

## XANES Study of the Oxidation State in Superconducting TbFeAsO<sub>0.85</sub>

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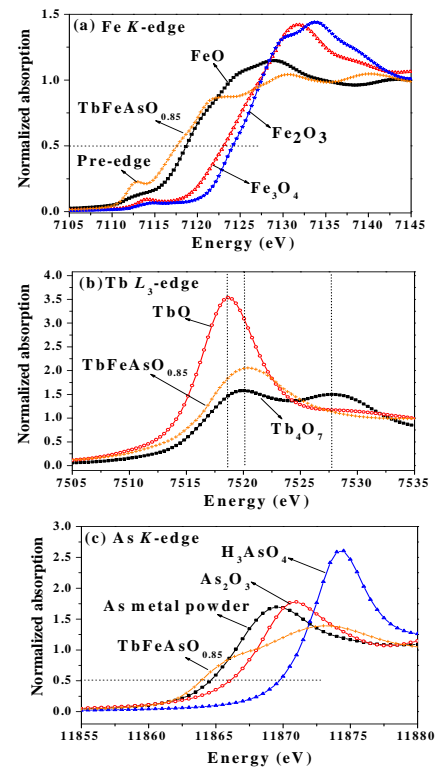
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Layered rare-earth metal oxypnictides (LaFeAsO) has emerged as a material of exceptional scientific interest due to the discovery of high temperature superconductivity. The strong interplay between structural, magnetic and superconducting properties in this class of materials has led to close comparisons with the physics of superconducting copper oxides. It has been also recognized that FeAs-based compounds could be a promising thermoelectric candidate in refrigeration applications around liquid nitrogen temperature. These aspects have generated several motivating studies by replacing La atoms by other lanthanide atoms (such as Tb and Dy) with an elevated critical temperature from 26 K to the highest of about 56 K.

On the other hand, the X-ray absorption spectroscopy (XAS) using synchrotron radiation is a powerful tool to investigate the structural and electronic properties of element of interest present in a sample. In this study, we focus on the oxidation state by measuring X-ray absorption near-edge structure (XANES) spectra. The Fe, As *K*-edges and the Tb *L*<sub>3</sub>-edge XANES spectra were recorded in transmission mode for synthesized powders mounted on a Scotch tape at a wiggler beamline BL17C with a double-crystal Si (111) monochromator for energy scanning.

The Fe *K*-edge XANES spectra of TbFeAsO<sub>0.85</sub> along with three standards, FeO (Fe<sup>2+</sup>), Fe<sub>3</sub>O<sub>4</sub> (Fe<sup>2.67+</sup>) and Fe<sub>2</sub>O<sub>3</sub> (Fe<sup>3+</sup>) are shown in Fig. 1(a). It is well known that the chemical shift of the main absorption edge to lower energy with decreasing valence of transition metals is a powerful tool for probing unknown valence of a transition metal. In Fig. 1(a), a dashed line at the absorption coefficient value of 0.5 is included to elucidate the chemical shift. The TbFeAsO<sub>0.85</sub> spectrum is close to, but slightly shifted to lower energy relative to the FeO (Fe<sup>2+</sup>) spectrum. This evidence indicates that electron configuration of Fe in the TbFeAsO<sub>0.85</sub> sample is an mixture of the basic *d*<sup>6</sup> (Fe<sup>2+</sup>) state and *d*<sup>7</sup> (plus ligand hole) configuration in the ground state. Moreover, the pre-edge peak around 7112 eV represents the 1*s*→3*d* transition, which is a dipole forbidden process. Such a pre-edge feature in TbFeAsO<sub>0.85</sub> is particularly stronger than other standard compounds due to the local tetragonal ligand field allowing dipole transitions into 3*d* related states. In Fig. 1(b), Tb *L*<sub>3</sub>-edge XANES spectra of TbFeAsO<sub>0.85</sub> together with two standards TbO (Tb<sup>2+</sup>) and Tb<sub>4</sub>O<sub>7</sub> (Tb<sup>3+</sup> and Tb<sup>4+</sup> mixture) compounds are shown. It is well known that the Tb<sub>4</sub>O<sub>7</sub> spectrum has two broad

peaks centered at ~7520 and ~7528 eV, reflecting the inhomogeneously mixed-valence nature of the sample. The peak position at ~7522 eV in Tb *L*<sub>3</sub>-edge XANES spectrum of TbFeAsO<sub>0.85</sub>, together with the absence of a second absorption peak, indicated that the Tb is neither tetravalent nor mixed valence, but instead is essentially Tb<sup>3+</sup> in this sample. Figure 1(c) shows As *K*-edge XANES spectra of TbFeAsO<sub>0.85</sub> sample with three standard compounds including As powder (As<sup>0</sup>), As<sub>2</sub>O<sub>3</sub> (As<sup>3+</sup>) and H<sub>3</sub>AsO<sub>4</sub> (As<sup>5+</sup>). In view of the absorption coefficient value of ~0.5, the As *K*-edge spectrum of TbFeAsO<sub>0.85</sub> is clearly shifted to lower energy relative to that of As powder, indicating that the oxidation number of As in TbFeAsO<sub>0.85</sub> is negative. Considering the valence of Fe and Tb, we assume that the oxidation state of As in TbFeAsO<sub>0.85</sub> is approximately 3-.



**Fig. 1:** (a) Fe *K*-edge XANES spectra of TbFeAsO<sub>0.85</sub> along with three standards of FeO (Fe<sup>2+</sup>), Fe<sub>3</sub>O<sub>4</sub> (Fe<sup>2.67+</sup>) and Fe<sub>2</sub>O<sub>3</sub> (Fe<sup>3+</sup>). (b) Tb *L*<sub>3</sub>-edge XANES spectra of TbFeAsO<sub>0.85</sub> together with two standards TbO (Tb<sup>2+</sup>) and Tb<sub>4</sub>O<sub>7</sub> (Tb<sup>3+</sup> and Tb<sup>4+</sup> mixture) compounds are shown. (c) As *K*-edge XANES spectra of TbFeAsO<sub>0.85</sub> with three standard of As metal powder (As<sup>0</sup>), As<sub>2</sub>O<sub>3</sub> (As<sup>3+</sup>) and H<sub>3</sub>AsO<sub>4</sub> (As<sup>5+</sup>).