$YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ Superlattices: Properties of Ultrathin Superconducting Layers Separated by Insulating Layers

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We have artificially varied the coupling between ultrathin $YBa_2Cu_3O_7$ layers by interposing insulating planes of $PrBa_2Cu_3O_7$ in multilayers and studied the consequences of decoupling 12-Å $YBa_2Cu_3O_7$ unit cells on the superconducting properties. We find that the T_c (midpoint) of a 12-Å/12-Å multilayer is 55 K, twice that of the corresponding alloy. T_c decreases linearly with further separation of the $YBa_2Cu_3O_7$ unit cells, the transition width increases and shows evidence of 2D fluctuations, and the influence of a magnetic field parallel to the layers is markedly reduced.

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The high-temperature superconductors (HTS) are well known for their high degree of anisotropy which reflects the naturally layered structure of these materials. It is widely appreciated that their layered structure and the coupling between neighboring Cu-O planes plays an important role in determining the superconducting properties as well as the basic pairing mechanism. In $YBa_2Cu_3O_7$ (YBCO) the two Cu-O planes of a unit cell responsible for superconductivity are separated from the next two Cu-O planes by a distance of $\simeq 12$ Å.[1] This large distance is the reason for the high degree of anisotropy. However, YBCO behaves as a three-dimensional anisotropic superconductor, at least near T_c.[2] In the compound $Bi_2Sr_2CaCu_2O_8$ similar groups of two Cu-O planes exist but their separation is $\simeq 31$ Å.[1] This compound is found to be much more anisotropic than YBCO and shows a behavior which is possibly related to two-dimensional fluctuations.[3] Although these materials are strongly anisotropic it is still unclear to which extent the two-dimensional nature is essential and to which extent the coupling between the planes is necessary for the presence of superconductivity. In order to further understand the physics of high-temperature superconductors it is of importance to study materials with different types of coupling between the Cu-O planes.

In this Letter we report the synthesis and properties of artificially produced multilayers containing ultrathin YBCO layers. Using thin-film deposition techniques we have been able to vary the coupling between superconducting Cu-O bilayers by interposing *insulating planes* of $PrBa_2Cu_3O_7$ (PrBCO). We report the consequences of progressively decoupling single (12-Å) YBCO superconducting layers on the superconducting properties, including the transition temperature, the transition width, and the behavior of the superconducting transition in a magnetic field parallel to the layers.

We recently demonstrated the ability to grow superlattices of $YBa_2Cu_3O_7/DyBa_2Cu_3O_7$ (Ref. 4) having modulation wavelengths Λ, determined by x-ray diffraction, as short as 24 Å; i.e., films in which one unit cell of YBCO alternates with one unit cell of DyBCO. No degradation of the superconducting properties due to the artificial interfaces was found; neither the transition temperature nor the residual-resistivity ratio were affected. We have used the same deposition technique to prepare $YBa_2Cu_3O_7/PrBa_2Cu_3O_7$ superlattices. Briefly, our films have been prepared by single-target dc planar magnetron sputtering.[5] Two stoichiometric targets of YBCO and PrBCO are mounted on two guns placed 180° apart in a UHV system. A computer-controlled stepping motor positions heated substrates in front of the desired gun for a given time and this process continues until the total multilayer thickness is obtained, about 1500 Å. We have used polished substrates of (100) MgO on which the films grow with the c axis perpendicular to the plane of the substrate.

Contrary to the other $RBa_2Cu_3O_7$ (RBCO, R denotes rare-earth element) compounds PrBCO is not a conductor and the Pr moments order at 17 K,[6] an anomalously high ordering temperature compared to the other RBCO compounds. Both the absence of superconductivity and the insulating state in PrBCO are not well understood at present, but are believed to be related to the intermediate valence of Pr and the presence of $4f$ states close to the Fermi level.[6] In order to check that PrBCO has the same properties when grown in thin-film form we have prepared single PrBCO thin films for which resistivity measurements show the expected semiconducting behavior.[6] The epitaxial growth of thick PrBCO on thick YBCO layers has recently been observed by Poppe *et al.*[7] with no corresponding effect on the superconducting properties of the bilayers. This is expected because of the large size of these structures compared to the superconducting coherence length. In our study the thickness

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of each layer is much smaller and a modification of the superconducting state is expected.

