RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 17 1 MAY 1993-I

Enhancement of flux pinning by Pr doping in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ ($0 \leq x \leq 0.4$)

L. M. Paulius,* C. C. Almasan, and M. B. Maple

Department of Physics and Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093

(Received 9 September 1992; revised manuscript received 1 March 1993)

Magnetic relaxation measurements in a magnetic field of 5 kOe at temperatures 5 K $\leq T \leq$ 90 K have been made on the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for $0 \leq x \leq 0.4$. The measurements reveal two peaks in the normalized logarithmic decay of the magnetization S as a function of temperature for the full range of Pr concentrations studied. The occurrence of the second peak in S could be a reflection of the softening of the flux lattice on approaching the melting line. Both the pinning energy at 27 K and the intragranular critical current density at 10 K exhibit maxima at $x = \approx 0.1$–0.2, with values that are about twice the corresponding values at $x = 0$.

One of the most challenging problems for the new high-temperature oxide superconductors is devising effective ways to increase flux pinning energies. A variety of techniques have been studied, including ion,[1] neutron,[2] and electron[3] irradiation, shock compaction,[4] and chemical doping.[5–7] In general, chemical doping increases the intragranular critical current density J_c through the formation of nonsuperconducting phases which provide regions where the superconducting order parameter is suppressed and fluxoids are pinned.

The objective of the investigation reported here is to explore an alternative method in which the chemical impurities are introduced substitutionally into the crystal lattice and the solute ions interact with the superconducting holes locally. Specifically, we have studied flux pinning in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system in which previous work[8,9] has yielded evidence that the substituted Pr ions interact with mobile holes in the CuO_2 planes, resulting in the localization of the holes and the breaking of the superconducting hole pairs. While the superconducting critical temperature T_c decreases monotonically with increasing Pr concentration from 92 K at $x = 0$ to 0 K at $x \approx 0.56$ in the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system, the depression of T_c is small for Pr concentrations in the range $0 \leq x \leq 0.1$ ($T_c \approx 88$ K for $x = 0.1$). Thus, doping with low concentrations of Pr could introduce pinning centers separated by distances on the order of the lattice constant without significantly decreasing T_c.

In this paper, we report the results of magnetic relaxation measurements in a magnetic field of 5 kOe at temperatures 5 $K \leq T \leq$ 90 K on the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system for $0 \leq x \leq 0.4$. The measurements reveal two peaks in the normalized logarithmic decay of the magnetization as a function of temperature for the full range of Pr concentrations studied. The existence of the second peak suggests the presence of two pinning effects; in particular, the second peak in S could be a reflection of the softening of the flux lattice on approaching the melting line. Both the pinning energy at 27 K and the intragranular critical current density at 10 K exhibit maxima in the range $x \approx 0.1$–0.2 as a function of Pr concentration, with values that are about twice the corresponding values at $x = 0$. The enhancement of the pinning may be due to the suppression of the superconducting order parameter in the vicinity of the Pr ions via a magnetic pair-breaking interaction.

The samples used for the present measurements were unaligned polycrystalline pellets prepared using the solid state reaction technique described in Ref. 10. X-ray diffraction patterns showed the samples to be single phase. The resistive transition widths $\Delta T_c \equiv T_{0.9} - T_{0.1}$, where T_n is the temperature at which the resistivity drops to a fraction n of its extrapolated normal state value, ranged from 0.7 K for $x = 0$ to 3.5 K for $x = 0.4$. Iodometric titration revealed oxygen concentrations of 6.95 ± 0.02.[10] Scanning electron microscopy (SEM) studies yielded an average grain size of ~ 12 μm for the $x = 0$ sample, and a range in the average grain size of 2 to 4 μm for the Pr doped samples with no apparent correlation between grain size and Pr concentration.

