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LA-UR- 93-2162

Title: Phase Separation and Superconductivity in Lanthanum-2-Copper-Oxygen-4+delta: Effects of Oxygen Diffusion

Author(s):
A.P. Reyes
P.C. Hammel
E.T. Ahrens
J.D. Thompson
P.C. Canfield
Z. Fisk
J.E. Schirber

Submitted to: Invited paper for Spectroscopies in Novel Superconductors, March 17-19, 1993, Santa Fe, NM

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Summary

Phase Separation and Superconductivity in $La_2CuO_{4+\delta}$: Effects of Oxygen Diffusion

Bulk magnetization measurements in oxygen annealed $La_2CuO_{4+\delta}$ shows an increase of superconducting transition temperature T_c when the sample is slowly cooled through 195K. ^{139}La NQR has been performed on this sample to examine the structural changes accompanying this phenomena. Data shows an appearance of an unusual feature in the spectra exhibiting a large distribution of local structures in the vicinity of lanthanum sites. The volume fraction of this anomalous structure increases with the cooling rate. These results are interpreted in terms of oxygen diffusing through the phase separated sample whose diffusion time is comparable to the cooling time. A picture consistent with the observed behavior of T_c with annealing temperature is obtained. The activation energy of the diffusion process derived from this model is in agreement with that obtained from direct measurements using oxygen tracers.

PHASE SEPARATION AND SUPERCONDUCTIVITY IN $La_2CuO_{4+\delta}$: EFFECTS OF OXYGEN DIFFUSION

A. P. REYES, P. C. HAMMEL, E. T. AHRENS, J. D. THOMPSON, P. C. CANFIELD†,
Z. FISK, and J. E. SCHIRBER*

Los Alamos National Laboratory, Los Alamos, New Mexico 87545
*Sandia National Laboratories, Albuquerque, New Mexico 87185

ABSTRACT

In oxygen-annealed $La_2CuO_{4+\delta}$ (δ 0.03), bulk magnetization measurements show an increase of 4K in the superconducting T_c when the sample is cooled slowly through a narrow temperature range near 195K. At this temperature, ^{139}La NQR spectra exhibit a concomitant appearance of an anomalous feature associated with the metallic phase whose spectral weight increases with cooling rate. The data suggests a distribution of local structures and annealing-dependent volume fraction on this part of the sample. Interpretation of these results in terms of oxygen diffusion in a phase separated material is considered and a picture consistent with the observed changes in T_c is obtained. Other possible origins of these anomal[illegible] the role they play in determining the superconducting properties of this system are discussed.

Keywords: NQR, NMR, high-T_c superconductivity, local structures, phase separation, oxygen mobility, La_2CuO_4

INTRODUCTION

Despite the numerous theoretical and experimental advances suggesting magnetism as the dominant mechanism in the superconductivity of the cuprates, it remains an open question whether the structural instability in these compounds provides the underlying framework.[1] Structural features with unusual behaviors may hold clues vital to the understanding of novel properties of these materials; a study of structural aspects in the superconducting oxides is very important. Recently, the existence of new superconducting phases in high-pressure oxygen-annealed $La_2CuO_{4+\delta}$ has been reported,[2] where three superconducting onsets were found depending on the cooling process. Such thermal history dependent T_c is also exhibited by other cuprates where a significant number of oxygen vacancies are present or the oxygen stoichiometry is not optimum for superconductivity.[2-8] Local structural arrangement of oxygen among the specific sites auxiliary to the CuO_2 planes has been invoked to explain these effects. For example, in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ an increase in T_c of 0–20K has been observed after various annealing times at room temperature.[3-5] It was suggested that during the anneal, local ordering of oxygen on the chain sites optimizes the number of hole carriers in the planes and thus T_c. The mechanism for the changes in T_c in the case of oxygen annealed $La_2CuO_{4+\delta}$ is less clear, but it was suggested that the phase separation process in this system plays a role.

