

values at the bond critical points for covalent interactions depends on the level of theory / basis set and the polarity of the bond, and can exceed 0.15 a.u. Because of the bias in the Laplacian introduced by the pseudoatom projection, the corresponding KED values can increase by a factor of five. Detailed analysis of model data suggests that errors introduced by approximate KED functionals and those that arise due to the pseudoatom projection, fortuitously cancel each other, especially for non-hydrogen atoms. We thus tend to conclude that the analysis has little physical relevance, even if, theoretical and experimental figures appear to be in good agreement.

Keywords: charge density, kinetic energy, topological analysis

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### Exploring pathways of structural phase transitions via experimental charge density analysis

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It has been a challenge to decipher the nature of a chemical bond between two atoms in a molecule and more so to evaluate the nature of interactions between molecules/ions in a crystal. Charge density analysis has gained immense importance in recent years, particularly because such studies allow one to observe and quantify chemical bonding beyond the criteria of mere geometry [1]. The theory of "Atoms in Molecules" [2,3] has not only provided a new pathway to evaluate derived properties on the basis of charge density measurements but also allows for comparison with theoretical estimates of such densities. Recent work in our laboratory is devoted to the analysis of complex inorganic sulfates in terms of bond paths, coordination spheres, electrostatic potential surfaces and in particular to observe the changes in one electron properties and the corresponding changes in chemistry across phase transitions with temperature. A new outlook to the definition of phase transitions in terms of the nature of the chemical bond pathways is observed.

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Keywords: charge density Inorganic Materials, phase transitions, properties

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### Intra and intermolecular electron density properties of fullerene derivatives: First C<sub>70</sub> examples

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Although recent technical and methodical advances made experimental electron density determinations also on larger molecules possible, fullerenes with 60 or more atoms are still a major challenge. Their investigation is complicated by the generally poor crystal quality and by the high mobility of these molecules in the crystal lattice. That is why only a few electron density studies are reported on highly substituted C<sub>60</sub> fullerenes, while no such investigation is known for a C<sub>70</sub> fullerene or its derivatives until now. Here we report on three further fullerene electron density investigations. They include for the first time (to our knowledge) two C<sub>70</sub> fullerene derivatives [C<sub>70</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>10</sub> [1] and C<sub>70</sub>(CF<sub>3</sub>)<sub>14</sub>] which have been studied based on data sets collected at the synchrotron beam lines F1 and D3 of the Hasylab, DESY. For a C<sub>60</sub> fullerene, C<sub>60</sub>(CF<sub>3</sub>)<sub>12</sub>, crystal quality was sufficient for a high resolution data collection under home laboratory conditions (MoKalpha, T= 20 K). The electron densities were topologically analyzed to yield quantitatively atomic and bond topological properties, which is of special interest in the C<sub>70</sub> case because even for free C<sub>70</sub> the number of chemically independent atoms (na=5) and bonds (nb=8) is substantially higher than for free C<sub>60</sub> (na=1, nb=2). In the case of C<sub>60</sub>(CF<sub>3</sub>)<sub>12</sub>, additional information about intermolecular electronic interactions in the crystal lattice was obtained which could be related to unusual physical properties of this compound such as low solubility and volatility [2]. Funding from the DFG (SPP 1188) is gratefully acknowledged.

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Keywords: fullerenes, C70, synchrotron radiation

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### Effects of crystal packing on the electron density of metal carbonyl complexes

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Carbonyl is the most important and versatile ligand in organometallic chemistry. The reference complexes are neutral M(CO)<sub>n</sub>, where carbonyl ligands are coordinated to a zero-valent transition metal atom. However, anionic and, more recently, cationic metal carbonyl complexes have been reported and their importance in organometallic chemistry is now well recognized. Structures and properties of ionic complexes may vary dramatically. For this reason, a quantum chemical investigation of the effects of electric field on the isolated CO molecule was undertaken, together with the analysis of chemical bonding. This allows studying the modifications of CO electron density due to coordination to the metal (separating the effects of the chemical bonding from those due to polarization). Periodic calculations were carried out on salts of ionic metal carbonyl complexes with several (hard and soft) counter-ions, with the purpose to analyze packing abilities of these species and the electron density polarization caused by the crystalline environment. For example, a species like [Co(CO)<sub>4</sub>]<sup>-</sup> was computed in known salts of Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, [NH(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>]<sup>+</sup> and the newly determined salt of [N(CH<sub>3</sub>)<sub>4</sub>]<sup>+</sup>. Similarly, [Fe(CO)<sub>6</sub>]<sup>2+</sup> was investigated as salt of [BF<sub>4</sub>]<sup>-</sup> and [Sb<sub>2</sub>F<sub>11</sub>]<sup>-</sup>.

