

Effect of praseodymium on the lattice dynamics and electronic structure of the Cu(1)-O(4) chain in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$

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$Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with $x=0.30$ and 0.45 has been studied by emission Mössbauer spectroscopy using ^{57}Co dopant. Cobalt substitutes for copper predominantly at the Cu(1) site, and one can extract information on the local electronic and vibrational state of the Cu(1)-O(4) chain from the Mössbauer spectra. The major coordination environments observed for the ^{57}Co dopant in $YBa_2Cu_3O_{7-\delta}$ are fourfold square planar (species A), fivefold trigonal bipyramidal (species B), and fivefold square pyramidal (species C). We have found that the reversible interconversion between species B and C, which was found earlier in $YBa_2Cu_3O_{7-\delta}$ and $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}$, is still observed in $Y_{0.7}Pr_{0.3}Ba_2Cu_3O_{7-\delta}$ with lower intensity, and it further diminishes in $Y_{0.55}Pr_{0.45}Ba_2Cu_3O_{7-\delta}$. This tendency shows that the out of the chain vibration of the O(4) oxygens is gradually damped as one approaches the critical Pr content where superconductivity is destroyed. This supports a phonon-assisted mechanism for high- T_c superconductivity in 1-2-3 compounds with significant contribution from the chains. We attribute the damping of the chain oxygen vibrations to the increase of the Cu(1)-Cu(1) distance along the chain with increasing Pr content. We have also concluded from Mössbauer isomer shifts that up to the critical Pr content where superconductivity disappears, the electronic density at the Cu(1) site seems to remain constant. This indicates that, in this region, any hybridization which takes place between Pr and sheet oxygens has no substantial influence on the chains. [S0163-1829(99)00417-8]

I. INTRODUCTION

The search for the mechanism of high-temperature superconductivity in 1-2-3 compounds initiated the investigation of the “anomalously” nonsuperconducting material

$PrBa_2Cu_3O_{7-\delta}$ and other, Pr-doped members of the 1-2-3 family. There is hope that once we find out why Pr kills superconductivity, it may shed light on the real mechanism of this phenomenon.

As $PrBa_2Cu_3O_{7-\delta}$ is perfectly isomorphous with the

‘‘classic’’ 90 K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, it is particularly interesting to study the mixed compound $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The topic attracted the attention of many research groups and the works have been reviewed.¹⁻³ It is observed that when Y is gradually substituted by Pr in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductivity vanishes at about 55% substitution level. The pure $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is not even metallic unlike other members of the 1-2-3 compounds.

For the mechanism of how Pr kills superconductivity, there have been proposed a few models, and the differences between them are not always well defined. The key problem is the nature of the interaction between Pr and the Cu(2)-O sheets where superconducting charge carriers are supposedly located. Pr is markedly different from most of its lanthanide relatives in its readiness to form also R^{4+} ions in addition to R^{3+} states. If the compound is considered strongly ionic, which is certainly not the case, Pr^{3+} may simply donate electrons to the sheets and reduce the concentration of charge carriers (holes) to a level where superconductivity dies out (*hole filling*). It is also plausible that due to high covalency, Pr 4*f* orbitals combine with Cu(2)-O electronic levels (*hybridization*), and this results in mobile hole depletion from the sheets by forcing the holes into localized states (*hole localization*). In the case of a much weaker interaction between Pr and its environment, the magnetic coupling between the Pr^{3+} ions and the sheets can still be responsible for the loss of superconducting charge carriers by *magnetic pair breaking*. Recent results seem to favor the hybridization mechanism for which also quantitative models have been proposed. Fehrenbacher and Rice⁴ (FR) suggested mixed valence $\text{Pr}^{\text{III}}/\text{Pr}^{\text{IV}}$ state. The mixed valence state of Pr is supported experimentally mostly by neutron-diffraction studies.⁵ In the FR model, mixed valency occurs by hole depletion from the superconducting $\text{Cu}3d\text{O}2p_\sigma$ band to an $\text{Pr}4f\text{O}2p$ band. They assumed rather localized states. Liechtenstein and Mazin further developed this model⁶ by assuming highly dispersive $\text{O}2p$ states contributing to the above-mentioned hole depleting band. An important feature of these models is that the Cu(1)-O chains are rather irrelevant from the point of view of Y to Pr substitution. One should also note that these models are valid for low and moderate Pr substitution level. Merz *et al.*⁷ performed near-edge X-ray-absorption fine structure experiments on $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ up to $x=0.8$ and could rule out hole filling and also charge transfer between the sheets and the chains. Their results are consistent with $\text{Pr}4f\text{O}2p_\pi$ hybridization.

