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# OXIDATION STATES OF THE "UNUSUAL" RARE EARTHS (R=Ce, Pr AND Tb) IN DOUBLE LAYER HIGH-T<sub>c</sub> SUPERCONDUCTORS

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**Abstract.** X-ray absorption and magnetization experiments are used to describe the oxidation states of the rare earths R=Ce, Pr and Tb in the double layer high-T<sub>c</sub> superconducting series  $\text{RBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$ . We obtained the same oxidation states for the rare earths in these two classes of compounds, namely, R=Ce tetravalent and R=Pr and Tb trivalent.

## 1. INTRODUCTION

It is well known that the compounds  $\text{RBa}_2\text{Cu}_3\text{O}_7$  (R=Y or rare earth) are superconducting below 92 K, except for the rare earth R=Ce, Pr or Tb. The reason for each exception is different.  $\text{PrBa}_2\text{Cu}_3\text{O}_7$  forms as a "single phase" material but does not superconduct [1]. Neither Ce nor Tb form this phase. For small doping concentrations Ce suppresses superconductivity in a manner similar to Pr whereas Tb does not influence T<sub>c</sub> at all [2]. It is interesting to note that all these three rare earths are redox active, and can be found in their trivalent and tetravalent oxidation states in nature. R=Ce has the lowest redox potential and therefore is expected to have the most stable tetravalent oxidation state. R=Pr and Tb have similar redox potentials and therefore may be expected to have the same oxidation state within a given structural series. However, the Pr 4f wave functions are far more extended than those of Tb and therefore both hybridization with higher shells and bonding effects are more likely for the Pr ions.

The double layer high-T<sub>c</sub> superconductors  $\text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$  form single phase compounds for all the rare earths, including Ce and Tb. The Pr and Tb analogs are both superconducting, whereas the Ce analog is not [3,4]. In addition to its superconductivity, the R=Tb analog also exhibits unusual magnetic properties [5].

Here we present X-ray absorption and susceptibility results comparing the oxidation states of Ce, Pr and Tb in the  $\text{RBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$  series.

