NMR evidence for two-step phase-separation in \(\text{Nd}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-\delta}\).

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By Cu NMR we studied the spin and charge structure in \(\text{Nd}_{2−x}\text{Ce}_x\text{CuO}_4−\delta\). For \(x = 0.15\), starting from a superconducting sample, the low temperature magnetic order in the sample reoxygenated under 1 bar oxygen at 900\(^{\circ}\)C, reveals a peculiar modulation of the internal field, indicative for a phase characterized by large charge droplets (‘Blob’-phase). By prolonged reoxygenation at 4 bar the blobs brake up and the spin structure changes to that of an ordered antiferromagnet (AF). We conclude that the superconductivity in the n-type systems competes with a genuine type I Mott-insulating state.

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At present an important issue in cuprate superconductivity is the nature of the electronic state(s) competing with the superconducting state (see \(^1\)\(^1\)\(^1\) and references therein). In the hole doped cuprates evidence has been accumulating that at low dopings this competitor is a stripe phase \(^1\). It is believed that these stripe phases find their origin in the microscopic incompatibility between the metallic- and Mott-insulating states \(^1\)\(^1\)\(^1\). Stripes are a-priori not a unique way of resolving this incompatibility. This was sharply formulated recently in terms of the analogy with superconductivity \(^1\); stripes can be viewed as the analogue of the type II superconductor while a type I behavior is also imaginable. In the latter the Mott-insulator and the metal/superconductor are immiscible and one expects a state characterized by droplets of metal/superconductor in a Mott-insulating background. The electron doped (n-type) superconductors are microscopically \(^2\) quite different from the hole doped ones, while also macroscopic properties seem distinct \(^2\). So far, no incommensurate spin fluctuations have been found by neutron scattering in this system \(^1\)\(^1\)\(^1\), arguing against stripe phases. Instead, recently it was reported that field induced \textit{commensurate} antiferromagnetism re-emerges in the superconducting state in the presence of an Abrikosov vortex lattice \(^1\), suggesting that the superconductivity competes with a conventional antiferromagnet.

Different from the p-type systems, the n-type systems stay insulating up to quite high dopings while the antiferromagnetism of half filling degrades quite slowly. In fact, Vajk et al. \(^1\) showed that the behavior of this antiferromagnet can be understood in detail assuming a random dilution of the Heisenberg quantum antiferromagnet, suggesting that the individual carriers stay strongly bound to impurity sites. Is the field induced antiferromagnet of a similar kind? Using NMR we will present here evidences that in between the superconductor and the strong pinning phase there is yet another phase. By re-oxygenating a superconducting \(\text{Nd}_{2−x}\text{Ce}_x\text{CuO}_4\) (NCCO) sample with \(x = 0.15\) up to the point that superconducting diamagnetism has disappeared we have detected a phase in a very small oxygen-doping range located in between the superconductor and the site diluted antiferromagnet. This phase is extremely sensitive to further oxygenation. Approximately one oxygen atom per 100 unit cells suffices to destroy this phase allowing a site-dilution antiferromagnet to take over. With NMR one can measure the \textit{amplitude} distribution of the magnetic moments. These show a double-peak distribution in this special phase. Extensive Monte-Carlo simulations on a representative model show that such a distribution will only arise in either a stripe phase or in a situation where \textit{large} droplets are formed. Since the neutron scattering appear to rule out the former we conclude that the superconductivity in the n-type systems competes with a genuine type I Mott-insulating state \(^1\).

\textbf{Experimental.} The experiments were performed on single crystals with \(x = 0.15\), 0.12 and 0.08. For \(x = 0.15\) the oxygen reduced sample (NCCOp) had a superconducting transition temperature of \(T_c = 21\text{ K}\). Half of the crystal (2x1x0.2 mm) was reoxygenated in air at 900\(^{\circ}\)C till no superconductivity could be detected in the SQUID-susceptibility measurement (sample NCCO1). After performing the full set of NMR measurements, the same sample was oxygenated further under 4 bar of oxygen at 850\(^{\circ}\)C for 20 hours (sample NCCO2), and NMR-scanned again. Sample preparation and characterization are described elsewhere \(^1\). The Cu NMR spectra were obtained with conventional phase coherent pulsed NMR between 4 and 350 K by sweeping the magnetic field at various constant frequencies. The NMR line-shift was determined by using a gyromagnetic ratio of 1.1285 MHz/kOe for \(^{63}\text{Cu}\) and \(K = 0.238\%\) of metallic Cu as a reference.

