

Planar ^{17}O NMR study of $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6+x}$ W. A. MacFarlane,* J. Bobroff, P. Mendels, L. Cyrot, H. Alloul, and N. Blanchard
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We report the planar ^{17}O NMR shift in Pr-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, which at $x = 1$ exhibits a characteristic pseudogap temperature dependence, confirming that Pr reduces the concentration of mobile holes in the CuO_2 planes. Our estimate of the rate of this counterdoping effect, obtained by comparison with the shift in pure samples with reduced oxygen content, is found insufficient to explain the observed reduction of T_c . From the temperature-dependent magnetic broadening of the ^{17}O NMR we conclude that the Pr moment and the local magnetic defect induced in the CuO_2 planes produce a long-range spin polarization in the planes, which is likely associated with the extra reduction of T_c . We find a qualitatively different behavior in the oxygen-depleted $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.6}$, i.e., the suppression of T_c is nearly the same, but the magnetic broadening of the ^{17}O NMR appears weaker. This difference may signal a weaker coupling of the Pr to the planes in the underdoped compound, which might be linked with the larger Pr to CuO_2 plane distance and correspondingly weaker hybridization.

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I. INTRODUCTION

Among the isostructural rare-earth analogs of the well-studied high- T_c system $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, only Pr/Y substitution suppresses superconductivity. The most widely accepted explanation of this effect is that it is due to counterdoping of the planes; i.e., the concentration of mobile holes in the planes is depleted, resulting in the *insulating* behavior found for $y \geq 0.6$ (e.g., Ref. 1). Several proposals for the origin of this counterdoping have been advanced; for example, the valence of Pr may be larger than $3+$ (e.g., Ref. 2), the large ionic radius of Pr^{3+} may influence the chain-plane charge transfer (similar to other large trivalent ions³), or strong hybridization of Pr with its neighboring planar oxygen may cause holes to be removed from the conduction band into localized⁴ or insulating-band⁵ states. X-ray and Cu NQR experiments⁶ apparently rule out the first two possibilities.

Planar ^{17}O NMR provides a sensitive probe of the spin susceptibility (χ_s) of the CuO_2 planes in the cuprate high- T_c superconductors. In particular, in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, $\chi_s(T)$ has been shown to be strongly dependent on the carrier content (n) of the planes, especially near T_c optimal doping.⁷ In the present work, we argue that determining $\chi_s(T)$ provides a measure of n in the normal state of $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$ ($\text{Pr}_y:\text{O}_7$). Such a local measurement of n , which is free of any influence of parasitic phases, quantitatively constrains models of counterdoping. Furthermore, we find a Curie-like line broadening of the ^{17}O NMR, indicating that the Pr ion is a magnetic perturbation which induces a long-range oscillatory spin polarization response in the CuO_2 planes, as has been found for Ni and Zn in-plane substitutions.⁸ This effect is somewhat analogous to the RKKY oscillations found in conventional metals containing

magnetic impurities. Such a perturbation may be responsible for the extra reduction of T_c , which is obtained after removing the net counterdoping effect.

Finally, motivated by results from underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ with Zn and Ni as in-plane Cu substitutions, which exhibit enhanced local magnetic effects and T_c reduction relative to optimal doping,⁸ we have also studied deoxygenated samples ($\text{Pr}_y:\text{O}_{6.6}$). The results indicate that Pr induces a weaker magnetic perturbation and is therefore less coupled to the CuO_2 planes in $\text{Pr}_y:\text{O}_{6.6}$.

After detailing the samples and technical aspects of the measurement, we present the results for $\text{Pr}_y:\text{O}_7$ then $\text{Pr}_y:\text{O}_{6.6}$. Then we discuss the data in relation to the results of other experiments.

