	Experiment title: XAFS Study of Superconducting $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$	<b>Experiment number:</b> <b>HE 1076</b>
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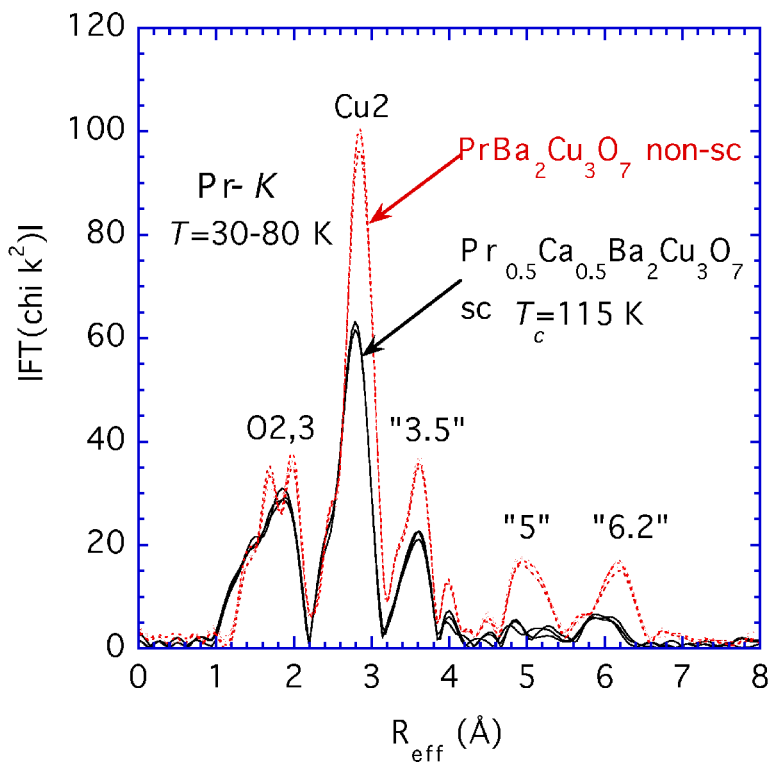
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## Report:

The absence of superconductivity in oxygen doped  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  (Pr-123) is a longstanding experimental and theoretical issue of the physics and chemistry of cuprate superconductors. However, cation doping of Pr-123, *e.g.* with  $\text{Y}^{3+}$  substituting  $\text{Pr}^{3+}$ , is well established to induce superconductivity. Also the partial substitution of  $\text{Pr}^{3+}$  with divalent  $\text{Ca}^{2+}$  was found to induce superconductivity, most recently in strongly doped bulk ceramics synthesized under high pressure [1].  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  exhibits  $T_{c\text{ onset}} = 115$  K, up to now the highest superconducting transition temperature in a lanthanide - 123 material.

We measured as a function of temperature (25 - 300 K) the *Pr K*- EXAFS (42 keV) of superconducting  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  with four different concentrations of calcium ( $x = 0.4, 0.5, 0.6$ ). Surprisingly the effect of different calcium concentrations on the EXAFS spectra turned out to be very weak. Measurements of two different preparations of  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_7$  ( $T_{c\text{ onset}} = 115$  K) yielded identical spectra. We checked carefully the effect of different background removal and normalization procedures on the low- $R_{\text{eff}}$  *nn* Pr-O<sub>2,3</sub> pair distribution functions (PDF). The analysis of the local atomic structure was performed using the FEFF6 code.

The comparison of the Fourier transforms spectra of superconducting  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  with those of nonsuperconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  is particularly instructive:



**Fig. 1** Fouriertransform spectra of the Pr *K* - EXAFS ( $k = 2 - 16 \text{ \AA}^{-1}$ ) in superconducting ( $\text{Pr}_{0.5}\text{Ca}_{0.5}$ )  $\text{Ba}_2\text{Cu}_3\text{O}_7$  (red stippled lines) compared to the Fouriertransform spectra of nonsuperconducting  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  (black drawn out lines). Several spectra between 30 and 80 K are co-plotted demonstrating the robustness of the normalization procedure. O2,3 and Cu2 indicate the *nn* and *nnn* shells of oxygen and copper in the planes, "3.5", "5", "6.2" multiple scattering (MS) configurations [2].

The PDFs of superconducting PrCa-123 and nonsuperconducting Pr-123 are significantly different. In superconducting PrCa-123 the prominent peak Cu2 (Pr-Cu2 pair) is dramatically decreased, and the high- $R_{\text{eff}}$  MS configurations at 5 Å ("5") and 6.2 Å ("6.2") are nearly completely wiped out. The strong reduction of the Cu2 peak is in line with our previous results from superconducting Y-123, also the broadened distribution of the *nn* Pr-O2,3 pairs. The suppression of the high- $R_{\text{eff}}$  peaks (governed by the nearly collinear MS paths Pr-O2,3-Ba, and Pr-Cu2-Ba) points to strong disorder in the "separating" Ba-O1(Apex) layers. Possibly a fraction of calcium atoms substitutes  $\text{Ba}^{2+}$  instead of  $\text{Pr}^{3+}$ , creates strongly disordered "separating" (Ba,Ca)-O1 layers, and thus destroys the collinearity of the three body scattering configurations around 5 Å and 6.2 Å. A subsequent EXAFS study of  $\text{Pr}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_7$  at the Ca *K*-edge (4 KeV) will yield the missing information on the possible occupation of the Ba-sites by calcium, and allow a combined analysis of the local structure in PrCa-123 from the Pr- and the Ca-EXAFS.

#### Literature:

- [1] Z.X. Zhao, K.Q. Li, G.C. Che, T. Homma, P.H. Hor, Physica C, Proc. M<sup>2</sup>HTSC 2000.
- [2] J. Röhler et al. in: NATO ASI E343, Kluwer Dordrecht, 1997, pp. 469-502.