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This paper repor s nuclear quadrupole resonance studies in superconducting $La_2CuO_{4+\delta}$. The role o. cooling was found to significantly alter the transition temperature by as much as 6K. Analysis of NQR data reveals a presence of a more disordered phase whose intensity increases as the cooling rate and a large shift in the NQR frequency. Abrupt shifts in the NQR frequency were also observed and were interpreted as a signature of local structural anomaly.

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NQR STUDY OF LOCAL STRUCTURES AND COOLING RATE DEPENDENT SUPERCONDUCTIVITY IN $La_2CuO_{4+\delta}$

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Structural properties of oxygen-annealed polycrystals of $La_2CuO_{4+\delta}$ ($\delta \sim 0.03$) have been studied using ^{139}La NQR spectroscopy. Superconducting critical temperatures were found to depend on the rate of cooling through a narrow temperature range at about 195K. Preliminary analysis of the ^{139}La NQR spectra suggest that the oxygen-rich phase-separated region is composed of two structurally distinct phases, both of which are metallic and super-conducting. One phase has a structure closely related to the stoichiometric oxygen-poor compound. The second shows a considerable amount of apical oxygen disorder, a large shift in NQR frequency ν_Q, and a volume fraction which increases with cooling rate. The formation of the second phase below ~200K is indicative of the freezing of CuO_6 octahedral tilting. Abrupt shifts in ν_Q above T_c were also observed for both phases, suggestive of a local structural anomaly or charge transfer to the Cu-O plane.

I. Introduction

Since the discovery of filamentary superconductivity in nearly stoichiometric La_2CuO_4 and a subsequent confirmation in mixed-phase oxygenated $La_2CuO_{4+\delta}$, phase separation in the cuprates has been the subject of many experimental and theoretical investigations.[1] It is well known that $La_2CuO_{4+\delta}$ segregates to form oxygen-rich and oxygen-poor (nearly-stoichiometric, $\delta \sim 0$) regions below the phase separation temperature $T_{ps} \sim$ 260K. Estimates based on NMR and NQR data show that the amount of holes doped into each region remains constant down to low temperatures.[2] While both phases have very closely related orthorhombic structures[3] due to the tilting of the CuO_6 octahedra, 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 $La_2CuO_{4+\delta}$ has been reported.[4] Three superconducting onsets were found depending on the cooling process. A more systematic study[5] on high quality samples indicated that the superconducting transition depends critically on the rate at which the sample is cooled through a very narrow range of temperature in the vicinity of 195K, and that the T_c's can vary by as much as 5K depending on the cooling rate. This cooling rate dependent T_c behavior has also been observed in $YBa_2Cu_3O_7$ samples,[6] where it has been interpreted that annealing at room temperature causes local ordering of oxygen in the chains which increases T_c. Indeed, many investigators believe that structural effects play a significant role in the superconductivity of the cuprates. It is therefore important to provide as much information as possible on the microscopic structure and its effects on superconductivity in these systems.

^{139}La nuclear quadrupole resonance (NQR) is a sensitive probe of local electronic, magnetic, and structural properties of the $La_2CuO_{4+\delta}$ system. Local magnetic fields at La sites due to ordered moments within the sample split otherwise degenerate nuclear quadrupole levels, while those of the paramagnetic part of the sample remain unsplit, providing a clear and unambiguous distinction between the antiferromagnetic phase and the non-magnetic metallic phase in the sample. [7-8]

II. Experiment

Samples of single crystal La_2CuO_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 hours. Superconducting transition temperatures were determined by a SQUID magnetometer, and their dependence on the cooling rate was studied systematically as described elsewhere.[5] 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 3300K/hr, whereas a *slow cool* run was a controlled cooldown at a rate of 9K/hr. We found sharp superconducting transition temperatures T_c of 25K for the fast cool run and 30K for the slow cool, with no broadening of the susceptibility curve, indicating a narrow distribution of T_c's. The NQR spectra were taken using a pulsed NMR spectrometer on the $\pm 7/2 \leftrightarrow \pm 5/2$ transition by sweeping the frequency with a calibrated signal source. The repetition rates and the bandwidths were kept constant for slow and fast cool runs. Fourier transform spectra were also taken whenever the peaks were close enough to be covered by the spectrometer bandwidth. The lines were then fitted to a Lorentzian function from which the center peak frequencies were determined. For broad non-Lorentzian lines, the centroid frequencies were calculated.

