Transport and NMR studies of the effect of Ni substitution on superconductivity and the normal-state pseudogap in $YBa_2Cu_4O_8$

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Resistance, thermopower, and ^{89}Y nuclear magnetic resonance (NMR) measurements have been carried out on $YBa_2(Cu_{1-x}Ni_x)_4O_8$ superconductors. Nickel substitution reduces both T_c and the pseudogap energy at almost the same rate as does Zn substitution, but unlike Zn substitution, there is no second peak in the ^{89}Y NMR spectra that can be attributed to Y atoms sited near a local moment. We show that this discrepancy is consistent with there being no local suppression of the normal-state pseudogap about the Ni impurity contrary to the case for Zn. [S0163-1829(96)03737-X]

INTRODUCTION

Atomic substitution in high-temperature superconducting cuprates and the concomitant change in T_c can in principle enable the pairing mechanism to be probed. Recent measurements on $YBa_2(Cu_{1-x}Zn_x)_4O_8$ and $YBa_2(Cu_{1-x}Ni_x)_4O_8$ have shown similar rates of decrease in T_c,[1,2] implying a common mechanism for the suppression of superconductivity. The decrease in T_c is rapid and $T_c=0$ when the total impurity content $c(=4x)$ is ~0.12.[2] This is inconsistent with previous studies on $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ and $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$,[3,4] where it was found that, for hole concentrations in the parent compound similar to that of $YBa_2Cu_4O_8$, T_c was suppressed to zero when the Zn content $c(=3x)$ was ~0.12 and the Ni content[4] was ~0.30. The different levels of impurity concentration required to suppress superconductivity was attributed to magnetic pair breaking[5] and a decrease in the pairing potential[6] for Zn substitution and to weak magnetic pair-breaking for Ni substitution.[6,7] These interpretations do not appear compatible with the results for Ni and Zn substitution in $YBa_2Cu_4O_8$. It is therefore important that a more detailed study of Ni and Zn substitutions in the high-T_c cuprates be made.

In the undoped state the high-T_c cuprates are antiferromagnetic insulators. Hole doping leads to the appearance of superconductivity in spite of the persistence of antiferromagnetic fluctuations as evidenced by a peak in χ'' near $\mathbf{q}=(\pi,\pi)$.[8] The temperature-dependent behavior of the heat capacity,[9] susceptibility,[10] NMR,[11] infrared conductivity,[12] thermopower and resistivity[13] have all been interpreted in terms of the opening up of a normal-state gap in the spin-charge spectrum. The normal-state gap is strongly correlated with hole concentration[14,15] and decreases to zero in the overdoped side near a hole concentration of $n=0.19$. Tallon *et al.*[14] have shown that the observed approximately parabolic relation between T_c and hole concentration, $T_c/T_{c,\max}=[1-82.6(n-0.16)^2]$, can be explained by the opening of the normal-state gap in the underdoped region and pair breaking on the overdoped side as evidenced by muon spin relaxation experiments.

We have recently shown from both NMR (Ref. 16) and thermopower[15] studies that the normal-state gap in $YBa_2(Cu_{1-x}Zn_x)_4O_8$ is locally suppressed about the Zn atom and away from the Zn atom there is initially a filling in of the gap without any change in the magnitude of the normal-state gap energy, E_g. The rapid decrease in the superconducting transition temperature for $YBa_2(Cu_{1-x}Zn_x)_4O_8$ with increasing Zn substitution has been attributed to magnetic pair-breaking by a moment induced on, or around, the Zn site.[17] The existence of magnetic moments in $YBa_2(Cu_{1-x}Zn_x)_4O_8$ and $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ is intriguing as Zn is nonmagnetic. What, therefore, is the behavior in $YBa_2Cu_4O_8$ where a magnetic impurity is substituted for Cu? Do the same features of local suppression of the normal-state gap and depression of T_c by pair breaking from local moments occur?

