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@C82, 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 L3 EXAFS spectra were measured at BL-12C with the fluorescence yield mode, using the Lysle detector at 20 K.

Results and discussion
Tm L3 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 C82 cage, previous NMR study suggested that the present cage is an isomer with C2v 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 Tm2O3. Then, we calculated the EXAFS curves for a number of possible Tm positions in the C82 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 C2v 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 C2v axis) and θ (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, θ=85º, 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.

References