

Palvadeau P., Rossat-Mignod J., *J. Phys. C: Solid State Phys.*, 1983, **16**, 5339.

**Keywords:** phase transitions, superstructure, TiOCl TiOBr VOCl

### P.20.10.3

*Acta Cryst.* (2005). A61, C471

#### Studies of the Magnetic Ordering in Polycrystalline Cr-Ru Alloys by Neutron Powder Diffraction

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The magnetic phase diagram of the Cr-Ru alloy system [1,2] shows that the spin density wave (SDW) ordering below the Néel temperature is incommensurate (I) for Ru concentrations ( $x$ ) < 1%, commensurate (C) for  $1\% < x < 17\%$ , with the formation of a superconducting state for  $x > 17\%$  [2].

Our approach to identify the nature of the magnetic ordering has always encompassed neutron diffraction studies on single crystal samples in which the different SDW orderings give rise to specific intensity distributions around the {100} reciprocal lattice position [3].

We here report experimental results from neutron powder diffraction studies of polycrystalline samples with  $x = 0.3\%$ ,  $12.5\%$  and  $15\%$  representative of the I and C phases. This has become an option with the availability of the upgraded neutron powder diffraction instrument at the SAFARI-1 research reactor.

The results demonstrate the viability of using diffraction pattern distributions from polycrystalline samples to research intricacies in the magnetic ordering of dilute alloys of Cr in future studies.

[1] Fawcett E., Alberts H.L., Galkin V. Yu., Yakhmi J.V., *Rev. Mod. Phys.*, 1994, **66**, 25. [2] Chatani K., Endoh Y., *J. Phys. Soc. Japan*. 2003 **72**, 17. [3] Boshoff A.H., Alberts H.L., du Plessis P. de V., Venter A.M., *J. Phys. Condens. Matter*, 2003 **5** 5353.

**Keywords:** neutron powder diffraction, spin-density wave, magnetic phases

### P.20.10.4

*Acta Cryst.* (2005). A61, C471

#### Magnetic Transitions in $\text{ErCo}_{10}\text{Mo}_{2-x}\text{M}_x$ ( $\text{M}=\text{Si}$ and $\text{V}$ )

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The intermetallic compounds of the type  $\text{R}(\text{T},\text{M})_{12}$  ( $\text{R}=\text{rare earths}$ ,  $\text{T}=\text{Fe, Co, Ni}$  and  $\text{M}=\text{stabilizing elements like Mo, Si, V}$  etc) that find many applications as permanent magnet materials exhibit tunable magnetic characteristics. Tuning of the magnetic anisotropy values, Curie and spin reorientation temperatures are made possible by replacing the constituting elements with others in specific proportions. X-ray powder diffraction and low field magnetization studies on  $\text{ErCo}_{10}\text{Mo}_{2-x}\text{M}_x$  ( $\text{M}=\text{Si, V}$ ) in the temperature range between 5K - 800K have revealed that:

i) all members of the family crystallize in  $\text{ThMn}_{12}$  type structure with tetragonal  $\text{I4/mmm}$  space group.

ii) Si for Mo replacement leads to a linear decrease of lattice parameters, a significant shift of  $T_c$  from 425K to 719K and a  $T_{sr}$  reduction from 139K to 74K.[1]

iii) V for Mo replacement leads to a linear decrease of lattice parameters, no significant change in  $T_c$  and a strong shift of primary  $T_{sr}$  from 139 to 350K.[2]

These findings together with structural and magnetic transition implications will be presented.

[1]Zhao Z.G., de Groot C.H., Brück E., Buschow K.H.J., de Boer F.R., *Physica B*, 1996, **228**, 214. [2] Brabers J.H.V.J., Zhou G.F., de Boer F.R., Buschow K.H.J., *J. Mag. Mag. Mat.*, 1993, **118**, 339-346.

**Keywords:** spin reorientation, Curie temperature, magnetic anisotropy

### P.20.10.5

*Acta Cryst.* (2005). A61, C471

#### X-ray Diffraction and Absorption Study under Strong Pulsed Magnetic Fields

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Diffraction experiments under non-ambient conditions have been developed for decades. Nowadays x-ray experiments over 100 GPa can be carried out using a diamond anvil cell. For ultra-low-temperature experiments, neutron and x-ray experiments below a few hundred mK are performed at several places. In contrast, diffraction experiments under strong magnetic field are limited below about 20T.