Figure 1 shows a θ-2θ x-ray diffractogram in the region of the (001) and (002) YBCO reflections for a $\Lambda = 48$ Å (24-Å/24-Å) YBCO/PrBCO sample. The well defined satellite peaks, characteristic of superlattice modulation, are indicated by the arrows. For each sample in this study the modulation wavelength Λ could be verified using the standard formula $\Lambda = \lambda_x/2(\sin\theta_i - \sin\theta_{i-1})$, where λ_x is the x-ray wavelength (1.542 Å here), and θ_{i-1}, θ_i are the positions of two adjacent x-ray peaks.

We have made several samples which consist of 12-Å/12-Å YBCO/PrBCO layers and find consistently a metallic behavior with a zero-resistance superconducting transition, T_{c0}, close to 50 K. The 24-Å/24-Å sample is also metallic with T_{c0} around 68 K. The presence of well defined satellite peaks as well as the difference in T_{c0} of these two samples demonstrates their layered nature. To rule out the possibility that strong interdiffusion between the Pr layers and the Y layers can explain the result for the 12-Å/12-Å sample, we have fabricated a $(Y_{0.5}Pr_{0.5})$BCO alloy by depositing 3 Å of YBCO alternating with 3 Å of PrBCO, thereby depositing 50% Y and 50% Pr in each rare-earth layer. The result is shown in Fig. 2. Here we display resistance, normalized at 100 K, versus temperature for the 50/50 alloy, the 12-Å/12-Å and 24-Å/24-Å multilayers, and a YBCO thin film on MgO. This YBCO film has a transition width of 2 K, and has been produced with the same deposition parameters as our series of multilayers. In agreement with results on ceramic samples we find for the 50/50 alloy a T_{c0} of about 20 K. The sharpness of the transition compared with the corresponding ceramic alloy[6] shows that this layer-by-layer construction produces homogeneous alloys.

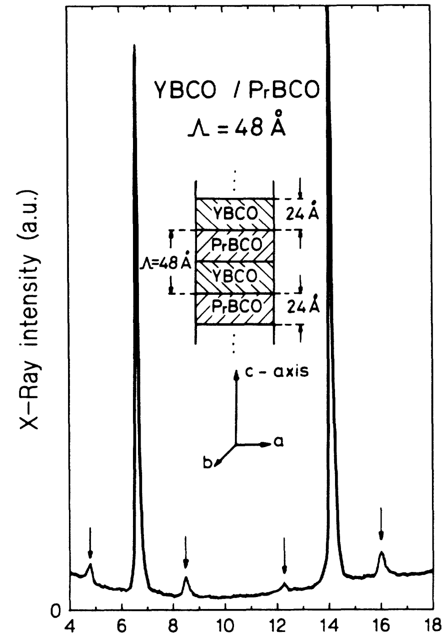

FIG. 1. θ-2θ x-ray diffractogram of a $\Lambda = 48$ Å (24-Å/24-Å) YBCO/PrBCO multilayer. The satellite peaks are indicated by the arrows. Inset: A schematic diagram of the multilayer indicating the direction of the c axis.

The major point of interest in Fig. 2 is that the behavior of the superlattices is strikingly different from that of the alloy. For the 12-Å/12-Å multilayer we find that (a) T_c is about twice that of the alloy, (b) the temperature coefficient of the resistivity is positive all the way to RT, showing metallic behavior, and (c) the resistive transition is very broad. (a) and (b) imply that the 12-Å/12-Å multilayer is well layered. In view of the well defined transition in the alloy it appears possible that the broad transitions in the 12-Å/12-Å and the 24-Å/24-Å samples are of intrinsic origin. Based on the Lorentz-Doniach (LD) theory of Josephson-coupled multilayers[8] we expect a change from 2D-like to 3D-like behavior as one approaches T_c. This crossover temperature is determined by the condition $\xi_c(T) = \Lambda/2$, where $\xi_c(T)$ is the temperature-dependent coherence length perpendicular to the layers. This crossover essentially marks the sharpening of the resistive transition. For our 12-Å/12-Å multilayer, $\Lambda = 24$ Å, the above criteria puts our film in the 2D region until a few percent of T_c. From this point of view the paraconductivity in these multilayers is to a very good approximation 2D in the entire temperature range above T_c. The simple 2D formula, $\sigma' = (e^2/16\hbar s) \times (T/T_c - 1)^{-1}$, in fact fits the data well near T_c (this is the dashed line in Fig. 2), in both magnitude and temperature dependence, for the 12-Å/12-Å multilayers with essentially only T_c as an adjustable parameter. In the above formula, s is taken to be the superconducting layer thickness ($s = 12$ Å and $T_c = 51.7$ K for the curve shown). This fit was made using the measured resistivity of the film and a linear dependence of the normal-state resistivity (ρ_n) on temperature. The resistivity was cal-

