# Valence Sensitive X-ray Fluorescence Holography of Magnetite

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X-ray fluorescence holography (XFH) is an atomic resolution, element sensitive experiment that can directly provide a 3-dimensional picture of the atoms surrounding a selected element in a material[1]. Fluorescent X-rays from the target element (reference wave) is scattered by the surrounding atoms (object wave), and their interference is recorded as holograms. A 3D atomic image can be directly reconstructed from the holograms by numerical processing.

In this presentation, we report a XFH experiment that is not only element sensitive, but is also sensitive to the electronic state of the atoms of the target element. Careful tuning of the incident X-ray energies, with respect to the shifts of the absorption edges of the different valence states of an element allows us to record valence sensitive holograms[2]. This allows the direct imaging of the local structure around the different valence states of the target element.

Magnetite ($Fe_3O_4$), is a classic mixed valence compound, where both $Fe^{2+}$ and $Fe^{3+}$ occupy octahedral B-sites, while $Fe^{3+}$ occupies tetrahedral A-sites. It has a metal-insulator transition upon cooling below 120 K, and is one of the most studied material in strongly correlated electron systems. We demonstrate this valence sensitive XFH experiment[3] on a magnetite reference sample, and show that Fe Kα holograms, and their corresponding atomic reconstruction can be obtained from all Fe cation as emitters, or separately for $Fe^{2+}$ cations only, or $Fe^{3+}$ cations only. The results of the experiment allow us to show that $Fe^{2+}$ emitters are in the octahedral sites, while $Fe^{3+}$ are on the tetrahedral sites.

Our results show that valence sensitive XFH is a promising new technique that can be used to address unresolved questions about the structure of mixed valence compounds by clarifying the difference in local atomic structure around the different ions in a crystal.

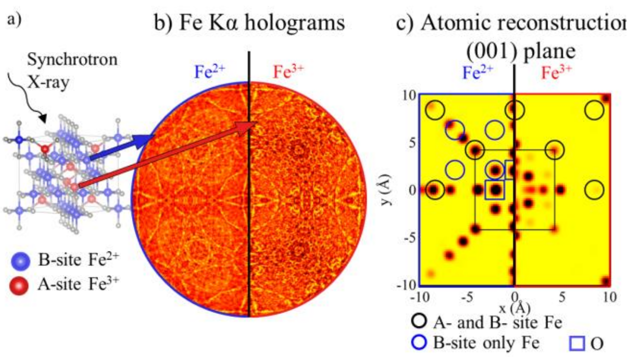


Figure 1. a) structure of $Fe_3O_4$, b) Fe Kα holograms of $Fe^{2+}$ (left) and $Fe^{3+}$ (right) ions and c), atomic images reconstructed from the holograms of $Fe^{2+}$ (left) and $Fe^{3+}$ (right).

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2. J. R. Stellhorn, *et al.*, *J. Appl. Crys.* **50**, 1 (2017).
3. A.K.R. Ang, *et al.*, *Phys. Status Solidi B*, in press (2018).