Origin of T_c suppression and magnetic ordering in $PrBa_2Cu_3O_{7-\delta}$

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The magnetic $4f$ excitation spectrum of $PrBa_2Cu_3O_{7-\delta}$ was measured by use of inelastic neutron scattering in a study of the ground-state properties of praseodymium. We analyzed the spectra in terms of crystal-field transition lines of a trivalent Pr ion. The absolute widths of the magnetic transition lines were found to be enhanced compared with those in stable $RBa_2Cu_3O_{7-\delta}$ compounds, where R is a rare-earth element. A distinct $|\mathbf{Q}|$ dependence of the inelastic magnetic intensities was found due to spatial magnetic correlations even above the unexpectedly high ordering temperature of the Pr magnetic moments. Both the enhanced width and the magnetic correlations are almost independent of the oxygen concentration. The enhanced widths indicate an increased hybridization between $4f$ electrons and electrons of the CuO_2 planes. This is certainly responsible for the T_c suppression in $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$, probably indirectly through the unexpectedly strong magnetic correlations (high ordering temperature) of the Pr magnetic moments caused by this enhanced hybridization.

I. INTRODUCTION

Since the discovery of high-T_c superconductivity in $YBa_2Cu_3O_7$, this so-called 1:2:3 system has been investigated extensively.[1,2] When discussing the role of magnetism in this system, one has to distinguish two distinctly different effects. First, superconductivity is suppressed by substitution of a few mole percent Cu by magnetic $3d$ elements like Fe or Ni, among others.[3] For $3d$ elements with an atomic number smaller than that of Mn, the suppression scales with the magnetic moment and therefore it can be explained by the theory of Abrikosov and Gor'kov (AG),[4] in which superconductivity is suppressed by spin-exchange scattering at a few mole percent of magnetic impurities. For $3d$ elements with a higher atomic number, additional structural effects may also play an important role. Second, and in contrast to the first case, the complete substitution of Y by magnetic rare-earth (R) elements does not affect the superconductivity significantly;[5] T_c may even be increased. A systematic correlation between T_c and the ionic radii of the element R (including $R=$Y) was found for R between Nd and Lu: T_c increases with decreasing ionic rare-earth radii.[6,7] Moreover, at low temperatures, magnetic order of the rare-earth ions and superconductivity coexist.[8] The highest magnetic ordering temperature found for R from Nd to Yb is that of gadolinium, $T_N \approx 2.25$ K.[8-10] This coexistence of magnetism and superconductivity can therefore be understood as two almost decoupled electronic subsystems, which are spatially separated in these layered structures of the 1:2:3 systems.[11]

From the above description one would expect for $PrBa_2Cu_3O_7$, $T_c=97$ K and $T_N \leq 0.5$ K. However, the Pr 1:2:3 system does not become superconducting at all, but behaves like a semiconductor,[12] and the magnetic ordering temperature of the Pr moments is, with $T_N \approx 17$ K, unexpectedly high. The latter was found in magnetic susceptibility,[13,14] specific heat,[13,14] muon spin resonance,[15] Mössbauer data on Gd impurities in $PrBa_2Cu_3O_{7-\delta}$ (Ref. 16) and in the temperature-

dependent intensity of a magnetic Bragg reflection by neutron diffraction.[17] Also $PrBa_2Cu_3O_6$ behaves anomalously when compared with other R $Ba_2Cu_3O_6$ systems. Its Néel temperature is about 8 K (Ref. 16) or even higher (see below), while those of the other rare-earth magnetic moments is only a few hundred mK.[10,18]

The impact of the Cu ions on the high-T_c properties also deserves interest. Some theories[19–22] suggest that for d elements magnetic order and superconductivity are caused by one single mechanism. The density of charge carriers seems to determine which of these two coherent ground states is formed. This density varies with the oxygen content in the 1:2:3 systems and with the Sr content in $La_{2-x}Sr_xCuO_4$. Thus, superconductivity in 1:2:3 systems depends strongly on the oxygen concentration: the O_7 system is superconducting, while the O_6 system is insulating and shows antiferromagnetic order of the Cu moments.[23] The magnetic order of the Cu moments and superconductivity are strictly mutually exclusive[24] in agreement with classical theories on superconductivity. (Interestingly, even a coexistence of magnetic order and superconductivity on the Cu-O planes was detected in $La_{1.85}Sr_{0.15}CuO_4$ by muon spin resonance.[25] However, this effect may be just an artifact due to sample inhomogeneities either in the oxygen concentration or in the density of charge exchange (CE), both yielding a separation of magnetically ordered and superconducting phases.) In all high-T_c superconductors, a strong sensitivity of T_c to the density of charge carriers was found.

The oxygen and its bonds to the neighboring atoms are certainly the key to most of the observed effects in the 1:2:3 systems. This is, for instance, reflected in the magnetic ordering of the rare-earth ions. The ordering temperature usually increases with increasing oxygen concentration,[10,18] for which the only known exception is Nd.[26] Generally it is thought that the CuO_2 planes carry the superconductivity because in high-T_c Bi-based superconductors[27] no Cu-O chains exist at all. Nevertheless, in 1:2:3 systems superconductivity is suppressed by taking the oxygen out of the Cu-O chains when decreasing the oxygen concentration from O_7 to O_6,[28] but it is not destroyed by the magnetic moment of the rare-earth ions, which are located very close to the CuO_2 planes. Thus, the role of the Cu-O chains for superconductivity in the 1:2:3 systems is still unclear.

Three possible mechanisms for the suppression of superconductivity in $PrBa_2Cu_3O_7$ are currently under discussion.

(1) Breaking of Cooper pairs by spin exchange scattering: According to the theory of Abrikosov and Gor'kov, Cooper pairs are broken via exchange scattering at *stable* magnetic moments.[4] This would imply an integral valency, such as Pr^{3+} or Pr^{4+}.

(2) Intermediate valency of Pr: It is suggested that an increased valence of Pr supplies additional conduction electrons to the Cu-O planes.[29] Consequently, the mobile electron holes are filled, thus destroying superconductivity.

(3) Enhanced hybridization may directly destroy the coherent state of Cooper pairs resulting in the suppression of T_c. This mechanism is discussed by Müller-Hartmann and Zittartz[30] for the Kondo regime.

These models result in two completely contrary dynamics of the Pr moment. For a stable moment, the magnetic relaxation rate would be very small ($\lesssim 1$ K$=0.086$ meV), while it would be enhanced for both an intermediate-valence Pr ion and for a slightly enhanced $4f$ hybridization ($\gtrsim 10$K$=0.86$ meV). As both configurations, Pr^{3+} and Pr^{4+}, are magnetic, an intermediate-valence Pr ion is expected to behave rather like Tm [see TmSe (Ref. 31)] than Ce or Yb,[32] i.e., at low temperature the quasielastic (QE) linewidth is expected to increase rapidly with increasing temperature, while it gets temperature independent at higher temperatures.

