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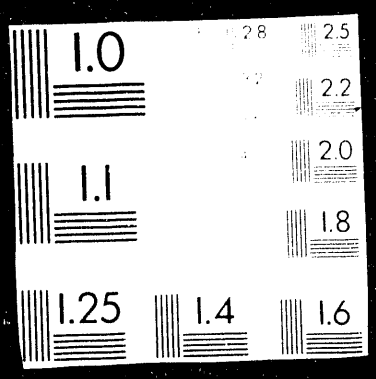

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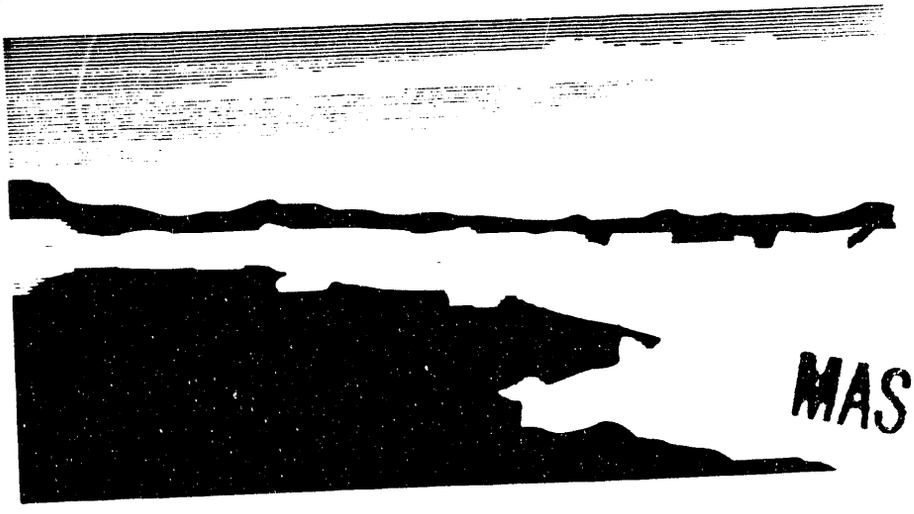



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# Local Structure in Oxygen-doped $La_2CuO_{4+\delta}$

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Oxygen doped $La_2CuO_{4+\delta}$ displays a rich variety of behaviors. Due to the unusually large mobility of the oxygen ions in $La_2CuO_{4+\delta}$ at high temperatures, it is the only cuprate which displays macroscopic phase separation of doped holes. We discuss our studies of $La_2CuO_{4+\delta}$ including phase separation, distributed local structure whose onset coincides with phase separation and the observation that in the presence of doped holes two distinct copper sites copper sites are generated, an observation which contrasts with results of diffraction studies. The importance of these phenomena for superconductivity is suggested by the observation that the superconducting transition temperature $T_c$ in this material changes by over 10% in response to altered cooling history.

We have presented the results of a study of this phase separation and pointed out some unusual features. Below a temperature $T_f$ the situation becomes similar to other cuprates since oxygen is no longer sufficiently mobile to allow further macroscopic phase separation. In this regime the magnetic behavior of metallic $La_2CuO_{4+\delta}$ is quite conventional in the context of the cuprates. However $^{139}La$ NMR spectroscopy [9] has shown the local structure of the La-O layer to be very sensitive to the presence of doped holes and to be strongly temperature dependent in this same regime. This sensitivity is evident in the $CuO_2$ planes where, in the presence of doped holes a second, distinct copper site is present. This provides an opportunity to explore the relationship between local structure and the novel magnetic behavior of the cuprates. Further experiments following this line of inquiry are planned.

