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^{139}La NMR study of phase separation in single-crystal $La_2CuO_{4+\delta}$

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We report a study of single-crystal $La_2CuO_{4+\delta}$, a 38-K superconductor produced by high-pressure oxygenation. We employ ^{139}La NMR to probe the behavior of copper spins in the CuO_2 planes. At low temperatures we observe two signals, one originating from regions of the crystal rich in oxygen and a second having no excess oxygen ($\delta \sim 0$). Upon warming through 265 ± 5 K, the volume fraction of the crystal poor in oxygen goes to zero. The magnetic shift of the peak intensity of the line originating in the oxygen-rich portion of the crystal does not change in the vicinity of 265 K. These observations provide direct microscopic evidence for phase separation in the crystal.

$La_2CuO_{4+\delta}$ is the parent compound for the copper oxide materials which become superconducting[1] around 40 K when hole doped. Because these compounds display many of the properties common to all of the cuprate superconductors, it is important that their properties be understood. In this paper we report a study of $La_2CuO_{4+\delta}$ in which the holes are doped into the compound by introducing additional oxygen through annealing in a 3-kbar oxygen atmosphere.[2] Neutron diffraction,[3-5] muon-spin rotation,[6] and transport and susceptibility measurements[7] show that in the temperature range between 200 and 280 K a separation into oxygen-rich and oxygen-poor phases occurs. The oxygen-poor phase is highly resistive while the oxygen-rich phase shows lower resistivity and becomes superconducting around 40 K.[7]

We report ^{139}La NMR measurements on a single crystal of oxygen doped $La_2CuO_{4+\delta}$ employed as a probe of the local crystalline environment which is very sensitive to hole doping. The behavior we observe is complex and gives clear evidence that regions of the crystal comprise a phase that is known from other studies to be magnetically ordered at low temperatures. Above 270 K a single, virtually unshifted line is observed; below 260 K two distinct features are observed, one is the same as that observed above 270 K and one is associated with the undoped ($\delta \sim 0$) compound. Above 260 K the volume fraction of crystal in the $\delta \sim 0$ phase decreases rapidly to zero. This observation supports the picture given earlier[7] which proposes that the phase separation is driven by the energy to be gained by forming a magnetically ordered phase.

The single-crystal sample was grown from a CuO flux. The final anneal was performed in a high-pressure (~ 3 kbar) oxygen atmosphere as described earlier;[2] the estimated value of δ resulting from this procedure is approximately 0.032.[8] T_c is 38 K; at low temperatures the shielding is nearly perfectly diamagnetic. The NMR spectra were taken with a standard pulsed NMR apparatus. The experiments reported here were performed at 52.59 MHz. The spin-echo signal intensity was recorded by means of a gated boxcar integrator as magnetic field was swept.

In Fig. 1 we show the ^{139}La NMR spectrum taken at three temperatures in a magnetic field of approximately 8.8 T applied parallel to the c axis (perpendicular to the CuO_2 planes). This field is sufficiently large that below the ordering temperature, the ordered Cu moments are expected to have a small ferromagnetic component parallel to the c axis.[1] The spectrum is composed of a nearly unshifted line and a doublet (split pair of lines) having a substantial shift. The series of spectra show the dramatic decrease of the intensity of the doublet above 250 K. The temperature dependence of shift of the doublet (average shift of the two lines in the doublet) is shown in Fig. 2. With increasing temperature the magnitude of the shift decreases slowly; at 260 K the uniform shift is 75% of its value at 40 K. The shift of the unsplit line (determined from the point of peak intensity since the line shape is changing with temperature below 250 K) is less than 0.05% throughout this temperature range and shows no change at the temperature at which the doublet vanishes.

The appearance of two features (the two lines in the doublet) requires that there be two distinct La sites in the phase of the crystal from which the doublet originates; two sites in the unit cell may become distinguishable as a result of magnetic ordering or a structural distortion. ^{139}La NMR spectra taken in two crystals of $La_2CuO_{4+\delta}$ for which $\delta \sim 0$ ($T_N = 320$ and 270 K) (Ref. 9) show splitting and a shift similar to the doublet feature we report here both above and below the Néel temperature. Thus, the splitting of the doublet is not the result of magnetic order, however we can identify the doublet in the $La_2CuO_{4.032}$ spectrum as arising from a phase of $La_2CuO_{4+\delta}$ having $\delta \sim 0$. The fact that this splitting persists above T_N in undoped crystals is not understood and is presently being investigated further. The ratio of oxygen-poor ($\delta \sim 0$) to oxygen-rich (metallic and superconducting) volumes of the crystal can be estimated from the area under the two spectral features if we assume them to have the same nuclear-spin lattice relaxation rate and the same T_2. The validity of this assumption is sup-