Static and time dependent magnetic measurements were performed on a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer over a temperature range 5 K $\leq T \leq$ 90 K and for applied magnetic fields H up to 50 kOe. A scan length of 3 cm was used to minimize the variations in field strength due to spatial inhomogeneities in the magnet ($\partial H < 0.048\%$). Magnetic relaxation measurements were performed by cooling the sample in zero field, waiting until the temperature was stable, applying a magnetic field of 5 kOe, and monitoring the magnetic moment every ~ 50 s for about one hour. At higher temperatures, we found that the decay of the magnetic moment was highly sensitive to very slight thermal instabilities.

In order to apply models of thermally activated flux motion to the magnetic relaxation data, the measurements must be performed with the sample in the fully critical state (i.e., flux penetrates throughout the entire sample). To determine the value of the external field required to reach the fully critical state, we measured the remnant moment as a function of the previously applied field. The inset of Fig. 1 is a log-log plot of $M_{\rm rem}$ vs H. The solid lines in the figure show how we extracted the value of $2H_{\rm fcs}$-$H_{\rm c1}$.[11,12] The determination of $H_{\rm fcs}$, performed at different temperatures, revealed that $H_{\rm fcs}$ decreases with increasing temperature. Figure 1 is a plot of

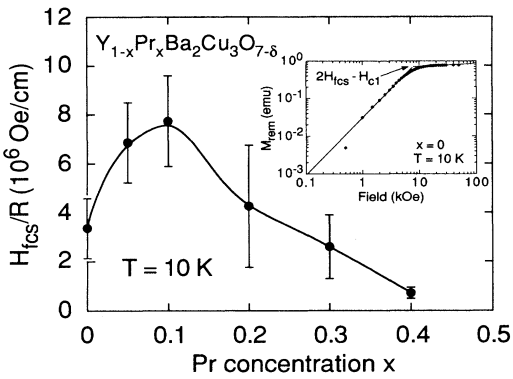

FIG. 1. Value of the fully critical field divided by the radius of the grains of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as a function of Pr concentration x measured at a temperature of 10 K. The error bars were calculated from the uncertainties in determining H_{fcs} and R. Inset: log-log plot of the remnant moment vs the value of the previously applied field for the $YBa_2Cu_3O_{7-\delta}$ sample measured at 10 K. The solid lines in the figure show how we extracted the value of $2H_{fcs}$-H_{c1}.

H_{fcs}/R as a function of Pr concentration, where H_{fcs} was normalized by the radius of the grains in order to eliminate the dependence of H_{fcs} on sample size. The error bars were calculated from the uncertainty in the values of H_{fcs} and R. All the relaxation measurements were taken in an applied field of 5 kOe because, for this value of H, all the samples investigated were in the fully critical state.

The relaxation of the magnetic moment was measured for samples with Pr concentrations $x=0$, 0.05, 0.1, 0.2, 0.3, and 0.4 at temperatures ranging from 5 to 90 K. Figure 2 is a plot of $M(t)/M(t_b)$ vs $\ln(t/t_b)$ for different x values, measured at $T=27$ K in a field of 5 kOe; $M(t)$ is the magnetic moment at time t and t_b is the time of the first measurement, which is ~ 500 s. For all x values, the decay of the magnetic moment is logarithmic in time with a decay rate which is largest for the $x=0$ sample, decreases with Pr concentration up to $x=0.2$, and then increases again for $x>0.2$. For the samples with $x=0.3$ and 0.4, the diamagnetic moments were corrected for the large paramagnetic signal of the Pr ions by fitting the normal state magnetization with a Curie-Weiss law. At each temperature, the corrected diamagnetic signal was obtained by subtracting the paramagnetic moment from the measured magnetic moment.

In the course of performing the measurements, we discovered that the decay of the magnetic moment at higher temperatures ($T \gtrsim 55$ K) was highly sensitive to the stability of the temperature. For example, for drifts in the temperature as small as 0.02 K at 86 K, strong deviations from logarithmic behavior were observed in the decay of the magnetic moment. To achieve greater temperature stability, we inserted a pause between the time the temperature was deemed "stable" by the magnetometer and the time the field was applied. For $55\ \text{K} \le T \le 60$ K, a 30 min pause was chosen to obtain a constant decay rate; for $T > 60$ K, a 90 min pause was required.