In this paper we address these questions using resistance, thermopower, and ^{89}Y NMR measurements on $YBa_2Cu_4O_8$ where Ni is progressively substituted for Cu. The $YBa_2Cu_4O_8$ parent compound consists of a double CuO_2 plane, the source of the superconductivity, and a double CuO chain. $YBa_2Cu_4O_8$ is an underdoped superconducting cuprate with a hole concentration estimated to be $n=0.12$.[16] The singular advantage of $YBa_2Cu_4O_8$ over $YBa_2Cu_3O_{7-\delta}$ for studying substitutions is that the oxygen content in the former is fixed while, for the latter, δ can vary from 0 to 1. Substitutional effects in $YBa_2Cu_3O_{7-\delta}$ can easily be confused by accompanying changes in oxygen content, moreover, oxygen disorder on the CuO chains in $YBa_2Cu_3O_{7-\delta}$ can lead to a broadening of the ^{89}Y NMR resonance and result in two peaks near optimal doping ($n=0.16$). Oxygen ordering effects also occur at reduced oxygen contents.[18] For all these reasons we have focused our investigations on $YBa_2Cu_4O_8$ and we will show that, unlike $YBa_2(Cu_{1-x}Zn_x)_4O_8$, there is no local suppression of the normal-state gap about the Ni atom in the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ compound.

EXPERIMENT

$YBa_2(Cu_{1-x}Ni_x)_4O_8$ samples, with $x=0$, 0.0125, 0.025, and 0.05, were prepared by decomposing a stoichiometric mix of Y_2O_3, $Ba(NO_3)_2$, CuO, and NiO for one hour in air at 700 °C. The samples were initially reacted for 6 h at 930 °C and an O_2 pressure of 6 MPa. This was followed by a further reaction at 940 °C for 24 h and three further reactions at 940 °C for 48 h each in an O_2 pressure of 6 MPa. The samples were reground after each reaction. The multiple reactions were essential to obtain homogeneous samples and x-ray diffraction (XRD) analysis of the final materials indicated that these were single phase. Previous XRD measurements have shown that $YBa_2(Cu_{1-x}Ni_x)_4O_8$ is single phase for Ni concentrations exceeding 0.05. Ni substitutes predominantly for the plane Cu(2) sites and the effect of Ni is to reduce the c-axis length.[2]

Variable-temperature ^{89}Y magic angle spinning (MAS) NMR measurements between 180 and 293 K were carried out using a Bruker MSL 360 spectrometer with a 8.45 T superconducting magnet. ^{89}Y MAS NMR measurements were also carried out near 130 K using a Varian Unity 500 spectrometer with a 11.74 T superconducting magnet. The samples were spun at ~2.5 kHz to remove the ^{89}Y-^{89}Y dipole interaction and hence reduce the ^{89}Y NMR linewidth. The ^{89}Y NMR shift was referenced to an aqueous solution of YCl_3. The two-pulse spin-echo technique was used to acquire the spectra where the delay between the 90° and 180° pulses was set to one rotor period. Spin-lattice relaxation time, T_1, measurements were made using a saturating 90° comb.

Four-terminal resistance and variable-temperature thermopower data were acquired between 10 and 300 K. The thermopower was calibrated against a Pb standard.

