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Precautions when interpreting EPR and dc magnetization measurements of high-T_c $RBa_2Cu_3O_{9-x}$-phase superconducting materials

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Many electron-paramagnetic-resonance (EPR) and magnetic susceptibility measurements for the high-T_c superconductors of the form $RBa_2Cu_3O_{9-x}$ (R=Y or a rare earth) have been reported. Excluding local moment resonances due solely to the R atoms, we show that all of the EPR measurements known to us are not intrinsic to the superconducting phase, but rather are due to low concentrations of spurious phases typically present in the samples. $BaCuO_2$ is found to be the main source of the low-temperature EPR signal and of the magnetic susceptibility which has been reported for $YBa_2Cu_3O_{9-x}$ above T_c.

I. INTRODUCTION

The static magnetic properties of the high-T_c (> 90 K) superconductors are clearly of great interest, and numerous measurements of the dc magnetic susceptibility of $YBa_2Cu_3O_{9-x}$ have been reported, with various authors attributing an average local moment of $\sim(0.1-0.5)\mu_B$ to the copper atoms.[1-5] The dynamic magnetic properties are also of great interest and could, in principle, be determined via observation of electron-paramagnetic-resonance (EPR) of the carriers, or other local moments. Were such data available, they might be extremely helpful in clarifying the nature of the superconducting mechanism. The primary purpose of this note is to demonstrate why great care must be taken in interpreting both the magnetic susceptibility and EPR experiments, and to explain why it is unlikely that any of the EPR measurements reported so far[5-10] for the usual granular-compressed-powder (GCP) samples of the form $RBa_2Cu_3O_{9-x}$ (R=Y or a rare earth), can be unambiguously related to the high-T_c superconducting phase. The primary problem is that significant quantities of spurious phases (most notably $BaCuO_2$) are readily present when the samples are made via the GCP method, and some of these phases have sufficiently strong magnetic properties to dominate over that of the high-T_c superconducting phase material.

II. INTERPRETATION OF EPR DATA IN $RBa_2Cu_3O_{9-x}$ HIGH-T_c SAMPLES

EPR signals in GCP samples of $RBa_2Cu_3O_{9-x}$ have been reported by several groups[5-9] for R=Y, and by ourselves[10] for R=Y, Pr, Nd, Eu, Gd, Ho, Er, and Yb. In general, two distinct EPR signals are observed; one usually observable only at low (< 40 K) temperatures,[6,7,10] and the other dominating the spectra at higher (> 40 K) temperatures.[5-10] We have termed these the LT and HT lines, respectively. The temperature dependences of the peak-to-peak linewidth ($\Delta H_{p.p.}$) and field for resonance (H_R) for the LT line were found to be quite similar for all the rare-earth or Y hosts.[10] An example of such data is presented in Fig. 1 for a $EuBa_2Cu_3O_{9-x}$ sample. In Fig. 1 we also present an example of data for an EPR signal which is typically observed in samples which were prepared by our standard GCP method,[10] but where the starting ingredients consisted of *only* $BaCO_3$ and CuO powders in various proportions. The EPR behavior observed in these nonsuperconducting samples is strikingly

