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Evidence for intrinsic impurities in the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ from ^{17}O nuclear magnetic resonance

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We have found that high quality crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) have intrinsic magnetic defects that depend on oxygen doping. Our ^{17}O nuclear magnetic resonance spectra provide evidence that local moments form in the CuO_2 plane in both normal and superconducting states. We suggest that these magnetic impurities are related to the electronic disorder that scanning tunneling microscopy experiments identify with the oxygen dopant atoms.

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Hole doping in cuprate superconductors controls the balance between magnetism and superconductivity. However, doping is also responsible for electronic disorder which may have serious consequences for superconductivity.[1] The usual doping scheme with $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) is to insert δ oxygen nonstoichiometrically in the crystal structure. Pan *et al.*[2] and McElroy *et al.*,[3] using scanning tunneling microscopy (STM), have found that oxygen dopants act like impurities, introducing nanoscale distributions in the pairing amplitude, which are correlated with an impurity resonance in the density of states.[3] Although it is still unclear where in the crystal, the dopant resides, nonetheless, its disturbance of the electronic environment has been the subject of considerable experimental and theoretical interest.[1–6] Here, we report that doping Bi-2212 with oxygen produces atomic scale magnetic field distributions, evident in our ^{17}O nuclear magnetic resonance (NMR) spectra. We show that the temperature dependent linewidths are associated with magnetic moments in the copper oxygen plane and that this local moment behavior exists in both superconducting and normal states. The magnetic field distribution of these impurities is reduced with increased doping as the system is displaced further from the antiferromagnetic region of the phase diagram. It is likely that these impurities are related to the disorder seen with STM.[3,4]

STM and NMR are both microscopic probes of electronic structure, complementary in the sense that one is sensitive to charge and the other to spin, well suited to investigate material defects. Both have been used to study chemical substitutions in the copper oxygen plane.[7–13,15] STM has powerful capability as a spectroscopic tool near the surface of the material.[2–5,12–14] NMR probes deeper, approximately equal to a penetration depth, and has selectivity for different atoms in the structure, oxygen in our case. Alloul *et al.* and Bobroff *et al.*[7,10,11] have used ^{17}O to investigate local magnetic field inhomogeneity in the CuO_2 plane for chemically doped *c*-axis aligned powders of $YBa_2Cu_3O_{7-\delta}$ (YBCO). They found a universal behavior in the normal state, a Curie-law temperature dependence of the ^{17}O NMR linewidth for various impurities (Ni, Zn, and Li) that substitute for planar copper. 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 for the Ruderman-Kittel-Kasuya-Yosida (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. In the work we report here, we observe similar behavior to be intrinsic to oxygen doped Bi-2212.

We have performed ^{17}O NMR on three crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) with differing amounts of nonstoichiometric δ oxygen varying from near optimal to overdoped. 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/h. The crystals were oxygen isotope exchanged in a circulating gas stream at ≈1 bar, enriched to 70% ^{17}O, at 650 °C for 48 h. After exchange, the crystals were annealed; for $T_C=75$ K (strongly overdoped), we chose 450 °C at 1 bar for 150 h. Similar procedures[18] 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 of 34, 48, 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 ≈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 an-

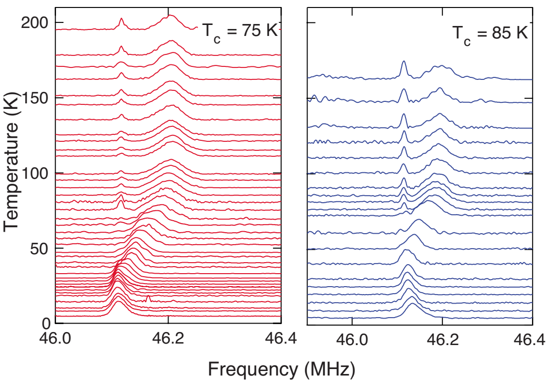

FIG. 1. (Color online) The central transition of ^{17}O NMR spectra of two overdoped Bi-2212 single crystals. The left plot is for T_C=75 K and the right is for T_C=85 K. The narrow line is for oxygen in the SrO plane O(2) and the broader line is for oxygen in the CuO$_2$ plane. The magnetic field H=8 T.

nealing, providing direct evidence that the effects we report here are solely attributable to doping.

Fourier transform of the NMR echo from $\pi/2$-π spin-echo sequences gave the spectra of the central transitions $\langle -\frac{1}{2} \leftrightarrow +\frac{1}{2} \rangle$, as 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 the Knight shift and linewidth (Figs. 2 and 3) as a function of temperature and doping in a magnetic field H=8 T.

There are two distinguishable oxygen sites in the NMR spectra identified in previous work[17] 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,[16] 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.

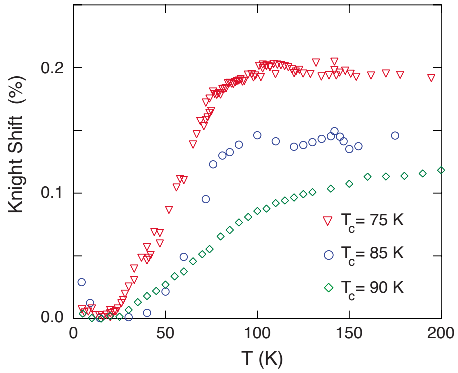

FIG. 2. (Color online) Temperature dependence of the Knight shift defined to be the first moment of the ^{17}O(1) central transition of each of three crystals.

