

## Polarization-dependent XANES study of $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Pr}_x\text{Cu}_2\text{O}_{8-\delta}$ insulating single crystal

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Pr doping has been extensively studied in cuprate superconductors to understand the mechanism of quenching of superconductivity in cuprate perovskites. Experience has revealed that it acts differently in different cuprate perovskites. We have made high resolution polarization XANES measurements on a Pr-doped single crystal within the ab-plane on the Cu K and Pr L<sub>III</sub> absorption edges to ascertain the valence state of Pr cation and thereby try learning how it is quenching superconductivity in the present case. Our results show that besides the Pr quenching holes the possibility of its localizing some holes through hybridization with O 2p and Cu 3d cannot be ruled out.

**Keywords:** Pr-doped BSCCO, polarized XANES, hybridization, hole quenching.

### 1. Introduction

Of all the different dopings Pr doping has been most extensively studied in cuprate superconductors to understand the mechanism of quenching of superconductivity in them (e.g., S.Venkatesh et al-1996; M. Khaled et al- 1997). In different cuprates it appears to have a different mechanism for influencing their superconducting properties. When Y in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  [YBCO (123)] is replaced by Pr and Ce it suppresses T<sub>c</sub> finally turning it an insulating compound. Similar results are obtained when Ca in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  [BSCCO (2212)] is replaced by Pr. The Abrikosov-Gor'kov pair breaking mechanism (C. Quitmann et al (1992)) could not explain the localization of charge carriers resulting into insulating behaviour of the system. Later, it was proposed that the Pr cation may be quenching the holes (for example M. Khalid et al (1998,1997)). It was finally discovered that the valence of Pr stays 3+ in the YBCO (123) system and hence there can be no quenching of holes by it. Later on, it was suggested that the itinerant holes perhaps get localized as a result of the Pr 4f- O 2p hybridization (Y. Nishihara et al (1999) and Z. Zou et al (1998a)). This explanation appears to have received wide acceptance. More recently, S. Gurman et al (1999) have concluded from their EXAFS study of Pr-doped YBCO (123) that there are two Pr-O distances in the lattice. With increase in Pr concentration the distances do not change but the statistical weight of the shorter distance goes on increasing. This may imply the presence of some local distortion in the lattice and the possibility that the Pr cation may occupy two different sites. Z. Zou et al (1998) have announced the synthesis of a superconducting pure  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Pr123) crystal. Very recently, V.N. Narozhnyi et al (1999) have from their magnetic susceptibility studies claimed that the superconductivity in Pr123 system perhaps derives from the fact

that only about one half of the nominal concentration of Pr occupies the Y-site and the other half vacancies are probably filled by non-magnetic Ba cation. There does seem to be no early end to the story of mysterious behavior of the Pr cation.

As far as BSCCO (2212) system is concerned it is highly anisotropic with a very large anisotropic ratio (R. Busch et al (1992)) which means that  $\text{CuO}_2$  interlayer coupling is very weak in it. Since Ca is located at the center of the  $\text{CuO}_2$  bilayer, the Pr substitution for Ca is likely to destroy the local superconductivity of the  $\text{CuO}_2$  block and also strongly affect the interlayer coupling. Moreover with Pr 3+ replacing Ca 2+ it will evidently lead to quenching of the holes and eventually turn the system insulating. In view of the above facts the role of Pr in the BSCCO (2212) system may not be as simple and straightforward as it is made out to be. It is for this reason that we have conducted the present study on the Pr-doped BSCCO (2212) insulating single crystal to further study the mechanism of quenching by Pr and any anisotropy or local distortion in the  $\text{CuO}_2$  plane of this system. Our results give an indication that Pr 4f hybridization with O 2p and Cu 3d orbitals may also be active alongside quenching of the holes by Pr.