Inelastic neutron scattering is an ideal tool to measure such a magnetic relaxation rate. Therefore, we have performed inelastic-neutron-scattering measurements on the Pr 1:2:3 systems. Moreover, the inelastic magnetic neutron-scattering response gives distinct information of the Pr valence (if stable) via crystal-field (CF) excitations. The Hund's rule ground state of Pr^{4+} (equivalent to Ce^{3+}) splits into three doublets and thus only two CF excitations can be observed at low temperatures, while that of Pr^{3+} splits into nine singlets, allowing six or possibly even more excitation transitions from the ground state. Inelastic-neutron-scattering results have been published by us,[33] by Skanthakamur *et al.*,[34] and by Soderholm, Goodman, and Loong,[35] showing a broad magnetic response in the spectra. This paper will give a detailed temperature-dependent analysis of the magnetic relaxation on the basis of the CF scheme published in Ref. 36.

II. EXPERIMENTS

$PrBa_2Cu_3O_{7-\delta}$ samples were prepared from a stoichiometric mixture of $BaCO_3$, Pr_2O_3, and CuO which was annealed three times at 950 °C in air for 12 h. After each annealing process the material was ground. Finally, the powder was pressed into pellets. The $PrBa_2Cu_3O_7$ sample was annealed at 950 °C in flowing oxygen for 12 h and then cooled down within another 12 h, while the $PrBa_2Cu_3O_6$ sample was annealed at 910 °C in argon atmosphere for 24 h and cooled down within 20 h.

Both samples were characterized by x-ray diffraction. For $PrBa_2Cu_3O_7$ the lattice parameters are $a=3.874$ Å, $b=3.928$ Å, and $c=11.710$ Å. This is in agreement with our neutron-diffraction results[37] and yields an orthorhombicity parameter of $d=(b-a)/(b+a)=6.92\times10^{-3}$. Although this value is 20% smaller than that of $YBa_2Cu_3O_7$, it fits nicely into the systematics of lattice parameter versus ionic radii.[6] Within the resolution of our x-ray diffractometer we were not able to detect any orthorhombic splitting of $PrBa_2Cu_3O_6$. This holds for the whole temperature range 4–300 K.[38] The room-temperature lattice parameters obtained from fits assuming tetragonal symmetry are $a=3.91$ Å and $c=11.85$ Å. The fraction of other phases was less than 2% in both samples.

Inelastic-neutron-scattering experiments were performed at the high-flux reactor (HFR) of the Institute

Laue-Langevin (ILL) in Grenoble. In order to achieve a high-energy resolution we have investigated $PrBa_2Cu_3O_7$ on the IN6 spectrometer with an incident energy of $E_0=3.14$ meV (cold neutrons) in the temperature range from 1.5 to 100 K. For elastic scattering the energy resolution was $\Delta E\approx 45$ μeV (HWHM). Additionally, we also measured $YBa_2Cu_3O_7$ as a nonmagnetic and $HoBa_2Cu_3O_7$ as a magnetic reference compound. The range of energy transfer available for neutrons is limited by the incident neutron energy on the energy-loss side and by the thermal occupation of excited states (detailed balance) on the energy-gain side of the neutrons. To gain information on the high-energy spectrum at low temperatures we performed additional experiments on the thermal-beam spectrometer IN4 (old version) with incident energies of 12.7, 50.8, and 115 meV at several temperatures. The energy resolutions (HWHM) were $\Delta E\approx 0.31$, 1.24, and 3.5 meV at the elastic line, respectively (see elastic peak in the corresponding spectra). In addition, we have also investigated $Pr_xY_{1-x}Ba_2Cu_3O_7$ with $x=0.1$, 0.4, and 0.7 and $PrBa_2Cu_3O_6$ on the IN4 spectrometer. In general, the energy resolution increases on the energy-loss (positive-energy transfer) side and degrades on the energy-gain side.

The scattering background, which depends on sample transmission, has been corrected by measuring both an empty sample holder and a cadmium plate at the sample position. To correct the efficiency of the detectors and to set the intensity to an absolute scale we have also measured a vanadium standard. Finally, we have performed an energy-dependent correction for the efficiency of the detectors as well as an angle and energy-dependent absorption correction taking into account the shape of the sample (for more details, see Ref. 32). In the spectra with $E_0\leq 12$ meV the contribution of multiple scattering is negligible. At such energies, Bragg scattering is too low to generate significant multiple scattering. However, in the spectra with $E_0\geq 30$ meV and at a low angle, multiple scattering is significant for the phonon contribution, but it is still negligible with respect to the magnetic response (for more details see Ref. 32).

Some spectra will be presented in a constant-$|\mathbf{Q}|$ mode. These spectra were rearranged by selecting just those time-of-flight (TOF) channels from all detectors having a value which falls into the given momentum transfer window $|\mathbf{Q}|\pm\Delta Q$. Due to the polycrystalline form of the samples this analysis can only be performed in terms of spherical $|\mathbf{Q}|$ shells, i.e., only an indirect relation between the $|\mathbf{Q}|$ dependence and the crystallographic directions is available.

For analyzing the magnetic contribution to the spectra, we used the paramagnetic scattering law $[d^2\sigma/d\hbar\omega\, d\Omega=(k_1/k_0)S(Q,\hbar\omega,T)]$ (for more details see Ref. 32):

$$S(\hbar\omega,Q,T)=\frac{1}{2}\left[\frac{g_N r_e}{\mu_B}\right]^2 F^2(Q)\frac{1}{1-e^{-\hbar\omega/k_BT}} \times\hbar\omega\chi_{\rm st}(T)P(\hbar\omega,Q,T)\ . \quad (1)$$

Here $F^2(Q)$ is the magnetic form factor which is related to the spatial extent of the scattering center and via the Kramers-Kronig relation the product $\hbar\omega\chi_{\rm st}P(\hbar\omega,Q,T)$ is the dynamic magnetic susceptibility χ'', which is related to the temporal behavior and to the strength of the local magnetic scattering center. Herein $\chi_{\rm st}(T)$ is the static magnetic susceptibility and $P(\hbar\omega,Q,T)$ is any spectral function (power law) which fulfills the normalization condition $\int_{-\infty}^{+\infty}P(\hbar\omega,Q,T)d(\hbar\omega)=1$. Usually, the spectral functions are found to be in good agreement with the Lorentzian. The expression containing the gyromagnetic ratio $g_n=-1.91$ of the neutrons, the classical electron radius $r_e=2.8\times10^{-13}$ cm, and the Bohr magneton μ_B is due to the transformation from the magnetic moment to the magnetic neutron cross section. This formula shows that the strength of the inelastic magnetic response is directly proportional to the static susceptibility, but only for narrow lines can one easily extract the localized magnetic moment from this intensity parameter.[39] To obtain the local magnetic moment which is related to a broad magnetic spectrum the total magnetic cross section has to be determined in the static approximation ($E_0\rightarrow\infty$ and $k_1/k_0=1$) by a numerical integration method using a somewhat uncertain cutoff energy E_c. All total intensities given here are based on $E_c=1.5$ eV, which was found to be a reasonable value (for more details see Ref. 39).