# Local Structure in Oxygen-doped $La_2CuO_{4+\delta}$

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## I. Introduction

The properties of both the normal and superconducting states of the high-$T_c$ cuprates are very unusual. Many aspects of these materials remain little understood. One such aspect is the structure of the cuprates; there is particular reason to be interested in structure which varies on local scales. There exists considerable experimental and theoretical support [1] for the presence of such effects and their importance in determining electronic behavior. There is also growing evidence [2, 3] that charge carriers in the cuprates tend to separate into regions of high and low density. In most cases this will also occur on a local distance scale only [3] because macroscopic phase separation is thwarted by long range coulomb forces which make the clumping of charge energetically unfavorable. An important question concerns the nature of the interaction between doped carriers and the local structure. $La_2CuO_4$ doped by the addition of excess oxygen is a superconductor ($T_c$ up to 45 K [4]) which is well suited to studying these phenomena, and the interactions between them.

The very high mobility of the oxygen dopants in $La_2CuO_{4+\delta}$ (in contrast to metal cations) allows macroscopic phase separation[5]. Here we will discuss our studies of $La_2CuO_{4+\delta}$ including phase separation, distributed local structure whose onset coincides with phase separation and the observation that in the presence of doped holes two distinct copper sites copper sites are generated, an observation which contrasts with results of diffraction studies. The importance of these phenomena for superconductivity is suggested by the observation that the superconducting transition temperature $T_c$ in this material changes by over 10% in response to altered cooling history.

## II. Phase Separation

The large mobility of oxygen dopants in high-pressure oxygen annealed $La_2CuO_{4+\delta}$ allows phase separation [5] in which oxygen-rich metallic domains coexist with oxygen-poor antiferromagnetic domains having characteristic dimensions of $\sim 10^3$ Å [6]. Using NMR techniques we are able to obtain estiimates [7] for the temperature dependence of the excess oxygen concentration in each phase. In the oxygen-poor AF phase we obtain this by exploiting the extreme sensitivity of the antiferromagnetic ordering temperature and thus the sub-lattice magnetization on $\delta$. In the oxygen-rich metallic phase, the spin susceptibility is very; sensitive to hole doping and thus to $\delta$. In Fig 1 we show the temperature dependence of the excess oxygen content [8] obtained in this way. The result is general agreement with phase diagrams obtained in other ways. We point out three distinctive features, however. The sides of the diagram are vertical below ~200 K; in the AF phase the deviation from verticality occurs just below $T_{PS}$ . As we will discuss below, this indicates a loss of oxygen mobility below 200 K,. There is a very rapid change in $\delta$ for both phases at the phase separation temperature $T_{PS}$ . One expects this to be continuous in one phase. Very little supercooling is possible since $T_{PS} = 265\text{K}$ is barely below room temperature where thermal equilibrium is certainly achieved through very

long waits. Such behavior may indicate that structural changes which onset [9] at this temperature may influence the phase separation. Finally, $T_{PS}$ coincides with the intersection of the vertical $\delta_{AF}(T)$ suggesting that the ability to form a long-range ordered antiferromagnet may play a driving role in phase separation.

**III. Oxygen mobility**

In order to better understand the phase diagram in Fig 1 we have employed $^{139}La$ nuclear spin lattice relaxation to probe the oxygen motion. It has been established [11] that relaxation in the AF phase of $La_2CuO_{4+\delta}$ is due to fluctuations of the electric field gradient (except perhaps in the immediate vicinity of $T_N$ ) and thus reflects the motion of oxygen ions neighboring the La site. Since magnetic relaxation is stronger in the more lightly doped materials it is likely that quadrupolar relaxation dominates the La nuclear relaxation in the metallic phase as well. Fig 2 shows the temperature dependence of the $(T_1T)^{-1}$ for the La site. The strong peak at 210 K indicates that the temperature at which the characteristic frequency for oxygen motion which is decreasing rapidly with temperature [12] crosses the Larmor frequency. This occurs at essentially the same temperature below which $\delta_M$ ceases to vary with temperature.

We conclude that below ~200 K the mobility of ox;ygen dopants in the metallic phase is insufficient to allow macroscopic phase separation thus preventing any further change in $\delta_M$. It appears that $\delta_{AF}$ varies only in a quite narrow range of temperature below $T_{PS}$ ; $\delta_{AF}$ is constant below about 240 K. This suggests that the mobility of oxygen varies differently with temperature in antiferromagnetic phase than in the metallic phase.

