Slow antiferromagnetic dynamics in the low-temperature tetragonal phase of $La_{2-x}Sr_xCuO_4$ as revealed by ESR of Gd spin probes

V. Kataev and B. Rameev
Kazan Institute for Technical Physics, Russian Academy of Sciences, 420029 Kazan, Russia

B. Büchner, M. Hücker, and R. Borowski
II. Physikalisches Institut, Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany

(Received 25 October 1996; revised manuscript received 12 November 1996)

Measuring the electron spin resonance 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 $La_{2-x}Sr_xCuO_4$. The data give evidence that at particular levels of Sr and Eu doping the frequency of the antiferromagnetic fluctuations ω_{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 $T \geqslant 8$ K, in contrast to the observation by neutron scattering of stripe ordering of spins below 50 K in a Nd-doped $La_{2-x}Sr_xCuO_4$ single crystal. In 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 characteristic property of the magnetism in the LTT structural phase may not be static magnetic order at elevated temperatures but rather extremely slow antiferromagnetic dynamics. [S0163-1829(97)50306-7]

The structural phase transition in $La_{2-x}Sr_xCuO_4$ 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 nonsuperconducting $La_{1.48}Nd_{0.4}Sr_{0.12}CuO_4$ 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 $La_{2-x}Sr_xCuO_4$.[4] Furthermore, this interpretation has been connected with an idea of a frustrated phase separation (see, e.g., Ref. 5) pointing at the importance of this observation for clarification of the nature of high-temperature superconductivity (HTSC).[5,6]

In this paper we present results of the study of the magnetic properties of the LTT phase of $La_{2-x-y}Eu_ySr_xCuO_4$ by means of electron spin resonance (ESR). As a spin probe in the ESR experiments a Gd^{3+} ion which substitutes for 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 ($8 \leqslant T \leqslant 300$ 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 $La_{2-x}Sr_xCuO_4$, in which part of La ions were substituted by Eu^{3+} (up to 12% relative to La), were prepared and characterized as described elsewhere.[7] Gd^{3+} ions were added in the 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 ($0.05 \leqslant x \leqslant 0.20$).[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 $La_{1.99-x-y}Sr_xGd_{0.01}Eu_yCuO_4$ 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 ΔH of the central component of the spectrum (encircled in inset of Fig. 1) are shown in Fig. 1. For $T > 80 - 100$ K, ΔH 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 ~8%. For these Eu contents ΔH 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

