

X-RAY MAGNETIC CIRCULAR DICHROISM FOR TRANSPARENT COBALT-DOPED ANATASE THIN FILM

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The ferromagnetism for a very small amount of Co ions in transparent Co-doped anatase thin film was observed at room temperature by fluorescence X-ray magnetic circular dichroism (XMCD). A 700 Å thickness film of Co_xTi_{1-x}O₂ (x = 0.07) on LaAlO₃ (001) was grown by the combinatorial laser molecular epitaxy technique in 10⁻⁵ to 10⁻⁶ torr of oxygen at 950 K and cooled down to 500 K. The XMCD measurements were carried out at the Co K absorption edge, by switching both magnetic field and circular polarization at the undulator beamline BL-39XU, SPring-8. The magnetic field of 1 T was applied parallel to the incident beam. A diffractive phase retarder of diamond was used to produce left- and right-circularly polarized X-rays in the 220 Laue geometry. The fluorescence intensity for the total reflection of the sample was measured in the 90° direction with 3 days accumulation of Rontec XFlash 1100 detector. The threshold energy of XANES spectra of the thin film coincided with that of CoFe₂O₄, showing that the Co ion is in the +2 oxidation state. The negative-to-positive dispersion-type XMCD spectra was observed in E = 7.725 keV region of the main edge and coincided with the highest energy XMCD signal of CoFe₂O₄. The magnitude of XMCD is comparable to the spin moment expected for the low-spin state (S = 1/2) of Co²⁺. No XMCD was observed at the pre-edge.

Keywords: FERROMAGNETISM XMCD THIN FILM

SEGMENTATION AND ELECTRONIC PROPERTIES OF FOUR DIPEPTIDES - A COMPARISON

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If transferability of amino acid and oligopeptide fragments to larger systems can be assumed, promising applications may be developed. It would allow to model the electron density of proteins from their fragments and thus to obtain more detailed information - beyond atomic resolution - compared to what can be achieved by protein crystallography. There are several ways of partitioning space. In a multipole refinement, the electron density $\rho(r)$ is the sum of atom centered multipole functions, which is already a sort of partitioning. Pichon Pesme et al. Follow this route, the transfer of multipole parameters [1]. In Baders theory of atoms in molecules [2] (AIM) partitioning is based on the electron density. A topological analysis of electron density then leads to a real-space description of density units associated with atoms or functional groups. The comparison of topological descriptors of $\rho(r)$ for several amino acids and oligopeptides [3] ($\rho(r|b)$ and $\nu\rho(r|b)$) at the bond critical point and it's position d) indicates a high degree of similarity for these values for the same type of atoms in a similar chemical environment. With integrated properties [4] (volume, charge) more properties of functional groups, although at high computational cost, are now accessible. Hirshfeld surfaces [5] provide a comparably easier and straightforward way of space partitioning. They are based on spherical electron densities and are easy to calculate. They divide the crystal into regions, where the contribution from the spherical atoms for the molecule or fragment exceeds the contribution from the sum over the crystal and only require cell data and atomic coordinates. In this work we have investigated the four dipeptides G-T, H-A, G-H and F-P. Their electron densities were determined by multipole fitted high resolution X-ray diffraction data (synchrotron radiation, CCD-detection). Integrated properties for these molecules are compared with each other, the volumes also to volumes obtained from Hirshfeld surfaces. We acknowledge financial support by BMBF (Project 05 647 KEA1), the DFG (LU 222/21-1, LU 222/22-2) and IDP Education Australia.

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Keywords: SYNCHROTRON RADIATION HIRSHFELD SURFACES ATOMIC PROPERTIES

CHARGE DENSITY AND TOPOLOGICAL ANALYSES OF A HIGH AND A LOW SPIN IRON(III) COMPLEXES

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Bond characterization of two Iron(III)-dithiocarbamate complexes, Fe(S₂CNC₄H₉)·C₆H₆ and Fe(S₂CNC₄H₉)·CH₂Cl₂ are studied by single crystal diffraction at 145K and molecular orbital calculation. The Fe³⁺ of the former complex is in a high spin state with S=5/2, that of the later one is in a low spin with S=1/2 at the temperature range of 5-300 K. Both complexes crystallize in monoclinic system with space group of P2₁/n and P2₁/c respectively.

Charge density distribution is undertaken through experiment and theory. The experimental approach is based on the multipole model whereas the theoretical approach is based on the DFT calculation. The purpose of this work is to observe the charge density redistribution at the iron site due to the bond formation and to demonstrate the differences in the electron density distribution of a high spin and a low spin state of Fe³⁺. Although the d-orbital populations of two spin states are not crisply different, the differences in the deformation density maps and in the VSCC of Laplacian at the iron center are significant. The apparent asphericity in electron density of the low spin species is not observed in that of the high spin case. The VSCC of the high spin state is almost spherical, no significant asphericity can be seen. In contrast, the VSCC of the low spin case shows a clear octahedral feature with six local charge concentrations around the iron center. This difference between two spin states can be best illustrated by the isovalue surface of Laplacian plots.

Keywords: CHARGE DENSITY LAPLACIAN DFT

CHARGE DENSITY STUDIES OF THE NICKEL(II) COMPLEX OF THE SCHIFF BASE OF (S)-N-BENZYLPROLINE (2-BENZOYLPHENYL)AMIDE AND GLYCINE

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Our efforts in asymmetric synthesis of α -amino acids are concentrated on development of chiral synthons - nickel(II) complexes of Schiff bases of (S)-N-benzylproline (2-benzoylphenyl)amide (BPB) and α -amino acids [1]. Previously, we used a combination of solution NMR [2], solid state NMR, X-ray crystallography and DFT calculations [3] to disclose the nature of the asymmetric induction achieved with chiral nickel complexes. The donation of electron density from the π -system of the benzyl ring to nickel orbitals was identified as important factor which might be used for creation of synthons with higher asymmetric induction. DFT B3LYP calculations confirmed a weak interaction, which decreases the distance between the plane of the benzyl group and the nickel atom [3]. Charge density studies were done using the X-ray source at the synchrotron beamline F1 in the HASYLAB/DESY, Hamburg with a CCD area detector at 100 K ($\lambda = 0.5604$ Å). We describe here the results of multipole refinement (on F² using XD [4] suite of programs) as well as the results of topological analysis.

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Keywords: CHARGE DENSITY, NICKEL COMPLEX, ASYMMETRIC SYNTHESIS