

Poster Sessions

physicochemical properties through the application of pressure and temperature as a result of changes in crystal packing and distortion/compression of coordination bonds. Measuring the structural changes of these complexes with relation to pressure and temperature allows for a greater insight into how these properties arise. Typically however it is difficult in current crystallographic studies to simultaneously alter the pressure and temperature of the experiment, due to the inherent difficulties associated with heating or cooling a diamond anvil cell, as well as difficulties in accurate and precise recording of the internal cell temperature.

Successfully merging the fields of low-temperature and high-pressure crystallography would however provide huge benefits to the study of structure-behaviour relationships. Low-temperature and high-pressure studies could be performed simultaneously or consecutively using the same crystal and experimental setup, allowing for improved modelling of complicated multi-variable phase changes. Significant improvements in data quality would be observed for high pressure studies conducted at low temperatures due to reduced thermal and vibrational motion. Secondary radiation damage to crystals is also temperature dependant thus lower temperature acquisition will prolong the lifespan of crystals under high-pressure study [1]. The desire for this combined approach has thus necessitated the design of a novel diamond anvil cell which can be successfully implemented for high-pressure low-temperature crystallographic studies.

[1] A.E. Goeta, J.A.K. Howard, *Chem. Soc. Rev.*, **2004**, *33*, 490–500.

Keywords: high-pressure, low-temperature, X-Ray

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Novel microfocus x-ray sources for high-pressure crystallography

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Diamond anvil cells (DAC's) are widely used for examining the crystal structure of materials under high pressure. The area of reciprocal space accessible in a high-pressure X-ray diffraction experiment is primarily restricted by the geometry of the DAC. For a typical high-pressure experiment using Mo radiation, only a small fraction of all reflections can be collected. This can be as low as 30% for triclinic crystal structures. Using radiation with a shorter wavelength, such as Ag-K_α, a larger portion of the reciprocal space is accessible, thus increasing the number of observations and the resolution of the data. However, because of the low intensity of conventional Ag sealed tubes, Ag sources are rarely used for high-pressure studies in the home lab.

Microfocus sealed tube sources have proven to deliver flux densities beyond that of traditional X-ray sources when combined with 2D focusing multilayer mirrors [1, 2]. The sharp beam profile of these sources produces a high flux density at the sample position, thus leading to strong diffracted intensities. Furthermore, the small beam cross-section significantly reduces the background that usually results from scattering at the gasket of the DAC. Therefore, this type of source presents a promising alternative to classical sealed tube sources currently being used in high-pressure crystallography.

We will be reporting on the latest developments on microfocus X-ray sources (Ag and Mo anodes) which enable a clear increase in intensity compared to other sealed tube sources. Selected results on the use of these sources in high-pressure crystallography will be presented.

[1] J. Wiesmann, J. Graf, C. Hoffmann, A. Hembd, C. Michaelsen, N. Yang, H. Cordes, B. He, U. Preckwinkel, K. Erlacher, *Particle & Particle Systems Characterization* **2009**, *26*, 112. [2] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G.M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2009**, *42*, 885.

Keywords: instrumentation, X-ray source, high-Pressure crystallography

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Silver the new gold standard for high pressure single crystal X-ray diffraction

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The advances in X-ray focusing optics have reignited the interest in alternative home laboratory source wavelengths. Ag X-radiation has several advantages to longer wavelengths, particularly for use with diamond anvil cells (DAC's), for high pressure diffraction experiments. The compression of the reciprocal lattice, from the shorter wavelength, allows significantly more data to be collected under restricted experimental conditions. Additionally the lower absorption and hence attenuation by the diamond anvils increases the usefulness of this wavelength for these experiments.

Previous attempts to utilize Ag radiation, from sealed tube X-ray sources, have been thwarted by the low incident flux levels achievable. The new Ag I μ S system [1] combats this problem by employing multilayer focusing optics which allow a high flux density to be achieved at the sample position even at low power levels (30W). The focused nature of the source also reduces unwanted interference in the X-ray diffraction pattern originating from the body of the DAC and the metal gasket forming the sample chamber.

