⁸⁹Y NMR study of Zn-induced local moments and pair breaking in $Y(Ba_{1-y}La_y)_2(Cu_{1-x}Zn_x)_4O_8$

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⁸⁹Y NMR measurements have been carried out and modeled for underdoped $Y(Ba_{1-y}La_{y})_{2}(Cu_{1-x}Zn_{x})_{4}O_{8}$ superconductors. We find that the data are well described by Zn inducing a local moment, leading to a spin-density oscillation and an additional ⁸⁹Y hyperfine field. We find an exchange energy increasing from ~ 50 to ~ 104 meV as the hole concentration is increased and an induced local moment which declines from 1.35 to $1.06\mu_{B}$. Magnetic pair breaking can fully account for the decrease in T_{c} with Zn substitution for the La-free materials. With progressive underdoping, magnetic pair breaking is increasingly unable to account for the decline in T_c with Zn substitution suggesting that Zn weakens the pairing interaction as in the spin-fluctuation pairing model.

Recent experiments have shown that there is a strong correlation between the magnetic properties and hightemperature superconductivity of superconducting cuprates. At low temperatures a gap in the normal-state spin-excitation spectrum exists that is strongly correlated with hole doping.¹ Measurements of the electronic entropy suggest that this gap occurs for the total excitation spectrum including charge degrees of freedom.² Drawing from these ideas, Tallon et al.³ have recently shown that the superconducting phase diagram can be explained by the opening of this normal-state gap on the underdoped side and pair breaking on the overdoped side due to excitations above the gap. The normal-state gap has been seen in heat capacity,⁴ susceptibility,² NMR,⁵ infrared conductivity,⁶ resistivity, and thermopower measurements⁷ but it should be distinguished from the "spin-gap" observed in neutron scattering.³ It is therefore important that the magnetic properties of high-temperature superconducting cuprates be fully investigated. In particular, investigating the way in which magnetic or nonmagnetic impurities suppress superconductivity should assist in the understanding of the superconductivity pairing mechanism. Monthoux and Pines⁸ have recently developed a spin-fluctuation-induced pairing theory in which they conclude that Zn substitution for Cu disrupts local magnetic order leading to a decrease in the pairing energy. Zn substitution is unusual in that in YBa₂Cu₃O_{7- δ} it generally produces no change in hole concentration⁷ but causes a rapid decrease in T_c and leads to the creation of local moments, even though Zn is nonmagnetic.⁹ By comparison, substitution of Cu by Ni leads only to a modest decrease in T_c with increasing Ni concentrations.¹⁰ Walstedt *et al.*¹¹ have performed ⁶³Cu NMR and susceptibility measurements on Zn-substituted $YBa_2Cu_3O_7$ and conclude that the decrease in T_c with increasing Zn content is not due to magnetic pair breaking. However Mahajan *et al.*¹² show from susceptibility and 89 Y Knight-shift measurements on Zn substituted YBa2Cu3O6.64 that the decrease in T_c with Zn substitution can be partially attributed to magnetic pair breaking with an exchange energy of $J \approx 75$ meV.

In this paper we report on ⁸⁹Y NMR measurements on Zn-substituted underdoped $Y(Ba_{1-\nu}La_{\nu})_2Cu_4O_8$. The ad-

vantage of the YBa₂Cu₄O₈ system is that it does not suffer from oxygen disorder. Oxygen disorder on the chains in YBa₂Cu₃O_{7- δ} can lead to an asymmetric peak and, near optimal doping, two peaks have been observed. Furthermore, as the oxygen content is reduced, oxygen vacancy ordering on the Cu-O chains is known to occur.¹³ Finally, Zn substitution in YBa₂Cu₃O_{7- δ} can result in changes in δ whereas in YBa₂Cu₄O₈ both the oxygen content and hole concentration remain fixed, even in La or Ca doped compounds.⁷ We will show by detailed modeling of our ⁸⁹Y NMR data that the local moment induced by Zn substitution is moderately dependent on hole concentration and that the decrease in T_c with Zn substitution, for all except the lowest hole concentration, can be wholly attributed to magnetic pair breaking.

