Oral presentation

Quantum Crystallographic Studies of Phase Transition in Minerals under Pressure

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Quantum Crystallography (QCr) uses various types of aspherical atomic electron densities (consequently aspherical atomic scattering factors) in the refinement of the structures of crystals and their electron densities against X-ray diffraction data. The main methods of QCr are: the refinement of multipole model of quantitative electron density distributions, the refinement of experimental wave functions and the refinement of the crystal structures using the Hirshfeld atom method (HAR). All these QCr methods provide better refinement results than the commonly used routine crystallography methods based on spherical atomic electron densities (IAM).

In this presentation, we will present the main ideas of the above mentioned QCr methods along with their applications to the studies of: structures of ices refined by HAR, redistribution of charge density with pressure in phase transitions of model minerals such as Calcite and Natrochalcite.

Structures and polymorphism of ice is absolutely fascinating. With HAR, we can get bond lengths to H-atoms equally reliable as those from neutron diffraction and also one can establish anisotropic ADP values for disordered H-atoms which are very similar to the neutron values of ADPs. Will also show real local structure of ices from PDF neutron powder studies.

An important biomineral, Calcite ($CaCO_3$) is one of the primary carriers of carbon in geochemical reservoirs. Carbonate rocks serve as hosts to various natural resources, including ores, oil, and gas, and are transported deep into the deep mantle at subduction zones. We traced a reversible phase transformation of Calcite to Calcite-II, from R-3c to P21/c symmetry at pressure ranging from 0.85 GPa to 2.07 GPa. The reversible phase transition takes place at 1.5GPa. It involves twinning of crystals into two domains. The decrease of pressure removed twinning in all crystals which regained the quality suitable for multipole modelling. Will present detailed changes of electron density at atoms under pressure.

Natrochalcite is a rare mineral and it possesses $H_3O_2^-$ units forming one of the shortest hydrogen bond (HB) reported so far in inorganic compounds. High pressure conditions can lead to the formation of an extremely short single-well HB in natrochalcite and to the phase transition connected with symmetry lowering above 2 GPa. It crystallizes in the monoclinic space group C2/m and it has usually emerald green colour. Natrochalcite gained ground in recent years as an anode material for lithium – ion batteries used in powering consumer electronics and vehicles. In this contribution, we will present details of changes of H-bonding in this mineral as a function of pressure as well as analyse variation of electronic parameters.

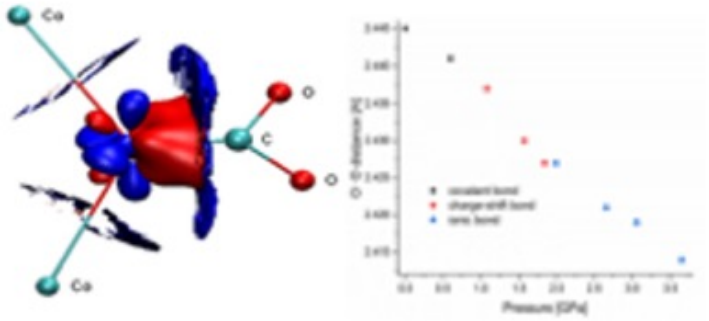

Figure 1. Difference in electron densities at Oxygen atom in Calcite (left) and the O-H…O distance vs. pressure for H-bonding in Natrochalcite (right)

KW, AH, PR and RG acknowledge a financial support within the Polish National Science Centre (NCN) OPUS21 grant number DEC-2021/41/B/ST4/03010