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Slow antiferromagnetic dynamics in the low temperature tetragonal phase of La\(_{2-x}\)Sr\(_x\)CuO\(_4\) as revealed by ESR of Gd spin probes

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Abstract

Measuring the ESR of Gd spin probes we have studied the magnetic properties of the copper oxide planes in the low temperature tetragonal (LTT) phase of Eu doped La\(_{2-x}\)Sr\(_x\)CuO\(_4\). The data give evidence that at particular levels of Sr and Eu doping the frequency of the antiferromagnetic fluctuations \(\omega_{sf}\) in the LTT phase dramatically decreases at low temperatures by almost three orders of magnitude. However, no static magnetic order has been found for \(T \geq 8\)K in contrast to the observation by neutron scattering of stripe ordering of spins below 50K in a Nd doped La\(_{2-x}\)Sr\(_x\)CuO\(_4\) single crystal. To our opinion static order in the Nd doped compound is induced due to the interaction between the Cu spins with the rare earth magnetic moments. Therefore, a really characteristic property of the magnetism in the LTT struc-
natural phase may be not static magnetic order at elevated temperatures but rather extremely slow antiferromagnetic dynamics.

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The structural phase transition in La$_{2-x}$Sr$_x$CuO$_4$ from the low temperature orthorhombic (LTO) phase to the low temperature tetragonal (LTT) phase [1,2] has recently attracted much attention. Neutron diffraction experiments on a non superconducting La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ single crystal show an unusual type of magnetic order below 50 K in the form of antiferromagnetic (AF) domains ('stripes') separated by walls in which holes are segregated [3]. It was argued that such stripe order is feasibly a result of pinning by particular direction of tilting of Cu–O octahedra in the LTT phase of dynamically correlated AF regions found earlier in superconducting La$_{2-x}$Sr$_x$CuO$_4$ [4]. Furthermore, this interpretation has been connected with an idea of a frustrated phase separation (see e.g. [5]) pointing at the importance of this observation for clarification of the nature of high temperature superconductivity (HTSC) [5,6].

In this Communication we present the first results of the systematic study of the magnetic properties of the LTT phase of La$_{2-x-y}$Eu$_y$Sr$_x$CuO$_4$ by means of ESR. As a spin probe in the ESR experiments a Gd$^{3+}$ ion which substitutes the rare earth (RE) site in the structure has been chosen. A simple qualitative analysis of the observed temperature dependence of the Gd$^{3+}$ ESR linewidth gives evidence that at certain concentrations of dopants the frequency of spin fluctuations in the CuO$_2$ planes with the LTT structure slows with lowering the temperature down to nearly $10^{10}$ sec$^{-1}$. However, within the temperature range of study ($8 \leq T \leq 300$ K) no signatures of a really static AF order have been observed in the samples investigated so far. This implies that in a frame of the stripe model spin correlations remain dynamic even in the LTT phase.

The polycrystalline samples of La$_{2-x}$Sr$_x$CuO$_4$ in which part of La ions was substituted by Eu$^{3+}$ (up to 12% relative to La) were prepared and characterized as described elsewhere [7]. Gd$^{3+}$ ions were added in amount of 1%. The role of Eu is to induce the transition to the LTT phase due to mismatch in ionic radii while hole concentration is tuned independently by Sr doping ($0.05 \leq x \leq 0.20$) [8]. In this respect the small percentage of Gd$^{3+}$ does not affect the relevant physical properties. Substitution by Eu instead of Nd was chosen mainly because Eu$^{3+}$ in its ground state possesses only Van–Vleck paramagnetism and the influence
on bulk susceptibility and ESR of thermally excited magnetic states lying 400 K above the ground state is much weaker in comparison to magnetic Nd$^{3+}$ ions and can be correctly subtracted \[9\]. Moreover, in the case of Eu substitution there is no influence of permanent magnetic moments at the RE sites on the magnetism of the CuO$_2$ planes.

Gd$^{3+}$ ESR spectra of $\text{La}_{1.99-x-y}\text{Sr}_x\text{Gd}_{0.01}\text{Eu}_y\text{CuO}_4$ measured at a frequency of 9.3 GHz show for all studied samples a fine structure due to the small splitting of the ground state multiplet $^8S_{7/2}$ of a Gd$^{3+}$ ion in the crystalline electrical field (see inset in Fig.1). The analysis of the spectra has been developed previously \[10,11\]. Typical temperature dependences of the width $\Delta H$ of the central component of the spectrum (encircled in inset of Fig.1) are shown in Fig.1. For $T > 80 - 100$ K $\Delta H$ increases linearly with temperature as $a + bT$. In agreement with our earlier findings \[11\] the slope $b = d(\Delta H)/dT$ increases with increasing the Sr (i.e. hole) concentration. At a fixed Sr content $b$ does not change significantly until the Eu concentration becomes higher than $\sim 8\%$. For these Eu contents $\Delta H$ increases due to relaxation via thermally excited magnetic states of Eu$^{3+}$ \[12\] which is appreciable for $T > 100$ K.

