

STRUCTURAL AND FUNCTIONAL ANALYSES OF DIHYDROOROTASE FROM *ESCHERICHIA COLI*

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Dihydroorotase plays a key role in pyrimidine biosynthesis by catalyzing the reversible interconversion of carbamoyl aspartate to dihydroorotate. The enzyme belongs to the amidohydrolase superfamily of proteins, which includes phosphotriesterase and urease, among others. High-resolution x-ray crystallographic analyses have shown that each active site of the dimeric enzyme contains a binuclear zinc metal center bridged by a carboxylated lysine residue. The enzyme was crystallized in the presence of its substrate, carbamoyl aspartate. Strikingly, dihydroorotate is observed bound in the active site of one subunit while carbamoyl aspartate is positioned in the active site of the second subunit. From the three-dimensional structures of the enzyme-bound substrate and product, it has been possible to propose a unique catalytic mechanism for this enzyme.

Keywords: AMIDOHYDROLASE SUPERFAMILY, PYRIMIDINE BIOSYNTHESIS, ENZYME MECHANISM

RESOLVING SPIN AND ORBIT MAGNETISM WITH X-RAY SCATTERING

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During the last decade, X-ray scattering methods have attracted renewed attention for the exploration of behavior of magnetic materials. The main driving factors for this strikingly increased interest center around the characteristics of synchrotron radiation: the adjustable polarization and the tunable energy of the photon beams. Indeed, the magnetic X-ray scattering cross-section is known to depend on the photon polarization state, both in the non-resonant and in the resonant scattering range, which can be reached by tuning the photon energy close to absorption edges. One particular field of application deals with the determination of orbital and spin momentum in magnetically ordered systems. In the non-resonant scattering regime, the observation of the polarization dependence of magnetic intensities allows the determination of form factors for the spin and the orbital momentum distributions. In the case of ferromagnetic systems, values of the magnetic moments from orbital momentum and the spin can be obtained through the analysis of x-ray dichroism experiments performed in the resonant regime. Particular examples from bulk and surface materials will be given to illustrate the wide range of applications of the x-ray methods to magnetism.

Keywords: MAGNETISM X-RAYS SCATTERING

MAGNETO ELECTRICITY AS REVEALED BY NEUTRON POLARIMETRY

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The magneto-electric (ME) effect, in which magnetization can be induced by the application of an electric field or vice-versa, has until recently only been studied using techniques which are unable to relate the sense and magnitude of the ME coefficients to the crystal structure. Zero-field neutron polarimetry overcomes this limitation since it allows components of scattered polarization transverse to, the incident polarization, to be measured. It is just such components, which are sensitive to the absolute configuration of magneto-electric structures. The magnetic moments in crystals exhibiting magneto-electricity can order in one or other of two 180° domains in which the magnetic moments point in opposite directions with respect to the arrangement of their ligand atoms. The two domains give opposite ME signals, so that in a multi-domain crystal the magnitude and sign of the ME effect measured depends on the domain populations. The sense of rotation of the neutron polarization scattered by such crystals is also opposite for the two domains. In magnetically annealed crystals in which the domains are unequally populated, spherical polarimetry allows the populations of the two types of 180° domains and the absolute spin configuration of the preferred domain to be determined. The technique has been used to determine the relationship between the absolute configuration of the dominant domain, and the relative directions of the electric and magnetic fields applied during magnetic annealing in Cr₂O₃, LiCoPO and LiNiPO₄. For Cr₂O₃ the technique has been further exploited to determine precise magnetic structure factors, analysis of which has given new insight into the microscopic origin of the ME effect.

Keywords: MAGNETO-ELECTRICITY NEUTRON POLARIMETRY NEUTRON DIFFRACTION

MOLECULAR MAGNETISM, FROM NEUTRON IMAGES TO THEORY

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Molecule-based magnetic compounds have attracted considerable interest in the last fifteen years mainly because of the technological importance of magnets. Indeed, such a class of compounds is supposed to fill a gap in the range of already existing materials, and several new applications, combining the specific properties of molecular compounds such as transparency, low density, solubility, electrical insulation or bio-compatibility, to magnetic properties, have already been invented. Many approaches exist in their engineering, ranging from purely organic, to 'mixed' approaches, where metallic centers are coupled by organic bridges. Due to the large diversity of organic chemistry, an infinite number of such combinations exists, and a dream for the future is to play with the different constituents to finely tune the sought properties. But such a dream requires a perfect understanding of all the magnetic couplings involved in these compounds.

In this context, neutron diffraction plays a key role, as the 'classical' spin polarized beam technique enables the magnetization distribution, that is the distribution of unpaired electrons responsible for the magnetic properties, to be determined precisely at any point of the molecules. Because it involves only the highest lying molecular orbitals, the magnetization distribution carries precious information on the electronic structure of the sample such as the nature of the ground state, the effects of chemical bonds (spin delocalization), the interactions with neighbors in the solid, or the spin polarization effects, and is therefore crucial to understand the coupling mechanisms. The magnetization distribution can also be obtained by first principle ab-initio calculations. These calculations always rely on approximations, and a question that often arises is to know whether the results obtained are reliable enough to calculate precisely exchange constants in these compounds. Therefore, a comparison between polarized neutron experimental results and ab-initio calculations provides stringent tests for these methods. During the presentation, an introduction to magnetic molecular compounds, to the experimental technique and to the different ab-initio methods will be made. A comparison between experimental and theoretical results will be illustrated by examples based on molecular materials.

Keywords: POLARIZED NEUTRON DIFFRACTION MAGNETIZATION DISTRIBUTION AB INITIO CALCULATIONS