III. Results and Discussion

Figure 1 shows the ^{139}La spectra at 200K, 160K and 4.2K for the $\pm7/2\leftrightarrow\pm5/2$ transition. The two peaks labeled AF come from the antiferromagnetic phase, while M1 comes from the metallic phase. The antiferromagnetic lines are split by the internal magnetic field as expected from first order perturbation theory. The coexistence of the AF and M1 lines is an evidence for phase separation. At high temperatures the M1 line is narrow, but it broadens somewhat as the sample is cooled. Its relative integrated intensity was determined to be nearly independent of temperature, and corresponds to about 10%-15% of the sample below 200K. Although not obviously visible at 4.2K, its existence is required to adequately fit the spectrum. Other workers[8] have also observed a weak $\pm3/2\leftrightarrow\pm1/2$ transition at ~6.35 MHz and 4.2K in superconducting $La_2CuO_{4+\delta}$. This line has been associated with the metallic phase since it is absent in undoped samples. Its resonance frequency is consistent with the NQR frequency of our M1 line.

A broad non-Lorentzian feature is also observed at lower frequencies (M2 in fig 1). Its integrated intensity is roughly 40% of the total. This line disappears above ~190K with no hysteresis. As shown in the figure, the magnitude of the M2 relative to the AF phase increases with the cooling rate. This prompts us to believe that M2 provides a clue to the cooling rate dependence of T_c in this material. An increase in the linewidth were also observed for all the lines upon cooling, as was also observed in nearly-stoichiometric samples.[9]

The positions of the NQR peaks are plotted in figure 2 as a function of temperature. The temperature dependence of the AF lines is consistent[9] with the undoped La_2CuO_4, but with a correspondingly lower T_N. The M1 line has the same NQR frequency ν_Q as the AF lines at all temperatures, except below ~T_c where large deviation occurs. The M2 line follows a similar temperature dependence as M1, suggesting that M2 is also a superconducting phase. 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 considerable disorder in the electric field gradient at La sites in this part of the sample. If this disordered EFG were due directly to the excess oxygen, it should also broaden the M1 line, which is not split and hence must arise from an oxygen-rich region. Apparently, near-neighbor shells ^{139}La nuclei around excess oxygen sites are completely "wiped-out" of the NQR line, and the most distant nuclei are not directly affected. Only these lanthanums which are farther away from any excess oxygen are seen in the spectra. The broadening of the M2 line, therefore, must come from another source.

One possibility has to do with the freezing of the CuO_6 octahedral tilts. The CuO_6 octahedra are intrinsically unstable to tilting distortions which can be stabilized by temperature dependent forces.[10] At high temperatures but below T_{ps}, these octahedral tilts may shift rapidly between the two degenerate HTT(110) and HTT($1\bar{1}0$) rotation axes,[10] causing the apical oxygens to move closer to the La atoms and change the electric field gradient. For fast cooling, more octahedra may be frozen in an intermediate (e.g., Pccn) symmetry contributing to broadening and increased intensity of the M2 phase. It is not clear from our data why T_c is reduced for fast cooling, but it may have some connection with a charge redistribution associated with this octahedral tilting as we shall discuss below.

What is the origin of the observed shift of the NQR frequency of the metallic lines at about T_c? Such behavior is also seen in superconducting and non-superconducting $La_{2-x}Ba_xCuO_4$.[11] Cu NQR in $YBa_2Cu_3O_7$ also exhibits a similar anomaly of roughly the same magnitude at T_c for both the chain and plane sites.[12] Generally, changes in NQR frequencies are structural in origin and can be caused by a true structural phase transition or changes in vibrational or torsional phonon modes. It appears though that lattice instability and changes in the local structure are common phenomena in the cuprates. A structural phase transition at ~40K has not been detected by neutrons in the present compound. However, atomic pair distribution analysis[13] on several cuprates reveal that in the vicinity of T_c, significant deviation of local structures from the crystallographic averages are present without forming long range order. Anomalies at ~T_c have also been observed in thermal expansion coefficient, elastic constants, and specific heat[14] both in undoped La_2CuO_4 and superconducting $La_{1.85}Sr_{0.15}CuO_4$.

A charge transfer mechanism, either alone or in conjunction with lattice effects, could also shift the NQR frequency. Any intra-atomic change in electric field gradient due to charge transfer also modifies the electronic configuration at La sites. This mechanism has been invoked in the YBCO system, where systematic changes in the Cu(1)-O(4) bond-length were observed to be related to T_c and oxygen deficiency.[15] The La-O layers can be thought of as charge reservoirs, analogous to Cu-O chains in $YBa_2Cu_3O_x$. Structural changes, such as tilting of $Cu\text{-}O_6$ octahedra, buckling of the Cu-O bonds, or bond-length compression could induce charge redistribution, either delocalizing or enhancing the density of hole-carriers on the CuO_2 layers. Their occurrence at T_c suggests that charge transfer and/or lattice instability are intimately connected to superconductivity.

