performance in electronegativity equalization methods discussed [9]. Finally, based on Hirshfeld-I derived density matrices [10], an AIM is formulated in momentum space.

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Keywords: density, quantum, charge

MS.34.3

Relativistic effects on the topology of the electron density

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The topological analysis of electron densities obtained either from X-ray diffraction experiments or from quantum chemical calculations provides detailed insight into the electronic structure of atoms and molecules. Of particular interest is the study of compounds containing (heavy) transition-metal elements, which is still a challenge for experiment as well as from a quantum-chemical point of view.

Accurate calculations on such systems need to take relativistic effects into account explicitly. Regarding the valence electron density distribution, these effects are often only included indirectly through relativistic effective core potentials. But as different variants of relativistic Hamiltonians have been developed all-electron calculations of heavy elements in combination with various electronic structure methods are feasible. In a previous study on the topology of the total electron density distribution of model systems $M(C_2H_2)$ (TM = Ni, Pd, Pt) calculated in different relativistic approximations we have compared several relativistic Hamiltonians with respect to their effect on the electron density in terms of a topological analysis [1].

In the present work we extended these studies to model systems containing lanthanide elements (for example $[La(CH_3)]^{2+}$ and $La(CH_3)_3$). Besides the investigation of relativistic effects on the topology of the electron density, we concentrated on two additional aspects: We analyzed the general polarization pattern of lanthanide atoms in metal organic complexes as revealed by the Laplacian of the electron density, $L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$, and the Electron Localization Function (ELF). For $L(\mathbf{r})$ it is known for example from studies on isolated La atoms that starting from $n = 5$ the valence shells can only be resolved as local maxima with $L(\mathbf{r}) < 0$ (see Figure a) [2] .

The results of our study indicate that the general pattern of local charge concentrations (LCCs) in the valence region of 6th row elements can still be observed in $L(\mathbf{r})$ and that in the case of the Lanthanum model complexes investigated this pattern shows a clear effect of the 4*f*-orbital contributions to the bonding molecular orbitals (see Figure b).

The second aspect of the present study concerns the possibility to recover the polarization patterns of such heavy elements by a multipolar refinement of structure factors calculated from electron density distributions obtained by relativistic density functional theory calculations. The results indicate that several independent sets of multipolar functions at one atomic site are required in order to fully recover the electron density distributions in the model-systems under investigation.
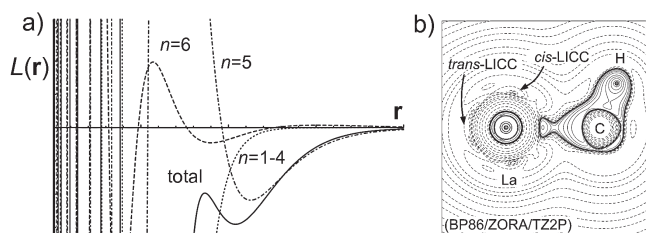
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Keywords: electron density, topology, relativistic effects

MS.34.4

Electron Deficient and Polycenter Bonds in γ-B_{28}

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The recently established superhard high-pressure γ-B_{28} polymorph of boron has grown a resurgence of interest in this element [1]. The crystal structure of γ-B_{28} consists of cubic closest packed icosahedral B_{12} units with B_2 dumbbell units placed on the octahedral sites. A charge-density study has been carried out in order to understand the nature of chemical interactions within γ-B_{28}. Charge densities of γ-B_{28} have been obtained by the multipole refinement using the computer program XD2006 [2] against low-temperature, high-resolution, single-crystal synchrotron X-ray diffraction data. Interpretation of the electron density with the aid of Bader's quantum theory of atoms in molecules (QTAIM) [3] reveals the existence of an one-electron-two-center bond between B_{12} units, which explains the covalent bonding mechanism in γ-B_{28}. The charge separation previously reported has been found to be a local phenomenon, driven by a unique polar-covalent two-electron-three-center bond between two boron atoms of the B_{12} unit and one boron atom of the B_2 unit.

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MS.34.5

Core and valence electron density distribution in a Ga^I NHC-analogue

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The background for the present study is the fact that the low oxidation state chemistry of the heavier main group elements has rapidly expanded over the past two decades [1] leading to a variety of fascinating complexes with unusual bonding patterns that are difficult to describe unambiguously using theoretical or experimental approaches. Complexes of this type are therefore ideally studied by experimental charge densities methods derived from accurate low-temperature single-crystal X-ray diffraction data, such as the one we have recently completed elucidating the unusual metal-metal bonding in a Mg^I-dimer complex [2]. In that study we discovered - in a combined theoretical and experimental approach - a surprising non-nuclear attractor between the two Mg-atoms.