III. RESULTS

In this paper we focus on the low-energy magnetic response, i.e., we present and discuss data taken with $E_0=3.14$ and 12.7 meV. The high-energy response taken with $E_0=115$ meV dealing with the CF splitting of the Pr ion is published separately.[36] The measurements with incident energies between these extremes do not contain any further relevant result. A brief summary of the CF results is given at the beginning of the discussion.

Figure 1 presents the comparison of the spectra of nonsuperconducting $PrBa_2Cu_3O_7$ and of superconducting $HoBa_2Cu_3O_7$ at $T=50$ both taken on the high-energy resolution spectrometer IN6 with $E_0=3.14$ meV. The spectra shown in Fig. 1 are obviously different: while the stable Ho 1:2:3 system shows very sharp CF transition lines, these lines are broadened in the Pr 1:2:3 system by a factor of about 5. The magnetic scattering response in $PrBa_2Cu_3O_7$ was fitted with three transition lines located at 1.5, 3.3, and 4.8 meV. The magnetic nature of these excitations is corroborated by comparison with $YBa_2Cu_3O_7$, where no such excitations are found, and by the fact that their $|\mathbf{Q}|$-dependent intensity agrees with the magnetic form factor. The Pr spectrum shown in Fig. 1 is the same as presented in our earlier work.[33] However, while all inelastic intensities down to -8 meV were interpreted as magnetic scattering in this early work, here the area between the dashed line and the experimental data points around -7 meV is interpreted as phonon states. This was proved by comparison with the nonmagnetic reference $YBa_2Cu_3O_7$ (see Fig. 2) at $T=5$ K as well as by the $|\mathbf{Q}|$ dependence of the spectra taken on $PrBa_2Cu_3O_7$ with $E_0=50.8$ meV at 5 K and with $E_0=3.14$ meV at 100 K. No quasielastic magnetic contribution is observed

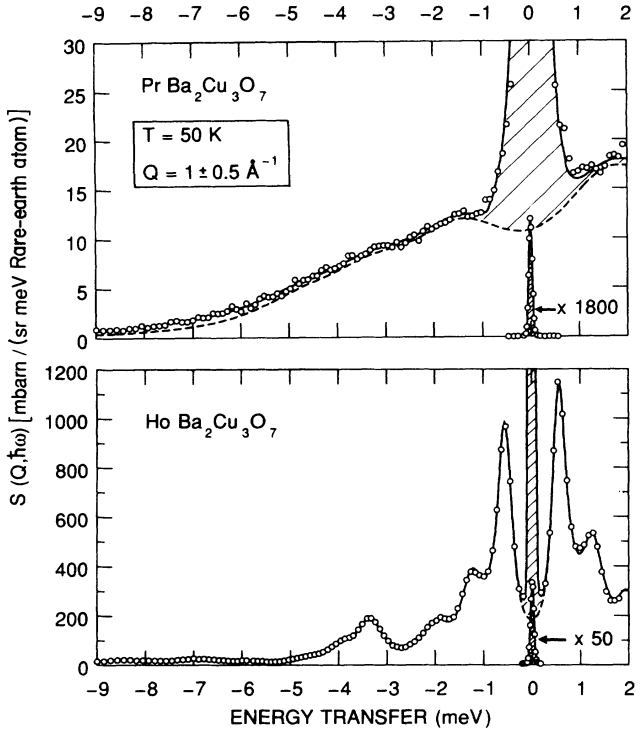

FIG. 1. Background corrected energy spectra of $PrBa_2Cu_3O_7$ and $HoBa_2Cu_3O_7$ obtained with an incident energy $E_0=3.14$ meV and at $T=50$ K on the IN6 spectrometer. The hatched area represents the nuclear elastic peak and the dashed line represents the magnetic scattering.

in the entire temperature range measured (i.e., 1.5–100 K).

In Fig. 3, three spectra are presented for $PrBa_2Cu_3O_7$ taken with $E_0=12.7$ meV at temperatures $T=5$, 10, and 30 K. They again show the three low-energy excitations. The magnetic nature of these excitations is verified by the same procedure as described above. The positions of these excitations—1.5, 3.3, and 4.8 meV at 30 and 50 K—are slightly shifted at $T=5$ K due to the magnetic order of the Pr ions. As fits with individual linewidths show the tendency for all inelastic linewidths to be identical, we have finally used just one common width for fitting all three lines at each temperature. All resulting line parameters coincide well using either data taken with $E_0=12.7$ meV or those taken with $E_0=3.14$ meV. The total intensity of these low-energy inelastic excitations is in good agreement with the intensity extracted from the CF parameters given in Ref. 36 (quasitriplet ground state, Γ_5 in the cubic approximation). The inelastic magnetic scattering on Pr in the 1:2:3 cuprates was also investigated as function of Pr concentration. Figure 4 presents low-temperature spectra of $Pr_xY_{1-x}Ba_2Cu_3O_7$ for $x=0.1$, 0.4, and 0.7. They again show three magnetic excitation lines. While the widths of the excitations at 3.3 and 4.8 meV are almost concentration independent, the width of the lowest excitation line at about 1.5 meV decreases rapidly with decreasing Pr concentration.

Figure 5 shows the $PrBa_2Cu_3O_6$ spectra at temperatures 5, 10, and 30 K. The spectrum taken at 30 K can be analyzed in terms of quasielastic scattering with mainly Gaussian character. The Gaussian linewidth is 2.4 meV, and its intensity of 3.55 b is about two-thirds of the total quasielastic magnetic intensity. The weaker Lorentzian contribution has a width of about 1.5 meV. The total quasielastic intensity is again compatible with a quasitriplet ground state (Γ_5 in the cubic approximation). At 10 and 5 K two distinct inelastic excitation lines of Gaussian characters are observed. The positions of the lines are increasing with decreasing temperature. This temperature dependence is shown in Fig. 6 for the lower one of the two excitations. Because of their rather large

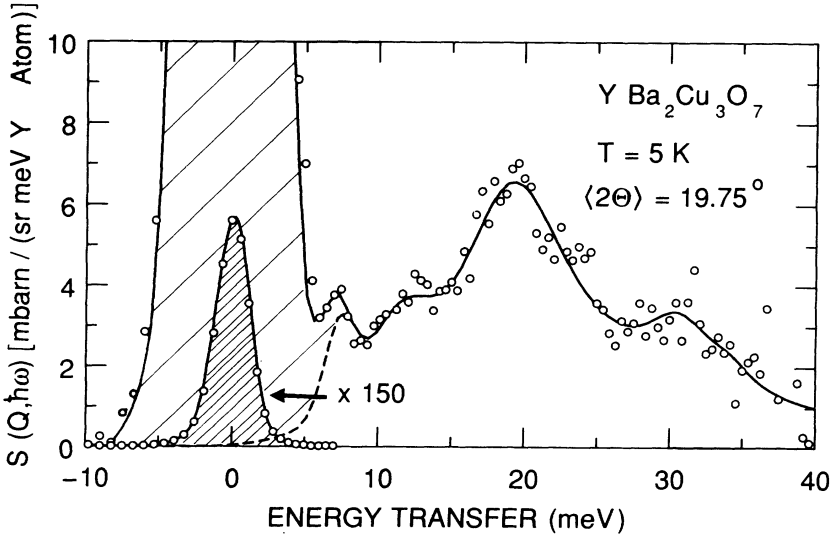

FIG. 2. Background corrected energy spectrum of $YBa_2Cu_3O_7$ obtained with an incident energy $E_0=50.8$ meV and at $T=5$ K on the IN4 spectrometer.