RESULTS AND ANALYSIS

In Fig. 1 we show the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ resistance data for $x=0$, 0.0125, 0.025, and 0.05 where it can be seen that Ni substitution dramatically decreases T_c. This is seen more clearly in the figure insert where we plot T_c versus x for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ and $YBa_2(Cu_{1-x}Zn_x)_4O_8$. It is apparent that both Ni and Zn substitution rapidly reduce T_c by approximately the same amount and that $T_c=0$ when the impurity concentration is $c\sim0.12$ per unit cell. This is consistent with recent results on well-prepared $YBa_2(Cu_{1-x}Zn_x)_4O_8$ and $YBa_2(Cu_{1-x}Ni_x)_4O_8$ where T_c decreases by similar amounts with Zn or Ni substitutions suggesting a common origin for the decline in T_c.[1,2] The thermopower data in Fig. 2(a) shows that the decline in T_c cannot be attributed to a decreasing hole concentration. The room-temperature thermopower is ~7 μV/K and, like Zn, is independent of Ni content. It has been shown that the room temperature thermopower for the high-T_c cuprates varies systematically with hole concentration being 70 μV/K at the onset of superconductivity ($n=0.05$) and decreasing exponentially to 1.5 μV/K at optimal doping ($n=0.16$) when $T_c=T_{c,\max}$ (Ref. 19). Thus a constant room-temperature thermopower across the series of Ni substitutions implies a constant hole concentration. We will also show later that the room-temperature ^{89}Y Knight shift for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ is approximately constant which again implies that Ni does not alter the CuO_2 plane hole concentration.

We have previously attributed the decrease in T_c with Zn substitution to magnetic pair breaking and modeled the ^{89}Y NMR data in terms of a local moment existing on the Zn atom resulting in a spin density oscillation and an additional ^{89}Y hyperfine field.[17] The appearance of a local moment on the Zn atom even though Zn is not magnetic is consistent with bulk susceptibility measurements on $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$.[5,20] We obtained an exchange-energy-local-moment product, $|JP_{\text{eff}}|$, of 110 meV. It can be seen in the insert to Fig. 1 that magnetic pair breaking using the full nonlinear Abrikosov-Gorkov theory[21] with $|JP_{\text{eff}}|=110$ meV satisfactorily accounts for the decrease in T_c with increasing Zn concentration in $YBa_2(Cu_{1-x}Zn_x)_4O_8$. If magnetic pair breaking is also responsible for the decrease in T_c with Ni substitution then from the full nonlinear

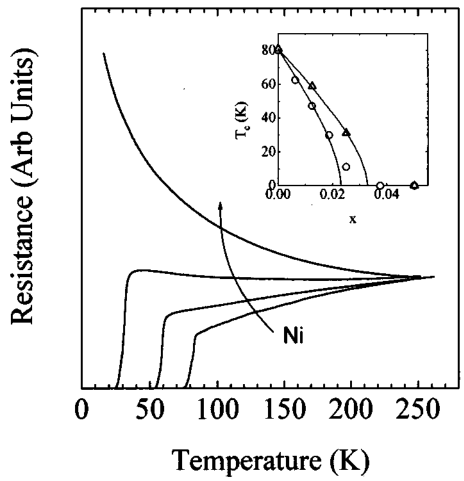

FIG. 1. Plot of resistance against temperature for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ with $x=0$, 0.0125, 0.025, and 0.05. Inset (○) T_c against Zn content for $YBa_2(Cu_{1-x}Zn_x)_4O_8$ where the solid curve is calculated using the full nonlinear Abrikosov-Gorkov theory with $|JP_{\text{eff}}|=110$ meV and (△) T_c against Ni content for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ where the solid curve is calculated using $|JP_{\text{eff}}|=92$ meV.

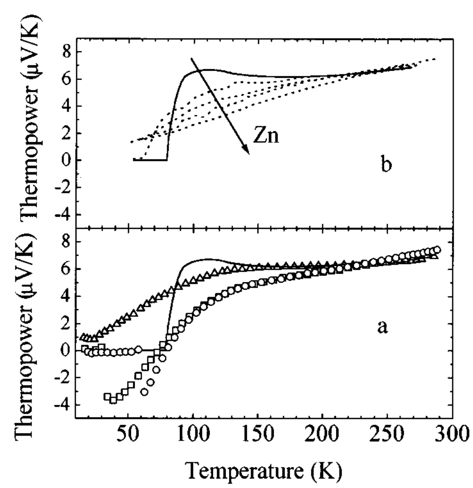

FIG. 2. (a) Plot of thermopower against temperature for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ with (solid line) $x=0$, (○) $x=0.0125$, (□) $x=0.025$, and (△) $x=0.05$. (b) Plot of thermopower against temperature for $YBa_2(Cu_{1-x}Zn_x)_4O_8$ with $x=0$, 0.006 25, 0.0125, 0.025, and 0.0375.