The XIPHOS diffraction facility [2] at Durham University has been expanded with the construction of a 'sister' diffractometer coupling a 4-circle Huber goniometer with a Bruker APEXII detector and a Ag I μ S source. This has allowed the exploration of a number of samples under high pressure to a greater resolution than previously accessible in the home laboratory. Of particular interest are compounds that exhibit different solid state phases which are dependent on the crystallization method employed (high pressure or low temperature).

[1] T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2009**, *42*, 885-891. [2] M.R. Probert, C.M. Robertson, J.A. Coome, J.A.K. Howard, B. Michell, A.E. Goeta, *J. Appl. Cryst.*, **2010**, *43*, 1415-1418.

Keywords: experimental, pressure, phase

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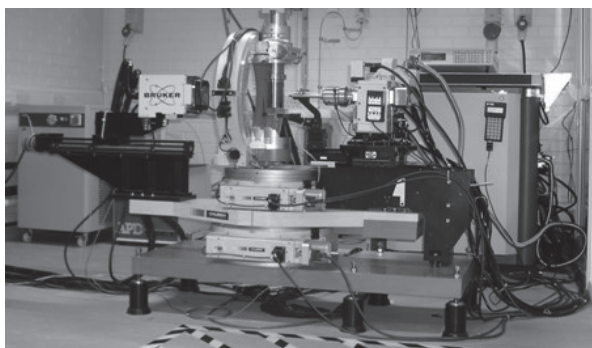
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The XIPHOS diffraction facility for extreme sample environments

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Pushing the boundaries of experimental single crystal diffraction, particularly in the home laboratory, requires significant deviation from off-the-shelf instrumentation. The XIPHOS diffraction facility

[1] has been designed for structural studies under extreme sample environments, combining equipment from several manufacturers along with custom designed components. The unique end product provides unparalleled access to 'in house' diffraction data allowing data collections to be performed at temperatures as low as 2.0 K. Operation and monitoring of the system, as well as data processing, requires novel approaches. In particular, the method of cooling means that several objects along with the sample are present in the primary X-ray beam and these features need to be accounted for. However, temperature is not the only thermodynamic variable to be explored through single crystal diffraction and there is growing interest in the field of structural studies under high pressure [2] and light irradiation [3]. Hence, the development of XIPHOS includes the controllable use of a combined range of temperatures, high pressures and/or irradiation wavelengths which expands the functionality of 'in-house' systems for the study of solid state phenomena.



[1] M.R. Probert, C.M. Robertson, J.A. Coome, J.A.K. Howard, B.C. Michell, A.E. Goeta *J. Appl. Cryst.* **2010**, *43*, 1415-1418. [2] E.V. Boldyreva *Acta Cryst.* **2008**, *A64*, 218-231. [3] P. Güttlich, H.A. Goodwin *Top. Curr. Chem.* **2004**, *234*.

Keywords: instrumentation, cryocrystallography, photocrystallography

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X-Ray resonant scattering - origin of Fe K Pre-Edge peak of magnetite

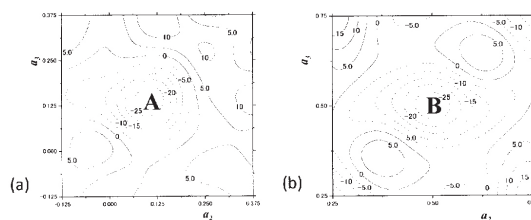
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The difference-Fourier synthesis between two sets of observed data was applied to X-ray resonant scattering (XRS). The XRS effect measured at a pre-edge of Fe K absorption edge makes it possible to give the information on a location of electrons resonantly scattered and therefore, of targeted atoms. The electron density can be estimated to subtract the resonant intensity at the pre-edge from off-edge intensity. Using a difference in the XRS pre-edge intensity measured at energy E_{on} and E_{off} , a difference in electron-density is given by $\Delta\rho(\mathbf{r}) = V^{-1} \sum_{\mathbf{hkl}} \{F(\mathbf{hkl})_{\text{on}} - F(\mathbf{hkl})_{\text{off}}\} \exp(-2\pi i \mathbf{k} \cdot \mathbf{r})$, where $F(\mathbf{hkl})$ and \mathbf{k} are the crystal structure factor and scattering vector, respectively, and then the termination effect of Fourier series is automatically corrected.