The Y(Ba_{1-y}La_y)₂(Cu_{1-x}Zn_x)₄O₈ samples were prepared by decomposing a stoichiometric mix of Y₂O₃, La(NO₃)₃·6H₂O, Ba(NO₃)₂, CuO, and ZnO powders in air at 700 °C. The samples were reacted for 6 h at 930 °C, 48 h at 940 °C, and a further 48 h at 940 °C in oxygen at a pressure of 6 MPa.¹⁴ All samples were reground after each sinter. X-ray diffraction analysis showed that the samples were single-phase material.

The ⁸⁹Y NMR signal was measured between 80 K and room temperature using a Varian Unity 500 spectrometer with a 11.74 T superconducting magnet. The roomtemperature measurements were made by magic angle spinning (MAS) using a Doty 5 mm high-speed MAS probe, and spinning speeds of 10 kHz to reduce the ⁸⁹Y NMR linewidth. Bloch decay spectra were acquired using a delay of 20 s between 90° pulses. Static temperature-dependent measurements were made using a Doty 5 mm probe, and ⁸⁹Y NMR spectra were acquired using the spin-echo technique with a 20 s delay at room temperature increasing to 150 s at 90 K to account for the increased spin-lattice relaxation time at low temperatures. The NMR shifts were measured relative to a 1m aqueous solution of YCl₃ which had a Larmor frequency of 24.49 MHz. Spin-lattice relaxation measurements were made at room temperature using a saturating 90° comb.

The substitution of La for Ba leads to a progressive underdoping of the parent compound and results in superconducting transition temperatures of 81, 64, and 44 K, for La contents of y=0, 0.05 and 0.1. From the $T_c/T_{c,\max}$ values

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FIG. ⁸⁹Y 1. NMR static spectra for (a) $YBa_2(Cu_{0.9625}Zn_{0.0375})_4O_8$ at 106 K, (b) $Y(Ba_{0.95}La_{0.05})_2$ $(Cu_{0.975}Zn_{0.025})_4O_8$ at 149 K, and (c) $Y(Ba_{0.9}La_{0.1})_2$ $(Cu_{0.975}Zn_{0.025})_4O_8$ at 109 K. The dotted curves are the fitted spectra using the spin density model described in the text for Y with a Zn nearest neighbor (satellite peak 2) and for Y away from the Zn impurity. The dashed curve is the total fitted spectra which has been Gaussian broadened to account for instrumental and processing broadening.

we estimate the hole concentrations¹⁵ to be p = 0.120, 0.098, and 0.080, respectively. We have previously shown that the effect of Zn is to dramatically decrease T_c without altering the hole concentration on the Cu-O planes¹⁶ and to locally suppress the normal-state gap about the Zn impurity without altering the gap energy away from the Zn impurity.

The effect of Zn on the low-temperature and room-temperature ⁸⁹Y NMR spectra can be seen in Figs. 1 and 2 for the $YBa_2(Cu_{0.9625}Zn_{0.0375})_4O_8$, $Y(Ba_{0.95}La_{0.05})_2(Cu_{0.975}Zn_{0.025})_4O_8$, and $Y(Ba_{0.9}La_{0.1})_2$ $(Cu_{0.975}Zn_{0.025})_4O_8$ samples. The low-temperature spectra are asymmetric and broader than the room-temperature spectra. We have previously shown that ⁸⁹Y NMR spectra from



FIG. 2. Room-temperature 89 Y static NMR spectra for (a) YBa₂(Cu_{0.9625}Zn_{0.0375})₄O₈, (b) Y(Ba_{0.95}La_{0.05})₂ (Cu_{0.975}Zn_{0.025})₄O₈, and (c) Y(Ba_{0.9}La_{0.1})₂(Cu_{0.975}Zn_{0.025})₄O₈. The dotted and dashed curves are as in Fig. 1.



FIG. 3. Room-temperature ⁸⁹Y NMR MAS spectra for (a) $YBa_2Cu_4O_8$, (b) $YBa_2(Cu_{0.9875}Zn_{0.0125})_4O_8$, and (c) $YBa_2(Cu_{0.9725}Zn_{0.0375})_4O_8$. The dotted curves and dashed curves are as in Fig. 1.

