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ELECTRON PARAMAGNETIC RESONANCE, ELECTRICAL RESISTIVITY, AND MAGNETIZATION STUDIES IN THE HIGH T_c SUPERCONDUCTORS $EuBa_2Cu_3O_{9-x}$ AND $EuBa_2(Cu_{1-y}M_y)_3O_{9-x}$ (M = Cr, Mn, Fe, Co, Ni, OR Zn)*

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We have measured electron paramagnetic resonance (EPR), electrical resistivity, and dc magnetic susceptibility from 2 K - 300 K for the high T_c oxide superconductor $EuBa_2Cu_3O_{9-x}$, either undoped or doped with 3d ions (Cr, Mn, Fe, Ni, Co, or Zn), which presumably substitute at the Cu sites. We have observed an EPR line at low temperatures ($T \leq 40$ K), which exhibits an increase in intensity and decrease in field for resonance as the temperature is lowered. The EPR linewidth is also temperature dependent and exhibits a minimum at about 15 K. In some of the samples another EPR signal is observed over the entire temperature range studied, with properties that depend on sample preparation conditions. This signal is likely to be due to small amounts of an additional phase. The behavior and origin of these EPR signals are discussed. The variation of T_c with 3d ion concentration over the range (1 - 8%) is also presented.

The discovery by Bednorz and Müller[1] of superconductivity above 30 K in La-Ba-Cu-O and the more recent discovery of superconductivity above 90 K in a series of oxide superconductors $RBa_2Cu_3O_{9-x}$, where R=Y[2,3] or rare earth ions,[4,5] has resulted in an unprecedented number of studies on these superconducting oxides. It appears that the R ions have a negligible interaction with the superconducting electrons in these compounds, since replacement by most R's , including those with local moments, does not change the high critical temperature, T_c.[4,5] It was suggested that the high temperature superconductivity is associated with a 2-D structure in which two layers of CuO_2 sandwich one CuO_3 chain, with two Ba^{2+} per unit cell.[6] Apparently the alkaline earth ions are only weakly coupled to the 2-D network of Cu-O sheets, since the substitution of Ba by Sr and/or Ca also has little effect on T_c.[7,8] Because the Cu ions seem to be the essential component of the conduction path in these oxides, it is important to determine whether substituting some of the Cu ions with other 3d ions, particularly those with with a local moment , results in a significant perturbation of their normal and superconducting properties. An additional reason to substitute local moment ions is that they may provide an atomic probe when observed via Electron Paramagnetic Resonance (EPR).

To investigate these ideas we have studied $EuBa_2(Cu_{1-y}M_y)_3O_{9-x}$ with M = Cr, Mn, Fe, Co, Ni or Zn and $0.01 \leq y \leq 0.15$. EPR, ac electrical resistivity , and dc magnetic susceptibility measurements were made over the temperature range 2 K - 300 K. Extensive studies of $RBa_2Cu_3O_{9-x}$ for R = Y, Pr, Nd, Gd, Ho, Er, or Yb , as well as fractional substitution of the R ions with Gd or Er, have also been made, and will be reported elsewhere.[9] Sample preparation techniques have been reported previously.[4,5] X-ray powder diffraction on these compounds confirmed them as > 97% single-phase materials with the desired orthorhombically distorted , oxygen deficient, perovskite-like structure.

Electrical resistivity measurements were made at 100 Hz using a four probe configuration. For $T > T_c$, the resistivity, ρ, showed a metallic behavior for low dopant concentrations, $y \leq 0.01$. At higher dopant concentrations, semiconducting-like behavior was typically observed above T_c. This type of behavior can be seen in Fig.(1a), where we present ρ vs T data for three different concentrations of Zn. In Fig.(1b) we present ρ vs T data for $EuBa_2Cu_3O_{9-x}$ and $EuBa_2(Cu_{0.95}M_{0.05})_3O_{9-x}$ with M = Fe, Co, Ni, or Zn . The critical temperature as a function of 3d dopant concentration (M = Cr, Fe, Co, Ni, or Zn) is shown in Fig (2). Although we have also added Mn as a dopant, we have not included these data in Fig.(2) because we have found that there is a lack of reproducibility of the suppression of T_c for the samples prepared to date.