**IV. Sensitivity of superconducting transition temperature to cooling history**

Many workers have observed that the superconducting transition temperature in oxygen doped $La_2CuO_{4+\delta}$ can be increased by slow cooling. We have studied this effect [10] with the goal of determining the temperatures and rates which are important for increasing $T_c$. In Fig 3 we have plotted the $T_c$ which results when the sample is held for times as short as 20 ?? minutes at various annealing temperatures. We observe that $T_c$ increases steadily with decreasing annealing temperature down to approximately 200 K. Annealing below this temperature results in a low $T_c$ similar to that achieved by rapid cooling from room temperature.

One might expect that this simply indicates that rapidly cooling the sample leaves $\delta_M$ at a lower value than is achieved by slow cooling and thus decreases $T_c$. While the magnitude of the change in $T_c$ is consistent with such an effect [10] the shape of the curve in Fig 3 is rather surprising. The mobility of oxygen in $La_{2-x}Sr_xCuO_4$ has been well studied [12]. A conventional Arrhenius behavior is observed with an activation energy U which varies slowly with x, but falls in the range of 0.7 to 1.1 eV. We find that a slow cooling rate $R_s$ of about 1 K/minute is sufficient to produce a higher $T_c$; a fast rate $R_f$ of only 3 K/minute will result in lower $T_c$. Thus the difference in time scales is small compared to the several orders of magnitude change in oxygen mobility between 250 K and 200 K. The small change in cooling rate should only affect the low temperature value of $\delta_M$ and thus $T_c$ in a narrow temperature range near a temperature $T_f$ (~200 K) where the ability of oxygen to move ~1000Å in a time scale of minutes is lost. We estimate the width of this range to be $\Delta T \approx \left(T_f^2/U\right)\ln\left(R_f/R_s\right) \approx 5\text{K}$. The result in Fig 3 shows that $T_c$ is changing with annealing temperature between room temperature and 200 K and so is

apparently inconsistent with this scenario. One rather unlikely explanation is that the temperature dependence of the oxygen mobility is very different in the oxygen doped material than in its Sr doped counterpart. More likely is that the observed sensitivity of $T_c$ to cooling rate is more complex, possibly related to the structural changes [9] taking place in the vicinity of $T_f$. This will be discussed further below.

## V. "Conventional" spin dynamics

In Fig 4 we show Knight shift and nuclear spin relaxation rate divided by temperature $(T_1T)^{-1}$ data for both copper and planar oxygen in the metallic phase. Knight shift measurement is the only way to obtain the metallic phase static susceptibility in the two phase region since the bulk susceptibility is also influenced by the AF phase. Below $T_f$, the susceptibility decreases monotonically with temperature; from these results it is apparent that below $T_f$ the behavior of the static susceptibility is characteristic of underdoped cuprates and, in particular, of $La_{2-x}Sr_xCuO_4$. Similarly, the nuclear relaxation rate below $T_f$ reflects copper spin dynamics which are typical of $La_{2-x}Sr_xCuO_4$ [13,14] and the cuprates in general [15]. The copper relaxation rate displays the characteristic form [14, 16] $KT_1T = a + bT$. Typically $^{63}(T_1T)^{-1}$ in the underdoped cuprates is maximum above $T_c$ and is decreasing at $T_c$. It is interesting that, as in the case of fully oxygenated $YBa_2Cu_3O_7$, [17] $^{63}(T_1T)^{-1}$ in Fig 4 maintains its maximum value with decreasing temperature down to $T_c$.

