139La NMR AND NQR STUDY OF THE TEMPERATURE DEPENDENT STRUCTURE OF La$_2$CuO$_{4+\delta}$

P. C. HAMMEL, E. T. AHRENS, A. P. REYES, R. H. HEFFNER, P. C. CANFIELD, S-W CHEONG, Z. FISK, and J. E. SCHIRBER*

Los Alamos National Laboratory, Los Alamos, NM 87545, and *Sandia National Labs, Albuquerque, NM 87185.

NMR and NQR reveal substantial structural changes in the metallic phase of La$_2$CuO$_{4+\delta}$ which occur below 220 K. The oxygen octahedra in the metallic phase are not tilted at phase separation; upon cooling to 40 K considerable tilt has developed. The low temperature structure is highly disordered.

1. Introduction

La$_2$CuO$_{4+\delta}$ has been extensively studied since the discovery of superconductivity at 39 K in the related compound La$_{1.85}$Sr$_{0.15}$CuO$_4$. La$_2$CuO$_{4+\delta}$ can also be made superconducting by doping with oxygen$^1$ alone. La$_2$CuO$_{4+\delta}$ displays a rich variety of behaviors including phase separation.$^2$

2. Experimental Procedure

We report results from two crystals; we will focus on the results from a 13 mg crystal with a $T_c$ of 38 K. Crystals of La$_2$CuO$_{4.0}$ were annealed as previously described$^3$ in a 3 kbar oxygen atmosphere. The phase separation temperature, $T_p$, is 265 K.$^4$ Below this temperature the crystal comprises two phases, one oxygen rich and metallic and a second ($\delta = 0$) which is antiferromagnetic (AF) and insulating.

The NMR and the NQR were performed using a conventional pulsed NMR apparatus. NMR spectra were obtained by sweeping magnetic field at fixed frequency. NQR spectra were obtained by two channel Fourier transform spectroscopy for narrow lines, or for broad lines by monitoring the area under the spin echo as the spectrometer frequency was varied.

3. Results

Fig. 1 shows NMR spectra for the 139La central (-1/2 to 1/2) transition taken at 40 K and 250 K. For these spectra the c-axis of the crystal (perpendicular to the CuO$_2$ planes) was oriented parallel to the applied magnetic field. The shift to high field of the AF phase spectrum results from the second order quadrupole interaction. This shift is proportional to the square of the angle between the electric field gradient (EFG) axis and the direction of the magnetic field for small angles and vanishes if they are parallel. Here, the field is parallel to the c-axis so the shift of the AF lines shows that the EFG axis is tipped away from the c-axis by about 10°. This is an expected consequence of the rotation of the oxygen octahedra associated with the orthorhombic distortion. The metallic phase peak is not shifted at 250 K.

In fig. 2 we show NQR spectra for two crystals.

![Figure 1](image-url)
with different $T_c$'s: $T_c = 38$ and $28$ K. The two lines at high and low frequency in the inset originate in the AF phase; they are split by the antiferromagnetic internal field. This spectrum provides the first direct proof that the oxygen-poor phase does indeed exhibit long range antiferromagnetic order; the onset of this order is discontinuous at $T_P$. The small width of the metallic line, comparable to the AF lines indicates the quality and homogeneity of the doped regions of the crystal. Were it not for the internal field in the antiferromagnetic phase all three lines would lie on top of each other. Thus both phases have identical quadrupole frequencies at $220$ K. Upon cooling to $100$ K the NQR spectrum for the metallic phase has changed dramatically. The line has shifted down in frequency by over $1$ MHz, broadened from approximately $30$ kHz to well over $1$ MHz, and developed a double peak structure. The NQR spectrum for the metallic phase in the $28$ K sample at $75$ K is similar to the $T_c = 38$ K spectrum except that the double peak structure is absent.

4. Discussion

The absence of a shift for the metallic NMR line at $250$ K shows that in the metallic phase, the EFG axis coincides with the crystalline c-axis; NQR data indicate that EFG is also axially symmetric. Thus the oxygen octahedra are not rotated although the phase is known to be orthorhombic. Because this shift is proportional to the square of the angle, this result cannot be explained by rapid motion amongst instantaneously rotated positions such that on the average the octahedron is not rotated.

Typically the NQR frequency, $v_Q$, increases with decreasing temperature due to thermal contraction. In the AF phase (and in La$_2$CuO$_{4.00}$), $v_Q$ increases by approximately $0.3$ MHz between $220$ K and $40$ K. That $v_Q$ decreases in the metallic phase indicates a substantial change in structure. The double peaked spectrum in the higher $T_c$ sample indicates that there are two La sites in the metallic phase. Interestingly this is absent in the $T_c = 28$ K sample.

The NMR spectra show that in the metallic phase the angle between the EFG axis and the c-axis is essentially zero at $250$ K but is distributed between $0$ and $10^\circ$ with a mean value around $5^\circ$ at $40$ K. This angle is closely associated with the tip angle of the oxygen octahedra away from the c-axis.

5. Conclusions

Using $^{139}$La NMR and NQR techniques we have observed substantial structural changes which occur in the metallic phase of oxygen doped La$_2$CuO$_{4+8}$ below $220$ K (phase separation occurs at $265$ K). At high temperature the oxygen octahedra are not tilted, but a tilt develops with decreasing temperature. The dramatic decrease in the quadrupole frequency and increase in the linewidth indicate a non-trivial change in structure and emphasize the loss of positional order. There are two distinct La sites at low temperature in the metallic phase as shown by the appearance of two peaks in the NQR spectrum.

We acknowledge the support of the US DOE.

1. J. E. Schirber et. al. Physica C 152, 121 (1988).
2. J. D. Jorgenson et. al., Phys. Rev. B 38, 11337 (1988).
3. K. F. McCarty, J. E. Schirber, S-W. Cheong, and Z. Fisk, Phys. Rev. B 43, 7883 (1991).
4. P. C. Hammel et. al., Phys. Rev. B 42, 6781 (1990).