II. SAMPLES

The powder samples were synthesized by conventional high-temperature solid-state reaction of Pr_6O_{11} , Y_2O_3 , BaO_2 , and CuO as detailed in Ref. 9. This synthesis procedure reproducibly results in a family $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$, of compounds with monotonically decreasing $T_c(y)$.¹⁰ Pr is not expected to affect the maximal oxygen uptake of the sample significantly,¹¹ and this was confirmed thermogravimetrically, i.e., $\delta x \leq 0.008$ for $y = 0.2$ relative to $y = 0$. The presence of Pr substituted on the Ba site can be detected by nuclear quadrupolar resonance (NQR) of the chain Cu as has been established by intentional Pr/Ba substitution.¹² The chain NQR spectrum for samples synthesized by us with the same procedure, but with much larger Pr content, is the same as that of pure $\text{YBa}_2\text{Cu}_3\text{O}_7$, indicating that for our samples Pr/Ba substitution is *negligible*. The samples were isotopically enriched by annealing in a $^{17}\text{O}_2$ -enriched atmosphere.

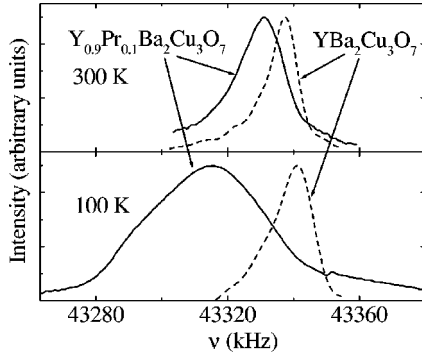


FIG. 1. The $^{17}\text{O}(2,3)$ NMR mainlines ($I_z = -\frac{1}{2} \leftrightarrow \frac{1}{2}$ transition) for pure YBCO_7 (dashed line) and $\text{Pr}_{0.1}\text{O}_7$ (solid line) at 300 K (top panel) and 100 K (bottom panel) from fast repetition (50 ms) spin-echo measurements. The downward shift of the peak position in the $\text{Pr}_{0.1}\text{O}_7$ case is due to the loss of susceptibility characteristic of the opening of the pseudogap. The left axis position corresponds to the zero of shift. The small feature at 43 350 kHz is an artifact of the rf irradiation frequency. The T -dependent broadening is also apparent.

Subsequent deoxidization was accomplished by vacuum annealing under thermogravimetric control. The samples were aligned by suspension in Stycast 1266 epoxy cured in a 7.5 T magnetic field. Alignment was checked using ^{89}Y NMR at 300 K. It was found that for $y \leq 0.1$, the samples were well aligned, but for $y = 0.2$, the powder did not completely align. However, systematic differences in the results due to imperfect alignment are negligible in comparison to the n -dependent contribution of $\chi_s(T)$.¹³

III. NMR TECHNICAL ASPECTS

A. Experimental method

Conventional spin-echo NMR spectra of the central transition of the plane oxygen [O(2,3)] were taken in the temperature range 80–350 K with the field aligned parallel to the c axis (except as noted above). The typical $\pi/2$ - τ - π sequence consisted of a $\sim 1 \mu\text{s}$ $\pi/2$ pulse and a τ of $\sim 100 \mu\text{s} \ll T_2$. The contrast in spin-lattice relaxation rates (T_1^{-1}) between the plane and apical O(4) oxygen sites was exploited (using fast repetition ~ 50 ms) to eliminate contamination from O(4). Typical Fourier-transformed spectra are illustrated in Fig. 1. From the raw spectra, the effect of Pr substitution is clearly to cause a temperature-dependent shift and broadening of the resonance. As shown below, the temperature-dependent shift is very similar to deoxidized pure YBCO_7 . We analyze the frequency spectra by extracting the peak position and the linewidth $\Delta\nu$ defined as twice the upper frequency half-width at half maximum. This definition of $\Delta\nu$ excludes the contribution to the linewidth of a slight inhomogeneity of n . This inhomogeneity of about $\pm 5\%$, which is also found in pure compounds, induces a larger broadening of the low-frequency side of the line.

