Magnetism of the LTT phase of Eu doped La$_{2-x}$Sr$_x$CuO$_4$

M. Hücker, J. Pommer, and B. Büchner

II. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany

V. Kataev, and B. Rameev

Kazan Inst. for Technical Physics, RAS-420029 Kazan

(February 23, 2022)

Abstract

The ESR signal of Gd spin probes (0.5 at %) as well as the static normal state susceptibility of Eu (J(Eu$^{3+}$) = 0) doped La$_{2-x}$Sr$_x$Eu$_y$CuO$_4$ reveal pronounced changes of the Cu magnetism at the structural transition from the orthorhombic to the low temperature tetragonal phase for all non-superconducting compositions. Both a jumplike decrease of $\chi$ as well as the ESR data show an increase of the in-plane magnetic correlation length in the LTT phase. From the Gd$^{3+}$ ESR linewidth we find that for specific Eu and Sr concentrations in the LTT phase the correlation length increases up to more than 100 lattice constants and the fluctuation frequency of the CuO$_2$ spin system slows down to $\sim 10^{10} - 10^{11}$ sec$^{-1}$. However, there is no static order above $T \sim 8$K in contrast to the LTT phase of Nd doped La$_{2-x}$Sr$_x$CuO$_4$ with pinned stripe correlations.
I. INTRODUCTION

The structural phase transition in rare earth doped \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) (LSCO) from the orthorhombic (LTO) to the low temperature (LT) tetragonal (LTT) phase has attracted much attention during the last years, since it manifests an intimate correlation between the buckling pattern, superconductivity and magnetic properties of the CuO\(_2\) planes in this compound [1–3]. In particular, for Nd doped LSCO it is known that for compositions with strongly suppressed superconductivity in the LTT phase static antiferromagnetic order occurs [4]. Moreover, recent neutron diffraction experiments by Tranquada et al. [5] give evidence that for these non superconducting stoichiometries static order at elevated temperatures does occur in form of spatially modulated stripes of spins and holes.

In this paper we show that also in the non superconducting LTT phase of Eu doped LSCO magnetism is affected dramatically due to the LT transition. However, even at lowest temperatures (~8K) we do not find static order but extremely slow antiferromagnetic dynamics. To our opinion the most obvious reason for this different behavior is a strong magnetic rare earth–Cu exchange interaction which is absent in the case of the nonmagnetic Eu\(^{3+}\) ions. If this explanation is correct, static order at elevated temperature may not be intrinsic for the non superconducting LTT phase.

II. EXPERIMENTAL

Polycrystalline samples of \( \text{La}_{2-x-y}\text{Sr}_x\text{Eu}_y\text{CuO}_4 \) with various Sr and Eu concentrations were prepared by a standard solid state reaction described elsewhere [6]. The role of Eu is to induce the structural transition LTO \( \rightarrow \) LTT, whereas the hole concentration is controlled independently by Sr doping. The static susceptibility was measured for \( \text{La}_{1.8-x}\text{Sr}_x\text{Eu}_0.2\text{CuO}_4 \) with \( 0.04 \leq x \leq 0.17 \) using a conventional Faraday balance in a magnetic field of 1 Tesla. The ESR experiments were performed at a frequency of 9.3GHz on \( \text{La}_{1.99-x-y}\text{Sr}_x\text{Eu}_y\text{Gd}_{0.01}\text{CuO}_4 \) samples using Gd\(^{3+}\) ions as spin probes. Such a small Gd concentration does not affect the relevant physical properties as rare earth substitution is used in any case to induce the LT transition.
III. RESULTS

A representative curve of the temperature dependence of the static magnetic susceptibility $\chi(T)$ of La$_2$CuO$_4$ doped with Sr and Eu is shown in Fig.1 (upper curve). For the analysis of $\chi(T)$ it is necessary to account for several contributions to the measured susceptibility. In principle it consists of temperature independent terms (such as core diamagnetism, Van Vleck paramagnetism of Cu$^{2+}$ ions), the spin $S = \frac{1}{2}$ magnetism of Cu$^{2+}$ and the Van Vleck paramagnetism of Eu$^{3+}$:

$$\chi(T) = \chi_0 + \chi_{\text{spin}}^{\text{Cu}^{2+}}(T) + \chi_{\text{VV}}^{\text{Eu}^{3+}}(T)$$

(1)