In contrast, due to some still unanswered questions, there is an increasing number of opinions considering the Cu(1)-O chains in 1-2-3 compounds as active participants in the mechanism of superconductivity. Blackstead *et al.* reported that even $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ can be superconducting on the microscopic scale,^{8,9} and a bulk superconductor can be fabricated by a sophisticated synthesis (recently confirmed by Zou *et al.*¹⁰). Their model which explains this and several major experimental findings about high- T_c superconductors assumes that superconductivity in 1-2-3 compounds is rooted in the Cu(1)-O chains and not in the sheets. They attribute the nonsuperconducting behavior of conventionally prepared $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ to substitution of Pr for Ba.¹¹ In this case, magnetic Pr^{3+} ions break superconducting pairs in the chains, and any hybridization in the sheets is irrelevant.¹²

Other reports also claim that, for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, Cu(1)-O chains may also contribute to superconductivity.¹³⁻¹⁵

Even if the role of the chains is not exclusive in this respect, it probably is not as passive as suggested by the charge reservoir scenario. Anelastic relaxation measurements made by Cannelli *et al.*¹⁶ indicated several processes taking place in $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ at different temperatures (O jumps, O ordering, phase transformations, etc.), which were found to be correlated with chain dynamics. From this point of view, an important feature of the Cu(1)-O chains is their zig-zag structure confirmed by neutron^{17,18} and x-ray¹⁹-diffraction results. This was the starting point for a model to interpret our earlier Mössbauer results on $\text{YBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ where we invoke a dynamic zig-zag chain.^{20,21} A similar displacement of chain oxygens was observed in the structurally closely related $\text{YBa}_2\text{Cu}_4\text{O}_8$ by Egami *et al.*²² using the pulsed neutron-scattering technique. The authors interpreted their finding as a sign of charge inhomogeneity in the planes due to charge-density waves (CDW’s), polarons, and bipolarons being possible driving forces for superconductivity. A scanning-tunneling microscopic study of the Cu(1)-O layers in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by Edwards *et al.*²³ gave real space evidence for some kind of collective phenomenon, maybe a CDW state, in which chain electrons participate. Other techniques like penetration depth measurements^{24,25} and heat conductivity measurements²⁶ were also supportive to the contribution of the chains to superconductivity.

In case of the significant role of the chains in the mechanism of high- T_c superconductivity, the presence of Pr at the rare-earth site should have some effect on the structure of the Cu(1)-O chains, and it may be observed by appropriate techniques which can probe the chains.

The emission version of ^{57}Fe Mössbauer spectroscopy is suitable to probe the Cu(1)-O chain after doping the material with ^{57}Co in an amount smaller than 50 ppm. The low doping level ensures minimal perturbation of the system, and ^{57}Co prefers to substitute the Cu(1) sites. The ^{57}Co impurity, as being chemically different from Cu, modifies its local environment to some extent like having generally a higher oxygen coordination number than that for Cu(1). Due to varying number of coordinated oxygens, one may consider it as multiple probing, i.e., instead of one probe *atom*, one has a series of probe *species* [$^{57}\text{Co}_m\text{O}_n$] (or [$^{57}\text{Fe}_m\text{O}_n$]) after the electron capture decay of ^{57}Co). Here usually $m=1$ because clusterization is not likely at such a low doping level, and $n=4, 5$, or 6 , as expected on the basis of chemical considerations. Species with different oxygen coordination numbers (different n) give different information about the material. In case of $\text{YBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, 4- and 5-coordinate species could be observed in the fully oxygenated material.²⁰ The four-coordinate one (species A, with isomer shift, $\delta=0.02$ mm/s and quadrupole splitting, $\Delta=1.97$ mm/s) proved to be stable in the whole oxygen stoichiometry range from 7 to 6, and its isomer shift sensitively monitored the decreasing oxygen content and the metal-to-insulator transition at oxygen stoichiometry of about 6.4.²⁷

The major five-coordinate species were not suitable for such a monitoring study as they ceased to exist in the samples via transforming into the four-coordinate one upon mild deoxygenation treatment. However, in the fully oxygenated material they provided a very useful tool to indicate the

dynamic motion of the Cu(1)-O chains. Reversible interconversion of two doublets in the Mössbauer spectra with variation in temperature could be observed. According to the model proposed by us, the two doublets represented five-coordinate species with trigonal-bipyramidal (species *B*, $\delta = 0.01$ mm/s, $\Delta = 0.99$ mm/s), and square-pyramidal (species *C*, $\delta = -0.12$ mm/s, $\Delta = 1.49$ mm/s) structures; the latter was more stable at higher temperatures. The interconversion took place in a relatively wide temperature range centered at about 280–290 K.²¹ The presence of five-coordinate species in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ with $M = \text{Co}$ and Fe up to $x = 0.1$ was observed also recently by Shi *et al.*²⁸ and a significant role in increasing T_c was attributed to these species as being responsible for creating specific local structures.

Considerable interconversion (we will refer to it as *B* to *C* interconversion throughout this paper) was also found recently in ^{57}Co -doped $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Ref. 29) with smaller transformation enthalpy. A large increase of the root-mean-square displacement of the Mössbauer dopant atom at the Cu(1) site was also observed in the same temperature range where the interconversion occurred.

In an earlier study, the *B* to *C* interconversion was absent in $\text{PrBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$,^{30,31} however, the Mössbauer parameters differed significantly from those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, which complicated the interpretation.

In the present study we have extended our interest to the compositions $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ in order to see the trend in *B* to *C* interconversion, and whether the Mössbauer parameters show any change in the still superconducting material, which would indicate change in the electron density at the Cu(1)-O(4) chain with possible relevance to the deleterious effect of Pr to superconductivity.