Over the time span measured, the observed decay of the magnetic moment is logarithmic to lowest order, consistent with the Anderson-Kim model of thermally activated flux motion.[13] Hence, the time dependence of the magnetic moment of a sample in the fully critical state can be expressed as[14]

$$M(t,T)=M_0(T)[1-\{kT/U(T)\}\ln(t/\tau)]\ , \qquad (1)$$

where $M_0(T)$ is the moment at time $t=0$ and temperature T, τ is the hopping time ($10^{-12}\ \text{s} < \tau < 10^{-6}$ s), and U represents the effective pinning energy. The unknown $M_0(T)$ can be eliminated from Eq. (1) by dividing the value of the magnetic moment at a particular time t_b. Hence, the normalized relaxation rate S is given by

$$S \equiv -\frac{1}{M(t_b)}\frac{dM(t)}{d\ln(t)} = \frac{1}{U/kT - \ln(t_b/\tau)}\ . \qquad (2)$$

Note that for convenience we have defined S_n as a positive value.

Figure 3 is a plot of S as a function of both temperature and Pr concentration with $5\ \text{K} \le T \le 90$ K and $0 \le x \le 0.4$. For all Pr concentrations measured, S exhibits two peaks; one at low temperatures (e.g., $T_1 \approx 25$ K for $x=0$) and another at higher temperatures (e.g.,

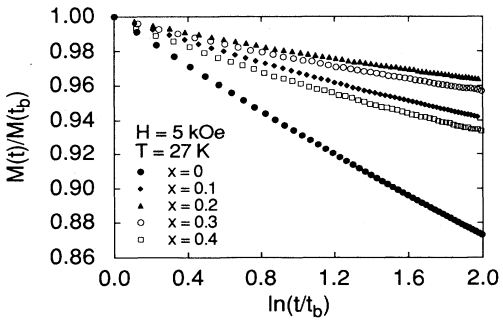

FIG. 2. Normalized magnetic moment of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ vs $\ln(t/t_b)$ for different Pr concentrations measured at $T=27$ K in an applied field of 5 kOe; $t_b \approx 500$ s is the time of the first measurement.

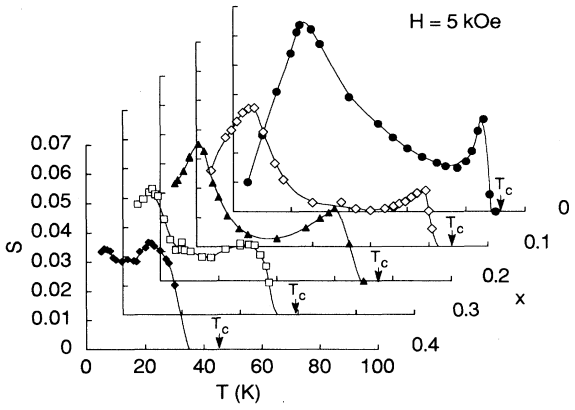

FIG. 3. Normalized decay rate of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ as a function of temperature and x, measured in an applied field of 5 kOe. Arrows indicate the value of the superconducting transition temperature T_c for different values of x. The solid lines are guides to the eye.

$T_2 \approx 85$ K for $x=0$). Both peaks in $S(T)$ shift to lower temperatures with increasing Pr concentration (e.g., $T_1 \approx 6$ K and $T_2 \approx 22$ K for $x=0.4$). The temperature at which the decay rate drops to zero was found to correspond to the irreversibility temperature.