## VI. Temperature dependent structure

We have observed [9] that the structure of $La_2CuO_{4+\delta}$ is very sensitive to the presence of doped holes as well as to temperature. In the high temperature tetragonal phase the apex oxygen is located directly above the copper [18]; the orthorhombic distortion in stoichiometric $La_2CuO_{4.0}$ the oxygen octahedra rotate causing a lateral displacement of the apex oxygen. The quadrupole shift of the $^{139}$La NMR frequency is a very sensitive local probe of the lateral displacement of the apex oxygen. The structure of the metallic phase contrasts with that of the antiferromagnetic phase: at temperatures above $T_{PS}$ which are nevertheless below the tetragonal to orthorhombic phase transition, the apex oxygen is *not* displaced, however as the temperature decreases below $T_{PS}$ a distribution of lateral displacements develops. At low temperatures a *uniform* distribution of displacements is approached. Recent neutron scattering data [19] indicate similar displacements which display long range correlations. Apparently there is a long wavelength, commensurate modulation of this lateral displacement. We have shown that this distribution is not a manifestation of the distortion surrounding an interstitial dopant; rather it is the response of the crystal to the presence of doped holes.

In the temperature regime where these lateral displacements are developing and below $T_f$ we see that the static and dynamic magnetic properties of the material are not unusual in the context of the cuprates. A consensus has yet to be reached as to explanation for this novel magnetic behavior; an understanding of the relationship between the temperature dependent structure and the evolution of the magnetic properties in $La_2CuO_{4+\delta}$ may provide vital clues concerning the novel magnetic behavior of the cuprates. One very important avenue of exploration is indicated by $^{139}$La NQR data showing a decrease of the NQR frequency with temperature in both oxygen doped [20]

and lightly Sr doped [21] in this same temperature regime. Since the introduction of interstitial oxygen would tend to reduce the distance between the La and apex-O ions, this would increase the NQR frequency; a straightforward explanation of the decrease would be a decrease of the average charge on the apex oxygens surrounding the La. A correlation between structural rearrangements and charge motion has been inferred from annealing experiments in $YBa_2Cu_3O_{7-y}$ [22]; related phenomena may be playing a role here as well.

## VII. Appearance of second copper site

Copper NQR spectroscopy provides a local probe of electric field gradients in the $CuO_2$ planes. Such spectroscopy in $La_{2-x}Sr_xCuO_4$ [23-26] has revealed the existence of two distinct copper sites. The number of copper sites in the second environment was found to increase with x; it is generally believed that the second site was differentiated by the close proximity of a Sr dopant. One of the most surprising results to come from the oxygen-doped material containing no Sr is the observation of an essentially *identical* copper NQR spectrum [9]. Noting that the oxygen dopant is interstitial while the Sr substitutes for La and that the ionic charge of the differs both in magnitude and sign, it is clear that the second site is differentiated not by the presence of the dopant but by a feature common to both materials: the presence of doped holes. The NQR spectrum in undoped $La_2CuO_{4+\delta}$ displays only a single line [27]. The larger width of the copper NQR lines in earlier NQR spectroscopy in $La_2CuO_{4+\delta}$ prevented the observation of a second site [28].

The existence of a second copper site in the planes is striking because it has not been observed in diffraction experiments, in spite of the fact that the substantial intensity of the minority copper NQR line shows that there are a considerable number of these copper sites. The feature distinguishing this site must be static on the time scale of the inverse NQR frequency (~35 MHz). This frequency is very sensitive to both changes in local structure and to altered hole occupation of different copper orbitals [28]; e.g. the second site may be differentiated by a small difference in the occupation of the $Cu(3z^2 - r^2)$ orbital as well as by a different local structure.

## VIII. Summary

Oxygen doped $La_2CuO_{4+\delta}$ displays a rich variety of behaviors. Due to the unusually large mobility of the oxygen ions in $La_2CuO_{4+\delta}$ at high temperatures, it is the only cuprate which displays macroscopic phase separation of doped holes. We have presented the results of a study of this phase separation and pointed out some unusual features. Below a temperature $T_f$ the situation becomes similar to other cuprates since oxygen is no longer sufficiently mobile to allow further macroscopic phase separation. In this regime the magnetic behavior of metallic $La_2CuO_{4+\delta}$ is quite conventional in the context of the cuprates. However $^{139}La$ NMR spectroscopy [9] has shown the local structure of the La-O layer to be very sensitive to the presence of doped holes and to be strongly temperature dependent in this same regime. This sensitivity is evident in the $CuO_2$ planes where, in the presence of doped holes a second, distinct copper site is present. This provides an opportunity to explore the relationship between local structure and the novel magnetic behavior of the cuprates. Further experiments following this line of inquiry are planned.

