

to understand the chemical behavior and properties of a specific organometallic complex. However, despite the vast information provided by crystal structures, it cannot always indicate how the complex will behave in solution state in the presence of other coordinating molecules. Therefore the use of various spectroscopic methods such as Nuclear Magnetic Resonance (NMR), Infrared Spectroscopy (IR) *etc.* in conjunction with crystallography allows a much better understanding into the chemical properties of a complex.

Our interest in homogenous catalysis, in particular, the Rhodium Monsanto process [1] which produces several million tons of acetic acid per annum has allowed us to explore both spectroscopic and crystallographic methods to better understand the catalytic cycle. Selecting catalysts which have been altered with various ligands with different stereo-electronic properties, it is possible to control the selectivities and rates of the catalytic reaction [2-4].

The precursor effect of the methanol carbonylation catalytic cycle was studied with various model complexes of the type $[\text{Rh}(\text{L},\text{L}'\text{-Bid})(\text{CO})(\text{PR}_3)]$ ($\text{L},\text{L}'\text{-Bid}$ = mono anionic bidentate ligand; PR_3 = alicyclic and aryl tertiary phosphine compounds). Crystallographic comparisons of the complexes were correlated with spectroscopic studies to determine the solid state and solution effects introduced by the selective variation in the substituents on the phosphorous atom [5-6].

[1] P.M. Maitlis, A. Haynes, G.J. Sunley, M.J. Howard., *J. Chem. Soc., Dalton Trans.*, **1996**, 2187. [2] C.M. Thomas, G. Süß-Fink, *Coord. Chem. Rev.*, **2003**, *243*, 125. [3] A. Roodt, S. Otto, G. Steyl, *Coord. Chem. Rev.*, **2003**, *245*, 121. [4] J.R. Dilworth, J.R. Miller, N. Wheatley, M.J. Baker, G.J. Sunley, *J. Chem. Soc. Comm.*, **1995**, 1579. [5] A. Brink, A. Roodt, H.G. Visser, *Acta Cryst.*, **2007**, *E63*, m2831. [6] A. Brink, A. Roodt, G. Steyl, H.G. Visser, *Dalton Trans.*, **2010**, *39*, 5572.

Keywords: crystallography, spectroscopy, rhodium

MS56.P02

Acta Cryst. (2011) **A67**, C582

Structural Origin of Ferromagnetism in Mn- and Co-doped Y_2O_3 Nanocrystals

Yun-Liang Soo, Tai-Sing Wu, Shih-Lin Chang *Department of Physics, National Tsing Hua University, Hsinchu (Taiwan)*. E-mail: soo@phys.nthu.edu.tw

Long-range-order and short-range-order structures in ferromagnetic Mn- and Co-doped Y_2O_3 nanocrystals prepared by a thermal decomposition method have been probed using x-ray diffraction (XRD) and extended x-ray absorption fine structure (EXAFS) techniques, respectively. These diluted magnetic oxides (DMO) are high-k dielectrics and exhibit ferromagnetism at room temperature. Our EXAFS results indicate that oxygen vacancies are present around the Mn and Co dopant atoms in the Y_2O_3 DMO host. To investigate the correlation between ferromagnetism and oxygen vacancies, the as-made sample were alternately annealed in oxygen and forming gas at a moderate annealing temperature. The EXAFS data reveals that the average number of oxygen vacancies surrounding magnetic dopant atoms is increased by oxygen annealing and decreased by forming-gas annealing. The XANES results also demonstrate consistent valency variations. Without appreciable changes in particle size, the saturation magnetization was found to increase with oxygen-vacancy concentration in these DMO samples. Our results strongly support the bound magnetic polaron model for ferromagnetism in these DMO nanocrystals.