Phase separation in $La_2CuO_{4+\delta}$ involves segregation of the excess oxygen into two macroscopic phases below a characteristic temperature T_{ps}.[9] One phase resembles the nearly stoichiometric insulating material which is poor in oxygen (δ 0.01) and antiferromagnetic. The other phase containing the excess oxygen (δ 0.06) is metallic and superconducting. The excess oxygen is incorporated into interstitial lattice positions between the La-O layers and tetrahedrally coordinated by four La atoms.[10] Estimates based on NMR and NQR data show that upon the completion of the phase separation process, the amount of excess oxygen in each region remains constant down to low temperatures.[11] In spite of the differences in the ground state properties and oxygen content, both phases have closely related orthorhombic structures.[9]

Our studies on high quality $La_2CuO_{4+\delta}$ (δ 0.03) samples revealed that the superconducting transition depends critically on the rate at which the sample is cooled through 195K, and that the

T_c's can vary by more than 4K depending on the cooling rate. We have employed ^{139}La NQR to search for accompanying structural changes occuring in the crucial cooling regime. A preliminary report of these results and related studies have appeared elsewhere.[11-13] This paper presents new analysis in terms of oxygen diffusion in the phase separated compound consistent with the observed thermal history dependent T_c.

EXPERIMENT

Samples of superconducting $La_2CuO_{4+\delta}$ were made from crushed crystals of nearly stoichiometric $La_2CuO_{4+\delta}$ that were oxidized in a 3 kbar oxygen atmosphere at 575°C for 12 hours. Estimates of the average oxygen composition based on similarly prepared crystals give $\delta \sim 0.03$ (Ref 10). D. C. susceptibility and superconducting transition temperatures (T_c) were determined by a Quantum Design SQUID magnetometer, and their dependence on the cooling rate was studied systematically. The inset of fig. 1 shows the thermal sequences used to locate the critical cooling regime necessary for optimum T_c. Initially, the sample was rapidly quenched from room temperature to 5K and T_c was measured upon warming. Then, for each 20K interval between 250K to 150K, the sample was slow-cooled at an average rate of 0.1K/min, followed by a rapid (~3K/min) cool to 5K and T_c was measured again upon warming up. For all these measurements, the sample is cooled at zero field and T_c was measured with an applied field of 10 Oe. For the NQR measurements, fast cool runs were carried out by pumping liquid helium into the sample cryostat through a capillary, cooling the sample at an average rate of 55K/min, whereas a slow cool run was a temperature controller-regulated cool down at 0.15K/min. The NQR spectra were taken on the ±7/2 ↔ ±5/2 transition using a pulsed NMR spectrometer by sweeping the frequency with a calibrated signal source or by taking the Fourier transform of the spin-echo. The spectra were fitted to a Lorentzian function to determine the center peak frequencies. The centroid frequencies were calculated for the broad non-Lorentzian lines.

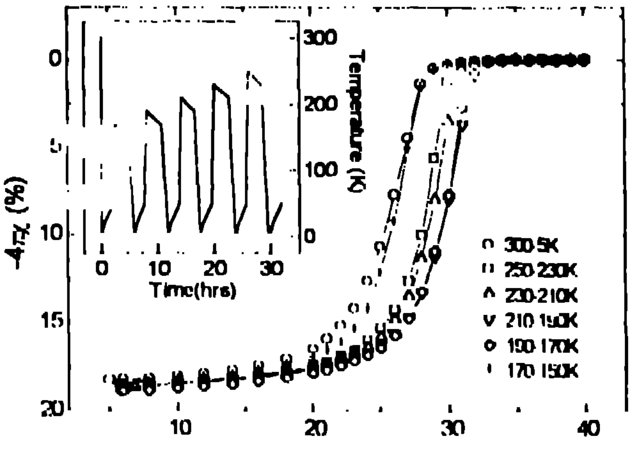

Fig. 1 Diamagnetic shielding curves for each 20K interval of slow-cooling. Inset: Cooling sequence for determining the critical cooling regime for T_c.

