

**P14.07.29***Acta Cryst.* (2008). A64, C574**Photomagnetic complexes. Structures of excited states**Helle Svendsen<sup>1</sup>, Jacob Overgaard<sup>1</sup>, Eric Collet<sup>2</sup>, Bo B Iversen<sup>1</sup><sup>1</sup>University of Aarhus, Department of Inorganic Chemistry, Langelandsgade 140, Aarhus, Dk-8000 Aarhus C, Dk-8000 Aarhus C, Denmark, <sup>2</sup>Groupe Matière Condensée et Matériaux, University Rennes1, France, E-mail: helle@chem.au.dk

Photoinduced magnetization is an interesting property in materials, with special focus on the development of new memory devices. We have synthesized a range of complexes with the general formula  $M1(DMF)_4(H_2O)_3(m-CN)M2(CN)_5 \cdot H_2O$  ( $M1M2DMF$ ), where M1 is a rare earth metal and M2 a transition metal. For NdFeDMF it has been shown that the material has a significant photoinduced magnetization. Upon UV irradiation the material stays in the excited state for several hours. The mechanism causing this large change in the magnetic susceptibility is not yet understood, and in order to understand the nature of the electronic transition it is crucial to know exactly which electrons are involved in the process. For that reason electron density studies are of great importance. The long lived metastable state makes it possible not only to study electron densities in the ground state but also in the excited state as well without the need for time resolution. As a first step towards excited state electron densities we have measured the structure in the excited state of NdFeDMF as well as four other complexes, which show the same behavior upon UV-illumination.

Keywords: photomagnetic complexes, excited state structures, lanthanide atoms

**P15.06.01***Acta Cryst.* (2008). A64, C574**Absolute intensity and phase of the resonant X-ray scattering from a germanium crystal**Enver Kh. Mukhamedzhanov<sup>1</sup>, Mikhail M. Borisov<sup>1</sup>, Andrey N. Morkovin<sup>1</sup>, Aleksey A. Antonenko<sup>2</sup>, Aleksey P. Oreshko<sup>2</sup>, Elena N. Ovchinnikova<sup>2</sup>, Vladimir E. Dmitrienko<sup>3</sup><sup>1</sup>Russian Research Center "Kurchatov Institute", Kurchatov Center of Synchrotron Radiation and Nanotechnology, Kurchatov square, 1, Moscow, Moscow, 123182, Russia, <sup>2</sup>Moscow State University, Moscow, 119992 Russia, <sup>3</sup>Shubnikov Institute of Crystallography, Russian Academy of Sciences, Leninskii pr. 59, Moscow, 119333 Russia, E-mail: enverh@npnet.ru

For understanding of the physics of resonant scattering, it is essential to measure not only the magnitude but also the phase of the scattering amplitude, both of them are strongly changed with energy. In contrast to the purely resonant 600 reflection in Ge crystal, 222 reflection is weakly allowed even in the non-resonance region. Thus the energy spectrum of the 222 reflection is caused by the interference of the weak non-resonant and purely resonant contributions to the tensor atomic factor. The 222 reflection near the germanium K absorption edge was studied on

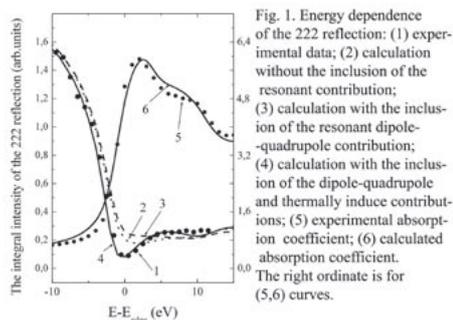


Fig. 1. Energy dependence of the 222 reflection: (1) experimental data; (2) calculation without the inclusion of the resonant contribution; (3) calculation with the inclusion of the resonant dipole-quadrupole contribution; (4) calculation with the inclusion of the dipole-quadrupole and thermally induced contributions; (5) experimental absorption coefficient; (6) calculated absorption coefficient. The right ordinate is for (5,6) curves.

the Kurchatov synchrotron radiation source (fig.1). The spectral dependence of the absolute intensity and phase of the resonant X-ray scattering from a Ge crystal was determined from the interference of the resonant and non-resonant contributions to the 222 reflection. The numerical simulation of the energy spectra of reflection with the inclusion of the temperature-independent dipole-quadrupole and thermally induced dipole-dipole contributions shows that the latter is dominant at room temperature. This work was supported by the Russian Foundation for Basic Research, project nos. 06-02-17249 and 07-02-00324.