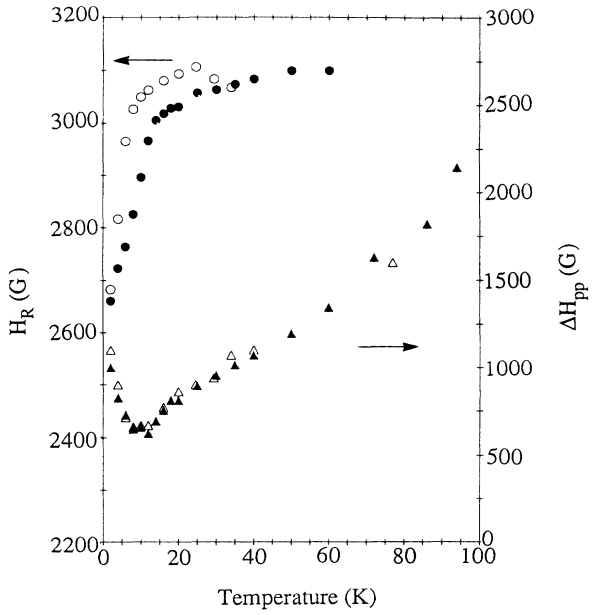

FIG. 1. Temperature dependence of the EPR peak-to-peak linewidth $\Delta H_{p.p.}$ (triangles) and field for resonance H_R (circles) for a $EuBa_2Cu_3O_{9-x}$ sample (open symbols) and a sample prepared from $BaCO_3$ and CuO only (closed symbols). For both samples the EPR signal was determined to originate from $BaCuO_2$. Measurements were made at a frequency of 9.2 GHz.

similar to that for the LT line observed in the superconducting RBa$_2$Cu$_3$O$_{9-x}$ samples.[6,7,10]

The major phases present in the samples made only with $BaCO_3$ and CuO powders were determined from x-ray powder diffraction measurements to be $BaCuO_2$, $BaCO_3$, and CuO. Neither pure $BaCO_3$ nor CuO were observed to exhibit an appreciable EPR signal at any temperature, which strongly suggests that the EPR signal observed in these samples arises from the $BaCuO_2$ phase. By varying the $BaCO_3$ to CuO starting ratios, we have prepared many samples which contain various amounts (10–93% mass fraction) of the $BaCuO_2$ phase. For these samples, as well as for numerous RBa$_2$Cu$_3$O$_{9-x}$ samples, we performed a careful, quantitative x-ray powder diffraction analysis, in combination with a determination of the LT EPR intensity per unit mass of sample. From the x-ray data, the amplitude of the most intense x-ray peak of each detectable phase was measured, and the mass fraction of each phase subsequently determined using standard procedures.[11] The mass absorption coefficients of each phase were taken into account, and numerous standards consisting of various known amounts of $BaCuO_2$, $BaCO_3$, CuO, and/or Eu$Ba_2Cu_3O_{9-x}$ were prepared for calibration purposes. This allowed the mass fraction of each phase to be determined to an accuracy of 10% or better, if the corresponding x-ray peak exhibited adequate signal-to-noise ratio. When necessary, large time constants and small angular sweep rates were used to improve the signal-to-noise ratio. The EPR intensities [taken as the amplitude times $(\Delta H_{\text{p.p.}})^2$] were determined at 6 K. Although we have taken into account the cavity Q factor, and normalized the EPR intensity per unit mass of sample, variations in sample size, shape, and position in the cavity limit the accuracy of our intensity measurements to $\sim$20% at best.

For the samples which were made from $BaCO_3$ and CuO only, we find that the intensity of the observed EPR line is proportional to the amount of $BaCuO_2$ present. The intensity is large enough that a $BaCuO_2$ mass fraction of $\leq 3\%$ would be sufficient to account for the intensity of the LT line observed in most of our RBa$_2$Cu$_3$O$_{9-x}$ samples. We also found that a majority of our RBa$_2$Cu$_3$O$_{9-x}$ samples (including those doped with $3d$ or $4f$ impurities) contained a detectable amount of $BaCuO_2$, and that the amount of $BaCuO_2$ present correlated well with the measured LT amplitude. The results are summarized in Fig. 2 for various RBa$_2$Cu$_3$O$_{9-x}$ superconducting samples, including a few doped with $3d$ impurities. Data points are shown for samples in which an appreciable amount of $BaCuO_2$ could be detected[12] and should not be taken as indicative of the amount of $BaCuO_2$ typically present for a particular rare-earth host R. The solid line in the figure indicates the expected dependence of the LT signal intensity on $BaCuO_2$ content, as deduced from a linear fit to the data of the samples made from $BaCO_3$ and CuO only. The value of the slope of this linear fit has a standard deviation of $\pm 30\%$, which is mainly due to errors in determining the LT intensity. The data points also have measurement errors of $\sim$30%. Considering the various measurement errors involved, the data points fit this line quite well.