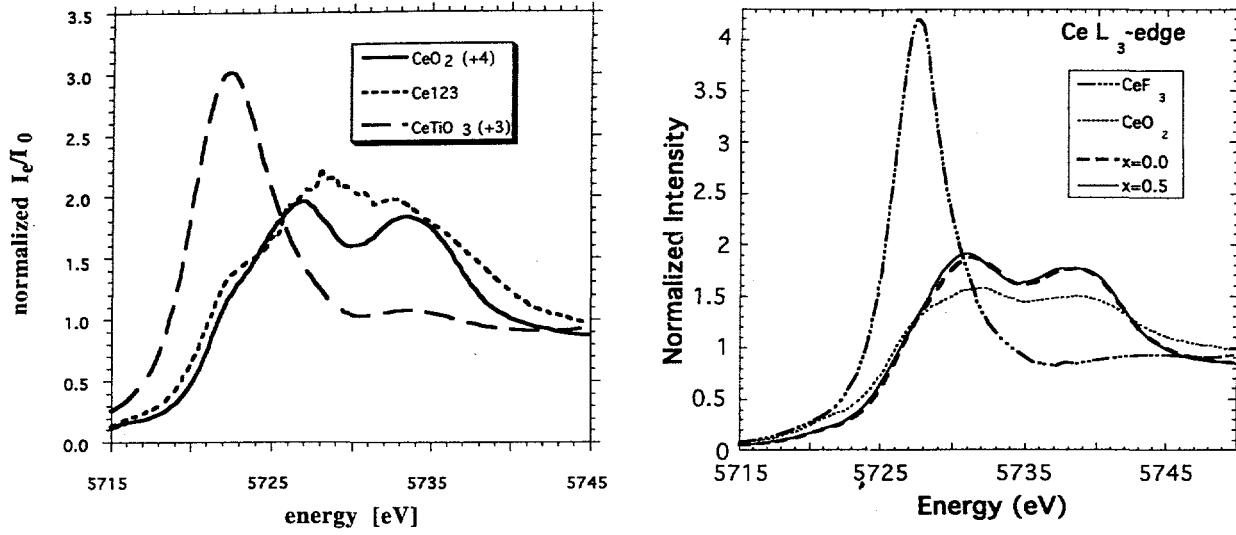
## 2. EXPERIMENTS

Polycrystalline samples for both series were prepared by standard sintering techniques. The single phase character of the samples was checked by X-ray powder diffraction and/or by neutron powder diffraction. R L<sub>3</sub>-edge X-ray absorption near edge structures (XANES) were collected at ambient temperature on beam line X-23A2 at the National Synchrotron Light Source (NSLS) and on the wiggler beam line 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL). X-23A2 at the NSLS is equipped with a Si<311> double-crystal monochromator ( $\Delta E/E=2.9 \times 10^{-5}$ ) and the beam line 4-1 at SSRL is equipped with a Si <111> double-crystal monochromator that gives an energy resolution of  $14.1 \times 10^{-5}$ . The magnetic susceptibilities were obtained from a superconducting quantum interference device (SQUID) magnetometer over the temperature range 10 to 300K using an applied field of 500 Oe.

## 3. RESULTS AND DISCUSSION

### 3.1 Ce doped compounds

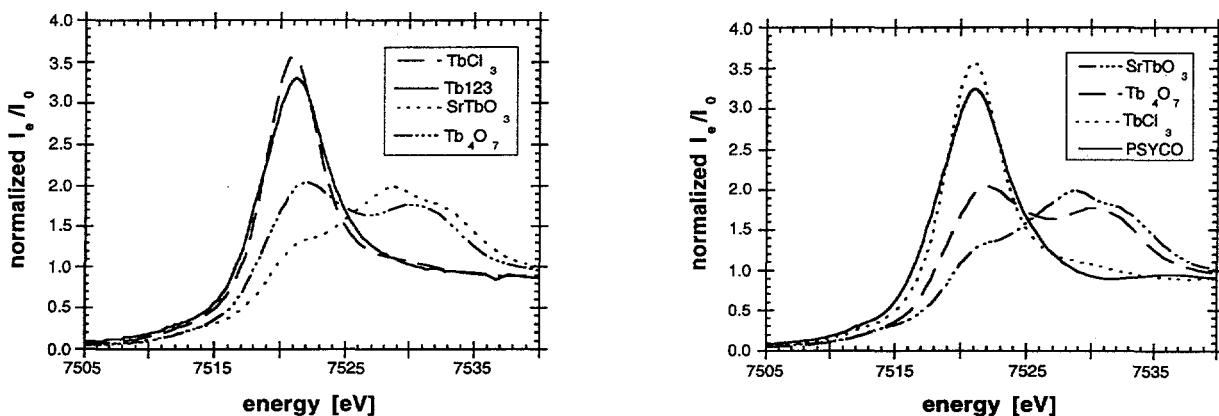
Figs. 1a and b show the measured L<sub>3</sub> X-ray absorption edges obtained from Ce in  $\text{Ce}_{0.2}\text{Y}_{0.8}\text{Ba}_2\text{Cu}_3\text{O}_7$  (a) and  $\text{Pb}_2\text{Sr}_2\text{Ce}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  (b) compared with trivalent  $\{\text{Ce}^{3+}\text{TiO}_3$  (a);  $\text{Ce}^{3+}\text{F}_3$  (b) and a tetravalent  $(\text{Ce}^{4+}\text{O}_2)$  standards. The L<sub>3</sub>-edge for the tetravalent oxidized Ce is composed of at least three transitions, as can be seen from the tetravalent standard [6]. The fingerprint of a trivalent oxidation state of Ce would be a single line at lower energies. Hence, in contrast to the other rare earth incorporated in these double layer perovskites, Ce is in a tetravalent oxidation state in both  $\text{RBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$  series. This is also confirmed by susceptibility results (not shown), where no effective magnetic moment is observed except the contributions from the Cu spins indicating no unpaired 4f electrons in both compounds.



