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

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NMR and NQR reveal substantial structural changes in the metallic phase of $\text{La}_2\text{CuO}_{4+\delta}$ 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

$\text{La}_2\text{CuO}_{4+\delta}$ has been extensively studied since the discovery of superconductivity at 39 K in the related compound $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. $\text{La}_2\text{CuO}_{4+\delta}$ can also be made superconducting by doping with oxygen¹ alone. $\text{La}_2\text{CuO}_{4+\delta}$ 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 $\text{La}_2\text{CuO}_{4.0}$ were annealed as previously described³ 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 ^{139}La 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

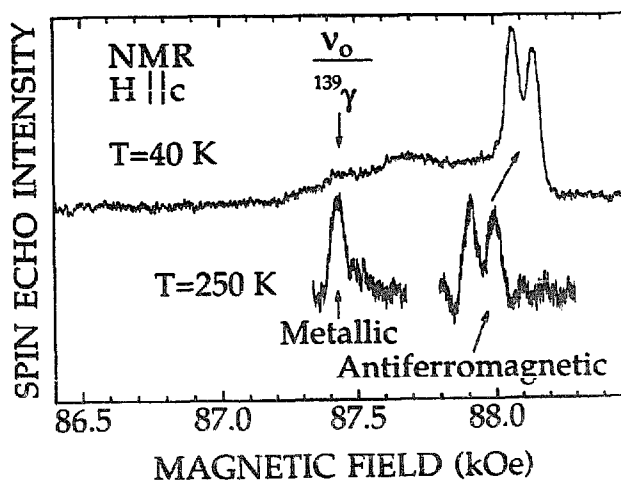


FIGURE 1
NMR spectra of a single crystal of $\text{La}_2\text{CuO}_{4+\delta}$ ($T_c = 38\text{ K}$) taken with the applied field oriented along the c-axis. At 250 K the metallic line is not shifted; it has broadened and shifted at 40 K.

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

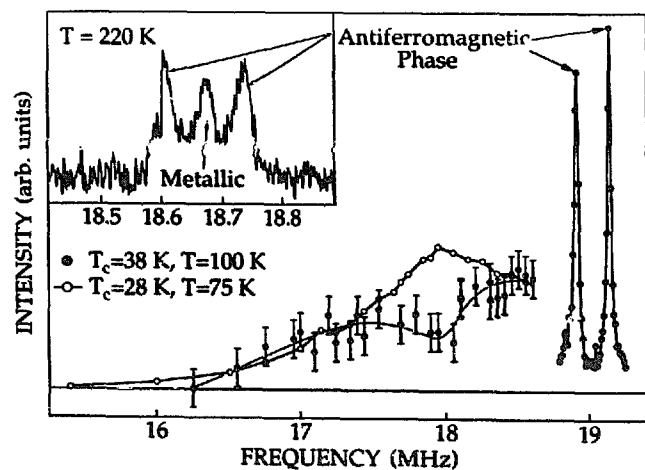


FIGURE 2

NQR spectra for the $T_c = 38$ K and 28 K crystals. At low temperature the metallic line has shifted, broadened tremendously, and two peaks have developed. The $T_c = 28$ K data taken at 75 K shows the shift and broadening but only a single peak.

indicate that EFG is also axially symmetric. Thus the oxygen octahedra are *not rotated* although the phase is known to be orthorhombic.² 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, ν_Q , increases with decreasing temperature due to thermal contraction. In the AF phase (and in $\text{La}_2\text{CuO}_{4.00}$), ν_Q increases by approximately 0.3 MHz between 220 K and 40 K. That ν_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° with a mean value around 5° 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 $\text{La}_2\text{CuO}_{4+\delta}$ 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.

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