II. EXPERIMENT

The $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ samples were prepared by solid-state synthesis from stoichiometric amounts of starting materials $\text{Ba}(\text{NO}_3)_2$, $\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$, Pr_6O_{11} , and $\text{Cu}(\text{OH})_2$ of at least 99.99% purity. Nitrates were used to avoid the formation of oxycarbonates during synthesis. Several cycles of thermal treatments in oxygen like $930^\circ\text{C}/24\text{h} + 600^\circ\text{C}/3\text{h} + 450^\circ\text{C}/10\text{h}$ were performed in order to obtain a single phase 1-2-3 compound. The quality of the material was checked by x-ray measurements, and no impurity phases could be detected.

The as-synthesized pellets were doped with ~ 100 MBq of carrier-free $^{57}\text{CoCl}_2$. To save the material from chemical degradation, the originally acidic (0.1 M HCl) solution was allowed to evaporate completely and the radioactive residue was transferred onto the pellets by using absolute ethanol. The diffusion of ^{57}Co into the bulk was carried out by a treatment at 900°C for 3–8 h in flowing oxygen followed by further oxygenation in the 450 – 550°C range for 4–24 h.

$\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ behaved somewhat differently from $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ from the point of view of the doping process. When the sample was subjected to a diffusion thermal treatment in the 900 – 950°C temperature range in oxygen for a long time (6–8 h), the resultant spectra were badly resolved due to broadened lines and a substantially larger

fraction of doublet *D* appeared. We attributed this behavior to a possible association of the dopant atoms with lattice defects and/or migration of the dopant to another lattice site (out of the chain). A possible exchange between Pr and Ba sites may also be taken into account. This “badly doped” stage is not advantageous for Mössbauer probing and could be eliminated by a longer (23 h) heating at 400°C in oxygen. This behavior was even more pronounced for $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

The onsets of superconducting transitions were monitored using the magnetically modulated microwave absorption technique. The experiments were carried out using a modified Varian *E-12* EPR spectrometer with an associated CTI Cryogenics closed-cycle refrigerator. The samples were mounted at the end of a sapphire rod and positioned at the center of a rectangular TE_{102} resonant microwave (~ 9.3 GHz) cavity. The magnetically modulated absorption was then studied as a function of temperature. The transition was marked by an appearance of the modulated microwave absorption which is not present in the normal state.³² The onset temperatures were found to be 65 and 42 K for the $x = 0.30$ and $x = 0.45$ samples, respectively. These values are 2–3 K higher than those measured by Peng *et al.*³³ by magnetic susceptibility measurements.

The Mössbauer measurements were performed between 80 and 430 K in a through-flow-type liquid-nitrogen cryostat (Leybold). The Mössbauer spectrometer was used in constant acceleration mode, and a PFC ($\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$) standard absorber with 0.50 mg/cm² ^{57}Fe was used. All isomer shifts throughout this paper are given relative to α iron at room temperature with the sign convention used in the transmission Mössbauer technique.

In the case of our earlier studies on $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and especially on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the pellets used for the emission Mössbauer measurements showed texture, i.e., the crystals of the materials had a preferred orientation of their *c* axis perpendicular to the surface of the pellet, and it caused asymmetry of the Mössbauer quadrupole doublets. So we have performed some reference measurement first. Mössbauer runs were taken at the magic angle between the normal vector of the plane of the pellets and the direction of the γ rays, where the asymmetry of the doublets vanishes,³⁴ and the resultant spectra did not show any difference within statistical error as compared to the normal ones, in both compounds. Thus, all Mössbauer spectra were recorded at normal geometry (pellet perpendicular to the γ radiation, which is preferable for a higher counting rate) and evaluated by using symmetrical Lorentzian doublets.

III. RESULTS AND DISCUSSION

Some examples of the Mössbauer spectra of $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ as a function of temperature can be seen in Fig. 1. The spectral envelopes are reminiscent of those of $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, however, the change of the envelopes from 80 to about 400 K is less pronounced. Computer fits of the spectra revealed the expected four doublets, *A*, *B*, *C*, and *D*. *A*, *B*, and *C* represent distorted square planar (maybe closer to tetrahedral), distorted trigonal bipyramidal, and distorted square pyramidal oxygen coordinations of the ^{57}Co (and inherently of the nu-

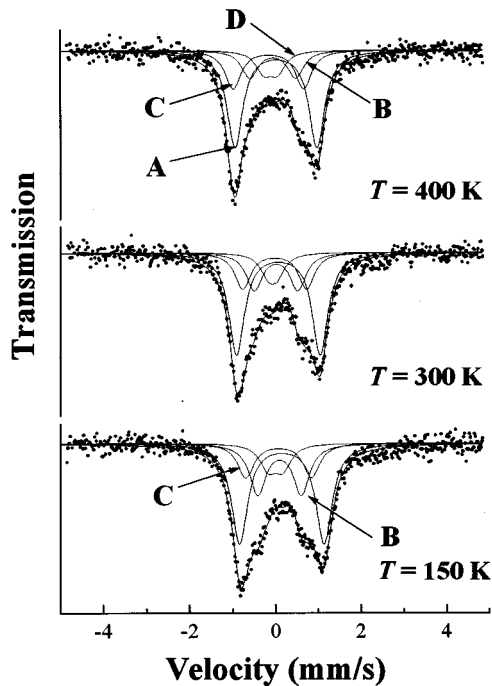


FIG. 1. Evaluated emission Mössbauer spectra of ^{57}Co -doped $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ at some selected temperatures. The velocity scale refers to α -Fe at room temperature and corresponds to the sign convention used in transmission geometry.

cleogenic ^{57}Fe) dopant, respectively.