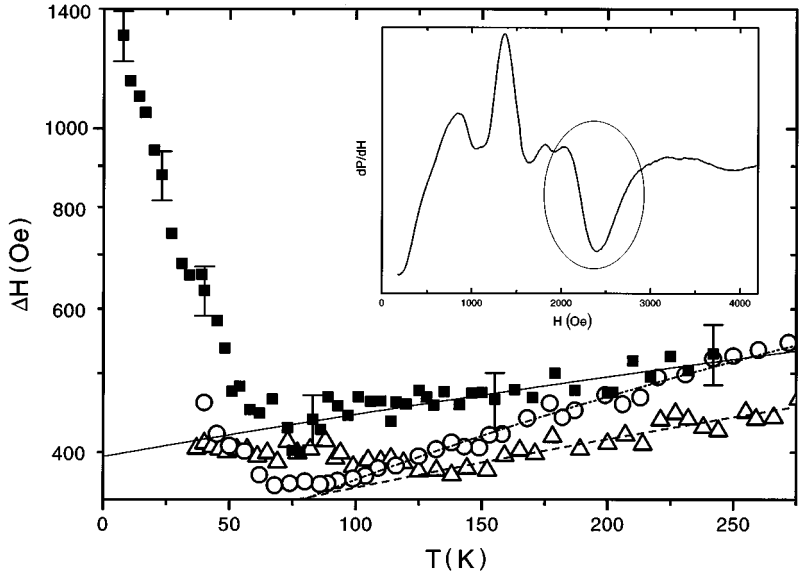

FIG. 1. Temperature dependence of the width of the central component of the Gd^{3+} ESR spectrum of $La_{1.99-x-y}Sr_xGd_{0.01}Eu_yCuO_4$ (symbols) together with corresponding linear fit $a+bT$ of its high-temperature part (straight lines): $x=0.10$, $y=0.0$ (Δ), dash line $309+0.53T$; $x=0.17$, $y=0.15$ (○), dash-dot line $272+0.98T$; $x=0.10$, $y=0.24$ (■), solid line $395+0.5T$. For the latter sample the contribution due to thermally excited magnetic states of Eu^{3+} lying above 400 K has been subtracted to keep the slope b the same as for the samples with lower Eu dopings. In the inset the fine-structure split ESR spectrum of Gd^{3+} is shown and the component for which $\Delta H(T)$ dependence is plotted in the main figure is encircled.

separately.[13] Hereafter we focus on the low-temperature $\Delta H(T)$ dependence of a single representative sample with the composition $La_{1.65}Sr_{0.1}Gd_{0.01}Eu_{0.24}CuO_4$, i.e., $x=0.10$, $y=0.24$. This compound is found to be in the nonsuperconducting LTT phase below ~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 $La_{2-x}Sr_xCuO_4$ 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 the Eu-free sample (see Fig. 1) which is nominally in the LTO phase. In our opinion, this is due to the fact that the Gd spin probe itself creates an LTT distortion of the lattice in the nearest surroundings 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]

$$\Delta H=(\Delta H)_0+(\Delta H)_{\mathrm{relax}}. \tag{1}$$

$(\Delta H)_0$ 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 $(\Delta H)_{\mathrm{relax}}$, 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 $(\Delta H)_{\mathrm{relax}}=M^2(1/\gamma T_1)$, where γ 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 $La_{2-x}Sr_xCuO_4$ gives a value $M^2\approx 0.5$ for the component of our interest. Thus, the Gd spin-relaxation rate reads

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

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 the inset of Fig. 2 the dependence of $(1/T_1)^{\mathrm{Gd}}$ versus temperature for the sample with $x=0.10$, $y=0.24$.

Similar to the general expression of the nuclear relaxation rate,[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 $\chi''(\mathbf{q},\omega)$ as

$$\frac{1}{T_1}=\frac{kTJ^2_{\mathrm{Gd\text{-}Cu}}}{(g_{\mathrm{Cu}}\mu_{\mathrm{B}}\hbar)^2}\lim_{\omega\to 0}\sum_{\mathbf{q}} f(\mathbf{q})\,\frac{\chi''(\mathbf{q},\omega)}{\omega}. \tag{3}$$

Here $J_{\mathrm{Gd\text{-}Cu}}$ 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 $f(\mathbf{q})$ is a geometrical form factor. However, $\chi''(\mathbf{q},\omega)$ in the layered cuprates is described differently in various theoretical approaches. This

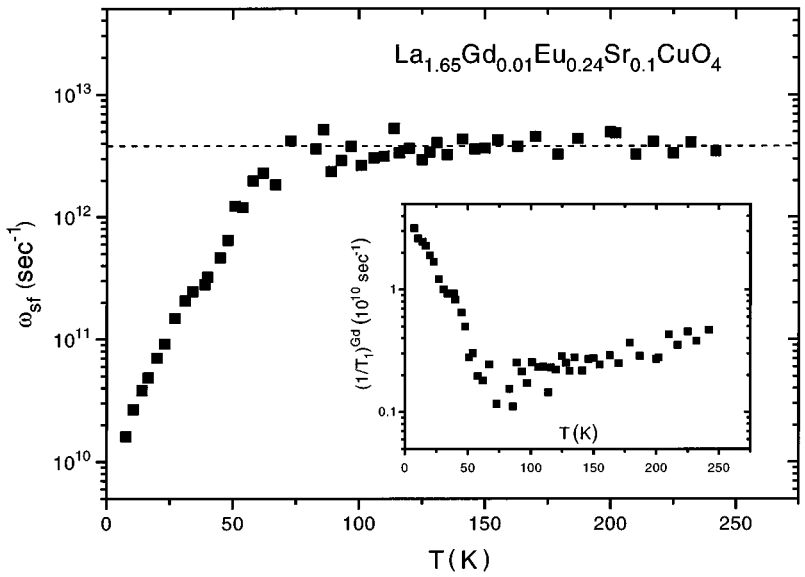

FIG. 2. Temperature dependence of the spin-fluctuation frequency for the $La_{1.65}Sr_{0.1}Gd_{0.01}Eu_{0.24}CuO_4$ sample estimated using Eq. (5). Inset: the Gd spin relaxation as a function of T extracted from the measured linewidth according to Eq. (2).

