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Multiferroic CuWO₄ under pressure: Comparison of PXRD and SXRD studies

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3d-transition metal tungstates are interesting due to their scintillating detection properties and their use for the search of rare events in particle physics. Cuproscheelite (CuWO₄) has been also proposed as a material for the production of positive electrodes of lithium rechargeable batteries. Furthermore, from the fundamental point of view, CuWO₄ has attracted attention as a multiferroic material with an intriguing magnetic phase diagram showing low dimension antiferromagnetism at 90 K; quite above the Neel temperature T_N = 23 K. The Jahn-Teller (JT) effect around the Cu²⁺ ions is responsible for this antiferromagnetic phase. Due to the JT distortion of the CuO₆ octahedra the symmetry of cuproscheelite is lowered from the monoclinic wolframite structure (SG. P2/c) to a triclinic distorted structure (SG. P1̄). Based on our optical absorption [1] and Raman spectroscopy [2] studies at high pressure (HP), it has been found that CuWO₄ undergoes a structural phase transition at 10 GPa. Otherwise, *ab initio* calculations [2] predict a wolframite-like structure for the HP phase. On top of that, according to calculations, the phase transformation involves an antiferromagnetic to ferromagnetic transition and a quenching of the JT distortion. In order to study the compressibility, solve the HP structure, and understand the mechanism of the phase transition, we have performed powder x-ray diffraction (PXRD) under different quasi-hydrostatic conditions up to 20 GPa. Experiments were performed at Diamond and APS synchrotrons. We also carried out single crystal x-ray diffraction (SXRD) at pressures smaller (7 GPa) and higher (13.4 GPa) than the transition pressure. These experiments were performed at HASYLAB synchrotron, Hamburg. Results showed that the compound's compressibility is affected by the presence of non-hydrostatic stresses. Depending upon the pressure-transmitting medium the bulk modulus of the low-pressure phase ranges from 139 to 171 GPa. We also found that only under non-hydrostatic conditions a second phase transition takes place at 17 GPa. On the other hand, SXRD experiments allowed us to solve the structure of the HP phase of CuWO₄, which has a monoclinic-type structure with space group P2/c. Interestingly, the JT effect plays an important role in this phase transition and, in contrast to the theoretical predictions, it is reduced but not suppressed.

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Phase transitions in carbon dioxide at high pressures and temperatures

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We report on the electronic, structural, and thermodynamic properties of carbon dioxide phases up to 200 GPa and 10 000 K obtained from first-principles theory. The liquid region of the phase diagram is divided into several regimes – molecular and polymeric among others, based on a detailed analysis of local structure and molecular composition. The finite-temperature stability of several solid phases has been examined and the melting curve has been calculated up to 150 GPa. Liquid free energies were evaluated explicitly using a new and efficient method. The issue of carbon-oxygen demixing in the Earth's mantle will also be addressed.

Keywords: pressure, transition, computation

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Is a more predictable QTAIM possible?

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The Quantum Theory of Atoms in Molecules (QTAIM) [1] has been extremely successful, providing an orbital invariant theory of chemical bonding based on an observable, the electron density, amenable to experimental determination. Two different operating modes coexist in the QTAIM. In the first, or local mode, chemical descriptors are correlated to the values of operator densities obtained a critical points. The second, or global mode, is based on basin averaged quantities. It is our opinion that the QTAIM has not reached the predictability of the standard Molecular Orbital (MO) paradigm due to the prevalence of the first mode over the second. A set of recent developments that expand both the scope and the predictive power of the QTAIM are considered here. We will first describe the Interacting Quantum Atoms (IQA) [2] approach, which provides an exact energetic decomposition within the QTAIM valid at general geometries. Then we will turn to how a statistical description of chemical bonds through the consideration of electron number distribution functions (EDF) [3] in real space may help recover many well-known concepts derived through MO pictures.

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Keywords: atoms in molecules, electron density, chemical bond

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Halogen bonding from charge density analysis

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Directional intermolecular interactions of diverse strengths [1],

[2] are favorite tools of crystal engineering, since the orientation of molecules in the solid state can be predicted with a reasonable degree of accuracy. Two such interactions stand out: hydrogen bonding and halogen bonding. The marked directionality of the hydrogen bond (HB) is well established and is the basis for efficient and reliable topologies of intermolecular motifs. The strength of the hydrogen bond can be estimated from high resolution X-ray diffraction as proposed by our group [3], [4] and this method based on the topological analysis of the electron density ρ at the HB critical point is now widely used.