Abrikosov-Gorkov theory we may fit the data by putting $|JP_{\mathrm{eff}}|=92$ meV as shown in the insert to Fig. 1. As mentioned earlier, the similar effect of Ni and Zn substitutions on T_c for $YBa_2Cu_4O_8$ is unlike that observed in $YBa_2Cu_3O_{7-\delta}$ and implies a common mechanism for the decline in T_c for these magnetic and nonmagnetic impurities.

It is possible that the different rates of decrease in T_c for $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ and $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ could be due to partial Ni substitution for Cu atoms on the Cu-O chain leading to a variation in hole concentration on the CuO_2 planes and an overestimate of the Ni concentration on the CuO_2 planes. This is consistent with annealing studies which show that $YBa_2(Cu_{1-x}Ni_x)_3O_{7-\delta}$ samples annealed at the same temperature and oxygen partial pressures have different δ values where the samples with the highest Ni concentrations have the lowest δ values. By contrast, the annealing of $YBa_2(Cu_{1-x}Zn_x)_3O_{7-\delta}$ samples under the same conditions leads to little or no significant variation in δ values.[4] Partial Ni substitution for Cu on the Cu-O chains would also explain the wide variety of experimental Ni moments ranging from 1.5 μ_B to 3.4 μ_B,[4,7,22] compared with the measured intrinsic Ni^{2+} moment of 3.2 μ_B.[23]

The temperature dependence of the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ thermopower data below 80 K for $x=0.0125$ and $x=0.025$, shown in Fig. 2, is unlike that observed in the other high-T_c superconductors with comparable room-temperature thermopowers. For temperatures below 80 K the thermopower is negative until $T=T_c$ when it becomes zero. The magnitude of the negative thermopower varies non-linearly with the Ni content and it has disappeared for the $x=0.05$ sample. The origin of this low temperature negative thermopower is unknown.

The $YBa_2(Cu_{1-x}Ni_x)_4O_8$ thermopower data in the temperature region from 80 to 220 K is also different from that observed in $YBa_2(Cu_{1-x}Zn_x)_4O_8$. In Fig. 2(b) we show the $YBa_2(Cu_{1-x}Zn_x)_4O_8$ thermopower plotted against temperature for $x=0$, 0.00625, 0.0125, 0.025, and 0.0375. From the ^{89}Y NMR data we showed that the normal-state gap energy changes by less than 25% as the Zn fraction increases from 0 to 0.15 but there is progressive filling in of the normal-state gap.[16] Thus we attributed the excess thermopower below 220 K for $x=0$ to the opening of the normal-state gap. The fact that the thermopower values are essentially identical above 220 K for all Zn concentrations but fan out below 220 K is consistent with a local picture in which the gap is suppressed near a Zn atom but remains unchanged away from a Zn atom. A study of La or Ca doped $YBa_2(Cu_{1-x}Zn_x)_4O_8$ showed that E_g, estimated in this way from the thermopower increases with decreasing hole concentration similar to the variation in E_g determined from ^{89}Y NMR measurements.[13] By contrast, below 220 K the $x=0.0125$ $YBa_2(Cu_{1-x}Ni_x)_4O_8$ sample has a thermopower which is much less than that for $YBa_2Cu_4O_8$ while the $x=0.05$ sample has a thermopower which is only slightly less than that for $YBa_2Cu_4O_8$. This may be related to the unusual negative thermopower data seen in the $x=0.0125$ and 0.025 $YBa_2(Cu_{1-x}Ni_x)_4O_8$ samples below 80 K.

