

XAFS studies of candidate dilute magnetic semiconductor materials

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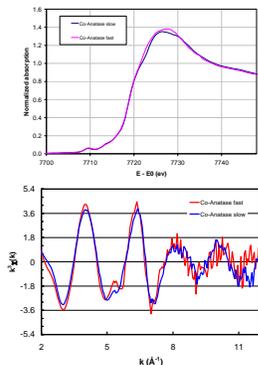
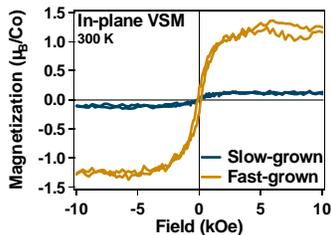
Introduction

The search for a dilute magnetic semiconductor with a high T_c has attracted much interest, and resulted in controversial and conflicting findings. These materials are needed for continued progress in spintronics as possible injectors of spin polarized carriers. XAFS studies at Sector 20 have proven to be extremely useful in characterizing candidate materials based on TiO_2 -anatase, hematite, and ZnO . To convert these materials into possible magnetic semiconductors, they need to be doped, typically with transition metals at the few percent level. The element specificity and sensitivity of XAFS allows these dopants to be studied in epitaxial films as thin as 20 nm. The near edge can be used to determine the valence of the dopant atoms, important for understanding the charge balance and whether metallic nanoparticles are forming. The EXAFS can determine the local atomic environment, verifying that substitutional doping is occurring and quantifying the lattice distortion at the dopant site.

Growth rate dependence of magnetism: Co- and Cr-doped anatase (see T.C. Kaspar et al. Phys. Rev. Lett. 95, 217203 (2005); T.C. Kaspar et al. Phys. Rev. B 73, 155327 (2006))

It was found that for Co doped anatase that the magnetism nearly disappears for slow grown (more ideal) films

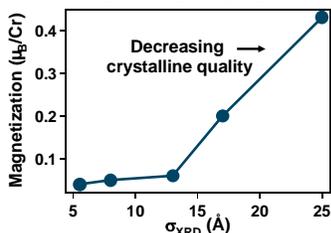
The local Co environment as determined by XAFS was unchanged.



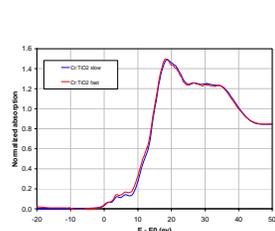
Cr-doped anatase was chosen as a model room temperature ferromagnetic materials system to study the role of crystalline structure in mediating ferromagnetic ordering.

Cr magnetism increases for poorer quality crystals

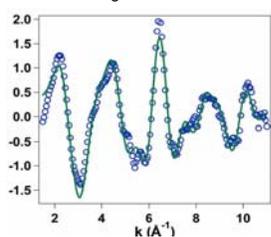
- Epitaxial particle-free films are obtained at all growth rates, with a uniform distribution of Cr and no segregation.
- A significant improvement in crystalline ordering is obtained by lowering the deposition rate from $\sim 0.1 \text{ \AA/s}$ to $\sim 0.015 \text{ \AA/s}$.



X-ray absorption measurements again show the Cr local environment and valence nearly unchanged



EXAFS fitting confirms a substitutional site

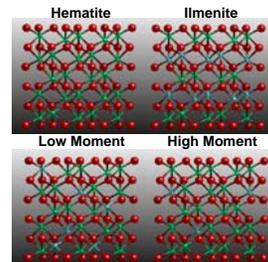


- Epitaxial Co- and Cr-doped anatase TiO_2 thin films of varying crystalline quality were deposited by OPAMBE.
- Locally the Cr or Co atoms have the same environment.
- Room temperature ferromagnetism was shown to require extended structural defects present in poor crystalline quality material; highly ordered material exhibits negligible ferromagnetism.
- These results directly contradict widely accepted magnetic ordering mechanisms for doped oxides involving bulk oxygen vacancies.

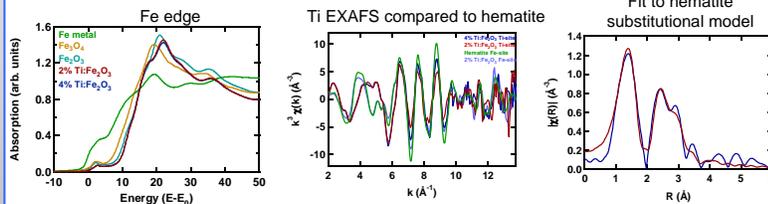
Ti doped hematite

Why Ti in hematite?

- $\alpha\text{-Fe}_2\text{O}_3$ is an antiferromagnetic semi-insulator
- $\alpha\text{-Fe}_2\text{O}_3$ can be doped n -type or p -type
- Fe atoms in adjacent layers are coupled antiferromagnetically (upper left)
- FeTiO_3 ilmenite is roughly isostructural with alternating Fe(II) & Ti(IV) layers (upper right)
- If Ti substitutes for Fe in alternating layers (lower right) \rightarrow ferrimagnetic with net magnetic moment gain of $\sim 4\mu_B/\text{Ti}$ atom
- If Ti substitutes randomly in layers (lower left) \rightarrow small net magnetic moment



XAFS from Ti doped hematite

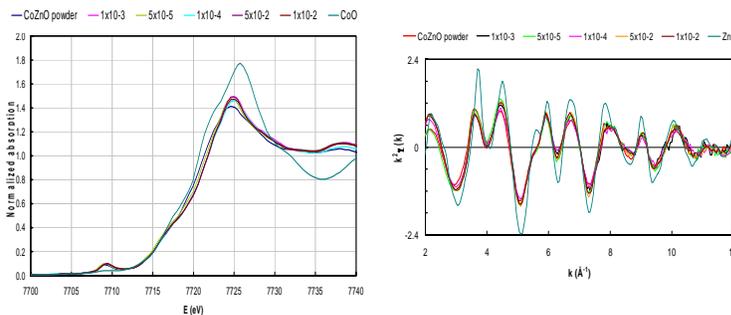


- Ti-doped hematite is grown epitaxially on sapphire by oxygen plasma MBE
- Ti(IV) acts as n -type electrical dopant in hematite
- Ti(IV) substitutes nearly randomly for Fe(III) in the $\alpha\text{-Fe}_2\text{O}_3$ lattice creating a distortion of local structure
- Ti substitution in adjacent configurations is nearly isoenergetic with alternate configuration confirmed by low net magnetic moment of $\sim 0.5 \mu_B/\text{Ti}$ atom

Initial results using pulsed laser deposition of Co doped ZnO collaboration with D. Gamelin and K. Kittelstved, Univ. of Washington

Pulsed laser deposition was used to grow epitaxial films of Co doped ZnO. To prevent metallic Co formation various partial pressures of O_2 were used. Below is the Co EXAFS and XANES from films grown at different pressures.

There is no evidence for Co metal at any pressure and the Co is obviously substituting for the Zn in the lattice.



Acknowledgements

This work was performed in the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Science and Engineering Physics under Project No. 10122. Use of the Advanced Photon Source was supported by the U.S. DOE, under Contract No. W-31-109-ENG-38.