The average Knight shift $^{17}K_c$ was extracted from the peak position as follows. We correct for the small second-order quadrupolar shift of the central line ($\nu_{1/2}^{(2)}$) assuming

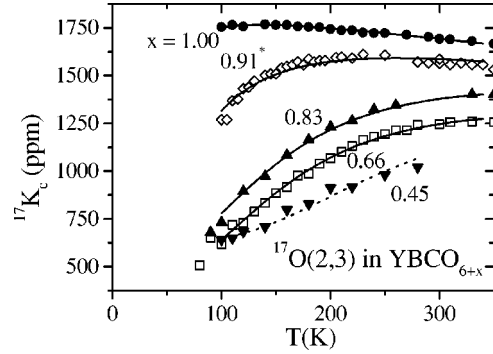


FIG. 2. Variation of the plane-oxygen temperature-dependent Knight shift for various dopings in YBCO_{6+x} . The fit curves are to a function of the form Eq. (1). The $x = 0.91$ points are obtained from scaling the ^{89}Y shift (Ref. 17). The data at $x = 0.45$ are from Ref. 18. Similar curves have been used to fit the ^{89}Y Knight shift (Ref. 7). The shift curve amounts to a very sensitive measurement of the average doping in the range $x = 0.8$ – 1.0 .

the same values of the quadrupolar interaction as in pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$.^{14,15} For the field along c , $\nu_{1/2}^{(2)}$ varies from 12.1 kHz ($x = 1$) to 10.6 kHz ($x = 0.6$) and is independent of temperature. These corrections are not large (less than 300 ppm at the experimental field), and are very weakly doping dependent. Thus, although one does expect changes in the average quadrupolar interaction with y between the extremes of $y = 0$ (Ref. 15) and $y = 1$ (Ref. 16), such effects are small compared to the T -dependent part of the shift.

B. Calibration of $^{17}K_c(2,3)$

In order to compare the shift effect to the doping effect of changing the oxygen content in pure YBCO_{6+x} , a set of curves was developed for $0.6 \leq x \leq 1$ to summarize the changes of the shift in terms of the single parameter x ; see Fig. 2. The function, based on a well-known phenomenological pseudogap T dependence,¹⁹ was of the form

$$^{17}K_c(T, x) = a(x) - bT + c\{1 - \tanh^2[T^*(x)/T]\}, \quad (1)$$

where T^* is a measure of the pseudogap. The T profile of the shift varies strongly with x for $x > 0.85$ (Fig. 2). The dependence of the shift is weaker^{14,18} for $x < 0.85$. In particular, for $0.6 < x < 0.85$, the main effect is a T -independent downward offset of $^{17}K_c$, while for $0.45 < x < 0.6$ there is additionally a compression of the variation of $^{17}K_c$, e.g., in the difference between 300 K and 100 K. Thus measurement of the T profile of the shift constitutes a measure of the doping level of the CuO_2 planes with high sensitivity near optimal doping and less sensitivity at lower doping.

IV. RESULTS FOR $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$

A. Shifts: The effect on doping

For the Pr_yO_7 samples, the measured shifts relative to the ^{17}O frequency in water are shown in Fig. 3 together with the curves for oxygen-depleted pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (from Fig. 2). Note that the spectra are featureless and that we do not resolve specific sites such as the near neighbors (NN) of

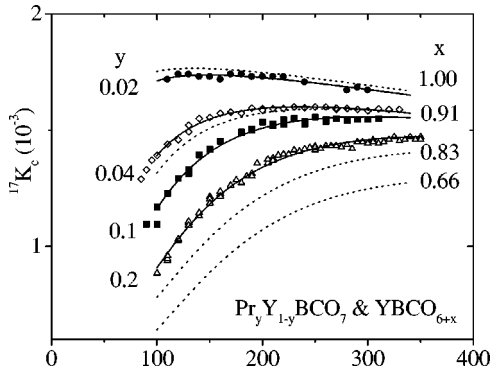


FIG. 3. $^{17}K_c$ for various Pr concentrations y in fully oxidized $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$ together with (solid) curves for deoxygenated $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. The dashed curves are fits to a phenomenological function indexed by a single parameter x^{eq} .

