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Magnetism and critical fields in the high-T_c superconductors $YBa_2Cu_3O_{7-x}S_x$ $(x=0,1)$: An ESR study

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We have used an ESR spectrometer to study magnetism and superconductivity in $YBa_2Cu_3O_{7-x}S_x$ $(x=0,1)$. All samples exhibited an ESR signal. All the superconducting samples showed a low-field signal due to transition from the Meissner state to the mixed state. We demonstrated a reverse relation between magnetism (ESR intensity) and superconductivity. The temperature dependence of the critical field H_{c1} is anomalous.

Since the initial discovery of high-temperature superconductivity in oxides[1] extensive research has been carried out in attempt to understand the mechanism of superconductivity and to find new superconductors.[1-4] Recently, Felner, Yeshurun, and Nowik[5] have discovered that $YBa_2Cu_3O_6S$ and $YBa_2Cu_3O_7$ have the same superconducting transition temperature, but the former exhibits a significantly larger Meissner effect (see inset of Fig. 1). This remarkable feature is not clearly understood at present. This Rapid Communication reports on magnetic and superconducting properties of the high-T_c superconductors $YBa_2Cu_3O_{7-x}S_x$ $(x=0,1)$. Using an ESR spectrometer[6] we have obtained valuable information on (a) the properties of the unpaired spins which contribute to the ESR line, (b) the lower critical field H_{c1}, and (c) the superconducting transition temperatures. This allows a better identification of the unpaired spins[7] and their effect on superconductivity. We believe that our results clarify somewhat the origin of the large Meissner effect for $YBa_2Cu_3O_6S$.

Measurements on four different samples [to be denoted by $YBa_2Cu_3O_7$(I), $YBa_2Cu_3O_7$(II), $YBa_2Cu_3O_7$-(quenched), and $YBa_2Cu_3O_6S$] are reported here. The method of preparation was described previously.[5] It is known that slow cooling of the melt down to room temperature stabilizes a superconducting orthorhombic phase while fast cooling and quenching leads to a nonsuperconducting state. Consequently, $YBa_2Cu_3O_7$(I) and $YBa_2Cu_3O_7$(II) were prepared by the slow-cooling procedure using different batches of starting materials. Both compounds exhibit superconductivity at $T_c \cong 89$ K.[8] $YBa_2Cu_3O_7$ (quenched) was prepared by fast cooling and quenching [using the same batch as for $YBa_2Cu_3O_7$(II)] and no evidence for superconductivity was observed down to $T=8$ K. $YBa_2Cu_3O_6S$ (in which an oxygen is replaced by a sulfur atom) was prepared by the slow-cooling procedure.[5] This sample is superconducting at $T_c \cong 89$ K (Ref. 8) and exhibits over 80% Meissner effect, as compared to about 25% Meissner effect in other materials (see the results of Felner, Yeshurun, and Nowik in the inset of Fig. 1). All the compounds exhibit a single phase. The superconducting material has an orthorhombic phase with lattice parameters of $a=3.822$ Å, $b=3.891$ Å, and $c=11.67$ Å for $YBa_2Cu_3O_7$(I), and $a=3.855$ Å, $b=3.914$ Å, and $c=11.75$ Å for $YBa_2Cu_3O_6S$.[5]

The measurements (including transition temperatures, critical fields, and ESR spectra) were conducted using a standard E-line spectrometer at X band frequency and TE_{011} cavity. The temperature was regulated and controlled by an "Air Product" helium flux system and mea-