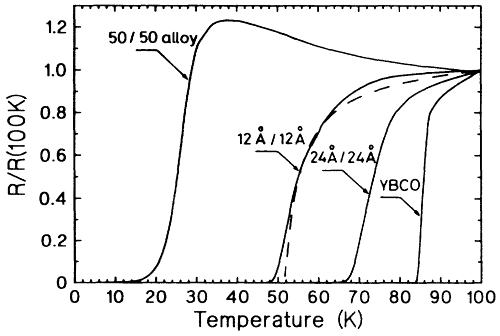

FIG. 2. Normalized resistance vs temperature from left to right for the 50/50 alloy, the 12-Å/12-Å and 24-Å/24-Å multilayers, and a YBCO film on MgO. The dashed line is the enhanced-fluctuation-conductivity fit discussed in the text.

culated as $1/\rho = 1/\rho_n + \sigma'$ and the resulting curve shown in Fig. 2 has been normalized by the measured resistivity at 100 K (592 $\mu\Omega\,\mathrm{cm}$). In addition, the magnitude of the fluctuation conductivity of the 24-Å/24-Å sample is also well fitted, taking $s = 24$ Å in the formula for the fluctuations. We also note that the conductivity at RT scales (within 15%) to the proportion of YBCO in the multilayer.

In order to further investigate the influence of the decoupling of the YBCO layers by the PrBCO layers on the superconducting properties, we have produced a series of YBCO/PrBCO multilayers keeping the thickness of the YBCO equal to 12 Å and varying the PrBCO thickness (d_{Pr}): 12-Å/24-Å, 12-Å/48-Å, and 12-Å/72-Å. The change from a 12-Å PrBCO to a 24-Å PrBCO separation of the YBCO leads to a shift in T_c and to a broadening of the transition close to T_{c0}. The same behavior is observed for the 24-Å/24-Å (shown in Fig. 2) and the 24-Å/12-Å samples. Thus when the thickness of the PrBCO is 24 Å or more the simple LD formula discussed above gives a poorer description of the resistive transition. This may result from critical fluctuations or possibly from a Kosterlitz-Thouless transition in these more two-dimensional samples. As explained by Bulaevskii, Ginzburg, and Sobyanin[9] the critical region can be very large in 2D (roughly the square root of the critical region, $t = \Delta T/T_c$, in 3D). If these films enter the critical regime before the superconducting layers couple, we would expect this type of broadening of the superconducting transition and, in addition, a renormalization of the mean-field parameters, for example, a change in T_c.

When the PrBCO thickness is increased beyond 24 Å we observe a regular shift of the whole transition to lower values without further broadening. Surprisingly, the dependence of T_c on d_{Pr} is close to linear as displayed in Fig. 3. Here T_c is defined as 10% of the normal-state resistance above the transition. This definition is consistent with our fluctuation-conductivity analysis. The fact that this plot extrapolates back to 60 K for $d_{\mathrm{Pr}} = 0$ suggests that two different mechanisms determine the T_c reduction in thse multilayers. A d_{Pr}-independent T_c reduction may be intrinsic to the single Cu-O double layer or it may be produced by the interaction of nearest-neighbor YBCO and PrBCO layers. We expect that some mixing of Pr atoms into the Y layer occurs. Furthermore, it is plausible that the nearest-neighbor Pr layer contains some Y atoms and thereby possibly a nonzero conductivity. A proximity effect, possibly enhanced by exchange scattering off the Pr atoms in this layer,[6] may account for a part of the T_c reduction in the limit $d_{\mathrm{Pr}} = 0$.

There are different possibilities to explain the linear decrease of T_c with increasing d_{Pr}. As discussed above, strong interdiffusion seems unlikely to occur because of the existence of a 12-Å/12-Å system with very different properties than the alloy. Interdiffusion, if any, appears limited to the nearest-neighbor Y and Pr layers. A proximity effect across the PrBCO layer also seem unlikely and would imply the presence in the multilayer of a coherent state across thick layers of PrBCO in spite of the insulating nature of this compound. A standard proximity calculation would also not predict a linear decrease of T_c unless the coherence length in the PrBCO is much longer than the largest d_{Pr}. The most interesting possibility is that the reduced T_c is related to a reduced coupling between the YBCO layers across the PrBCO and reflects the intrinsic behavior of a single Cu-O double layer. This would suggest that a small but finite coupling between the Cu-O double layers is necessary in order to produce superconductivity.

