Quantum Impurities and the Neutron Resonance Peak in $YBa_2Cu_3O_7$: Ni versus Zn

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The influence of magnetic ($S = 1$) and nonmagnetic ($S = 0$) impurities on the spin dynamics of an optimally doped high temperature superconductor is compared in $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ ($T_c = 80$ K) and $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$ ($T_c = 78$ K). In the Ni-substituted system, the magnetic resonance peak (which is observed at $E_r \simeq 40$ meV in the pure system) shifts to lower energy with a preserved E_r/T_c ratio while the shift is much smaller upon Zn substitution. By contrast Zn, but not Ni, restores significant spin fluctuations around 40 meV in the normal state. These observations are discussed in the light of models proposed for the magnetic resonance peak.

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Magnetic and nonmagnetic impurities have long been exploited to elucidate the microscopic nature of the superconducting state. In the cuprate superconductors, substitution by divalent transition metals for copper offers a particularly attractive way of introducing such impurities, as these preserve the doping level and introduce only minimal structural disorder. The effects of these impurities on the superconducting properties are unusual and in many ways opposite to those observed in conventional superconductors. In particular, nonmagnetic Zn^{2+} ions ($3d^{10}, S = 0$) induce a T_c reduction (~ -12 K/% Zn) almost 3 times larger than magnetic Ni^{2+} ions ($3d^8, S = 1$) [1,2]. Strong-correlation models attribute the large effects of Zn impurities to a disruption of either local antiferromagnetic [3] or resonating-valence-bond [4] correlations by spin vacancies, which can lead to a spatially extended bound state. Magnetic Ni impurities, on the other hand, are coupled to their environment through exchange interactions and hence act as a much weaker, local scattering center. Alternative models based on a local charge imbalance induced by differences in the hybridization of the transition metal ion with oxygen ligands have also been proposed to explain the disparate effects of Zn and Ni, without expressly invoking strong correlations [5].

Here we explore the interplay between both types of impurity and collective spin excitations in the $YBa_2Cu_3O_7$ system by inelastic neutron scattering (INS). In pure $YBa_2Cu_3O_7$, the spin excitation spectrum is dominated by a magnetic resonance peak [6–10] that is located at the antiferromagnetic (AF) wave vector $\mathbf{Q}_{AF} = (\pi/a, \pi/a)$ and energy $E_r \simeq 40$ meV and disappears above T_c. The recent discovery of a similar magnetic resonance peak in the superconducting state of $Bi_2Sr_2CaCu_2O_{8+\delta}$ [11] demonstrates that this collective spin excitation is a generic feature of the cuprates. There have been many attempts to explain this unusual mode theoretically and link it to the mechanism of high temperature superconductivity. Through impurity substitutions, it is possible to vary the superconducting transition temperature without changing the carrier concentration, so that the influence of both parameters on the resonance peak can be separated. However, the first step in an attempt to follow this program in lightly Zn-substituted $YBa_2Cu_3O_7$ yielded entirely unexpected results [12,13]. In particular, spin excitations around E_r were found to increase in intensity and persist above T_c. In order to find out which of these findings are general consequences of disorder in the CuO_2 planes and which can be ascribed to the purported resonant scattering of carriers from Zn impurities, we have undertaken an analogous investigation of Ni-substituted $YBa_2Cu_3O_7$.

We present a comparative study of spin excitation spectra in two samples that were chosen because of their closely similar transition temperatures: $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ ($T_c = 80$ K) and $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$ ($T_c = 78$ K). Both crystals were grown using the top seed melt texturing method and had volumes of ~ 2 cm^3. The samples were heat treated to achieve full oxygenation [12], and the Ni/Cu and Zn/Cu ratios were deduced from the reduction of T_c as compared to the pure system. The Ni content and homogeneity were cross-checked by microprobe measurements. INS experiments on Ni and Zn substituted samples have been performed on the triple axis spectrometers 2T at the Laboratoire Léon Brillouin, Saclay, and IN8 at the Institut Laue Langevin, Grenoble (France). A focusing Cu(110) monochromator and PG(002) analyzer were used and a pyrolytic graphite filter was inserted into the scattered beam in order to remove higher order contamination. The data were taken with a

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fixed final energy of 35 meV, and with the crystals in two different orientations where wave vector transfers of the form $\mathbf{Q} = (H, H, L)$ and $(3H, H, L)$, respectively, were accessible. Throughout this Letter, the wave vector $\mathbf{Q}$ is indexed in units of the reciprocal tetragonal lattice vectors $2\pi/a = 2\pi/b = 1.63$ Å^{-1} and $2\pi/c = 0.53$ Å^{-1}. In this notation the $(\pi/a, \pi/a)$ wave vector parallel to the CuO_2 planes corresponds to points of the form $(h/2, k/2)$ with h and k odd integers. Because of the well known intensity modulation of the low energy spin excitations due to interlayer interactions [6–10], the data were taken at $L = 1.7l$ where l is an odd integer.