The remarkable feature of $\Delta H(T)$ is the qualitative change of its behavior in the low temperature region where a pronounced broadening of the Gd$^{3+}$ ESR spectrum is observed (see Fig.1). This effect was found to depend on both Sr and Eu content. In particular, at a fixed Sr concentration $x$ the broadening increases with increasing the Eu concentration $y$. The details of the doping dependence will be published separately \[13\]. Hereafter we focus on the low temperature $\Delta H(T)$ dependence of a single representative sample with the composition $\text{La}_{1.65}\text{Sr}_{0.1}\text{Gd}_{0.01}\text{Eu}_{0.24}\text{CuO}_4$, i.e. $x = 0.10$, $y = 0.24$. This compound is found to be in the non superconducting LTT phase below $\sim 130$ K \[8\]. For this sample the broadening of the Gd$^{3+}$ ESR linewidth is most pronounced and the observation of the ESR spectrum is not obscured by the large field dependent drift of the base line due to superconductivity.

As we have shown earlier \[11\], the linear temperature dependence of the Gd$^{3+}$ ESR linewidth in the normal state of the LTO phase of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a result of the Korringa
relaxation of Gd spins due to a small but finite exchange coupling of Gd$^{3+}$ ions to the mobile holes in the CuO$_2$ planes. As the Gd ion probes the spin dynamics of the copper oxide planes, a very pronounced deviation of $\Delta H(T)$ from linearity in the low temperature region observed in the LTT phase for the Eu doped sample is obviously due to strong changes of the spectrum of spin excitations in these key elements of the structure of HTSC compounds. At this point one should mention that a small deviation from the linear $\Delta H(T)$ dependence is noticeable even for Eu free sample (see Fig.1) which is nominally in the LTO phase. To our opinion, this is due to the fact that Gd spin probe itself creates an LTT distortion of the lattice in the nearest surrounding and therefore may locally modify the spin dynamics in the CuO$_2$ plane.

To evaluate the influence of the Cu spin dynamics on spin relaxation of Gd$^{3+}$ ions we first recall that the measured ESR linewidth of magnetic ions in metals is usually separated into two parts [14]:

$$\Delta H = (\Delta H)_0 + (\Delta H)_{\text{relax}}. \quad (1)$$

$(\Delta H)_0$ is the so called residual width which arises due to a number of static reasons such as inhomogeneities of the crystal field potential and local magnetic fields, hyperfine coupling, anisotropic spin–spin interactions, etc. The second, homogeneous, contribution $(\Delta H)_{\text{relax}}$, which is most important in our analysis of $\Delta H(T)$, is determined by the spin relaxation of an ion. For the case of the fine structure split ESR spectrum of a Gd$^{3+}$ ion the relaxation determined part of the width of an individual component is related to the spin relaxation rate $1/T_1$ as $(\Delta H)_{\text{relax}} = M^2(1/\gamma T_1)$, where $\gamma$ is the gyromagnetic ratio and $M$ is the matrix element of the corresponding Zeeman transition [14]. Computer modeling of the ESR spectra of Gd$^{3+}$ in La$_{2-x}$Sr$_x$CuO$_4$ gives a value $M^2 \approx 0.5$ for the component of our interest. Thus, the Gd spin relaxation rate reads:

$$\left(\frac{1}{T_1}\right)^{\text{Gd}} = \frac{\gamma}{M^2}[\Delta H - (\Delta H)_0]. \quad (2)$$

Assuming $(\Delta H)_0$ to be equal to the parameter $a$ of the high temperature linear fit $a + bT$
of the $\Delta H(T)$ dependence (see Fig.1), we plot in inset of Fig.2 the dependence of $(1/T_1)^{Gd}$ versus temperature for the sample with $x = 0.10, y = 0.24$.