The $YBa_2(Cu_{1-x}Ni_x)_4O_8$ ^{89}Y MAS NMR spectra are shown at different temperatures in Fig. 3 for $x=0.0125$ and in Figs. 4 and 5 for $x=0.025$. The dip near -120 ppm in Fig. 3(a) originates from a noise spike. In some spectra we also observe a second weaker peak near 150 ppm with $T_1<0.2$ s compared with a $YBa_2Cu_4O_8$ T_1 of 15.7 s. The fast relaxing peak disappears upon further reactions at 940 °C and in an O_2 atmosphere at 6 MPa and hence we attribute it to regions of very high Ni concentration. There is no evidence of the second peak which was observed in the $YBa_2(Cu_{1-x}Zn_x)_4O_8$ low temperature ^{89}Y static NMR spectra.[17] In the case of $YBa_2(Cu_{1-x}Zn_x)_4O_8$ the second peak was attributed to the four Y atoms which are nearest neighbors to the magnetic moment induced on the Zn atom. This second peak was modeled with an NMR shift of $K_{nn}(T)=K_c(T)+7K_0/8$ where $K_c(T)$ is a Curie shift proportional to $1/T$ and is produced by transferred hyperfine coupling from the local moment on the Zn atom to the Y atom. The temperature-independent K_0 is the high temperature limit ^{89}Y Knight shift and was attributed to a local suppression of the normal-state gap about the Zn atom. The two peaks in the

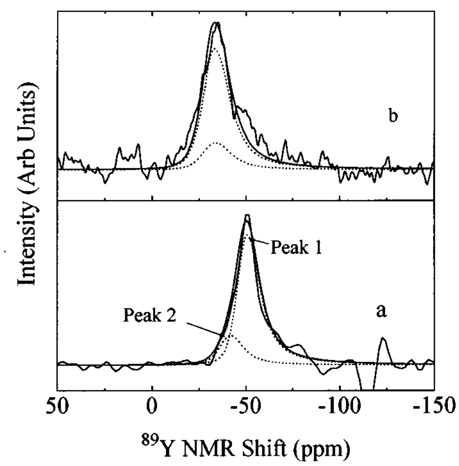

FIG. 3. Plot of ^{89}Y MAS NMR spectra for $YBa_2(Cu_{0.9875}Ni_{0.0125})_4O_8$ at temperatures of (a) 293 K and (b) 206 K. The dashed curves are fits to the data using the model described in the text. The dotted curves are the modeled ^{89}Y MAS NMR spectra from the Y atoms which are not nearest neighbor to the Ni impurity (peak 1) and the Y atoms which are nearest neighbors to the Ni impurity (peak 2).

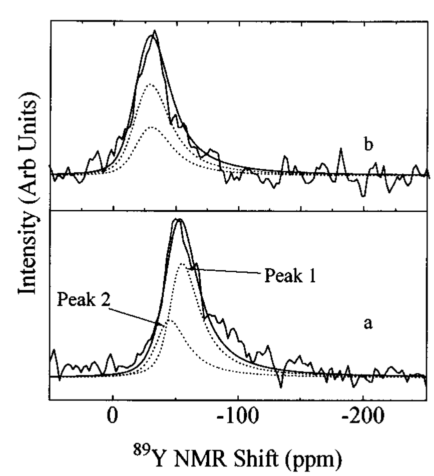

FIG. 4. Plot of ^{89}Y MAS NMR spectra for $YBa_2(Cu_{0.975}Ni_{0.025})_4O_8$ at temperatures of (a) 293 K and (b) 210 K. The dashed and dotted curves are as in Fig. 3.