The Cu NMR spectra were studied for two orientations \((B_{\text{appl}}||c)\) and \((B_{\text{appl}}||ab)\) of the crystals with respect to applied external magnetic field \(B_{\text{appl}}\). An example for \(x = 0.15\) with \(B_{\text{appl}}||c\) is shown in Fig. 1 at high tem...
the Cu-sites only - the internal field effects are so large we concentrate on the low temperature field profiles on W mental relaxation probability I normalized product of the line intensity (field, as deduced from
FIG. 2: (a) Amplitude distribution of the internal field for central transitions of the two copper isotopes $^{63}$Cu and $^{65}$Cu and are superposed on a relatively broad background which likely originates from quadrupole satellites with small quadrupole frequencies. For characterization of the samples, we measured the $T$ dependencies of the normalized product of the line intensity ($I$)(corrected for $T_2$ effects) and $T$, the NMR line-sift $^{63}$K, and the fundamental relaxation probability $W_I$. [13, 14, 15, 16]. Here we concentrate on the low temperature field profiles on the Cu-sites only - the internal field effects are so large that the role of the Nd-moments can be neglected.

FIG. 2: (a) Amplitude distribution of the internal field for NCCO1 at 5 K. The solid line gives the profile of the hyperfine field, as deduced from $B \parallel c$. From the data for $B \perp c$ the antiferromagnetic alignment of the electron spins in the $(a, b)$-plane appears to be strongly disordered, see text. (b) Simple reconstruction of the internal field distribution for a one and two dimensional spin structure. In 1D the radial coordinate $r$ with (incommensurate) wavevector $k_r$ have to be read as $x$ and $k_x$. In 2 D cylindrical symmetry is assumed.

**Analysis of the low temperature profiles.** In the presence of the static hyperfine magnetic field $B_{hf}$ on the copper nuclei produced by ordered Cu$^{2+}$ spins, one should observe two Cu NMR lines at $B = [B_{appl}^2 + B_{hf}^2 + 2B_{appl}B_{hf} \cos \alpha]^{0.5}$, where $\alpha$ is the angle between the directions of $B_{appl}$ and $B_{hf}$. It is known from neutron scattering experiments on Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ [8] that the Cu$^{2+}$ spins are ordered antiferromagnetically in the $ab$-plane. Therefore, for $B_{appl}||c$ ($\alpha = 90^0)$ only one Cu NMR resonance is expected at a lower value than the field calculated from the gyromagnetic ratio, $B_0$. For those nuclei, where for some reason the internal field is cancelled, the resonance will be unshifted. The Cu NMR spectra recorded for $B_{appl}||c$ for $x = 0.08, 0.13$ and 0.15 can indeed be qualitatively explained in this way: for $x = 0.15$, see Fig. 3, part of the nuclei mainly feel the external field (resonate at the fields of Fig. 4) and the remainder experiences an internal field in addition. At lower doping the line shifts are larger. The spectra for $B_{appl}||ab$, see Fig. 4, seem to be composed out of at least two lines of different intensities. This difference is not due to $T_2$ or different $\pi/2$-conditions, because these are similar for both peaks ($T_{2}^{-1} = 23(1) \times 10^3$ s$^{-1}$ and $\pi/2 = 2$ μs).

For a quantitative analysis, the low-temperature copper NMR spectra of NCCO1 at 5 K were simulated by exact diagonalization of the nuclear spin Hamiltonian $\mathcal{H}$ with effective spin $I = 1/2$ (the quadrupolar interaction is weak compared to the magnetic interaction) for both isotopes $^{63}$Cu and $^{65}$Cu. For $B \parallel c$, $\mathcal{H}$ can be written as $\mathcal{H} = \gamma_0 HB_{appl}I_z + \gamma_0 BH_{hf}(I_x \cos \varphi + I_y \sin \varphi) + \gamma h B_1 I_x$, where the $z$-direction is along the crystallographic $c$-axis and $\varphi$ is angle between $B_{hf}$ and the rf-field $B_1$ (along the $x$-axis); for $B \perp c$, $I_z$ has to be replaced by $I_y$. $B_{appl} \perp B_1$ in all experiments and the AF coupled electron spins are assumed to be always in the $(a, b)$ plane. The amplitude distribution of the internal field $P(B_{hf})$ was obtained via Monte-Carlo optimization to reproduce the data for $B \parallel c$, see Fig. 4a. Analysis of the $B \perp c$ data (Fig. 4b) with this pure in-plane AF spin model indicates that the alignment of the electron spins is rather disordered in the $(a, b)$-plane, and on average show a field induced canted of some 20 degrees, which does not influence significantly the distribution $P(B_{hf})$ in Fig. 4a.