Pr. However, such local measurements have been carried out using the ^{89}Y NMR of the NN sites of Pr.²⁰ These results lead us to anticipate that the ^{17}O NN sites of the Pr are wiped out of the present spectra, which are thus representative of the average χ_s far from the Pr. The data from the Pr-doped samples can be compared with curves obtained by interpolation between those of the deoxygenated YBCO samples. The excellent fits which are obtained indicate that $^{17}K_c$ follows the deoxygenated behavior quite closely. The fact the Pr data are well fit by the calibration curves *over the whole temperature range* confirms that changes in T -independent shift contributions due to Pr substitution are negligible.

In both the deoxygenated and Pr-doped data, the opening of the pseudogap is apparent in the temperature profile of $^{17}K_c$. While there is no detailed theoretical understanding of the electronic structure of the doped CuO_2 planes [from which one could calculate $\chi_s(n, T)$], the resemblance is so strong (Fig. 3) that it is quite reasonable to assume a common origin for the evolution of the T profiles, i.e., a reduction of n . Moreover, measurements of quite different properties (e.g., Ref. 21) also find evidence of a reduction of n . Henceforth, we will simply assume this is the case and proceed with an analysis based on the phenomenological model of Eq. (1). From the fits, we can thus extract a value for the equivalent oxygen concentration x^{eq} as a function of Pr content y , which is reported in Fig. 4 together with a linear fit.

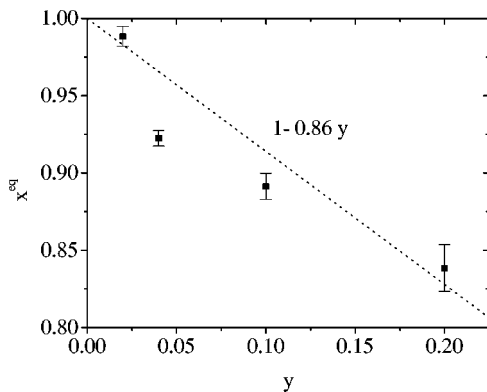


FIG. 4. The equivalent oxygenation as a function of Pr concentration y in $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$.

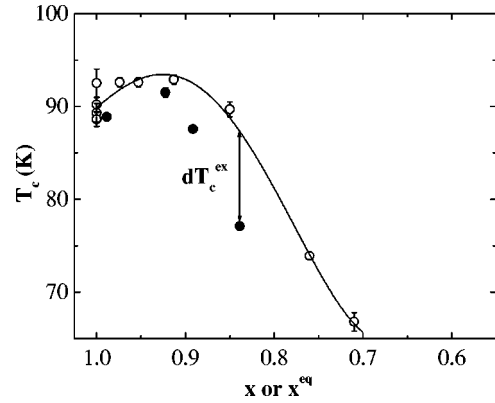


FIG. 5. T_c as a function of x for pure $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (open points) and of x^{eq} for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$ (solid points) where all the samples are from the same source and all the values of T_c were obtained by extrapolating the linear midtransition region of the field cooled (typically $B=30$ G) dc magnetic susceptibility (χ) to the zero of χ .

The decrease of T_c with y is much more rapid than expected from counterdoping alone. This can be seen by comparing $T_c(x)$ for the oxygen-depleted materials with $T_c(x^{\text{eq}})$ (Fig. 5). The difference between the two curves clearly shows that another mechanism of T_c suppression is present. The excess reduction in T_c , ΔT_c^{ex} , has been extracted as shown in Fig. 5 and is plotted as a function of Pr concentration in Fig. 6. The slope of $\Delta T_c^{\text{ex}}(y)$ is about 0.51 K/%.

