Taipei, Taiwan. [b]*Department of Material Science, University of Hyogo, Himeji, Japan.* E-mail: wangyu@ntu.edu.tw

A six-coordinated iron(II) complex, t-$Fe(tzpy)_2(NCS)_2$ (tzpy = 3-(2-pyridyl)[1,2,3]triazolo[1,5-a]pyridine), undergoes a graduate spin transition from a paramagnetic high spin state ($^5T_2$, S = 2, HS-1) above 200K to a diamagnetic low spin state ($^1A_1$, S = 0, LS-1) below 75 K according to the magnetic measurement. The crystal structures of both HS-1 and LS-1 are studied at 298 and 40K respectively. Significant differences in Fe-N distances and in coordination geometries of Fe do occur during the spin transition. The electronic configuration of Fe in both HS and LS states is monitored by Fe K- & L-edge absorption. In addition, the ligand C-N stretching frequency can also be followed through the spin transition.

A light-induced-excited-spin-state-trapping phenomenon (LIESST) is observed by pumping the crystal with 532nm laser at 40K, where a relatively long-lived high spin state (HS-2) occurred. The molecular and crystal structure of this HS-2 state is investigated using pump and probe mode. The excitation can be easily detected by XRD, XAS and IR spectroscopy. The molecular structure and electronic configuration of Fe of HS-2 state are very similar to those of HS-1. The relaxation from such HS-2 state to the low spin state (LS-2) is followed via C-N stretching frequency at various temperature.

Keywords: spin-crossover, X-ray absorption spectroscopy, excited spin state

P.14.04.1

Structure Refinements of Protein-ligand Complex by the Maximum Entropy Method

Makoto Sakata[a], Takuya Kajikawa[a], Eiji Nishibori[a], Hideo Ago[b], Keisuke Hamada[b], Jun Ishijima[b], Masashi Miyano[b], [a]*Department of Applied Physics, Nagoya University, Nagoya, Japan.* [b]*RIKEN/SPring-8, Harima, Hyogo, Japan.* E-mail: sakata@cc.nagoya-u.ac.jp

It is important to have detailed structural information of protein crystal to understand functions of a protein. Particularly, interaction between protein and ligand molecule is a fundamental aspect of protein crystallography. The experimental techniques of protein crystallography have been very rapidly improved due to, for example, advent of Synchrotron Radiation source. Hence, it becomes rather usual to collect fairly good quality data set for a protein crystal. The analytical techniques for structure determination of protein crystals have also drastically improved. However, the structure refinement method still remains in an old fashion, i. e. Fourier method.

For materials with simple structure, more sophisticated method called the Maximum Entropy Method (MEM)[1] is now commonly used to obtain accurate electron density distributions. In order to demonstrate the ability of MEM for structure refinement in protein crystallography, the complex of ribose-5-phosphate isomerase(Rpi)[2] between both ribose 5-phosphate(R5P) and arabinose-5-phosphate (A5P) are refined by MEM. Isomerization to ribulose-5-phosphate proceed only for R5P but not for A5P. The MEM density maps revealed very clearly the structural differences between Rpi/R5P and Rpi/A5P.

[1] Sakata M., Sato M., *Acta Cryst.*, 1990, **A46**, 263. [2] Hamada K. *et al., J. Biol. Chem.*, 2003, **278**(49), 49183.

Keywords: protein structure refinement, maximum entropy method, Rpi

P.14.04.2

Maximum Entropy and Fourier Study on Electron Density of MnO, LaCoO$_3$ and MgSiO$_3$

Mikiko Tada[a], Shin Ishikawa[a], Makoto Sakata[b], Kouichi Ohkubo[a], Toru Kyomen[a], Eiji Nishibori[b], Satoshi Sasaki[a], [a]*Materials and Structure Lab., Tokyo Institute of Technology.* [b]*Department of Applied Physics, Nagoya University, Japan.* E-mail: tada@lipro.msl.titech.ac.jp

The maximum entropy method (MEM) gives us the deduced electron-density distribution without the use of any structure model [1]. On the other hands, the difference-Fourier (D-FR) method is well known to estimate the accurate electron-density through the Fourier transform. We have examined the validity to apply the MEM for electron-density studies in physically meaningful and relatively complicated structures. In this study, the MEM and D-FR maps derived from single-crystal X-ray diffraction data were compared for three materials, i.e. MnO, LaCoO$_3$ and MgSiO$_3$, after optimizing MEM parameters such as resolution and constraint condition.

MnO gave the anisotropic distribution of Mn 3d-electrons in the NaCl structure, although Mn^{2+} ions should be spherically distributed in the regular-octahedral coordination. LaCoO$_3$ has a maximum of susceptibility in the temperature range of 100 K, where Co^{3+} ions may have an intermediated spin-state. The temperature dependence of electron density was examined in this study. In a chain of SiO$_4$ tetrahedra in MgSiO$_3$, two Si-O bridging bonds and the other two non-bridging bonds had different covalent characters. It is conclusive that electron-density distributions deduced by the MEM are well compared with those estimated from the D-FR calculation.