### 2. Experimental

The pristine  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  and the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_{8-\delta}$  were grown by the usual flux method through the process of solid state fusion. These were then characterized by XRD and the c-axis lattice parameters obtained by least square fitting analysis of the (001) XRD reflection peaks. The c-axis length turned out to be 30.584 Å for the pristine crystal and 30.357 Å for the Pr-doped system. The values are identical to those reported by X. F. Sun et al (1999). The Pr-doping content analyzed by electron probe micro analysis (EPMA) turned out to be consistent with the nominal composition  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_{8-\delta}$  within the experimental error. Temperature dependent (DC) magnetic susceptibility for Pr-doped crystal was also measured by the SQUID magnetometer. For this a DC magnetic field of 20 gauss was applied parallel to the c-axis (Fig.1).

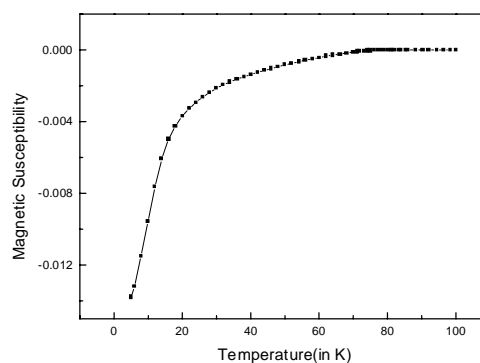


Fig.1:- Temperature dependent DC magnetic susceptibility measurement by SQUID with a DC magnetic field of 20 Gauss applied parallel to the c-axis

The polarized Cu K and Pr L<sub>III</sub> absorption edge measurements were made at SRRC, Taiwan at the BL 17 C (wiggler-C) beamline employing fluorescence detection in an array of nine detectors and yielding a resolution of ~0.5 eV at the Cu-K edge. We have carried out this study using polarized X-ray absorption spectroscopy method to measure the Pr L<sub>III</sub> and the Cu K-edges in different orientations. However, because of the paramount importance of the  $\text{CuO}_2$  plane to superconductivity we have confined over orientation dependence to within the ab plane- E//a, E//b and E//a<sup>45</sup>.

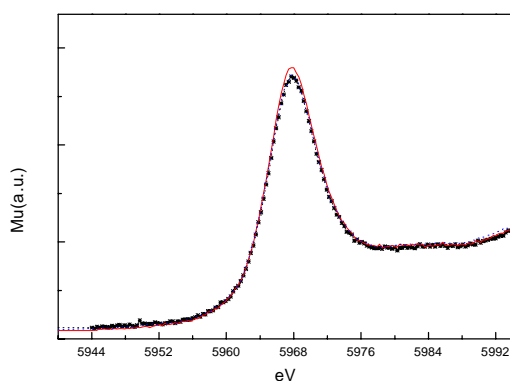
### 3. Results and Discussion

Figures 2 and 3 show the background corrected and normalized polarized XANES spectra of Pr  $L_{III}$ - and Cu K-edges respectively from a Pr-doped  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_{8-\delta}$  insulating single crystal. The three spectra in each case pertain the  $E\sim//a$ ,  $E\sim//b$  and  $E\sim45^\circ$  orientations. The energy positions of the various fine structures including to the absorption edge for the Cu K XANES as determined from the first and second derivatives of the corresponding spectra are shown in table 1.

**Table 1:** Energy (eV) of absorption edge and of various features in the Cu K edge spectra

Polarization	P	A	$E_0$
$E\sim//a$	8977.10	8982.43	8989.3
$E\sim//a^{45}$	8977.86	8982.21	8993.2
$E\sim//b$	8977.33	8982.21	8989.3
Polarization	$B_1$	$B_2$	$B_3$
$E\sim//a$	8992.98	8994.59	8998.17
$E\sim//a^{45}$	9000.57	8994.80	9002.22
$E\sim//b$	8993.43	8994.80	8998.55

