

building blocks. Barbituric acid molecule seems to be a valuable component in designing of new materials possessing prospective properties i.e NLO properties [1,2,3]. Organic materials modified with inorganic components are interesting from the viewpoint of their outstanding properties as NLO materials i.e. high SHG response, appropriate mechanical and optical resistance. Recently we have discovered the usage of barbituric acid and selected inorganic metal salts to form polar structures such as cadmium barbiturate dihydrate (Iba2) or copper barbiturate trihydrate (Fdd2) [4]. Moreover we have obtained centrosymmetric structure of silver barbiturate hydrate (P2(1)/m), which can be further modified to obtain the polar structure. For those three structures experimental charge density study and its topological properties were analyzed using XD2006 package [5]. The studies revealed different topological features for the three oxygen atoms of the barbituric acid. Molecular recognition and the formation of specific hydrogen patterns in all of the examined structures seems to have origin in the resonance structures of the barbituric acid molecule.

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Keywords: crystal engineering, experimental charge densities, nonlinear optics

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Anharmonic Nuclear Motion in Charge Density Studies. Regine Herbst-Irmer, Julian Henn, Kathrin Meindl. *Institute of Inorganic Chemistry, University of Göttingen, Germany*
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In some of our recent charge density studies we had severe problems in appropriately refining the model to a flat and featureless residual density. In 9-diphenylthiophosphinoyl-anthracene unreasonable high residual density peaks remained close to the sulfur atoms [1]. These peaks disappeared only when Gram-Charlier anharmonic coefficients were introduced. Data sets at 15 K, 100 K and room temperature were collected. For all temperatures a typical shashlik-like residual density pattern could be found [2]. Although the room temperature data set was not of the quality and resolution sufficient for a multipole refinement, this pattern was also present and could be removed by refining anharmonic Gram-Charlier-coefficients. This was observed with a spherical-atom as well as with an invariom refinement [3, 4]. However, the drop in the R-value was only small.

There are two independent molecules in the asymmetric unit that differ in their amount of vibration but have similar geometrical parameters. Therefore, also the anharmonic motion differs.

Calculations with theoretical data showed that the amount of noise and thus the quality of data seems to be important for the detection and successful refinement of anharmonic motion [2]. The dependence of temperature, resolution, data quality and vibration on the Gram-Charlier coefficients will be presented.

The correlation with further parameters of a multipole refinement will be discussed.

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Keywords: charge density, anharmonic refinement, residual electron density

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Chemical Experimental Charge Density Study of γ -B₂₈. Swastik Mondal^a, Sander van Smaalen^a, Andreas Schönleber^a, Yaroslav Filinchuk^b, Dmitry Chernyshov^b, Evgeniya Yu. Zarechnaya^c, Leonid Dubrovinsky^c, Natalia Dubrovinskaia^{d,a}, ^a*Laboratory of Crystallography, University of Bayreuth, Germany*, ^b*Swiss-Norwegian Beam line, ESRF, Grenoble, France*, ^c*Bayerisches Geoinstitut, University of Bayreuth, Germany*, ^d*Mineralphysics, Institute of Earth Sciences, University of Heidelberg, Germany*
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The latest discovery of γ -B₂₈, a superhard, high-pressure form of boron [1,2] has attracted much attention due to unique properties of this material. The present electron density study of γ -B₂₈ has been undertaken in order to extract experimental information about peculiarities of chemical bonding in γ -B₂₈. The study has been carried out using low-temperature, high-resolution, single-crystal synchrotron X-ray diffraction data. Electron densities of γ -B₂₈ have been obtained by the multipole refinement using the computer program XD2006 [3], and by the maximum entropy method (MEM) using the computer program BayMEM [4]. Experimental charge densities have been analyzed with the aid of Bader's *Atoms in Molecule* (AIM) theory [5]. Quantitative interpretation of the electron density using Bader analysis reveals the polar-covalent nature of chemical bonding in γ -B₂₈. Detailed analysis of the charge transfer is provided.

