Pis'ma v ZhETF, vol. 80, iss. 3, pp. 221 – 225 © 2004 August 10

# Pseudogap behavior of nuclear spin relaxation in high $T_c$ superconductors in terms of phase separation

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Submitted 7 July 2004

We analyze anew experiments on the NMR in cuprates and find an important information on their phase separation and its stripe character hidden in the dependence of $1/^{63}T_1$ on degree of doping. In a broad class of materials $1/^{63}T_1$ is the sum of two terms: the temperature independent one attributed to "incommensurate" stripes that occur at external doping, and an "universal" temperature dependent term ascribed to moving metallic and antiferromagnetic sub-phases. We argue that the frustrated first order phase transition in a broad temperature interval bears a dynamical character.

PACS: 74.25.Ha, 74.72.–h, 76.60.–k

Soon after the discovery of high temperature superconductivity (HTSC) in cuprates by Bednorz and Muller in 1986 it was suggested theoretically [1] that the materials should manifest a tendency to inherent phase segregation involving both lattice and electronic degrees of freedom. Later other models revealed similar tendency to an inhomogeneous electronic ground state [2 – 5]. (For an experimental summary see e.g., [6 – 8]). It is currently common to discuss microscopic phase separation (PS) in cuprates as a pattern of the alternating spin-charge stripes [9], dynamical or pinned by static defects seen, e.g., in $(LaNd)_{2-x}Sr_xCuO_4$ [10] with Nd doping.

The most intriguing phenomenon in the normal state of cuprates is the pseudogap (PG) seen as a new energy scale or a crossover temperature, $T^*$, in NMR, tunneling spectra, resistivity etc. (for review see, e.g., [11, 12]). We address this highly debated issue by considering the PG regime as a regime of the phase segregation.

Our premise is that $T^*(x)$ marks a temperature below which the system enters mesoscopic dynamical regime of a frustrated 1st order phase transition with sizes of the sub-phases' determined by electroneutrality [1, 13]. Unlike [14, 15], changes in the normal properties below such a $T^*$ come not from a symmetry breaking but due to interweaving of regions with different holes content.

The NMR fingerprints of a static stripe phase were observed for the low temperature tetragonal (LTT) compounds $(LaEu)_{2-x}Sr_xCuO_4$ [16] and $(LaNd)_{2-x}Sr_xCuO_4$ [17]. Dynamical features are seen in inelastic neutron experiments at frequencies $10^{12}$–$10^{13}\,s^{-1}$, exceeding the NMR scale.

In the present paper we analyze anew vast *experimental* data on nuclear spin relaxation in cuprates to show that for a broad class of materials $^{63}T_1^{-1}$ in the PG regime is the *sum of the two terms*: the temperature independent one that we attribute to stripes caused by the presence of dopants and an "universal" temperature dependent term related to the moving metallic and antiferromagnetic (AF) subphases. We argue that for LSCO $T^*$ is above the "dome" of superconductivity (SC).

For a guidance we adopt a qualitative two-band view [1, 13]. Basic to it is the assumption that in absence of interactions the energy spectrum of holes for $CuO_2$ plane consists of an itinerant band and the periodic array of local levels identified with the $d^9$ Cu-configuration. Although hole concentration is not a thermodynamic variable, we suggest that doping is accompanied by changes in the charge transfer gap and implements a 1-st order Mott transition. (The low temperature Hall effect 18 – 20] show that the number of the itinerant holes rapidly increases up to one per unit cell near $x = 0.15$.)

New features in [1, 13] as compared to other models [2 – 5] concern Cu spins: 1) a hole on a $d^9$ Cu site is bound by the lattice (remnants of the Jahn-Teller effect); 2) a local hole on a $d^9$ Cu-site distorts surrounding lattice so that the distortions on different sites interact with each other. The elastic energy minimizes itself by bringing occupied Cu sites together, thus forming nuclei of a dense "liquid" phase of local centers' (in the language of the lattice "liquid-gas"). It is the *lattice* that triggers "liquid-gas" transition! An exchange between

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holes' spins on the neighboring sites tends to organize spins of "liquid" AF sub-phase.

For holes localized on Cu's in the $CuO_2$ plane the lattice "liquid-gas" transition at some $T^*$ is well-known from the exact solution of the familiar 2D Ising-problem. Taking hole-doped $La_{1-x}Sr_xCuO_4$, for the sake of argument, missing (with respect to the Sr ionicity) holes' density in the AF area must be recompensated by local metallic inclusions or droplets with higher hole's content.