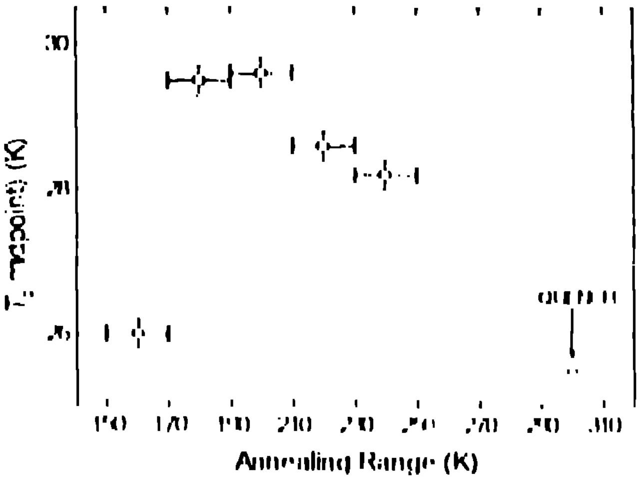

Fig. 2 Plot of the midpoint T_c obtained for each 20K temperature annealing interval shown as horizontal error bars. The vertical error bars represent the transition widths. The dotted line is a guide to the eye.

RESULTS

Susceptibility measurements and cooling rate dependent T_c

The zero field cooled diamagnetic susceptibility, corrected for sample shape demagnetization is plotted in fig. 1. The

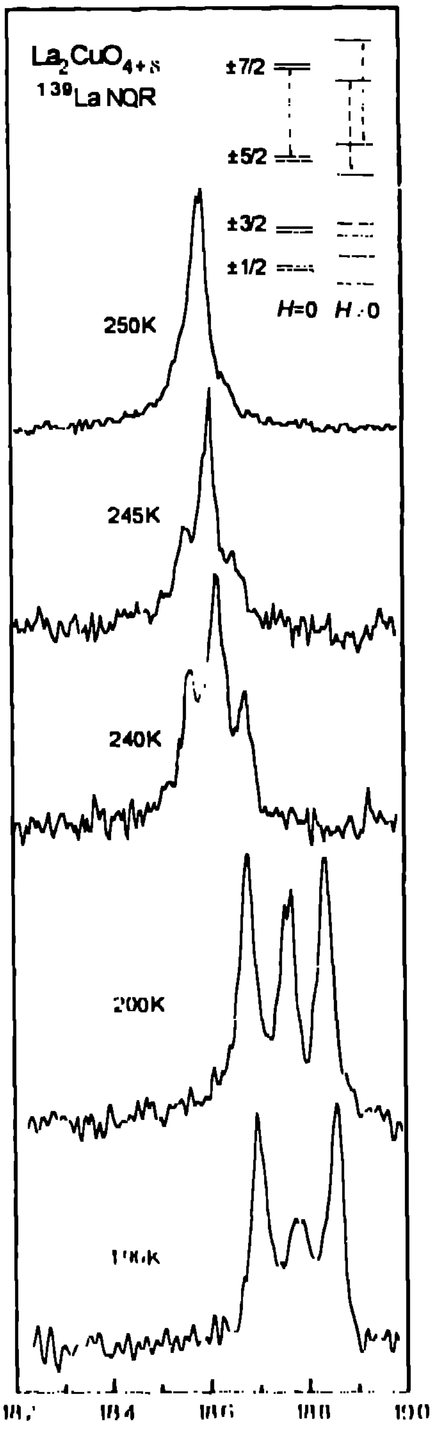

Fig. 3. Temperature dependence of the ^{139}La spectra through the phase separation temperature. The central peak arises from the metallic phase and the two outermost peaks originate from the antiferromagnetic phase. Inset: Nuclear energy level diagram for $I = 7/2$ and $\eta = 0$. Zeeman perturbs quadrupole hamiltonian appropriate for La_2CuO_4. The spectral features correspond to

