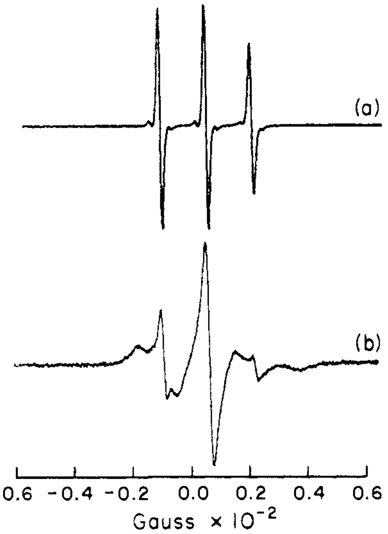

Figure 3. EPR spectra of (a) **1b** and (b) 5′-d(CGCGAATT*CGCG) (100 μM in duplex DNA, 100 mM NaCl, 10 mM phosphate, pH 7.0, 0.1 mM EDTA, 0 °C). In spectrum (b), the origin of the signal representing $\tau_r < 1$ ns (ca. 15%) which is superimposed upon the $\tau_r \approx 5$ ns signal is under investigation.

broadening[13] [T(5),T(6) > G(4) > G(3) > G(2)] which is anticipated based on the distance of these iminos from the two spin labels (see Figure 1). Reduction of the spin label (excess sodium dithionite) eliminates this differential line broadening effect.

On the basis of simple hydrodynamic considerations,[14] anisotropic tumbling in the 4–7 ns range is expected for an aqueous dodecamer duplex at 0 °C. The EPR spectra of **1b** and the spin labeled dodecamer are shown in Figure 3. As calculated from these spectra,[15] **1b** has a rotational correlation time (τ_r) shorter than 0.3 ns; in contrast, the labeled dodecamer has a τ_r of roughly 5 ns at 0 °C. That this τ_r is calculated from the EPR data without any correction for subnanosecond internal dynamics of the probe independent of the DNA[5] is a strong indication that the motion of the spin probe is well correlated with the motion of the DNA.

These studies unequivocally demonstrate (1) that the nitroxide moiety is compatible with phosphoramidite-mediated DNA synthesis, (2) that attachment of a bulky and hydrophobic nitroxide can be accommodated without disruption of DNA secondary structure,[16] and (3) that a nondisruptive spin probe can be sufficiently rigidly constrained to correlate its motion with that of the DNA to which it is attached. These findings provide a foundation for further DNA local dynamics studies in which this probe is incorporated into base sequences of biological relevance in much larger duplex DNAs. This probe should likewise find use in dynamics studies of other unusual DNA structures (i.e., hairpins, mismatches, bulges) and may have utility as a paramagnetic marker in structural studies of DNA by NMR. These studies are in progress, and the results will be reported in due course.

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Electronic Absorptions in the High T_c Superconductor $YBa_2Cu_3O_x$

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Superconductivity in metals and alloys has been well-explained by the theory of Bardeen, Cooper, and Schrieffer (BCS)[1] in which electrons are paired by a phonon-mediated, attractive interaction. The theory predicts the correct order of magnitude of the transition temperature, T_c, and a dependence of T_c on the isotopic mass of the metal. The recently-discovered ceramic superconductor,[2] $YBa_2Cu_3O_x$ with a T_c of 93 K and the virtual absence of an isotopic effect,[3,4] suggests the presence here of a different pairing mechanism. That an electronic *excit*ation (the *exciton* interaction) could provide such an interaction and give very high T_c's had been suggested previously.[5] It should be noted that the term "exciton" in the context of superconductivity does not refer to Frenkel or Wannier excitons. A strong electronic absorption has, in fact, been seen in reflectivity studies of polycrystalline samples of $YBa_2Cu_3O_x$[6] and the related compound $La_{2-x}Sr_xCuO_4$[7-9] at 0.37 and 0.5 eV, respectively. For $La_{2-x}Sr_xCuO_4$ the absorption strength varies with x in the same manner as does T_c. This suggested that an exciton interaction might be present. However, Bozovic et al.[10] found no such absorption peak in high quality, oriented films of $YBa_2Cu_3O_x$ and suggested that it was due to an impurity or surface artifact not related to superconductivity and thus did not provide evidence of an exciton interaction. Here we report spectroscopic studies of high-purity samples of $YBa_2Cu_3O_x$ as well as several impurity phases that we have identified as possible contaminants. We show that this low-lying electronic transition is characteristic of $YBa_2Cu_3O_x$, is not due to an impurity phase, and does correlate with T_c and then discuss its possible connection to an exciton interaction.

