Fe K-edge XANES analysis of Dicyano(phthalocyaninato)iron Compounds with multiple scattering theory

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The dicyano(phthalocyaninato)iron molecular conductor shows the giant negative magnetoresistance (GMR) effect at low temperature [1]. TPP[Fe(Pc)L_2]_2 (TPP=tetraphenylphosphonium, Pc=phthalocyanine, L=CN, Cl, Br) system has strong intramolecular interaction between the local spin moment caused by 3d electrons of Fe and π-electrons of Pc ring. The origin of GMR effect is considered to the charge ordering of the Pc unit which is derived from the Coulomb interaction of the nearest neighbor molecule [2]. The GMR intensity depends on the ligand [3] and obeys the spectrochemical series. In order to investigate the electronic structure about Fe atom with varying ligand, we measured Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectra, which include the information about geometrical and electronic structures around the X-ray absorbing atom. The observed spectra with varying L show the absorption edge shift of ca. 3 eV. In the case of L=CN, the temperature dependent and magnetic field dependent spectra are also measured. These spectra show the change of main peak intensity. In order to analyze these spectral changes, we have performed first principle molecular orbital calculation to obtain the electronic structure of these molecules by using Gaussian09. XANES spectra are calculated by multiple scattering theory [4]. The result of molecular orbital calculation shows that the decreasing of Fe charge also obeys the spectrochemical series. Calculated XANES spectra which take account of the electronic structure obtained by molecular orbital calculation reproduce the observed spectra.