superconducting transition widths, defined by 20-80% points on the susceptibility curve remain fairly narrow for each cooling sequence, averaging at about 4.2K° with less than 1K° variation. This indicates a macroscopically uniform superconducting phase. In Fig. 2, the superconducting transitions, determined from the midpoints of the susceptibility curve are plotted as a function of the temperature interval within which the sample was slow cooled. This interval is indicated by the horizontal error bar. The vertical error bar denotes the transition width. The quenched samples produce T_c of ~25K. The highest bulk T_c of 29.6K is achieved for the slow cooling range between 210–190K but is slightly reduced for the 190–170K range. From this we estimate that the critical cooling range which optimizes T_c is 195±10K. The striking feature is that annealing at temperatures higher than 210K actually produces a lower T_c if one then passes rapidly through the critical temperature band. This suggests that a change occurs around 200K which requires some time to proceed to the optimum condition. We found that the material with optimal T_c can also be produced by annealing the sample at 195K for at least 20 minutes; longer anneals produce identical T_c. Assuming this anneal is equivalent to slow-cooling through 195±10K over 20 minutes, one gets a rough estimate of the optimal cooling rate of 1K/min for the high T_c phase. We note that this critical temperature is much below the phase separation temperature, T_{ps} ~ 250K, and more importantly, slow-cooling through T_{ps} does not optimize T_c. These results are completely reproducible and each step in the process is independent of any previous thermal history.

Nuclear quadrupole resonance spectra

Underlying structural effects that might accompany the observed phenomenon can be investigated using ^{139}La nuclear quadrupole resonance (NQR) spectroscopy. NQR sensitively probes the local charge distribution around a nucleus and provides an excellent tool for studying the electronic, magnetic, and structural properties of solids. The nuclear resonance is primarily determined by the nuclear quadrupole moment Q and the electric field gradient (EFG), $V_{ij} = \partial^2 V/\partial x_i \partial x_j$, where V is the electrostatic potential at the nuclear site.[18] The crystalline EFG interacts with the quadrupole moment of the probe nucleus and alters the energy of various nuclear spin states. In zero magnetic field and EFG of axial symmetry, the quadrupole Hamiltonian gives rise to nuclear energy levels degenerate in ±m. For ^{139}La isotope, the spin $I = 7/2$ and

$$E^{o}_{m} = (1/21)h\nu_Q[3m^2 - 63/4],$$

where ν_Q is the quadrupole frequency which is proportional to the product of the EFG and Q. A perturbing external (or internal) magnetic field H removes this degeneracy, which

$$E_m = E^\circ_m \pm m\gamma hH\cos\theta,$$

where γ is the nuclear gyromagnetic ratio and θ is the angle between the field and the principal symmetry axis of the EFG. In stoichiometric La_2CuO_4, there exists a single unique La crystallographic site. For the ±7/2 ↔ ±5/2 transition, a single peak in the NQR spectrum is expected in the metallic phase corresponding to this site, whereas in the AF phase below the Néel temperature T_N, the presence of a dipolar or transferred hyperfine field from ordered Cu^{2+} moments gives rise to a doublet (see inset, Fig. 3). The doublet arises from the splitting of the otherwise degenerate levels and not from the opposing sublattice magnetization.

In fig. 3 we show the evolution of ^{139}La spectra for the ±7/2 ↔ ±5/2 transition through the phase separation temperature, $T_{ps} \sim 250K$. Above this temperature, only a single lanthanum peak is observed indicating a uniform metallic phase. Below T_{ps}, two peaks originating from the antiferromagnetic phase develop without broadening of the original metallic line. The coexistence of these lines is an excellent and unambiguous demonstration that the sample undergoes phase segregation. This behavior is entirely reversible, implying that the phase separation process is an equilibrium phenomenon. It is important to note that the metallic line was never observed in the parent compound ($\delta \sim 0$) below T_N. Interestingly, the quadrupole frequencies extracted from the data are identical in both phases. This is indicative of the fact that although one phase is devoid of excess oxygen, the underlying local structure surrounding the lanthanums does not change drastically after phase separation occurs. The temperature dependence of the splitting of the AF peaks extrapolates to an effective Néel temperature not very far from T_{ps}, $T_N \sim T_{ps}$.

At lower temperatures (not shown), the relative intensity of the central peak metallic line decreases monotonically down to ~160K where it becomes independent of temperature, corresponding to about 5-10% of the total NQR signal. Although not obviously visible at 4.2K, its existence is required to adequately fit the spectrum. Evidence for its existence at low temperatures is the observation by other workers[17-18] of a La NQR signal at 6.3 MHz corresponding to ±3/2 ↔ ±1/2 transition, consistent with the signal we observed. This signal was associated with the metallic phase since it is absent in undoped samples.