We speculate that tiny structure of sub-phases leads to strong fluctuations in islands' sizes and positions [1]. Boundaries between them move rapidly. Moving boundary itself is due to the new notion that a Cu-site can merely loose spins when a "metallic" regions crosses over the position of that $^{63}$Cu nuclear spin. Experimentally one sees only one nuclear resonance frequency, this provides a strict evidence in favor of the dynamical picture.

In what follows we address only $1/^{63}T_1$ behaviour because for cuprates AF fluctuations prevail over the Korringa mechanisms.

We now turn to experimental data on $1/^{63}T_1$ for a number of cuprates. At high enough temperatures itinerant holes and Cu $d^9$ states form a homogeneous phase. In particular we will also address means to determine $T^*$, which because of the Coulomb effects manifests itself only as a start of a new fluctuation regime.

A widespread view is that PG $T^*(x)$ is a density of states (DOS) crossover. In the $(T, x)$ plane it crosses the SC "dome", $T_c$ (see e.g. in [22, 21]). We take a different view. In Fig.1a we collected data on $1/^{63}T_1$ in LSCO from [23]. The following comments are of relevance here: 1) according to [24] $1/^{63}T_1(T)$ at higher temperatures tends to $2.7\,\mathrm{ms}^{-1}$ *for all* Sr concentrations, in spite of considerable spread seen in Fig.1a. Beginning of deviation from that value could be a definition of $T^*(x)$; 2) note that $1/^{63}T_1$ i.e. dissipation, monotonically decreases with the decrease of disorder from small $x$ to 0.24; 3) after an appropriate *vertical* offset all curves in Fig.1a collapse onto the $T$ dependence of $1/^{63}T_1$ for the "optimal" $x = 0.15$ above 50 K (Fig.1b). Same tendency is seen in Fig.2a,b for YBCO (6.5) doped with Ca: the data in Fig.2a for different $z$ in $Y_{1-z}Ca_zBa_2\,Cu_3\,O_{6.5}$ [25] all fall on the top of each other in Fig.2b.

This prompts us to verify whether same "off-settings" of the $1/^{63}T_1$ data apply to a broader group of materials. The stoichiometric $YBa_2Cu_4O_8$ possesses no structural or defect disorder and we adjust all data to the $1/^{63}T_1$ behaviour for this material [21]. Fig.2c shows that after a vertical shift in $1/^{63}T_1$ all the materials indeed follow the same "universal" temperature dependence above their $T_c$ and below 300 K. In other words, in this temperature range the nuclear spin relaxation in these cuprates is a sum of contributions from two parallel processes:

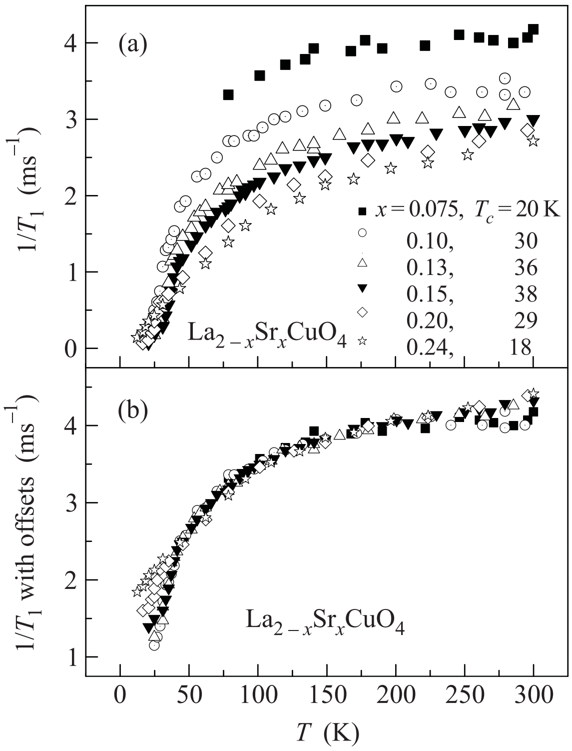


Fig.1. The temperature dependence of $1/^{63}T_1(x)$ for LSCO: a) the plots for different $x$ and $T_c$ (see inset) are taken from [23], at higher temperatures all of them converge to the same value of 2.7 ms$^{-1}$ [24]; b) the same dependences collapsing to the single curve after the corresponding vertical offsets

$$1/^{63}T_1 = 1/^{63}\overline{T}_1(x) + 1/^{63}\widetilde{T}_1(T). \qquad (1)$$

In eq.(1) $1/^{63}\overline{T}_1(x)$ depends on a material and a degree of disorder (x), but does not depend on temperature, while $1/^{63}\widetilde{T}_1(T)$, depends only on temperature, is the same for all these compounds and coincides with the $1/^{63}T_1$ for the two chains YBCO 124 above its $T_c = 62$ K.