The low-temperature peak in the $YBa_2Cu_3O_{7-\delta}$ sample is consistent with previous measurements on this system.[14–16] However, to our knowledge, this is the first time that the second peak in $S(T)$ has been observed in $YBa_2Cu_3O_{7-\delta}$. The observation of this second peak depends critically on the elimination of thermal instabilities which can cause large deviations from logarithmic decay at higher temperatures. Almasan *et al.*[17] found two peaks in $S(T)$ in the electron-doped $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ compound, indicating that this is possibly a general behavior for the cuprates. The existence of two peaks suggests the presence of two different pinning effects;[17] in particular, the second peak in S could be a reflection of the softening of the flux lattice on approaching the melting line which has been discussed, for example, by Vinokur, Feigel'man, and Geshkenbein.[18]

The pinning energy U was calculated from the decay rate S using Eq. (2). For the $x=0$ sample, $U(10\text{ K})=0.056$ eV, which is within the range of values (~ 0.02 to ~ 0.2 eV) reported in the literature for $YBa_2Cu_3O_{7-\delta}$.[14,19] For all of the Pr concentrations studied, the pinning energy was found to increase with temperature, which is consistent with a distribution of pinning energies[20] or with a nonlinear dependence of U on J.[21] In order to compare the effects of Pr doping on the pinning energy for the full range of Pr concentrations, we calculated U from magnetic relaxation measurements taken at different temperatures for all the x values. For temperatures between ~ 15 and ~ 70 K, the pinning energy vs Pr doping shows a maximum. These results are consistent with the increase in $U(x)$ for $x \lesssim 0.1$, previously reported in Ref. 22. The concentration at which this maximum occurs decreases with increasing temperature. The calculated value of U at 27 K is plotted vs x in Fig. 4 and exhibits a maximum at $x=0.20$, which is a factor of ~ 2 larger than the value of the undoped sample. This temperature was chosen because it is the highest temperature for which all samples exhibit magnetic relaxation.

To compare these results with the behavior of the intragranular critical current density J_c, we calculated J_c from the measurements of $H_{\rm fcs}$ at 10 K. In the case of a cylindrical sample of radius R, with the field applied parallel to the axis of the cylinder, the critical current derived from the Bean model is given by[11]

$$J_c = \frac{10(H_{\rm fcs}-H_{c1})}{4\pi R}\ , \tag{3}$$

where J_c is in A/cm^2, R is the average grain size (in cm), and H_{c1} is the lower critical field (in Oe). The values of $H_{c1}(x)$ were calculated, following Ref. 23, from values of the penetration depth $\lambda(x)$ deduced from μSR experiments[24] Treating the samples as dirty superconductors [$\xi(x) \propto T^{-1/2}$] would change the values of $J_c(x)$ by only a few percent. The values of $J_c(x)$ calculated from Eq. (3) are shown in the inset of Fig. 4 where $J_c(x)/J_c(0)$ is plotted vs x, with $J_c(0)=(2.4\pm 0.5)\times 10^6$ A/cm^2. Although the maxima occur at slightly different concentrations, the behavior of J_c is qualitatively similar to the behavior of the pinning energy. The critical current density increases with Pr concentration up to $x \approx 0.1$ and then decreases for $x \gtrsim 0.1$. The difference in the value of x which corresponds to the peak in $U(x)$ and $J_c(x)$ may be due to errors in estimating J_c (caused by uncertainties in determining R and $H_{\rm fcs}$).

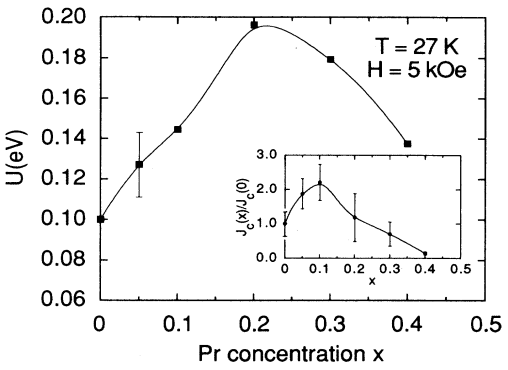

FIG. 4. Pinning energy U vs Pr concentration x for $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ calculated from the magnetic relaxation data taken at 27 K in an applied field of 5 kOe. We calculated U by setting the hopping time $\tau=10^{-9}$ s and the error bar reflects the uncertainty in τ. Inset: Intragranular critical current density as a function of Pr concentration. Current densities are normalized to the value for the $x=0$ sample. The error bars were calculated from the uncertainties in determining R and $H_{\rm fcs}$. The solid lines in both graphs are guides to the eye.