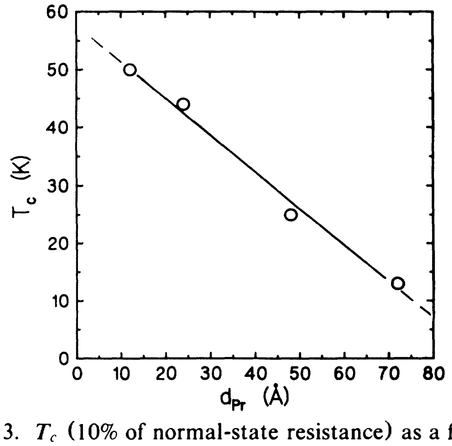

FIG. 3. T_c (10% of normal-state resistance) as a function of the PrBCO thickness for a series of multilayers with constant 12-Å YBCO layers.

Figure 4 shows resistive transitions in an applied field parallel to the Cu-O planes for the 50/50 alloy, the 12-Å/48-Å, 12-Å/12-Å, and 24-Å/24-Å multilayers, and, finally, a YBCO film on MgO. Our results show the evolution of the transitions in a parallel field as the coupling between Cu-O bilayers is varied, going from strongly coupled, YBCO and $(\mathrm{Y_{0.5}Pr_{0.5}})$BCO, to pro-

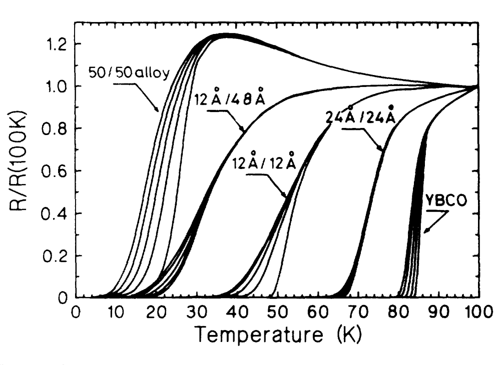

FIG. 4. Resistive transitions in field from left to right for the 50/50 alloy, the 12-Å/48-Å, 12-Å/12-Å, and 24-Å/24-Å multilayers, and YBCO film on MgO. The different curves are for 0, 1, 3, 6, and 9 T.

gressively decoupled YBCO layers, 12-Å/12-Å, 24-Å/24-Å, and 12-Å/48-Å multilayers. Qualitatively, the point on the $R(T)$ curve at which the curves in field separate moves from the onset of the transition towards the zero-resistance point as the coupling between the layers decreases. Our results also show that as the coupling decreases and the films become more two dimensional, their superconducting transitions become increasingly field independent. Furthermore, the 12-Å/12-Å and 24-Å/24-Å multilayers show a tendency towards saturation of the field dependence above 6 T, which may be an indication of a dimensional crossover in the upper critical field.[8] Note there that there could be a small misalignment ($<1°$) between the applied field and the CuO_2 planes. We estimate that a 1° misalignment would result, if present, in an additional broadening of 4% in the resistive transitions of YBCO and of the alloy (the anisotropy between $H_{c2\parallel}$ and $H_{c2\perp}$ is $\simeq 5$ for both), 9% for the 12-Å/12-Å multilayer (anisotropy $\simeq 10$), and 45% for the 24-Å/24-Å multilayer for which the anisotropy is at least 50. A perfect alignment would not markedly change Fig. 4, but these estimates indicate that the small broadening observed in the foot of the resistive transition for the 24-Å/24-Å multilayer could be even smaller.

Another interesting point is that the effect of a parallel field on the character of the resistive transition of the 12-Å/12-Å multilayer seems to be qualitatively similar to the effect of interposing thicker PrBCO layers. This can be seen in comparing the shape of the transition for the 12-Å/12-Å multilayer in a magnetic field to that observed in the 12-Å/48-Å multilayer in zero field. This happens certainly because the flux lines tend to be located between the YBCO layers. Finally, comparing the broadening of the transition due to the field observed for the various samples shown in Fig. 4, we note that there is no obvious increase in the transition width with increasing T_c, as would be expected in a thermally activated flux-flow model. A detailed analysis of the behavior of these films in a magnetic field will be presented in a forthcoming publication.

In conclusion, we have studied the superconductivity in multilayers containing ultrathin (12-Å or 24-Å) YBCO layers separated by 12 Å or more of insulating PrBCO layers. A linear reduction of T_c is observed with increasing thickness of the PrBCO layer, suggesting that a minimum interlayer coupling is necessary for superconductivity to occur in the individual 12-Å YBCO layers. The behavior seen in a magnetic field parallel to the layers demonstrates the increased decoupling of the layers as the PrBCO thickness is increased.

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