Further scrutiny of the NQR spectra at low temperatures reveals that the metallic line evolves into a broad non-Lorentzian feature at lower frequencies (Fig. 4). This broad line is absent in the parent compound . The large width of this feature indicates that a significant number of lanthanum sites experience a broad distribution of EFG's. This signal becomes visible only below 200K and grows stronger rapidly as temperature is decreased. Below ~160K, its integrated intensity is roughly constant and constitutes a fairly large portion (about 50%) of the total intensity. Fig. 4 shows the effect of the slow and fast cooling on the spectra at 4.2K. The data are normalized such that the total integrated area of both spectra are equal, i.e. the total number of nuclei are conserved.[ref] We found that for the fast cool, the total fractional volume of the metallic phase (the central peak and the broad feature) shows a 10% increase over its value for the slow cool, with the corresponding decrease in the intensity of the antiferromagnetic lines.

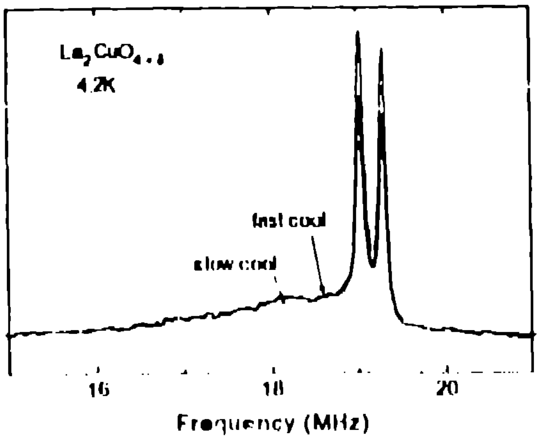

Fig. 4 La spectra at 4.2K for slow and fast cool runs. The data are normalized against the total area. No correction due to T_1 has been made (see text)

DISCUSSION

NQR spectra and interstitial oxygen

NQR is a local probe sensitive to structural distortions from the average local positions over length scale of a few lattice constants. Although the NQR data are not sufficient to determine the exact local structure in the vicinity of the La probe, the observation that changes in the NQR spectra accompany the changes that we observe in T_c lead us to briefly consider some situations where details of oxygen configuration could have an effect on the La spectra and the superconductivity of La_2CuO_4.

The large width of the metallic line at low temperaures indicate a considerable distribution in the electric field gradient (EFG) at the La probe site. One may speculate that this distribution results from the incorporation of interstitial oxygen between the La–O layers causing huge lattice distortions and variations in the ionic charges of the atoms in the layer. However, this hypothesis is inconsistent with the following arguments. Using a point charge model,[19] we calculated the EFG's at La sites due to an interstitial oxygen and found that an excess oxygen greatly affects only its nearest neighbor lanthanums such that they would experience 2–3 times the EFG (and hence its resonance frequency) that it would have if the oxygen were absent. Obviously, due to the substantial distortion of the local lattice in the immediate vicinity of an interstitial oxygen, these lanthanum nuclei around excess oxygen sites are completely shifted off-scale, and the most distant nuclei are not directly affected. Only those lanthanums which are farther away from any excess oxygen are seen in the spectra. Because the excess oxygen is very dilute in these samples, only about 10% of these La nuclei are affected. Thus, the distribution of local EFG's indicated by the width of the metallic line cannot be simply due to the presence of the interstitial oxygen, rather, some modification of structure resulting from the introduction of excess holes by these oxygens must be considered.

Perovskites are known to have an inherent instability towards CuO_6 octahedral tilting which is the system's response to relieve the local strains caused by bond length mismatches among various atoms. This has been observed in a number of high T_c oxides.[20] A distribution of the tilt angle of these octahedra as well as a distribution of Cu-apical oxygen bond lengths would also explain the broadening of the metallic line. Our NMR results[21-22] from oxygenated single crystal of $La_2CuO_{4+\delta}$ show the development of a tilt of the EFG at the La site as the sample is cooled below 200K. Whether the tilts of the EFG axes are caused by the octahedral tilts directly, or indirectly, via subsequent changes in the La-apical oxygen distances the evolution of the NMR spectra is consistent with the change in the degree of these EFG tilts. A substantial distribution of these tilts effectively produces a number of inequivalent La sites that could account for observed large inhomogeneity in the NQR line.