As we are interested in possible changes of the magnetism of the CuO$_2$ planes as a function of temperature it is necessary to subtract the dominant magnetic contribution of europium from the total susceptibility curve. This can be done rather accurately using a theoretical Van Vleck [7] fit (see fig.1). After its subtraction the remaining signal $\chi - \chi(\text{Eu}^{3+})$ shows a jump-like decrease with lowering temperature at $\sim$123K which clearly corresponds with the structural LT transition LTO $\rightarrow$ LTT at $T_{LT}$. The amplitude of this jump amounts to about 5% of the susceptibility of the corresponding Eu free La$_{2-x}$Sr$_x$CuO$_4$ compounds ($\sim 1 \cdot 10^{-4}$emu/mol) [8]. Furthermore, one can see a sign change of the temperature slope of the signal immediately below $T_{LT}$. It is known that the positive temperature slope of $\chi_{\text{spin}}^{\text{Cu}^{2+}}$ in the LTO phase reflects the strong antiferromagnetic Cu spin correlations in a two dimensional (2D) $S = \frac{1}{2}$ Heisenberg antiferromagnet. Hence, the observed drop of $\chi_{\text{spin}}^{\text{Cu}^{2+}}$ at $T_{LT}$ can be naturally explained as being due to the larger magnetic inplane correlation length $\xi_{2D}$ in the LTT phase and consequently to a smaller value of $\chi_{\text{spin}}^{\text{Cu}^{2+}}$.

The Sr dependence of this anomaly in the susceptibility at the structural transition is summarized in Fig.2. In this plot we show changes of $\chi - \chi(\text{Eu}^{3+})$ relative to a linear fit of the data points in the LTO phase immediately above $T_{LT}$. With increasing hole concentration the jump at $T_{LT}$ becomes smaller and is scarcely resolvable for $x=0.17$. From this we have to conclude that the enhancement of the inplane correlation length $\xi_{2D}$ due to the structural changes at $T_{LT}$ becomes smaller when the hole concentration is increased. However, the absence of the jump in $\chi_{\text{spin}}^{\text{Cu}^{2+}}$ for $x > 0.17$ is not related to some qualitative change of the structural LT transition, which is observable up to much higher Sr concentrations ($x \sim 0.24$). In contrast, we found that its disappearance rather correlates with an
electronic phase boundary within the LTT phase caused by a critical buckling of the CuO$_2$ planes [1].

This phase boundary is related to a critical Sr content $x_c$ that separates the LTT phase into a non superconducting part ($x < x_c$) and a superconducting part ($x > x_c$). Indeed, all these compounds presented in Fig.2 do not exhibit bulk superconductivity, whereas without europium they do (except $x=0.04$). It is worth to mention that the sample with $x=0.17$ already is very close to this critical concentration $x_c$ as has been shown for a similar set of samples [2].

To summarize, the presented results of the static susceptibility measurements show that the LT transition significantly enhances the inplane correlation length $\xi_{2D}$, but only if the LTT phase is not superconducting.

The same conclusion emerges from the ESR study. The ESR spectra of La$_{1.99-x-y}$Sr$_x$Eu$_y$Gd$_{0.01}$CuO$_4$ have been measured in the temperature range 8K<T<300K. The fine structure of the spectra (see inset in Fig.3) observed for all samples is due to the small splitting of the ground state multiplet $^8S_{7/2}$ of Gd$^{3+}$ in the crystalline electrical field. The width of the central component of the spectrum (encircled in inset of Fig.3) as a function of temperature is shown in Fig.1 for two representative La$_{1.89-y}$Sr$_{0.1}$Eu$_y$Gd$_{0.01}$CuO$_4$ compounds. One is not Eu doped and hence is a superconductor ($T_c \sim 25$K) without LTO $\rightarrow$ LTT transition. For the second sample with a very high Eu content ($y=0.24$) the LT transition does occur at $T_{LT} \sim 130$K and superconductivity is completely supressed. In the normal state of the LTO phase $\Delta H$ increases linearly with temperature for both samples. This is due to the Korringa relaxation of Gd spins caused by a small exchange coupling of Gd$^{3+}$ ions to the mobile holes in the CuO$_2$ planes [3]. The important feature of the Eu doped sample is a very strong increase of the linewidth at low temperatures, i.e. in the LTT phase.

To explain such a profound effect it is necessary to consider a coupling of the Gd spins to antiferromagnetic (AF) spin fluctuations in the CuO$_2$ planes. Due to the magnetic exchange interaction between Gd$^{3+}$ and Cu$^{2+}$ions ($J_{Cu-Gd}$) the relaxation rate $1/T_1$ of the Gd$^{3+}$ spin state serves as a probe for the Cu spin fluctuation frequency $\omega_{sf}$: $1/T_1 \propto J_{Cu-Gd}^2 \chi_{Cu} T / \omega_{sf}$. Since $1/T_1$ determines the homogeneous part of the width $\Delta H$ of the components of the Gd ESR spectrum, estimates of $\omega_{sf}$ can be obtained from the temperature dependence of $\Delta H$ [4]. In the LTO phase AF fluctuations with the frequency of the order of $10^{13}$ sec$^{-1}$ do not contribute significantly to the Gd ESR linewidth.
Thus, a strong increase of $\Delta H$ corresponds to a dramatic slowing down of the Cu$^{2+}$ spin dynamics in the LTT phase. The estimated fluctuation frequency decreases by two orders of magnitude down to $\omega_{sf} \sim 10^{10} - 10^{11} \text{sec}^{-1}$ at $T \sim 10\text{K}$ \cite{10}. If we assume that $\omega_{sf} \sim 1/\xi_{2D}^2$ \cite{11}, then the magnetic correlation length $\xi_{2D}$ of the hole doped CuO$_2$ planes should increase up to more than 100 lattice constants. Remarkably, the continuous increase of the linewidth $\Delta H$ down to the lowest temperatures of the measurements, indicates that the Cu spins remain dynamic rather then turning into an AF ordered state.

