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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 gradual spin transition from a paramagnetic high spin state (⁵T₂, S = 2, HS-1) above 200 K to a diamagnetic low spin state (¹A₁, 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 40 K 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 532 nm laser at 40 K, 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

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

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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

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Maximum Entropy and Fourier Study on Electron Density of MnO, LaCoO₃ and MgSiO₃

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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, LaCoO₃ and MgSiO₃, after optimizing MEM parameters such as resolution and constraint condition.

MnO gave the anisotropic distribution of Mn 3d-electrons in the NaCl structure, although Mn²⁺ ions should be spherically distributed in the regular-octahedral coordination. LaCoO₃ has a maximum of susceptibility in the temperature range of 100 K, where Co³⁺ ions may have an intermediated spin-state. The temperature dependence of electron density was examined in this study. In a chain of SiO₄ tetrahedra in MgSiO₃, 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

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Electron Density in Cubic SrTiO₃ from γ -ray Diffraction

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The electron density and atomic displacements in the prototype perovskite SrTiO₃ have been studied using extensive and accurate γ -ray diffraction data ($\lambda = 0.0392$ 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 $I_{\text{obs}}/I_{\text{kin}}$ 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 SrTiO₃ 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: $q(\text{Sr}) = 1.18$ |e|, $q(\text{Ti}) = 3.10$ |e| and $q(\text{O}) = -1.42$ |e|.

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

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

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High-resolution Magnetic Compton Profile of Iron

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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 $\Delta p \sim 0.4$ 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