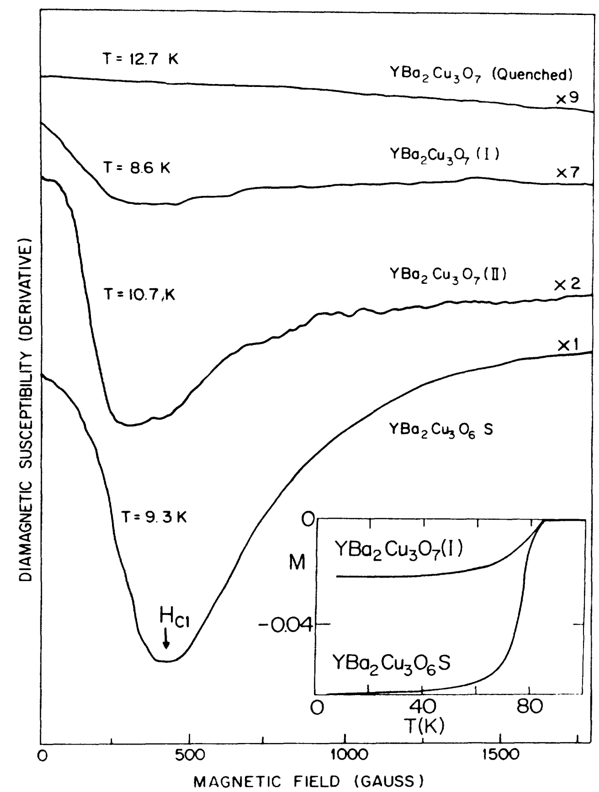

FIG. 1. Derivatives of the "superconducting" signal vs magnetic field. This signal is due to change in the diamagnetic susceptibility upon transition from the Meissner state to the mixed state. The minimum yields H_{c1}. Inset: magnetism M (in emu/g) vs temperature measured using a SQUID magnetometer and an external field of $H=2$ G (Ref. 5). Note that the diamagnetic susceptibility for $YBa_2Cu_3O_6S$ is significantly larger than that of $YBa_2Cu_3O_7$(I) and roughly scales with the intensity of the superconducting signals. Inset was taken from Felner, Yeshurun, and Nowik (Ref. 5).

sured using Au(Fe) versus chromel thermocouple. To compare signal intensities, we used the same quantity (approximately 80 mg) of powdered samples inside a quartz tube for all our experiments. This corresponds to a filling factor of $\eta \cong 10^{-3}$. The superconducting transition temperature is indicated by a dramatic increase of the cavity resonance frequency, by $\Delta\nu \cong 15$ MHz, and a significant improvement of the cavity Q factor and coupling. The cavity quality factor changes from $Q \cong 1500 \pm 200$ for the loaded cavity in the normal state to $Q = 3000 \pm 300$ in the superconducting state (we note that the Q value of the unloaded cavity in $Q_0 = 4000 \pm 300$). An external magnetic field above 500 G has a significant effect on the coupling and the Q factor (due to low H_{c1}). Other microwave properties will be published elsewhere. We would like to emphasize, however, that the dramatic change in Q upon transition to the superconducting state for such a small filling factor may suggest that superconducting cavities can be constructed. In the past, superconducting cavities with a quality factor as high as $Q \cong 10^8$ were built and used for various applications.[9]

Generally speaking, the low-temperature spectra exhibit two types of signals: a low-field "superconducting" signal which appears below T_c for all the superconducting samples (Fig. 1) and an ESR signal which appears below 50 K for all our compounds (Fig. 2). Figure 1 exhibits the low-field signal at low temperatures. This signal is due to changes in the diamagnetic susceptibility $\Delta\chi_{\rm dia}$ upon transition from the Meissner state to the mixed state[10] (actually, Fig. 1 exhibits the first derivative of such a transition due to the phase-sensitive detection). The relative intensities of the signals in Fig. 1 were very carefully determined by taking into consideration the cavity Q factor and the spectrometer sensitivity. Nevertheless, we estimate a possible error up to 100%. Note that the signal intensities in Fig. 1 are directly related to the percentage of the Meissner effect. For instance, the signal intensity is the largest for $YBa_2Cu_3O_6S$, consistent with the large Meissner effect of this compound as measured by low-field magnetization (see inset of Fig. 1). The minima in Fig. 1 yield directly the lower critical field H_{c1}. Figure 3 is a plot of H_{c1} versus temperature for the various samples. It should be emphasized that H_{c1} was measured in a consistent way by increasing the temperatures for all our samples. No attempts were made to measure possible irreversibilities by first magnetic field cooling.

Figure 2 exhibits the ESR spectra for the various samples at low temperatures. The intensities are normalized to allow a comparison. As seen, the ESR intensity significantly varies from sample to sample, being the largest for $YBa_2Cu_3O_7$(quenched), which is not superconducting. The signal intensity of this sample is larger by several orders of magnitude than that associated with the superconducting $YBa_2Cu_3O_6S$ sample. Note also that the linewidth and the field for resonance vary from sample to sample. The linewidth is largest for $YBa_2Cu_3O_7$ (quenched) (Fig. 2). The field for resonance and the ESR linewidth for the various samples are plotted as a function of temperature in Fig. 4. It can be seen that the field for resonance and the linewidth of $YBa_2Cu_3O_6S$ are almost temperature independent, while those of the other samples (and particularly the quenched sample), are strongly temperature dependent (Fig. 4). The ESR signal intensity I increases dramatically with decreasing temperature roughly as $I \sim \exp(-T/T_0)$; T_0 varies between 5 and 11 K for the various samples.[7] This is consistent with the first observation of Shaltiel *et al.*[7] This feature is not understood at present.