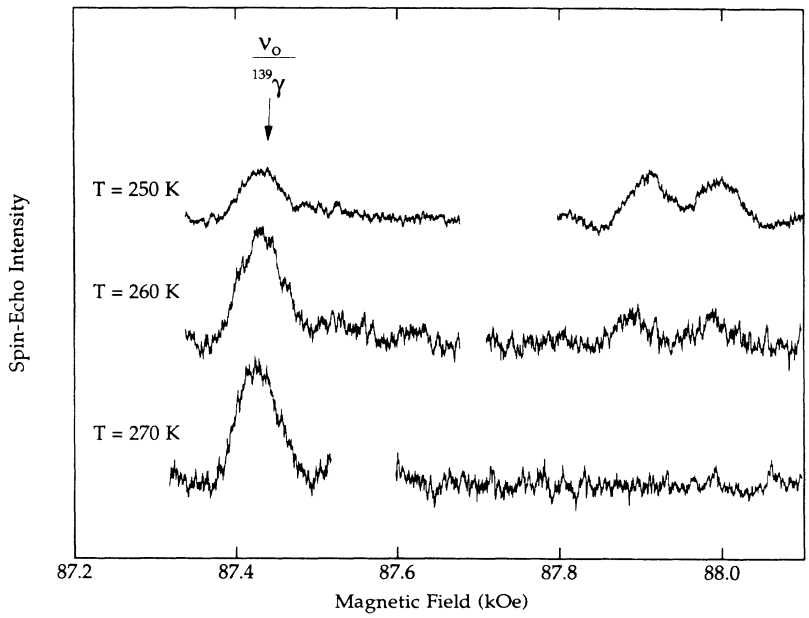

FIG. 1. ^{139}La NMR field swept spectrum of the central transition taken at three temperatures. The spectrometer frequency ν_0 is 52.59 MHz, $^{139}\gamma$ is the ^{139}La nuclear gyromagnetic ratio (the arrow indicates the magnetic field at which the unshifted resonance would occur). The spectrum consists of a single nearly unshifted line and a doublet. The doublet vanishes above 260 K. Note the uniform shift of the doublet is to higher fields and is larger than the splitting of the two lines in the doublet. This shift and splitting remain finite as the amplitude of the signal diminishes to zero.

ported by the observation that the intensity ratios are roughly independent of repetition rate and separation between the excitation pulses. Within this assumption we estimate the fraction of the crystal which is oxygen rich to be 0.25 ($\pm$0.05) at 220 K, a fraction smaller than previously observed.[4,6] The difficulty of using the NMR intensity to accurately measure the number of La nuclei in the two phases makes a quantitative analysis of the temperature dependence of these fractions difficult and this will not be undertaken here. It is apparent, however, that intensity moves from the doublet to the single unshifted line with increasing temperature and that by 270 K the doublet has vanished entirely. This is not simply the result of warming above T_N since spectra from undoped crystals ($\delta \sim 0$) show a similar feature above T_N. The vanishing of the doublet shows that above the transition temperature of 265 $\pm$ 5 K the crystal contains no oxygen-poor phase.

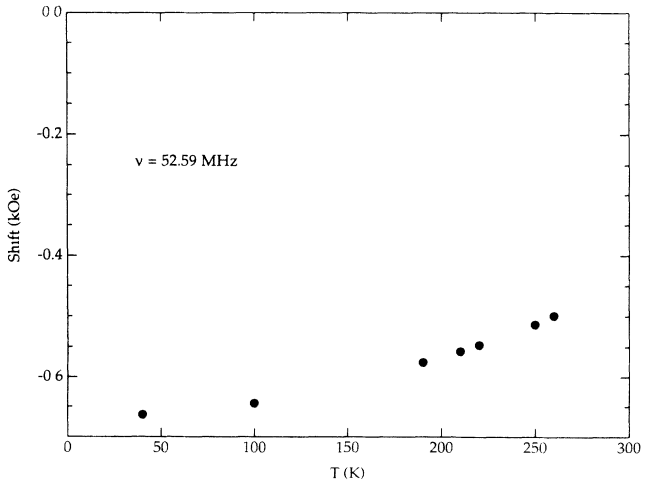

FIG. 2. The temperature dependence of the uniform shift of the doublet (given by the average of the shift of the two lines). The signal vanishes with increasing temperature between 260 and 270 K but the shift is diminished by only 25% from its $T=0$ value.

The unshifted line is due to that portion of the crystal having moderate hole doping both above and below the phase separation temperature. In both cases these regions are metallic but phase separation increases their hole doping.[7] Both the very small shift of this NMR signal and the absence of a change in this shift due to the change in doping which occurs as a result of phase separation suggest a weak hyperfine coupling between the La nucleus and the hole spins. The existence of axial symmetry about the direction of the applied field (c axis) (Ref. 10) at the La site means that there also will be no second-order quadrupole shift. The doped phase appears to be changed little upon warming through 265 K; the increase of the fraction of the crystal this phase occupies is observable as an increase in intensity of this line.

Neutron-scattering results[11] show δ to be extremely small in the oxygen-poor phase. Experience with $La_{2-x}Sr_xCuO_4$ indicates that low hole doping leads to a large Néel temperature. Thus it is likely that magnetic order develops simultaneously with the phase separation. Earlier discussions of the possible driving force behind such a phase separation have pointed out[7,12,13] that it may occur because the system can gain energy by expelling the doped holes from regions of the crystal which may then magnetically order thus lowering the energy of the crystal as a

whole. The special feature of the oxygen-loaded material is that the extra oxygens appear to be mobile and can maintain overall charge neutrality by their motion, thus allowing the holes in the CuO_2 planes to condense. It is an interesting fact that T_c of the resultant oxygen-rich phase is very close to the maximum observed in $La_{2-x}Sr_xCuO_4$ as x, and thus hole doping, is varied. The suggestion one draws from this is that hole dopings near but below this value are unstable, and a metastable hole density in $La_{2-x}Sr_xCuO_4$ for $x < 0.15$ is enforced by the inability of Sr atoms to follow and thus compensate a condensation of the holes in the CuO_2 planes.

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