Local magnetic order in superconducting $YBa_2(Cu_{1-x}M_x)_3O_7$ (M=Co,Fe)

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We have examined the local magnetic order which is introduced into $YBa_2Cu_3O_7$ by substituting low levels (1–4 %) of Co or Fe. The order is evidenced through the appearance of an internal field on the spin of $^{170}Yb^{3+}$ Mössbauer probes diluted at the Y^{3+} sites. Low substitution levels only marginally influence the superconducting properties, yet introduce local magnetic order over the whole sample volume. The local order concerns the Cu sublattices and fluctuates with rates that depend on the substituted ion, its concentration, and the temperature. [S0163-1829(97)01737-2]

In the cuprate superconductors, Cu-based magnetism and superconductivity both depend strongly on the hole density, and the interrelation between the two states remains a center of interest. The evolution of the superconducting and magnetic properties is well evidenced by the $YBa_2Cu_3O_x$ system, which displays a number of the generic properties of the cuprates. Here the hole and condensate densities are governed by the oxygen level and its spatial distribution. In the fully oxidized ($x\sim7$) superconducting samples ($T_c\sim92$ K), neutron scattering measurements evidence spin excitations above a gap of the order of $3.5T_c$ (Refs. 1 and 2) and no excitations at low energies.[3] In the fully deoxidized ($x\sim6$) nonsuperconducting samples, neutron diffraction measurements[4,5] show that the Cu(2) of the Cu-O bilayers orders antiferromagnetically ($T_N\sim400$ K). Increasing the oxygen level up from the fully deoxidized state leads to a reduction in the size of the long-range correlated moments, to reductions of the correlation lengths, and to the introduction of temperature-dependent fluctuations of the correlated moments. Superconductivity is introduced and magnetic ordering disappears when the oxygen level is increased through the range $x\sim6.4$ to ~6.6, where a gap opens in the spin excitation spectrum with a size which rescales with the value of T_c.[1,6] In the intermediate oxygen level range, where T_c remains relatively low, phase separation into hole-rich and hole-poor regions can occur and cluster spin-glass magnetic order continues to exist in parts of the sample up to sample-averaged oxygen levels of $x\sim6.55$.[7–9] A crossover from a magnetically ordered Cu(2) state to a superconducting state also occurs when Y is substituted for Pr in $PrBa_2Cu_3O_7$,[10] and at intermediate substitution levels, the samples show superconductivity, with relatively low T_c values, and spin-glass magnetic order. This coexistence again probably arises through phase separation. For the above samples, when T_c remains high and the whole sample volume is superconducting, Cu(2) magnetic order is absent.

We present results which show that the substitution of low levels of Co or Fe into $YBa_2Cu_3O_7$ only slightly reduces T_c below the optimum value, yet introduces locally magnetically ordered Cu moments, with spin-glass-like behavior, over the whole sample volume. To detect the static or fluctuating ordered moments, we examine the static or fluctuating internal field they produce on paramagnetic $^{170}Yb^{3+}$ Mössbauer probes diluted at the Y^{3+} sites.[11] The measured signal comprises a contribution from each of the probes in the sample. The present approach is analogous to that followed by the muon-spin rotation-relaxation (μSR) technique, which has been extensively used to study magnetic ordering in the cuprates,[8,10] where the static or fluctuating internal fields are detected on implanted interstitial positive muon probes.

The $^{170}Yb^{3+}$ probes are nonintrusive in that their presence has essentially no influence on superconductivity or on any Cu-based magnetic order. They are randomly distributed at the Y^{3+} sites and thus provide information on the local magnetic properties over the whole sample volume. [That the distribution is random is shown by the Mössbauer analysis: In addition to the main spectrum due to isolated Yb^{3+}, used to extract information concerning the internal fields, there is a second, minor spectrum which is identified with Yb^{3+} dimers. The relative intensity of this spectrum (for $Yb^{3+}/Y^{3+}=0.025$ it is $\sim25\%$) roughly scales with the Yb^{3+} concentration, so showing that the probes are distributed randomly.] When substituted into $YBa_2Cu_3O_7$, the Yb^{3+} ion has a $S'=1/2$ ground state, well separated from the excited crystal field levels. For the isolated Yb^{3+} ions in the studied temperature range of up to 60 K, there are no fluctuations between the ground-state sublevels on the Mössbauer frequency scale ($\sim5\times10^9$ s^{-1}), which is defined by the Yb^{3+} hyperfine interaction.[11] In this case, the Mössbauer absorption is interpreted with the standard slow paramagnetic relaxation Hamiltonian