It is interesting to pinpoint specific atoms by extracting some electrons resonantly scattered. For example, the position of 1s electrons can be estimated from the *shell structure factors* to be the balance between X-ray resonant scattering (XRS) and total intensity [1]. Recently, the electron-density analysis of magnetite has revealed the overlapping of magnetic electron orbitals among neighboring atoms,

by making use of the intensity difference in resonant X-ray magnetic scattering between left- and right-circular polarizations [2]. Magnetite has the crystal structure of inverse-spinel type of $[\text{Fe}^{3+}]^{\text{A}}[\text{Fe}^{2+}\text{Fe}^{3+}]^{\text{B}}\text{O}_4$, where only Fe^{3+} occupies the tetrahedral A sites and Fe^{2+} and Fe^{3+} equally occupy the octahedral B sites. It is known that in X-ray absorption experiments magnetite has a pre-edge structure at the Fe K edge. Although the pre-edge peak is considered as a dipole-transition mechanism of Fe^{3+} in the tetrahedral sites, the site symmetry of the octahedral sites is $-3m$ and gives another possibility on the origin with super-exchange interaction of A-O-B sites.

Magnetite used in this study has a cell dimension of $a = 8.4000(3)$ Å with the space group of $Fd-3m$. Synchrotron experiments were performed at BL-6C of the Photon Factory using a conventional Rigaku AFC5 four-circle diffractometer. Si(111) double-crystal monochromator and diamond(001) phase retarder were used to produce circularly polarized X-rays at the Fe K edge. Intensity data for 354 reflections were collected in the range $2\theta \leq 90^\circ$ with an ω - 2θ step scan mode. Figure 1 shows the electron-density maps of magnetite on the planes passing through (a) A and (b) B sites, respectively. Contours are at intervals of $0.5 \text{ e}/\text{\AA}^3$, where the numbers in maps are magnified by 10 and solid lines are zero and positive and broken lines are negative. negative peaks appear around A and B sites in heights of -2.7 and $-2.9 \text{ e}/\text{\AA}^3$, respectively. It is suggested that the pre-edge peak of magnetite originates in both A and B sites.



[1] S. Sasaki, K. Tsukimura, *J. Phys. Soc. Jpn.* **1987**, *56*, 437-440. [2] Y. Kaneko, M. Okube, S. Sasaki, *Am. Inst. Phys. Conf. Proc.* **2010**, *1234*, 871-874.

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Electron-density distribution of Fe_3O_4 on resonant X-Ray magnetic scattering

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A combination of resonant X-ray magnetic scattering (RXMS) [1-3] and difference-Fourier synthesis makes it possible to visualize the distribution of magnetic electrons. RXMS is a useful tool to examine the magnetic structure associated with specific electronic states such as $3d-4p$ interactions. The electron-density maps can be synthesized on the basis of a difference in the RXMS intensity between left- and right-circular polarizations.

The crystal structure of magnetite Fe_3O_4 is of inverse-spinel type, where there are tetrahedral A site occupied by Fe^{3+} and octahedral B site occupied equally by Fe^{2+} and Fe^{3+} . The magnetic and electronic properties are influenced by the cation distribution of Fe atoms in two kinds of the sites. X-ray magnetic circular dichroism (XMCD) of magnetite gives a dispersive signal at a pre-edge of Fe K absorption edge, which is observable by site-specific magnetic electrons.