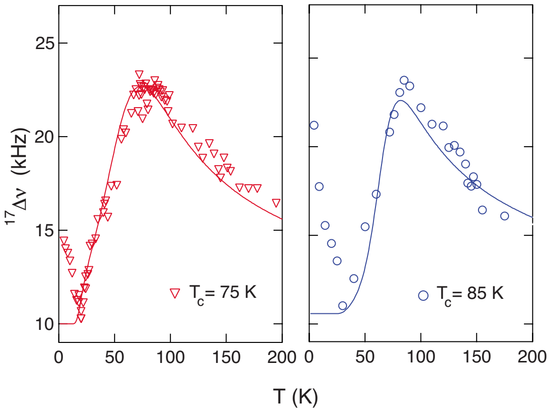

FIG. 3. (Color online) The linewidth of the ^{17}O(1) central transition calculated as the square root of the second moment as a function of temperature. The solid curves are from Eq. (1). The sharp upturn in data near 30 K marks the vortex freezing transition (Ref. 16).

In the superconducting state, the frequency of the O(1) resonance peak decreases with temperature below the superconducting 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.*[7] in the normal state of cation-substituted YBCO. In the superconductive state, vortex supercurrents generate an inhomogeneous field distribution, which make a quantitative interpretation more complex,[15] 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,[19] permitting us to extend measurement of local moment impurities well be-

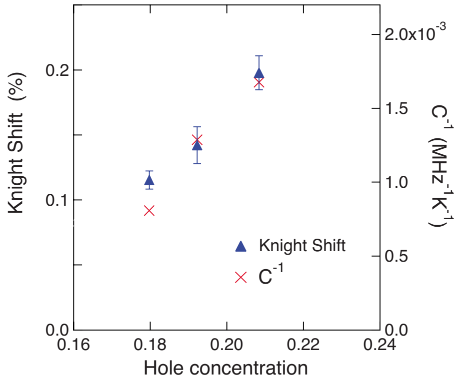

FIG. 4. (Color online) The Knight shift and inverse Curie constant as a function of hole concentration. The hole concentration in the CuO_2 plane is related to T_C by Ref. 20 $T_C/T_{C\,max}=1-82.6\,(p-0.16)^2$. The nonstoichiometric oxygen content δ was determined independently from annealing conditions (Ref. 27) giving the values of δ close to the hole concentration.

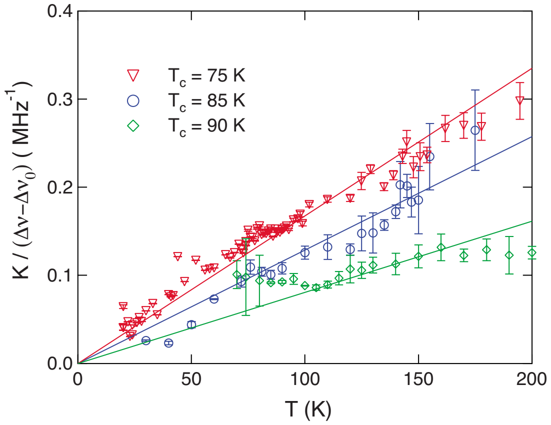

FIG. 5. (Color online) The Knight shift (first moment of the spectrum) divided by the linewidth (defined as the square root of the second moment), $K/(\Delta\nu-\Delta\nu_0)$, is plotted against temperature. A straight line through the origin indicates a Curie law with slope of the inverse Curie constant.

low 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[16] 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 the Knight shift over the whole temperature range can be represented by a simple phenomenological expression,

$$\Delta\nu(T) = \Delta\nu_0 + K(T)HC/T, \qquad (1)$$

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, ≈ 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, $K(T \gg T_C)$.

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 indicate 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 leading to deviations from the Curie-law behavior.

The magnetization of YBCO samples with Ni and Zn substituted for copper in the CuO_2 plane has a Curie temperature dependence in the normal state[21–23] that is correlated with a corresponding temperature dependence of the NMR linewidth, indicating the existence of paramagnetic moments.[7,10,11,24] 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[25] of the magnetization in a magnetic field of 5 T rule out the latter, similar to the results of Takigawa and Mitzi.[26]

We propose that the broadening of the $^{17}O(1)$ spectrum originates from local moments in the copper oxygen plane, which are associated with oxygen doping. The exact placement of the nonstoichiometric oxygen is still an open question;[3] 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.[7,10,11] 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.*[3] used 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 nonstoichiometric oxygen. Second, 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.* found dI/dV, immediately above the oxygen dopant atom, to be modified by superconductivity up to a bias of ≈ -200 mV from E_F, which may be sufficient to suppress the RKKY interaction.

In conclusion, we report NMR spectra of ^{17}O(1) in different oxygen doped Bi-2212 single crystals. We have found a simple relation between the temperature dependent Knight shift and linewidth, which indicates the existence of an inhomogeneous magnetic field distribution from magnetic impurities. We associate these with the oxygen dopant, intrinsic to Bi-2212, and we find that their magnetic effects persist unmodified from the normal state to well below T_C.

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