NQR study of local structure and cooling rate-dependent superconductivity in La$_2$CuO$_4$+$\delta$

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NQR study of local structure and cooling rate-dependent superconductivity in La$_2$CuO$_{4+\delta}$

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Preliminary results of structural studies in oxygen-annealed La$_2$CuO$_{4+\delta}$($\delta$~0.03) using $^{139}$La nuclear quadrupole resonance (NQR) spectroscopy are reported. Superconducting critical temperatures were found to depend on the rate of cooling through a narrow temperature range near 195 K. Analysis of the $^{139}$La NQR spectra reveal that lanthanum atoms in the oxygen-rich metallic region occupy two sites having different local environments. One site has a structural configuration closely related to the stoichiometric oxygen-poor compound. The second appears only below 200 K and exhibits a large shift and broad distribution of NQR frequency $\nu_Q$. Changes in $\nu_Q$ in the vicinity of the superconducting transition were also observed for both metallic sites. Possible origins of these anomalies and their connection to superconductivity are discussed.

Since the discovery of filamentary superconductivity in nearly stoichiometric La$_2$CuO$_4$ and the subsequent observation of bulk superconductivity in mixed-phase high-pressure oxygenated La$_2$CuO$_{4+\delta}$ phase separation in the cuprates has been the subject of many experimental and theoretical investigations. La$_2$CuO$_{4+\delta}$ segregates to form oxygen-rich and oxygen-poor (nearly-stoichiometric, $\delta$~0) regions below the phase separation temperature $T_{ph}$~250 K. Estimates based on NMR and NQR data show that the amount of holes doped into each region remains constant down to low temperatures. While both phases have very closely related orthorhombic structures, the oxygen-rich region is metallic and superconducting while the oxygen-poor region exhibits antiferromagnetic order. Recently, the existence of new superconducting phases in high-pressure oxygen annealed La$_2$CuO$_{4+\delta}$ has been reported, where three superconducting onsets were found depending on the cooling process. Our studies on high quality samples revealed that the superconducting transition depends critically on the rate at which the sample is cooled through $\sim$195 K, and that the $T_C$'s can vary by as much as 5 K depending on the cooling rate. Similar phenomena has been associated with structural effects in YBa$_2$Cu$_3$O$_7$ samples, where annealing at room temperature increases $T_C$ due to local ordering of oxygen in the chains. Indeed, many investigators believe that structural effects play a direct role in the superconductivity of the cuprates. It is therefore important to investigate the microscopic structure and its effects on superconductivity in these systems.

Nuclear quadrupole resonance (NQR) sensitively probes the local charge distribution around a nucleus and provides an excellent tool for studying the electronic, magnetic, and structural properties of superconducting La$_2$CuO$_{4+\delta}$. For example, $^{139}$La NQR unambiguously distinguishes the metallic from the antiferromagnetic phase in this system. In the metallic phase, the quadrupolar energy levels of the La nuclei ($I=7/2$) are doubly degenerate in $m$; each $m\rightarrow m\pm 1$ transition gives rise to a single peak in the NQR spectrum. Below $T_N$, a local magnetic field due to the ordered moments removes this degeneracy and splits the NQR resonance line.

Samples of single crystal La$_2$CuO$_4$ were prepared using conventional techniques. These were crushed into powder, oxygenated in a bomb under 3 kbar of pressure and annealed at 525 °C for 12 h. Estimates of the oxygen composition give $\delta$~0.03. Superconducting transition temperatures ($T_C$) were determined by a SQUID magnetometer, and their dependence on the cooling rate was studied systematically. A fast cool ("quenched") NQR run was performed by pumping liquid helium into the sample cryostat through a capillary, cooling the sample at an average rate of 3300 K/h, whereas a slow cool run was a controlled cool down at a rate of 9 K/h. We found superconducting transitions at $\sim$25 K for the fast cool run and $\sim$30 K for the slow cool, with no broadening of the susceptibility curve, indicating a narrow distribution of $T_C$'s and that the superconducting phase remains macroscopically uniform. The NQR spectra were taken using a pulsed NMR spectrometer by sweeping the frequency with a calibrated signal source. Fourier transform spectra were also taken for the narrow spectral features and then fitted to a Lorentzian function to determine the center peak frequencies. The centroid frequencies were calculated for the broad non-Lorentzian lines.

Figure 1 shows the $^{139}$La spectra at various temperatures for the $\pm 7/2\rightarrow\pm 5/2$ transition. Split by the internal magnetic field, the doublet labeled AF originate from the antiferromagnetic phase while the singlet denoted as M1 arises from the metallic phase. The coexistence of the AF and M1 lines provides direct evidence of phase separation. At high temperatures, the M1 line is narrow, but it broadens somewhat as the sample is cooled. Its relative integrated intensity decreases monotonically down to $\sim$160 K where it becomes independent of temperature, corresponding to about 5%-10% of the total NQR signal. Although not obviously visible at 4.2 K, the existence of M1 is required to adequately fit the spectrum. This result is sup-
FIG. 1. $^{171}$La NQR spectra at 200, 160, and 4.2 K. The intensities for the slow and fast cool data are normalized against the antiferromagnetic peaks.

