small magnetic fields, studied theoretically by de Gennes for insulating Josephson junctions.[14] The two limiting cases of Josephson junction behavior in a magnetic field are (i) very weak magnetic fields where the magnetic field decays exponentially along the junction and (ii) stronger fields, where the magnetic field completely penetrates the junction. The very weak field behavior holds for fields

$$H \ll H_{c1}^{\rm Jos} \cong \Phi_0/(2\lambda\delta) \ , \quad (1)$$

where λ is the London magnetic field penetration depth, $\Phi_0 = ch/2e = 2\times 10^{-7}$ G is the flux quantum, and

$$\delta = (hc^2/16\pi e I_m \lambda)^{1/2} \quad (2)$$

is the characteristic penetration depth of very weak fields into the junction with I_m the zero-field critical current density through the junction. The magnetic field within the junction decays exponentially as

$$h(y) = H\exp(-y/\delta) \ , \quad (3)$$

where $y=0$ corresponds to the intersection of the junction and the sample surface and H is the field at the surface of the sample.

For strong fields with

$$H \gg H_{c1}^{\rm Jos} \cong \Phi_0/(2\lambda\delta) \ , \quad (4)$$

the magnetic field is nearly uniform along the junction, $h(y) \cong H$. The currents become periodic with wavelength

$$L = \Phi_0/(2\lambda H) \ , \quad (5)$$

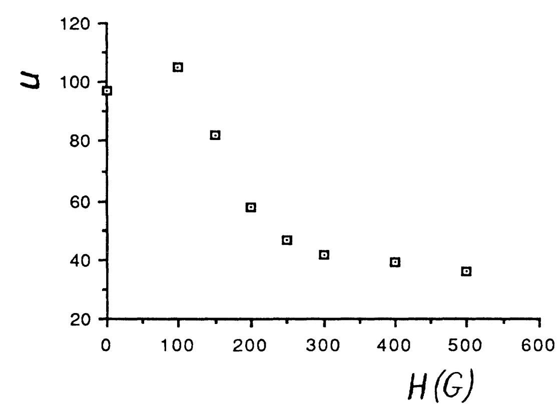

FIG. 5. Suppression of the huge low-field peak by brief exposure to magnetic field. Dependence of the peak height on the field to which $La_{1.85}Sr_{0.15}CuO_4$ sample had been exposed is plotted ($T = 31$ K).

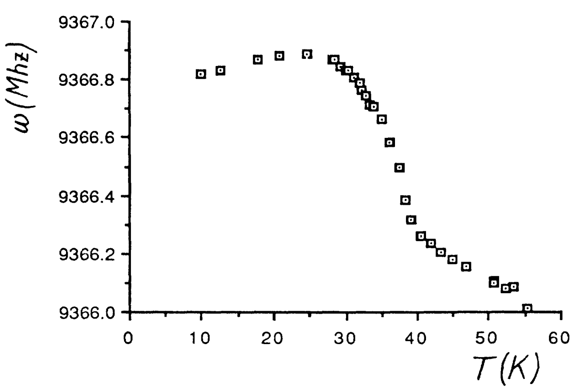

FIG. 6. Temperature dependence of the standing microwave frequency ω in the cavity loaded by $La_{1.85}Sr_{0.15}CuO_4$. The temperature dependence of the standing microwave frequency in the cavity loaded by just the quartz tube with the thermocouple but without the sample was subtracted.

and are given by

$$I_x = I_m \sin[2\pi(y - y_0)/L] \; , \tag{6}$$

with each period carrying one quantum of flux. This structure resembles an array of vortex lines in the plane of the junction and occurs in type-I superconductors as well as in type-II superconductors below the lower critical field H_{c1}.

The maximum current through a Josephson junction varies as[14]

$$J_c(H,T) = I_m(T)(d/2\pi)[\sin(\pi H/H_0]/(H/H_0) \; , \tag{7}$$

with

$$H_0 = \Phi_0/2d\lambda \; , \tag{8}$$

where d is the width of the junction. Critical current measurements[6] give $H_0 = 7$ G for $YBa_2Cu_3O_7$. This value is consistent with the position of the low-field peak that we observe for $YBa_2Cu_3O_7$. The field H_{c1}^{Jos} as well as H_0 should be much smaller than H_{c1}. The correlation between the temperature dependence of the critical current[6] and trapped flux[4] and the height of the low-field peak are apparent. Suppression of the critical current by previous exposure to a magnetic field[6] and suppression of the low-field peak signal by similar previous field exposure should also be related.