One supporting evidence that excess oxygen are not responsible for the anomaly in the La spectra is from the copper NQR in the same compound. We observed that the Cu NQR spectrum exhibits two distinct copper sites in the metallic phase, in contrast to the single site expected on the basis of crystallography.[22] This is essentially identical with what is seen in $La_{2-x}Sr_xCuO_4$ samples[23] where a complete crystallographic site substitution of Sr for La, as opposed to interstitial occupation as in oxygen, occurs. The quadrupole frequency extracted from the data agrees very well in both compounds. This similarity is highly unusual and not expected to result from the two similar crystallographic sites that are only charge-differentiated by either the oxygen or strontium neighbors. Rather, the feature which distinguishes the second copper site must be common to both materials and independent of the detailed method of doping. This result therefore suggests that the doped holes due to these dopants are primary contributors to intrinsic inhomogeneity in the local structure of this compound.

Phase separation and oxygen diffusion

We note that the temperature at which the broad metallic feature begins to appear (~200K) is the same temperature through which slow cooling optimizes T_c. Together with the observed increase of the volume fraction of the metallic phase for fast-cooling, these important results suggest that the relative concentration of the two coexisting phases have a special significance to the electronic properties of the system which may be connected to superconductivity.

Our data shows that the final low temperature oxygen configuration within the sample is dependent on the cooling rate through 195±10K. This requires a rapid loss in the mobility of excess oxygen below ~200K. Such freezing of oxygen motion can be effectively probed by the La spin-lattice relaxation (T_1). We have determined previously[11] that at high temperatures, the La relaxation is not magnetic but rather quadrupolar in origin, caused by fluctuations in the electric field gradient due to the hopping motion of the oxygens. This is reasonable since the highly mobile excess oxygen alters a La–O bond distance considerably and the EFG is strongly affected. The measured temperature dependence of the La relaxation rate, details of which are discussed elsewhere,[29] shows a maximum at ~210K at nuclear Larmor frequency $\nu_L = 50$ MHz. A maximum in $1/T_1$ is expected to occur when ν_L is comparable the inverse correlation time of the hopping motion. Our calculations from this data, using the activation energy of 1.13±0.12 eV obtained from ^{18}O diffusion measurements[30] in $La_{2-x}Sr_xCuO_{4-y}$ suggest that by 180K, it would take an average of 18 minutes for the excess oxygen to travel the ~1000Å (Ref. 9) distance required to form metallic domains. This is in agreement with the observed critical rate necessary for producing the phase with optimal T_c. It is important to note that the oxygens are unexpectedly highly mobile at and even below T_{ps} and their mobility does not diminish until ~180K.

This result allows us to consider an interpretation of the T_c data in terms of the phase separation process, oxygen mobility and the observed volume change in the metallic phase as a function of cooling rate. The temperature dependence of the excess oxygen content in the insulating and metallic phases during the phase separation process have been determined by Hammel and co-workers[11] using ^{17}O NMR Knight shifts and La NQR data. The resulting phase diagram,^{ref} reproduced in fig. 6, shows a miscibility gap opening discontinuously below T_{ps} ~ 250K. At about 200K and below the excess oxygen content δ in each region of the sample remains constant, consistent with the freezing of oxygen motion. There is a regime $200 < T < 250$K where the excess oxygen concentration in the metallic phase has a strong temperature dependence within which the oxygens must migrate enough distance in order to form the metallic domains in a time determined by its diffusion rate. For a sufficiently high cooling rate, it is then possible for the system to freeze in a state with a non-equilibrium concentration of oxygen in the metallic phase[11] and consequently give a less than optimal amount of hole doping for superconductivity. In other words, consider a case where the sample is quenched from room temperature to a very low temperature. Initially [illegible] are uniformly distributed and the sample is metallic. When the sample cools and reaches T_{ps}, the oxygens start to segregate. Because this process is so slow and the cooling rate is very fast the oxygens would not have time to move far enough before the sample reaches the freezeout temperature. The system ends up having small regions of very little excess oxygen which become the antiferromagnetic phase, while the rest of the sample containing all the