The dc magnetic susceptibility, χ, was measured with a SQUID magnetometer[10] from 6 K to 300 K in magnetic fields from 50 G to 10 kG. In Fig.(3) we present χ vs T for $EuBa_2(Cu_{1-y}Zn_y)_3O_{9-x}$ with y = 0.01 and 0.05. Similar data were obtained for the other 3d dopants. We note the large suppression of the diamagnetism below T_c with increasing Zn dopant concentration.

The EPR measurements were made on powdered material (grain size ~ 10 μm) using an X-band superheterodyne spectrometer over the temperature range 1.5 K - 300 K. Below T_c the microwave impedance of the sample is strongly dependent on field and temperature, giving rise to a baseline signal that exhibits significant variations and hysteresis. For most samples we are able to discern a Lorentzian EPR signal superimposed on the field dependent baseline variations. (Some caution must be exercised in this process because the baseline variations at low field, < 500 G, can often appear to mimic a Lorentzian type of signal.)

Below ~ 40 K, an anti-symmetric ($A/B \equiv 1.0$) Lorentzian EPR line is observed for pure or doped samples, including those whose T_c is < 2 K (e.g., sample "E" in Fig.(1a)). We will refer to this EPR signal as the low temperature (LT) line. The properties of the LT line, as the temperature is decreased from 40 K, are: (a) the intensity continuously increases; (b) the EPR linewidth, ΔH_{pp}, decreases until ~ 15 K and then sharply increases, as shown in Fig.(4a); (c) the resonance field, H_R, at 9.2 GHz remains constant down to ~ 15 K and then sharply decreases, as shown in Fig.(4b).

In addition to the EPR line just described, we often observed a partially resolved spectrum similar to that found for Cu^{2+} ions in an orthorhombic host, with $g_1 \sim 2.27$, $g_2 \sim 2.12$, and $g_3 \sim 2.05$. When present, this spectrum is observable over the full temperature

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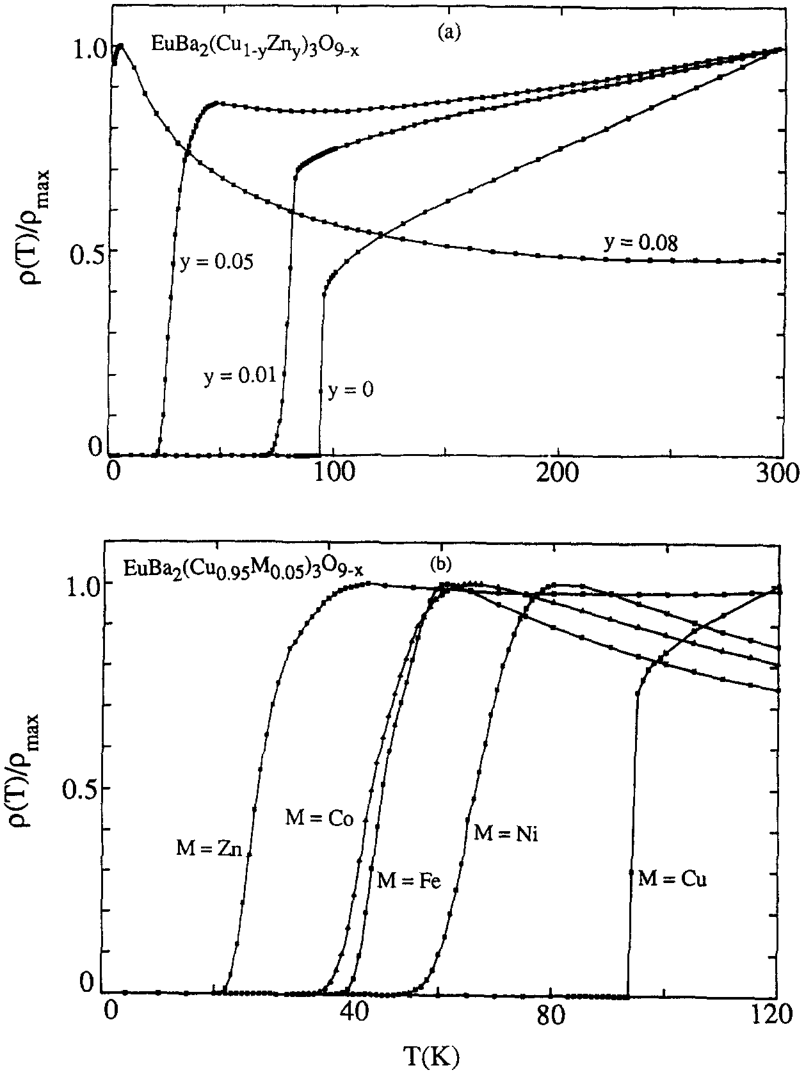