Figure 1(a) shows a typical constant-energy scan for $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ which reveals that, at temperatures below $T_c = 80$ K, a magnetic signal is present and peaked at $\mathbf{Q}_{\mathrm{AF}}$. With increasing temperature, the magnetic intensity diminishes drastically, and above T_c only an upper limit corresponding to about 1/3 of the low temperature intensity can be established, as in pure $YBa_2Cu_3O_7$ [9,10]. A series of constant-energy scans at low temperature shows that neither the q width nor the peak position exhibit any strong energy dependence. The intrinsic q width of the magnetic scattering, $\Delta Q = 0.49 \pm 0.07$ Å^{-1}, was extracted by fitting these profiles to Gaussians. It is larger than $\Delta Q \simeq 0.25$ Å^{-1} which characterizes the magnetic resonance peak in both pure and 0.5% Zn substituted systems [12].

In order to extract the energy dependence of the additional scattering below T_c, two energy scans have been performed at low temperature ($T \ll T_c$) and at $T = T_c + 7$ K, with the wave vector fixed at $\mathbf{Q}_{\mathrm{AF}}$. Their difference is reported in Fig. 2(a). As shown in the figure, the enhancement of the magnetic intensity in the superconducting state is concentrated around a characteristic energy of 35 meV. Deconvolution of the instrumental resolution (width 5 meV) yields an intrinsic energy width of $\Delta E \sim 11$ meV. The negative difference at low energy stems from phonon scattering (determined independently through constant-energy scans).

The magnetic intensity has then been converted to the imaginary part of the dynamical magnetic susceptibility χ'' after correction by the detailed balance and magnetic form factors and calibrated against optical phonons according to a standard procedure [12]. The temperature dependence of $\chi''(\mathbf{Q}_{\mathrm{AF}}, 35\ \mathrm{meV})$, shown in Fig. 3(a), exhibits a marked upturn at T_c, and an order-parameter-like curve in the superconducting state: the telltale signature of the resonance peak in the pure system. The energy-integrated magnetic spectral weight at low temperature in the energy range probed by the neutron experiment, $\int dE\, \chi''(\mathbf{Q}_{\mathrm{AF}}, E)$, is $1.6 \pm 0.5\mu_B^2$. Within the errors, this result is identical to that previously obtained in pure $YBa_2Cu_3O_7$. At *fixed* $\mathbf{Q} = \mathbf{Q}_{\mathrm{AF}}$, damping by the Ni impurities thus leads to a mere redistribution of the spectral weight of the resonance peak. However, as a consequence of the broadening of the resonance peak in momentum space the spectral weight obtained after

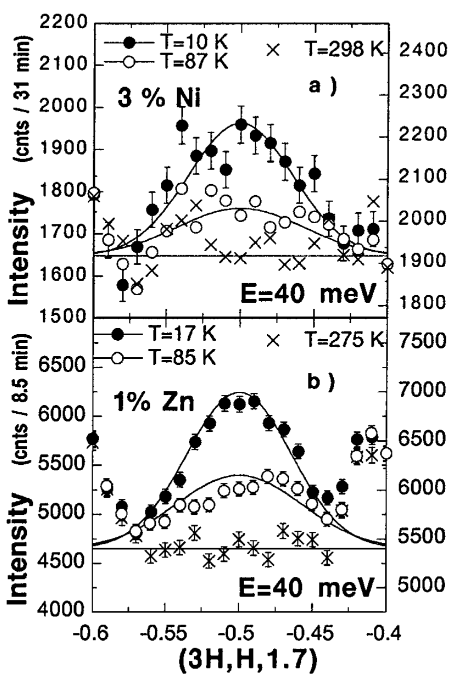

FIG. 1. Constant-energy scans performed at 40 meV around $\mathbf{Q}_{\mathrm{AF}} = (-1.5, -0.5, 1.7)$ along the (3, 1, 0) direction: (a) $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$, (b) $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$. The right scale corresponds to data close to room temperature. The peaks have been fitted to Gaussians.

