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L_3-x-ray absorption spectroscopy is used together with inelastic neutron scattering and magnetic susceptibility measurements to characterize the Tb oxidation state and bonding in the high-T_c related materials $Y_{1-x}Tb_xBa_2Cu_3O_7$ and $Pb_2Sr_2TbCu_3O_8$. The Tb is found to be essentially trivalent in both compounds with no indications of significant hybridization. However, there is evidence of significant Tb-Tb magnetic interactions in $Pb_2Sr_2TbCu_3O_8$ that persist to temperatures much higher than the Tb long-range ordering temperature.

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INTRODUCTION

$RBa_2Cu_3O_7$ (R=rare earth) was the first series of compounds for which it was discovered that a diamagnetic ion (Y) could be replaced by a magnetic rare earth without influencing the high T_c superconducting properties [1]. It was noted at the time that there were three R-ions that could not be substituted to produce a superconductor; Ce, Pr and Tb. Interestingly, these are also the three R ions that have an accessible tetravalent state, and are sometimes found as R^{4+} in the solid state. As a result of this correlation between samples that were not superconducting, and the presence of an ion with a stable tetravalent state, it has been argued that superconductivity is destroyed in these cases by an *in situ* redox reaction of the form [2];

$$R^{3+}Ba_2Cu_3^{2.3+}O_7 \rightarrow R^{4+}Ba_2Cu_3^{2+}O_7.$$

There has been a variety of studies centered on this hypothesis. Taken as a whole, a wide range of studies on the R=Pr analogue strongly suggest that this mechanism is incorrect [3, 4] and the Pr ion appears to be essentially trivalent. The suppression of superconductivity is then associated with a more complex interaction involving the Pr-localized f-states and the CuO conduction electrons [5, 6].

There has been considerably less work done on the roles of Ce and Tb in suppressing T_c. At least in part, this is because the Ce and Tb do not from isostructural analogues of the $RBa_2Cu_3O_7$ series. However, a comparative study of partially substituted $Y_{1-x}R_xBa_2Cu_3O_7$ thin film samples, made by *in situ* laser ablation, revealed that Tb does not behave in the same manner as Ce or Pr [7] when it is incorporated into a superconducting phase. Whereas the partial substitution of Pr or Ce have detrimental effects on sample conductivity and superconductivity, Tb was found to substitute for Y up to $x \approx 0.75$ without deliterious effects on either the normal state conductivity or the superconducting critical temperature. On the other hand, Ce and Pr both increase resistivity in the normal state and monotonically decrease T_c with increasing x. In this manuscript we report on our efforts to understand further the role of Tb in influencing the conducting and magnetic properties of high-T_c related materials.

We have chosen to look at $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$ and $Pb_2Sr_2TbCu_3O_8$. We chose the small doping level for the former compound because it has been found that samples made by conventional, solid-state synthetic techniques are multiphase when Tb replaces more than 20% of the Y. The 10% doping level is well below the saturation limit, and therefore we should be able to look at Tb in the compound of interest, and not in an impurity phase. $Pb_2Sr_2TbCu_3O_8$ was chosen because it is the parent of the superconductor $Pb_2Sr_2Tb_{0.5}Ca_{0.5}Cu_3O_8$ that shows resistivity and superconductivity behaviours that are in line with the other R-members of the series [8]. We have chosen to look at these materials by x-ray absorption near edge spectroscopy (XANES), inelastic neutron scattering (INS) and magnetic susceptibility in order to quantify the oxidation state of Tb in these compounds, to look for any evidence of the f-state interactions that were observed in the INS spectra obtained from $PrBa_2Cu_3O_7$ [9], and to investigate any Tb-Tb interactions similar to those seen in $HoBa_2Cu_3O_7$ [10].

EXPERIMENTAL SECTION

Samples were prepared by standard, solid-state techniques [11, 12]. Neutron and x-ray diffraction data show the samples to be single phase. Tb L_3-edge data were collected at ambient temperature on beamline X23-A2 at the National Sychrotron Light Source. This beamline is equiped with a Si <311> double-crystal monochromator to provide both good energy resolution and effective harmonic rejection of the second-order Bragg reflections. The experiments were performed in the electron-yield mode to minimize sample thickness effects. Inelastic neutron scattering experiments were carried out on the High-Resolution-Medium-Energy Chopper Spectrometer (HRMECS) at the Intense Pulsed Neutron Source (IPNS) located at Argonne National Laboratory. The incident neutron energy was 80 meV. The raw data are corrected for detector efficiency and background by standard procedures. The magnetic susceptibility was measured as a function of temperature using a 5 Tesla SQUID magnetometer. Further details are outlined elsewhere [13].

