Intrinsic Impurity in the High Temperature Superconductor Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

Bo Chen, Sutirtha Mukhopadhyay, W. P. Halperin, 
Department of Physics and Astronomy, 
Northwestern University, Evanston, Illinois 60208

Prasenjit Guptasarma 
Department of Physics, 
University of Wisconsin-Milwaukee, Wisconsin, 53211

D. G. Hinks 
Materials Science and Technology Division, 
Argonne National Laboratory, Argonne, Illinois, 60439 
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The $^{17}$O NMR spectra of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) single crystals were measured in the temperature range from 4 K to 200 K and magnetic fields from 3 to 29 T, reported here principally at 8 T. The NMR linewidth of the oxygen in the CuO$_2$ plane was found to be magnetically broadened with the temperature dependence of a Curie law where the Curie coefficient decreases with increased doping. This inhomogeneous magnetism is an impurity effect intrinsic to oxygen doping and persists unmodified into the superconducting state.

Cuprate high temperature superconductivity emerges from the insulating antiferromagnetic parent compound by chemically doping the system with extra charge. In the case of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) this is accomplished by inserting $\delta$-oxygen non-stoichiometrically in the crystal structure. The doped holes drive the system away from antiferromagnetism giving rise to superconductivity in a classic dome shaped region in the temperature-dopant phase plane. Hole doping controls the balance between magnetism and superconductivity. But scanning tunneling microscopy (STM) measurements show that doping also produces nano-scale electronic disorder. Neither the doping dependence of $T_c$ nor depairing effects from spatial electronic inhomogeneities are well-understood as yet. Nonetheless, it seems from nuclear magnetic resonance (NMR) measurements that magnetic moments emerge where there is local suppression of the superconducting order parameter.

We find that oxygen doping also generates magnetic moments in the copper oxygen plane and that this local moment behavior persists deep into the superconducting state. The effect of these impurities is reduced with increased doping as the system is displaced further from the antiferromagnetic region of the phase diagram. It remains an open question as to how these moments are formed and if their effect on superconductivity is deleterious.

STM and NMR are both microscopic probes of electronic structure and have been used to study the effect of chemical impurities in the copper oxygen plane in cuprates. STM has powerful capability as a spectroscopic tool but is limited to the charge degrees of freedom within $\approx$ 1 nm of the free surface. NMR is a complementary probe with spin-sensitivity greater than a penetration depth from the surface with selectivity for different atoms in the structure, oxygen in our case. It is easily studied as a function of temperature and over a wide range of magnetic fields. Alloul and Bobroff et al. have used $^{17}$O to investigate local magnetic field inhomogeneity in the CuO$_2$ plane for chemically doped $c$-axis aligned powders of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO). They found a universal behavior, a Curie temperature dependence, of the $^{17}$O NMR linewidth for various impurities (Ni, Zn, and Li) that substitute for copper in the CuO$_2$ plane. Alloul et al. proposed that the chemical substitution for copper atoms in the CuO$_2$ plane breaks the in-plane, spin-singlet correlations of neighboring copper atoms, giving rise to an uncompensated local magnetic moment that couples through an oscillating hyperfine interaction to the $^{17}$O NMR such as might be expected.

FIG. 1: The central transition of $^{17}$O NMR spectra of two over doped Bi-2212 single crystals. The left plot is for $T_c$ = 75 K and the right is for $T_c$ = 85 K. The narrow line is for oxygen in the SrO plane, O(2), and the broader line is for oxygen in the CuO$_2$ plane. The magnetic field is $H = 8$ T.
for the RKKY interaction. As a result the width of the NMR spectrum is increased symmetrically and proportional to the magnetization of the local moment having the temperature dependence of a Curie law. Here we report similar behavior to be intrinsic to oxygen doped Bi-2212.

We have performed $^{17}$O NMR on three crystals of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ (Bi-2212) with differing amounts of non-stoichiometric $\delta$-oxygen varying from near-optimal to over-doped. The crystals were grown by the floating-zone technique using a two-mirror image furnace. Cationic homogeneity was ensured by maintaining the same stoichiometry on the top and bottom rods and a very slow growth rate of 0.1 mm/hr. The crystals were oxygen isotope exchanged in a circulating gas stream at $\approx$ 1 bar, enriched to 70% $^{17}$O, at 650 $^\circ$C for 48 hours. After exchange the crystals were annealed; for $T_c = 75$ K (strongly overdoped) we chose 450 $^\circ$C at 1 bar for 150 hr. Similar procedures at lower partial pressures and higher annealing temperatures were used to reduce the doping for the other crystals giving transition temperatures determined from low field susceptibility, $T_c = 90$, 85, and 75 K, and with weights 34 mg, 48 mg, and 28 mg, respectively. Prior to $^{17}$O exchange the $T_c$ of these crystals was 95 K with optimal doping, the highest yet reported, indicative of high cationic homogeneity and chemical purity. After exchange the concentration of $^{17}$O was estimated to be $\approx$ 60%. As a procedural check we processed two crystals at the same time giving $T_c = 85$ K. Then one of these was reannealed to give $T_c = 90$ K. The NMR spectra of both crystals were found to be identical before the final annealing, providing direct evidence that the effects we report here are solely attributable to doping.