Similar to the general expression of the nuclear relaxation rate \[\text{[15]},\] the spin relaxation of the Gd$^{3+}$ ions due to their coupling with the CuO$_2$ planes can be written in terms of the dynamic susceptibility of the planes $\chi''(q, \omega)$ as:

$$\frac{1}{T_1} = \frac{kT \cdot J_{Gd-Cu}^2}{(g_{Cu} \mu_B \hbar)^2} \lim_{\omega \to 0} \sum_q f(q) \frac{\chi''(q, \omega)}{\omega}.$$  \hspace{1cm} (3)

Here $J_{Gd-Cu}$ is a coupling constant which determines the strength of the exchange interaction between Gd and Cu spins, $g_{Cu}$ is the g–factor of Cu, and $f(q)$ is a geometrical form factor. However, $\chi''(q, \omega)$ in the layered cuprates is described differently in various theoretical approaches. This makes a quantitative interpretation of the data model dependent as will be discussed in a separate publication \[\text{[13]}\]. Fortunately, as we shall see below, a considerable qualitative insight into the low frequency spin dynamics in Eu doped La$_{2-x}$Sr$_x$CuO$_4$ can be already provided if we rewrite Eq.3 in a simplified form:

$$\frac{1}{T_1} \sim \frac{k \cdot J_{Gd-Cu}^2}{(g_{Cu} \mu_B \hbar)^2} \chi_0 \cdot \frac{T}{\omega_{sf}},$$  \hspace{1cm} (4)

where $\chi_0$ is the measured static susceptibility and $\omega_{sf}$ is the frequency of the spin fluctuations in the CuO$_2$ plane. Then, combining (4) and (3) we obtain:

$$\omega_{sf} \sim \frac{k \cdot J_{Gd-Cu}^2 M^2 \chi_0}{(g_{Cu} \mu_B \hbar)^2} \cdot \frac{T}{\Delta H - (\Delta H)_0}. $$  \hspace{1cm} (5)

To extract the values of $\omega_{sf}$ from the experimental data using (5) one has to know $J_{Gd-Cu}$ and $\chi_0$. An estimate of the strength of the rare earth Cu exchange coupling in the hole doped lanthanum copper oxide can be obtained from recent specific heat measurements of La$_{2-x-y}$Nd$_y$Sr$_x$CuO$_4$ which show for samples with suppressed superconductivity in the LTT phase a Schottky anomaly at low temperatures \[\text{[16]}\]. It can be attributed to the splitting of the ground state Kramers doublet of Nd$^{3+}$ due to slowly fluctuating or even static magnetic field $H_{int} \sim J_{RE-Cu} < \mu_{Cu} >$ of the order of 1 T transferred from the Cu spin lattice. Similar low temperature specific heat has also been observed in Gd doped La$_{2-x}$Sr$_x$CuO$_4$ samples with
the LTT structure [17]. Although in this case the interpretation of the Schottky anomaly
is more complicated due to the crystalline field fine structure splitting of the ground state
multiplet of the Gd$^{3+}$ ion, the estimate gives a similar value of the transferred magnetic field
at the RE site [18]. Taking the value of $<\mu_{\text{Cu}}>$ ≃ 0.5$\mu_{\text{B}}$ we obtain $J_{\text{RE-Cu}} \sim 5$ K.

Measurements of the static susceptibility on samples with similar stoichiometry but
without Gd show that $\chi_0$ changes with temperature not more than within a factor of
two. Therefore, for the following estimates it can be taken as constant with a value
$\chi_0 \approx 2 \cdot 10^{-4}$ emu/mole.

With these values of the exchange constant and static susceptibility we plot in Fig.2 the
temperature dependence of the spin fluctuation frequency evaluated from the experimental
data according to (5). As it can be seen from this Figure, $\omega_{\text{sf}}$ is temperature independent
above $\sim 75$ K. Although the obtained energy scale of these fluctuations $\hbar \omega_{\text{sf}} \approx 40$ K is
consistent with that probed in the NMR experiments on La$_{2-x}$Sr$_x$CuO$_4$ (see e.g., the analysis
in Ref. [19]), its value is, of course, sensitive to the choice of parameters in (5). However,
most important is that the temperature dependence of $\omega_{\text{sf}}$ presented in Fig.2 demonstrates
a qualitative change of the spin dynamics in the LTT phase at low temperatures. A steep
decrease of the fluctuation frequency below $\sim 70$ K by more than two orders of magnitude
points at a dramatic slowing of spin fluctuations in the CuO$_2$ planes with the LTT structure.
Such slowing of spin dynamics has a profound effect on the spin relaxation of Gd ions
leading to strong enhancement of $(1/T_1)^{\text{Gd}}$ and, consequently, to the experimentally observed
broadening of the Gd$^{3+}$ ESR line. A similar pronounced increase of $(1/T_1)$ of Cu nuclei
has been found for insulating La$_2$CuO$_4$ at temperatures approaching the Neel transition
temperature $T_N$ (see e.g., Ref. [20]). Although in the case of Eu doped La$_{2-x}$Sr$_x$CuO$_4$ a
strong tendency of the system to long range order at $T_N > 0$ at finite levels of hole doping
is evident from the data, a really static AF order is not found within the temperature
range of study. It would manifest itself in a narrowing and splitting of the Gd$^{3+}$ ESR
spectrum. Instead we observe in the LTT phase a very slow spin dynamics of AF correlated
regions. A quantitative evaluation of the spatial extent of these correlations (i.e. the AF
correlation length $\xi$) from the ESR data requires a particular model of spin relaxation in the cuprates. We defer such analysis to a further publication \[13\]. Here we only mention that the phenomenological model of the nuclear spin lattice relaxation developed by Millis, Monien and Pines (MMP) \[21\] seems to be applicable in our case \[22\]. In the frames of this model we arrive at the result that the correlation length $\xi$ in the hole doped CuO$_2$ planes with the LTT structure increases up to more that 100 lattice constants \[13\]. This should correspond to a dramatic decrease of the fluctuation frequency down to $\sim 10^{10}$ sec$^{-1}$ which matches well with our above made qualitative estimates (see Fig.2).