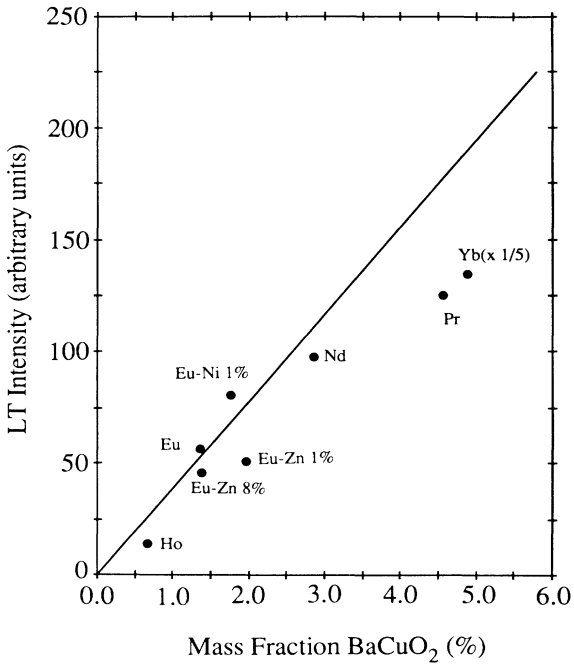

FIG. 2. Intensity of the LT EPR signal (normalized per unit mass of sample) observed for various RBa$_2$Cu$_3$O$_{9-x}$ samples or Eu$Ba_2Cu_3O_{9-x}$ samples doped with Zn or Ni as a function of the mass fraction of $BaCuO_2$ present in the sample. The Yb data point is plotted with both the LT intensity (680 units) and mass fraction of $BaCuO_2$ (24.6%) reduced by a factor of 5 to facilitate the presentation of the data. The solid line indicates the expected dependence of the EPR intensity on $BaCuO_2$ content, as described in the text. Both the line and the data points contain measurement errors of $\sim$30%.

The results presented in Figs. 1 and 2 strongly indicate that $BaCuO_2$ is responsible for the LT EPR signal observed by ourselves[10] and other investigators[6,7] in the RBa$_2$Cu$_3$O$_{9-x}$ superconductors.[13] Further evidence supporting this conclusion is that, for all superconducting samples in which no $BaCuO_2$ was detected by x-ray diffraction, the LT signal intensity was weak enough that the amount of $BaCuO_2$ needed to produce this intensity would not have been detectable by x-ray diffraction. Also, for a few samples, no LT line was observed at all, nor was any $BaCuO_2$ detected.

The HT signal, when resolved, has $g_x = 2.27$, $g_y = 2.12$, and $g_z = 2.05$, and is most likely due to Cu^{2+} in a noncubic site. We suggest that the HT signal also cannot be unambiguously associated with the RBa$_2$Cu$_3$O$_{9-x}$ phase because of the following. (a) There are no changes in the HT linewidth or field for resonance which we can associate with T_c. (b) The HT signal amplitudes increase with time for samples left at room temperature, sometimes increasing by as much as two orders of magnitude over a period of two weeks, but without any noticeable changes in either the x-ray spectra or T_c. (c) We can find similar HT signals and time dependence in samples made with only the $BaCO_3$ and CuO powders. (d) We find pure

Y_2BaCuO_5 (the so-called green phase) to have a very strong HT signal, such that the presence of $< 1\%$ of this phase would account for the HT signals observed in the $YBa_2Cu_3O_{9-x}$ superconducting samples.[14]

III. dc MAGNETIC SUSCEPTIBILITY

We have mentioned that measurements of the dc magnetic susceptibility χ for $YBa_2Cu_3O_{9-x}$ have been reported, which, if interpreted as being associated with the Cu ions, would correspond to an average moment ranging from ~ 0.1 to $0.5\ \mu_B$ per ion.[1-5] Of course such measurements represent a sum of the contributions from all the sample constituents. Since we have found that there are always small quantities of spurious phases present in our GCP samples, and some of these give observable EPR signals, they must also contribute to the total dc magnetization. We have measured a sample containing a 93% mass fraction of $BaCuO_2$ (the remainder being $BaCO_3$, which was determined to give a negligible contribution to χ), and present a plot of $1/\chi$ versus temperature (adjusted to 100% $BaCuO_2$) in Fig. 3. At high temperature we find an effective magnetic moment of $1.72\mu_B$ per Cu ion in agreement with other published values.[15,16] As the temperature is lowered, the effective moment increases, reaching a value of $3.16\mu_B$ below 30 K. Thus, at high temperatures a mass fraction of $BaCuO_2$ ranging from 0.3% to 8% would explain the reported results. This is in agreement with similar qualitative conclusions reached by other groups.[1,2,5]