On the other hand, the *halogen bonding* interaction has been much less investigated. It occurs in the systems C–Hal \cdots X (X = L, Hal) where an organic halogen atom approaches either a Lewis base (L) or a halogen atom (Hal). Halogen bonding can be as effective as hydrogen bonding for driving highly specific crystal packing motifs, as synthons. It finds its origin in the anisotropy of ρ around the halogen nucleus, leading to a smaller effective atomic radius along the extended C–Hal bond axis than in the direction perpendicular to this axis, a feature called polar flattening.

In a recent experimental charge density analysis of hexachlorobenzene (C₆Cl₆) [5] we have confirmed the anisotropy of the electron distribution around the chlorine nuclei, leading to the formation of electrophilic and nucleophilic sites in the valence-shell charge concentration of chlorines. In the crystal structure of C₆Cl₆, main halogen \cdots halogen interactions are thus electrophilic-nucleophilic in nature, being established between oppositely polarized regions in front of each other within a Cl₃-synthon. The Atoms in Molecules theory [6] has been applied to crystalline C₆Cl₆, demonstrating those features and indicating that the electron density properties at Hal \cdots Hal bond critical points correlate with the strength of the observed interactions.

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Keywords: electron density, halogen bonding, topological analysis

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Joint densities and density matrices refinements: First attempts and first results

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Although analysis of joint experimental data as diverse as x-rays structure factors, polarized neutron flipping ratios, neutron structure factors, CBED measurements, x-ray Compton magnetic (and non magnetic) profiles, among others, is theoretically feasible and desirable, to this day only few attempts have been made

We will remind some of the important strategies that have been elaborated in the past and we will propose a new possible way of combining and exploiting the richness of the diversity of experimental methods.

We will show that as long as the data are issued from elastic coherent

scattering experiments only marginal changes have to be made to the usual pseudo-atoms model. This will be illustrated with recent results obtained on magnetic compounds.

We will finally address a critical discussion concerning the difficulties occurring in combining real and momentum space data.

Keywords: density matrices refinement

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Quantitative information on polarization of ED from multipolar model – possible?

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We performed systematic analysis of electrostatic properties of a molecule estimated from Hansen-Coppens multipolar model [1] of crystal density. We verified an accuracy of electrostatic properties estimated from the multipolar model, and whether it is enough to study changes of electrostatic properties caused by crystal field effect.

For the purpose of the study, perturbation of electron density of individual molecule was induced by cluster of atom charges, dipoles and quadrupoles surrounding molecule, as to simulate influence of crystal environment. Perturbed and unperturbed wave functions were calculated on the bases of the same crystal geometries of a few amino acids and dipeptides. In following step, electrostatic properties were derived directly from either perturbed or unperturbed wave functions. Moreover, multipolar models were fitted to the subsequent theoretical perturbed and unperturbed electron densities.

Comparison of the electrostatic properties obtained either directly from the perturbed theoretical densities, or from SAPT(DFT) [2] calculations, with the results derived directly from wavefunctions of isolated molecules, gave us possibility to study influence of crystal field on electrostatic properties. We characterized trends in changes of electrostatic properties due to polarization of electron density induced by crystal field.

Additional analysis of the electrostatic properties obtained from corresponding multipolar models fitted to the theoretical electron densities enabled us to check whether systematic information about the trends could be derived from multipolar models. Multipolar models fitted to the theoretical electron densities of a crystals, obtained in periodic calculations, were also studied.

The study revealed that electrostatic properties obtained from the multipolar models fitted to the electron densities are significantly different than ones obtained directly from the densities. Electrostatic properties of isolated molecule are reproduced better by multipolar models than electrostatic properties of molecules in crystal. Perturbation of electron density due to crystal field is hardly described by the multipolar models. The main difference in description of valence electron density between purely theoretical models and Hansen-Coppens multipolar models of the same theoretical densities occurred in the very positions of nuclei, where density is not exactly defined in multipolar refinement due to Fourier truncation error.

It seems that electrostatic properties obtained from multipolar models fitted either to theoretical, or experimental electron density of a crystal, have similar accuracy to those estimated with the use of the aspherical pseudoatom databases [3]. Nevertheless, qualitative analyses only could be performed with the electrostatic properties obtained with the use of both method.

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