In the present study we apply the experimental charge density technique to the only known example of a four-membered Ga^I N-heterocyclic carbene analogue, $[:Ga^I(Giso)]$ (Giso = $[(DipN)_2CN(C_6H_{11})_2]^-$.[3] The compound is stabilized by incorporation of a very bulky guanidinate ligand,[4] and exhibits a two-coordinate gallium centre, formally in the +1 oxidation state and bearing a lone pair of electrons. A theoretical study of a model of it indicated that the Ga lone pair possesses a high degree of s-character from NBO analysis but nevertheless exhibits sufficient directionality for the heterocycle to behave as an unconventional gallium σ-donor ligand towards transition metal fragments.

The experimental charge density of the compound has been determined by multipole modeling of 90 K X-ray diffraction data and compared to theoretical results. In order to achieve a satisfactory refinement of the multipole model for both experimental and theoretical structure factors, it was found necessary to modify the description of the dependency of the Ga core-electrons using two separate radial scaling parameters. This leads to a multipole model in which the Ga core *s*- and *p*-electrons are expanded by ~4%, while Ga *3d*-electrons are contracted by ca 5% [5] Notably essentially identical values for these changes result both from theory and experiment. The most surprising result from the final multipole model is the significant perturbation of the core density which is attributed to chemical bonding, and the presentation will provide a detailed analysis of the core density changes and compare it with theoretical results.

In the analysis of the valence density, evidence for significant lone pair density on Ga is found in the electron density and derived properties such as the electrostatic potential, despite the formal +1 oxidation state and partial positive charge of this atom. There will be ample description of the valence density in order to provide evidence for the behavior of the lone pair density.

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MS.35.1

Kinetic anomalies of crystal growth: object, novelty and implication

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Crystal growth rates in solutions versus temperature were established as non-monotonous in the form of irregular oscillations and termed as "kinetic anomalies". The establishers [1], [2] as well as other authors determined the oscillation spectra for 12 randomly chosen soluble salts, showed some of their specific and similar features, and related them to supposed structural transformations in the medium. Meanwhile, the essences of the transformations, their belonging to adsorption layer or solution bulk, the nature of each the maximum, etc. are not clear. We elaborate novel approach needed urgently to attack the problem supposing anomalies to be of a principal significance for deciphering crystal growth mechanisms and crystal synthesis.

Electrochemical reduction of metals, we introduced for this purpose [3], [4], widen experimental resources principally while grounds of crystallization are the same as for salts. Using this method, we determined the anomalies for Cu, Hg, and Cu-amalgams and compared their behavior with conditions. Particularly, anomalies of Cu-reduction are similar to those of $CuSO_4 5H_2O$-growth and anomalies of amalgam-reduction are combined of those for pure Cu- and Hg-reduction. Average intensities of anomaly peaks of Cu-amalgams decrease with increasing Hg concentration in amalgams, but transition interval from solid amalgams to liquid ones is not well-defined. Anomalies of Cu-reduction in nitrate and sulphate solutions are similar. They change definitely with solution concentration and adding admixtures modifying solution structure. The concentration changes correlate with changes of ion pair contents solution. The admixtures of ethanol cause temperature behavior of anomalies coordinated with change of entropy of ion dissolution, maximum of chemical shift of water proton, minimum of heat excess of mixing water and ethanol, and minimum of partial molar volume of ethanol. As a whole we concluded the anomalies to be arisen in the solution bulk and extended to the adsorption layer as well as assumed that temperature reorganization in hydration shells of ions results in kinetic anomalies. It also means that kinetic anomalies caused by specific features of crystal growth mechanism and they should appear in all water-soluble systems independently on the moving force.

To a conclusion, kinetic anomalies of crystal growth have a significant impact on crystal growth. They result in non-monotonic variations of crystal habit displayed for $NaClO_3$- and $KClO_3$-crystals grown from aqueous solutions as well as for Cu precipitated by electrocrystallization. Also, as displayed on the example of $Na(Cl,Br)O_3$-crystals, anomalies result in non-monotonic distribution of isomorphic components within a crystal body causing zoning [4]. These effects should be taken into account at crystal growing. Significantly, anomaly features contain hard-to-reach information on the medium structure and may be used for analyses of molecular processes at crystal growth. Introduction of electrocrystallization makes available accelerated obtaining data of a high accuracy.

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