makes a quantitative interpretation of the data model dependent, as will be discussed in a separate publication.[13] Fortunately, as we shall see below, a considerable qualitative insight into the low-frequency spin dynamics in Eu-doped $La_{2-x}Sr_xCuO_4$ can be already provided if we rewrite Eq. (3) in a simplified form:

$$\frac{1}{T_1} \sim \frac{kJ_{\text{Gd-Cu}}^2}{(g_{\text{Cu}}\mu_{\text{B}}\hbar)^2}\,\chi_0\,\frac{T}{\omega_{\text{sf}}}, \tag{4}$$

where χ_0 is the measured static susceptibility and ω_{sf} is the frequency of the spin fluctuations in the CuO_2 plane. Then, combining Eqs. (2) and (4) we obtain

$$\omega_{\text{sf}} \sim \frac{kJ_{\text{Gd-Cu}}^2 M^2 \chi_0}{(g_{\text{Cu}}\mu_{\text{B}}\hbar)^2\gamma}\,\frac{T}{\Delta H-(\Delta H)_0}\,. \tag{5}$$

To extract the values of ω_{sf} from the experimental data using Eq. (5) one has to know $J_{\text{Gd-Cu}}$ and χ_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 $La_{2-x-y}Nd_ySr_xCuO_4$ which show for samples with suppressed superconductivity in the LTT phase a Schottky anomaly at low temperatures.[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 $H_{\text{int}} \sim J_{\text{RE-Cu}}\langle\mu_{\text{Cu}}\rangle$ of the order of 1 T transferred from the Cu spin lattice. Similar low-temperature specific heat has also been observed in Gd-doped $La_{2-x}Sr_xCuO_4$ 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 $\langle\mu_{\text{Cu}}\rangle \simeq 0.5\mu_{\text{B}}$ we obtain $J_{\text{RE-Cu}} \sim 5$ K.

Measurements of the static susceptibility on samples with similar stoichiometry but without Gd show that χ_0 changes with temperature not more than within a factor of 2. Therefore, for the following estimates it can be taken as constant with a value $\chi_0 \approx 2\times10^{-4}$ 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 Eq. (5). As can be seen from Fig. 2, ω_{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 $La_{2-x}Sr_xCuO_4$ (see, e.g., the analysis in Ref. 19), its value is, of course, sensitive to the choice of parameters in Eq. (5). However, most important is that the temperature dependence of ω_{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_2CuO_4 at temperatures approaching the Néel transition temperature T_N (see, e.g., Ref. 20). Although in the case of Eu-doped $La_{2-x}Sr_xCuO_4$, 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 ξ) from the ESR data requires a particular model of spin relaxation in the cuprates. Results of such analysis will be published elsewhere.[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 ξ in the hole-doped CuO_2 planes with the LTT structure increases up to more than 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-presented qualitative estimates (see Fig. 2).

However, we emphasize that independent of 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 slow fluctuation frequency $\omega_{sf} \sim 10^{10}-10^{11}$ sec^{-1} from the point of view of ESR. However, in muon spin relaxation (μSR) experiments with characteristic frequency $\sim 10^6$ sec^{-1}, magnetic order in $La_{1.85-x}Nd_xSr_{0.15}CuO_4$ has also been observed at rather high $T \sim 28$ K.[23] In contrast to this, μSR results on the Eu-doped $La_{2-x}Sr_xCuO_4$ with $0.018 \leqslant x \leqslant 0.08$ 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 $La_{2-x}Sr_xCuO_4$. 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.