**Figs. 1a and b:** Ce L<sub>3</sub>-edge XANES of  $\text{Ce}_{0.2}\text{Y}_{0.8}\text{Ba}_2\text{Cu}_3\text{O}_7$  (Ce123),  $\text{CeTiO}_3$  and  $\text{CeO}_2$  (left) and  $\text{Pb}_2\text{Sr}_2\text{Ce}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$  ( $x=0$  and 0.5),  $\text{CeF}_3$  and  $\text{CeO}_2$  (right) obtained through electron-yield detection at ambient temperature.

### 3.2 Tb doped compounds

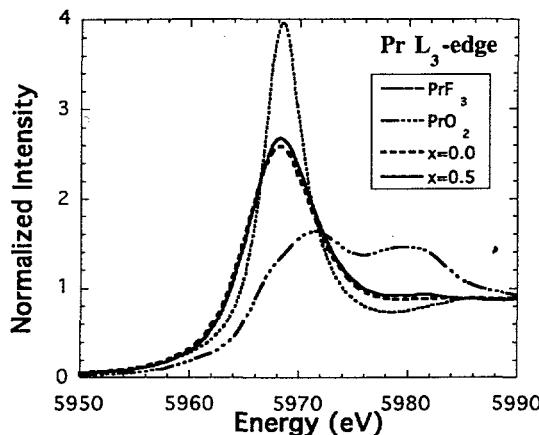
Figs. 2a and b show the measured L<sub>3</sub> x-ray absorption edges obtained from Tb in  $\text{Tb}_{0.1}\text{Y}_{0.9}\text{Ba}_2\text{Cu}_3\text{O}_7$  (a) and  $\text{Pb}_2\text{Sr}_2\text{TbCu}_3\text{O}_8$  (b) compared with trivalent Tb in  $(\text{Tb}^{3+}\text{Cl}_3)$ , a mixed valent standard ( $\text{Tb}_4^{3.5+}\text{O}_7$ ) and a tetravalent standard ( $\text{SrTb}^{4+}\text{O}_3$ ). The L<sub>3</sub>-edge in the tetravalent oxidized Tb is composed again of at least three transitions, two strong ones in the mixed-valent compound as can be seen from the standards. The fingerprint of trivalent Tb is a single line at lower energies. Hence, Tb is in a trivalent oxidation state in both the  $\text{RBa}_2\text{Cu}_3\text{O}_7$  and  $\text{Pb}_2\text{Sr}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_8$  compounds. This is also confirmed by the susceptibility results (not shown), where an effective magnetic moment of  $9.7 \mu_B$  is observed, which is very close to the value expected for trivalent Tb.



**Figs. 2a and b:** Tb L<sub>3</sub>-edge XANES of  $\text{Tb}_{0.1}\text{Y}_{0.9}\text{Ba}_2\text{Cu}_3\text{O}_7$ ,  $\text{TbCl}_3$ ,  $\text{Tb}_4\text{O}_7$  and  $\text{SrTbO}_3$  (left),  $\text{Pb}_2\text{Sr}_2\text{TbCu}_3\text{O}_8$ ,  $\text{TbCl}_3$ ,  $\text{Tb}_4\text{O}_7$  and  $\text{SrTbO}_3$  (right) obtained through electron-yield detection at ambient temperature.