RESULTS AND DISCUSSION

The Tb L_3-edge X-ray absorption near edge structure (XANES) for the superconductor $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$ and $Pb_2Sr_2TbCu_3O_8$ are compared to those obtained from samples with Tb in well defined trivalent and tetravalent oxidation states. As can be seen from Figure 1a, the energy position of the resonant "white line" and the overall edge shape together establish that Tb is essentially trivalent. Similar results are shown in Figure 1b for Tb in $Pb_2Sr_2TbCu_3O_8$.

A close inspection of the data in Figure 1 reveals that the white-line feature at the Tb edges of the data obtained from the superconductor-related materials are slightly broader than those obtained from the trivalent standard $TbCl_3 \cdot 6H_2O$. In order to determine if this broadening is structural in nature or whether it is an indication of significant Tb hybridization, we performed a similar experiment on $ErBa_2Cu_3O_7$ [11]. We chose the Er analogue because it has been extensively studied and there has been no indication that the Er is hybridizing, or in any way interacting with the CuO states to influence the superconducting properties. Therefore, any broadening of the Tb over the Er white-line may suggest some type of Tb - CuO hybridizaiton or bonding effects that may influence superconductivity. However, we see a similar broadening in the Er data obtained from $ErCl_3 \cdot 6H_2O$ relative to those obtained from $ErBa_2Cu_3O_7$. From this result we conclude that there is no evidence from XANES data for any significant bonding or hybridization that may interfere with the CuO superconductivity.

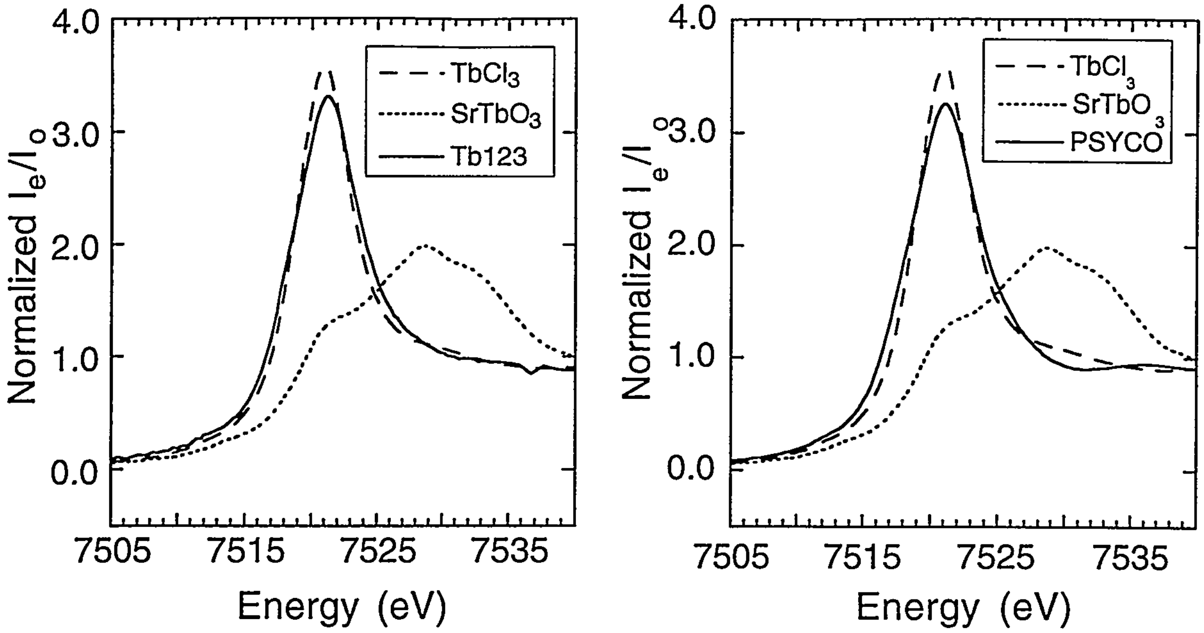

Figure 1: The Tb L3 edge XANES spectra of (a) $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$ and (b) $Pb_2Sr_2TbCu_3O_8$ (PSYCO) are compared with representative trivalent ($TbCl_3 \cdot 6H_2O$) and tetravalent ($SrTbO_3$) standards. These data are used to conclude that Tb is trivalent in the superconductor-related materials.