YBa(Cu_{1-x}Zn_x)₄O₈ samples can be modeled as consisting of two peaks.¹⁶ The satellite peak (peak 2 in Fig. 1) was attributed to Y adjacent to a Zn atom while the main peak (peak 1 in Fig. 1) was associated with Y atoms which are not nearest neighbors to a Zn atom. The effect of Zn substitution can also be seen in Figs. 3 and 4 where we show the room temperature ⁸⁹Y NMR MAS spectra for YBa₂Cu₄O₈, YBa₂(Cu_{0.9875}Zn_{0.0125})₄O₈, and YBa₂(Cu_{0.9625}Zn_{0.0375})₄O₈ and the corresponding linewidths as a function of Zn. The MAS spectra are much narrower than the static spectra due to the removal of dipole-dipole broadening and hence it is possible to see that the ⁸⁹Y NMR linewidth becomes larger with Zn substitution.

The ⁸⁹Y NMR spectra in Figs. 1–3 and the corresponding linewidth data in Fig. 4 are modeled by considering the effect of local moments which are known to be induced by Zn substitution for planar Cu atoms.⁹ The local moments induce a spatially varying static spin density that can be described by the exchange Hamiltonian $H_{ex} = -J \Sigma_{r'} S^L \cdot S(r')$ where S^L is the local moment spin operator, S(r') is the conduction band carrier spin operator and J is the exchange energy. Walstedt *et al.*¹¹ have used the formalism of



FIG. 4. ⁸⁹Y NMR MAS linewidths plotted against Zn content for $YBa_2(Cu_{1-x}Zn_x) {}_4O_8$ samples after subtraction of instrumental broadening. Experimental data (\blacksquare) and fitted spectral widths (\triangle) using the model described in the text.

Pennington and Slichter¹⁷ to show that the resultant spin at site $\mathbf{r}' = (n_x, n_y)$ is $S_z = -|\rho J| (\xi/a) \beta^{1/2} \langle S_z^L \rangle$ $\times (4\pi)^{-2}(-1)^{nx+ny} \Sigma_{\mathbf{r}'} \exp(-|\mathbf{r}+\mathbf{r}'|^2/4\xi^2)$ where ρ is the spin density of states, β is the conduction-band dynamicsusceptibility scale parameter, ξ is the antiferromagnetic coherence length, and a is the average lattice parameter in the ab plane. The ⁸⁹Y hyperfine field arising from the spin density oscillation is $H(\mathbf{r}) = D_{Cu} \Sigma S_z(\mathbf{r} + \mathbf{r}')$ where $D_{Cu} = -3$ kG (Ref. 18) and the sum is over the eight nearest Cu atoms. The ⁸⁹Y NMR data were fitted by randomly distributing Zn on two 100×100 square lattices to simulate the two CuO₂ planes, computing the spin on each copper and then adding up the spins about each Y atom. The fitted spectra from Y with Zn as a nearest neighbor (satellite peak) and Y where Zn is not a nearest neighbor (main peak) are shown in Figs. 1-3. The fitted spectra were summed and then convoluted with a Gaussian to account for the instrumental and processing-induced spectral broadening. It can be seen in Figs. 1-3 that this model describes the data well. In particular, this model also accounts for the increase in the roomtemperature MAS linewidths as shown in Fig. 4. The ξ values were estimated from the neutron-scattering data of Rossat-Mignod *et al.* (ξ =1.2*a*, 1.5*a*, and 2.4*a* for 0, 0.05, and 0.1 La).¹⁹ The parameter evaluated by fitting our NMR data is $\gamma = |D_{Cu}\rho J|\beta^{1/2} \langle S_z^L \rangle / (B16\pi^2)$, where B is the magnetic field. We find that $\gamma = 34 \times 10^{-6}$, 31×10^{-6} , and 21×10^{-6} for the 0, 0.05, and 0.1 La, respectively. Taking²⁰ $\beta^{1/2}=10$ and $\rho=3$ states/eV (Ref. 12) we find that $|JP_{eff}| = 110, 100, and 68 \text{ meV}$ for each La concentration, respectively, where $P_{\rm eff}$ is the size of the local moment in μ_B . The reduction in $|JP_{eff}|$ with underdoping results primarily from the increasing correlation length ξ .