[1] Sakata M., Sato M., *Acta Crystallogr.*, 1990, **A46**, 263.

Keywords: maximum-entropy method, Fourier methods, electron density distribution

P.14.05.1

Electron Density in Cubic SrTiO$_3$ from γ–ray Diffraction

Wolfgang Jauch[a], Manfred Reehuis[b], [a]*Hahn-Meitner-Institut, Berlin, Germany.* [b]*Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany.* E-mail: jauch@hmi.de

The electron density and atomic displacements in the prototype perovskite SrTiO$_3$ have been studied using extensive and accurate γ-ray diffraction data (λ = 0.0392 Å) at room temperature. The 6 strongest structure factors have been determined under extinction-free conditions by means of an extended-face thin-crystal plate in Laue geometry, so that the lowest I_{obs}/I_{kin} ratio was 0.98 for the full data set. The maximum thermal diffuse scattering contribution was only 3% at $\sin\theta/\lambda = 1.72$ Å^{-1}.

The thermal displacement parameters are in good agreement with lattice dynamical calculations as well as with neutron diffraction results. Contrary to simple expectation, anharmonic motion effects are negligible for all atoms. This finding is consistent with a previous γ-ray study which revealed SrTiO$_3$ as a harmonic system at $T_c + 5$ K [1], *i.e.* very close to the antiferrodistortive phase transition.

The charge density was modeled using *VALRAY*. The population of the 3d subshell on Ti is found to be 0.200(45) |e|, *i.e.* close to zero, in agreement with the observed magnetic behaviour. The electronic properties at the bond critical points indicate ionic Ti-O and Sr-O interactions of different strength which is corroborated by the net charges of the atomic basins: q(Sr) = 1.18 |e|, q(Ti) = 3.10 |e| and q(O) = −1.42 |e|.

[1] Jauch W., Palmer A., *Phys. Rev. B*, 1999, **60**, 590.

Keywords: γ-ray diffraction, charge density inorganic compounds, perovskite oxides

P.14.05.2

High-resolution Magnetic Compton Profile of Iron

Masayoshi Itou[a], Yoshiharu Sakurai[a], Akihisa Koizumi[b], Nobuhiko Sakai[b], [a]*Japan Synchrotron Research Institute, Hyogo, Japan.* [b]*University of Hyogo, Hyogo, Japan.* E-mail: mito@spring8.or.jp

A high-resolution magnetic Compton profile of ferromagnetic iron was measured with a momentum resolution of 0.14 atomic units. The results are compared with those obtained by FLAPW calculations [1].

Most of the magnetic Compton experiments have been performed with an energy dispersive spectrometer using a solid-state detector. With such detectors it is impossible to achieve a momentum resolution better than Δp ~ 0.4 atomic units. With a wavelength dispersive spectrometer, a higher resolution measurement can be performed. However, it usually takes a couple of weeks to acquire significant data

sets. Therefore, there are only two reports of high-resolution magnetic Compton experiments [2, 3] in this decade.

A new setup of the Cauchois-type x-ray spectrometer for Compton scattering experiments installed on BL08W at SPring-8 allows us to perform high-resolution experiments within a reasonable beam time. This spectrometer employs an X-ray image intensifier as a position sensitive detector. Using this spectrometer, a high-resolution magnetic Compton profile of iron single-crystal was measured with a momentum resolution of 0.14 atomic units. The statistical accuracy is approximately 4% at $p_z=0$. The experiment shows a good agreement with the theoretical prediction [1].

[1] Kubo Y., Asano S., *Phys. Rev. B*, 1990, **42**, 4431. [2] Sakurai Y. *et.al.*, *J. Condens. Matter*, 1994, **6**, 9469. [3] Cooper M. J. *et. al.*, *J. Phys. Chem. Solids*, 2000, **61**, 512.

P.14.05.3
The Effect of Fourier Series Truncation Errors on the Electron Density Distribution of $LiMn_2O_4$
Nobuo Ishizawa, Kenji Tateishi, Douglas du Boulay, *Ceramics Research Laboratory, Nagoya Institute of Technology, Tajimi 507-0071, Japan.* E-mail: ishizawa@nitech.ac.jp

The effect of Fourier series truncation errors on the electron density distribution (EDD) of $LiMn_2O_4$ has been examined using the single-crystal synchrotron X-ray diffraction data and the molecular dynamics (MD) simulation[1]. The MD crystal structure factors obtained from each MD snapshot taken at 2fs intervals in real space were time-averaged and then reversely Fourier transformed to calculate EDD in a similar way to the X-ray data. The EDD thus obtained in the range $\sin\theta/\lambda < 3.33$ Å^{-1} was scarcely affected by the series truncation errors, indicating unambiguously that a small portion of Li does exist close to interstitial positions near the 16c site of the space group Fd3m. The residual EDD assuming a partial structure with eliminating Li atoms also reproduced a mostly correct picture about the distribution of interstitial Li atoms, even though the value of $\sin\theta/\lambda$ of the MD data was reduced to 0.80 Å^{-1}. The interpretation of EDD obtained from the single-crystal synchrotron X-ray diffraction data was thus verified and reinforced from the MD simulation, not only by looking at the real space distribution of atoms in the snapshots but also by a close examination of their Fourier transform.