IV. Conclusion

In summary, we investigated the effects of the cooling rate on the microstructures of superconducting $La_2CuO_{4+\delta}$ using ^{139}La NQR. We observed the appearance of an additional phase whose behavior resembles that of the metallic phase, but whose intensity increases with the rate of cooling. Charge transfer associated with octahedral tilting has been invoked to explain the cooling rate dependent superconductivity. We also observed anomalies in La NQR frequencies near T_c which we attributed to changes in local structures.

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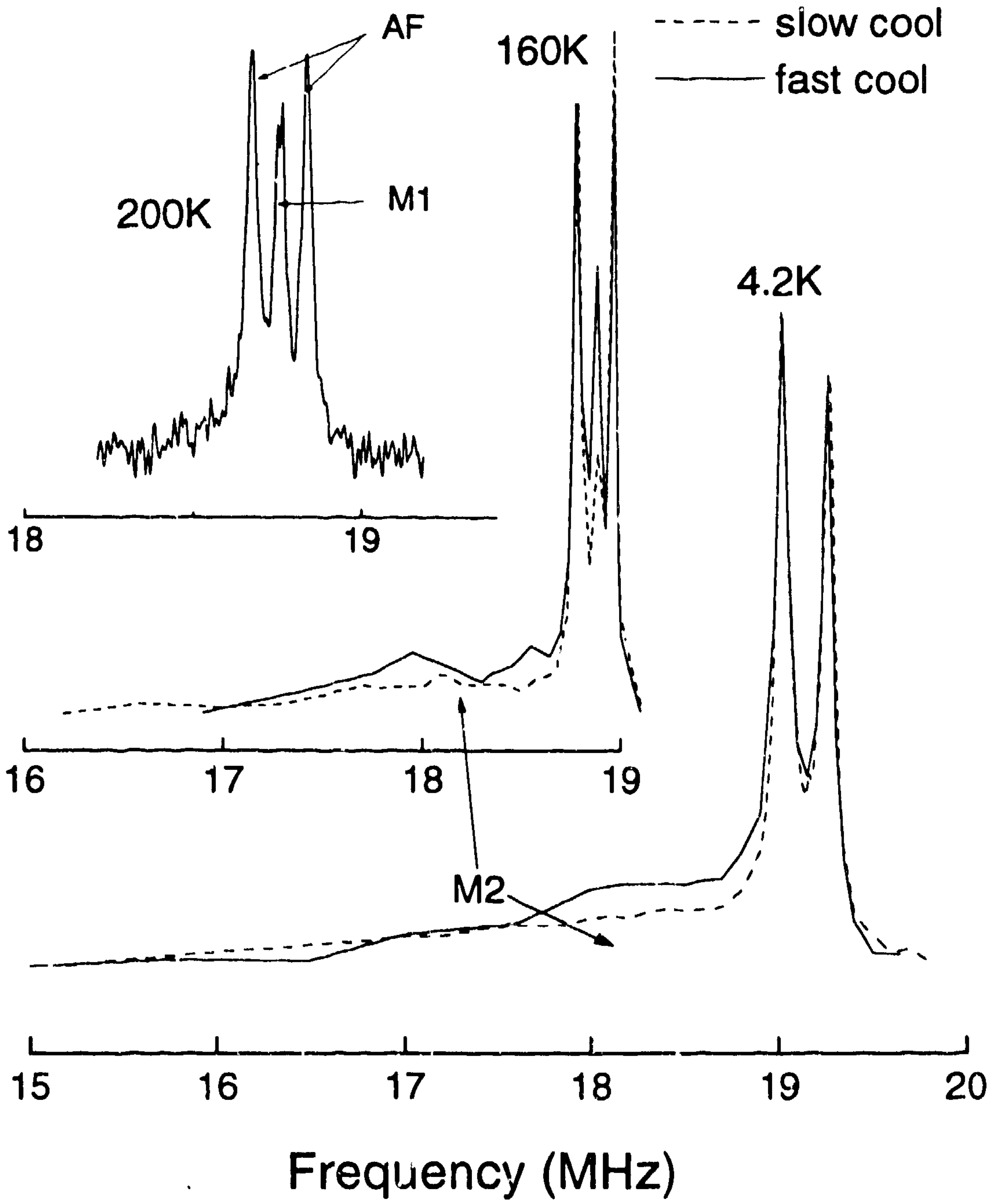