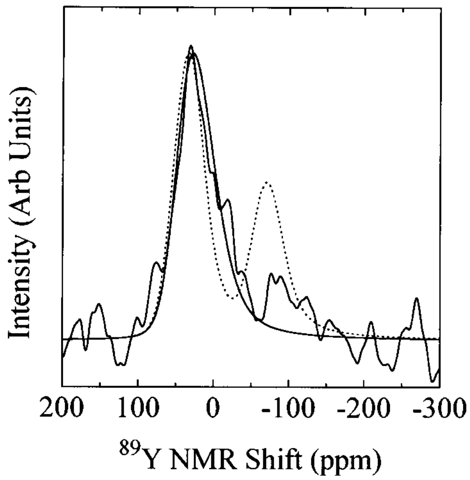

FIG. 5. Plot of the 126 K ^{89}Y MAS NMR spectra for $YBa_2(Cu_{0.95}Ni_{0.025})_4O_8$. The spectra is broadened by 300 Hz to decrease the noise. Also included is the fitted data using the model described in the text (solid smooth curve) and the expected spectra if there was a local suppression of the normal-state gap (dotted curve).

$YBa_2(Cu_{1-x}Zn_x)_4O_8$ NMR low temperature spectra were clearly observed by varying the delay between the 90° and 180° pulses. Short delays produced spectra that were peaked near the resonance position from Y atoms that are nearest neighbors to the Zn impurity while long delays produced spectra that were peaked near the resonance position from Y atoms that are not nearest neighbors to the Zn impurity. This is consistent with a local suppression of the normal-state gap leading to the low temperature T_1 from Y atoms nearest neighbor to the Zn impurity being much less that T_1 from Y atoms which are not nearest neighbors to the Zn impurity. No second peak or change in spectral shape was observed in the low temperature $YBa_2(Cu_{1-x}Ni_x)_4O_8$ ^{89}Y NMR MAS spectra when the delay between the 90° and 180° pulses was varied. A possible explanation is that there are in fact two peaks but they remain overlapping at all temperatures. The likely scenario is that for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ there is no local suppression of the normal-state gap about the Ni impurity and hence only a single T_1 value. Thus K_0 for Y adjacent to Ni has the same temperature dependence as Y remote from Ni due to the presence of the pseudogap in both cases. The Knight shift for the two cases differs only by the additional Curie term for the former. We note that this scenario is consistent with Cu NMR and nuclear quadrupole resonance measurements on Ni and Zn substituted $YBa_2Cu_3O_7$ by Ishida *et al.*[24] They found that a 1% concentration of Zn was sufficient to dramatically reduce the Cu $1/T_1T$ peak from Cu near Zn at low temperatures implying a local suppression of the antiferromagnetic correlations and the normal-state gap. They also found an increase in the Cu NMR shift at low temperatures. However, Ni concentrations of up to 5% do not lead to a suppression of the low temperature peak in $1/T_1T$ or an increase in the low temperature Cu NMR shift implying that Ni does not significantly affect the antiferromagnetic fluctuations.

To enable a comparison with $YBa_2(Cu_{1-x}Zn_x)_4O_8$ we invoke a magnetic moment on the Ni atom leading to a spin density oscillation about the Ni atom and an additional ^{89}Y hyperfine field. We model the $YBa_2(Cu_{1-x}Ni_x)O_8$ ^{89}Y NMR spectra by including an exchange Hamiltonian of the form $H_{ex}=-J\Sigma_{r'}\mathbf{S}^L\cdot\mathbf{S}(r')$, where $\mathbf{S}^L$ is the local-moment spin operator, $\mathbf{S}(r')$ is the conduction-band carrier spin operator, and J is the exchange energy. In a manner similar to Walstedt *et al.*[20] we use the formalism of Pennington and Slichter[25] to show that the resultant spin at site $\mathbf{r}'=(n_x,n_y)$ is

$$S_z=(-1)^{nx+ny}|\rho J|(\xi/a)\beta^{1/2}\langle S_z^L\rangle(4\pi)^{-2}$$
$$\times\Sigma^{r'}\exp(-|\mathbf{r}+\mathbf{r}'|^2/4\xi^2),$$