The variation of the ESR field for resonance with temperature (Fig. 4), as observed, for instance, in $YBa_2Cu_3O_7$(quenched), is probably associated with spin-spin interaction effects. These interactions produce an internal field which shifts the resonance line towards lower fields (Fig. 4), suggesting a *ferromagnetic type of interaction*. The near independence on temperature of the field

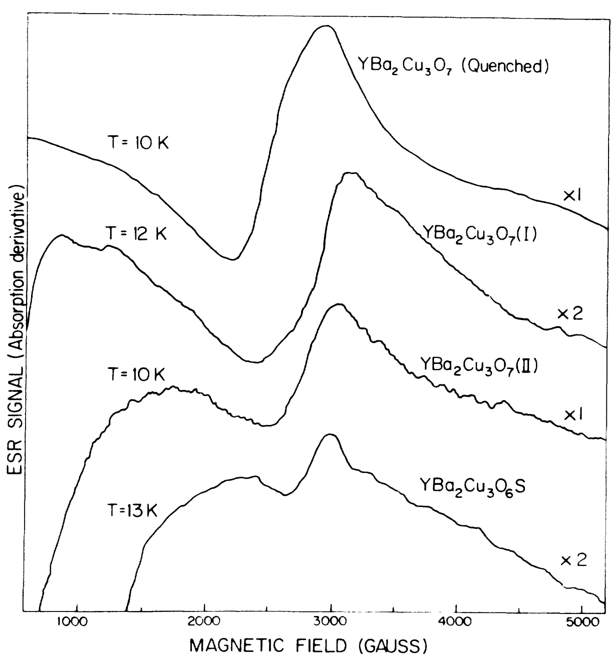

FIG. 2. ESR signals (absorption derivatives) at low temperatures. Note the variation of the signal intensities, which are largest for the quenched sample and smallest for $YBa_2Cu_3O_6S$.

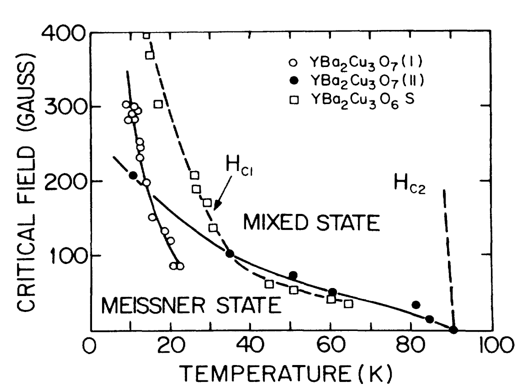

FIG. 3. The critical field H_{c1} vs temperature. Solid and dashed lines are visual aids.

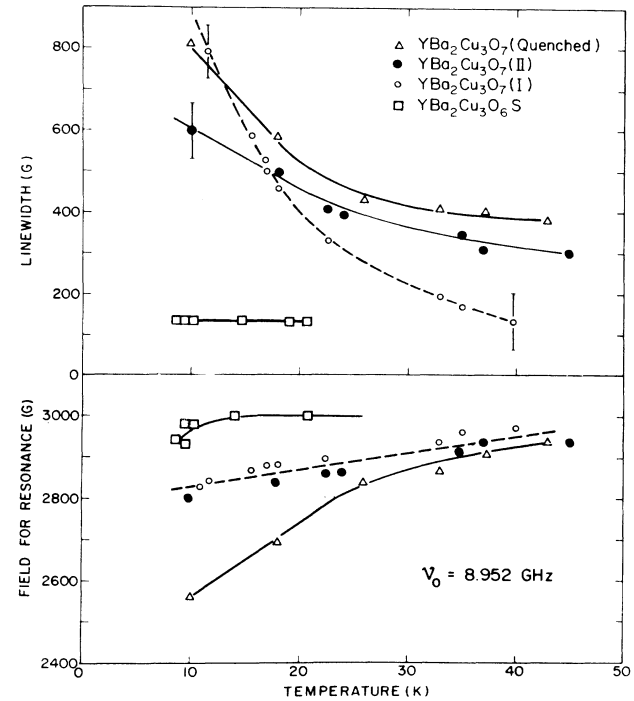

FIG. 4. ESR linewidth and field for resonance as a function of temperature. Solid and dashed lines are visual aids.

