density gradient vector field according to the "atoms in molecule"-theory of Bader [3]. To evaluate the atomic volumes and charges the program TOPXD [4] was used.

In order to examine the transferabillity of smaller fragments the topology of submolecular parts of the three molecules were compared with each other and with those of the Matta study.

[1] Matta C.F., J. *Phys. Chem.*, 2001, **A 105**, 11088. [2] Koritsanszky T. *et al.*, *XD*, Freie Universitaet Berlin. User Manual, 2001. [3] Bader R.F.W., *Atoms in Molecules*, Clarendon Press, Oxford, 1994. [4] Volkov A., Gatti C., Abramov Y., Coppens P., *Acta Cryst.*, 2000, **A56**, 332.
Keywords: charge density studies, CCD detectors, low temperature

P.14.01.6
Thymidin Invariom Transfer and Multipole Refinement of a 20K Data Set: a Comparison
Christian B. Hübschle[a], Birger Dittrich[b], Marc Messerschmidt[a], Peter Luger[a]. *[a]Institut für Chemie / Kristallographie, Freie Universität Berlin, Germany. [b]University of Western Australia, Perth, Australia.* E-mail: cheubsch@chemie.fu-berlin.de

Nucleosides play a key role in life. Therefore they are interesting compounds for X-Ray charge density studies, because this would help to understand their biological function in more detail. The invariom aproach[1] uses small theoretically calculated model compounds to derrive the multipole populations without the need of high resolution data, because they are kept unrefined.

Thymidin, which is one of the DNA nucleosides, was measured at 20K with Mo-K_α radiation up to a resolution of $\sin\theta/\lambda=1.1\text{Å}^{-1}$. After the spherical refinement of the structure a multipole refinement was executed and also the recently developed invariom transfer was applied. A topological analysis was done in both approaches.

The results of the invariom transfer, the multipole refinement and the theoretical calculations were compared to have a better guess about the quality of the new approach.

[1] Dittrich B., Korisánszky T., Luger P., *Angew. Chem. Int. Ed.*, 2004, **38**, 1397.
Keywords: charge density studies, nucleosides, high resolution

P.14.01.7
Experimental Electron Density and Topological Analysis of D- and DL- Camphoric Anhydride
Kumaradhas Poomani, Tibor Koritsanszkyb, *Periyar University, Department of Physics, Salem - 636011, 636011 Salem, Tamil Nadu, India.* E-mail: kumaradhas@yahoo.com

Parameter indeterminacies often encountered during pseudoatom modeling of non-centrosymmetric structures unavoidably bias the results of experimental charge density studies [1,2]. A comparative analysis of high-resolution X-ray data of both crystal forms of Camphoric Anhydride $C_{10}H_{14}O_3$ was performed to learn about model restrictions applicable to reduce correlations between least-squares parameter estimates and the transferability of experimental pseudoatoms. The title compound is an ideal candidate for such a study, since the two enantiomers have very similar crystal packing and thus density differences due to different intermolecular forces are expected to be negligible. All intensity data were collected at 100K using SMART 1K CCD area detector with Mo K_α radiation up to a resolution corresponding to $(\sin\theta/\lambda)_{max} = 1.1\text{Å}^{-1}$. The multipole refinement and the analysis of the static densities were performed using the XD program suite. The results obtained by different constrained models will be presented in terms of local and integrated topological properties of the densities.

[1] Spackman M.A., Byrom P.G., *Acta Cryst.*, 1997, **B53**, 553. [2] El Haouzi A., Hansen N.K., Le Hènaff, C., Portas L., *Acta Cryst.*, 1996, **A52**, 291. [3] Koritsanszky T., Richter T., Macchi P., Volkov A., Gatti C., Howard S., Mallinson P.R., Farrugia L., Su Z., Hansen N.K, *XD: a Computer Program Package for Multipole Refinement and Topological Analysis of Electron Densities from Diffraction Data*, 2003.