Let us compare this result with former studies. Previous Cu NMR measurements for Pr-substituted samples also found underdoped behavior in both the plane copper shift and spin lattice relaxation temperature dependence.²² Also using simultaneous Ca/Y and Pr/Y substitution a somewhat larger slope of $\Delta T_c^{\text{ex}}(y)$ was inferred.¹ But in both cases there was no direct measurement of the counterdoping effect of Pr. Here the specific advantages of the ^{17}O NMR, such as its high sensitivity and intrinsically narrow resonance, together with the systematics of our study have allowed us to reach accurate quantitative conclusions.

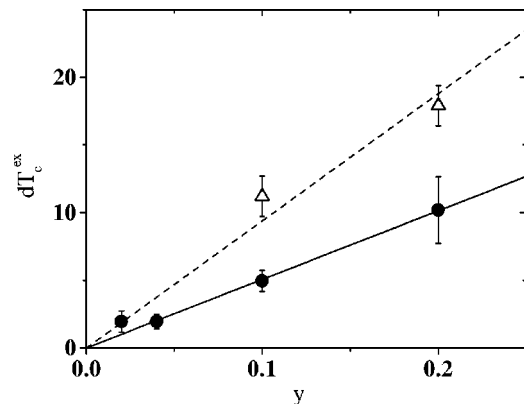


FIG. 6. Solid points: the excess reduction of T_c as defined in the previous figure as a function of Pr concentration y for $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_7$. Open points: reduction of T_c from its $y=0$ value [59.5(1.0) K] in $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.6}$.

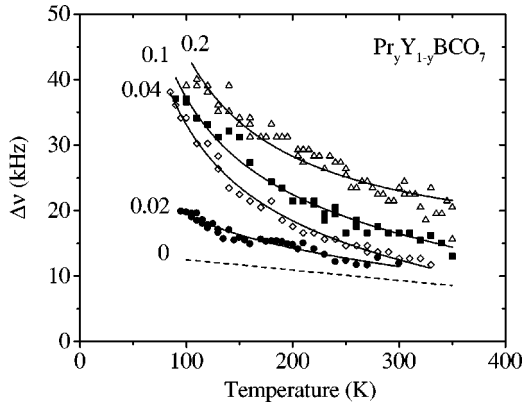


FIG. 7. The widths of the O(2,3) main lines and the width in pure $\text{YBa}_2\text{Cu}_3\text{O}_7$ (dashed line). $y=0.02$ (circles), 0.04 (diamonds), 0.1 (squares), and 0.2 (triangles).

If we extrapolate from the dilute regime of our measurements, the observed counterdoping effect is already sufficient to explain the metal-insulator transition at $y \approx 0.6$, where $x^{\text{eq}} \approx 0.4$. But as the decrease of T_c is even larger than that obtained from the counterdoping alone, we expect a nonsuperconducting part of the phase diagram whose ground state is likely an insulating magnetically disordered state, similar to Zn substituted samples.²³

B. Broadening: Magnetic effects

We can gain more insight into the effects induced by Pr substitution and more specifically on the origin of ΔT_c^{ex} from the ^{17}O linewidths $\Delta\nu$. The observed $\Delta\nu$ are presented in Fig. 7 together with that of the pure system. It is apparent that there is an excess broadening related to the Pr concentration which increases as $T \rightarrow 0$. As Pr is a paramagnetic ion with a local susceptibility possessing a Curie T^{-1} component, it is natural to associate the line broadening with such a magnetic contribution. Indeed $\Delta\nu(T)$ in $\text{Pr}_y\text{:O}_7$ scales approximately with the Pr susceptibility.²⁴ To interpret this broadening, we move now to a discussion of its origin.

The spatial distribution of local fields due to randomly placed magnetic impurities is expected to give rise to a broadening of the host nuclear resonance lines which scales with the impurity contribution to the susceptibility, typically a Curie law for dilute weakly interacting impurities. In contrast, dilute *nonmagnetic* disorder generally produces a temperature-independent broadening due, for example, to a distribution of electric field gradients.