Looking at the Pr  $L_{III}$  spectra in figure 2 for the three orientations of the electric vector but for a very small increase in the intensity of the white line for the  $E\sim//a^{45^\circ}$  case we find that the spectra are almost identical. The change is too small to warrant any significance. However, the more interesting aspect of this spectrum is the huge one component white line arising from  $2p\rightarrow 5d$  hole transition. This unambiguously points out the Pr being in a univalent  $3+$  state. Its absorption and peak energy values also support this conclusion. In a mixed valence state  $3+$  and  $4+$  the white line of Pr is a two component peak (A. Bianconi et al., (1987)). Also, compared to above mixed valence spectrum the absorption edge does not show any fine structure at all, which may mean that Pr replaces Ca in the lattice and has likewise an isotropic environment. Both the single peaked structure of the  $L_{III}$  white line as well as near total absence of any fine structure on the edge tend to strongly indicate that almost all of Pr occupies the Ca-site.

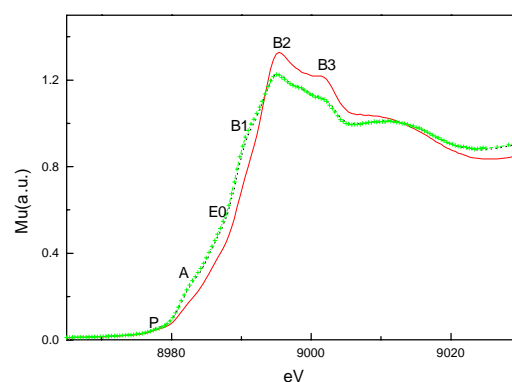


**Fig 2** Polarised Pr  $L_{III}$  edge in  $E\sim//a$  [\*\*\*],  $E\sim//b$  [.....] and  $E\sim//a^{45}$  deg [solid line] orientations from  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_{8-\delta}$  single crystal.

Turning our attention to Cu K spectra in figure 3, one cannot fail to notice a lot of fine structure on the absorption edge and a shift in their position with orientation. Of the three spectra two pertain to the polarization  $E\sim//a$  (dotted) and  $E\sim//b$  (dashed) while the third (solid line) corresponds to  $E\sim//a^{45^\circ}$ . In other words, the first two correspond to the Cu-Cu direction and the third to the Cu-O-Cu direction in the plane. The Cu K spectra show all the characteristic features observed in cuprates with a square planer geometry. Let us

first confine our attention to the dramatic behavior of the changes in spectra with polarization.

From figure 3 and table 1 one can immediately see the shift of absorption edge of  $\sim +3.9$  eV in  $E\sim//a^{45}$  case. What is more astonishing is that the main peak  $B_2$  does not show any appreciable shift which implies that the absorption edge is rising more sharply in the Cu-O-Cu case. Also, one does not notice any significant changes in the energy position of the other XANES peak. The shift of the absorption edge may probably indicate a higher valence for Cu in this orientation due to proximity of O ions with doping holes in this direction. It is also worthy of note that the  $E\sim//a$  and  $E\sim//b$  spectra are almost identical in all respect. Saini et al (1998) in their report on similar study on pristine superconducting BSCCO (2212) at 30 K do not observe any such edge shift. The shift in the present case must therefore owe its origin to the presence of Pr cation. The whole spectrum gives the feeling as if the presence of higher valent Pr cation is tightly squeezing the bound states into a smaller energy span since no change is observed in energy position of either the quadrupole pre-peak or the main peak  $B_2$  in these spectra



**Fig 3** Polarised Cu K-edge in  $E\sim//a$  [.....],  $E\sim//b$  [---] and  $E\sim//a^{45}$  deg. [solid line] orientations from  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Pr}_{0.6}\text{Cu}_2\text{O}_{8-\delta}$  single crystal.

