

m23.o01**Symmetry and physical aspects of the near-edge resonant "forbidden" reflections**Vladimir E. Dmitrienko^a, E.N. Ovchinnikova^b, A.A. Antonenko^b, K.A. Kozlovskaya^b, A. Kirfel^c, S.P. Collins^d, D. Cabaret^e, R.V. Vedrinski^f, J. Kokubun^g, K. Ishida^g^aInstitute of Crystallography, Moscow, 119333 Russia, ^bMoscow State University, Russia, ^cBonn University, Germany, ^dDiamond Light Source, UK, ^eUniversity Pierre and Marie Curie, France, ^fRostov State University, Rostov-Don, Russia, ^gTokyo University of Science, Japan. E-mail: dmitrien@ns.crys.ras.ru**Keywords: anisotropic anomalous dispersion, forbidden reflections, polarized XAS**

Symmetry restrictions on the X-ray polarization anisotropy of scattering factors, which are important for the near-edge resonant diffraction, are surveyed. The main emphasis is made on the anisotropy-induced "forbidden" reflections because they are most sensitive to the environment of resonant atoms. A recent review can be found in [1]. An important physical feature of the resonant anisotropy is that it is extremely sensitive to small violations of local symmetry, for example, to thermal atomic motion or disorder. The anisotropic scattering amplitude can be expanded as a function of the wave vectors of initial and diffracted beams so that the dipole-dipole, dipole-quadrupole, etc. contributions can be considered separately. The dipole-quadrupole term is especially interesting because its symmetrical part is similar to the thermal-motion-induced term whereas its antisymmetrical part describes local chirality of atoms even in centrosymmetric crystals like hematite or anatase [2]. The phase problem can be solved for the "forbidden" reflections using their interference with the multiple-wave contributions from non-forbidden reflections [3]. Theoretical ideas are illustrated by experimental data for Ge, Fe₂O₃, Cr₂O₃, Ge, TiO₂ and other crystals and by simulations using different approaches, namely, the full multiple-scattering method employing a cluster muffin-tin potential and pseudopotential ab initio calculations. Possible physical applications of the "forbidden" reflections are discussed. This work was partly supported by the INTAS grant 01-0822 and by a travel grant of Russian Foundation for Basic Research.

- [1] Dmitrienko V.E., Ishida K., Kirfel A., Ovchinnikova E.N., *Acta Cryst.*, 2005, A61, 481 (free access to this review at www.iucr.org).
 [2] Dmitrienko V.E., Ovchinnikova E.N., *Acta Cryst.*, 2001, 57, 642.
 [3] Kokubun J., Ishida K., Cabaret D. et al., *Phys. Rev. B*, 2004, 69, 245103.

m23.o02**Study of charge ordering by resonant diffraction**

Yves Joly, Elena Nazarenko, Emilio Lorenzo

*Laboratoire de Cristallographie, BP166 38042 Grenoble Cedex 09, France. E-mail: yves.joly@grenoble.cnrs.fr***Keywords: ab initio periodical and cluster calculations, X-ray resonant scattering, charge transfer**

Resonant X-ray diffraction (RXD) is a technique where both the power of site selective diffraction and the power of local absorption spectroscopy regarding atomic species are combined to the best. Reflections are recorded over some tens electronvolts around the absorption edge of the elements present in the material, where they show strong energy and angular dependencies. This phenomenon is due to the virtual photon absorption-emission associated with the resonant transition of an electron from a core level to some intermediate state above the Fermi level. By virtue of the dependence on the core level state energy and the three dimensional electronic structure of the intermediate state, this technique is specially suited to study charge, orbital or spin orderings and associated geometrical distortions. In the case of charge ordering, we exploit the fact that atoms with closely related site symmetries but with barely different charges exhibit resonances at slightly different energies. Here we show that the sensitivity of this effect allows for quantitative estimations of the charge disproportion. Opposite to fluorescence or absorption measurements, the power of diffraction relies on the capability of detecting differences that are even smaller than the inverse lifetime of the core hole level. Clearly, not all Bragg reflections are sensitive to charge ordering, and the failure in detecting charge ordering signatures in previous RXD work on magnetite is partly related to an incomplete choice of them. To account for the uncertainty of the crystallographic structure and the fact that the charge ordering must be disentangled from the associated atomic displacements, a complete methodology is proposed. It needs a very important set of experimental data, first principle simulations and the use of objective confidence factors for comparing experiment and theory. As main example we apply the method to the evidence and quantitative evaluation of the charge ordering in the low temperature phase of magnetite. We found in this case ± 0.12 and ± 0.10 charge disproportions between the four iron octahedral sites. Relative sensitivity on spin ordering, Jahn-Teller distortion and orbital ordering is also shown and compared on different transition metal oxide compounds.