Having established that Tb is essentially trivalent in these two materials, it is then possible to use previously established trends in crystal-field splittings of rare-earth ground multiplets established across the R series in $RBa_2Cu_3O_7$ [9] to predict the energy splittings and inelastic neutron scattering data expected for our sample containing 10% Tb in $YBa_2Cu_3O_7$. This analysis indicates that we have neither the resolution nor the flux available to collect useful data on this sample. However, similar calculations based on the crystal-field established for the isostructural compounds $Pb_2Sr_2RCu_3O_8$ (R = Ho, Er) [14] indicate that there are magnetic transitions that should be observable in INS data from this compound. Whereas the Tb sits in a site with relatively low symmetry [15], the oxygen near neighbours have tetragonal symmetry. The Tb^{3+} J=6 multiplet should be split into three doublets and 7 singlets in tetragonal symmetry. The results from such an experiment are shown in Figure 2. There are three transitions between crystal-field states observable in the data, at 30, 37, and 60 meV. The magnetic origin of these tranistions is confirmed by their decreasing intensity with increasing momentum transfer Q of the neutrons (not shown).

The observation of magnetic transitions in this energy range provide clear, confirming evidence that Tb is trivalent in this compound because tetravalent Tb (f^7) has no orbital moment (L=0) and therefore the J=7/2 ground-multiplet is not significantly split by the crystal field. In addition, the magnetic lines shown in Figure 2 are not broadened, as was the case for the magnetic transitions in $PrBa_2Cu_3O_7$ [9], where the broadening has been attributed to hybridization of the f-states with the CuO conduction states [6].

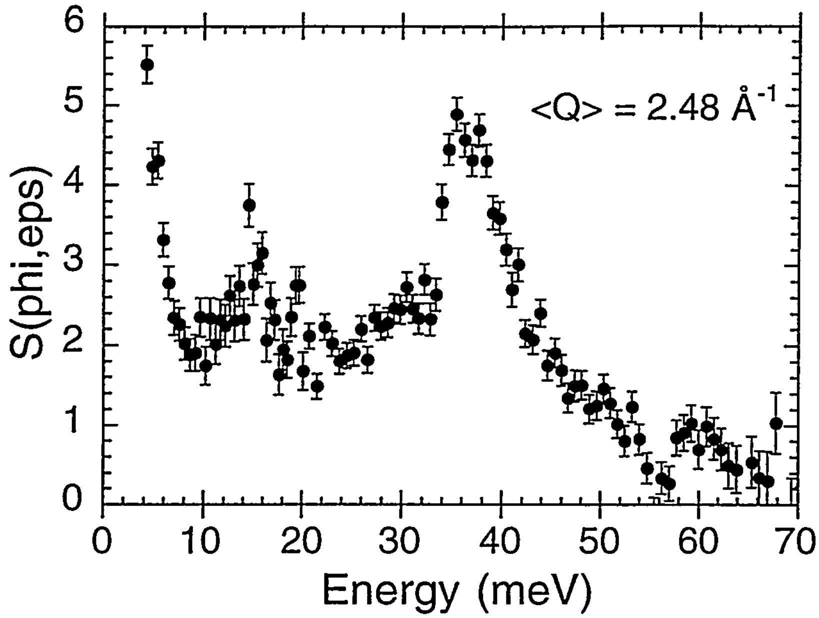

Figure 2: The inelastic neutron scattering spectrum of $Pb_2Sr_2TbCu_3O_8$ obtained at 20 K with an incident neutron energy of E_i=80 meV. The Q- and temperature-dependences of these data (not shown) lead us to the conclusion that the peaks at 30, 37 and 60 meV are magnetic in origin.

The energies and intensities of the three lines observed agree well with those predicted from our initial calculations. Using the higher, tetragonal symmetry to model our data would require 5 independent crystal-field parameters, B^0_2,B^0_4,B^4_4,B^0_6, andB^4_6. However, we can use a simple, geometrical model to constrain the relationships within the fourth and sixth rank parameters. With this constraint, we can obtain a good fit to the three observed INS line positions and their intensities [13].