width only an upper limit of about 1 meV can be given at $T=15$ K for the excitation at the lower energy. Both the temperature-dependent position of the inelastic lines for $T \leq 15$ K and the Gaussian character of the quasielastic scattering (see discussion below) at $T=30$ K give strong indications for magnetic ordering of the Pr moments. The ordering of our $PrBa_2Cu_3O_6$ sample is expected to be at 12 ± 2 K from Fig. 6, i.e., slightly above the value observed by other authors.[16]

Specific-heat and bulk susceptibility data on $PrBa_2Cu_3O_6$ samples prepared in our laboratory by the same procedure as described above show a peak between 10 and 11 K,[40] which is compatible with the lower border of the temperature range for T_N given by the inelastic-neutron-scattering results. Only bulk susceptibility data exist for $PrBa_2Cu_3O_7$, which was used for our inelastic-neutron-scattering experiment. They show a weak kink at about 17 K, which is compatible with other data in the literature (e.g., Refs. 13 and 14).

IV. DISCUSSION

For a better understanding of the data presented above we will first discuss briefly our CF analysis published in Ref. 36, which was mainly based on the high-energy transitions observed with $E_0=115$ meV. The CF scheme derived for orthorhombic symmetry consists of nine singlets and allows for seven ground-state excitations, of which two have low energies and five of them have energies larger than 60 meV. Four of these high-energy transitions could be clearly detected, while the fifth has a too small intensity. As the CF scheme of Pr^{4+} has only three doublets allowing for two ground-state excitations, the

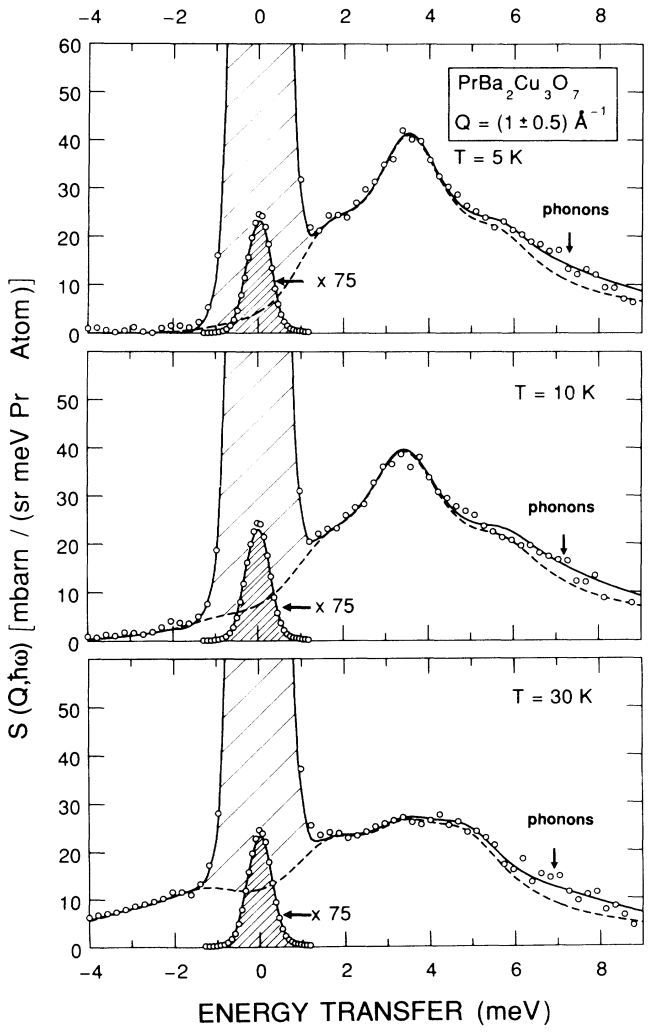

FIG. 3. Background corrected constant-$|\mathbf{Q}|$ spectra of $PrBa_2Cu_3O_7$ obtained with an incident energy $E_0=12.7$ meV on the IN4 spectrometer. The hatched area represents the nuclear elastic peak and the dashed line represents the magnetic scattering. Thus, the nonhatched area between the dashed and solid lines are due to phonon scattering.

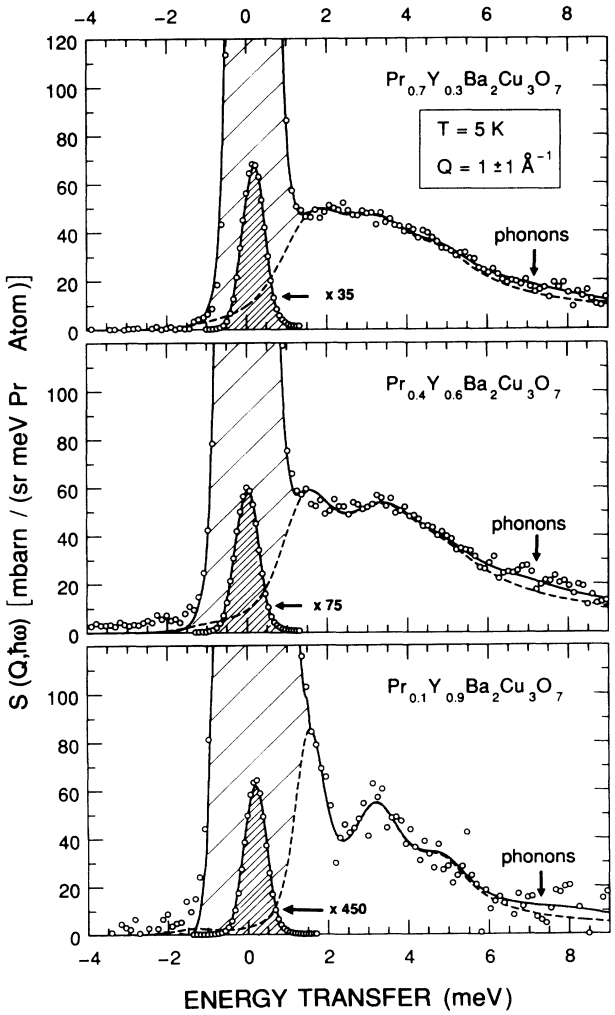

FIG. 4. Background corrected constant-$|\mathbf{Q}|$ spectra of $Pr_xY_{1-x}Ba_2Cu_3O_7$ with $x=0.7$, 0.4, and 0.1 obtained with an incident energy $E_0=12.7$ meV and at $T=5$ K on the IN4 spectrometer. The hatched area represents the nuclear elastic peak and the dashed line represents the magnetic scattering. Thus, the nonhatched area between the dashed and the solid lines are due to phonon scattering.