The pre-edge peak P due to dipole forbidden but quadrupole allowed transition is clearly seen in all the three spectra. As can be seen from table 1 its position changes only slightly in the three spectra. From figure 3 it can be noticed that the intensity of the pre-peak  $1s\rightarrow 3d_{x^2-y^2}$  transition is slightly greater in the  $E\sim//a$  and the  $E\sim//b$  cases as compared to the  $E\sim//a^{45}$  case. This transition probability varies with  $\sin^2\theta$ , where  $\theta$  is the angle between the photon electric field and the Cu-O bond when no structural distortion is present in the plane (J.E. Hahn et al (1982); A.V. Narlikar et al (1999)). It implies therefore that its intensity should be maximum in the  $E\sim//a$  and the  $E\sim//b$  geometry in the present case and should be nearly zero in the  $E\sim//a^{45}$  degree. Since it is very much present in our spectrum in this direction also there may be local distortions present in the ab plane in the system. However, one cannot rule out a small possible contribution from vibrationally coupled dipole transition due to phonons getting excited in the absorption process. Unlike Saini et al (1998) we also observe a significant change in the intensities of the multiple scattering peaks  $B_2$  and  $B_3$ . Besides these  $E\sim//a$  and  $E\sim//b$  reveal another shoulder  $B_1$  just below the main peak  $B_2$ .

### 4. Conclusions

Of course, substitution of Pr for Ca quenches superconductivity in the BSCCO (2212) system. Our results indicate that Pr is in  $3+$  valence state and is in all probability occupying the Ca site and

hence it must be quenching itinerant holes. However, the significant shift observed in the Cu K-edge and presence of the pre-peak in Cu-O-Cu direction suggest local distortion in the CuO<sub>2</sub> plane due to presence of Pr in the lattice and the possibility of Pr 4f hybridization with O2p and Cu 3d orbitals.

### 5. Acknowledgement:

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### References

- Bianconi, A., Davoli, I., Della Longa, S., Garcia, J., Garg, K.B., Kotani, A. & Marcelli, A. (1987). Theoretical and Experimental aspects of valence fluctuation and heavy fermions; Ed. Gupta, L.C. & Malik, S.K. : Plenum, pp.243-251.
- Busch, R. (1992). Phys. Rev. Lett. **69**, 522-525
- Gurman, S., Amiss, J., Venkatesh, S., Singhal, R.K. & Garg, K.B., (1999) J. Phys. Cond. Matter **11**, 1847-53
- Hahn, J. E., Scott, R.A., Hodson, K.O., Doniach, S., Desjardins, S.R. & Solomon, E.I. (1982). Chem Phys. Lett. **88**, 595-98
- Khaled, M., Saini, N.L., Gurman, S.J., Amiss, J.C. and Garg, K.B., (1997) J. de Physique IV (France) **7**, C2 1121-1122.
- Narlikar, A.V., Gupta, A., Samanta S.B., Chen, C., Hu, Y., Wondre, F., Wanklyn, B.M. & Hodby, J.W. (1999). Phil. Mag. B **79**, 717-728.
- Naroznhyi, V.N., Eckert, D., Fuchs, G., Nenkov, K., Uvarova, T.G., & Muller, K.-H. (1999) arXiv:cond.mat/9909110, 1-2.
- Nishihara, Y., Zou, Z., Ye, J., Oka, K., Minawa, T., Kawanaka, H. & Bando, H. (1999). Bull. Mater. Sci. **22**, 257-263.
- Quitmann C. et al., (1992) Phys. Rev. B **46**, 11813-816
- Saini, N.L., Lanzara, A. & Bianconi, A., (1998) Phys. Rev. B **58**, 11768-11773.
- Sun, X.F., Zhao, X., Li, X.-G. & Ku, H.C. (1999). Phys. Rev. B **59**, 8978-8983.
- Venkatesh, S., Khaled, M., Saini, N.L., Studer, F. and Garg, K.B., (1996) Solid State Commun. **100**, 773-77
- Zou, Z., Oka, K., Ito, T. & Nishihara, Y. (1997). Jpn. J. Appl. Phys. **36**, L 18- 23
- Zou, Z., Ye, J., Oka, K., Ito, T. & Nishihara, Y. (1998). Phys. Rev. Lett. **80**, 1074-1077.