$$\mathcal{H}=\vec{S}'\cdot\mathbf{A}\cdot\vec{I}-\beta\vec{H}\cdot\mathbf{g}\cdot\vec{S}'. \quad (1)$$

The first term in Eq. (1) is the hyperfine interaction with **A** the hyperfine tensor and the second a Zeeman term where the field $\vec{H}$, if present, acts on the Yb^{3+} effective spin with **g** its effective g tensor. The Mössbauer transitions take place between the two ensembles of ''static'' electronuclear Breit-Rabi levels formed, according to Eq. (1), by combining $S'=1/2$, respectively, with the ground ($I_g=0$) and excited ($I_{ex}=2$) nuclear states linked by the ^{170}Yb Mössbauer transition. In the absence of any internal field (the case of unsubstituted $YBa_2Cu_3O_7$), the line shapes are governed only by the hyperfine interaction. When the line shape analysis evidences the presence of an internal field on the $^{170}Yb^{3+}$

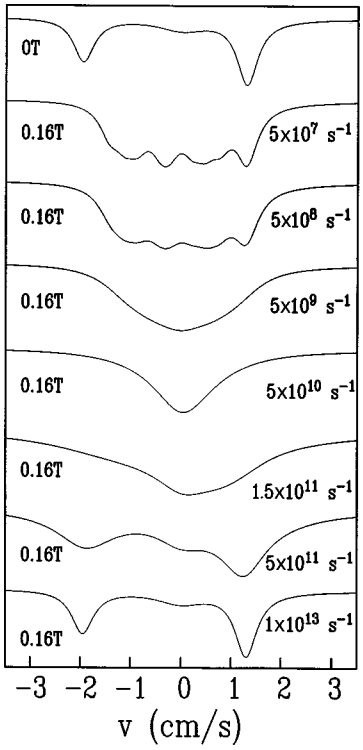

FIG. 1. Simulated Mössbauer line shapes with the hyperfine parameters and g values for $^{170}Yb^{3+}$ in $YBa_2Cu_3O_x$. Topmost: no internal field on the Yb^{3+}. For the remainder, an internal field of 0.16 T is present and fluctuates at the rates shown. When the rate is below 1.0×10^8 s^{-1}, the field is ''static.'' When the rate is high enough (bottommost), the line shape returns to that for no internal field (topmost). An appropriate subspectrum, centered at $v=0$ cm/s, due to the Yb^{3+} dimers, observed experimentally is also included.

probe, then this is an indication of magnetic ordering in the vicinity of the probe. The detected internal field is attributed to the combined influence of the molecular and dipolar fields arising from the neighboring ordered moments.[11]

The sensitivity of the technique is illustrated in Fig. 1 which presents line shapes simulated with the appropriate hyperfine parameters and g values for Yb^{3+}.[11] There is a marked difference between the case for no internal field (corresponding to unsubstituted $YBa_2Cu_3O_7$) and for the case of an internal field of 0.16 T which is representative of the experimental values to be encountered below. Figure 1 also illustrates a second feature of the present technique: The line shapes depend on the fluctuation rate of the internal field, which can thus be followed over a fairly wide range. Figure 1 shows the evolution as a function of the fluctuation frequency of the field (of size 0.16 T) obtained using Eq. (1) with the line shapes calculated by allowing the field to fluctuate stochastically.[11,12] The evolution through the three characteristic line shapes (initially split, then collapsed, and finally resplit) identifies, respectively, ''static'' magnetic order, fluctuating magnetic order with an average fluctuation rate near the middle of the accessible frequency window, and fluctuating order with rates above the window. For this last case, the Zeeman term no longer influences the line shape because it is ''motionally narrowed.'' The present technique has been used previously to examine the local magnetic order in $YBa_2Cu_3O_x$ (Ref. 11) and in $Y_{1-x}Pr_xBa_2Cu_3O_7$ (Ref. 13). The results are in basic agreement with specific features established by neutron[4,5,7] and μSR (Refs. 10 and 14) measurements.