valence was proved to be close to trivalence ($\nu < 3.1$). This CF scheme is in agreement with the fact that no QE magnetic scattering could be observed. For $PrBa_2Cu_3O_6$ the spectra look quite similar. Probably due to its tetragonal symmetry—a slight orthorhombic splitting cannot be excluded—the three singlets observed at 0–1.5–3.3 meV in the O_7 system are almost degenerated in the O_6 system. A splitting of the quasitriplet ground state into a singlet and a doublet as expected for tetragonal symmetry cannot be ruled out, but an upper limit of such a splitting is about 2 meV. The complete set of CF parameters derived by Nekvasil, based on his superposition model[41] and including J mixing, is given in Ref. 36. Although the main features of the spectra are in agreement with the result of Soderholm *et al.*,[42] there are significant differences in the results of the CF analysis. Soderholm *et al.* interpret peaks at about 45 and 50 meV as CF excitations, while we can clearly relate these peaks in our spectra to the density of phonon states because the intensities increase with increasing $|\mathbf{Q}|$.[36,37]

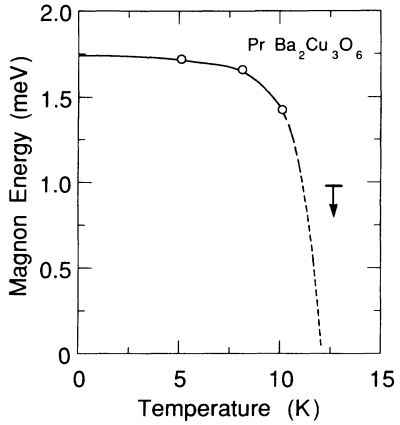

FIG. 6. Magnon peak position as function of temperature for $PrBa_2Cu_3O_6$.

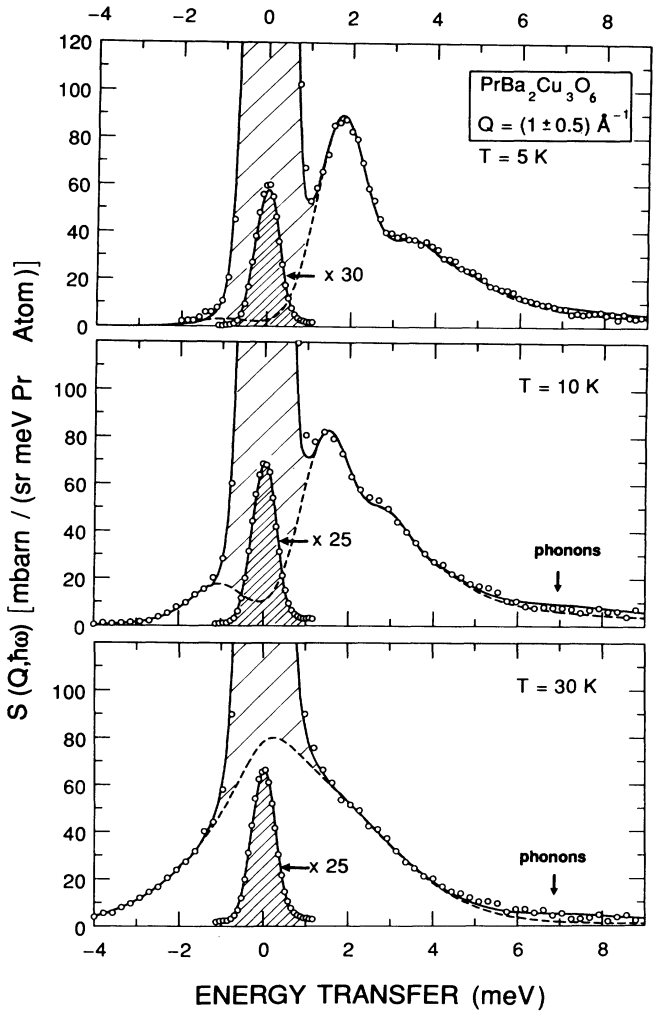

FIG. 5. Background corrected constant-$|\mathbf{Q}|$ spectra of $PrBa_2Cu_3O_6$ obtained with an incident energy $E_0 = 12.7$ meV on the IN4 spectrometer. The hatched area represents the nuclear elastic peak and the dashed line represents the magnetic scattering. Thus, the nonhatched area between the dashed and the solid lines are due to phonon scattering.

If simplifying the orthorhombic CF scheme of $PrBa_2Cu_3O_7$ found by Nekvasil *et al.*[36] to cubic symmetry, it could be roughly approximated by the two CF parameters $W \approx +2.35$ meV and $x \approx 0.76$, using the nomenclature of Lea, Leask, and Wolf.[43] The Γ_5 ground state (triplet), following from this set of parameters, has a rather large magnetic cross section of about 4 b. In fact, in orthorhombic symmetry this Γ_5 state is split into three nonmagnetic singlets and the remaining magnetism is of van Vleck type. Due to the rather low splitting energies of this triplet and due to the broadening of the levels, one may still discuss the magnetic features in terms of a broadened magnetic "quasitriplet" (Γ_5), which has a significant density of states close to $\hbar\omega = 0$ in the dynamic susceptibility $\chi''(\hbar\omega)$.

As discussed above the splitting of the Γ_5 triplet results into two low-energy transitions. This is contrary to the observation of three such lines at $T = 5$ K. First, one may believe that the existence of three instead of the expected two transitions is an artifact due to dispersion of the CF states caused by the internal magnetic field in the antiferromagnetically ordered phase. However, the spectra obtained for different Pr concentrations in $Pr_xY_{1-x}Ba_2Cu_3O_7$ still show these three excitation lines at $T = 5$ K (see Fig. 4), although, especially in the low-concentration sample ($x = 0.1$), magnetic order of the Pr ions can clearly be excluded. Therefore, a mechanism other than magnetic ordering must be responsible for the surplus line at low energies. On the one hand, the decrease of the linewidth of the excitation at 1.5 meV with decreasing Pr concentration seems to be a good indication that this line is a pure CF excitation between a sharp ground state and a just as sharp first excited state. On the other hand, the enhanced widths of the two excitations at 3.3 and 4.8 meV are almost unchanged as function of temperature and of Pr concentration. This indicates that the upper of the three "ground-state" singlets, probably a Γ_1,[36] behaves anomalously. A possible reason may be electron-phonon coupling leading to two

broadened mixed modes (the CF-Γ_1 and acoustic phonon modes). This mechanism was successfully used by Thalmeier and Fulde[44] to explain the observed splitting of the CF excitation in $CeAl_2$.[45] Also, a mechanism causing just an energy dispersion of the third level (Γ_1) may be thinkable.