The hardest cation,  $\text{Li}^+$ , shows a very large polarising power which is able to invert the deformations in the metal carbonyl geometry and produce stronger interion bonds.

Keywords: ionic metal carbonyls, electric field, intermolecular interactions

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### XAO analysis of the 5d-occupation in rare-earth complexes with high potential as quantum

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The 4f and 5d electron density distribution (EDD) in  $\text{MB}_6$  ( $\text{M}=\text{Ce}, \text{Sm}$ ) were investigated by the X-ray Atomic Orbital analysis (XAO). In XAO each atom is divided into the groups of sub-shell electrons (s/p/d/f) and they are treated as pseudo-atoms, which enables to analyze non-stoichiometric compounds keeping the crystal neutral. Since orthonormal condition is obeyed in XAO, the electron population on each AO is obtained reliably, which cannot be done by spectroscopic methods. The EDD of  $\text{CeB}_6$  measured at several temperatures from 100 K to 535 K revealed the flow of Ce-4f electrons to B-B bonds connecting  $\text{B}_6$  octahedrons below room temperature. However, above room temperature electrons are donated to Ce-5d orbitals and fill the  $5d(j=5/2)\Gamma_8$  and  $\Gamma_7$  orbitals at 430 and 535 K, respectively [1]. On the other hand,  $\text{SmB}_6$  exhibited electron flow from  $\text{B}_6$  to Sm and filled  $5d(j=5/2)\Gamma_8$  orbitals below room temperature while 4f populations do not change significantly. The occupied 5d orbitals seem to be common among the rare-earth complexes. The energy difference between 4f and 5d states in  $[\text{Ce}(\text{OH})_2]^{3+}$  were 3.7-4.0 eV [2]. If electrons of fully occupied 5d orbitals are transferred to 4f orbitals, the emitted UV light can be an energy source getting energy from discarded heat below 473K. Rare-earth complexes can be effective quantum energy materials.

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### 3D view of mesoscopic internal structure by coherent hard X-ray diffraction

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X-ray diffraction microscopy is a novel method of structural analysis in nanoscience. Diffraction limited sub-micrometer resolution becomes possible by reconstructing a sample image directly from the coherent diffraction data without aid of lenses. High penetration power of x-rays allows three-dimensional structural analysis for thick samples in a non-destructive manner. We have been performing x-ray diffraction microscope experiments by using hard x-rays from SPring-8 for a variety of samples in materials science and biology. Here, we report some recent results of our studies. In materials science application, we measured an aluminum alloy sample, and observed an internal high electron-density structure in the three-dimensional reconstruction [1]. We interpret that the high electron-density structure originates from sub-micrometer sized precipitates, which play an important role in practical applications in controlling the strength of the alloy. In biological application, we measured human chromosomes [2]. We, for the first time, succeeded in three-dimensional electron density mapping of a cell organelle by using hard x-rays. It is important because it is directly connected with x-ray crystallography, which is currently the most powerful method of the atomic structure analysis for proteins. Though electron cryotomography has been an almost unique method of cell structural analysis at high spatial-resolution, x-ray diffraction microscopy has definite advantage for thicker samples. Prospects for x-ray diffraction microscopy using future x-ray free electron laser are also discussed. [1] Takahashi Y., Nishino Y., Ishikawa T., Matsubara E., *Appl. Phys. Lett.*, 2007, 90, 184105. [2] Nishino Y., Takahashi Y., Imamoto N., Ishikawa T., Maeshima K., 2008, submitted.

Keywords: X-ray microtomography, nanostructures, phase reconstruction

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### Femtosecond dynamic diffraction imaging: X-ray snapshots of ultra-fast nanoscale phenomena

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The ultrafast pulses from X-ray free-electron lasers are ushering in extraordinary new capabilities in X-ray imaging, including potentially the imaging of isolated objects at near-atomic resolution. Of particular interest is the ability to study transient material dynamics, and ultimately determine the structures of proteins, viruses and macromolecules that cannot be crystallized. The FEL X-ray beam is sufficiently intense that the specimen can be completely destroyed by the pulse, but that destruction only happens after the X-ray pulse has passed through the object. The scattering pattern from the object will therefore give structural information about the undamaged object. An extensive program of research has been