where ρ is the spin density of states, ξ is the antiferromagnetic correlation length [1.2a (Ref. 26)], β is the conduction-band dynamic-susceptibility scale parameter, and a is the average lattice parameter in the ab plane. The resultant ^{89}Y 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. 27) and the sum is over the eight nearest Cu atoms. We model the ^{89}Y MAS NMR spectra in Figs. 3–5 using two 100×100 lattices to represent the two Cu-O planes with Ni randomly distributed throughout both layers and take $\beta^{1/2}=10$ (Ref. 28) and $\rho=3$ states/eV (Ref. 5). We use the $|JP_{eff}|=92$ meV required to account for the decrease in T_c if magnetic pair breaking is occurring. The position of the ^{89}Y resonance from Y atoms which are nearest neighbor to the Ni impurity, $K_{NN}(T)$, was modeled in terms of there being no local suppression of the normal-state gap. Thus $K_{NN}(T)=K_c(T)+7K(T)/8$ where $K(T)$ is now temperature dependent and equal to $K(T)$ from Y atoms which are not nearest neighbors to the Ni impurity. We show in Figs. 3–5 that this model can successfully describe the data. The experimental and fitted data in Fig. 5 were Gaussian broadened to reduce experimental noise. Unlike $YBa_2(Cu_{1-x}Zn_x)_4O_8$, skewed Lorenzians and intrinsic linewidths of 8 and 23 ppm are required to fit the ^{89}Y MAS NMR spectra compared with a $YBa_2Cu_4O_8$ linewidth of 5 ppm. We attribute the asymmetry and broader intrinsic resonances to Ni-induced disorder. This is consistent with the larger superconducting transition widths observed in the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ compound. We also show in Fig. 5 the expected ^{89}Y NMR spectra if there were a local suppression of the normal-state gap about the Ni impurity resulting in $K(T)$ being replaced by K_0. The satellite peak would then be well separated from the main peak and it is clear that this is not supported by the data.

We show in Fig. 6 that T_1 at 293 K is similar for both Ni and Zn substituted $YBa_2Cu_4O_8$ and that there is a weak dependence of T_1 on impurity concentration, implying similar spin-lattice relaxation mechanisms for both Ni and Zn impurities. Within the magnetic pair-breaking model discussed above the small decrease in T_1 can be attributed to the indirect Ruderman-Kittel-Kasuya-Yosida mechanism where there is exchange coupling of the local moment to the conduction band electrons and then exchange coupling to the ^{89}Y nuclear moment. Direct dipolar coupling of a Ni or Zn moment to the ^{89}Y nuclear moment is unlikely as it should result in a dramatic reduction in T_1. An example of direct dipole coupling leading to a large decrease in T_1 is $Y_{1-y}Gd_yBa_2Cu_4O_8$ where Gd^{3+} with a magnetic moment of 8.0 μ_B is substituted for nonmagnetic ^{89}Y. We have found

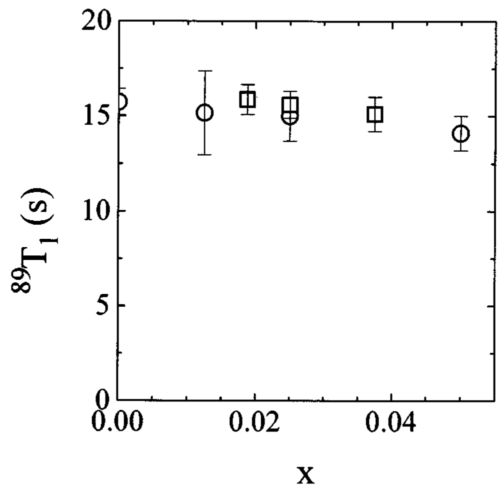

FIG. 6. Plot of the 293 K ^{89}Y spin-lattice relaxation time, T_1, against impurity content for (□) $YBa_2(Cu_{1-x}Zn_x)_4O_8$ and (○) $YBa_2(Cu_{1-x}Ni_x)_4O_8$.

