Substituting Y in orthorhombic \((Y, RE)Ba_2Cu_3O_7\) by any rare-earth element \(RE\) has generally little effect on the superconducting properties. For \(RE = Pr\), however, superconductivity is completely suppressed. To elucidate this effect we have studied the unoccupied electronic structure of \(Pr_xY_{1-x}Ba_2Cu_3O_7-y\) \((x = 0.0, 0.4, 0.8)\) by polarization-dependent \(O1s\) x-ray absorption spectroscopy on detwinned single crystals. Along with the comparison of undoped \((y \approx 0.9)\) to the doped materials \((y \approx 0.1)\), this allows a test of the current theoretical explanations for the suppression of superconductivity. While we can rule out models involving hole filling or charge transfer from planes to chains our data is consistent with approaches based on \(Pr4f-O2p_x\) hybridization.

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1. INTRODUCTION

Among the rare-earth-based cuprates that are isostructural to \(YBa_2Cu_3O_{7-\delta}\), the \(PrBa_2Cu_3O_{7-\delta}\) compound is an intriguing exception since it shows neither metallic nor superconducting behavior.\(^1\)\(^,\)\(^2\) Upon substituting \(Pr\) in the \(Pr_xY_{1-x}Ba_2Cu_3O_{7-\delta}\) system, the superconducting transition temperature \(T_c\) decreases\(^3\)\(^,\)\(^4\) and finally vanishes for \(Pr\) fractions \(x\)
beyond 0.55. This transition seems to be accompanied by a change from metallic to semiconducting characteristics.\(^4\)

Since Pr\(_{x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) has all the features that are considered essential for high-temperature superconductivity in YBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\), such as CuO\(_2\) planes, CuO\(_3\) chains, and apical oxygen atoms, differences in the electronic structure and in the distribution of holes between these structural units may reveal key parameters for high temperature superconductivity in REBa\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) and, therefore, might help to close in on the mechanism that underlies superconductivity. In order to explain the \(T_c\) suppression in the \(p\)-type system Pr\(_{x}\)Y\(_{1-x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\), up to now several models have been competing while still no general agreement on the Pr valence has been reached. The prevailing proposals can be divided into three main categories: (i) filling of initially delocalized holes in the CuO\(_2\) planes, (ii) magnetic interaction and/or localization effects mediated through hybridization of Pr\(_{4f}\) with O\(_{2p}\) states in the planes, and (iii) gradual hole transfer from the planes to the chains.

The aim of our investigation is to distinguish between the various models by carefully examining the electronic structure of Pr\(_{x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) close to the Fermi level. For this, we have conducted O\(_{1s}\) near-edge x-ray absorption fine structure (NEXAFS) studies of Pr\(_{x}\)Y\(_{1-x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\).

### 2. EXPERIMENTAL

We have grown Pr\(_{x}\)Y\(_{1-x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) single crystals using standard methods.\(^5\) For \(x = 0.0\) and 0.8, the samples were grown in an Y\(_{2}\)O\(_{3}\)-stabilized ZrO\(_{2}\) crucible while the Pr\(_{0.4}\)Y\(_{0.6}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) crystals were grown in a BaZrO\(_{3}\) crucible.\(^5\) Crystals with \(x = 0.0\) and 0.8 from the same batches were characterized by EDX and neutron diffraction for impurities, stoichiometry, and structural parameters. The oxygen content of Pr\(_{x}\)Y\(_{1-x}\)Ba\(_{2}\)Cu\(_{3}\)O\(_{7-\delta}\) (\(x = 0.8, 0.0\)) was determined to 6.91 ± 0.01. Oxygen deficient samples were obtained by annealing as-grown crystals of the same batch at 650 °C in a vacuum of about \(10^{-9}\) mbar for several days.

The O\(_{1s}\) absorption spectra were obtained using polarized synchrotron radiation from beamline U4B at the National Synchrotron Light Source, Brookhaven. Applying dipole selection rules, the unoccupied part of the O\(_{2p}\) final states can be reached from the initial O\(_{1s}\) core level. Therefore, polarization-dependent NEXAFS measurements on detwinned single crystals are a powerful method to distinguish whether the hole states have in-plane or out-of-plane orbital character in the CuO\(_2\) planes or if they are situated in the CuO\(_3\) chains. We have recorded our spectra in the fluorescence yield detection mode, using a multi-element Ge detector, to avoid surface sensi-