In the $x = 0.12, 0.08$ samples the computations give a single peak at a field $\sim 3$ T, consistent with a simple commensurate antiferromagnet. However, in the slightly oxygenated $x = 0.15$ sample this spin-amplitude distribution is quite structured: the peak at 2.4 T (corresponding with a reduced moment of $\sim 0.14 \mu_B$) is asymmetric showing a slow decrease on the smaller moment side, while a second peak at vanishing internal field corresponds with sites where the internal fields have completely disappeared.

**Interpretation.** If the internal-field distribution would arise from a stripe-like spin structure with wave vector $k_x$, we would have $P(B) = d(k_x x)/dB$ and hence
that both stripe like structures (comparable to the 1D case) and charge blobs (2D case) are compatible with the experimental data. Furthermore the needed zero field region in 2D is larger than in 1D (due to the transferred hyperfine interaction the size of the blobs with zero spin exceeds the zero field region).

The size enters into the problem even stronger because of the specific form of the hamiltonian. The internal field has not only a on-site contribution $A$, but also the transferred hyperfine interaction $B \approx A/4$, which gives a field of opposite sign and hence in a droplet a non-zero field will be generated on zero-spin sites (in a stripe configuration zero field states are easier to generate because it is an anti-domain boundary). To make this case more persuasive we performed Monte-Carlo simulations on a classical model designed to interpolate smoothly between stripe-like and droplet-like ground state textures. This is a classical, spin-full lattice gas model which is similar to the model introduced by Stojkovic et al. It builds in the quantum-physical ingredient that electrons/holes (‘charge’, $\sim (1-n_i)$) cause anti-phase boundaries in the spin system by a ‘charge mediated’ exchange interaction coupling the spins antiferromagnetically across the charge, $H_{spin} = J \sum x,y S_{x,y} \cdot (S_{x+1,y} + S_{x+1,y}) + J_1 \sum x,y S_{x,y} \cdot \{[(1-n_{x,y+1}) S_{x+1,y+2} + (1-n_{x+1,y}) S_{x,y+2}] \text{ with } J, J_1 \geq 0 \}$. The frustration in the spin system is released by the formation of charged domain walls. The frustrated phase separation motive is build in by balancing the spin-mediated attractive charge-charge interactions with a repulsive $1/r$ Coulomb interaction of strength $Q$ between the charges, which we cutoff at 10 sites (beyond the inter-stripe distance) for reasons of numerical efficiency. We take a XY spin system and the spin-orientational disorder is build in by a spin pinning potential, breaking the ground-state degeneracy by choosing a direction (up to spin reflection) for the antiferromagnetic background, as well as providing an inhomogeneous charge potential. It has the form $H_{Pot} = -V_\text{C} \sum x,y S_{x,y} \cdot P_{x,y}$, where $P_{x,y} = \sum_{x',y'} A_{x',y'} e^{i \Theta_{x',y'}} \exp(-\sqrt{(x-x')^2 + (y-y')^2}/R)$ with $R$ the correlation length over which the antiferromagnetic background is allowed to rotate. The angle $\Theta_{x',y'}$ is chosen randomly with a uniform distribution and amplitude $A_{x',y'} = \text{Random}[0,1]$. Finally we also incorporate a quenched disorder potential acting on the charge in the form $V_\text{C} = \text{Random}[0,1]$.

Despite its simplicity this simple model is capable of generating quite complex ground states, ranging from highly disordered droplet patterns ($J_1 \rightarrow 0$) to very orderly stripe patterns $J_1, J \gg Q, V_S$. In the simulations we used small but finite temperatures and thermal annealing, mimicking the effects of quantum fluctuations in smearing the sharp textures in this classical model. Two typical outcomes are illustrated in Figs. 3-4.