Sintered pellets of fully-oxygenated $YBa_2Cu_3O_7$ samples were prepared by standard ceramic techniques.[11,12] Oxygen-deficient samples were prepared by heating the fully-oxygenated sample under argon at elevated temperatures (500 °C for $x = 6.6$; 570 °C for $x = 6.4$; 700 °C for $x = 6.2$; 800 °C for $x = 6.0$) until the desired oxygen content was achieved and then slowly cooling to room temperature in the inert atmosphere. The oxygen content of these samples was measured gravimetrically. X-ray powder diffraction studies were performed on a Rigaku XRD instrument

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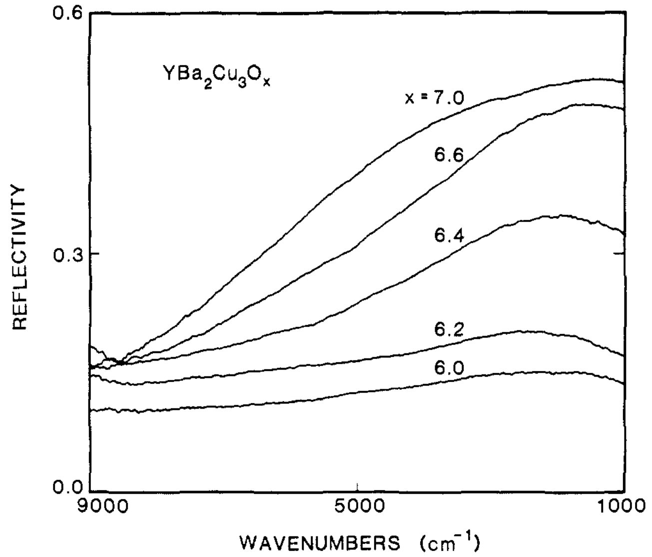

Figure 1. Reflectance spectra of $YBa_2Cu_3O_x$ for values for x between 6 and 7.

by using Cu Kα radiation. Spectroscopic studies were performed as described by Kamaras et al.[6] on an IBM 98 FTIR spectrophotometer. Impurity phases were prepared according to literature methods and were studied as above.[13,14] Four-point measurements were made of the resistivity.

The purity of the $YBa_2Cu_3O_7$ samples was estimated by X-ray powder diffraction to be in excess of 99% (the detection limit of our instrument). All lines in the pattern were indexed, and the cell constants were calculated in agreement with previously reported values.[15]

Reflectance spectra of a single $YBa_2Cu_3O_x$ pellet at several oxygen contents are presented in Figure 1. There is a broad electronic transition in the mid-to-near IR which decreases in intensity as x decreases from 7 to 6 and is restored upon reoxygenation. As it is unlikely that surface morphology will change appreciably or reversibly with oxygen content we believe that the feature is a bulk property. We also show that it is unlikely to be due to an impurity phase.

We have identified CuO, Y_2O_3, $BaCuO_2$, $Y_2Cu_2O_5$, Y_2BaCuO_5, and $BaCO_3$ as stable phases under the reaction conditions employed in the synthesis of $YBa_2Cu_3O_7$. We have measured the reflectance spectra of each of these compounds between 1000 and 9000 cm^{-1} and find no evidence of a low-lying electronic transition in any of them. It thus seems likely that the broad band is intrinsic to $YBa_2Cu_3O_7$. However, our observation does not rule out the possibility of absorption by a defect-like impurity generated in the oxygenation step.