Keywords: resonant scattering, synchrotron radiation, tensor atomic factor

**P15.06.02***Acta Cryst.* (2008). A64, C574**Quantitative evaluation of quadrupole transition effect in ATS scattering from magnetite, Fe<sub>3</sub>O<sub>4</sub>**

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ATS (anisotropic tensor of the susceptibility) scattering can be observed in *forbidden* Bragg reflections near absorption edge with synchrotron radiation. Magnetite has a spinel structure, in which the Fe atoms occupy the tetrahedral A site and the octahedral B site. The ATS scattering with dipole-dipole (d-d) transition process is allowed for the B site but not allowed for the A site. For the A site, therefore, we must consider higher dipole-quadrupole (d-q) transition. We previously studied the energy and azimuthal angle dependence of the 002 and 006 forbidden reflections. In the energy spectrum we found a main resonant peak just above the Fe K-edge and a second peak in the pre-edge region. From the ratio of the two reflections intensities we concluded that the main peak was mainly caused by d-d scattering from the B site and the pre-edge peak by d-q scattering from the A site. However, we did not quantitatively estimate each contribution because the azimuth dependence is completely same for the both transitions. In the present work, in order to evaluate the quantitative contribution from the A and B sites, we measured detailed azimuth dependence of the 046 forbidden reflection at the two resonant energies. Furthermore we measured separately each energy spectrum of the d-d or d-q scattering by utilizing the X-ray polarization property. From least-squares analysis of the azimuth dependence, we evaluated absolute value of the anisotropic tensorial element for the d-d and d-q scattering factors,  $f(dd)$  and  $f(dq)$ . We obtained the ratio of the ATS scattering factors  $f(dd):f(dq) = 3:2$  at the main resonance, while  $f(dd):f(dq) = 1:4$  at the pre-edge resonance. Thus we have found that the d-q scattering from the A site has unexpectedly large effect on the both resonance.

Keywords: X-ray resonant scattering, magnetite, quadrupole transition

**P15.10.03***Acta Cryst.* (2008). A64, C574-575**Twenty-four beam X-ray diffraction in a two-plate Fabry-Perot silicon crystal cavity**Shih-Lin Chang<sup>1,3</sup>, Mau-Sen Chiu<sup>2</sup>, Yuriy P. Stetsko<sup>3</sup><sup>1</sup>National Tsing Hua University, Physics Department, 101, Section 2, Kuang Fu Rd. Physics Dept., Hsinchu, Taiwan, 300, Taiwan, <sup>2</sup>National

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The dynamical interaction in a simultaneous twenty-four beam diffraction in a two-plate silicon cavity assembly for 14.4388 keV X-rays is studied, where the diffracted X-rays are reflected back and forth between the two crystal plates via the (12 4 0) reflection. The dynamical theory of X-ray diffraction with a Cartesian coordinate system is employed to calculate the interference pattern due to Fabry-Perot type resonance. The calculated intensity distribution of the transmitted beam is in good agreement with the measured one. The dispersion surface, linear absorption coefficients, wavefield intensities, and excitations of mode are also calculated. The formation of standing waves and phase change under the cavity resonance condition will be discussed.

Keywords: twenty-four beam diffraction, X-ray cavity, dynamical interaction

## P15.06.04

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### Site-selective determination of coordination symmetries by anisotropic anomalous X-ray scattering

