MS26 Quantum mechanical models for dynamics and diffuse scattering

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X-ray diffraction and periodic DFT calculations for modelling of hydrogen atoms in a mineral - pinnoite

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Abstract

High resolution charge density experiments are still rarely carried out in the studies of minerals. Accurate modelling of hydrogen atoms from X-ray diffraction is challenging due to low scattering power of H. Here, we present a combined dynamic quantum crystallography approach to overcome the experimental shortcomings from X-rays.

Pinnoite, $Mg[B_2O(OH)_6]$ was first described by Staute in 1884 [1]. This diborate mineral, consists of $Mg(OH)_6$ octahedra sharing all OH groups with $B_2O(OH)_6$ double tetrahedra. The lattice framework forms void channels along [001]. The exact structure of pinnoite was under review over the last decades. It was solved in $P4_2$ or $P4_2/n$ space groups [2,3].

High-resolution single-crystal X-ray diffraction data were collected up to 0.4 Å resolution at 293 K for natural pinnoite. Based on reflection extinction conditions the space group, $P4_2/n$ was chosen. The specimen originated from an Inder boron deposit in Kazakhstan. It contained needle-like crystals of excellent quality, free of any elemental impurities. The morphology and chemical composition of single crystals were examined on scanning electron microscope, equipped with energy dispersive spectrometer.

We obtained lattice dynamics model of pinnoite, from periodic DFT calculations, run in Crystal17 [4] software. Next, we refined the vibrational frequencies against the single crystal X-ray diffraction data, using NOMORE [5] package. The resultant accurate ADPs of hydrogen atoms, were further implemented to the charge density refinement (XD package [6]) of pinnoite.

The quantitative experimental charge density distribution was determined with Hansen-Coppens multipole formalism [7], getting R(F)=1.48%. Each boron atom is tetrahedrally coordinated by four oxygen atoms, three of which form O(1)-H(1), O(2)-H(2), O(3)-H(3) hydroxyl groups, whereas O(4) links two symmetrically equivalent boron atoms. The Bader [8] atomic basins were determined and charges were integrated from electron density within each basin: q^{Mg} =+1.5; $q^{O(1)}$ = -1.3; $q^{O(2)}$ = -1.2; $q^{O(3)}$ = -1.3; $q^{O(4)}$ = -1.5; $q^{B(1)}$ = +2.5; $q^{H(1)}$ = +0.5; $q^{H(2)}$ = +0.6; $q^{H(3)}$ = +0.5. The crystal maintained $P4_2/n$ symmetry, in pressures of 2.7GPa and 4GPa, generated in a diamond anvil cell. The model of electron density distribution determined here serves as a reference for ongoing high pressure studies.

References

1.   H. Staute, Berichte Der Deutschen Chemischen Gesellschaft, 17 (1884) 1584–1586.
2.   J. Krogh-Moe, Acta Cryst, 23 (1967) 500–501.
3.   F. Paton, S.G.G. MacDonald, Acta Cryst, 10 (1957) 653–656.
4.   R. Dovesi, R. Orlando, A. Erba, C.M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De La Pierre, P. D'Arco, Y. Noël, M. Causà, M. Rérat, B. Kirtman, International Journal of Quantum Chemistry, 114 (2014) 1287–1317.
5.   A.A. Hoser, A.Ø. Madsen, Acta Cryst A, 72 (2016) 206–214.
6.   A. Volkov, P. Macchi, L.J. Farrugia, C. Gatti, P. Mallinson, T. Richter, T. Koritsanszky, XD2016 - A Computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors (2016).
7.   N.K. Hansen, P. Coppens, Acta Crystallographica Section A: Crystal Physics, Diffraction, Theoretical and General Crystallography, 34 (1978) 909–921.
8.   R.F.W. Bader, Atoms in Molecules: A Quantum Theory, Clarendon Press, (1994).