### 3.3 Pr doped compounds

Fig. 3 shows the measured  $L_3$  X-ray absorption edges obtained from Pr in  $Pb_2Sr_2Pr_{1-x}Ca_xCu_3O_8$  compared with a trivalent Pr in  $(Pr^{3+}F_3)$  and a tetravalent Pr standard  $(Pr^{4+}O_2)$ . The  $L_3$  edge in the tetravalent oxidized Pr is composed of at least two transitions as can be seen from Fig. 3. The fingerprint of a trivalent oxidation state of Pr is a single line at lower energies. Hence, Pr is in a trivalent oxidation state in the  $Pb_2Sr_2R_{1-x}Ca_xCu_3O_8$  structure. Here, we did not show any results on  $PrBa_2Cu_3O_7$ , because these XANES results are published in the literature [7, 8]. The susceptibility results (not shown), are consistent with an observed effective magnetic moment of  $2.7 \mu_B$ , intermediate between the free-ion expectation values for trivalent and tetravalent Pr. However, this intermediate moment is well understood in terms of the crystalline electric field interaction, which splits the  $^3H_4$  ground-state of the trivalent Pr ions [9].



**Fig. 3:** Pr  $L_3$ -edge XANES of  $Pb_2Sr_2Pr_{1-x}Ca_xCu_3O_8$ , ( $x=0, 0.5$ )  $PrF_3$  and  $PrO_2$  obtained through electron-yield detection at ambient temperature.

### 4. CONCLUSIONS

We present XANES and susceptibility results on the "exceptions" Pr, Ce and Tb in the two superconducting series  $RBa_2Cu_3O_7$  and  $Pb_2Sr_2Pr_{1-x}Ca_xCu_3O_8$ . These results strongly indicate that Ce is tetravalent in both series whereas Pr and Tb are both trivalent. The tetravalent oxidation state of Ce explains why superconductivity is suppressed upon Ce doping (reduction of the carrier concentration) and also explains why  $CeBa_2Cu_3O_7$  does not form. The trivalent oxidation state of Tb is in accordance with the fact that  $T_c$  is not suppressed upon Tb doping. The reason why  $TbBa_2Cu_3O_7$  does not form lies in the chemical stability of the  $TbBaO_3$ , which is formed during the normal solid state reaction [10]. For Pr, which is also in the trivalent oxidation state, the much more extended 4f wave functions (compared to Tb) allow hybridization with the  $CuO_2$  bands, which effectively suppresses superconductivity.

### ACKNOWLEDGMENT

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- 1 L. Soderholm, K. Zhang, D. G. Hinks, M. A. Beno, J. D. Jorgenson, C. U. Segre, and I. K. Schuller, *Nature* **328**, 604 (1987).
- 2 C. R. Fincher, Jr., and G. B. Blanchet, *Phys. Rev. Lett.* **67**, 2902 (1991).
- 3 U. Staub, L. Soderholm, S. Skanthakumar, and M. R. Antonio, *Phys. Rev. B* **52**, 9736 (1995).
- 4 S. Skanthakumar and L. Soderholm, *Phys. Rev. B* **53**, 920 (1996).
- 5 U. Staub, L. Soderholm, S. Skanthakumar, S. Rosenkranz, C. Ritter, and W. Kaguny, *Europhys. Lett.* **34**, 447 (1996).
- 6 M. Gasgnier, G. Schiffmacher, L. Albert, P. E. Caro, H. Dexpert, J. M. Esteva, C. Blancard, and R. C. Karnatak, *J. Less-Common Met.* **156**, 59 (1989).
- 7 F. W. Lytle, G. v. d. Laan, and R. B. Greegor, *Phys. Rev. B* **41**, 8955 (1990).
- 8 E. E. Alp, L. Soderholm, G. K. Shenoy, D. G. Hinks, B. W. Veal, and P. A. Montano, *Physica B* **150**, 74 (1988).
- 9 U. Staub, S. Skanthakumar, L. Soderholm, and R. Osborn, *J. Alloys Compds.* (to be published).
- 10 U. Staub, M. R. Antonio, L. Soderholm, M. Guillaume, W. Hengeler, and A. Furrer, *Phys. Rev. B* **50**, 7085 (1994).