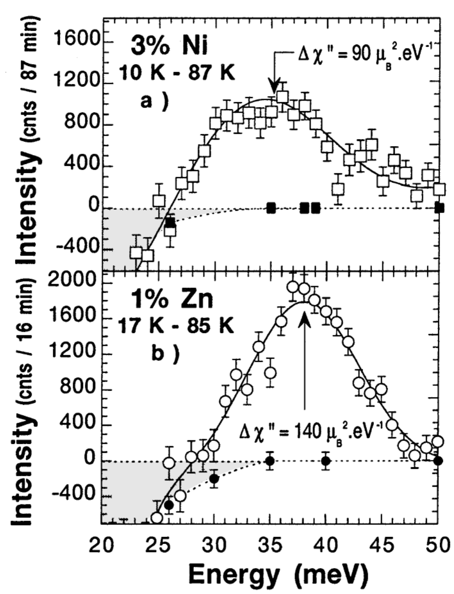

FIG. 2. Difference spectrum of the neutron intensities at low temperature and $T_c + 7$ K, at $\mathbf{Q}_{\mathrm{AF}} = (-1.5, -0.5, 1.7)$: (a) $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$, (b) $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ (open symbols). Full symbols correspond to the reference level of magnetic scattering and is determined from the difference of constant-energy scans at both temperatures. This level becomes slightly negative with decreasing energy (shaded area), owing to the thermal enhancement of the nuclear background. Lines are guides to the eye.

both integrating over energy *and* **Q** averaging over the two-dimensional Brillouin zone ($\sim 0.2\mu_B^2$) is almost 5 times larger than in pure $YBa_2Cu_3O_7$ ($0.043\mu_B^2$). This situation is closely analogous to pristine, optimally doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ ($E_r = 43$ meV) which is also thought to contain a small number of intrinsic defects [14].

The absolute unit calibration also allowed us to quantify the upper limit on the normal-state intensity: Within the range of our measurements (20–50 meV), χ'' does not exceed $45\mu_B^2 eV^{-1}$ in the normal state. Note that this upper limit, shown as a dashed line in Fig. 3(a), has been pushed below the limit previously established for pure $YBa_2Cu_3O_7$ ($70\mu_B^2 eV^{-1}$) due to various improvements in the experiments [15]. All features of the magnetic response in both superconducting and normal states of $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ are thus closely analogous to the pure system. The resonance peak is broadened and shifted down in energy, but the ratio $E_r/k_BT_c \sim 5$ is preserved. Further, 3% Ni substitution induces no measurable changes in the normal-state spectrum.

The situation is very different for Zn impurities. In order to compare the effects of Zn and Ni on an equal level, we now discuss neutron measurements taken on a $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$ crystal whose $T_c = 78$ K is almost identical to that of $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$. Again, the magnetic signal is peaked at $\mathbf{Q}_{AF}$ [Fig. 1(b)], but only about half of it is removed upon increasing the temperature up to T_c. Above T_c, the magnetic response gradually fades away and completely vanishes at room temperature (Fig. 3). Its intrinsic q width, $\Delta Q = 0.44 \pm 0.07$ Å^{-1}, is larger than in the pure system (0.25 Å^{-1}) but comparable to $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$. A difference scan in the energy range $E = 20-50$ meV (analogous to that reported above for the Ni-substituted system) shows that the enhanced $\chi''(\mathbf{Q}_{AF}, \omega)$ in the superconducting state is concentrated around a characteristic energy ~38 meV, with an intrinsic energy width $\Delta E \sim 9$ meV [Fig. 2(b)].