The analysis of the spectra revealed B to C interconversion, however, a smaller fraction of B converted to C as compared to the case of $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (Table I). The plot of the relative spectral contributions of the four species as a function of temperature is shown in Fig. 2. We have calculated the thermodynamical parameters of the B to C equilibrium with the usual $\ln([C]/[B])$ vs $1/T$ plot,^{20,21} and found $\Delta H = 7.3$ kJ/mol and $\Delta S = 29$ J/mol K for the formation of C . These values are smaller than those found for $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

We have checked the temperature variation of the total spectral area of $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, and a behavior similar to that of $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ was found. The total area of the Mössbauer spectra is determined by the mean amplitude of the vibration of the Mössbauer probe; the larger the amplitude the smaller is the observed area. We observe an anomalous change in the decrease of the area around 200–220 °C (Fig. 3) which coincides with the onset

TABLE I. The extent of the B to C interconversion in the 80–400 K temperature range in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ at various Pr contents, and the calculated thermodynamical parameters. A = spectral area, ΔH = transformation enthalpy, ΔS = transformation entropy.

Pr content (x)	$\Delta A(B)/A(B+C)$	ΔH (kJ/mol)	ΔS (J/mol K)
0	0.63	31(4)	111(18)
0.10	0.56	12(1)	50(8)
0.30	0.32	7.3(5)	29(6)
0.45	0.17	2.6(8)	6(3)

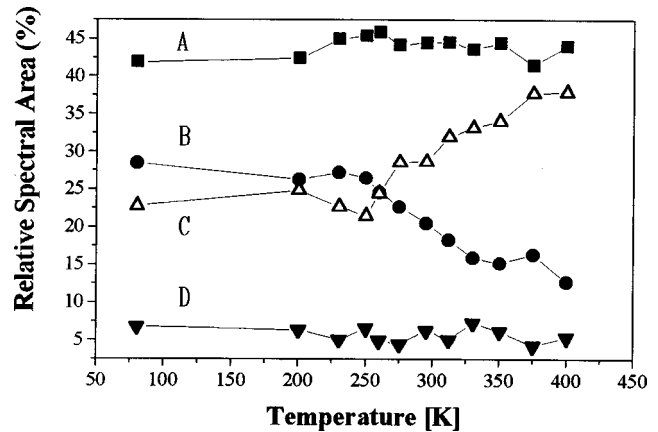


FIG. 2. Plot of the relative spectral area of the four species as a function of temperature in $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The B to C transformation is weaker than that observed earlier in $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

of the B to C interconversion. A detailed comparison of the plot with that of the $\text{Y}_{0.9}\text{Pr}_{0.1}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ compound²⁹ is not possible because of the paucity of measurements.

As far as the Mössbauer parameters are concerned, species A and C do not show any remarkable change as compared to the previous samples containing less Pr. The isomer shift of species B , however, seems to be changing (decreasing), and the same can be said about species D where this is a tendency already from zero Pr content.

As was mentioned before, the $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ sample proved to be more problematic from the point of view of the optimal doping process (i.e., optimal thermal history) as compared to $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$. Even after prolonged and repeated heat treatments at 900 °C and then at 400 °C, both in oxygen, the lines in the Mössbauer spectra were broadened, indicating some distributions in the local environments of the Mössbauer dopant. Two efforts were made to bring the two materials $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ and $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, to the same state by treating them simultaneously for the same time in the same furnace. The first trial used a maximum temperature of 600 °C, which allows the diffusion of oxygen in the

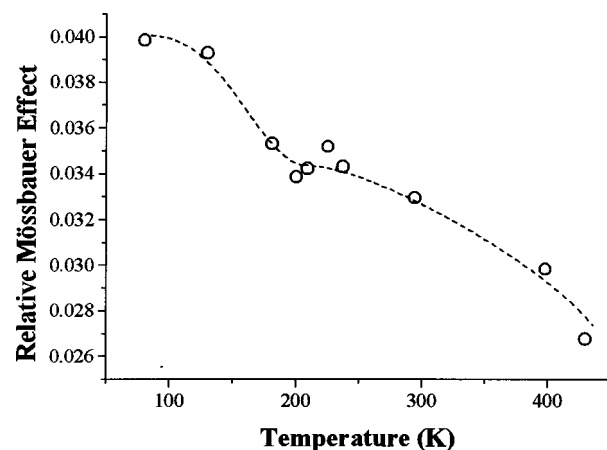


FIG. 3. Plot of the total spectral area vs temperature for ^{57}Co -doped $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The dashed line is only a guide to the eye.