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[8] Fig 2 of ref. 7 contains an error in the value of $\delta_M$ for the oxygen-rich phase. The values are obtained by comparison of the metallic phase susceptibility with that of $La_{1.85}Ca_{0.15}CuO_4$, L. Reven et al., *Phys. Rev. B* 43, 466 (1991). I am grateful to F.C. Chou for bringing to my attention subsequent work (A.R. Moodenbough et al., *Physica C 198*, 103 (1992)) showing that the solubility limit for Ca in this compound is approximately 0.10 thus indicating a lower hole doping for this compound than one would assume based on the nominal Ca concentration. Fig 1 here shows the corrected phase diagram.

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Figure Captions

Fig 1 Phase separation in $La_2CuO_{4+\delta}$. Temperature is plotted against the excess oxygen content $\delta$.. Note that $\delta$ is independent of temperature below 235 K for the AF phase and 200 K for the metallic phase and the very abrupt change in $\delta$ for both phases.

Fig 2 $^{139}$La spin lattice relaxation rate plotted as $(T_1T)^{-1}$ vs. temperature. The sharp peak at 210 K indicates the time scale for some oxygen motion important for $^{139}$La spin lattice relaxation is equal to the inverse of the Larmor frequency (~35 MHz).

Fig 3. Dependence of superconducting $T_c$ on annealing temperature. The large width of the peak in the curve argues against a mechanism involving incomplete phase separation.