The size of the local moment per Zn atom is estimated from the ⁸⁹Y NMR shift of the satellite peak by noting that in the absence of Zn, the ⁸⁹Y NMR shift is (Ref. 21) $K=8D\chi_s/g\mu_B+\sigma$ where χ_s is the static spin susceptibility per planar CuO₂ unit due to the transferred hyperfine interaction between Y and the electrons in the conduction band, g is the electron g factor, and σ is the chemical shift [152 ppm (Ref. 22)]. Thus we write the ⁸⁹Y NMR shift of the satellite peak for Zn substituted samples as

$$K = 7D_{\rm Cu}\chi_s/(g\mu_B) + D_{\rm Zn}\chi_c/(g\mu_B) + \sigma, \qquad (1)$$

where D_{Zn} is the transferred hyperfine coupling constant from the spin on the Zn site to the ⁸⁹Y nuclei and χ_c is the static susceptibility of the induced moment per Zn atom. We express χ_c in a manner similar to χ_s leading to

$$\chi_c = \chi_m / (cN_A), \tag{2}$$

where χ_m is the molar susceptibility of the local moments, c(=4x) is the Zn fraction per formula unit, and N_A is Avogadro's constant. Thus,

$$\chi_c = (\mu_B^2 P_{\text{eff}}^2) / (3k_B T).$$
 (3)

The temperature dependence of the 89 Y NMR shift of the satellite peak is shown in Fig. 5 for $YBa_2(Cu_{0.9875}Zn_{0.0125})_4O_8, \quad YBa_2(Cu_{0.9625}Zn_{0.0375})_4O_8, Y(Ba_{0.95}La_{0.05})_2(Cu_{0.975}Zn_{0.025})_4O_8, \text{ and } Y(Ba_{0.9}La_{0.1})_2 (Cu_{0.975}Zn_{0.025})_4O_8$. The NMR shift of this peak is independent.



FIG. 5. ⁸⁹Y NMR shift of the satellite peak plotted as a function of temperature for (\bigcirc) YBa₂(Cu_{0.9875}Zn_{0.0125})₄O₈, (\square) YBa₂(Cu_{0.9875}Zn_{0.0125})₄O₈, (\bigcirc) Y(Ba_{0.95}La_{0.05})₂(Cu_{0.975}Zn_{0.025})₄O₈, (\bigcirc) Y(Ba_{0.95}La_{0.05})₂(Cu_{0.975}Zn_{0.025})₄O₈, and (\triangle) Y(Ba_{0.9}La_{0.1})₂(Cu_{0.975}Zn_{0.025})₄O₈. The curves are 35 +9500/*T* for no La (solid curve), 25+10 500/*T* for 0.05 La (dashed curve), and 15+11 000/*T* for 0.1 La (dotted curve). Inset: ⁸⁹Y room-temperature spin-lattice relaxation rate (1/*T*₁) as a function of Zn content for YBa₂(Cu_{1-x}Zn_x)₄O₈. The solid line is the best fit line to Eq. (4) with |*JP*_{eff}| = 110 meV.

dent of Zn content as expected from Eqs. (1) and (3). Thus for $Y(Ba_{1-y}La_y)_2(Cu_{1-x}Zn_x)_4O_8$, we find that the NMR shift is K = 9500/T + 35, 10 500/T + 25, and 11 000/T + 15 for 0, 0.05, and 0.1 La. The constant term is $\frac{7}{8}$ times the Knight shift for the corresponding superconductors without Zn. To estimate the size of the induced local moment we take $D_{7n} = D_{Cu}$. This assumption is consistent with the observation that both Cu and Zn have 3d outermost occupied levels and implies that both the conduction-band wave functions and Zn impurity wave functions at the Fermi level are similar. Previous thermopower data showed that the Fermi level is independent of Zn concentration,¹⁶ which is consistent with the Zn-O orbital being within the Cu-O conduction band. The resultant effective moments per Zn atom are 1.06, 1.12, and $1.35\mu_B$ which are slightly greater than the value of $P_{\text{eff}} \approx 1$ found by Walstedt *et al.*¹¹ from susceptibility measurements on $YBa_2(Cu_{1-x}Zn_x)_3O_7$ and the value *et al*.¹² of $P_{\rm eff} \approx 0.86$ used by Mahajan in $YBa_2(Cu_{1-x}Zn_x)_3O_{6.64}$. Thus, we find that the induced moment is moderately dependent on hole doping. The corresponding values of the exchange energy obtained from the estimates of P_{eff} and the fitted γD values are J = 104, 89, and50 meV for La contents of 0, 0.05, and 0.1, respectively. By comparison Walstedt *et al.*¹¹ deduced J=5 meV from ⁶³Cu NMR measurements on YBa₂(Cu_{1-x}Zn_x)₃O₇ and Mahajan *et al.*¹² estimated J = 75 meV from ⁸⁹Y NMR measurements on $YBa_2(Cu_{1-x}Zn_x)_3O_{6.64}$. The latter compound is in a similar, though slightly lower, doping state to our 5% La substituted $YBa_2Cu_4O_8$ samples and hence its J values is in reasonable agreement with the *p*-dependent values we report.