The effectiveness of Pr as a pinning site in $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ for concentrations up to ~ 0.2 is presumably due to a local suppression of the superconducting order parameter in the vicinity of the Pr ions. One mechanism for this effect could be magnetic pair breaking via a spin-dependent exchange interaction between the superconducting holes and the paramagnetic Pr ions. Hybridization of the Pr $4f$ localized states and the CuO_2 valence-band states has been suggested as a possible mechanism for filling (or localizing) holes in the CuO_2 planes and generating the antiferromagnetic exchange interaction via the Schrieffer-Wolf transformation.[8,9]

The peaks in the pinning energy and the critical current density could be the result of the competition between the mechanism that increases the pinning energy and the effects that decrease it. Two possible causes of the latter are the suppression of the superconductivity and the decreasing distance between pinning centers. The decrease in U follows from the fact that U is proportional to ξH_c^2, which decreases with decreasing T_c, where H_c is the thermodynamic critical field. A decrease in U due to the decrease in the distance between pinning centers may occur when the distance between adjacent pinning centers becomes smaller than the core of the fluxoid ($\sim 2\xi$), so that a fluxoid can move more easily from one site to another. As a rough approximation, the relationship between the size of the core of the fluxoids and

the distance between ions can be estimated by assuming that the ions are uniformly distributed throughout the material and by averaging the coherence lengths and lattice parameters of the three different directions. This simple calculation yields a distance between Pr ions of $\sim 2\xi$ and, hence, the position of the peak in $U(x)$, at a concentration of $x \approx 0.1$.

To compare the effectiveness of Pr with that of another paramagnetic lanthanide solute an increasing pinning in $YBa_2Cu_3O_{7-\delta}$, we measured the magnetic relaxation of $Y_{0.9}Ho_{0.1}Ba_2Cu_3O_{7-\delta}$. The Ho ion does not suppress superconductivity in $YBa_2Cu_3O_{7-\delta}$ and has a magnetic moment that is three times larger than that of the Pr ion. We found an increase in the pinning energy in the sample doped with Ho, but only by half as much as for the corresponding $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_{7-\delta}$ sample. This indicates that the effect of the Pr ions involves more than just introducing disorder into the system. It also implies that any spin-dependent interaction between the lanthanide solute ions and the superconducting charge carriers, and, in turn, the fluxoids, depends on the strength of the interaction rather than the magnitude of the lanthanide magnetic moment.

In summary, we present the results of magnetic relaxation measurements on $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ in a field of 5 kOe for $0 \leq x \leq 0.4$ and 5 K $\leq T \leq$ 90 K. The normalized magnetic decay rate shows two peaks as a function of temperature for all Pr concentrations measured. The peaks shift to lower temperatures with increasing Pr concentration. The existence of two peaks suggests the presence of two different pinning effects; in particular, the second peak in S could be a reflection of the softening of the flux lattice on approaching the melting line. Both the pinning energy $U(x)$ at 27 K, calculated from the relaxation measurements, and the critical current density $J_c(x)$ at 10 K, calculated from the Bean model, show maxima which occur at $x \approx 0.1-0.2$. The increase in the pinning energy may be due to the local suppression of the superconducting order parameter by the Pr ions via magnetic pair breaking. The measurements reported here show that the addition of Pr increases the pinning energy in $YBa_2Cu_3O_{7-\delta}$ and suggests that Pr substitution could be used in conjunction with other methods to improve the critical current density of this important high-T_c material.

This research was supported by the U.S. Department of Energy under Grant No. DE-FG03-86ER-45230.

*Present address: Department of Physics, Western Michigan University, Kalamazoo, MI 49008.

[1]B. Roas, B. Hensel, G. Saemann-Ischenko, and L. Schultz, Appl. Phys. Lett. **54**, 1051 (1989).

[2]A. Umezawa, G. W. Crabtree, J. Z. Liu, H. W. Weber, W. K. Kwok, L. H. Nunez, and H. Claus, Phys. Rev. B **36**, 7151 (1987).