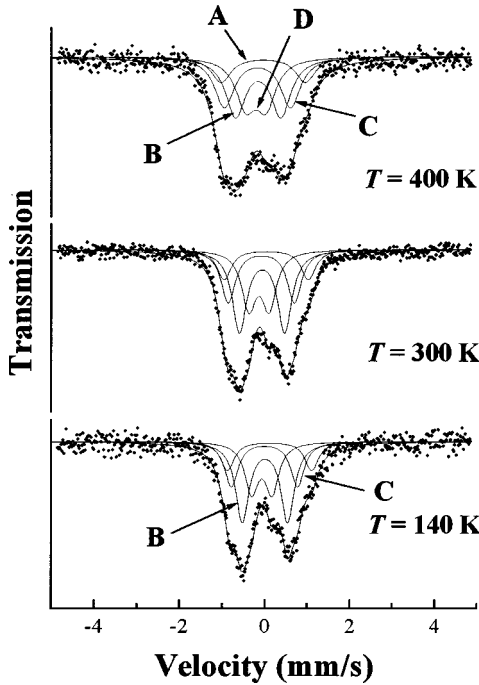


FIG. 4. Evaluated emission Mössbauer spectra of ^{57}Co -doped $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ at some selected temperatures. The velocity scale refers to α -Fe at room temperature and corresponds to the sign convention used in transmission geometry.

lattice and did not have any significant effect. Only a 900 °C treatment, where the cobalt dopant can also migrate, altered the Mössbauer spectrum of $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$ appreciably, but it did not become identical with that of $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, indicating the effect of increased Pr content.

Evaluation of the spectra (Fig. 4) revealed the well known set of four species, *A*, *B*, *C*, and *D* with usual parameters for species *A* and *C*, and confirmed the effect of Pr on the isomer shift of *B* (Table II). Species *D* did not change convincingly.

B to *C* interconversion was considerably reduced and was limited to only 17% of the spectral area of doublets *B*+*C* (Fig. 5). The thermodynamical parameters of the *B* to *C* equilibrium were found to be $\Delta H = 2.6$ kJ/mol and $\Delta S = 5.6$ J/mol K for the formation of *C*. No anomaly was found on the total area vs temperature curve on the basis of six measurements in the 80 to 373 K range (Fig. 6). Surprisingly, the abundance of species *D* increased considerably.

As the most important conclusions may be drawn from a comparison of the present data with those obtained on other

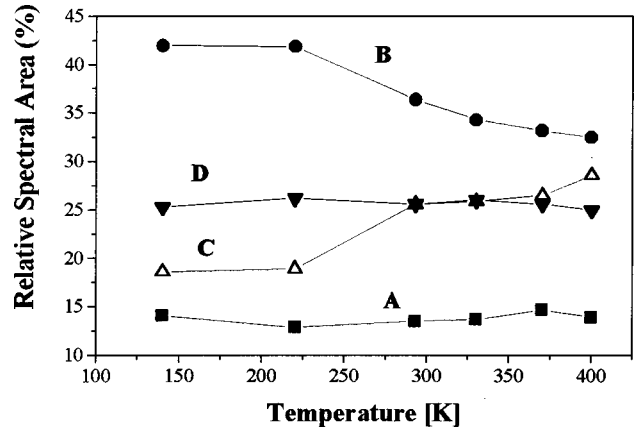


FIG. 5. Plot of the relative spectral area of the four species as a function of temperature in $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The *B* to *C* transformation is weaker than that observed in $\text{Y}_{0.7}\text{Pr}_{0.3}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$.

compositions (i.e., different Pr contents), we have revisited our earlier Mössbauer emission results on $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{1-\delta}$ with $x = 0$ (Refs. 20, 21) and $x = 0.1$.²⁹ There are two aspects of the results which are worthy of discussion: the fate of the *B* to *C* interconversion and the change of the Mössbauer parameters, as a function of the Pr content.

Table I compiles data relevant to the *B* to *C* interconversion for the four different compositions. One can see that with the increase of the Pr content, a clear tendency of the killing of *B* to *C* interconversion is revealed. The fraction of *B* (or *C*) which participates in the interconversion is diminished first, and it seems to fade away completely just around the Pr content critical to superconductivity ($x = 0.55$). The same can be stated on the thermodynamical parameters of the interconversion. It appears that the energetical difference between species *B* and *C* somehow decreases with increasing Pr content, and this may reflect that their structures gradually get closer to each other. The observed anomalies on the total spectral area vs temperature curves are also fading away as the Pr content grows from $x = 0.10$ to $x = 0.30$ to $x = 0.45$. [For $\text{YBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, this effect was not searched for.] To rationalize these findings and their implications on the possible mechanism of high- T_c superconductivity, let us take a closer look at our model for the assignment of species *A*, *B*, and *C*.

We have assigned species *B* to a distorted trigonal bipyramidal arrangement of oxygens around ^{57}Co at the Cu(1) site, including two O(4), two O(1) and one O(5) atoms (see

TABLE II. Room-temperature Mössbauer isomer shifts δ (given relative to α iron) and quadrupole splittings Δ of the doublets representing the four species found in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$. The typical error of the listed values is ~ 0.02 mm/s for species *A*, *B*, and *C*, and about 2 to 5 times as much for the minor species *D*.