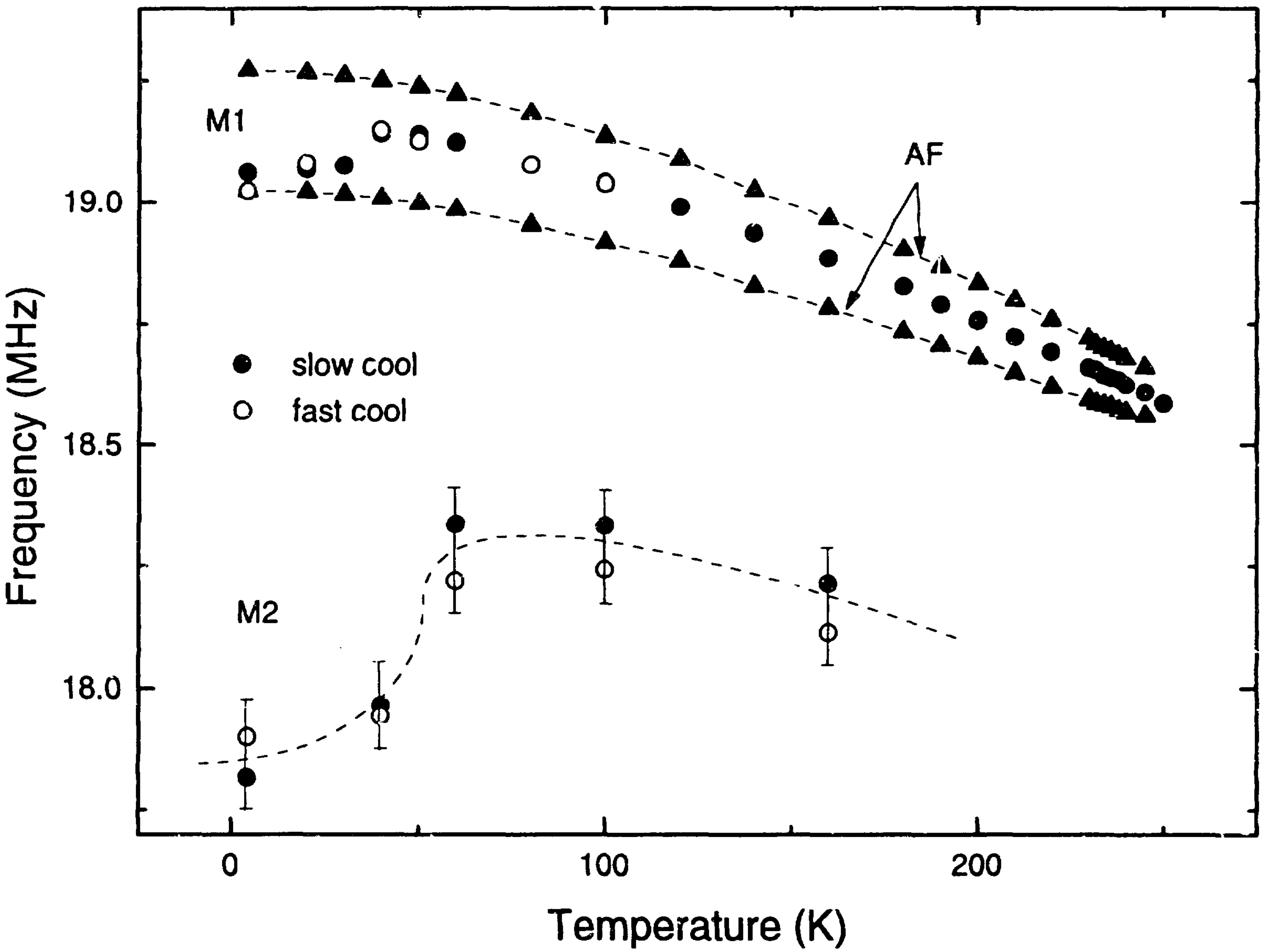
FIGURE CAPTIONS

Fig.1 ^{139}La NQR spectra at 200K, 160K and 4.2K. The intensities for the slow and fast cool data are normalized against the antiferromagnetic peaks.

Fig.2 Temperature dependence of positions of NQR peaks in figure 1. The M2 peaks are obtained from the first moment after subtracting contributions from other peaks. Lines are guides to the eye.



AF
M1
200K
18
19
160K
slow cool
fast cool
16
17
18
19
4.2K
M2
15
16
17
18
19
20
Frequency (MHz)



M1
AF
slow cool
fast cool
M2
19.0
18.5
18.0
0
100
200
Frequency (MHz)
Temperature (K)