Fourier transform of the NMR echo from $\pi/2 - \pi$ spin-echo sequences gave the spectra of the central transitions $\langle -1/2 \leftrightarrow +1/2 \rangle$ shown in Fig. 1. Measurements were performed as a function of temperature from 4 to 200 K over a range of magnetic field from 3 to 29 T parallel to the c-axis. Here we discuss our most extensive measurements of Knight shift and linewidth (Fig. 2 and 3) as a function of temperature and doping in a magnetic field of $H = 8$ T.

There are two distinguishable oxygen sites in the NMR spectra identified in previous work as the oxygen in the CuO$_2$ plane, O(1), and the oxygen in the SrO plane, O(2). The central transitions are shown in Fig. 1 where the broad resonance is from O(1) and a narrow, partially saturated, resonance is from O(2). The much narrower NMR spectrum from O(2) indicates a more homogeneous electronic environment in the SrO plane compared to the conduction plane. Additionally, the position of the O(2) resonance does not change significantly with temperature and its spin-lattice relaxation time is an order of magnitude longer as a consequence of the fact that O(2) is more weakly coupled to the electronic excitations in the CuO$_2$ plane, as compared to O(1). In contrast, the O(1) NMR central transition, Fig. 1, is relatively broad. The central transition linewidth is similar to its satellites and proportional to magnetic field demonstrating that the spatial inhomogeneity is from local magnetic fields and that quadrupolar broadening from a distribution of electric field gradients in the copper oxygen plane is insignificant. We exploit the long spin-lattice relaxation time of O(2) to suppress it using fast pulse repetition for temperatures below 40 K and we explicitly subtract it from the spectrum at higher temperatures where it can be resolved.

![FIG. 2: Temperature dependence of the Knight shift defined to be the first moment of the $^{17}$O(1) central transition of each of three crystals.](image1)

![FIG. 3: The linewidth of the $^{17}$O(1) central transition, calculated as the square root of the second moment as a function of temperature. The solid curves are from Eq. 1. The sharp up-turn in data near 30 K marks the vortex freezing transition.](image2)
perconducting transition, Fig. 2, approaching its zero Knight shift position, $K(0)$, near 30 K. This reduction is expected for a spin-singlet superconductor where $K(T)$ follows the temperature dependence of the spin susceptibility. Well above the superconducting transition temperature, $K(T)$ approaches a temperature independent value that increases with hole doping as shown in Fig. 4. This general trend is expected; in a simple metal the spin susceptibility is proportional to the electronic density of states.

The linewidth of O(1), Fig. 3, has an unusual Curie temperature dependence in the normal state. This observation and its extension to the superconducting state is the main focus of our work. Such a Curie behavior comes from paramagnetic moments that produce a static inhomogeneous distribution of magnetic field throughout the sample, thereby broadening the NMR spectrum increasingly with decreasing temperature as was first observed by Alloul et al.\textsuperscript{15} in the normal state of cation-substituted YBCO. In the superconductive state, vortex supercurrents generate an inhomogeneous field distribution that make a quantitative interpretation more complex,\textsuperscript{20} except in the vortex liquid region where rapid vortex motion on the NMR time scale, averages this inhomogeneity to zero. In the case of Bi-2212, in contrast with YBCO, the vortex liquid state occupies a wide temperature range due to its high anisotropy\textsuperscript{16} permitting us to extend measurement of local moment impurities well below $T_c$. In our samples vortex freezing is identified with the sharp increase of the linewidth with decreasing temperature near 30 K, Fig. 3, from which we have determined\textsuperscript{15} the freezing phase diagram up to $H \approx 30$ T.

The strong decrease in linewidth with decreasing temperature that we observe in the superconducting state, Fig. 3, must therefore be a consequence of some combination of local moment behavior and superconductivity. The narrowing of the spectrum seems, at first sight, to parallel that of the temperature dependent Knight shift suggesting that either the conduction electrons are crucial to the formation of these local moments or, at the very least, our sensitivity to them through the hyperfine interaction is interrupted as conduction electrons condense into a singlet, Cooper-pair, state. In fact, we have found that the relation between the linewidth and Knight shift over the whole temperature range can be represented by a simple phenomenological expression:

$$\Delta \nu(T) = \Delta \nu_0 + K(T) \cdot H \cdot C / T,$$

where $\Delta \nu$ is the observed linewidth, $K(T)$ is the Knight shift, $T$ is the temperature, and $C$ is a Curie constant. $\Delta \nu_0$ denotes the temperature independent intrinsic linewidth determined by extrapolating the decreasing linewidth to a temperature where $K(T)$ approaches zero. For each sample this is proportional to the field, $\approx 1$ kHz/T. Our fits to Eq.1 are given by the solid curves in Fig. 3 with only the Curie constant as an adjustable parameter. Here $K(T)$ in the formula is replaced by a numerical representation of the data in Fig. 2. The resulting values for $C^{-1}$ are plotted in Fig. 4 and appear to vary with hole concentration in a manner similar to the high temperature value of the Knight shift, $K(T >> T_c)$.