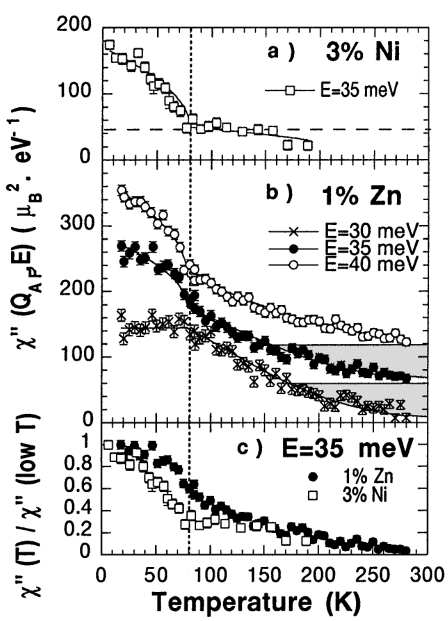

FIG. 3. Temperature dependence of $\chi''(\mathbf{Q}_{AF}, E)$: (a) $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$, $E = 35$ meV. (b) $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$, $E = 30$, 35, 40 meV. Data sets are shifted from one another by $60\mu_B^2 eV^{-1}$. The dashed line in (a) corresponds to the upper limit of magnetic response left in the normal state. (c) χ'' at 35 meV normalized to low temperature in both samples.

All of these features are closely analogous to those observed in $YBa_2(Cu_{0.995}Zn_{0.005})_3O_7$. It is, in fact, surprising that the energy widths of the magnetic response in both systems are identical (but much larger than in the pure system) despite the factor-of-2 difference in Zn concentration. The present data set is, however, more comprehensive and reveals a subtle but distinct difference between the normal-state and superconducting-state response functions that had gone unnoticed before. Specifically, the temperature dependences of $\chi''(\mathbf{Q}_{AF}, 35\text{ meV})$ and $\chi''(\mathbf{Q}_{AF}, 40\text{ meV})$ [close to the maximum of the difference scan of Fig. 2(b)] show inflection points near T_c, whereas no such feature is apparent in the temperature dependence of $\chi''(\mathbf{Q}_{AF}, 30\text{ meV})$ (farther away from the maximum). Moreover, above T_c, $\chi''(\mathbf{Q}_{AF}, 30\text{ meV})$ is actually larger than $\chi''(\mathbf{Q}_{AF}, 35\text{ meV})$ and $\chi''(\mathbf{Q}_{AF}, 40\text{ meV})$. Taken together, these observations imply that the characteristic energy of the normal-state response is somewhat lower than the one in the superconducting state.

We can summarize the experimental observations as follows. While the width of the resonance peak is very sensitive to both types of impurities (and hence presumably to any type of disorder), there are also pronounced differences in the magnetic response functions of lightly Zn- and Ni-substituted $YBa_2Cu_3O_7$ with identical T_c. Whereas Ni impurities do not measurably enhance the normal-state response, a broad peak with characteristic energy comparable to (but somewhat lower than) the energy of the resonance peak in pure $YBa_2Cu_3O_7$ appears in the normal-state response of Zn-substituted systems. In the superconducting state, on the other hand, the impurity-induced shift of the magnetic response is larger in the Ni-substituted system.

Theoretical work on the interplay between collective spin excitations and quantum impurities in high temperature superconductors is just beginning. Bulut [16] has introduced a model that attributes the normal-state peak in Zn-substituted systems to impurity-induced umklapp scattering. In the framework of this model, the weaker modification of the normal-state response by Ni [Fig. 3(c)] could simply be a consequence of the weaker scattering cross section of Ni. To explain the stronger shift of the resonance peak due to Ni impurities in the superconducting state, one may have to resort to models that also address the microscopic mechanism underlying the large difference in scattering cross sections. On a phenomenological level, our data are consistent with a scenario in which Zn impurities are surrounded by extended regions whose magnetic properties are strongly modified already far above T_c, and in which superconductivity never develops [13]; superconductivity is then confined to (perhaps only rather narrow) regions far from the Zn impurities. This would explain why Zn impurities all but eradicate the effect of superconductivity on the spin excitations which is so readily apparent in the pure system.

In $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$, on the other hand, there is no indication that impurities disrupt the spin correlations over an extended range. Rather, our data suggest that the magnetic response is not essentially different from that of a homogeneous system. This scenario is also consistent with NMR experiments. While these have uncovered a variety of unusual effects in Zn-substituted $YBa_2Cu_3O_7$ (such as at least two different ^{63}Cu relaxation times that have been attributed to copper sites at different distances to the Zn impurities [17], or local moments on copper sites adjacent to Zn [18]), no such effects have been reported for Ni-substituted systems.