Single-phase polycrystalline samples of $Y_{0.975}{}^{170}Yb_{0.025}Ba_2(Cu_{1-x}M_x)_3O_7$ ($M=$Co,Fe, $x=0.01-0.04$) were made using the standard carbonate method with five intermediate grindings to ensure homogeneity and a final ambiant pressure oxygen anneal to optimize T_c. The Co and Fe enter the chain sites (uniquely for Co, predominantly for Fe). The real oxygen level of the samples varies slightly with the substitution level, but is written here simply as 7. The substitution of Fe or Co leads to an underdoped state[15] and was found to lower the superconducting transition temperatures by amounts in agreement with the literature.[16] Our susceptibility measurements show essentially unchanged Meissner and screening fractions. In Fig. 2 we present the ^{170}Yb Mössbauer line shapes ($I_g=0$, $I_{ex}=2$, $E_\gamma=84$ keV, 1 mm/s=68 MHz, source Tm^*B_{12}) observed in superconducting $YBa_2(Cu_{1-x}M_x)_3O_7$ with $M_x=Co_{0.02}$

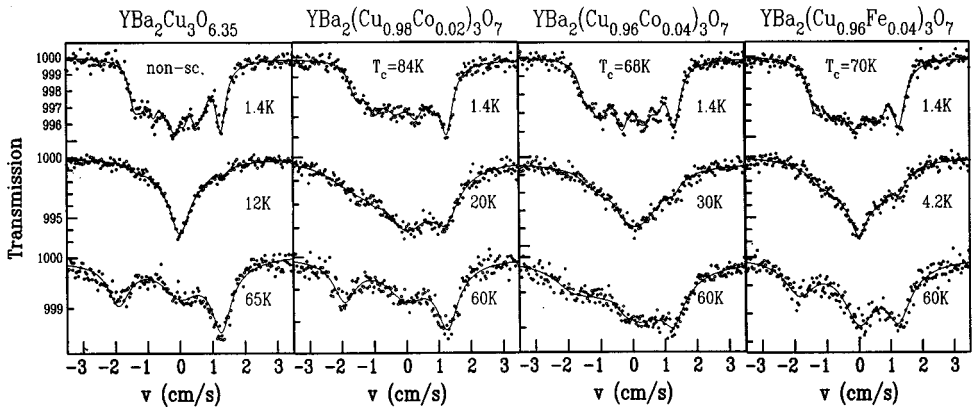

FIG. 2. Mössbauer absorption of $^{170}Yb^{3+}$ probes diluted into nonsuperconducting $YBa_2Cu_3O_{6.35}$ and into superconducting $YBa_2(Cu_{0.98}Co_{0.02})_3O_7$, $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$, and $YBa_2(Cu_{0.96}Fe_{0.04})_3O_7$. At 1.4 K in each of the samples, magnetic order is evidenced through the presence of ''static'' internal fields on the spins of all the isolated probes. At higher temperatures, the absorption is fitted by allowing the fields to fluctuate and by including a distribution in the local rates. Each total line fit also includes a separate minor subspectrum due to Yb^{3+} dimers.