Keywords: charge density, non-centrosymmetry, multipole model

P.14.01.8
Light on Phase IV in $Ce_{0.7}La_{0.3}B_6$
Dan Mannix[a], Y. Tanaka[b], D. Carbone[c], N. Bernhoeft[d], K. Katsumata[b], S. Kunii[e], *[a]XMaS UK CRG beamline, ESRF, Grenoble, France. [b]RIKEN Institute, SPRING-8, Japan. [c]ESRF, Grenoble, France. [d]CEA-Grenoble, Grenoble, France. [e]Department of Physics, Tohoku University, Sendai, Japan.* E-mail: danny@esrf.fr

The Γ_8 ground state of CeB_6, which may support, dipole, quadrupole and octupole moments, is responsible for its complex low temperature phase diagram. On cooling from the paramagnetic phase (Phase I), antiferroquadrupole (AFQ) order occurs below $T_Q=3.3K$ (Phase II). Upon further cooling, antiferromagnetic order (AFM) additionally sets in below $T_N=2.2K$ (Phase III). The substitution La ions for Ce, gives rise to a recently discovered new phase (Phase IV) in $Ce_xLa_{1-x}B_6$. For x~0.7, the ground state condenses from the paramagnetic phase into phase IV, below $T_{IV}=1.5K$. However, since its discovery, the nature of phase IV has confounded researchers, because the various experimental results are irreconcilable with either AFQ or AFM order [1].

We report on new resonant X-ray scattering (RXS) studies of phase IV, taken at the XMaS beamline of the ESRF. The E2 RXS cross-section can be expressed as a multipole expansion sensitive to dipole, quadrupole, octupole and hexadecapole moments [2]. From our investigation, we have discovered an E2 RXS feature, for which the azimuth dependence can be reconciled with an ordered octupole moment in phase IV. The results give, to our knowledge, the first direct evidence for a new order parameter in the $Ce_{0.7}La_{0.3}B_6$ ground.

[1] *For a review see*: Kubo K., Kuramoto Y., *J. Phys. Soc. Jpn.*, 2004, **73**, 216.
[2] Hill J.P., McMorrow D.F., *Acta. Cryst.*, 1996, **A52**, 236.
Keywords: resonant X-ray scattering, multipole order, spin and charge density

P.14.01.9
Anisotropic Displacement Parameters (ADPs) of Hydrogen Atoms. Can Invariom Modeling Contribute?
Birger Dittrich, Andrew Whitten, Mark A. Spackman, *Department of Chemistry, University of Western Australia, Nedlands 6009, WA, Australia.* E-mail: birger@cyllene.uwa.edu.au

Recently we have introduced invarioms (intermolecular transferable pseudoatoms) [1] and have shown that invariom modeling improves molecular geometry [2] for all atoms including hydrogens and overcomes the shortcomings of the independent atom model (IAM). Such modeling also improves the description of the thermal motion parameters as quantified with the Hirshfeld test.

To answer the title question we computed for a variety of small molecules hydrogen ADPs as described in [4], implemented in the XD [5] suite. In that procedure the internal displacements for all atoms are calculated by an *ab initio* methods, and then subtracted from the experimental data that also contain the external modes. The molecular C,N,O-skeleton is then fitted as a rigid body to the remains of the experimental ADPs. Finally these contributions are, together with the theoretical internal modes, assigned to the riding hydrogen atoms. These hydrogen ADPs are compared with results from an invariom structure refinement and to room temperature neutron data.

[1] Dittrich B., Koritsanszky T., Luger P., *Angew. Chem. Int. Ed.*, 2004, **43**, 2718. [2] Dittrich B., Huebschle C. B., Kalinowski R., Girnt, D., Luger P., *Acta Cryst. A, accepted.* [3] Hansen N.K., Coppens P., *Acta Cryst.*, 1978, **A34**, 909. [4] Flaig R., Koritsanszky T., Zobel D., LugerP., *J. Am. Chem. Soc.*, 1998, **120**, 2227. [5] Koritsanszky T., Richter T., Macci P., Gatti C., Howard S., Mallinson P.R., Farrugia L., Su Z.W., Hansen N.K., *XD*, Freie Universitat Berlin, Berlin, 2003.
Keywords: charge density, thermal parameters, ab initio calculations