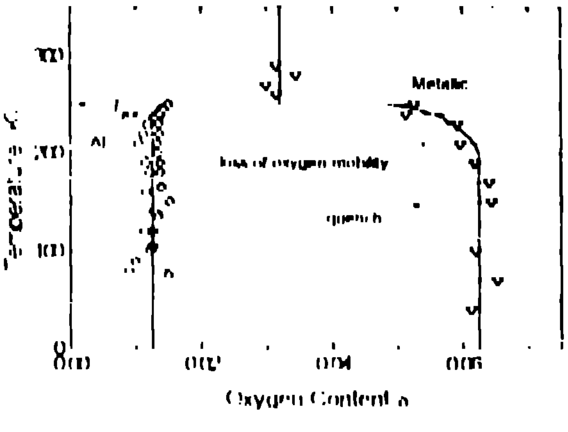

Fig. 6. Excess oxygen phase diagram of superconducting $La_2CuO_{4+\delta}$ from Hammel *et al.* (Ref. 11). The line labeled "quench" is estimated by the lever rule using the determined volume change from the slow to fast cool NQR spectra. The corresponding shift for the AF phase is not shown.

excess oxygens remains metallic. In the phase diagram of fig. 6, the line corresponding to the metallic δ would be shifted toward a smaller value. On the other hand, if the sample is slow cooled or is annealed just above the freeze-out, more efficient segregation would take place. Larger AF domains and smaller metallic regions are formed. The smaller metallic regions contain most of the oxygens. Consequently, a larger concentration of holes are doped into this phase and this leads to a higher T_c. Thus, the metallic phase with higher T_c occupies a smaller volume. Our estimate for the change in δ given the measured volume change from the La spectra is $\Delta\delta = 0.009$. This can be roughly translated to a change in T_c using the known dependence of T_c on hole concentration in $La_{2-x}Sr_xCuO_4$ (Refs. 32 and 33) and assuming linear correspondence between δ and x. We obtained $\Delta T_c \sim 5.5K$, in close agreement with the measured value of ~4.6K.

SUMMARY

In summary, ^{139}La NQR spectroscopy has clearly demonstrated that phase separation occurs in oxygen-annealed superconducting $La_2CuO_{4+\delta}$ and provided clues to understanding the effects of the cooling rate on the local structures of this compound. We observed the appearance of a spectral anomaly in the lanthanum lines coming from the metallic phase, but which appears only below 200K. Modeling of the NQR spectrum for random distributions of interstitial oxygen as well as local structural distortions involving CuO_6 octahedra had shown that NQR frequency shifts that were observed for the metalllic sites cannot be explained by the presence of the oxygen in the interstitial sites. The observed inhomogeneity in structure is not a manifestation of a local distortion around interstitial oxygen but rather an intrinsic response of the system to the presence of holes doped by these oxygens.

The superconducting transitions vary by more than 4K and show a strong sensitivity to cooling rate in the temperature regime 195±10K, the same temperature where the anomalous feature in the ^{139}La NQR appears. The data also indicate a cooling rate dependence to the metallic volume fraction. The La relaxation rate data and the excess oxygen phase diagram suggest that oxygen mobility is lost around this temperature. We have interpretated the T_c data based on these results and found that it is consistent with the fact that the observed cooling-rate dependent superconductivity is a volume effect phenomenon in which the hole doped into the metallic phase is not optimized for superconductivity. These results could have profound implications on experimental measurements of the physical properties of this system that are sensitive to amount of hole doping. These also illustrate how a rich variety of physics can be studied where perturbations from hole doping can be varied without extrinsic modification of the sample composition.

ACKNOWLEDGMENTS

We are grateful to R. H. Heffner and B. Büchner for stimulating discussions. Work at Los Alamos was performed under the auspices of the U. S. Department of Energy.

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The value of the low temperature oxygen content along the metallic boundary in the diagram on p.145 of Ref. 11 should be positioned at $\delta = 0.063$.

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