Figure 1 : Normalized electrical resistivity as a function of temperature for:
(a) $EuBa_2(Cu_{1-y}Zn_y)_3O_{9-x}$ with y = 0, 0.01, 0.05, and 0.08.
(b) $EuBa_2Cu_3O_{9-x}$ and
$EuBa_2(Cu_{0.95}M_{0.05})_3O_{9-x}$ with M = Fe, Co, Ni or Zn .

range (2 K - 300 K). We will refer to this as the high temperature (HT) spectrum. The intensity of the HT spectrum varied greatly from sample to sample, even though the samples were characterized by X-ray diffraction as having only the $EuBa_2Cu_3O_{9-x}$ phase present. In most samples the HT spectrum is either relatively weak, or is not observed, so it is unlikely that it is characteristic of the $EuBa_2Cu_3O_{9-x}$ phase. Also, the HT spectrum should not be a consequence of the presence of small amounts of Eu_2BaCuO_5 (green phase), since we found that this phase by itself exhibits no significant EPR signal. This is in contrast to the case for R = Y, where we have found that Y_2BaCuO_5 gives such a large HT spectrum intensity that the presence of even a fraction of 1% of this phase in $YBa_2Cu_3O_{9-x}$ would give a HT spectrum comparable in intensity to that found in our samples with R = Eu. At present, the origin of this sample dependent HT spectrum is unknown, but it may arise from another phase in amounts small enough ($\leq 2\%$) to escape detection by X-ray diffraction. Additional investigations are underway and will be reported separately.

We did not observe any additional EPR signals in samples doped with Cr, Fe, Co, Ni, or Zn. While we have observed an additional EPR line in some Mn doped samples, we find that its presence is sample-dependent. With EPR there is always the concern that an observed signal derives from a spurious phase, and this remains a possibility until the location of the Mn dopant is determined.

None of the EPR signals observed to date have any features which correlate with the superconducting transition. More explicitly, the HT spectrum, when present, is unaffected upon crossing T_c. The LT line, as previously discussed, is present in all samples, with a qualitatively similar temperature dependence for H_R and ΔH_{pp}, even for those samples which are non-superconducting (i.e., $EuBa_2[Cu_{0.92}Zn_{0.08}]_3O_{9-x}$, as well as $PrBa_2Cu_3O_{9-x}$ and several of the superconducting samples that were subsequently Ar annealed to partially deplete the oxygen). In some of the samples that were doped with Mn, we also observe an EPR line attributed to the Mn^{2+} ion and again find no anomaly as we pass through T_c.

