

m13.p14**X-ray diffraction study of chemical bonds under external electric field**Semen Gorfman^a, Oleg Schmidt^a, Marcus Schmidt^b, Horst Borrmann^b, Yuri Grin^b, Vladimir Tsirelson^c, Ullrich Pietsch^a^aUniversity of Siegen, Germany. ^bMax-Planck Institute for Chemical Physics of Solids, Dresden, Germany. ^cMendeleev University of Chemical Technology, Moscow, Russia E-mail: gorfman@physik.uni-siegen.de**Keywords:** single-crystal diffraction, chemical bonding, crystal physics

The physical properties of crystals such as dielectric polarization and piezoelectricity are well studied on macroscopic level. They are described by the tensors of dielectric susceptibilities and piezoelectric constants. In most cases their atomistic origin is not always clear. The evaluation of the structural origin of these phenomena requires *in-situ* measurement of the microscopic structural response under influence of an external perturbation. One possible experiment of this type is to monitor the change of X-ray diffraction intensities by a crystal under a permanent external electric field. Because the effect is small ($\Delta I/I < 0.01$) it has to be measured by means of the synchrotron radiation [2]. The shifts of diffraction peak positions are related to the change of crystal lattice parameters (converse piezoelectric effect). The variations of Bragg intensities are associated with the change of the fractional atomic coordinates (dielectric polarization). From one side electric field induced atomic displacements may be related to crystal dielectric properties. From other side they are directly connected to features of electron density and chemical bonding of studied crystal. Thus the microscopic information, derived from the electric field induced change of the electron density is related to crystal physical properties. Recently [1], we applied this strategy to investigate the site selective response in α -GaPO₄ to a permanent external electric field. Here we have shown that the response of a crystal rather depends on the pseudoatomic charges of consistent atoms than to the strength of chemical bond. Therefore the PO₄ with stronger bond strength deforms slightly larger compared with the GaO₄ tetrahedra with smaller bond strength due to the higher pseudoatomic charge of P atom compared with Ga one. This outcome can be verified by inspection of other semi-covalent ternary compounds such as ZnSiP₂ or similar chalcopyrite compounds. These are iso-structural to ZnS structure and contain two different bonds with different bond strength and pseudoatomic charges. The chalcopyrite ZnSiP₂ crystals were grown by chemical transport reactions and prepared for synchrotron diffraction studies under external electric field. The electron density in this crystalline compound is investigated on the basis of density functional theory. The strength Zn-P and Si-P chemical bonds are studied and the pseudoatomic charges of Zn, P and Si atoms are determined. On the basis of the previous results the reaction of ZnSiP₂ crystals to an external electric field is predicted.

[1] Gorfman, S.V.; Tsirelson, V.G.; Pucher, A.; Morgenroth, W.; Pietsch, U. *Acta Cryst.* A62, 1-10, (2006).[2] Gorfman, S.V.; Tsirelson, V.; Pietsch, U. *Acta Cryst.* A61, 387-396, (2005).**m13.p15****Comparison of Crystal Structures Formed by Similar Molecules with Different Functional Groups**

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Crystal structures formed by molecules with similar carbon skeleton but possessing different small substituents have been analyzed. These were naphthalenes, anthracenes, alkanes, and adamantanes. Methyl, hydroxyl, carboxyl, halogen, nitro, cyano and several other groups were regarded as substituents. The Cambridge Structural Database has been used as the main source of information. It was confirmed that arrangements of molecules in crystals affected not only by the chemical nature of substituents itself but also by the number of these and their mutual displacement. Some relations between the presence of particular groups in the definite positions and probable crystal structures of substances have been found. This work was partially supported by RFBR (grant 05-03-32946a).