The local *magnetic* field always contains the direct dipolar field of the impurity moments, but in metallic systems the field distribution sampled by the nuclei is usually dominated by (RKKY) spin polarization of the conduction band. Let us first demonstrate that the computed dipolar fields are negligible compared to the measured broadening. Although the precise nature of the Pr moment is still controversial,²⁵ its contribution to the macroscopic susceptibility is accounted for (in this T range) by a $\approx 2.7\mu_B$ Curie term plus a constant. In the dilute limit, the dipolar broadening may be estimated²⁶ as

$$\Delta\nu = \frac{8\pi}{9\sqrt{3}} nD \langle S_z \rangle,$$

where n is the volume concentration of the randomly placed impurities, D is the dipolar coupling to the nuclei with gyromagnetic ratio γ_n , i.e., $D = 2\mu_B\gamma_n$, and $\langle S_z \rangle$ is the thermodynamically averaged impurity spin polarization, proportional to the impurity susceptibility. Substituting the values for the Pr moment and the oxygen nuclei yields

$$\Delta\nu = \frac{3840(\text{kHz K})y}{T}.$$

For 4% Pr, the variation of this width between 300 K and 80 K is less than 1.4 kHz, more than an order of magnitude smaller than the observed value.²⁷ Thus the Curie-like broadening of the ^{17}O NMR must be due to an induced long-range spin polarization associated with a coupling of the Pr magnetic defect to the plane carriers. Such an effect is not observed for other rare earths for which a dipolar contribution is sufficient to explain the NMR widths. We discuss in Sec. VI the possible origins of this coupling.

V. RESULTS FOR $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.6}$

The reported *decrease* in the effectiveness of Pr in reducing T_c in $\text{Pr}_y\text{:O}_{6.6}$ (Ref. 28) suggests that the influence of Pr is weaker in the underdoped region of the phase diagram than at optimal doping. In contrast, our value of $\Delta T_c/y$ (0.94 K/%) is more than twice this previous report (triangles, Fig. 6) and has about the same magnitude as the T_c reduction for $\text{Pr}_y\text{:O}_7$. To investigate the role of Pr substitution in the deoxygenated samples, we studied the ^{17}O NMR in two $\text{Pr}_y\text{:O}_{6.6}$ samples corresponding to the highest Pr concentrations studied at full oxygenation in the previous section, $y = 0.1$ and 0.2 .

In the pure samples, the variation of the NMR shifts with oxygen content is much weaker in the underdoped regime than near optimal doping (see Fig. 2). Only a small reduction of the difference of $^{17}K_c$ between 100 and 300 K is observed, from $x = 0.65$ to $x = 0.45$, so that one cannot obtain a very accurate determination of the counterdoping from NMR. The data for both the $y = 0.1$ and 0.2 samples appear to be simply shifted versions of that for the unsubstituted $x = 0.6$ sample (Fig. 8). This observed change in the T -independent shift contribution appears too large to be of quadrupolar origin (see above), especially since no such effect was found in the O_7 composition. It is also large relative to the (T -independent) orbital shift, about 100 ppm in YBCO_7 . Such behavior precludes a quantitative estimate of the underdoping effect since the calibration of Sec. IV B does not apply. However, the absence of a reduction of the difference of $^{17}K_c$ between 100 K and 300 K with increasing Pr content suggests that again counterdoping is insufficient to explain the ~ 20 K decrease of T_c observed for $y = 0.2$.