Recently, we have developed very small pulsed magnets [1]. Typical dimensions of the coils are 20 mm in diameter and 25 mm in length. Hence, the coil is readily attached to the cold head of a conventional closed cycle refrigerator, and is easily installed in a conventional x-ray diffractometer. Although the coils are small, magnetic fields above 30 T can be generated. Using this miniature coil and intense synchrotron x-rays, we conducted x-ray diffraction experiments under strong pulsed magnetic fields at beamline BL22XU at SPring-8. The field induced structural phase transition around 9 T in  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  and the valence transition around 26 T in  $\text{YbInCu}_4$  were clearly observed. Our new plan for x-ray absorption experiments under pulsed magnetic fields is also presented.

[1] Matsuda Y.H., et al., *Physica B*, 2004, **346-347**, 519.

**Keywords:** pulsed magnetic field, magnetic structural phase transition, valence fluctuations

### P.20.10.6

*Acta Cryst.* (2005). A61, C471

#### Magnetic field induced polymorphism of $\text{R}_5\text{T}_4$ compounds

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Structural rearrangements triggered by a magnetic field are rare compared to temperature and/or pressure induced polymorphism. While the latter is routinely probed *in situ* by temperature and pressure dependent powder diffraction, the most common tools employed in detecting magnetic field induced polymorphism remain bulk field-dependent measurements of the physical properties, e.g., the electrical resistance, magnetization and strain. On one hand, discontinuities in these macroscopic properties serve as suitable evidence of a structural phase transition, but on the other hand, they provide no clues about its atomic-scale mechanism. By successfully coupling a rotating anode powder diffractometer with a continuous-flow cryostat and a split-coil superconducting magnet we were able to obtain excellent-quality Rietveld-ready powder diffraction data between 2.5 K and 315 K in 0 to 4 T magnetic fields. This allowed us to study the magnetic field-induced polymorphism in several polycrystalline compounds from the  $\text{R}_5\text{T}_4$  family, where  $\text{R} = \text{lanthanide metal}$ ,  $\text{T} = \text{Si, Ge and/or Sn}$ .

This research was supported by the Division of Materials Science of the Office of Basic Energy Sciences of the US DOE under contract No. W-7405-ENG-82.

**Keywords:** phase transitions, powder diffractometry, structural physical properties

### P.20.12.1

*Acta Cryst.* (2005). A61, C471-C472

#### When 2+2 isn't 4

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Recently much work has gone into examining the photoexcited HS state of iron(II) spin crossover compounds in full structural detail[1]. So far this work has focused on compounds closely related to the early work with either two neutral tridentate ligands or two

neutral didentate and two mononegative ligands (usually thiocyanate)[1,2].

Using a single tetradentate ligand [3] we present variable temperature results on [(tpa)Fe(NCS)<sub>2</sub>] (tpa = tris(pyridine-2-ylmethyl)amine) crystallised with a variety of solvents. The variation in solvent with the concomitant change in the hydrogen bonding significantly affects the position of the HS ↔ LS crossover. Furthermore we report on our initial results from determining the structures of photoinduced metastable HS states.

[1] Money V. A., Elhaik J., Radosavljevic Evans I., Halcrow M. A., Howard J. A. K., *J. Chem. Soc., Dalton Trans.*, 2004, 65. [2] Marchivie M., Guionneau P., Howard J. A. K., Goeta A. E., Chastanet G., Létard J-F, Chasseau D., *J. Am. Chem. Soc.*, 2002, **124**, 194-195. [3] Højland F., Toftlund H., Yde-Andersen S., *Acta Chem. Scand.*, 1983, **A37**, 251-257.

**Keywords:** spin crossover, iron, phase transitions

#### P.20.12.2

*Acta Cryst.* (2005). **A61**, C472

#### Synthetic and Structural Studies on Photoactivated Complexes

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**Photocrystallography**[1] is the technique for determining the structure of molecules in their excited state. Single crystal X-ray diffraction studies have been carried out on a number of complexes that have metastable or microsecond lifetimes[2]. These are very challenging experiments and it is difficult to maximise the level of excitation without destroying the crystal. In order to overcome these difficulties we are investigating several new strategies.

