

MS54.P22

Acta Cryst. (2011) A67, C581**The forms of fluorite crystals as an important factor for prospect evaluation of mineralization (in case of deposits of tajikistan)**

Fayziev Abdulkhak, *Department of mineral deposits, Institute of Geology, Academy of Sciences of the Republic of Tajikistan, Dushanbe.*
E-mail: faiziev38@mail.ru

Tajikistan is the fluorite-bearing region where minerals are extracted for the needs of the economy since the thirties of last century. There are many known fluorite deposits of different genetic types: carbonatite, pegmatite, greisen, skarn, hydrothermal, sedimentary-epigenetic. Fluorite is associated mineral in deposits of many kinds. Its industrial amounts there are in different silver-polymetallic sites.

Fluorite crystals occur in all genetic types of mineral deposits. However, a very wide variety of crystal-morphology forms are characterized in hydrothermal manifestations. Fluorite crystals were the subject of mining as an optical material in some of them. Unique by the cleanness, transparency and value Druze Crystals of optical fluorite were found in the Cooley Kalon Field in Zeravshan Range where the size of the largest crystal reached 25 cm in diameter and weighed 24 kg. Crystals of optical fluorite were mined in other ore fields (Mogov, Kaznok). Fluorite crystals have cubic, octahedral and rhombododecaedric habitus forms and thereof combinations. In addition, there are more faces in tetragontrioctaedr (hkk), geksaoktaedr (hkl), tetrageksaedr (hko) and trigontritetraedr (hkk) positions. Some patterns, which can be used for prospecting and evaluation of the fluor spar deposits, were identified in detailed study of the crystals. Thus, the morphological change of one form of fluorite crystals to other was detected both in time and space. Changing shapes of crystals in time is expressed in their evolution from cube to octahedron, sometimes rhombododecaedr, from early to late generations of minerals. By slice study of deposits, habitus forms of crystals from cube to the octahedron, sometimes rhombododecaedr, has been established from early to later generations. The greatest interest has the change of crystal forms in space, i.e. along the rising of ore bodies as the ore-bearing mineral-solution moves up from source of hydrothermal vents. It is expressed in the finding of fluorite crystals of different habitus types in different hypsometric levels. It is allowing you to use this relationship for practical purposes. Change of some forms in other ore fields of different regions in Tajikistan subjects to the general rule but has some specific features. In the fields of northern Tajikistan, modified habitus forms of fluorite crystals from the lower to the upper levels of the deposit comes from the octahedron by cuboctahedron, cubo-rhombododecaedr and rhombododecaedr to the cube. For deposits of Central Tajikistan in the upper horizons, the crystals have a cubic habitus of facets (110) and (111), rarely (hkk); in the middle horizons the cuboctahedron crystals with approximately equal development of both forms are dominated, while at the lower levels octahedral shape complicated by the faces of the cube are present. In deposits of the Pamirs, the lower parts of the veins have developed octahedral crystals; in the middle – the rhombododecaedric, and in the upper – the cubic habit types with (hkk), (hkl) sides and rarely (hko) are present.

Generalized model for the evolution of simple forms of fluorite crystals and combinations thereof from below upwards, from lower to upper levels of the deposit, has the order: (111) → 111 + (110) + (100) → (110) → (100) + (110) + (hkk) + (hkl) + (hko) → (100).

Such zoning in the distribution of fluorite crystals can be used to assess the level of erosional truncation and for prognosis of fluorite mineralization at depth. It was successfully implemented in prospecting and evaluation work for fluor spar mineralization in Central Tajikistan and the Pamirs.

Keywords: Fluorite, Crystal, Mineralization

MS55.P01

Acta Cryst. (2011) A67, C581**Study of charge stripes and charge density waves using x-ray scattering**

Chao-hung Du,^a S.-H. Lee,^a C.-L. Huang,^a Y.-C. Lai,^a P.-F. Wu,^a F. C. Chou,^b ^aDepartment of Physics, Tamkang University, Tamsui 25137, (Taiwan). ^bCenter for Condensed Matter Science, National Taiwan University, Taipei 10617, (Taiwan). E-mail: chd@mail.tku.edu.tw

Modulated structures due to the modulation in charge densities are observed in many material systems, especially in low dimensional materials, in common, and often accompany the occurrence of unusual transport behavior. In order to understand these unusual physical properties, it is therefore essential to study the correlations between the modulations and the transport behavior. Among the probes used for studying the charge modulations, synchrotron x-ray scattering has the merits of sensitivity to charges and high spatial resolution over others. Using synchrotron x-ray scattering, we report the study of charge modulations on both materials of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ (LSNO) and $2T\text{-TiSe}_2$ (TS). LSNO is isostructural to the high T_c superconductor $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, but it doesn't show superconductivity with any concentrations of Sr [1]. One of the reasons is ascribed to the formation of static charge modulations. Using high resolution x-ray scattering on 3 high quality single crystals of LSNO, with $x = 0.225, 0.333, \text{ and } 0.4$, we observed the satellite reflections due to the formation of charge modulations. The q-wavevectors of the modulation vary with the hole concentrations, and the modulation are also observed to be two-dimensional in nature. Using azimuthal scan, the modulation are also demonstrated to show a two-fold symmetry, which is in agreement with the characteristic of charge stripes forming in the ab plane.

By contrast, $2T\text{-TiSe}_2$ possesses a modulated structure due to the formation of charge density waves at low temperature. With a small amount of doping of Cu, $2T\text{-TiSe}_2$ shows superconductivity at about 4K [2]. It was believed that both electronic states of superconductivity and CDWs compete with each other, however, experimentally, it has been demonstrated that both states can coexist with each other in some low-dimensional system, such as NbSe_2 . In the case of $2T\text{-Cu}_x\text{TiSe}_2$, Cu atoms could be regarded as the impurities to the CDWs, and result in the deformation of the CDW modulation. Using synchrotron X-rays, the spatial resolution can be easily reached as high as 10^{-4} \AA^{-1} , x-ray scattering is therefore an ideal probe for studying the deformation of the modulated structure or lattice distortion. Using high resolution x-ray scattering on the parent compound $2T\text{-TiSe}_2$, we have observed that TS possesses two types of modulation. One has the wavevector of $q=(0.5 \ 0.5 \ 0.5)$, and the other is $(0.5 \ 0 \ 0.5)$.

[1] H. Yoshizawa, T. Kakeshita, R. Kajimoto, T. Tanabe, T. Katsufuji, Y. Tokura, *Physical Rev. B*, **2000**, *61*, R854. [2] E. Morosan, H.W. Zandbergen, B.S. Dennis, J.W.G. Bos, Y. Onose, T. Klimczuk, A.P. Ramirez, R.J. Cava, *Nature Physics* **2006**, *2*, 544.

Keywords: CDW, modulation, x-ray scattering

MS56.P01

Acta Cryst. (2011) A67, C581-C582**Under the microscope: crystallographic and spectroscopic study of Rh(I) complexes**

Alice Brink,^a Hendrik G. Visser,^a and Andreas Roodt,^a ^aDepartment of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein 9300, (South Africa). E-mail: alice.brink@gmail.com

The use of X-ray crystallography to determine the absolute coordination and structure is an undeniable advantage in trying

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