$\propto \int_0^{B/B_{\text{max}}} P(B) dB$. Using the experimental outcome for $P(B_{\text{hf}})$ the integration leads to the 1D-wave depicted in Fig. 2); note that because the Cu-nuclei that experience $B_{\text{hf}}$ have regular lattice positions, the wave vector needs to be incommensurate to realize such a field distribution at the Cu-sites. The peak of $P(B_{\text{hf}})$ at zero internal field in Fig. 2 would then correspond with the nodes. However, the field profile for a radially symmetric two dimensional spin profile can be generated similarly via $(k_x r)^2 \propto \int_0^{B/B_{\text{max}}} P(B) dB$ and is given in the same figure. These simple calculations are only meant to show FIG. 3: 2D map of the blob (a) and stripe (b) results from thermalized averaged MC simulations, obtained with the hamiltonian discussed in the text. The spin-orientational disorder in the $(a, b)$-plane is represented by a difference in color (complementary colors correspond to opposite aligned spins), while the color intensity corresponds to the spin value. The spin-zero regions (black), as also seen in experiment, are found in the stripe simulations, but are almost absent for small blobs. The parameters for the blob and stripe panels are $(J = 1, V_C = 0)$: $J_1 = 0.2, Q = 0.2, V_S = 0.2, R = 10$, $T = 0.4$ and $J_1 = 1, Q = 0.4, V_S = 0.2, R = 10$ with $T = 0.3$.

$\propto \int_0^{B/B_{\text{max}}} P(B) dB$. Using the experimental outcome for $P(B_{\text{hf}})$ the integration leads to the 1D-wave depicted in Fig. 2; note that because the Cu-nuclei that experience $B_{\text{hf}}$ have regular lattice positions, the wave vector needs to be incommensurate to realize such a field distribution at the Cu-sites. The peak of $P(B_{\text{hf}})$ at zero internal field in Fig. 2 would then correspond with the nodes. However, the field profile for a radially symmetric two dimensional spin profile can be generated similarly via $(k_x r)^2 \propto \int_0^{B/B_{\text{max}}} P(B) dB$ and is given in the same figure. These simple calculations are only meant to show

FIG. 4: Blob results from the MC simulations - a thermalized result for larger blobs than in the previous figure. Only if blobs are sufficiently large, zero field sites can be generated in the presence of the transferred hyperfine interaction. For still larger blobs the zero field contribution will further increase. Parameter values are $J = 1, T = 0.3, J_1 = 0, Q = 0.04, V_S = 0.2$ with $R = 10$ and $V_C = -1.5$.
We have extensively scanned the parameter space of this model. Invariably, we find that a double peak structure is easily associated with stripe like patterns (Fig. 4), but these configurations invariably lead to incommensurate scattering amplitudes, which are not observed experimentally. When droplets are formed instead, the zero-moment peak is always lacking for small droplets (Fig. 3 and Fig. 4). Only droplets of 2 nm or more (25 sites or larger) mimic the peculiarities of the NMR spectra. This adds confidence to our claim that the double peak structure in the local moment distribution is the NMR fingerprint signalling the presence of large charge blobs.

In summary, we have presented evidence demonstrating that the n-type cuprate superconductor is in a direct competition with a phase where the charge carriers form large droplets in a commensurate antiferromagnetic background. This phase is in turn extremely sensitive to the chemical conditions. Tiny amounts of excess oxygen suffice to destroy both superconductivity and the large droplet phase, in favor of a phase where the charge carriers are strongly bound to the impurities.

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FIG. 5: Copper NMR spectra (the intensity in arbitrary units along the vertical axis is plotted against the magnetic field value in Tesla) at 5 K for NCCO1 and NCCO2 (a). The lines in (b) are fits with an optimized internal field distribution, see text.

How to reconcile our findings with the neutron scattering evidences favoring the site-diluted antiferromagnet? The NMR sample has a volume of 1 mm$^3$, much smaller than typical neutron targets and we found the large droplet phase by almost continuously monitoring the disappearance of the superconducting state while the sample was oxygenated. Apparently, the large droplet phase in the NCCO1 sample is linked to the presence of a tiny amount of apical oxygens ($\delta \sim 0.005$ for NCCO1). The result for continuing the oxygenation of NCCO1 in 4 bar of oxygen as used in other studies is given in Fig. 5. The data show clearly that in NCCO2 the phase of NCCO1 is suppressed in favor of a new phase. Applying a similar analysis as before, we find that this new phase is characteristic of an antiferromagnet with an internal field of 3 T - the phase seen in the neutron data. Although it is hard to arrive at precise numbers, it seems that one extra oxygen per roughly 100 unit cells suffices to fracture the droplets and to favor a state where the charge carriers are strongly bound to impurities. As the superconductor, the large droplet insulating phase shows an extreme sensitivity to oxygen concentration explaining why this phase has been missed in the neutron scattering studies.

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