Poster Presentation

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A lattice-dynamical refinement approach based on periodic ab-initio calculations

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The use of synchrotron radiation and large area detectors has increased the quality and quantity of X-ray and neutron diffraction data within the last decades. These advances call for new and better approaches to model and to interpret the data. Elastic X-ray diffraction corresponds to the Fourier transform of the thermally averaged electron density in the unit cell. This density is normally approximated as the convolution of a sum of static atomic densities and the thermal motion of the individual atoms. The static densities and thermal motion are equally important: Together they conform the entire model refined against a single set of measured data, and they must both be modeled correctly, or neither is. The advent of high-performance computers has made it feasible to obtain lattice-dynamical models based on periodic quantum-mechanical calculations, to describe the concerted motion of atoms and molecules through the crystal. Our recent calculations of Debye-Waller factors based on periodic ab-initio calculations for various molecular test systems [1] has prepared the ground for proposing the refinement of quantum-mechanically derived normal modes of vibration against diffraction experiments. As opposed to the standard approach using independent atomic motion, some of the advantages and possibilities that emerge are: 1. A physically reasonable picture of the molecular motion in the crystal. 2. Refinement against data obtained at multiple temperatures in a common model. 3. Modeling thermal diffuse scattering. 4. Reduction of the number of model parameters. 5. Anisotropic motion of H atoms. The approach is computationally expensive, but may prove useful for electron density studies, studies of thermal effects in crystals, i.e. studies of thermochromic and thermoelectric compounds, solid-state phase-transitions and to derive thermodynamic properties, e.g. free energies of polymorphic crystals. We will introduce the method and present some first results for model systems.

[1] *A. Ø. Madsen, B. Civalleri, M. Ferrabone, et al, Acta Cryst. A, 2013, 69, 309–321*

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