Pr content (<i>x</i>)	$\delta(A)$ mm/s	$\Delta(A)$ mm/s	$\delta(B)$ mm/s	$\Delta(B)$ mm/s	$\delta(C)$ mm/s	$\Delta(C)$ mm/s	$\delta(D)$ mm/s	$\Delta(D)$ mm/s
0	0.03	2.00	0.05	0.98	-0.09	1.54	0.18	0.59
0.10	0.02	1.97	0.01	1.00	-0.10	1.46	-0.18	0.35
0.30	0.03	1.95	-0.02	1.02	-0.10	1.48	-0.20	0.32
0.45	-0.01	1.98	-0.10	1.06	-0.12	1.56	-0.17	0.47

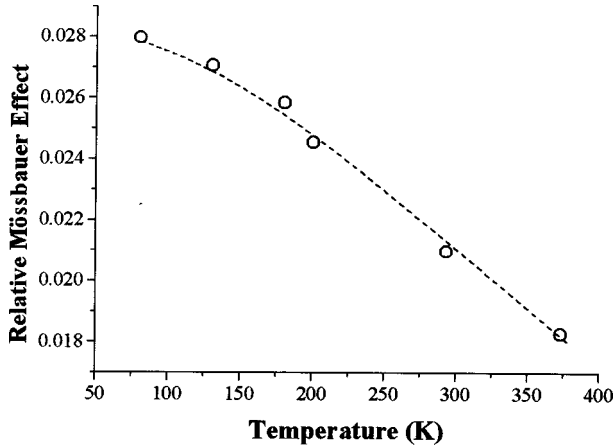


FIG. 6. Plot of the total spectral area vs temperature for ^{57}Co -doped $\text{Y}_{0.55}\text{Pr}_{0.45}\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The dashed line is only a guide to the eye.

Fig. 7). The formation of *B* requires two adjacent O(4)'s to be displaced on the same side of the zig-zag structured chain, which is a severe perturbation of the chain structure. Upon raising the temperature, one of the two O(4)'s jumps back to the opposite side of the chain (formation of Species *C*) and thus the original zig-zag structure of the chain is restored. The smaller the displacement of the O(4) atoms in the chain, the smaller the energy (and structural) difference between species *B* and *C*. The disappearance of the *B* to *C* interconversion can be explained by either diminishing displacement

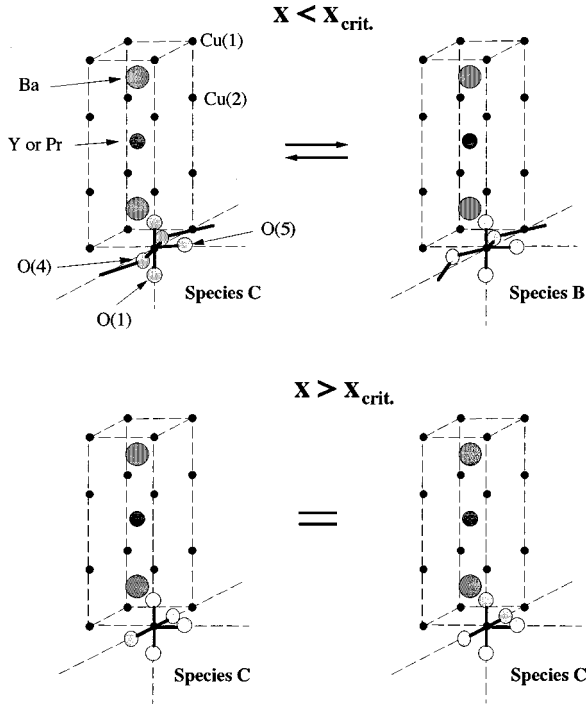


FIG. 7. The killing of the *B* to *C* interconversion by the effect of praseodymium in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ as a result of increasing Cu(1)-Cu(1) distance. From among the oxygens of the unit cell, only those coordinating the ^{57}Co -substituted Cu(1) site are shown. We assume that the straightening of the zig-zag Cu(1)-O(4) chain takes place around the Pr concentration critical to superconductivity ($x_{\text{crit}}=0.55$).

of the O(4) atoms, or a transformation of the dynamic zig-zag structure into a static one (i.e., when the chain becomes more rigid). The latter is unlikely because the temperature of the *B* to *C* interconversion did not change appreciably with the Pr content. On the other hand, it is clearly shown by structural data provided by neutron-diffraction⁵ and x-ray studies^{35,36} that the Cu(1)-Cu(1) distance along the chain (i.e., lattice parameter *b*) increases with Pr substitution at the Y site. In $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the exact position of the O(4) atoms are 0.015 nm off the chain, according to a high-resolution neutron-diffraction study.¹⁷ One may assume that this displacement is basically caused by the insufficient Cu(1)-Cu(1) distance, that is, the optimal Cu(1)-O(4) bond length is larger than one half of the Cu(1)-Cu(1) distance, thus the O(4) atoms are forced into the off-chain position. One can estimate the optimal Cu(1)-O(4) bond length from the displacement (0.015 nm) and from the Cu(1)-Cu(1) distance. Using the data from Ref. 5, $b=0.3883$ nm (at 10 K); an optimal bond length of 0.1947 nm is obtained. This means that if the Cu(1)-Cu(1) distance was $2 \times 0.1947 = 0.3894$ nm, the displacement of the O(4) atoms would not be necessary and the Cu-O chains could acquire a straight configuration. In this case, the out of the chain O(4) vibrations must be damped considerably. Furthermore, as a consequence for the Mössbauer results, in a straight chain, there is much less driving force for the formation of species *B*. In $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $b=0.3918$,⁵ which is higher than twice the optimal Cu(1)-O(4) bond length, providing a ready explanation for the disappearance of the *B* to *C* interconversion due to the absence of the zig-zag structure. This is consistent with our earlier finding that the *B* to *C* interconversion was not observed in $\text{PrBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$.³¹