The authors would like to thank G. Khaliullin, W. Brenig, and G. Teitel'baum for helpful discussions. The work in Cologne was supported by the Deutsche Forschungsgemeinschaft through SFB 341 and the work in Kazan was supported in part by the State HTSC Program of the Russian Ministry of Sciences (Project No. 940045) and by the Russian Foundation for Basic Research under Grant No. 95-02-05942. One of us (V.K.) acknowledges NATO support under Collaborative Research Grant No. HTECH.EV 960286.

[1] B. Büchner *et al.*, Physica C **185-189**, 903 (1991).
[2] M. K. Crawford *et al.*, Phys. Rev. B **44**, 7749 (1991).
[3] J. M. Tranquada *et al.*, Nature (London) **375**, 561 (1995); Phys. Rev. B **54**, 7489 (1996).
[4] S. Cheong *et al.*, Phys. Rev. Lett. **67**, 1791 (1991); T. Mason *et al.*, *ibid.* **68**, 1414 (1992); T. Thurston *et al.*, Phys. Rev. B **46**, 9128 (1992).
[5] V. J. Emery and S. A. Kivelson, Physica C **235-240**, 189 (1994); **263**, 44 (1996); U. Löw *et al.*, Phys. Rev. Lett. **72**, 1918 (1994); M. I. Salkola, V. J. Emery, and S. A. Kivelson, *ibid.* **77**, 155 (1996).
[6] H. Eskes *et al.*, Phys. Rev. B **54**, R723 (1996).
[7] M. Breuer *et al.*, Physica C **208**, 217 (1993).
[8] B. Büchner *et al.*, J. Low Temp. Phys. **95**, 285 (1994); B. Büchner *et al.*, Physica C **235-240**, 281 (1994).
[9] M. Hücker, Diplomarbeit, Universität zu Köln, 1994.
[10] V. E. Kataev *et al.*, JETP Lett. **48**, 476 (1988).
[11] V. E. Kataev *et al.*, JETP Lett. **56**, 385 (1992); V. E. Kataev *et al.*, Phys. Rev. B **48**, 13 042 (1993).
[12] R. D. Zysler *et al.*, Phys. Rev. B **44**, 9467 (1991).
[13] V. Kataev *et al.* (unpublished).
[14] S. E. Barnes, Adv. Phys. **30**, 801 (1981).
[15] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).
[16] Q. Nguyen, Diplomarbeit, Universität zu Köln, 1995.
[17] G. Czjzeck *et al.* (unpublished).
[18] C. Rettori *et al.* [Phys. Rev. B **47**, 8156 (1993)] have explained the splitting of the Gd^{3+} ESR spectrum in the insulating AF ordered La_2CuO_4 single crystal using the value of H_{int} at the RE site of the order of 0.1 T. This smaller value is possibly due to the presence of interstitial oxygen typical for samples with $x=0$. We emphasize that the value of the transferred field of the order of 1 T yields an upper limit of the RE-Cu exchange and thus an *upper* limit of the fluctuation frequency ω_{sf}.
[19] H. Monien, P. Monthoux, and D. Pines, Phys. Rev. B **43**, 275 (1991).
[20] T. Imai *et al.*, Phys. Rev. Lett. **70**, 1002 (1993).
[21] A. J. Millis, H. Monien, and D. Pines, Phys. Rev. B **42**, 167 (1990); H. Monien, D. Pines, and M. Takigawa, *ibid.* **43**, 258 (1991).
[22] Although the assumption of the MMP model that $\chi''(\mathbf{q},\omega)$ is peaked at the AF wave vector $\mathbf{Q}(\pi/a,\pi/a)$ contradicts with the results of the neutron-scattering measurements which observe incommensurate spin correlations (see Refs. 4 and 3), there are reasonable possibilities to reconcile this contradiction. See, e.g., a discussion by V. Barzykin, D. Pines, and D. Thelen, Phys. Rev. B **50**, 16 052 (1994) and Y. Zha, V. Barzykin, and D. Pines, *ibid.* **54**, 7561 (1996).
[23] W. Wagener *et al.* (unpublished).
[24] W. Wagener *et al.* (unpublished).