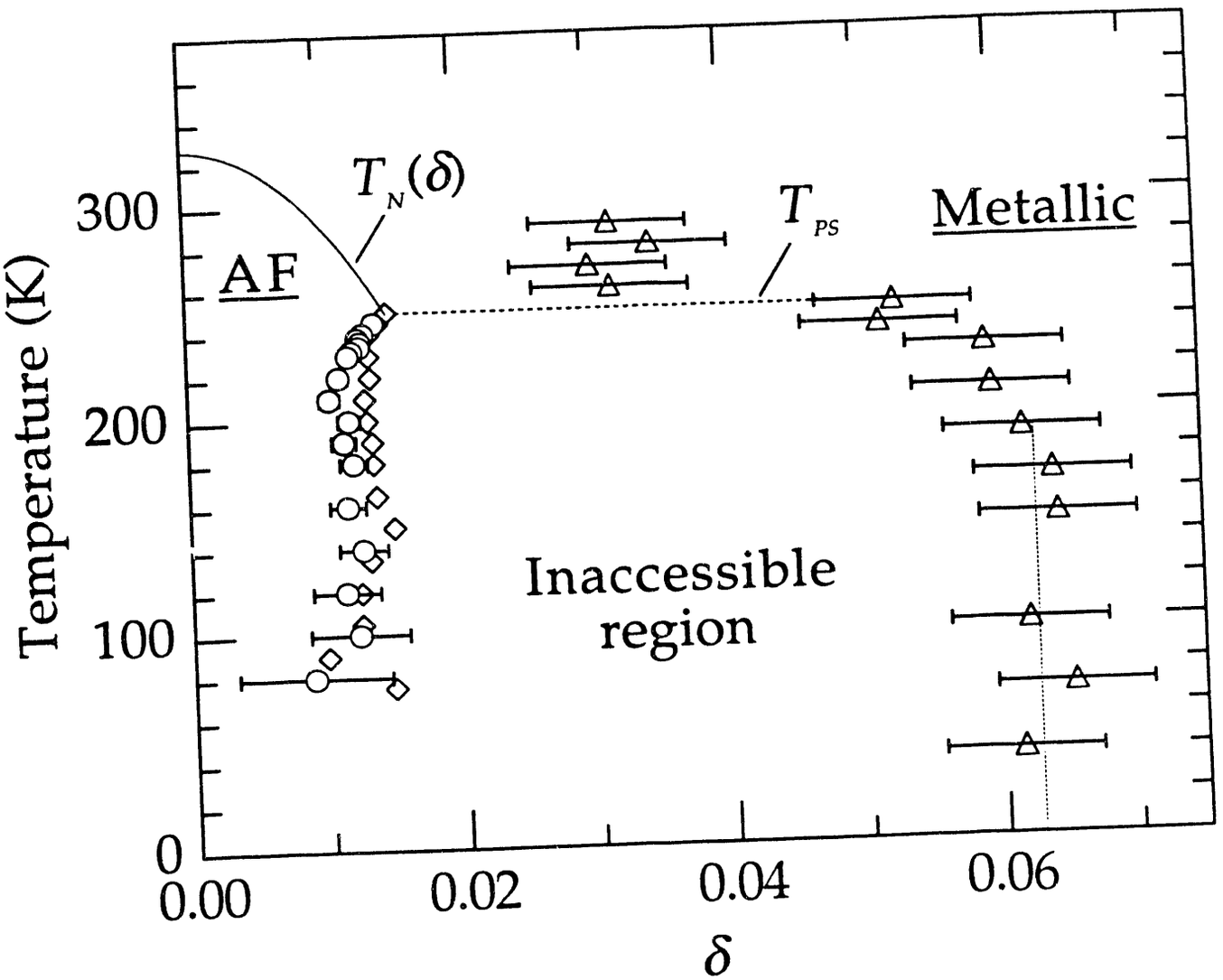


Fig 1

*Hammel et al. "Local Structure in Oxygen Doped $La_2CuO_{4+\delta}$*

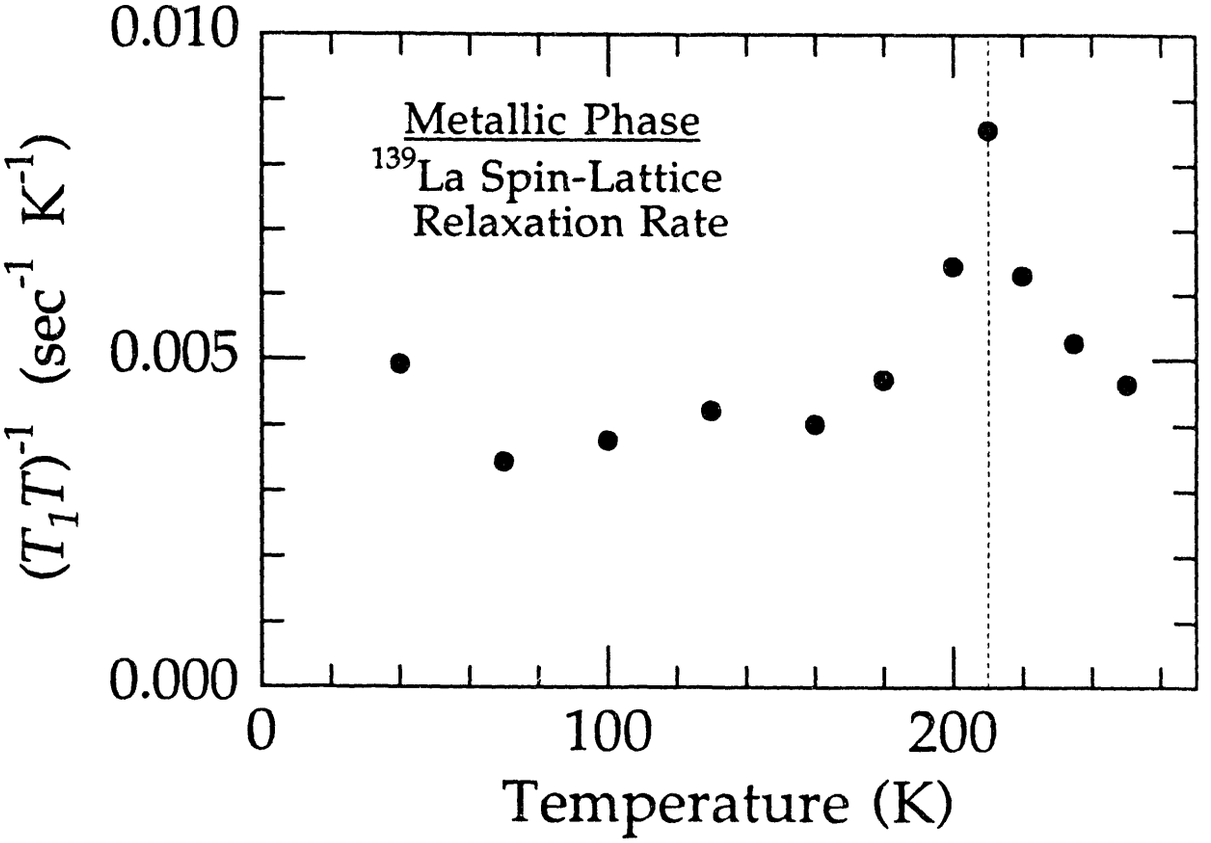


Fig 2

*Hammel et al. "Local Structure in