In general, one may expect to find certain features in the temperature dependence of the linewidth and field for resonance of local moments placed in type II superconductors. These features typically arise from : (a) inhomogeneities of the magnetic field

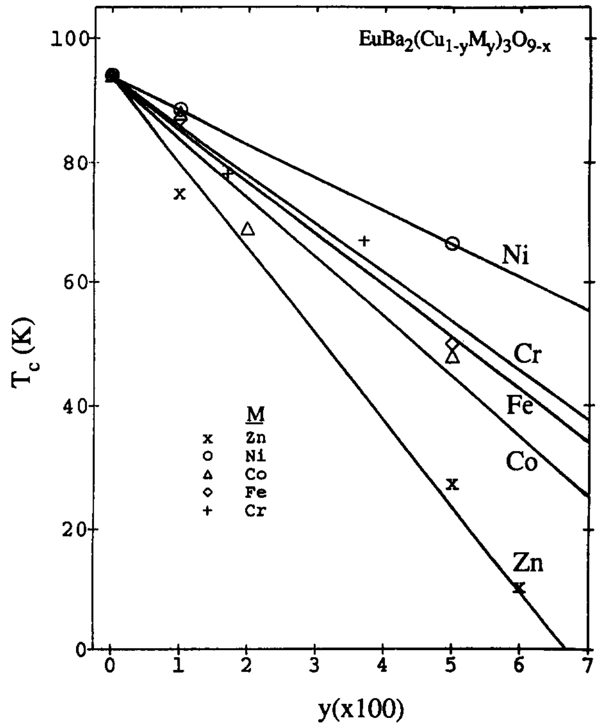

Figure 2 : Critical temperature, T_c, as a function of dopant concentration, y for $EuBa_2(Cu_{1-y}M_y)_3O_{9-x}$ with M= Cr, Fe, Co, Ni, or Zn. The solid lines are drawn as a linear representation of the data points.

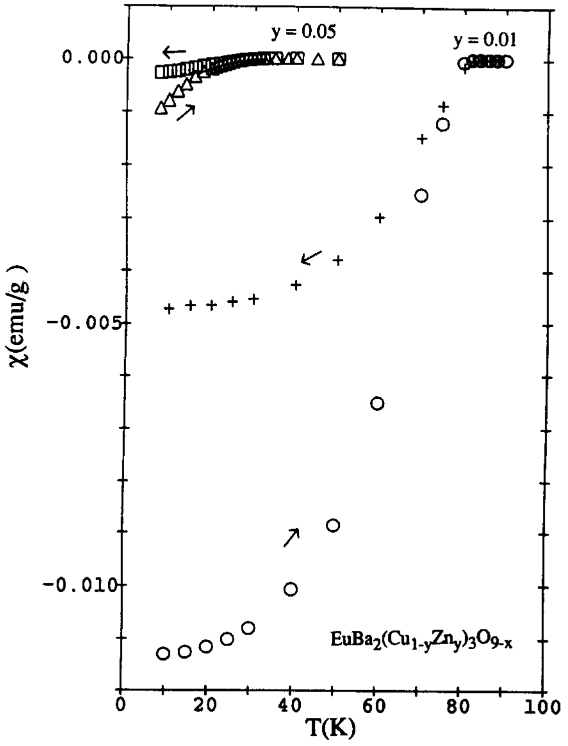

Figure 3: The magnetic susceptibility per gram as a function of temperature, taken in a dc field of ~50 G, for $EuBa_2(Cu_{0.99}Zn_{0.01})_3O_{9-x}$ and $EuBa_2(Cu_{0.95}Zn_{0.05})_3O_{9-x}$. The arrows indicate that the data were taken by either field cooling (←) or zero field cooling (→).