The experimental $|JP_{eff}|$ value for YBa₂(Cu_{1-x}Zn_x)₄O₈ can be used to estimate the change in the ⁸⁹Y NMR spin lattice relaxation rates expected with Zn substitution. Gio-

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vannini and Heeger²³ have shown that the spin density oscillation induced by the local moment results in a spin lattice relaxation time that can be expressed as,

$$T_1(c) = T_1(c=0) / [1 + (6c \langle S_z^L \rangle J_{\text{eff}}^2 / \pi E_F g \mu_B)], \quad (4)$$

where $J_{\text{eff}} \approx 4J$ (Ref. 11) and E_F is the Fermi energy. The experimental room-temperature spin-lattice relaxation rates are shown in the insert in Fig. 5. Also plotted are the theoretical spin-lattice relaxation rates as determined from Eq. (4) and using $|JP_{\text{eff}}| = 107$ meV. We find that the experimental spin-lattice relaxation rates are consistent with the deduced $|JP_{\text{eff}}|$.

The decrease in T_c from magnetic pair breaking can be estimated from the experimental $|JP_{\rm eff}|$ values. Using the Abrikosov-Gorkov²⁴ formula T_c should decrease by $\Delta T_c = \frac{7}{96} \pi^2 c \rho J_{\rm eff}^2 S(S+1)/k_B$, for small magnetic-impurity concentrations. However, as S(S+1) can be estimated from the size of the induced moment per Zn atom, $P_{\rm eff} \mu_B = g [S(S+1)]^{1/2} \mu_B$,²⁵ then the Abrikosov-Gorkov formula can be rewritten as

$$\Delta T_{c} = \frac{7}{96} \pi^{2} c \rho |JP_{\text{eff}}|^{2} / g^{2} k_{B}.$$
 (5)

Thus using the fitted $|JP_{\rm eff}|$ value of 110 meV we find magnetic pair breaking in the YBa₂(Cu_{0.975}Zn_{0.025})₄O₈ sample should cause T_c to decrease by ~61 K, which is close to the experimental value of $\Delta T_c = 69$ K. Indeed, when the full nonlinear Abrikosov-Gorkov theory is used the pair-broken depression of T_c agrees remarkably well with the observed data. Figure 6 shows the observed T_c values plotted as a function of Zn fraction for 0, 5, and 10% La, while the solid curves are the Abrikosov-Gorkov theory using the above-deduced $|JP_{\rm eff}|$ values. It can be seen that magnetic pair breaking can fully account for the decrease in T_c for the La-free superconductors but not for the very under-



FIG. 6. T_c plotted as a function of Zn content for $0 (\bullet)$, 0.05 (\blacksquare), and 0.1 (\blacktriangle) La content. The solid curves are from the Abrikosov-Gorkov theory using the deduced $|JP_{eff}|$ values.

doped superconductors Zn strongly reduces the pairing potential while near optimal doping the pairing potential is only moderately reduced. These results are consistent with the spin fluctuation model of Monthoux and Pines⁸ which presents a reduction in the pairing potential with Zn substitution which is strongly increasing with the antiferromagnetic correlation length.

In summary, we have performed ⁸⁹Y NMR measurements on underdoped YBa_{2-y}La_y(Cu_{1-x}Zn_x)₄O₈ samples and modeled the data using the formalism of Pennington and Slichter. The local moment induced by the Zn atoms increases moderately with hole doping while the exchange energy increases rapidly. From the deduced exchange energy we find that magnetic pair breaking by the induced local moments can fully explain the rapid depression in T_c with Zn substitution for La-free samples. However, as the samples become more underdoped magnetic pair breaking is increasingly unable to account for the observed decline in T_c which probably occurs predominantly via a reducing pairing interaction.

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