We can also make a direct comparison of our raw data with Eq. 1. In Fig. 5 we plot, for each measured O(1) spectrum, the ratio of its first moment to the square root of its second moment (subtracting the fixed background contribution). The raw data in this form indicates a Curie law, Eq. 1, if it is a straight line passing through the origin. We conclude that this is the correct temperature dependence of the local moment behavior for both normal and superconducting states for the two overdoped crystals. For the optimally doped crystal we suspect that the pseudogap contributes to the temperature dependent Knight shift sufficiently that there are deviations from the Curie law behavior.

![FIG. 4: Knight shift and inverse Curie constant as a function of hole concentration. The hole concentration in the CuO$_2$ plane is related to $T_c$ by $T_c/T_{c_{max}} = 1 - 82.6 (p - 0.16)$\textsuperscript{7}. The non-stoichiometric oxygen content, $\delta$, was determined independently from annealing conditions\textsuperscript{22} giving values of $\delta$ close to the hole concentration.](image)

The magnetization of YBCO samples with Ni, and Zn substituted for copper in the CuO$_2$-plane have a Curie temperature dependence in the normal state\textsuperscript{20,21,22} that is correlated with a corresponding temperature dependence of the NMR linewidth, indicating the existence of paramagnetic moments\textsuperscript{16,23}. The similar behavior that we observe associate with oxygen doping. However, if chemical impurities were to be present, in order to broaden the NMR spectra as reported for YBCO, we would require 1.5% Zn or 1.0% Ni. Our measurements of the magnetization in a magnetic field of 5 T, rule out the latter.

We propose that the broadening of the $^{17}$O(1) spectrum originates from local moments in the copper oxygen plane that are associated with oxygen doping. The exact placement of the non-stoichiometric oxygen is still an open question\textsuperscript{23}; nonetheless, we conjecture that this
dopant modifies the spin state of an adjacent copper atom in the CuO$_2$ plane thereby introducing a local moment in a manner similar to that which was proposed to account for local moment formation in YBCO. The attendant inhomogeneous electronic structure is transferred through the hyperfine interaction to the oxygen nucleus in the CuO$_2$ plane. It was argued previously in the YBCO work that an RKKY mechanism would produce positive and negative excursions of the local magnetic field giving a symmetrically broadened NMR spectrum. This feature is also a characteristic aspect of our data. McElroy et al. use STM imaging spectroscopy to find disorder in the electronic structure of pure Bi-2212, specifically associated with the oxygen dopant and directly correlated to local suppression of the superconducting coherence peaks. Our interpretation of the $^{17}$O NMR spectra is that the electronic disorder observed by STM has an associated magnetic moment that forms in the CuO$_2$ plane. However, there are several issues that remain unresolved. First, it is not clear how such intrinsic moments form from non-stoichiometric oxygen. Secondly, the RKKY mechanism generally requires electron states far from the Fermi surface and should be relatively insensitive to superconductivity which affects only those states on the gap scale, close to the Fermi energy, $E_F$. Our observation of a strongly temperature dependent narrowing of the $^{17}$O NMR spectra in the superconducting state would be compatible with an RKKY mechanism only if superconductivity modifies the density of states far from $E_F$. In fact there is some indication that this might be the case. In their tunneling measurements McElroy et al. find $dI/dV$, immediately above the oxygen dopant atom, to be modified by superconductivity up to a bias of $\approx -200$ mV from $E_F$, which may be sufficient to suppress the RKKY interaction.

In conclusion, we have found a simple relation between the temperature dependent Knight shift and NMR linewidth of $^{17}$O(1) spectra in Bi-2212 single crystals that indicates the existence of an inhomogeneous magnetic field distribution from local moments in the CuO$_2$ plane. We find a Curie-law behavior for the linewidth that decreases with increased oxygen doping. Consequently we identify the local moments with the oxygen dopant, intrinsic to Bi-2212, and we find they persist in the superconducting state. However, the mechanism for formation of the magnetic moments is not known and the effect of superconductivity on the hyperfine interaction between these moments and the probe nucleus, $^{17}$O, needs additional clarification.

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