Equations (1)–(8), derived for the case of a Josephson junction between two semi-infinite superconducting regions, are applicable only when the grain diameter D is much larger than both the London penetration depth λ and the penetration distance δ into the junction. For the case $D < \lambda$ or $D < \delta$, penetration of the magnetic field is determined primarily by grain size and microstructure and should be relatively insensitive to increase in λ and δ as the temperature is increased. This is presumably the explanation of the observed independence of the low-field peak position with temperature for the high-T_c superconducting oxides.

In the region of very weak magnetic fields (1), both microwave magnetic field and modulation field decay exponentially within the junction and the signal from the superconductor is weak. For magnetic fields stronger than H_{c1}^{Jos}, we are in the domain of complete penetration of the magnetic field into the junction and the response of the superconductor to the modulation and microwave fields strongly increases. As the magnetic field is further increased, the response slowly decreases because of the decrease in total current through the junction (7).

Prior exposure to a magnetic field suppresses the low-field peak only if the magnetic field to which the sample had been exposed exceeds a certain critical value (Fig. 5). This is consistent with the dependence of the zero-field critical current on the maximum magnetic field to which the sample had been exposed.[6] The critical current is also suppressed by prior exposure to a magnetic field if the field exceeds a threshold value, which Kwak, Venturini, Ginley, and Fu[6] identify with H_{c1}. The analogy between the dependence of the low-field peak on the maximum prior magnetic field and the similar dependence of the critical current suggests that the threshold field that suppresses the low-field peak may also be identified with H_{c1}.

The observed temperature dependence of the low-field peak height suggests that the peak height is proportional to the magnetoresistance of the superconducting oxide. The resistance of a periodic array of all-niobium superconducting islands,[15] weakly coupled by Josephson junctions, is observed to decrease exponentially in the transition region

$$R(H,T) = R_n \exp[-\alpha(H)J_c(H,T)\Phi_0/(k_B T)] \; , \tag{9}$$

where R_n is the junction resistance in the normal state, $J_c(H,T)$ is the critical current per junction, and $\alpha(H)$ is a coefficient dependent both on the number of superconducting islands and on the magnetic field. For $\alpha(0) > \alpha(H_0/2)$ and $J_c(0,T) > J_c(H,T)$ we expect $R(0) \gg R(H_0/2)$ and $R(0,T) - R(H_0/2,T) \cong R(0)$.

According to the BCS theory, the maximum critical current density through a Josephson junction is[14]

$$I_m(T) \sim [eh/(m\xi_0)]n(T)P_j \; , \tag{10}$$

where $\xi_0 = 0.18hv_F/k_B T_c$ is the correlation length at 0 K (v_F is the Fermi velocity), P_j is a transmission coefficient across an insulating wall of the Josephson junction, $n(T)$ is the concentration of Cooper pairs, which according to the BCS theory is proportional to $T_c - T$ in the transition region. Therefore, in the transition region we expect $I_m(T) \propto (T_c - T)$ and $J(H,T) \propto (T_c - T)$. We also expect

$$R(H_0/2) - R(0) = R_n\{\exp[-\beta_1(T_c - T)/T] - \exp[-\beta_0(T_c - T)/T]\} \; , \tag{11}$$

where from (9) β_1 is a coefficient corresponding to the field $H_0/2$ and β_0 is a coefficient corresponding to zero field with $\beta_0 \gg \beta_1$. Thus, if the signal from the superconducting oxide is proportional to the magnetoresistance, the huge low-field peak height should decrease exponentially with $(T_c - T)/T$, as observed. The observed exponential decrease of resistance of an array of superconducting islands weakly coupled by Josephson junctions suggests that the resistance is caused by the motion of vortices.[15]

Sign reversal of small modulation-amplitude signals when the magnetic field sweep direction is changed is also consistent with sign reversal of the magnetic moment when the magnetic field sweep direction is changed as observed by Kwak *et al.*[6] For large modulation amplitudes the sign of the magnetic field change is determined mostly by the ac modulation field and the resulting signal is a composite of opposite sweep directions. Thus, the decrease in hysteresis and the nonlinearity of peak signal versus modulation amplitude may be understood.

To conclude, microwave studies with an EPR spectrometer offer a valuable method for the investigation of magnetic behavior and grain decoupling in the high-T_c superconducting oxides.

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