If, as both neutron and NMR experiments indicate, the spin dynamics of $YBa_2(Cu_{1-x}Ni_x)_3O_7$ is indeed amenable to an "effective medium" description, our measurements can be directly compared to current models of the spin excitations in the cuprates, most of which do not explicitly incorporate disorder. Specifically, recent theoretical interpretations of the resonance peak fall into two categories, attributing the mode to collective modes in the particle-particle [19] and particle-hole (e.g., Refs. [20,21]) channels, respectively. In the former model, the magnetic resonance peak is identified with the so-called π excitation that can be visualized as a spin triplet pair of electrons with center of mass momentum $(\pi/a, \pi/a)$. The resonance peak can be ascribed to resonant scattering of Cooper pairs into π pairs [19]. In this model, the intensity of the magnetic resonance peak is controlled by the magnitude of the d-wave order parameter, whereas the mode energy depends on hole doping only.

The competing model attributes the magnetic resonance peak to a magnonlike bound state that is pulled below the continuum of spin flip excitations by antiferromagnetic interactions [21]. As this resonant excitation is a consequence of a delicate interplay between the superconducting gap, the shape of the Fermi surface in the normal state, and the antiferromagnetic spin correlations, its energy should be very sensitive to the magnitude of the gap. At least in the optimally doped and overdoped regimes of the phase diagram, where "pseudogap" effects are not important, the gap is expected to scale with T_c. The shift of the magnetic resonance peak upon Ni substitution, which reduces T_c without changing the hole content, therefore appears inconsistent with a description in terms of the π mode. In contrast, the fact that the ratio E_r/T_c remains constant suggests that the collective mode and the superconducting gap are renormalized in the same way, which is consistent with the spin-exciton scenario for the magnetic resonance peak [21]. Of course, a direct measurement of the superconducting gap is required to confirm this interpretation. Finally, we note that the impurity broadening of magnonlike excitations in d-wave superconductors predicted using general arguments [22] is in good overall agreement with the widths of the resonance peaks reported here.

In conclusion, our INS data show that the spin excitation spectra of $YBa_2(Cu_{0.97}Ni_{0.03})_3O_7$ and $YBa_2(Cu_{0.99}Zn_{0.01})_3O_7$ are still dominated by a magnetic resonance peak below T_c, but that the two types of impurity affect the spin correlations in very different ways. The interplay between quantum impurities and collective spin dynamics in the cuprates is therefore a surprisingly rich new field of investigation.

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[1] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 7458 (1988).
[2] P. Mendels *et al.*, Europhys. Lett. **46**, 678 (1999).
[3] D. Poilblanc *et al.*, Phys. Rev. B **50**, 13 020 (1994).
[4] R. Kilian *et al.*, Phys. Rev. B **59**, 14 432 (1999).
[5] R. P. Gupta and M. Gupta, Phys. Rev. B **59**, 3381 (1999).
[6] J. Rossat-Mignod *et al.*, Physica (Amsterdam) **185-189C**, 86 (1991).
[7] H. A. Mook *et al.*, Phys. Rev. Lett. **70**, 3490 (1993).
[8] H. F. Fong *et al.*, Phys. Rev. Lett. **75**, 316 (1995).
[9] P. Bourges *et al.*, Phys. Rev. B **53**, 876 (1996).
[10] H. F. Fong *et al.*, Phys. Rev. B **54**, 6708 (1996).
[11] H. F. Fong *et al.*, Nature (London) **398**, 588 (1999).
[12] H. F. Fong *et al.*, Phys. Rev. Lett. **82**, 1939 (1999).
[13] Y. Sidis *et al.*, Phys. Rev. B **53**, 6811 (1996).
[14] Y. Kitaoka *et al.*, J. Phys. Soc. Jpn. **63**, 2052 (1994).
[15] P. Bourges *et al.*, in *High Temperature Superconductivity*, edited by S. E. Barnes *et al.*, AIP Conf. Proc. No. 483 (AIP, Amsterdam, 1999), pp. 207–212.
[16] N. Bulut, cond-mat/9909437; cond-mat/9908266.
[17] K. Ishida *et al.*, J. Phys. Soc. Jpn. **62**, 2803 (1993).
[18] A. V. Mahajan *et al.*, Phys. Rev. Lett. **72**, 3100 (1994).
[19] E. Demler *et al.*, Phys. Rev. B **58**, 5719 (1998).
[20] J. Brinckmann and P. A. Lee, Phys. Rev. Lett. **82**, 2915 (1999).
[21] F. Onufrieva and P. Pfeuty, cond-mat/9903097.
[22] M. Vojta *et al.*, cond-mat/9912020.