Let us now consider the Pr-induced broadening of the ^{17}O line, which has been linked for YBCO_7 with magnetic effects associated with the Pr. This extra linewidth is quite small for the sample with $y = 0.1$. For $y = 0.2$ it is larger and

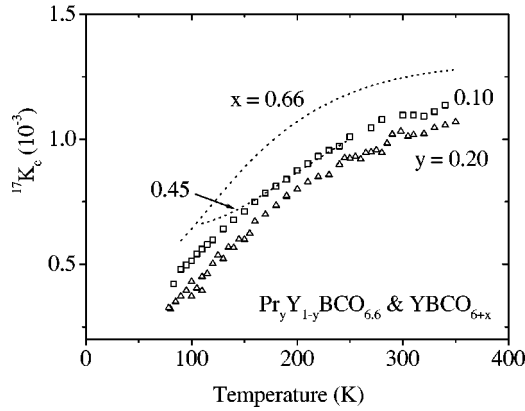


FIG. 8. $^{17}K_c$ for various Pr concentrations y in deoxygenated $\text{Pr}_y\text{Y}_{1-y}\text{Ba}_2\text{Cu}_3\text{O}_{6.6}$ (points) together with curves for deoxygenated $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (curves).

increases very rapidly at low T in the underdoped regime (Fig. 9), much faster than a Curie law. This is reminiscent of the situation encountered in underdoped $\text{YBCO}_{6.6}$ for substitution of the plane Cu by a magnetic ion, such as Ni,⁸ where the rapid T variation of the width has been shown to be a consequence of the T -dependent enhanced magnetic response $\chi'(\mathbf{q})$ of the underdoped planes. There is no reason to expect this characteristic of the underdoped planes to be altered by Pr substitution, so a detailed comparison with the case of Ni may be instructive. For Ni/plane Cu substitution, the broadening $\Delta\nu(100\text{ K})$ of the plane oxygen NMR was found to be 3–4 times larger than near optimal doping, while the magnitude of the susceptibility of Ni does not change significantly with oxygen content. However, here $\Delta\nu(100\text{ K})$ for the same concentration y of Pr is *smaller* for $\text{Pr}_y:\text{O}_{6.6}$ compared to $\text{Pr}_y:\text{O}_7$. As for the Pr effective moment, its magnitude is not significantly modified from $x=1$ to $x=0.6$ by the changes in crystalline electric field at the Pr site.^{24,29,30} Therefore the large decrease in linewidth compared to the $\text{Pr}_y:\text{O}_7$ linewidth data indicates that the coupling of the Pr moment to the planes is reduced in the underdoped state. We discuss this point in the next section together with the data in the optimally doped composition.

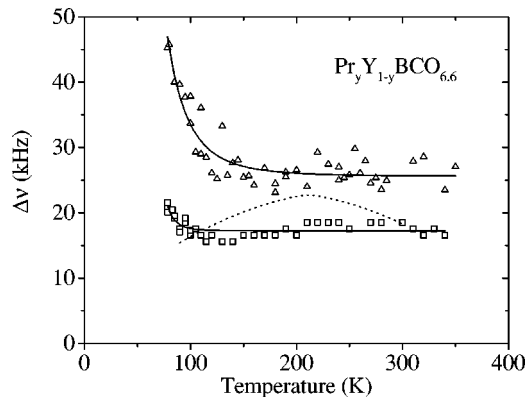


FIG. 9. The widths of the O(2,3) main line and the temperature dependence of the width in pure $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ (dashed line). Here $y=0.1$ (squares) and 0.2 (triangles).

VI. DISCUSSION

The data presented here demonstrate unambiguously that in $\text{Pr}_y:\text{O}_7$ Pr acts not only as a counterdopant (reducing n), but also as a magnetic defect. This is reflected in the long-range oscillatory spin polarization which gives rise to the broadening of the plane oxygen NMR. The magnetic defect couples strongly to the CuO_2 planes in YBCO_7 , while the coupling apparently decreases for deoxygenated samples.

The effective local magnetic moment of the Pr ion couples directly to the planes, in contrast to the moments of other rare-earth ions substituted on the Y site. Indeed the ordering temperature of the Pr moments [17 K (Ref. 31)] in pure nonmetallic PrBaCuO_7 is much larger than the ordering temperature of Gd in GdBaCuO_7 , which is a high T_c superconductor,³² indicating stronger superexchange paths through the planes for Pr than for Gd. Such a coupling via, for example, hybridization of Pr with its near-neighbor oxygens as suggested by Fehrenbacher and Rice⁴ would also result in a magnetic pair breaking effect.