[3]Y. Matsui, E. Takayama-Muromachi, and K. Kato, Jpn. J. Appl. Phys. **26**, L1183 (1987).

[4]C. L. Seaman, E. A. Early, M. B. Maple, W. J. Nellis, J. B. Holt, M. Kamegai, and G. S. Smith, in *Shock Compression of Condensed Matter-1989,* edited by S. C. Schmidt, J. N. Johnson, and L. W. Davison (North-Holland, New York, 1990), pp. 571–574.

[5]D. Shi, M. S. Boley, U. Whelp, J. G. Chen, and Y. Liao, Phys. Rev. B **40**, 5255 (1989).

[6]F. Mizuno, H. Masuda, I. Hirabayashi, and S. Tanaka, in *High-Temperature Superconductors: Fundamental Properties and Novel Materials Processing,* edited by J. Narayan, C. W. Chu, L. F. Schneemeyer, and D. K. Christen (Materials Research Society, Pittsburgh, PA, 1990), pp. 955–958.

[7]M. Murakami, S. Gotah, H. Fujimoto, N. Koshizuka, and S. Tanaka (unpublished).

[8]M. B. Maple, J. M. Ferreira, R. R. Hake, B. W. Lee, J. J. Neumeier, C. L. Seaman, K. N. Yang, and H. Zhou, J. Less-Common Met. **149**, 405 (1989), and references cited therein.

[9]M. B. Maple, N. Y. Ayoub, J. Beille, T. Bjornholm, Y. Dalichaouch, E. A. Early, S. Ghamaty, B. W. Lee, J. T. Markert, J. J. Neumeier, G. Nieva, L. M. Paulius, I. K. Schuller, C. L. Seaman, and P. K. Tsai, in *Transport Properties of Superconductors,* edited by R. Nicolsky (World Scientific, New York, 1990), pp. 536–556, and references cited therein.

[10]J. J. Neumeier, T. Bjørnholm, M. B. Maple, J. J. Rhyne, and J. A. Gotaas, Physica C **166**, (1990).

[11]C. P. Bean, Phys. Rev. Lett. **8**, 250 (1962).

[12]L. M. Paulius, C. C. Almasan, and M. B. Maple (unpublished).

[13]P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. **36**, 39 (1964).

[14]C. W. Hagen and R. Griessen, in *Studies of High Temperature Superconductors,* edited by A. V. Narlikar (Nova Science, New York, 1989), Vol. 3, p. 159.

[15]Y. Yeshurun and A. P. Malozemoff, Phys. Rev. Lett. **60**, 2202 (1988).

[16]M. Tuomien and A. M. Goldman, Phys. Rev. B **37**, 548 (1988).

[17]C. C. Almasan, C. L. Seaman, Y. Dalichaouch, and M. B. Maple, Physica C **174**, 93 (1991).

[18]V. M. Vinokur, M. V. Feigel'man, and V. B. Geshkenbein, Phys. Rev. Lett. **67**, 915 (1991).

[19]Y. Yeshurun, A. P. Malozemoff, F. Holtzberg, and T. R. Dinger, Phys. Rev. B **38**, 11 828 (1988).

[20]G. M. Stollman, B. Dam, J. H. P. Emmen, and J. Pankert, Physica C **162–164**, 1191 (1989).

[21]S. T. Weir, Solid State Commun. **77**, 839 (1991).

[22]L. M. Paulius, P. K. Tsai, J. J. Neumeier, M. B. Maple, K. C. Chen, and K. S. Mazdiyasni, Appl. Phys. Lett. **58**, 1792 (1991).

[23]R. A. Klemm and J. R. Clem, Phys. Rev. B **21**, 1868 (1980).

[24]C. L. Seaman, J. J. Neumeier, M. B. Maple, L. P. Le, G. M. Luke, B. J. Sternlieb, Y. J. Uemura, J. H. Brewer, R. Kadono, R. F. Kiefl, S. R. Krietzman, and T. M. Riseman, Phys. Rev. B **42**, 6801 (1990).