

## Tm L<sub>III</sub> EXAFS STUDY OF Tm@C<sub>82</sub>

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### Introduction

Geometry of the metal encapsulated in a fullerene has been studied by several methods, such as NMR, TEM and powder diffraction with the MEM analysis. EXAFS is a method of the local structure analysis and it is challenging to study how EXAFS can give us the geometrical information on such a complicated sample as metallofullerenes. We have applied EXAFS structure analysis to Tm@C<sub>82</sub>, which was well purified and characterized by NMR.

### Experimental

Sample preparation and EXAFS experiments are just same as those reported in the same Proceedings. Tm L<sub>3</sub> EXAFS spectra were measured at BL-12C with the fluorescence yield mode, using the Lytle detector at 20 K.

### Results and discussion

Tm L<sub>3</sub> EXAFS and its Fourier transformed spectra are shown in Figs. 1 and 2, respectively, as a solid line. Although there are 9 isomers in the C<sub>82</sub> cage, previous NMR study suggested that the present cage is an isomer with C<sub>2v</sub> symmetry. In order to obtain geometrical information of Tm in the cage, we used the non-empirical EXAFS simulation program, FEFF8[1]. First, we confirmed that FEFF8 program well reproduced the EXAFS oscillation of Tm<sub>2</sub>O<sub>3</sub>. Then, we calculated the EXAFS curves for a number of possible Tm positions in the C<sub>82</sub> cage, assuming that the cage is not distorted and that the Debye temperature is 600K. For comparison with the experimental curve, the *r*-factor was calculated for each proposed structure.

It is found that the Tm atom is distinctly not on the C<sub>2v</sub> symmetry axis, as opposed to the prediction by NMR[2]. We searched the best fit Tm position by using three parameters; *r* (averaged distance from the nearest neighbor hexagonal C atoms), *d* (deviation from the C<sub>2v</sub> axis) and  $\theta$  (angle from the C-C bond around the rotation axis). After calculating the EXAFS curves and *r*-factors for 240 cases, we determined the best fit parameters as follows, *r*=2.55 Å, *d*=0.15 Å,  $\theta$ =85°, as shown in Fig.3.

Simulated curves with best fit parameters are shown as broken lines in Figs.1 and 2. Discrepancy between NMR and EXAFS can be reconciled by the temperature difference; EXAFS was measured at 20K, while NMR experiments were done at RT.

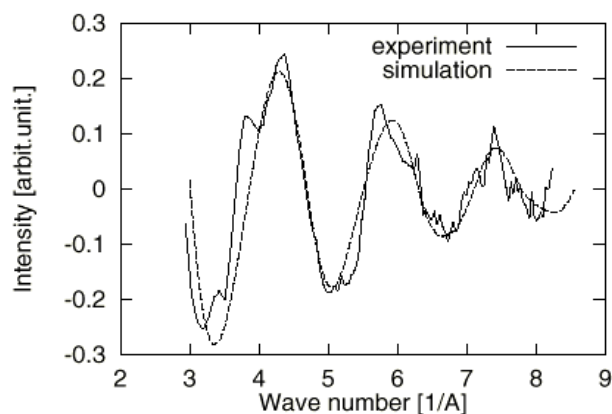


Fig. 1 Tm L<sub>3</sub> EXAFS oscillation from Tm@C<sub>82</sub>

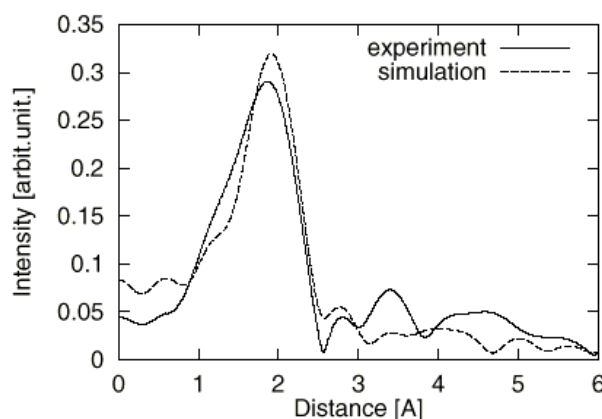


Fig.2 Fourier transforms of Fig.1

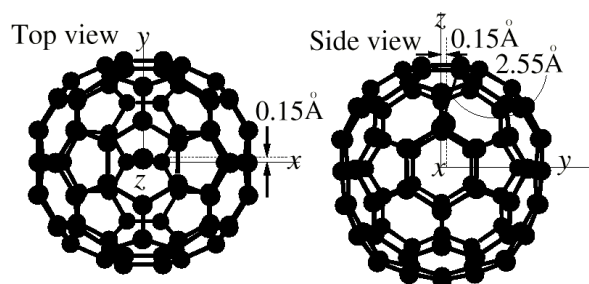


Fig.3 Proposed position of Tm in the C<sub>82</sub> cage.

### References

- [1] A.L.Ankudinov, et al., Phys. Rev. B58, 7565(1998).
- [2] Y.Miyake et al, 19<sup>th</sup> Fullerene general symposium, 2A13, 78 (2000)