Time-resolved X-ray diffraction experiments including those performed at XFEL sources require modification of data analysis procedures as sample destruction in the X-ray and/or laser beam typically requires multi-crystal data collection. Modifications introduced include a scaling technique for relative scaling within multi-crystal data sets, use of the RATIO technique in which measured I_{ON}/I_{OFF} ratios are used in combination with conventional data [1], and the use of refinement methods [2] and R-factors [3] specific for dynamic-structure crystallography. The procedures have been applied to several sets of Laue data collected at beamline 14-ID at the Advanced Photon Source [4]. The extended bandwidth of the pink Laue technique allows use of one or a few X-ray pulses per data frame, thus minimizing crystal damage by laser exposure and optimizing the attainable time-resolution.

Results for the α-modification of $Rh_2(\mu\text{-}PNP)_2(PNP)_2$ $(BPh_4)_2$ ($PNP = CH_3N(P(OCH_3)_2)_2$, Ph = phenyl) (**1**) show a shortening of the Rh-Rh distance of 0.136(8) Å and significant displacements of the ligands on excitation. This may be compared with those on an earlier monochromatic study of the $[Rh_2(1,8\text{-diisocyano-p-menthane})_4]^{2+}$ ion in which a Rh-Rh shortening of 0.85(5) Å was observed [5]. The polychromatic results on (**1**) are clearly the more accurate ones. They are not well reproduced by isolated molecule calculations, but can be accounted for quantitatively by taking into account the confining effect of the crystal environment with the QM/MM (Quantum Mechanics/Molecular Mechanics) method [6], thus underlining the differences between isolated molecules and molecules in crystals. Additional data have been collected on a number of phosphorescent Cu(I)-phenanthroline chromophores which are candidates for use in photovoltaic cells.

The modified Laue method is capable of producing excited state structures at atomic resolution of a quality compatible with or better than those of monochromatic synchrotron experiments. The modifications described are relevant for monochromatic data sets collected at X-ray Free Electron Laser sources.

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Keywords: time-resolved diffraction, laue method, excited state

MS.45.5

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Dynamic Investigation of photoinduced phase transition in prussian blue analogs by picosecond time-resolved XAFS

Shunsuke Nozawa,[a] Tokushi Sato,[a] Ayana Tomita,[b] Manabu Hoshino,[b] Hiroko Tokoro,[c] Shin-ichi Ohkoshi,[c] Shin-ichi Adachi,[a] Shin-ya Koshihara,[b] [a]*Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, (Japan).* [b]*Department of Chemistry and Materials Science, Tokyo Institute of Technology, Meguro-ku, (Japan).* [c]*Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, (Japan).* E-mail: noz@post.kek.jp

Prussian blue analogs have recently attracted great interest due to their various characteristics in the photoinduced phase transition (PIPT) as a photo-induced magnetization as well as photo-induced structural change.[1], [2] The investigation of the dynamics of PIPT allows us to obtain information how the photo-excitation in the single site expands into a macroscopic phase transition. Picosecond time-resolved XAFS experiments were performed on the NW14A at the Photon Factory Advanced Ring (PF-AR).[3], [4] The time-resolved XAFS spectra were collected by the pump-probe technique with a femtosecond laser system. In EXAFS and XANES regions, transient features attributed to the PIPT were obtained at 100 ps resolution. The detailed results will be presented.

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X-ray diffraction methods as a complementary tool for analyses of historical objects

Carolina Cardell, *Departament of Mineralogy and Petrology, University of Granada, Av/Fuentenueva s/n, 18071 Granada, (Spain).* E-mail: cardell@ugr.es

This presentation summarizes the research done by our team using different X-ray diffraction (XRD) methods to characterize historical objects such as paintings, ceramics, metals and stones. Also pigments and salts are typified since XRD is essential for analyzing materials with similar elemental composition but differing mineralogy. Our goals are to apply XRD methods as non-destructive, routine laboratory analyses combined with complementary techniques to fully characterize historical items, and thus, to draw artistic/archaeological conclusions and supply information to enable conservation/restoration interventions.

X-ray thermodiffraction (XRTD) is a powerful tool to track time-resolved, *in situ* mineralogical and phase transitions of varied materials such as pigments and hydrated salts. Using XRTD we studied the azurite decarbonation process [1] and sulfate-rich salt dehydration. New routines for 2D mapping allow us to better interpret reaction trends and kinetic rates [2].

Micro-XRD is a non-destructive technique that enables direct analysis of small (<1mm) artwork samples. Via micro-XRD we characterized pigments used in Islamic palaces from Granada (e.g. the Alhambra), bricks, potteries, enamels, bronze artifacts, patinas and stones, as well as newly formed minerals (salts and high T silicates) [3]. We used a single-crystal diffractometer and the software XRD2Dscan [4] to transform Debye-Scherrer rings into conventional powder diffractograms. The microtextural data of crystalline phases obtained from the Debye-Scherrer rings were used to determine crystal sizes of mineral grains and quantify grain sizes of phases present in the same layer. This novel micro-XRD application used on painting samples sheds light on the nature, manufacture and weathering of pigments [5].

Grazing incidence XRD (GIXRD) is a potent method for surface characterization of thin films and monolayers such as metal and alloys, providing information on corrosion processes. Few papers are published on the application of GIXRD to artworks, and most focus

on metallic artifacts with simple structures unlike those of paintings. Our ongoing investigation is devoted to optimizing GIXRD analytical routines to obtain the best quality diffractograms in complex, small and uneven painting samples [6].