Keywords: ferromagnetic, high-k, exafs

MS56.P03

Acta Cryst. (2011) **A67**, C582

The X-ray Extended Range Technique for high accuracy XAS for comparison and improvement to theoretical modeling

Nicholas A. Rae, Christopher T. Chantler, *School of Physics, The University of Melbourne, Victoria, (Australia)*. Email: nrae@ph.unimelb.edu.au

The x-ray atomic form factor is the fundamental parameter describing the interaction of x rays with matter. Accurate values of the mass attenuation coefficient and hence of the dielectric function are vital for many areas of x-ray science. A wide range of atomic, molecular, and solid-state features can be calculated given accurate values of x-ray atomic form factors of the constituent elements. However, large discrepancies between different theoretical calculations exist, and are largest in the important absorption edge regions [1,2]. We have developed the X-ray Extended Range Technique (XERT) to measure x-ray mass attenuation coefficients to accuracies as low as 0.02% [3,4,5]. From these measurements the form factors are derived and used help improve theoretical approaches. Two recent reviews have discussed experimental details [6,7].

We present measurements of the x-ray mass attenuation coefficients of zinc, selenium and zinc selenide are measured between 7.2 keV and 15.2 keV with an absolute accuracy of 0.044% - 0.197% and a relative accuracy down to 0.006%, making this the most accurate determination of any attenuation coefficient on a bending-magnet beamline [8]. The measurements invite improvements in theoretical calculations of mass attenuation coefficients. Comparison between zinc, selenium and zinc selenide measurements tests the effect of structure and bonding, and the sum rule in theoretical calculations of the mass attenuation coefficient. In particular theoretical calculations of XAFS and XANES [9] are compared to the measurements.

[1] C.T. Chantler, *J. Phys. Chem. Ref. Data* **1995**, *24*, 71-591. [2] C.Q. Tran, C.T. Chantler, Z. Barnea, *Physical Review Letters* **2003**, *90*, 257401. [3] N.A. Rae, C.T. Chantler, Z. Barnea, M.D. de Jonge, C.Q. Tran, J.R. Hester, *Physical Review A - Atomic, Molecular, and Optical Physics* **2010**, *81*, 022904-1-10. [4] M.T. Islam, N.A. Rae, J.L. Glover, Z. Barnea, M.D. de Jonge, C.Q. Tran, J. Wang, C.T. Chantler, *Physical Review A - Atomic, Molecular, and Optical Physics* **2010**, *81*, 022903-1-9. [5] C.T. Chantler, Z. Barnea, C.Q. Tran, J. Tiller, D. Paterson, *Optical and Quantum Electronics* **1999**, *31*, 495-505. [6] C.T. Chantler, *Radiation Physics and Chemistry* **2010**, *79*, 117-123. [7] C.T. Chantler, *European Physical Journal ST* **2009**, *169*, 147-153. [8] N.A. Rae, J.L. Glover, C.T. Chantler, *Nuclear Instruments and Methods in Physics Research, A* **2010**, *619*, 47-50. [9] J.L. Glover, C.T. Chantler, Z. Barnea, N.A. Rae, C.Q. Tran, *Journal of Physics B: Atomic, Molecular and Optical Physics* **2010**, *43*, 085001-1-15

Keywords: XAFS, XANES, zinc selenide

MS56.P04

Acta Cryst. (2011) **A67**, C582-C583

Modulation excitation spectroscopy adapted to Crystallography

Rocco Caliandro,^a Wouter van Beek,^{b,c} Marco Milanese,^c Atsushi Urakawa,^d Dmitry Chernyshov,^b Davide Viterbo,^c Luca Palin,^c Hermann Emerich,^b *Institute of Crystallography CNR, Bari Italy*. ^bSwiss Norwegian BeamLines at ESRF, Grenoble, (France). ^cDISTA – Università del Piemonte Orientale “A. Avogadro”, Alessandria, (Italy). ^dInstitute of Chemical Research of Catalonia (ICIQ), Tarragona, (Spain). E-mail: rocco.caliandro@ic.cnr.it

Modulation excitation spectroscopy is a powerful and well established technique to investigate the dynamic behavior of chemical