[1] Tateishi K. *et al.*, *Annual Report of Ceram. Res. Lab.*,2005, **4**, *in press*.

P.14.05.4
Ultra-high Resolution Data for Charge Densities Studies
Maksymilian Chruszcz[a], Marcin Cymborowski[a], Anna Makal[b], Zbyszek Otwinowski[c], Krzysztof Wozniak[b], Wladek Minor[a], [a]*University of Virginia, Charlottesville, Virginia 22908, USA.* [b]*University of Warsaw, 02-093 Warsaw, Poland.* [c]*UT Southwestern Medical Center at Dallas, Dallas, Texas 75390, USA.* E-mail: maks@iwonka.med.virginia.edu

X-ray diffraction is at present the main experimental technique to obtain the electron density distribution in crystals. Use of the new advanced area detectors allows measuring the ultra-high resolution data almost routinely. Speed of data collection and its quality is optimized when an integrated system for data collection, reduction and structure solution is used. The presented system allows for immediate control of the data quality in terms of such parameters as diffraction limit, completeness, and redundancy during the experiment. The experiment simulation module may minimize the influence of profile overlap and detector obstructions on data completeness. The further optimization can be accomplished by the use of specifically adjusted oscillation angle for each scan. The precise determination of diffraction intensities in the resolution shells between 0.7Å and 0.38Å is achieved by separate treatment of $K_{\alpha1}$-$K_{\alpha2}$ split. The ultra-high resolution, high quality data allow for precise analysis of interactions continua for all pairs of interacting atoms. The application of this approach to several systems will be presented.

P.14.05.5
Electron Density and Electrostatic Potential Study of an Organic Phosphate
Elies Molins[a], Ignasi Mata[b], Enrique Espinosa[c], [a]*ICMAB-CSIC, Barcelona, Spain.* [b]*SpLine-CSIC, Grenoble, France.* [c]*LIMSAG, Dijon, France.* E-mail: elies.molins@icmab.es

The electron density of the phosphate of L-histidinium phosphoric acid (LHP), experimentally obtained by X-ray and neutron diffraction data, is used for a detailed study involving *ab initio* calculations and topological analysis of both the electron density and the electrostatic potential [1][2].

As the L-histidinium presents a large dipolar moment and LHP crystals are non-centrosymmetric, this material has potential non-linear optical properties. These properties strongly depend on the crystal packing which, in this case, involve very short hydrogen bonds.

The results of this analysis on the LHP electron density allow a good characterization of the intermolecular interactions and a better understanding of the crystal packing. Moreover, the topological analysis of the electrostatic potential proves to be a useful tool to study the interaction of the molecules with its environment.

[1] Bouhmaida N., Dutheil M., Ghermani N.E., Becker P., *J. Chem. Phys.*, 2002, **116**, 6196. [2] Leboeuf M., Köster A.M., Jug K., Salahub D.R., *J. Chem. Phys.*, 1999, **111**, 4893.

P.14.05.6
Accurate Charge Densities in under a Day with a Home X-ray Source
A. Alan Pinkerton[a], Vladimir V. Zhurov[a,b], Elizabeth A. Zhurova[a], Yu-Sheng Chen[a], [a]*Department of Chemistry, University of Toledo, Toledo, OH 43606, USA.* [b]*Karpov' Institute of Physical Chemistry, Moscow, Russia.* E-mail: apinker@uoft02.utoledo.edu

The assembly and evaluation of a new in-lab facility for the rapid collection of charge density quality diffraction data will be presented. The system uses an 18 kW Mo rotating anode generator, graphite monochromator, large curved image plate, and an open flow helium cryostat. The rational for the choice and operating conditions of each of the components will be discussed. The need and application of a flood field correction will be demonstrated. Data integration with the program *VIIPP* [1] was shown to be superior to any other program available to us. Proof of principle experiments have been carried out in under a day. The quality of the diffraction data obtained at 15 K to $(\sin\theta/\lambda)_{max} = 1.32$ Å^{-1} has been evaluated from the statistics provided by SORTAV [2], and by the quality of the multipole refinements [3] as judged by final R factors, residual maps, deformation density maps, etc. Although not as fast as a synchrotron experiment, a home source is always available, is more stable than most synchrotrons, and has no travel overhead associated with its use.

[1] Zhurova E.A., Zhurov V.V., Tanaka K., *Acta Cryst.*, 1999, **B55**, 917. [2] Blessing R.H., *Cryst. Rev.*, 1987, **1**, 3. [3] Koritsanszky T., Howard S., Mallison P.R., Su Z., Ritcher T., Hansen N.K., *XD. A computer Program Package for Multipole Refinement and Analysis of Electron Densities from Diffraction Data. User's Manual*, University of Berlin, Germany, 1995.

P.14.06.1
Topological Analysis of Charge Densities in Polymorphs of 3-acetylcoumarin
Parthapratim Munshi, Tayur N. Guru Row, *Solid State and Structural*