for resonance and linewidth for the case of $YBa_2Cu_3O_6S$, suggests, therefore, the absence of strong interaction effects. This is consistent with the relatively small ESR intensity for $YBa_2Cu_3O_6S$ and allows an estimation of the *true* g value to be $g = 2.05 \pm 0.01$. This roughly agrees with the g value of localized d hole on Cu^{2+}.[7,11] The very similar temperature dependence of the ESR intensity suggests that the ESR lines originate with the same type of localized holes in all our samples. The observation of a strong resonance in the quenched sample (which is not a superconductor) perhaps suggests that the localized holes may originate from regions in the samples which are not superconducting. If we write the stoichiometry of our $YBa_2Cu_3O_7$ as[3]

$$Y^{3+}(Ba^{2+})_2(Cu_{1-\delta}{}^{2+}Cu_{\delta}{}^{3+})_3(O^{2-})_{9-y} ,$$

the condition for charge neutrality requires $2y = 5 - 3\delta$ (Ref. 3) and for our case $y = 2$ and $\delta \approx 0.33$. Kamimura[3] has suggested that the d hole in Cu^{2+} (d^9 configuration) occupies the $|x^2 - y^2\rangle$ orbitals. The extra hole in Cu^{3+} (d^8 configuration) occupies a $|3z^2 - r^2\rangle$ orbital due to the Jahn-Teller distortion. In the normal state these d holes are mostly mobile.[3] Superconductivity is associated with pairing of the d holes (possibly via bipolarons[3] or other mechanisms[12]). Our results, however, suggest the formation of localized d holes, probably in nonsuperconducting regions of the samples which give rise to the ESR intensity.

Certainly, a most interesting feature of our results is the reverse relationship between the ESR signal intensity and the "superconducting" signal intensity. Figures 1 and 2 suggest that the stronger the ESR intensity, the weaker the superconducting signal and vice versa. This may suggest competition between (antiferromagnetic) pairing[3] and magnetic fluctuations.

Schmeltzer[4] has suggested recently a model which considered antiferromagnetic exchange interactions in the d hole liquid. He has shown that the free energy of the system can be separated into two terms: a term which yields superconductivity, i.e., Bose-like condensation at the zero wave vector ($q = 0$) and a term due to antiferromagnetic fluctuations at $q \sim \pi/a$. He then argued that at high temperatures (~ 100 K) the magnetic fluctuations may be completely suppressed, probably due to disorder which is always present in these oxides. In the framework of this model, magnetic fluctuations are important at low temperatures and there is a competition between superconductivity and magnetism.

The critical field H_{c1} versus temperature indicates two different slopes at high and low temperatures. The upward inflection occurs around $T \cong 30$ K. Such an inflection occurs also in multilayered superconductors due to the low dimensionality[13] and Josephson coupled multilayers.[14] It may occur also in granular materials[15] or in the presence of two condensation temperatures (probably due to the two-band model). However, much work is needed before definite statements can be made. From Fig. 3, we find for $YBa_2Cu_3O_6S$ $H_{c1}(0) \cong 600$ G by extrapolation. Using the relations $H_{c1} = (H_c \ln\kappa)/1.414\kappa$ and $H_{c2} = 1.414\kappa\, H_c$ (Refs. 16 and 17), where H_c is the thermodynamical critical field and κ is the ratio of penetration depth to coherent length, we estimate $H_{c2}(0) = 1.38 \times 10^6$ G and $H_c = 13$ kG using $\kappa \approx 70$.[16,17] This value is close to previous estimates.[16,18]

We conclude our paper as follows. Superconductivity in $YBa_2Cu_3O_{7-x}S_x$ ($x = 0,1$) is probably due to pairing of mobile d holes. However, in the preparation process, the formation of localized d holes cannot be completely eliminated. These localized d holes give rise to an ESR signal at low temperatures; its shift and linewidth suggest ferromagnetic interaction. Such an interaction can destroy superconductivity. Indeed, our experimental results suggest that samples which exhibit a strong ESR signal, are less superconductive and vice versa. Thus, a delicate balance exists between superconductivity and magnetism which can be controlled chemically by heat treatment and disorder. The large Meissner effect in $YBa_2Cu_3O_6S$ is partially related, we believe, to the relatively small number of localized d holes. However, the exact role of the sulfur atom is not completely clear.

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