In a recent paper, Orenstein and Rapkine[16] appear to resolve the discrepancy between the film and polycrystalline data. They show that reflection of light from a randomly oriented polycrystalline sample of a 2-D metal exhibits a shift in the free-electron (Drude-like) absorption to create a peak at higher energy. We are in essential agreement with this.

The structure of $YBa_2Cu_3O_7$ has been shown to be an orthorhombic, tripled perovskite consisting of Y sheets, Ba–O sheets, CuO_2 sheets, and CuO_3 ribbons.[17,18] As the material is deoxygenated, oxygen is removed from the ribbons, and the unit cell becomes tetragonal. The two-dimensional CuO_2 sheets remain intact and two-coordinate copper sites are formed[19,20] from the ribbons. The fully-oxygenated samples, $x = 7$, have T_c's above 90 K which decrease to 55 K at $x = 6.7$. Below $x = 6.5$, the materials become semiconducting and no longer superconduct. We believe the 2-D metallic behavior results from conduction in the sheets *and* along the chains but with limited movement along the *c*-axis perpendicular to the sheets.

In the BCS model, each electron near the Fermi energy is paired with another. This pairing results from a phonon–electron interaction in which momenta, ranging in value from near zero to about twice the Fermi momentum, is exchanged between the pair. We[21] have suggested that in $YBa_2Cu_3O_7$, the interactions between conduction electrons in the sheets is mediated by electronic excitations involving the ribbons rather than by phonons alone. These excitations involve finite momenta exchange just as for the phonon case.

Band structure calculations by Mattheiss et al.[22] suggest that the conduction electrons reside in the CuO_2 *sheets* in a partially filled band formed from the overlap of Cu $d_{x^2-y^2}$ orbitals with O_{p_x} and O_{p_y}. They also show that several bands formed from overlap of Cu and O orbitals on the CuO_3 *ribbons* straddle the Fermi level. Electronic particle-hole excitations within the CuO_3 ribbons can then couple electrostatically to the conduction electrons[19] in the sheets. This is what is meant by the exciton interaction.

The above excitations *cannot* be observed in direct optical transitions because of their finite momenta. They might be observed in phonon-assisted transitions but this would be weak and masked by the strong free-electron (Drude-like) absorption. They might be seen in highly disordered samples where the Fourier components of the disorder would allow the lattice to absorb the momentum or in high-resolution electron energy loss experiments where the scattered electron could accept the excess momenta. In the absence of such a direct observation, evidence for the existence of electrons *capable* of such excitations in the ribbons can be drawn from the free-electron contribution of the ribbons to the IR reflectance. This contribution is seen to decrease from $x = 7$ to $x = 6.5$ as oxygen is removed from the ribbons, leaving only that due to the sheets. The reflectance spectra we show is evidence of this contribution.

We argue that T_c is suppressed as oxygen is removed from the ribbons because of a breaking up of the 1D Cu–O dispersion curves[23] and an increase in the number of electrons at E_F. These two effects then serve to destroy superconductivity by filling the electronic excited states in the ribbons, thereby freezing out the motion of these electrons.

In summary, we have confirmed the presence in $YBa_2Cu_3O_x$ of a broad reflectance feature in the range 1000–9000 cm^{-1} and shown it to be reversibly dependent on the bulk oxygen content and thus not a surface phenomenon. We have also shown that this absorption is not due to impurity phases. Rather, it seems to be a free-electron absorption by quasi-free carriers in the ribbons. Such carriers could provide an exciton interaction which would explain the high T_c. We suggest that deoxygenation results in structural disruption of the ribbons and filling of the previously partially filled Cu–O bands, thus destroying the states required for high T_c superconductivity.

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