The wavefunctions obtained from this single-ion crystal-field modeling can be used to calculate directly the Tb-sublattice magnetic susceptibility for comparison with the experimentally determined data shown in Figure 3. The calculated susceptibility deviates significantly from that determined experimentally for temperatures less than about 120 °K. A less pronounced deviation, expressed in the form of a theta parameter, was also observed for $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$ [11], where it was suggested that it was due to the presence of a Tb-Tb interaction.

In order to probe this possibility, a $Pb_2Sr_2Y_{0.95}Tb_{0.05}Cu_3O_8$ sample was prepared and the susceptibility measured, as shown in Figure 3. There is a considerable difference between the full R=Tb sample and the R = 5% Tb sample. This difference is attributed to thedilution of the

Tb-Tb interactions by the diamagnetic Y. It can be seen that whereas there is a much closer agreement between the diluted sample and the calculated susceptibility, there is still indications in the experimental data of persisting Tb-Tb interactions at low temperatures. Independent evidence for Tb-Tb correlations comes from the observation, by neutron diffraction [16] and calorimetry [17], of long range ordering of the Tb moments at $T_N = 5.5$ K. Inelastic neutron scattering experiments support our interpretation that there are Tb-Tb interactions that persist to temperatures as high as 120 K [13]. This interaction is currently under further study.

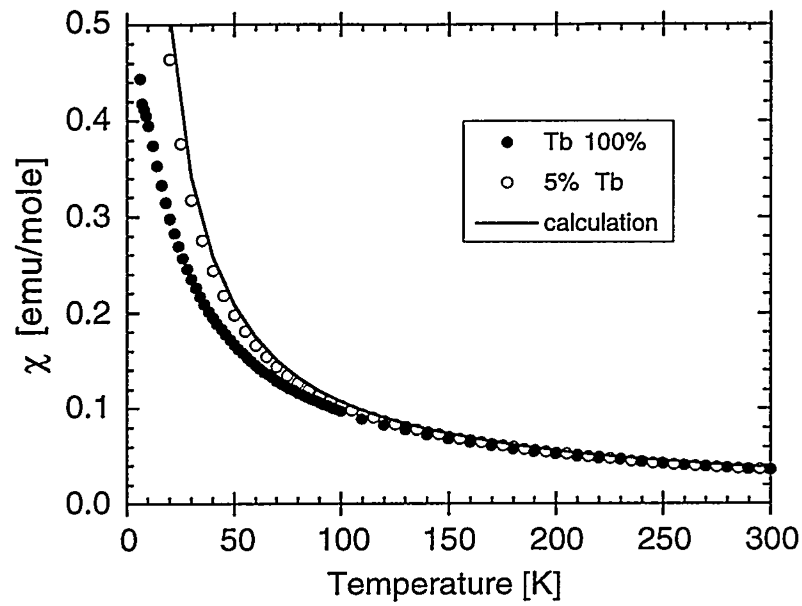

Figure 3. The magnetic susceptibility data obtained from a powdered sample of $Pb_2Sr_2TbCu_3O_8$ (solid circles) compared with a 5% substituted Tb in a diamagnetic, isostructural $Pb_2Sr_2YCu_3O_8$ host (open circles) to form $Pb_2Sr_2Y_{0.95}Tb_{0.05}Cu_3O_8$. The single-ion susceptibility calculated based on the INS results is shown as the solid line.

It is clear from this work that Tb is trivalent in these superconductor-related materials, and that the reason that some Tb samples are not superconducting is not simply the result of a charge transfer from Tb to the CuO planes. There is also no evidence for significant hybridization of the Tb f-states with the CuO conduction states. We believe that the absence of superconductivity in Tb-based samples is only indirectly related to the stability of tetravalent Tb. In samples prepared under oxidizing environments, particularly those samples containing Ba, the relative stability of $BaTb^{4+}O_3$ is probably the single most important reason that these samples are not superconducting.

CONCLUSIONS

Tb in the superconductor-related materials $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_7$ and $Pb_2Sr_2TbCu_3O_8$ has been found to be essentially trivalent. Unlike previous work on $PrBa_2Cu_3O_7$, there is no evidence of

Tb - CuO interactions that may interfere with superconductivity. However, there is independent evidence of significant Tb-Tb magnetic interactions that persist well above the reported ordering temperature of 5.5 K.

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