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Based on an experiment of Kirfel and Petcov on rutile (136)  $P4_2/mnm$ , which verified anisotropic anomalous scattering (AAS) by measuring 'Forbidden Reflection near Edge Diffraction' (FRED), we aimed to extend the results with allowed reflections to extract more tensor symmetries of the Ti scattering factor tensor  $f_{ij}$  by fitting the model of AAS to the experimental data. Results from DFT calculations will also be presented. Furthermore we intended to study possible restrictions for atomic site occupation of unknown structures in an identified space group due to these local symmetry relations exemplary for this model structure. Experiments were carried out at DESY/HASYLAB BL C using a Si (111) double crystal monochromator tuned to an energy of 4985 eV. An automated optimization and  $\Psi$ -scan routine for a sample setup with rotating degree of freedom assured AAS measurements at the reflection maxima. The rutile samples investigated were  $10 \times 10 \times 1$  mm<sup>3</sup> wafers in (001), (110) and (111) orientation and  $\Psi$ -scans were measured for the reflections 001, 220, 110 and 111. Ti occupies Wyckoff site  $2a$ , its tensor symmetry must follow the local symmetry  $m.mm$  leaving 3 complex elements  $f_{11}, f_{12}, f_{33}$ . Simulations showed dependencies: 001 to  $f_{12}$ , 220 to  $f_{11}-f_{33}$ , 110 to  $f_{11}-f_{33}$ , 111 to  $f_{12}$ . For the 001 reflection intensity real and imaginary part correlate, but the 111 intensity displays asymmetric influence so the ambiguity is separable. The measured data show clear evidence of AAS and the 001 FRED and 111 intensities could be fitted:  $f''_{Ti} d'_{12} = -5.44 * 0.5(8)$ ,  $f''_{Ti} d''_{12} = 3.98 * 1.4(2)$ . Since  $f_{13}$  and  $f_{23}$  were refined to zero, the positioning of Ti within the unit cell would by inverse symmetry arguments with respect to site symmetry only be consistent on Wyckoff sites  $a, b, e, f, g$  (out of  $k$ ).

Keywords: anisotropic anomalous dispersion, X-ray resonant scattering, anomalous scattering methods

## P15.06.05

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### Resonant X-ray diffraction study of low temperature magnetite

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Magnetite was one of the first magnetic materials discovered, and has historically been cited as the model charge ordered system. However, the low temperature structure is yet to be fully resolved, complicating our understanding of the nature of the superstructural ordering. We have conducted resonant x-ray scattering, examining the pre- and post sample polarisation dependence at the iron K-edge in order to probe the (0 0 odd)<sub>C</sub> and forbidden (0 0 half integer)<sub>C</sub> reflections.

Keywords: resonant scattering, anomalous diffraction, X-ray charge-density analysis

## P15.06.06

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### Orbital ordering and the impurity effect in layered manganites

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The charge, spin, and orbital ordering states in perovskite-type transition metal oxides and the doped compounds have attracted much interest because of their intriguing phenomena such as high T<sub>c</sub> superconductivity, colossal magnetoresistance effect, magnetoelectric effect and so on. Impurity ions substituted for the transition metal ions in these compounds effect a change in the local electronic state. In this study we have investigated the impurity effect on the charge/orbital ordering of layered manganites by using resonant x-ray scattering (RXS). A layered manganite La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub> shows charge and orbital ordering below about 220 K. We have studied how the ordering state is changed by the substitution of Cr, Fe, Ga ions for Mn ions by using RXS at absorption edge energy (EA) of Cr, Fe, Ga as well as Mn. The RXS at Mn EA in La<sub>0.5</sub>Sr<sub>1.5</sub>Mn<sub>0.97</sub>Cr<sub>0.03</sub>O<sub>4</sub> has almost the same intensity as that in the pure compound La<sub>0.5</sub>Sr<sub>1.5</sub>MnO<sub>4</sub>. In contrast, we could not observe any RXS intensity at Mn EA in La<sub>0.5</sub>Sr<sub>1.5</sub>Mn<sub>0.97</sub>Fe<sub>0.03</sub>O<sub>4</sub>. These results indicate that the charge and orbital ordering state is not changed by the substitution of Cr but the orderings collapse by the substitution of Fe. Moreover, the most interesting result is the Ga substitution effect. The RXS at Mn EA in La<sub>0.5</sub>Sr<sub>1.5</sub>Mn<sub>0.97</sub>Ga<sub>0.03</sub>O<sub>4</sub> has four times larger intensity than that of the pure compound: The orderings in La<sub>0.5</sub>Sr<sub>1.5</sub>Mn<sub>0.97</sub>Ga<sub>0.03</sub>O<sub>4</sub> become strong by the substitution. We have