One can now conclude that the disappearance of the *B* to *C* interconversion is a sign of the straightening of the Cu(1)-O(4) chain, and it indicates that the out of the chain vibration of the O(4) atoms can be important for the mechanism of high- T_c superconductivity in the 1-2-3 compounds. Our reasoning is illustrated in Fig. 7.

As shown in Table I the decrease of the *B* to *C* interconversion means a simultaneous decrease of the convertible fraction of *B* + *C* and of the thermodynamical parameters. From our model suggested above, however, one may expect only the latter. The decrease in the convertible fraction can perhaps be attributed to the nonhomogeneous effect of Pr to the lattice parameters. It is possible that the elongation of the chain is higher in the vicinity of a Pr atom, resulting in a complete extinction of the *B* to *C* interconversion, while in farther regions, the interconversion is still on but with smaller transformation enthalpy and entropy.

Another question also arises as to why should species *B* be present at all in 1-2-3 compounds with large concentration of Pr? It seems that Pr substitution introduces lattice defects which can freeze the structure of the five-coordinate species. A scenario suggested by Cannelli *et al.*¹⁶ is very likely, namely, if a whole set of adjacent O(4) atoms can be situated on the same side of the chain (and it would be enhanced by Pr substitution), it would cause freezing of species *B*. It may be mentioned here that in $\text{PrBa}_2\text{Cu}_3(^{57}\text{Co})\text{O}_{7-\delta}$, where one expects a straight chain, and, because it is not a mixed compound with a lot of defects, only two major species were

observed,³⁰ only one of them being a five-coordinate one, most likely *C*.

Table II shows the room-temperature Mössbauer data of the four species observed for the four different compositions.

The isomer shifts of *A* and *C* are almost constant up to $x=0.45$, only a very slight decrease can be seen. Their quadrupole splittings are practically constant. These findings are perfectly consistent with our model, as the structure of these species do not depend on the displacement of the O(4) atoms in the chain. The situation for species *B* is completely different, as the displacement of the O(4) atoms determines the distortion of the trigonal bipyramid (see Fig. 7). As the chain straightens, the distortion grows (from the point of view of an ideal trigonal bipyramidal structure) and finally reaches the structure of *C*. This implies that during this process, the Mössbauer parameters of *B* should be getting closer and closer to those of *C*, and that is exactly what happens to the isomer shift (Table II). The change of the quadrupole splitting of *B* is slower. Most probably, a rather sudden change can be anticipated when the symmetry of this species switches from distorted trigonal to a quasitragonal, i.e., when the Co, the two O(4) and the two O(1) atoms become fully coplanar.

Our model and the recently accumulated results permit some more discussion of the observed isomer shift values for species *A*, *B*, and *C* in connection with the electronic structure of the chains. First, the substantially smaller isomer shift for *C* than that for *B* should deserve explanation. As the coordination numbers for the two species are the same, and there is no special reason to believe that the valence state of the central iron atom changes, and, furthermore, the chains are metallic, the conduction electrons can be assumed responsible for the big difference. It is fairly reasonable in our model, as species *C* appears to be an integral part of the metallic chain. On the other hand, species *B* represents a severe perturbation of the chain, and its electron system is probably rather isolated. It means more localized *d* electrons at the central Fe atom, and consequently a higher isomer shift for *B*. In this scenario, the isomer shift of species *A* is rather surprising as being much higher than that of species *C*, despite the lower coordination number. One has to assume that the four-coordinate species *A* has a structure very far from the square-planar oxygen arrangement, most probably a tetrahedral one. As a tetrahedral coordination is uncommon in the chain, in harmony with the above reasoning, it will result in a partial structural isolation, that is, more localized *d* electrons for iron. The localization of the *d* electrons overcompensates the effect of the lower coordination number and results in a higher isomer shift than that for species *C*.³⁷

On the basis of the variation of the Mössbauer isomer shifts of the major species *A*, *B*, and *C* with the Pr content, we can conclude that only the isomer shift of species *B* varies significantly, but it is an intrinsic property of the varying structure of this species. If hole filling by Pr were to occur in the Cu(2) sheets, and if a fraction of that charge were to transfer onto the Cu(1)-O chains, then the *d*-electron density would increase in the chains resulting in an increase of the isomer shifts of species *A* and *C*. On the contrary, we observe no appreciable change (Table II).