The decomposition (1) into two parallel dissipation processes show that usual definitions of $T^*$ [22] have no grounds. In Fig.1a the LSCO data with $x < 0.15$ are spread even above 250 K. As a rough estimate for $T^*$, it is much higher than the SC onset temperature.

Fig.3 and Table present the dependence on $x$ for $1/^{63}\overline{T}_1$ in $La_{2-x}Sr_xCuO_4$ and provide the "offsets" (i.e. $1/^{63}\overline{T}_1$-terms) for other materials. We return to discussion of the two terms of eq.(1) later.

The observation that is central for the following is that in all the materials with non-zero $1/^{63}\overline{T}_1$ incommensurate (IC) peaks have been observed in neutron

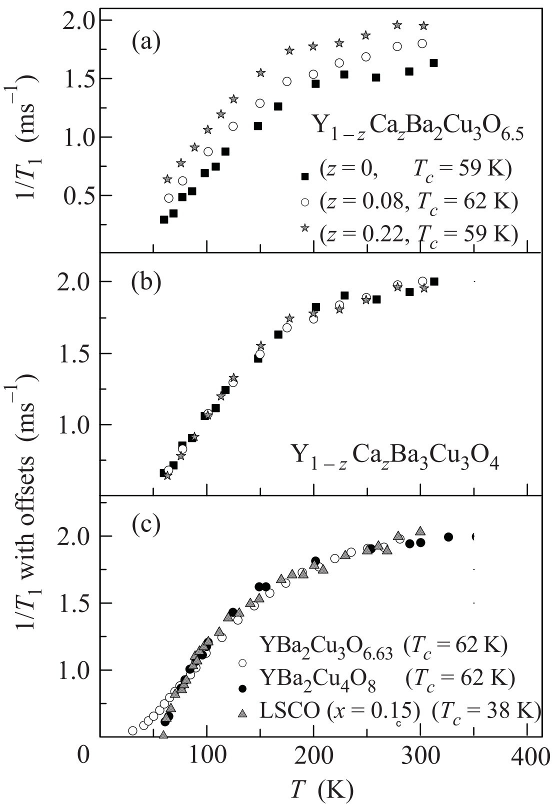


Fig.2. The temperature dependence of $1/^{63}T_1$ for different compounds: a) for $Y_{1-z}Ca_zBa_2Cu_3O_{6.5}$ with different Ca content $z$ [25]; b) the same curves overlayed at each other by the vertical offsets; c) the $1/^{63}T_1$ for YBCO (123) [26] overlayed with that for LSCO [23] and YBCO (124) [21]

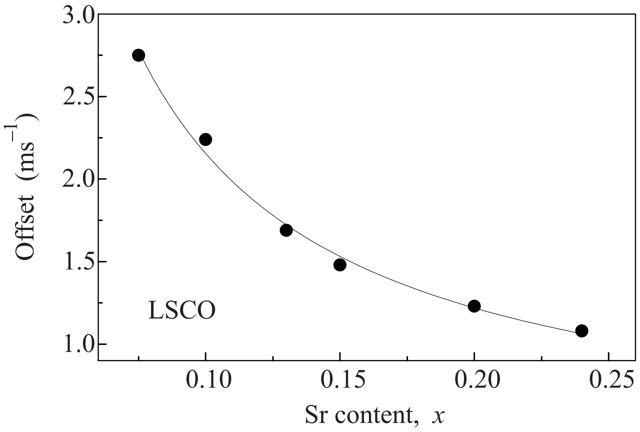


Fig.3. The offset $1/^{63}\overline{T}_1(x)$ vs Sr content $x$ for LSCO (relative to that for YBCO 124), line is a guide for eyes

| Material | | Offset |
|---|---|---|
| YBCO 124 | | 0 |
| BISCO-u | $T_c = 90$ K | 0.11 |
| BISCO-o | $T_c = 77$ K | 0.15 |
| YBCO 123 | Ca = 0 | 0.13 |
| YBCO 123 | Ca = 0.08 | 0.26 |
| YBCO 123 | Ca = 0.22 | 0.45 |
| LSCO | Sr = 0.15 | 1.47 |

The offsets for some other compounds (data for underdoped (u) and overdoped (o) BISCCO 2212 deduced from [27]; to compare BISCCO with LSCO and YBCO materials the hyperfine constants have to be properly adjusted).

scattering [28]. Peaks are close to the $[\pi,\pi]$ – point: at $[\pi(1\pm\delta),\pi]$ and $[\pi,\pi(1\pm\delta)]$ [10]. We will now look for the connection between these two phenomena.