A broad non-Lorentzian feature is also observed at lower frequencies (M2 in Fig. 1). This signal becomes visible only below 200 K and grows stronger rapidly as temperature is decreased. Below ~160 K, its integrated intensity is roughly constant and constitutes about 50% of the total area. At a given temperature, the integrated intensity of M2 is independent of cooling rate although the line appears to be narrower for fast cool runs.

The positions of the NQR peaks as a function of temperature are shown in Fig. 2. The temperature dependence of the frequencies of the AF lines is consistent with the undoped La$_2$CuO$_4$ (Ref. 2). The M1 lines has the same NQR frequency $\nu_0$ as the AF lines at all temperatures, except in the neighborhood of $T_c$ where a substantial deviation occurs. Within experimental error, we found no difference in the peak positions for all the lines as a function of cooling rate.

The large width and non-Lorentzian shape of the M2 line indicate a considerable distribution in the electric field gradient (EFG) at the La probe site which is sensitive to local structures over a length scale of ~10 Å. This distribution could result from the incorporation of interstitial oxygen between the LaO layers causing huge lattice distortions and variations in the ionic charges of the atoms in the layer. However, we believe this not to be the case. The substantial distortion of the local lattice in the immediate vicinity of an interstitial oxygen means that near-neighbor shells of lanthanum nuclei around excess oxygen sites are completely "wiped-out" of the NQR line, and the most distant nuclei are not directly affected. Only those lanthanums that are farther away from any excess oxygen are seen in the spectra. The fact that M2 line follows a similar temperature dependence as M1 and that both lines are not split indicate that both signals must originate from the same oxygen-rich metallic phase, so that if the large width of M2 were due directly to the interstitial oxygen, the M1 line should be broadened as well. Note that M1 is narrow above and below $T_c$. Thus the distribution of local EFGs indicated by the width of the M2 line cannot be simply due to the presence of the interstitial oxygen, rather, some modification of structure associated with the introduction of excess holes by these oxygens must be considered.

A distribution of the tilt angle of the CuO$_6$ octahedra (as are known to occur in Sr and Ba doped compound$^{[15]}$) or a distribution of Cu-apical oxygen bond lengths would not be inconsistent with this broadening. Previous NMR results from oxygenated single crystal La$_2$CuO$_{4+8}$ show the development of a tilt of the EFG at the La site as the sample is cooled below 200 K (Ref. 11). Whether the tilts of the EFG axes are caused by the CuO$_6$, octahedral tilts directly, or indirectly, via subsequent changes in the La-apical oxygen distances, the evolution of the spectra is consistent with the change in the degree of these tilts. A substantial distribution of these tilts effectively produce a number of inequivalent La sites that could account for observed large width of the NQR line.

It is not clear from our data why $T_c$ is reduced for fast cooling. However, we note that the temperature at which the M2 line begins to appear (~200 K) is the same temperature through which slow cooling optimizes $T_c$. Although the NQR data are not sufficient to determine the exact local structure in the vicinity of La probe, this important observation suggests that structural anomalies hap-
pennu at this temperature may be connected to supercon-
ductivity.

The observed shift of the NQR frequency \( v_Q \) of the
metallic lines in the vicinity of \( T_c \) raises an issue about the
role of local lattice changes in the superconductivity of
these materials. This anomaly in \( v_Q \) seems to be fairly com-
mon, as it also occurs in La and Cu NQR in
\( \text{La}_2\text{Ba}_4\text{Cu}_9\text{O}_{14} \) and \( \text{YBa}_2\text{Cu}_3\text{O}_7 \), respectively.\(^{12}\) Generally,
shifts in NQR frequencies are structural in origin and can
be caused by changes in vibrational or torsional phonon
modes or a true structural phase transition. Although no
structural phase transition has been detected near 40 K by
neutrons in this compound, atomic pair distribution anal-
ysis on several cuprates reveal that in the vicinity of \( T_c \), a
significant deviation of local structures from the crystallo-
graphic averages exists without forming long-range or-
der.\(^{13}\) Anomalies at \( \sim T_c \) have also been observed in ther-
mal expansion coefficient, elastic constants, and specific
heat both in undoped \( \text{La}_2\text{CuO}_4 \) and superconducting
\( \text{La}_{1.55}\text{Sr}_{0.15}\text{CuO}_4 \) (Ref. 14).

In summary, we investigated the effects of the cooling
rate on the microstructures of superconducting
\( \text{La}_2\text{CuO}_{4+\delta} \) using \(^{139}\)La NQR. We observed the appearance
of an additional La lines which we argued to be coming
from the metallic phase, but which appears only below
200 K, the same temperature through which slow cooling
is critical for \( T_c \). We also observed shifts in La NQR fre-
cuencies near \( T_c \), an anomaly whose origin is attributed
to changes in the local structures. Complementary NMR ex-
periments in oxygenated single crystals are currently in
progress.

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\(^{1}\) See, for example, Proceedings of the International School on Phase Sep-
oration in Cuprate Superconductors (Erice, Italy), edited by K. A.
Muller (World Scientific, Singapore, in press).


\(^{3}\) T. Egami, S. J. L. Billinge, T. M. Rice, and A. Migliori for stimulating discussions. We also thank D. E. MacLaughlin for useful comments on the manu-
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