These findings are consistent with those models which restrict the effect of Pr to the superconducting sheets, so the

FR model⁴ which assumes hybridization of the Pr4*f* orbitals with 2*p* orbitals of the eight nearest-neighbor oxygens. Either this model or its modified version by Liechtenstein and Mazin⁶ consider the superconducting Cu-O *pdσ* band to be isolated from the chains. It is worth noting here, however, that both models apply to small or moderate Pr doping levels.³⁸ Above the critical Pr content, there are Mössbauer data available on PrBa₂Cu₃(⁵⁷Co)O_{7-δ} only,³⁰ and the isomer shifts are anomalously high, which may indicate increase of the *d* density at the chains. Clearly some more data on intermediate Pr contents (between 45 and 100%) are needed to settle this question.

The striking result of our study, however, is the disappearance of the *B* to *C* interconversion which lends more credence to models assuming an active role of the chains in the mechanism of high-*T_c* superconductivity. In this respect, hybridization between Pr and sheet oxygens may not be very relevant to the question of superconductivity suppression by Pr, just as recently claimed by Blackstead and Dow.¹² Let us note here that the substantial advantage of the Liechtenstein-Mazin model against the original FR model, namely, that it explains the decreasing *T_c* suppression rate upon bond contraction caused by host *R* substitution in R_{1-x}Pr_xBa₂Cu₃O_{7-δ},³⁹ readily follows also from our *B* to *C* interconversion scenario. If the Cu(1)-Cu(1) distance becomes shorter, one has to introduce more Pr to “straighten the chain” and that destroys superconductivity.

Recently, there have been published reports on superconducting PrBa₂Cu₃O_{7-δ} prepared by a special synthesis, a traveling-solvent floating-zone technique.¹⁰ This strange behavior of the compound has been assigned to local structural inhomogeneities and/or possible mutual substitution of Pr and Ba. The substitution of Pr for the Ba site in 1-2-3 compounds seems to be well established by now,^{40,41} and its effect on the chain structure is not known exactly, but it may be responsible for the badly resolved Mössbauer spectra observed by us after some heat treatments in Y_{0.7}Pr_{0.3}Ba₂Cu₃(⁵⁷Co)O_{7-δ}, but especially in Y_{0.55}Pr_{0.4}Ba₂Cu₃(⁵⁷Co)O_{7-δ}. Pr at the Ba site may destroy *B* to *C* interconversion and broaden Mössbauer lines. From the point of view of the chains, is the remarkable observation of Shi *et al.* who found that a macroscopic amount of Co and especially Fe impurity (up to 10–20% Cu substitution) depresses the *T_c* suppression rate in YBa₂Cu₃O_{7-δ} when the synthesis is carried out in a high pressure atmosphere of oxygen.²⁸ They attributed it to excess oxygen brought into the chains by the dopants resulting in the formation of dopant centered local structures.

At this point, it is very interesting to note that going from Pr_{0.3} to Pr_{0.45} substitution, there is a dramatic increase in the abundance of species *D* at the expense of *A*. The amount of *B* also increases. This observation also supports that for the Pr_{0.45} compound, a fair proportion of Pr is substituting the Ba site. It is plausible that Pr³⁺ substitution at the Ba²⁺ site helps accommodate O²⁻ in the sixth position in the chain [O(5) site] also. The small quadrupole splitting and the significantly negative isomer shift of species *D* would be consistent with a sixfold coordinated species. (In the previous cases, i.e., at lower Pr content, the abundance of *D* was so small that its parameters were not reliable enough for a serious site assignment.). The five- and six-coordinate species form at the expense of the four-coordinate species *A* in the

oxygen-rich environment created by the nearby Pr^{3+} substituted at the Ba^{2+} site. From our Mössbauer data, we cannot make a quantitative estimate for the subdivision of Pr between the two sites because it is possible that the ^{57}Co dopant shows a preference for oxygen-rich regions of the Cu(1)-O chain near Pr-substituted Ba sites.

For the present state of affairs, it is difficult to judge what is the cause and effect in the relation of chain properties and superconductivity, but the correlations between the B and C interconversion, T_c , the oxygen content of the chains interrelated with substitution of Ba^{2+} by Pr^{3+} , all seem to support the importance of chain dynamics.

IV. SUMMARY

We have microprobed the electron density and the dynamics of the Cu(1)-O chain with increasing Pr substitution using ^{57}Co (^{57}Fe) Mössbauer dopants in $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$. The absence of change in the isomer shifts of some chain-related Co(Fe)-O species indicated that, below the Pr concentration critical to superconductivity, hole filling in the Cu(2)-O sheets does not occur, assuming that it would also effect the electron density at the chains. Any hybridization in the sheets involving Pr, also leaves the chains unaffected.

The reversible interconversion between two five-coordinate species with different configurations, which is triggered by oscillation of O(4) between two potential wells on either side of the chain, is gradually depressed by increasing Pr concentration, and becomes quite small for the $\text{Pr}_{0.45}$ compound. A possible explanation of this phenomenon is the increase of lattice parameter b resulting in straightening of the originally zig-zag structured Cu(1)-O(4) chains.

These results are consistent with models which invoke an active role of the anharmonic dynamics of the chains in the mechanism of high- T_c superconductivity in 1-2-3 compounds.

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