Oxygen Doped $La_2CuO_{4-\delta}$*

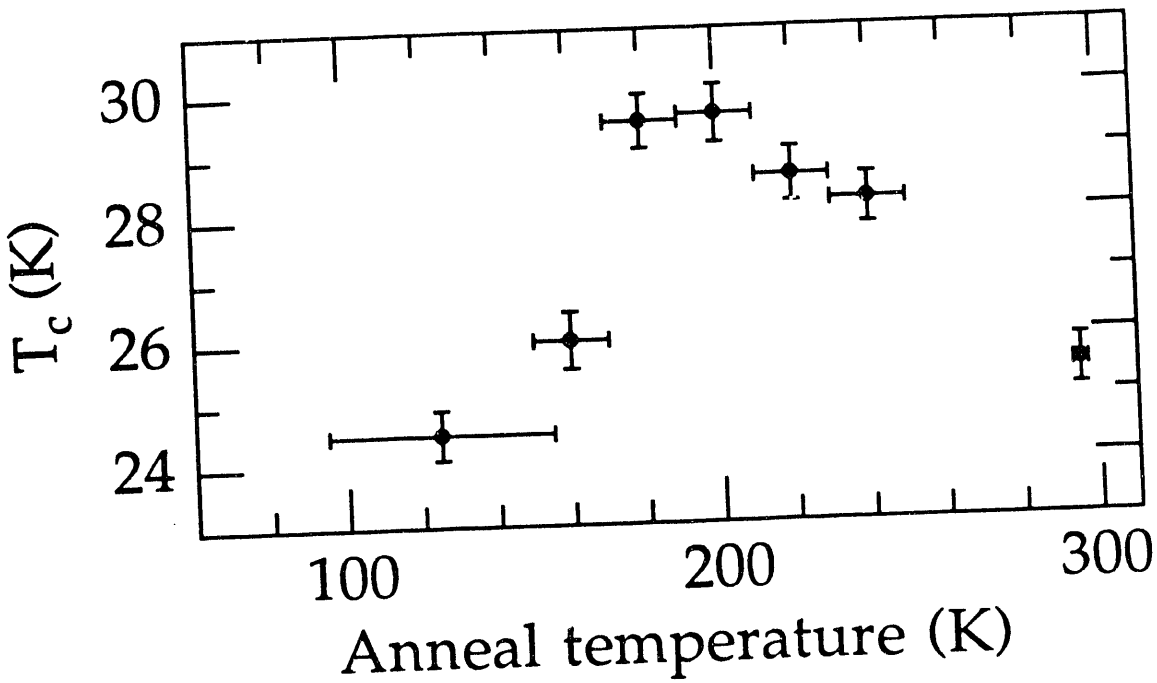


Fig 3

*Hammel et al. "Local Structure in Oxygen Doped $La_2CuO_{4=\delta}$*


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