($T_c = 84$ K), $Co_{0.04}$ ($T_c = 68$ K), and $Fe_{0.04}$ ($T_c = 70$ K). Figure 2 also shows the line shapes observed in nonsuperconducting $YBa_2Cu_3O_{6.35}$.[11] All the experimental data for the isolated Yb^{3+} ions can be interpreted with the slow paramagnetic relaxation Hamiltonian of Eq. (1) with the field $\vec{H}$ ''static'' or fluctuating. Each line fit contains an appropriate minor contribution due to Yb^{3+} dimers. At 1.4 K in each of the samples, all of the isolated $^{170}Yb^{3+}$ probes experience a ''static'' field. (The line shapes are basically similar to those in Fig. 1 for rates below 1×10^8 s^{-1}.) For nonsuperconducting $YBa_2Cu_3O_{6.35}$ and superconducting $YBa_2(Cu_{0.96}Fe_{0.04})_3O_7$, the mean value of the local field is ~ 0.22 T, for $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$ it is ~ 0.14 T, and for $YBa_2(Cu_{0.98}Co_{0.02})_3O_7 \sim 0.08$ T. In all cases the fields show a distribution in size of up to $\sim 30\%$ of the mean value. These ''static'' fields can only arise from ''static'' correlated magnetic moments in the vicinity of each probe. For Co substitution levels as low as 2%, we find that (short-range correlated) magnetic order is visible over the whole sample volume. For the 1% Co level at 1.4 K, a field is detected on the majority of the probes, showing that local magnetic order exists over the major part of the sample volume. For the 1% Fe level at 1.4 K, local magnetic order is also detected over part of the sample.

When the temperature is increased, the spectral line shape for each of the samples first tends to collapse and then to split again. This behavior is analogous to that shown in Fig. 1 and is due to the thermally driven increases in the fluctuation rates of the fields acting on the spins of the $^{170}Yb^{3+}$ probes. In each of the samples we detect the coexistence of quite different local fluctuation rates and we find that the average fluctuation rate slows down as the temperature is lowered. This is symptomatic of spin-glass behavior. The existence of a wide distribution in the local rates is clearly seen, for example, for the $YBa_2(Cu_{0.98}Co_{0.02})_3O_7$ sample where the line shape does not collapse to a single line at a single intermediate temperature. Figure 3 presents the thermal dependence of the average fluctuation rates. The vertical bars represent the approximate range of the rates that are simultaneously present.

As shown in Fig. 3, the upper threshold of the accessible frequency window changes slightly (it depends on the size of the field). For $YBa_2(Cu_{0.98}Co_{0.02})_3O_7$, the threshold is exceeded on average below 40 K, whereas for $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$, the average rate is still within the window at 60 K. For $YBa_2(Cu_{0.96}Fe_{0.04})_3O_7$, the threshold is exceeded on average near 20 K, and at 60 K, some of the rates are within the window and some are above the upper threshold. The fluctuation rates show a weaker thermal variation for $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$ than for $YBa_2(Cu_{0.98}Co_{0.02})_3O_7$ and a very much weaker variation for $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$ than for $YBa_2(Cu_{0.96}Fe_{0.04})_3O_7$. The substitution of Co rather than Fe thus leads to a more strongly coupled system which is less easily set fluctuating by increases in temperature. Increasing the substitution level also leads to a more strongly coupled system. The differences between the details of the local magnetic ordering introduced by the Co and Fe substitutions probably stem from the different single-ion magnetic moments and anisotropies of the two ions. Further details concerning the magnetic properties reported here are expected from planned μSR and neutron scattering measurements.