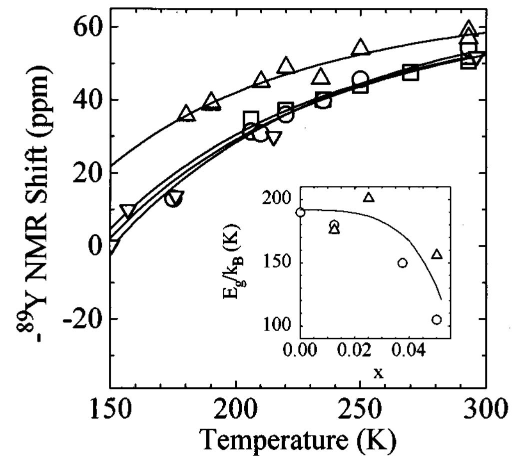

FIG. 7. Plot of the ^{89}Y NMR shift against temperature for $YBa_2(Cu_{1-x}Ni_x)_4O_8$ with (▽) $x=0$, (□) $x=0.0125$, (○) $x=0.025$, and (△) $x=0.05$. The solid lines are the best fit to the data using Eq. (2) without any filling in of the gap. Inset; The x-dependence of the normal-state gaps for (○) $YBa_2(Cu_{1-x}Zn_x)_4O_8$ and (△) $YBa_2(Cu_{1-x}Ni_x)_4O_8$. The solid line is a guide to the eye.

that for a Gd content of only $y=0.01$, T_1 is reduced from 15.7 to 5.2 s while a Ni content of $c=0.2$ leads to a ΔT_1 of only (1.6 ± 1.6) s.

In Fig. 7 we show the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ ^{89}Y NMR shifts for Y atoms which are not nearest neighbor to the Ni atom plotted against temperature. The constant room temperature ^{89}Y NMR shift is consistent with a constant hole concentration on the CuO_2 planes.[29,30] We have previously modeled the $YBa_2(Cu_{1-x}Zn_x)_4O_8$ ^{89}Y NMR and high field Gd^{3+} ESR data by a step function in the density of states leading to an ^{89}Y NMR shift of[16]

$$K(T)=K_0\mathrm{sech}^2(E_g/2k_BT)+K_g+\sigma, \qquad (1)$$

where K_g is proportional to the density of states within the gap and K_0 is proportional to the difference between the density of states above the gap and within the gap. The step function is located at the gap energy E_g. As noted, we have previously shown that there is a local suppression of the gap about the Zn impurity and away from the Zn atom there is a progressive filling in of the gap with Zn substitution. The E_g values obtained by fitting the Knight shift data to Eq. (1) are plotted in the insert to Fig. 7. As there is no evidence of a local suppression of the normal-state gap about the Ni impurity in $YBa_2(Cu_{1-x}Ni_x)_4O_8$, we therefore fit the $YBa_2(Cu_{1-x}Ni_x)_4O_8$ ^{89}Y NMR shift with $K_g=0$ implying no filling in of the gap and show the fitted curves in Fig. 7. The fitted normal-state gaps are $E_g/k_B=190$, 186, 200, and 156 K for $x=0$, 0.0125, 0.025, and 0.05. The E_g values for Ni and Zn substitution are shown in the insert to Fig. 7. Extension of the MAS data to lower temperatures would help define E_g values more accurately (for Ni substitution) but it can be seen that for both Ni and Zn substitution E_g is approximately constant until $x>0.025$ after which it decreases sharply.

CONCLUSION

In conclusion we have performed resistance, thermopower, and ^{89}Y MAS NMR measurements on $YBa_2(Cu_{1-x}Ni_x)_4O_8$ compounds. Unlike $YBa_2(Cu_{1-x}Zn_x)_4O_8$ there is no well separated second peak in the ^{89}Y NMR spectra that can be attributed to Y atoms near the Ni impurity. This discrepancy finds a simple interpretation in the occurrence of a local moment induced on the Ni atom which couples strongly to the conduction band carriers but with no local suppression of the normal-state gap near the Ni impurity.

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