We are developing methods of studying metastable and excited state structures using X-ray **powder diffraction**. This relies on significant structural changes in the molecules such as isomerism, and in the initial investigations we are studying the linkage isomerism of [Ru(SO<sub>2</sub>)(NH<sub>3</sub>)<sub>4</sub>L][X<sub>n</sub>] (L=Cl, X=Cl, n=1; L=H<sub>2</sub>O, X=MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>, n=2) where the coordination mode of the SO<sub>2</sub> changes from μ<sub>1</sub>-S to μ<sub>2</sub>-S-O under illumination by a bright white light source. The μ<sub>2</sub>-S-O isomer is metastable at temperatures below 120K.

In a related series of synthetic studies, we are co-crystallizing the ruthenium complexes with cyclodextrin molecules, so that the cations may be held in the cyclodextrin pocket. Then if photocrystallographic studies are carried out on these systems, higher levels of excitation may be observed because the SO<sub>2</sub> group will be free to isomerise shielded from the rest of the crystal structure by the cyclodextrin cage.

[1] Coppens P., Ma B., Gerlits O., Zhang Y., Kulshrestha P., *Cryst. Eng. Comm.*, 2002, **4**, 1. [2] Novozhilova I.V., Volkov A.V., Coppens P., *J. Am. Chem. Soc.*, 2003, **125**(4), 1079-1087.

**Keywords:** photocrystallography, powder diffraction, crystal engineering

#### P.20.12.3

*Acta Cryst.* (2005). **A61**, C472

#### Charge Density Study of Photo-Excited State in Spin Crossover Complex

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The spin crossover complexes are widely recognized for the temperature and photo-induced transitions from low-spin (LS: S=0) to high-spin (HS: S=2) state of the Fe<sup>2+</sup> ions. By the photo-excitation at low temperature the HS state is trapped even after the photo-irradiation. This phenomenon is called Light Induced Excited Spin State Trapping (LIESST). Here we have found the photo-excited state in [Fe(ptz)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub> [1] and Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>, at 92K. At this temperature the LIESST phenomenon is not observed. The experimental and analytical methods used are as follows.

The powder diffraction data of the complexes were measured at 92K under 532nm CW laser irradiation by using Large Debye-

Scherrer Camera installed at BL02B2, SPring-8. An imaging plate was used as a detector to collect whole powder patterns simultaneously. The N<sub>2</sub> gas flow type system was combined with the laser system for the low-temperature measurements. As a result, the volume ratio of the photo-excited phase reached to approximately 90%. The charge density obtained by using the MEM/Rietveld method revealed the distinguished difference between the photo and temperature-induced HS state in the Fe-N bonding nature. In the talk, the detail including the LIESST phase will be presented.

[1] Moritomo Y., et al., *J. Phys. Soc. Jpn.*, 2002, **71**, 2609.

**Keywords:** photo-excited structure, spin crossover complex, charge density study

#### P.20.12.4

*Acta Cryst.* (2005). **A61**, C472

#### Thermal and Light-Induced Polymorphism in Fe(II) Spin Crossover Materials

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In certain Fe(II) complexes, the energy difference between the high spin (HS) and low spin (LS) state is of the order of  $k_bT$ . In these materials it is possible to induce a spin crossover (SCO) by a change of temperature, application of pressure and more interesting for potential applications, by light irradiation [1].

Materials such as Fe[H<sub>2</sub>BPz<sub>2</sub>]<sub>2</sub>L (Pz = pyrazol L = 2,2'-bipyridine (1) or 1,10-phenanthroline (2)) have been shown to exhibit Light-Induced Excited Spin-State Trapping (LIESST) when irradiated at low temperature [2]. In 2, the thermal SCO is coupled with a structural change from C2/c to P1, which is retained on irradiation, giving a new high spin structure [3].

Another SCO material, the coordination polymer {Fe(Bpe)<sub>2</sub>[Ag(CN)<sub>2</sub>]} (3) exhibits an incomplete SCO transition [4], the structural consequences which include an effect complementary to the "Thermal and Light-Induced Polymorphism" seen in 2.

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**Keywords:** spin crossover, LIESST, coordination polymers