IV. CONCLUSION

In conclusion, we have shown that in the LTT phase of Eu doped La$_{2-x}$Sr$_x$CuO$_4$ both the static susceptibility and the Gd$^{3+}$ ESR linewidth indicate a pronounced increase of the Cu spin correlation length for all non superconducting samples. However, in contrast to the observation of static stripe order of spins and charges in the LTT phase of Nd doped La$_{2-x}$Sr$_x$CuO$_4$ below 50K, for the Eu doped compounds we find no evidence for a static order even at 8K.

This work was supported by the Deutsche Forschungsgemeinschaft through SFB 341. M.H. acknowledges support by the Graduiertenstipendium des Landes Nordrhein-Westfalen. The work of V.K. and B.R. 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 (project No.95-02-05942). V.K. acknowledges NATO support under Collaborative Research Grant No. HTECH.EV 960286.
REFERENCES

[1] B. Büchner, M. Breuer, A. Freimuth, and A.P. Kampf, Phys. Rev. Lett. 73, 1841 (1994); M.K. Crawford et al., Phys. Rev. B 44, 7749 (1991)

[2] B. Büchner et al., Physica C 235-240, 235 (1994);

[3] J.D. Axe, and M.K. Crawford, J. Low Temp. Phys. 95, 271 (1994)

[4] M. Breuer et al., Z. Phys. B 92, 331 (1993)

[5] J.M. Tranquada et al., Nature 375, 561 (1995); J.M. Tranquada et al., Phys. Rev. B 52, 3581 (1995)

[6] M. Breuer et al., Physica C 208, 217 (1993)

[7] J.H. van Vleck, The Theorie of Electric and Magnetic Susceptibilities, Oxford University Press

[8] H. Takagi et al., Phys. Rev. B 40, 2254 (1989); D.C. Johnston, Phys. Rev. Lett. 68, 957 (1989)

[9] V.E.Kataev et al., JETP Lett. 56, 385 (1992); V.E.Kataev et al., Phys. Rev. B48, 13042 (1993).

[10] V.Kataev et al., Phys. Rev. B55, (1997);

[11] A.J.Millis, H.Monien and D.Pines, Phys.Rev. B42, 167 (1990); H.Monien, D.Pines and M.Takigawa, ibid, 43 258 (1991)
FIGURES

FIG. 1. Static susceptibility of La$_{1.76}$Sr$_{0.04}$Eu$_{0.2}$CuO$_4$. The total measured signal $\chi$, the Van Vleck fit $\chi(Eu^{3+})$ which takes the Eu magnetism into account and the difference $\chi - \chi(Eu^{3+})$ are shown. Inset: changes of $\chi - \chi(Eu^{3+})$ at the LTO $\rightarrow$ LTT transition on expanded scale.

FIG. 2. Deviations of the static magnetic susceptibility $\chi - \chi(Eu^{3+})$ of La$_{1.76}$Sr$_{0.04}$Eu$_{0.2}$CuO$_4$ with 0.04<$x$<0.17 from a linear fit in the LTO phase (curves are shifted). The jumplike anomaly at $T_{LT} \sim 130$K is due to the LT transition and decreases with decreasing buckling of the CuO$_2$ planes. All samples are no bulk superconductors.

FIG. 3. Temperature dependence of the linewidth $\Delta H$ of the encircled component (inset) of the Gd$^{3+}$ ESR spectrum of La$_{1.89-y}$Sr$_{0.1}Eu_y$Gd$_{0.01}$CuO$_4$ with y=0.0 and 0.24. Remarkable is the pronounced broadening of the spectra in the LTT phase of the non superconducting sample. For this sample the contribution due to thermally excited states of Eu$^{3+}$ laying above 400K has been subtracted.
La$_{1.76}$ Sr$_{0.04}$ Eu$_{0.2}$ CuO$_{4+\delta}$

$T_{LT} = 123\text{K}$

(as measured)

$\chi$

$\chi$ (Eu$^{3+}$)

(Van Vleck Fit)

$\chi - \chi$ (Eu$^{3+}$)

$T_{LT}$

LTT

LTO

$\chi - \chi$ (Eu$^{3+}$)

$T_{LT}$

$\chi$ (10$^{-4}$ emu/mol)

$T$ (K)
La$_{1.8-x}$Sr$_x$Eu$_{0.2}$CuO$_4$

$\chi - \chi$(Eu$^{3+}$) - Fit(LTO)

$\chi$ (10$^{-5}$emu/mol)

T (K)

LTT  LTO

$x = 0.04$

$T_{LT}$

$0.08$

$0.12$

$0.15$

$0.17$