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Keywords: boron, charge density, X-ray diffraction

FA4-MS37-P07

Direct visualization of disordered polymer chain structure in polyoxymethylene crystal by MEM. Kunihisa Sugimoto^a, Sono Sasaki^b, Kohji Tashiro^c, Yoshie Nakamura^d, Masaki Takata^{d,e}, ^a*JASRI/SPring-8, Hyogo, 679-5198 Japan*, ^b*Kyoto Institute of*

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Of particular interest is the relationship between chemical bonding and property for polymer materials since the number of X-ray charge density study was very few due to the difficulty of crystallinity control of single crystal sample. Thus, the charge density study of polymer material is a challenging task. In order to reveal the bonding nature, MEM (Maximum Entropy Method) charge density study of the polyoxymethylene (POM, $-(\text{CH}_2\text{O})_n-$) were carried out by synchrotron radiation (SR) X-ray diffraction experiment using the best quality single crystal at SPring-8 BL02B1.

The data with high counting statistics were measured at 123 K by the combination of high brilliance SR and the large cylindrical Imaging Plate (IP) camera. From the fiber pattern of POM recorded on IP, the integrated intensities of each Bragg reflections were obtained and corrected to the observed structure factors. The obtained X-ray pattern represented a typical feature of uniaxially-oriented POM structure on the basis of helical chain molecule.

The preliminary structure analysis was done by SHLEX-97 software with the 9/5 helical chain structure model reported by Hengstenberg *et al.* in 1927[1]. However, the analysis presented an inconclusive answer even for the fundamental structure and the *R*-factor was 17.1%. This result coincides with the existence of the none-indexed X-ray spots of the present pattern. The possibility of another structure model such as the 29/16 helical chain model by Tashiro *et al.* [2] should be also examined.

The MEM ought to allow visualizing charge density, which is consistent with the observed data. In fact, the MEM charge density based on the 9/5 helical chain model revealed the charge densities based on the mixture of several helical period structures. Even though the examination of bonding nature is still in progress, the existence of disordered and/or random feature of helical POM is uncovered in the charge density level for the first time.

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Keywords: polymers, maximum-entropy method, charge density studies

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Electron charge density and topological analysis of coumarin dye. Yvon Bibila Mayaya Bisseyou^a, Christian Jelsch^a, Benoit Guillot^a, Janos Angyan^a, Claude Lecomte^a Noël Lugan^b, ^aCRM2, Institut Jean Barriol, Nancy Université, France, ^bLab. Chimie Coordination. Toulouse.

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The electron-density distribution of coumarin-102, a laser dye has been investigated from high-resolution X-ray diffraction data collected at 100K, and from data based on theoretically calculated structure factors (VASP)[1], using the Hansen &

Coppens[2] multipolar atom model. Topological properties of the refined charge density have been determined using the Bader[3] “atoms in molecules” theory. Analysis of deformation electron density peak heights and topological features indicate that the chromen-2-one ring system has a delocalized π electron cloud in resonance with the N amino atom. The molecular electrostatic potential and dipolar moment were estimated from both theoretical and experimental multipolar models, and reveal an asymmetric character of the charge distribution along the molecule. This polarization effect is due to a substantial charge delocalization within the molecule. Moreover, C—H...O contacts are observed in the crystal packing, and are confirmed as true hydrogen bonds by the presence of (3,-1) critical points along H...O paths.

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Keywords: electron-density distribution, high-resolution X-ray diffraction, topological properties of charge

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ELECTRON CHARGE DENSITY DISTRIBUTION IN AN ORGANIC COMPOUND : THE 4,4 DIMETHYL CYANO BIPHENYL (DMACB).

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At room temperature, the 4,4 dimethylamino-cyanobiphenyl (DMACB) appears in two polymorphic structures: orthorhombic and monoclinic forms. In the present work, we shall focus on the monoclinic form of this compound which has a centrosymmetric structure with the space group Cc. The molecular dipole moment has been estimated experimentally [1].

High resolution single crystal diffraction experiment was performed at low temperature with MoK α radiation. The crystal structure was refined using the multipolar model of Hansen and Coppens (1978) [2]. The molecular electron charge density distribution is described accurately. The study reveals the nature of inter-molecular interactions including charge transfer. The results could be analyzed in more detail, if they were complemented by a quantum chemistry calculation. The electronic structure of this molecule has been investigated theoretically by the Semi-empirical and Ab initio calculations. The agreement between the experimental and theoretical results such as: atomic net charge, molecular dipole moment, electrostatic potential and electron density was satisfactory. All these results will be presented in the meeting. The figure below gives the charge density distribution in the phenyl plane.