Telling “twin molecules” apart in the solid state world: charge density approach

Yulia V. Nelyubina, Mikhail Yu. Antipin, Konstantin A. Lyssenko, X-ray Structural Center, A.N. Nesmeyanov Institute of Organoelement Compounds, Moscow (Russia). E-mail: unelya@xrlab.ineos.ac.ru

Chemical compounds that tend to form crystals with several independent species (Z>1, often pseudosymmetric) or exist as several polymorphic modifications are an evergreen challenge of the solid state world. Encountering these “twins” (molecules or crystals of the same chemical nature) significantly complicates the scientific efforts of many crystallographers. In the case of Z>1, however, they mostly have to go to the efforts of averaging, as such molecules are usually believed to be identical. Meanwhile, the self-association of these species, like the interactions between counterners, can cause the electron density redistribution that makes them distinct. As a result, the crystal structures and thus the related properties cannot be predicted based on the quantum chemical calculations of an isolated molecule.

Theoretical methods were elaborated to rationalize the crystal structures with Z’>2 [1], but many systems have more than two independent species; therefore, to assess the degree to which they are different and how it is related to the crystal environment can be a challenge difficult to overcome. The similar questions can be addressed to the polymorphic modifications. Judging whether a distinction between the “twins” is significant is still based mostly on the comparison of geometrical parameters; interconnecting a molecular or crystal structure with the physicochemical properties of the resulting materials (e.g., their stability), on some empirical principles of crystal formation (dense packing, strength of interactions between species, etc. [1]). These approaches are, however, too rough approximations of the complex situation in a real crystal and provide no qualitative information on the matter. Much more powerful is the topological analysis of the electron density distribution within the “atoms in molecules” theory [2]. It allows accurately evaluating the net properties of molecules (e.g., their charge) and the energy of interactions they form in a crystal (and so the energy of a crystal lattice), hence distinguishing the “twins” at both the molecular and supramolecular levels.

We tested this approach on a series of Z’>1 crystals and polymorphs with intermolecular interactions of various strength: from classical H-bonds (as in paracetamol [3]) to weak van-der-Waals contacts (as in a sildone imine derivative [4]). It proved to be an effective tool to identify and quantify even subtle differences between the molecules and their crystal environments [4] and thus to correlate the charge transfer and mutual polarization due to the self-association with the interaction energy, while revealing some important implications for crystal engineering. In summary, Z’>1 systems should be dealt with care, as neglecting even faint distinction between the independent species (those caused by the weakest interactions) can have measurable consequences; the “cost” for a crystal structure being sometimes high [5]. This approach also allowed estimating the stability of polymorphic modifications, the isoenergetic ones and those violating the “density approach”, in the latter case it helped to reveal the interactions that are responsible for this [3].

Study was financially supported by RFBR (grant 10-03-00578).


Keywords: charge density, polymorphs, Z’>1 systems

MS24.P06

Looking at nanoscale properties in macro-systems with x-ray diffraction imaging

Andrei Nikulin,* Daniele Pelliccia,* Barry Muddle,* School of Physics, Monash University, Clayton, Victoria 3800 (Australia); *Department of Materials Engineering, Monash University, Clayton, Victoria 3800 (Australia). E-mail: Andrei.Nikulin@monash.edu

A feature of emerging nanotechnology is the development of novel materials based on the dispersion of nano-particles in a broad variety of matrices. Applications of such materials range from novel paints and coatings, to a new generation of light alloys, advanced photonics and telecommunication devices, cosmetics and novel biomedical