Historical objects comprise a wide variety of composite materials made up of inorganic and organic components. To attain a full material characterization, other analytical techniques are essential in addition to XRD methods, such as microscopic techniques that provide key information on artwork microtexture, structure and composition via the use of mineral maps obtained from SEM-EDX analyses. Also application of Raman microscopy is crucial since it non-destructively identifies amorphous, poorly ordered and crystalline phases of small size (1µm). We have demonstrated the benefits of combining XRD methods together with Raman microscopy and SEM-EDX analyses in painting samples and patinas [5], [7].

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Synthetic or manufactured ancient pigments studied by means of synchrotron radiation–based methods

Pauline Martinetto,[a] Catherine Dejoie,[b] Michel Anne,[a] Eric Dooryhée,[c] Louise Samain,[d] Pierre Bordet,[a] Jean-Louis Hodeau,[a] Philippe Walter,[e] *[a]Institut Néel, CNRS-UJF, Grenoble, (France). [b]Lawrence Berkeley National Laboratory-ALS, Berkeley, (USA). [c]Brookhaven National Laboratory-NSLS II, Upton, (USA). [d]Institut de Physique Nucléaire, Atomique et de Spectroscopie et Centre Européen d'Archéométrie, Liège, (Belgique). [e]Centre de Recherche et de Restauration des Musées de France, CNRS, Paris, (France).* E-mail: pauline.martinetto@grenoble.cnrs.fr

Although recent use of laboratory X-ray powder microdiffractometers showed promising results on very small or multi-layer samples [1], synchrotron facilities produce X-ray beams (both tunable in energy and size) which allows a lot of combinations, well adapted to the heterogeneity of ancient materials. X-ray powder diffraction is thus combined with fluorescence and absorption to identify pigments in paint layers [2] and to understand manufacturing or alteration processes [3]. We shall illustrate through three examples the different possibilities offered by synchrotron radiation–based methods to study synthetic or manufactured ancient pigments. These pigments are often ill-ordered (because of their synthesis, their processing or their ageing) and remain difficult to be studied by using traditional diffraction methods. We use modern reproductions as references in order to consolidate data treatment and to interpret the results obtained on Cultural Heritage materials. The first example concerns Maya Blue, an artificial pigment manufactured in pre-Columbian Mesoamerica [4], one of the best examples of organic-inorganic hybrid materials. Its durability is due to a unique association after heating together indigo and a particular clay. Combining thermogravimetric analysis and synchrotron X-ray powder diffraction data with molecular modelling, we are able to propose a new explanation of the chemical stability and the durability of Maya Blue [5]. The second example will deal with Prussian Blue. This artificial pigment, accidentally discovered in Berlin in 1704 and very popular in the 18th and 19th centuries, shows a tendency to fade under light [6]. The degradation process seems related to the crystalline quality of the powders, depending of the method of preparation. In the case of ill-ordered powders, we have recorded the total scattering signal at 100 keV and we are currently carrying out Pair Distribution Function (PDF) analysis in order to provide suitable data for structural investigations of Prussian blue. The third pigment which will be discussed, galena (PbS), was extensively studied several years ago as main ingredient of ancient Egyptian cosmetics [7]. Actually, thermal treatments are commonly used nowadays to prepare eye make-up of different colors based on galena in northern Africa, but heating processing of galena in Ancient Egypt remains an opened question. We have recently performed Laue micro diffraction experiments on both artificially heated galena crystals and archaeological powders, in order to compare the thickness of the oxidized layers and the formed phases.

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Quantitative characterization of japanese ancient swords through time of flight neutron diffraction and energy resolved neutron imaging

Francesco Grazzi,[a] Elisa Barzagli,[a] Antonella Scherillo,[a,b] Stefan Hartmann,[c] Francesco Civita,[d] Riccardo Franci,[d] Eberhard Lehmann,[c] Marco Zoppi,[a] *[a]Consiglio Nazionale delle Ricerche, Istituto dei Sistemi Complessi, Sesto Fiorentino (Italy). [b]Science and Technology Facility Council, ISIS Neutron Source, Didcot (UK). [c] Paul Scherrer Institut, SINQ Neutron Source, Villigen (CH). [d]Museo Stibbert, Firenze (Italy).* E-mail: francesco.grazzi@isc.cnr.it

A total of nine broken Japanese swords pertaining to a period ranging from 14th until 19th century have been analysed through neutron diffraction and neutron imaging techniques [1]. The samples are the lower part of ancient swords broken approximatively at 50-60 mm from the beginning of the blade. They are signed and the authorship and attribution can be accurately identified. The samples have been made available by the Stibbert Museum staff as test samples for non destructive characterization through innovative methods.

Neutron diffraction has been applied on all the selected samples by using the INES diffractometer at the ISIS pulsed neutron source in UK [2]. The measurements have been performed on the average gauge volume both in the tang and in the blade in order to determine the quantitative distribution of the metal and non metal phases. The cementite to ferrite ratio has been used in order to quantify the carbon content. The comparative analysis of the phase distribution among the samples permitted to identify peculiar characteristics related to the forging traditions and periods of the Japanese history. I.e. the carbon content, the fayalite amount, the presence of wuestite and troilite has been comparatively checked. On few selected samples