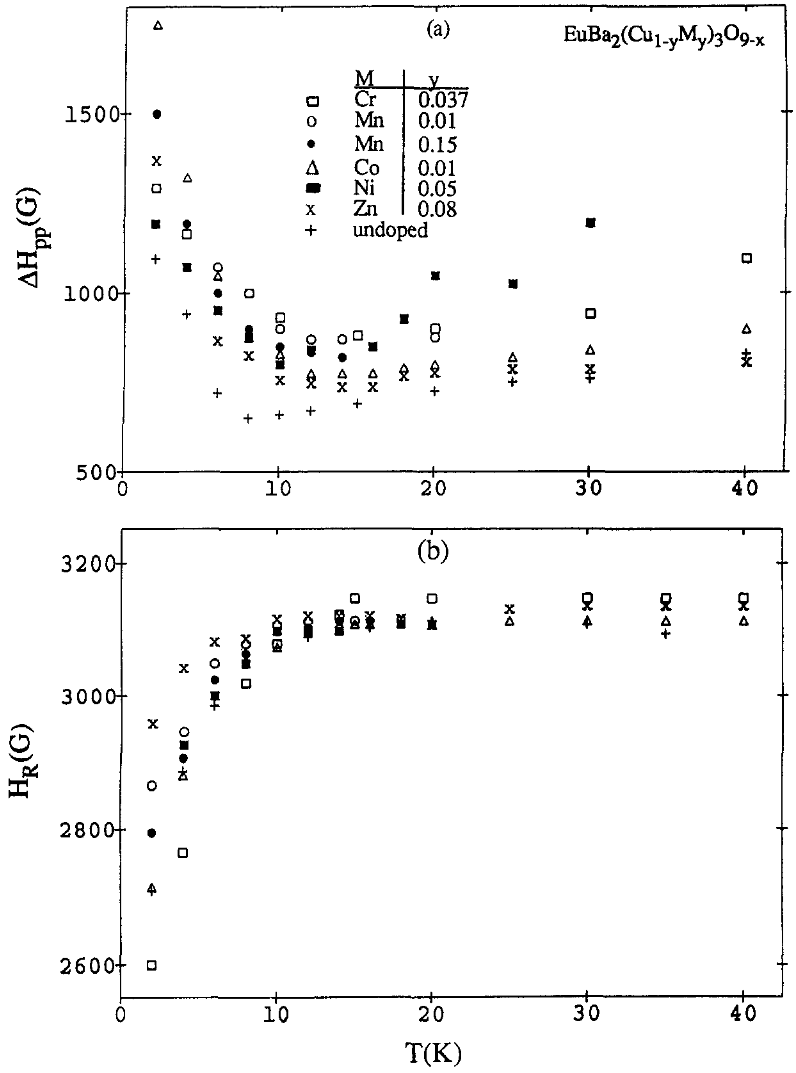

Figure 4. Properties of the low temperature (LT) EPR line as a function of temperature for $EuBa_2(Cu_{1-y}M_y)_3O_{9-x}$ with M = Cr, Mn, Co, Ni, or Zn; and y as indicated in the figure.

(a) The peak-to-peak linewidth, ΔH_{pp}, and

(b) the field for resonance, H_R at a frequency of 9.2 GHz.

when $H_{c1} < H_R < H_{c2}$, (b) changes in the effects of spin-orbit interactions upon spin relaxation, or (c) the diminution of the electronic susceptibility below T_c.[11,12] However, none of these effects would appear to be able to account for the temperature dependences of the signals we have observed. Instead, it is likely that the large shifts of the field for resonance are due to an internal rearrangement of an underlying spin system. It is also most likely that the changes in linewidth are not due to real changes in spin relaxation, but are rather a reflection of the large shifts in H_R, which may be inhomogeneously felt throughout the sample. Measurements of the spin lattice relaxation time, T_1, are underway to clarify this question. We have specific experiments in progress to determine whether there is a temperature dependence of the susceptibility which can be correlated with the temperature dependence of H_R and ΔH_{pp} observed for the LT line. We suggest that an examination of neutron scattering data might also be insightful.

We conclude with a comment concerning the resistivity data shown in Fig.(2). The data indicate that there is no correlation between the free ion magnetic moment of the 3d impurity ions and their effectiveness in depressing T_c. This is in contrast to standard BCS superconductors where magnetic impurities are particularly effective in suppressing T_c. Most striking is that the non-magnetic Zn, which one would expect to be Zn^{2+}, is even more effective in depressing T_c than the magnetic 3d ions. One possible explanation is that the different 3d ions replace the Cu preferentially on sites of different importance for the superconductivity. Another is that substitution of the different 3d ions may change electron density or other variables to such an extent that these changes become more important in determining T_c than the spin-dependent scattering of conduction electrons by these ions.

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