We will now turn to discuss the consequences of our inelastic-neutron-scattering results on the three possible models for explaining the T_c suppression in $PrBa_2Cu_3O_7$ given in the Introduction. For that we will focus in the following on the energy range around the quasitriplet ground state, i.e., $\hbar\omega \lesssim 8$ meV. In the first subsection we will discuss the anomalous large width of CF levels with respect to a possible explanation for the suppression of T_c in $PrBa_2Cu_3O_7$ and in the second subsection we will focus on the magnetic correlations of Pr moments.

A. Valence of praseodymium and 4*f* hybridization effects

The determination of the Pr valence is a key point. Neumeier *et al.*[29] analyzed the distances of the Cu atoms in the planes of $R\ Ba_2Cu_3O_7$ (including R=Y) as a function of the trivalent ionic diameter. As expected they found an increase of the Cu(2)-Cu(2) distance with ionic diameter for all rare-earth atoms, except for Pr. From this relation linear interpolation between the trivalent and tetravalent ionic radii of Pr yields a Pr valence of 3.3. Also, a lower effective moment extracted from static susceptibility measurements up to 400 K was given as an argument for the intermediate valence of Pr.[46,47] Therefore, Neumeier *et al.* claim a hole-filling mechanism as the origin for the T_c suppression in $PrBa_2Cu_3O_7$. However, other types of experiments raise strong doubts on a valence larger than 3.1 (e.g., Ref. 48).

The temperature dependence of the magnetic relaxation rate is able to give some additional information regarding the stability of the Pr ground state. In Fig. 7, the width of excitation lines in nonsuperconducting $PrBa_2Cu_3O_7$ and, for comparison, that of the excitation at about 3.3 meV in superconducting $HoBa_2Cu_3O_7$ is shown as a function of temperature. We chose Ho as a reference because Ho^{3+} as well as Pr^{3+} are non-Kramers ions, which implies that in orthorhombic symmetry the Hund's rule ground state splits completely into singlets. The CF splitting of Ho in this system was analyzed by Furrer, Brüesch, and Unternährer.[49] The linewidth of the Ho CF excitation at 3.3 meV is about 0.25 meV and shows only a weak temperature dependence between 12 and 100 K, especially when compared with its increase at temperatures $T > 100$ K.[37] Such a nearly constant behavior was also found for the inelastic excitation in $ErBa_2Cu_3O_7$ (Ref. 50) as well as for the quasielastic line in $NdBa_2Cu_3O_{7-\delta}$.[51] Hence, this seems to be a quite common property of 1:2:3 systems regardless of their oxygen concentration.[51] However, the observed change in the slope at about 100 K (Refs. 50 and 51) is an uncommon property compared to intermetallic rare-earth compounds like $R\ Pd_3$, $R\ Al_2$,[52] and many others. For further discussion of this anomaly we refer to Ref. 51. The width of the excitation line in $PrBa_2Cu_3O_7$ is already about 1.1 meV at T=1.5 K and is only slightly increasing to about 1.5 meV at T=100 K, i.e., it is about five times larger than in the Ho system in this range of temperatures.

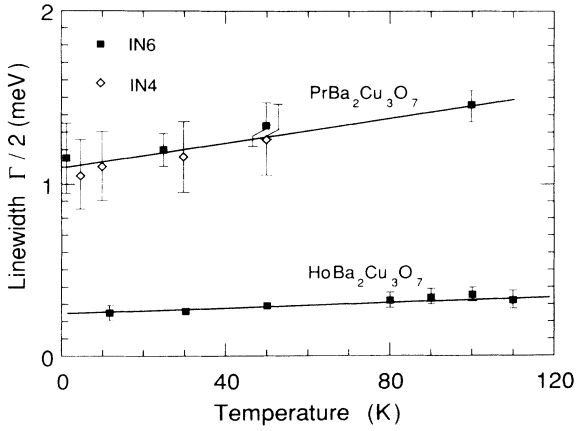

FIG. 7. The widths of the inelastic excitations in $PrBa_2Cu_3O_7$ and of the inelastic line at 3.3 meV in $HoBa_2Cu_3O_7$ as a function of temperature.

Because of a lack of $PrBa_2Cu_3O_6$ data above T=30 K, a detailed analysis of the temperature dependence cannot be given for this system. The magnetic spectrum at T=30 K shows again a broadening, which may smear out a possible CF excitation. The Lorentzian linewidth is rather compatible with that found for $PrBa_2Cu_3O_7$. Qualitatively, our spectra look the same as those taken by Gering and Renker.[53] Their spectra at higher temperatures show a further broadening. The shape of the quasielastic line is expected to change its character from Gaussian to Lorentzian with increasing temperature (compare Refs. 54–59). When the widths of the Lorentzian-shaped component are compared, the broadening effects in both systems, $PrBa_2Cu_3O_6$ and $PrBa_2Cu_3O_7$, are found to be roughly of the same magnitude.

This enhanced width indicates a hybridization of the 4*f* electrons with surroundings electrons. However, a strong intermediate valency of Pr is rather unlikely because the width is still much smaller than in typical intermediate-valence compounds like $CePd_3$, $YbCu_2Si_2$,[32] and many others. Moreover, the relaxation behavior of intermediate-valence Pr is expected to be similar to that of Tm because both mixing valence states are magnetic. Thus, a comparison to strongly intermediate-valence TmSe should be even more relevant. But the width of Pr in the 1:2:3 cuprate does not show a rapid increase with temperature and is therefore with 1.5 meV also much smaller than that of TmSe (7 meV) at T=100 K.[31] This clear difference to intermediate-valence compounds makes a strong intermediate valence of Pr in $PrBa_2Cu_3O_7$ very unlikely.

A further argument against a strong intermediate valence of the Pr ions comes from the total magnetic cross section, which can be obtained by integrating (see Ref. 39) the total magnetic spectrum including the high-energy CF excitations (see Ref. 36). We found a total

magnetic cross section of $\sigma_{mag} \approx 10$ b corresponding to $\mu_{eff} \approx 4.05 \mu_B$. In view of the fact that this observed value is much larger than the effective moment of Pr^{4+} ($2.54 \mu_B$) and even slightly overestimated with respect to the effective moment of Pr^{3+} ($3.58 \mu_B$), we find that not only the observed number of transition lines exclude tetravalence, but also the magnetic moment observed from the magnetic neutron-scattering spectra. (The overestimation of the experimental intensities is only due to the high-energy excitations. These are larger by a factor of about 2 compared to the ones derived from the CF parameters. We argue[36] that the free-ion form factor used in our analysis is no longer valid due to J mixing and therefore causes this discrepancy. The intensity of the low-energy excitations is in rather good agreement with those extracted from the CF parameters.) An effective magnetic moment close to that of Pr^{4+} as extracted from static susceptibility measurements up to 300 K (e.g., Refs. 46 and 47) is rather doubtful because in that temperature range the effective moment is still reduced by the large CF splitting of about 90 meV. Calculations of the static susceptibility using the CF parameters of Ref. 36 still show a curvature up to 1000 K. Just above this temperature the slope of $1/\chi$ versus T is roughly in agreement with the full Pr^{3+} moment.[40] Therefore, only static susceptibility measurements up to 1000 K would result in a more accurate estimate of the effective Pr moment. Unfortunately, such measurements cannot be performed because at such high temperatures the sample will lose its oxygen.

