# XANES STUDY OF METALOFULLERENES

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## Introduction

The chemical valency of metals encapsulated in fullerenes is fundamental information to understand the chemical bonding of metals and fullerenes. Core-level absorption edge shift is a useful measure of chemical valency. We have measured L-edge XANES spectra of several rare-earth metals for metallofullerenes and estimated the valency of the metals in fullerenes.

## Experimental

Rare earth metal encapsulated fullerenes were synthesized with the conventional method and purified with the liquid chromatography. Samples obtained are,
Three isomers of Tm@C82, Tm@C84, Tm2@C82, TmHo@C82, three isomers of Eu@C82.
Tm-L3, Ho-L3, and Eu-L3 XANES spectra were measured at BL-12C with Si(111) crystal monochromator. Since all the samples were of limited amount( <5 mg), each sample was concentrated in a small pit of a glass plate by dropping and drying the $CS_2$ solution repeatedly. Measurements were performed with the fluorescence yield mode, using the Lytle detector.

## Results and discussion

Fig. 1 shows the Tm L3 XANES spectra of Tm encapsulated fullerenes as well as that of Tm2O3. Intensity of each spectrum is normalized at 8748 eV. As is clearly seen, all three isomers of Tm@C82 have the absorption edge at 8640 eV, which is 7 eV lower than the reference sample, $Tm_2O_3$[1]. Tm ion has usually +3 valency as in the case of $Tm_2O_3$, and only a few compounds, TmS and TmTe have $Tm^{2+}$ ions, whose edge energy is 7 eV lower than that of $Tm_2O_3$. Thus, we can conclude that the valency of Tm of Tm@C82 is +2. In contrast, Tm atoms in TmHo@C82 and $Tm_2$@C82 have +3 valency.

Fig.2 shows that Ho of TmHo@C82 has +3 valency. It is also found that Eu atoms in Eu@C82 have +2 valency. C82 has an inside diameter of 8-9 Å, and ionic radii of $Tm^{2+}$ and $Tm^{3+}$ are 1.03Å and 0.88Å, respectively [2]. It is known that Sm@C82 has $Sm^{2+}$, while Ho@C82 has $Ho^{3+}$. The valency of the metal in the C82 cage might be determined by the counterbalance of the third ionization potential of the metal and the electron affinity of the cage, Coulombic interactions and also by the ionic sizes.

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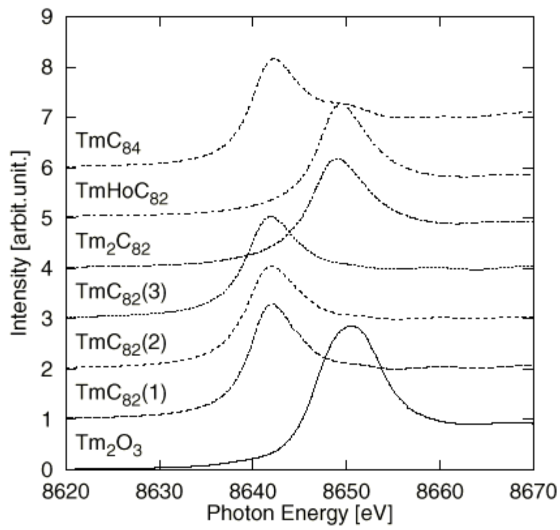


Fig.1 Tm L3 XANES from several Tm encapsulated fullerenes

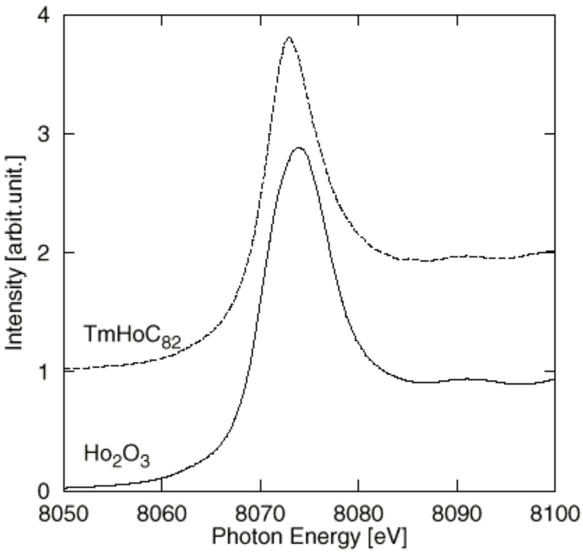


Fig.2 Ho L3 XANES from TmHo@C82

## References

[1] H.Launois, et al., Phys. Rev. Lett. 44, 1271(1980).
[2] R.D.Shannon, Acta Cryst. A32, 751(1976)