Discovery of IC spin fluctuations presented a challenge for explaining the NMR results for the oxygen spin relaxation times: hyperfine field "leaks" originated by the AF incommensurate fluctuations, would considerably increase the oxygen's relaxation rates, but this was not seen experimentally. Slichter (see in Ref.[29]) interpreted these contradictions in terms of "discommensurations": a periodic array of soliton-like walls separating regions with a short-range AF order. Unlike neutrons, the NMR as a local probe, does not feel the overall periodicity.

As a theory attempt to put the IC peaks into the context of the *dynamical* PS separation, consider first a stoichiometric material like YBCO 124. Below some $T^*$ we expect the system to break-up into sub-phases – the one with a richer content of the Cu-spins ("AF"-phase), and the second – with an excess of carriers [1, 13]. The system passes $T^*$ gradually and remains macroscopically homogeneous. PS would express itself in strong fluctuations that provide for the $1/^{63}\widetilde{T}_1(T)$ – term in eq. (1).

At doping the system (LSCO) must screen excess charge ($Sr^{2+}$) in AF regions. External doping introduces features that may have something to do with pinning or structural changes. For the Nd doped LSCO, $La_{2-x-y}Nd_ySr_xCuO_4$ (for the summary below see experiments: [30–33]), doping of $La_{1.6}Nd_{0.4}CuO_4$ with Sr reproduces all features, including SC at lower temperatures, of $La_{1-x}Sr_xCuO_4$ itself with that important difference that "stripes" easily become static. *Elastic lattice/charge* IC peaks were seen in [32] at $\pi[2\pm\delta,0,0]$ with the lattice distortions along the modulation direction (IC peaks positions in [32] are defined by $\epsilon=\delta/2$). Lattice peaks appear first at cooling, followed by the static magnetic peaks. According to [32], pinning of IC distortions can be ascribed to the pattern of the octahedra tilts and redistribution of the Cu–O – bonds in the LTT phase that sets in LaNdSCO at higher temperatures [30]. (Unlike the high temperature tetragonal phase (HTT) the LTT phase contains four formula units per primitive cell). Strips of AF ordered phase alternate with "metallic" domain walls. Such strip arrangement by itself is nothing but an optimization of the competing Coulomb and lattice forces [3].

Note that the stripes at low temperature finally acquire a long range order even in LSCO (at smaller $x$ [34]), breaking the symmetry of the ground state. The way of the "coexistence" of SC and the stripe order in the same sample remains unresolved: one view treats the new stripe symmetry as a superstructure superimposed on the Fermi surface that change the energy spectrum like any SDW/CDW can do it (e.g. [9]). Another plausible alternative would be a spatially inhomogeneous coexistence of the nonsuperconducting IC AF phase and a "metallic" phase with strong fluctuations.

Coexistence of a SC and the IC AF phases at low temperatures was confirmed recently by the neutron diffraction experiments [35] for $La_{2-x}Sr_xCuO_4$ ($x = 0.10$) in the vortex state. (The coexistence of SC and AF formations was found also from the $\mu$SR spectra [36]).

One can now say that with the temperature increase the static phase coexistence melts into the dynamical regime governed by the Coulomb interactions. "Discommensurations" suggested by Slichter (see in [29]) ought to be corrected: IC excitations should indeed consist of alternating strips of the short-range AF order, but separated by walls that store the compensating charge. Direct correspondence between $x$ and $\delta$: $\delta/2$ ($\equiv \epsilon$) $\approx x$ found for $0.05 \leq x \leq 1/8$ saturates for $x > 1/8$ at $\delta \approx 1/4$ [37]. Fig.3 allows to consider the tendency as an increase in the share of the "metallic" fraction.

We shall now make an attempt to agree on a semi-quantitative level the observed IC magnetic peaks in $La_{2-x}Sr_xCuO_4$ with the values of the first term in eq. (1). We concentrate on $La_{1.86}Sr_{0.14}CuO_4$ for which the most detailed data are available [38].

