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Linear Dichroism in the Fe K-edge of Magnetite

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Fe3O4 is a well known inverse spinel compound with numerous applications for e.g. MRI contrast enhancement, hyperthermia treatment, drug delivery, etc. With particle sizes on the nano –scale, magnetite becomes chemically active and its electronic and magnetic structure changes as a function of the size. An in situ probe of the Fe electronic structure is possible using hard X-ray spectroscopy where an Fe 1s core electron is excited to a level just above the Fermi energy. Such excitations are referred to as K absorption pre-edges. The excited state decays with a certain lifetime and the core hole is filled via several possible decay channels. A highly probable decay channel is the K alpha fluorescence where a 2p electron fills the 1s level emitting K alpha X-rays. By monitoring the K alpha fluorescence intensity as a function of the incoming photoexcitation energy we gain information on the absorption cross-section at the K pre-edges and hence the electronic structure. The exact nature of the pre-edges is poorly understood owing to the fact that three different Fe sites in magnetite contribute to the spectra. In order to elucidate the electronic transitions that give rise to the pre-edge we performed linear dichroism(LD) experiments where the relative orientations between crystal axes, X-ray polarization and magnetic field are varied. Based on the LD experimental results obtained from the bulk magnetite we assign spectral features to specific Fe sites and interpret the spectral changes that magnetite undergoes when its particle size is reduced to a few nanometers.

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