Additionally such a hybridization should change the superexchange interaction between the Cu hole spins adjacent to the Pr ion. Such a local perturbation in the Cu-Cu interactions may induce an extended magnetic defect in the plane, as does any in-plane perturbation. This magnetic defect would contribute both to the induced spin polarization and the T_c depression, similar to Zn and Ni impurities.³³

We do not at this stage have enough detailed information regarding the local magnetic properties around the Pr impurities to distinguish between these two contributions, as the NMR line of Fig. 1 is comprised only of distant oxygen nuclei.

We can, however, qualitatively consider the likely evolution of these effects with decreasing x —that is, deoxygenation. The established increase of the Pr-O(2,3) distance due to removal of chain oxygen^{30,34} is compatible with a weaker effect of Pr in the underdoped regime. In particular it could cause *both* a decrease of the exchange coupling of the Pr moment to the planes *and* a weaker induced magnetic defect in the planes. The former may be responsible for the monotonic decrease of the Pr ordering temperature to about 11 K as $x \rightarrow 6$ found in PrBCO_x .^{30,31,35}

Another important method of characterizing the Pr defect is through its effect on charge transport—i.e., the residual resistivity ρ_0 . The anomalous behavior of in-plane Zn defects³⁶ and radiation-induced disorder³⁷ has been studied in detail, and the correlation between the reduction in T_c and the increase in ρ_0 has been found to depend strongly on n . Without resorting to a microscopic formulation of the impurity scattering or its effect on T_c , it is of interest to ask whether the Pr defect behaves qualitatively differently to the in-plane defects.³⁸ Until now such a comparison was not possible as the counterdoping effect could not be separated from the scattering. Our measurements provide $\Delta T_c = \Delta T_c^{\text{ex}}$ and n at full oxygenation, but transport data on high-quality single crystals are lacking. Some measurements on $\text{Pr}_y:\text{O}_7$ have been reported and compared to radiation damage.³⁹ However, we find that ρ_0 from Ref. 39 is unreasonably large. Indeed, for a 10% reduction of T_c , $\rho_0 \approx 5600\ \Omega/\text{plane}$ while

for Zn it corresponds to $\Delta\rho_0 < 1000 \text{ } \Omega/\text{plane}$. In order to see if this difference indicates that Pr is quite distinct from Zn, it will be necessary to confirm the reported values of ρ_0 . Other techniques, such as microwave and optical conductivity, which yield the impurity contribution to the carrier scattering rate, are also of interest in a better quantitative analysis of ΔT_c^{ex} .

VII. CONCLUSION

In conclusion, from measurements of planar ^{17}O NMR, we are able to deduce the net hole doping in the planes accurately in $\text{Pr}_y:\text{O}_7$. Counterdoping by Pr is observed at $\text{Pr}_y:\text{O}_7$, but is not sufficient to explain the reduction of T_c . The rate of counterdoping (summarized by $x^{\text{eq}} \approx 1 - 0.86y$) is important both as a constraint on theories of the T_c suppression and as a means of interpreting the results of other experiments in which the doping level is not directly mea-

sured. We suggest that the excess loss of T_c is related to scattering of the remaining mobile holes in the CuO_2 planes by the Pr defects. This might be confirmed by obtaining accurate estimates of the residual resistivity due to Pr and reliably obtaining the correlation $\Delta T_c^{\text{ex}}(n, \Delta\rho_0)$. It has been demonstrated that the Pr defect induces an in-plane magnetic response which is due to the coupling of the Pr moment itself to the planes and to the local modification of superexchange between copper holes near Pr. In $\text{Pr}_y:\text{O}_{6.6}$, the smaller influence of the magnetic perturbation can be attributed to the increase of the Pr-O distance.

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