All the above arguments show clearly that a strong intermediate valence of Pr can be excluded in the 1:2:3 cuprates. Nevertheless, a small intermediate valence of $v \lesssim 3.1$ cannot be excluded from our neutron-scattering result as well as from most other experimental methods because all these determinations contain an uncertainty which is particularly large for valences close to an integral value. Based on such a weak intermediate valence, a hole-filling mechanism like that suggested by Neumeier *et al.*[29] is rather unlikely to explain the T_c suppression in $PrBa_2Cu_3O_7$ because such a small amount of additional electrons ($\lesssim 0.1$ per unit cell) will not be sufficient for a complete filling of all holes on the Cu-O_2 planes. In fact, results of the electron-energy-loss spectroscopy by Fink *et al.*,[60] who found evidence against hole filling, support this statement.

Let us now discuss the Pr anomaly in context with Ce and Tb, which do not form single-phase samples with 1:2:3 stoichometry.[61] Very often it is the size of the Pr and Ce ion which is called for the origin of all the observed anomalies in Pr and Ce 1:2:3 cuprates. However, this size argument can be ruled out because it does not hold for Tb, the size of which is just between Gd and Dy, both being good superconductors. A more important property of Ce and Pr at the beginning of the lanthanides and Tb at the beginning of the second half of the lanthanides seems to be the common tendency to donate electrons. As already discussed in the Introduction, this agrees nicely with the finding that oxygen acts as an electron acceptor and thus a comparison to the rare-earth oxides may be useful. While the standard composition of rare-earth oxides is usually R_2O_3 with a rare-earth valence of 3, the above three elements form an oxide with different standard compositions: Ce(IV)O_2, Pr_6(III,IV)O_{11}, and Tb_4(III,IV)O_7.

In Pr_6O_{11} two different Pr sites exist: one occupied by a Pr^{3+} and the other by an intermediate-valence Pr ion. This yields an average valence of about 3.17 as found by L_{III}-edge measurements.[62] The inelastic magnetic neutron-scattering response[63] of Pr_6O_{11} consists of very narrow CF excitations and a broadened, almost quasielastic, magnetic scattering. The narrow CF lines are related to Pr^{3+}, while the broad quasielastic line supports the idea that the second crystallographic site is occupied by an intermediate-valence Pr ion. There is, however, only a single type of rare-earth site in the rare-earth 1:2:3 cuprates. This implies an enhanced interaction of the Pr $4f$ electrons with the surroundings. Because of the analogy to the oxides it seems that a direct interaction with the copper electrons is rather unlikely, but that an enhanced hybridization of the $4f$ electrons with the oxygen electrons is the origin for most of the anomalies observed in $PrBa_2Cu_3O_{7-\delta}$.

Thus, the hybridization of $4f$ electrons with electrons of the CuO_2 plane may be thought to destroy directly the coherent superconducting state. This model was successfully applied by Müller-Hartmann and Zittartz[30] to explain the suppression of T_c in the Kondo system $La_xCe_{1-x}Al_2$ with its negative exchange constant J_{ex}. There the concentration-dependent suppression of T_c differs from classical Abrikosov-Gor'kov (AG) behavior yielding a stronger suppression with increasing Ce concentration than expected.[64] However, Peng *et al.*[65] were able to fit the T_c suppression of $Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}$ ($0 < x < 0.5$) in terms of the theory of Abrikosov and Gor'kov[4] with an exchange constant $N(0)J_{ex}^2 = 7.08 \times 10^{-4}$ eV atom states/spin direction. Therefore, the application of the above model seems to fail in the case of $PrBa_2Cu_3O_7$.

Comparing $PrBa_2Cu_3O_{7-\delta}$ with superconducting $Pr_xLa_{1.85-x}Sr_{0.15}CuO_4$ and with the n-type doped Pr superconductor $Pr_{1.84}Ce_{0.16}CuO_4$, a remarkable difference in the CF level scheme is observed. While the Pr 1:2:3 cuprate has a quasitriplet ground state (see above), which implies strong intensity in the dynamic magnetic response close to $\hbar\omega = 0$ meV, the CF ground state in the Pr 2:1:4 cuprates is a singlet and the first excited level has an energy of $\Delta \geq 7$ meV. As the width of the transition line is much smaller than this excitation energy, there is no intensity close to $\hbar\omega = 0$ in the dynamic susceptibility χ''. This explains why the Pr moments in the 2:1:4 cuprates do not order at all or at very low temperatures. The clearly nonmagnetic ground state of Pr in the 2:1:4 system is either due to a larger splitting of the cubic Γ_5 state than observed in the Pr 1:2:3 cuprates (see, e.g., Refs. 66–68) or due to a reversed CF scheme with a nonmagnetic Γ_4 ground state in cubic approximation. This will be discussed in more details in Ref. 69.

The different CF ground states are probably related to the different coordination of surrounding oxygen atoms. On the one hand, the nonmagnetic ground state of the Pr

2:1:4 cuprates allows for superconductivity. On the other hand, the strong magnetic quasitriplet ground state of the Pr 1:2:3 cuprate allows magnetic order of the Pr moments and may be responsible for the suppression of superconductivity. Therefore, we will now turn to consider the question whether the unexpected high ordering temperature of Pr in $PrBa_2Cu_3O_{7-\delta}$ can be related to the suppression of superconductivity.

B. Magnetic correlations

In $PrBa_2Cu_3O_6$ the appearance of additional magnon lines (compare Figs. 5 and 6) gives clear evidence for magnetic ordering. From a different point of view, the splitting of the quasitriplet ground state into three singlets is due to the internal magnetic field, and the transition between these singlets observed in the low-temperature spectra may be called magnon excitations. Such a proof cannot be given for $PrBa_2Cu_3O_7$ due to small differences in crystal symmetry. In tetragonal $PrBa_2Cu_3O_6$ the CF ground state seems to be threefold degenerated with respect to the enhanced width of these levels (compare spectrum at $T=30$ K in Fig. 5). This quasitriplet ground state is split for $T<T_N$ by an internal magnetic field giving rise to the observation of magnon lines. In contrast to that, our $PrBa_2Cu_3O_7$ sample is clearly orthorhombic and its orthorhombicity parameter (see Sec. II) fits into the systematics of rare earths. This leads to a splitting of the quasitriplet into a level sequence 0–1.5–3.3 meV. As the crystal field dominates the internal magnetic field, the internal magnetic field causes only a slight shift of the inelastic CF excitations. The magnetic ordering is also reflected by a variation of the line position as function of $|\mathbf{Q}|$ for both oxygen concentrations. But our polycrystalline data do not allow for a detailed dispersion analysis.