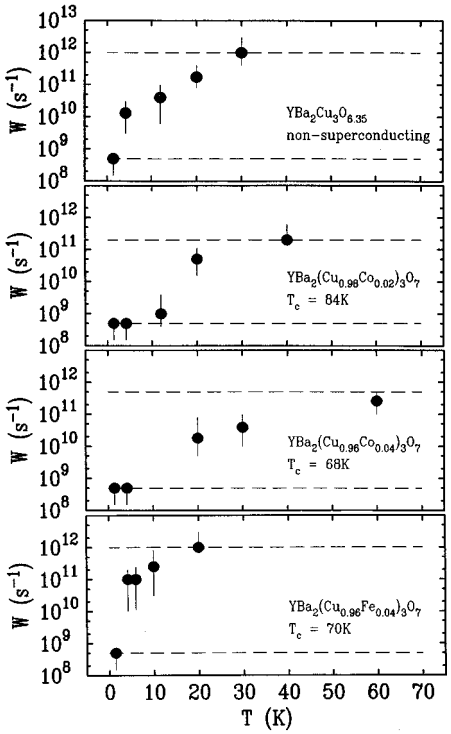

FIG. 3. Temperature dependence of the average fluctuation rate of the internal field acting on the spin of isolated $^{170}Yb^{3+}$ Mössbauer probes in nonsuperconducting $YBa_2Cu_3O_{6.35}$ and in superconducting $YBa_2(Cu_{0.98}Co_{0.02})_3O_7$, $YBa_2(Cu_{0.96}Co_{0.04})_3O_7$, and $YBa_2(Cu_{0.96}Fe_{0.04})_3O_7$. The dashed lines indicate the accessible frequency window with the upper limit depending on the observed strength of the field. The fluctuation rates of the field correspond to the fluctuation rates of the short-range correlated moments which are at the origin of the field.

We now consider the possible origins of the internal field, focusing chiefly on the case of the Co substitutions. The dipolar fields on the Yb^{3+} spin coming from assumed isolated and blocked Co moments are too small to account for the observed fields: Assuming Co moments of $2\mu_B$, the dipolar field will show a wide distribution with an upper limit of only 14 mT. In fact, the substituted Co, which occupies only the Cu(1) site and pulls in extra oxygen, forms dimers and clusters.[17] These clusters will presumably be magnetically coupled at low temperatures and the dipolar fields they create will still show a wide distribution with an average value much lower than the measured value. Rather, we identify the observed fields as coming from locally ordered Cu moments which themselves are introduced by substituting Co. For 2% Co (the lowest level which introduces magnetic order over the whole sample volume) and assuming a random distribution of Co dimers, these would be separated on average by roughly six lattice spacings (a or b). That such low densities trigger local magnetic ordering over the whole sample indicates that the order must involve extensive long-range (oscillatory?) polarization of the Cu moments.

This long-range polarization will involve the Cu(1)-O chains into which the Co is substituted. However, the purely dipolar field coming from induced Cu(1) moments will not be large enough to account for the fields observed on the

Yb^{3+} which are sandwiched between the Cu(2)-O biplanes and are rather distant from the chains. Direct superexchange between the chain moments and the Yb^{3+} is also inoperative because the cations of the chains and the Yb^{3+} do not share a common oxygen neighbor. Cation-anion-anion-cation superexchange, passing through two intermediate oxygens, can exist,[18] but such interactions are not common. We suggest that the field produced on the Yb^{3+} contains a significant contribution coming from interactions with locally correlated Cu(2) moments which are also introduced by the substitution of Co. In this respect, we recall that in $YBa_2Cu_3O_6$, where only the Cu(2) carries ordered moments, the Yb^{3+} experiences internal fields of a size ($\sim$0.16 T) (Ref. 11) comparable to those observed here. Previous neutron diffraction measurements have shown that the low level substitutions into $YBa_2Cu_3O_7$ do not introduce long-range magnetic order[19] (although this becomes visible when the substitution level is high enough to remove superconductivity[20]) whereas Cu nuclear quadrupole resonance (NQR) measurements have evidenced some induced Cu moments and magnetic ordering.[21,22] Neutron time-of-flight measurements have shown that spin-glass-like freezing is present[23,24] with the freezing attributed to the blocking of the spin fluctuations of the substituted magnetic cations.

In conclusion, from measurements of the internal field appearing on paramagnetic $^{170}Yb^{3+}$ Mössbauer probes diluted at the Y^{3+} sites, we find that substituting low levels of Co or Fe into $YBa_2Cu_3O_7$, such that the T_c remains high, introduces spin-glass-like magnetic ordering over the whole sample volume. The correlated moments which develop with the Co/Fe substitutions concern the Cu(1) and Cu(2) sublattices. The local probe Mössbauer technique, as used here, is well suited to the study of the static or fluctuating magnetic order which can be identified even if the local correlations extend only over distances comparable to that of the unit cell. The present results indicate that in underdoped superconducting cuprates with high T_c values, it is possible for superconductivity and local Cu(2) magnetic order to coexist.

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