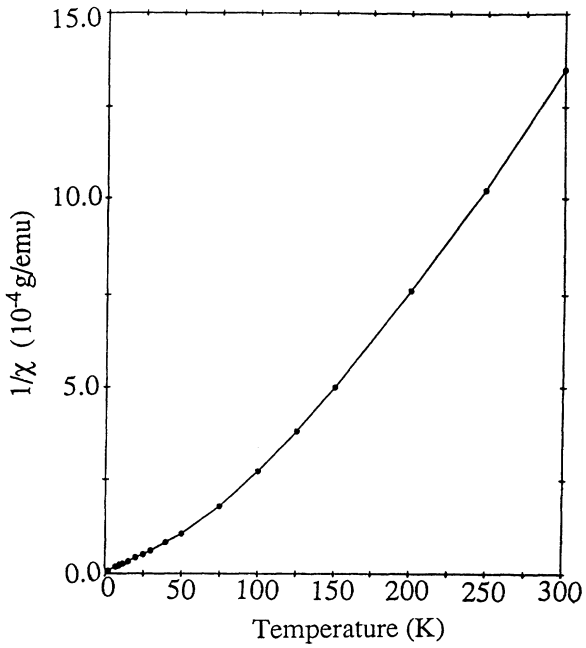

FIG. 3. $1/\chi$ vs temperature data for $BaCuO_2$ measured in a dc magnetic field of 3.0 kG. The solid line is a guide to the eye.

IV. SUMMARY

We have shown that the LT EPR line observed in GCP samples of the $RBa_2Cu_3O_{9-x}$ superconductors is most likely due to the presence of $BaCuO_2$ and is not to be interpreted as intrinsic to the superconducting material. We have also shown that the HT signal cannot be unambiguously attributed to the $RBa_2Cu_3O_{9-x}$ phase, although it is not clear what phase (or phases) gives rise to this signal. In addition, the dc magnetic susceptibility of $BaCuO_2$ can be large enough to dominate over any intrinsic paramagnetic contribution from $RBa_2Cu_3O_{9-x}$ (when R=Y or a nonmagnetic rare earth) in the normal state. From x-ray measurements we find that impurity phases (especially $BaCuO_2$) are typically present in the $RBa_2Cu_3O_{9-x}$ oxide systems, and we caution that, even for future work utilizing single crystals, particular care must be taken to ensure that EPR and magnetic-susceptibility measurements reflect only the intrinsic properties of the high-T_c superconducting material.

Note added in proof. Similar conclusions for the HT line were recently reached by G. J. Bowden *et al.*, J. Phys. C **20**, L545 (1987).

ACKNOWLEDGMENTS

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[11]See, for example, B. D. Cullity, *Elements of X-Ray Diffraction* (Addison-Wesley, Reading, MA, 1978).

[12]At best we could detect the presence of $BaCuO_2$ whenever the amplitude of the major $BaCuO_2$ x-ray peak was $\geq 0.2\%$ of the major $RBa_2Cu_3O_{9-x}$ peak amplitude. Assuming no other impurity phases to be present, this corresponds to a detectable $BaCuO_2$ mass fraction of $\geq 0.5\%$ (or atomic fraction of $\geq 1.5\%$).

[13]Of course, $BaCuO_2$ is not responsible for any local moment resonance which may arise from the R atoms, such as for R=Gd.

[14]For pure Eu_2BaCuO_5 we do not observe an appreciable HT signal, but nonetheless still frequently observe an HT signal in the $EuBa_2Cu_3O_{9-x}$ samples. This is evidence that other spurious phases may exhibit similar HT signals.

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