The $|\mathbf{Q}|$ dependence of the inelastic intensity is another clear indication for magnetic order in both $PrBa_2Cu_3O_6$ and $PrBa_2Cu_3O_7$. For all three low-energy lines the intensities show qualitatively the same $|\mathbf{Q}|$ dependence. Therefore, in Fig. 8 the sum of these intensities is presented as function of $|\mathbf{Q}|$ for both oxygen concentrations. No significant differences could be detected as function of oxygen concentration. The zone boundary of the first Brillouin zone (BZ) in the c and in the a or b directions are indicated by arrows. The minimum at about 2.1 Å reflects the zone-center behavior of the second BZ (ab plane), i.e., it agrees well with the decrease for $|\mathbf{Q}|\rightarrow 0$ (zone center of the first BZ). Such a $|\mathbf{Q}|$ dependence is typical for spatial magnetic correlations like magnons. It does not occur for pure inelastic crystal-field excitations such as the 3.3-meV excitation line in $HoBa_2Cu_3O_7$, which does not show any distinct $|\mathbf{Q}|$ dependence[37] besides the mandatory magnetic form factor. However, it is impossible to derive an ordering temperature from the $|\mathbf{Q}|$ dependence alone, because short-range correlations survive above the ordering temperature with a $|\mathbf{Q}|$-dependent intensity similar to that below T_N. Such a behavior is well known from other ordering f systems, e.g., URu_2Si_2.[70] In $PrBa_2Cu_3O_6$ these spatial correlations above the ordering temperature are also represented by the Gaussian character of the quasielastic line at $T=30$ K. This is again a quite common feature for f systems, e.g., Yb_3Pd_4,[54] $YbAuCu_4$,[55] $CeAu_2Si_2$,[56] $CeCu_2Ge_2$,[57] $CeAg_2Si_2$,[58] and U_2Zn_{17},[59] to list some of the many examples.

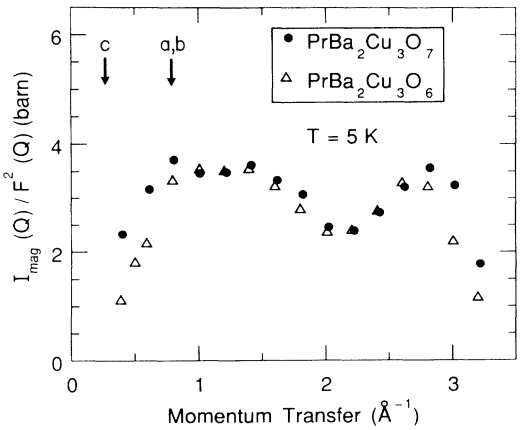

FIG. 8. The intensity of the inelastic excitations at about 3.3 meV in $PrBa_2Cu_3O_7$ (solid circles) and $PrBa_2Cu_3O_6$ (open triangles) as function of momentum transfer Q.

As mentioned above the ordering temperature of the Pr 1:2:3 systems is much higher than expected by scaling from the other rare-earth 1:2:3 cuprates. On the one hand, strong hybridization due to intermediate valence may coexist with magnetic order if both valence states are magnetic, as observed, for instance, in TmSe.[71,31] On the other hand, if one valence state is nonmagnetic, as in Ce or Yb compounds, the strong intermediate valence suppresses magnetic order. However, even for Ce and Yb, the onset of hybridization is able to cause an increase in the ordering temperature compared with almost stable Ce or Yb systems.[72] One example for the latter case is $CeRh_2Si_2$, which compared to other members of the CeM_2Si_2 series has a higher ordering temperature, but also shows larger magnetic relaxation rates.[56] Thus, the observed enhanced magnetic relaxation behavior in the Pr 1:2:3 systems may also be the origin for the unexpected high magnetic ordering temperatures.

In fact, without any hybridization the three singlets of the quasitriplet would be well separated resulting in a clearly nonmagnetic Pr ground state, i.e., there would be no magnetic contribution at about $\hbar\omega=0$ (static magnetic moment) and therefore no magnetic order at all. In other words, the width of the inelastic excitation lines determines the magnitude of the magnetic contribution at $\hbar\omega=0$, which finally allows for magnetic order in $PrBa_2Cu_3O_7$ and determines the ordered magnetic moment.

The above arguments show that the magnetism of the Pr ions may play an important role in suppressing superconductivity in $PrBa_2Cu_3O_7$. Of course, as the other rare earths with even a larger magnetic moment than Pr do not suppress superconductivity in the 1:2:3 cuprates, a pair-breaking mechanism via exchange scattering in the sense of Abrikosov and Gor'kov must be triggered by a special property of the Pr ion. This may be the tendency

of Pr to donate $4f$ electrons resulting in a hybridization of the $4f$ electrons with electrons of the CuO_2 planes. As the Pr ground state in the 2:1:4 cuprates is clearly nonmagnetic, such a hybridization cannot be proved for these systems by measuring the width of low-energy excitations (no magnetic scattering at low energies up to 7 meV).[69] Compared to the other rare-earth 1:2:3 cuprates, the $4f$ hybridization may cause quite different magnetic spatial correlations between the Pr moments, which are still strong enough at about $T=100$ K to suppress superconductivity. Thus, a modified AG mechanism could be successful in explaining the suppression of superconductivity in $Pr_xY_{1-x}Ba_2Cu_3O_7$.

V. CONCLUSION

We have shown that the magnetic relaxation of Pr in the 1:2:3 systems is anomalously strong compared with that of the other rare earths. Comparisons to rare-earth oxides suggest an enhanced $4f$ hybridization with the oxygen electrons. Nevertheless, the spectra favor a valence close to trivalence, i.e., the valence must be *less than 3.1*. That excludes the hole-filling mechanism as an origin for the suppression of superconductivity in $PrBa_2Cu_3O_7$, especially if keeping in mind the electron-energy-loss spectroscopy data by Fink *et al.*[60] The enhanced hybridization yields both the unexpectedly high magnetic ordering temperatures as well as the suppression of superconductivity. However, we cannot determine whether the $4f$ hybridization will directly destroy the superconductivity or whether anomalous magnetic correlations between the Pr moments, caused by this $4f$ hybridization, will be the origin for the suppression of superconductivity. Both a simple Abrikosov and Gor'kov[4] mechanism and the Kondo mechanism in the sense of Müller-Hartmann and Zittartz[30] can be excluded.

The low-temperature and low-energy magnetic response is not yet satisfactorily understood. There are three causes for inelastic excitations at low temperatures: CF excitations, excitations of magnon character, and a Kondo peak (see, e.g., Ref. 73) due to $4f$ hybridization effects. It will be very hard, if not impossible, to separate these three origins of an inelastic magnetic response at low temperatures. Moreover, it seems that phonon-electron interactions will give rise to further complications.

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