With the notation from [39]

$$1/T_1 = \frac{k_B T}{2\mu_B^2 \hbar^2 \omega} \sum_i F(Q_i) \int \frac{d^2 q}{(2\pi)^2} \chi''(q, \omega \to 0) \quad (2)$$

where $Q_i$ stands for one peak, hyperfine "tensor" $F(Q) = \{A_\perp + 2B[\cos(Q_x) + \cos(Q_y)]\}^2$ and for $\chi''(q, \omega \to 0)$ we take near single peak, say $[\pi(1-\delta), \pi]$

$$\chi''(q, \omega) = \frac{\chi''_{\text{peak}}(T)\omega}{[1 + (x\xi_x)^2 + (y\xi_y)^2]^2} \qquad (3)$$

where $(x, y) = (q_x - \pi(1-\delta); q_y - \pi)$ and $\xi_x$ and $\xi_y$ are the correlation lengths in the two proper directions. After integration the contribution from stripes with $q$ along the $x$-direction is

$$1/^{63}T_1 = \frac{k_B T}{\pi \mu_B^2 \hbar \xi_x \xi_y} \{A_\perp - 2B[\cos(\pi\delta) + 1]\}^2 \chi''_{\text{peak}}. \qquad (4)$$

Experimentally [38] $\chi''_{\text{peak}}(T) \propto T^{-2}$ and for $x = 0.14$ $\delta = 0.245 \sim 1/4$. Assuming the $T^{-1}$ dependence [38] only for the one of $\xi$'s, $\xi_x$ and using for $A_\perp$ and $B$ the known values [39] one obtains: $1/^{63}T_1 = (4/\xi_y)\,\text{ms}^{-1}$. With the AF correlation length $\xi_y \sim 4$ this is the correct order of magnitude.

The descending dependence of the offset (Fig.3) agrees qualitatively with the behavior of $\delta(x)$ [37] in eq.(4). For a quantitative description one need to know the $x$-dependence for $\chi''_{\text{peak}}(T)$. Such data in the absolute units are absent yet except [38]. In addition, with the $x$-increase buckling in the $CuO_2$-planes is known to decrease diminishing pinning effects and making the local symmetry of the $CuO_2$-unit same as in other materials from the class with small offset in Fig.3. The system grows metallic with a high holes' content [18–20].

Thus the only "pseudogap" feature in the NMR data that survives in Fig.2c is the one for YBCO 124: a change of the regime between 130 and 180 K. Similar drop in the width for the Ho-crystal field excitations was found in [40] for another 124-compound, Ho-124, in about the same temperature interval. It would be tempting to view the regime change again in the PS-terms. However, note that the AF fluctuations cancel at the Ho-positions, and the relaxation seen in [40] looks as "metallic" Korringa law. In [40] DOS's, as characterizing linear slops in T-dependencies outside the crossover interval, are almost the same, so that whatever means the transitional area in Fig.2c for Ho-124, it is not a simple gap opening [21]. Recall that properties of both YBCO 124 and the optimally doped LSCO (for review see [11]) are unusual in a very broad temperature interval and are best understood in terms of the "marginal" Fermi liquid model [41]. Therefore we leave the origin of the "universal " term in eq.(1) open to further discussions.

Two words regarding our choice $(\xi_x, \xi_y)$. We assumed anisotropic spin correlation widths with the one along *commensurate* AF direction temperature independent. The asymmetry is expected, although the experimental verification remains to be done. Rapid growth of the width of the neutron peak along modulation direction, $q_x$, (linear in temperature [38]) reflects the low energy cost for magnetic excitations in LSCO ($x = 0.14$) (the width from the stripes "bending" should have given the $T^{1/2}$ dependence for both $\xi$'s).

To summarize, we have found that in a temperature interval above $T_c$ and below some $T^* \sim 300$ K the nuclear spin relaxation for a broad class of cuprates comes from two independent mechanisms: relaxation on the "stripe"-like excitations that leads to a temperature independent contribution to $1/^{63}T_1$ (originating due to the presence of external doping or disorder), and an "universal" temperature dependent term. For $La_{1.86}Sr_{0.14}CuO_4$ we obtained a correct quantitative estimate for the value of the first term. We argue that the whole pattern fits well the notion of the dynamical PS into coexisting metallic and IC magnetic phases. Experimentally, it seems that with the temperature decrease dynamical PS acquires the static character with the IC symmetry breaking for AF phase dictated by the competition between the lattice and the Coulomb forces.

One of the authors (L.P.G) expresses his gratitude to T. Egami, C. P. Slichter and J. Haase for interesting discussions. The work of L.P.G. was supported by the NHMFL through NSF cooperative agreement DMR-9527035 and the State of Florida, that of G.B.T. through the RFBR Grant # 04-02-17137.

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