However, we emphasize that independent on a particular theoretical model the mere fact of the strong enhancement of the Gd$^{3+}$ spin relaxation upon lowering T shows a rapid slowing down of AF fluctuations and the absence of long range AF order at elevated temperatures. This is in contrast to the results of Tranquada et al. \[3\] whose neutron scattering data show static ordering of spins and charges in a La$_{1.48}$Nd$_{0.4}$Sr$_{0.12}$CuO$_4$ single crystal already below 50 K. This contradiction could be due to different characteristic energies of neutron diffraction and ESR experiments, respectively. The stripe correlations may be already static from the point of view of neutron scattering but, in fact, remain dynamic with a very slowly fluctuation frequency $\omega_{sf} \sim 10^{10} - 10^{11}$ sec$^{-1}$ from the point of view of ESR. However, in $\mu$SR experiments with characteristic frequency $\sim 10^6$ sec$^{-1}$ magnetic order in La$_{1.85-x}$Nd$_x$Sr$_{0.15}$CuO$_4$ has also been observed at rather high T $\sim 28$ K \[23\]. In contrast to this, first $\mu$SR results on the Eu doped system show no signs of magnetic order at elevated temperatures \[24\]. Hence, static magnetic order occurs possibly due to interaction of the Cu spin system with magnetic moments of Nd which obviously is not the case for Eu doped La$_{2-x}$Sr$_x$CuO$_4$.

Therefore, from our data we conclude that the main feature of magnetism of the LTT structural phase of the lanthanum strontium copper oxide and its possible relation to HTSC is not AF order but rather a dramatic slowing down of spin dynamics.

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FIGURES

FIG. 1. Temperature dependence of the width of the central component of the \( \text{Gd}^{3+} \) ESR spectrum of \( \text{La}_{1.99-x-y}\text{Sr}_x\text{Gd}_{0.01}\text{Eu}_y\text{CuO}_4 \) (symbols) together with corresponding linear fit \( a + bT \) of its high temperature part (straight lines): \( x = 0.10, \ y = 0.0 \) (\( \triangle \)), dash line \( 309 + 0.53T \); \( x = 0.17, \ y = 0.15 \) (\( \bigcirc \)), dash–dot line \( 272 + 0.98T \); \( x = 0.10, \ y = 0.24 \) (\( \blacksquare \)), solid line \( 395 + 0.5T \).

For the latter sample the contribution due to thermally excited magnetic states of \( \text{Eu}^{3+} \) lying above 400 K has been subtracted so that to keep the slope \( b \) the same as for the samples with lower Eu dopings. In inset the fine structure split ESR spectrum of \( \text{Gd}^{3+} \) is shown and the component which \( \Delta H(T) \) dependence is plotted in the main figure is encircled.

FIG. 2. Temperature dependence of the spin fluctuation frequency for the \( \text{La}_{1.65}\text{Sr}_{0.1}\text{Gd}_{0.01}-\text{Eu}_{0.24}\text{CuO}_4 \) sample estimated using (5). Inset: the Gd spin relaxation as a function of \( T \) extracted from the measured linewidth according to (2).
La$_{1.65}$Gd$_{0.01}$Eu$_{0.24}$Sr$_{0.1}$CuO$_4$

![Graph showing the relationship between temperature (T) and angular frequency ($\omega_{sf}$) for La$_{1.65}$Gd$_{0.01}$Eu$_{0.24}$Sr$_{0.1}$CuO$_4$.](image)

- Horizontal axis: Temperature (T), K
- Vertical axis: Angular frequency ($\omega_{sf}$), sec$^{-1}$

Inset graph:
- Vertical axis: $(1/T_1)$, $10^{10}$ sec$^{-1}$
- Horizontal axis: Temperature (T), K