

topic of research of several recent papers within the field of magneto-structural correlations. [1] Symmetry rules [2] give an explanation of the occurrence of ferro- or antiferromagnetic interactions in polynuclear compounds with transition metals; however the application of them to *f*-block elements is still unclear. The main advantage of the use of Gd(III) resides in its spin-only formalism, since its first excited state is well separated from its ground state. However the shielding of the inner electron orbits by the *f*-electrons promotes that the values of magnetic coupling are weak, which means that are hard to measure and easily confused with other interactions as the ligand field.

In the quest of clarify magneto-structural correlations in these complexes, we have synthesized three new digadolinium(III) complexes with hexa-, hepta- and octanoate ligands [caproate (cap), enanthate (ena) and caprylate (capy), respectively] of formulae  $[\text{Gd}_2(\text{cap})_6(\text{H}_2\text{O})_4]$  (**1**),  $[\text{Gd}_2(\text{ena})_6(\text{H}_2\text{O})_4]$  (**2**) and  $[\text{Gd}_2(\text{capy})_6(\text{H}_2\text{O})_4]$  (**3**) and their structures have been determined by X-ray diffraction on single crystals. Their structures consist of neutral and isolated digadolinium(III) units, containing six monocarboxylate ligands and four coordinated water molecules, where the aliphatic tails pointing to the *a* direction in all cases. The hydrophobic character of this tails avoids the inclusion of any crystallographic water molecule. The bridging skeleton within the Gd(III) units is built by a  $\mu\text{O}(1):\kappa^2\text{O}(1)\text{O}(2)$  framework where the values of the intramolecular Gd–Gd separation are 4.133(2) (**1**), 4.1150(13) (**2**) and 4.1378(7) (**3**) Å and those of the Gd–O–Gd angle are 113.69(15) (**1**), 113.2(2) (**2**) and 113.90(12) (**3**)°. This structural pattern has already been observed in previously reported complexes whose structure and magnetic properties were reported.[3]

Magnetic susceptibility measurements in the temperature range 1.9–300 K reveal the occurrence of a weak intramolecular antiferromagnetic interaction in **2** [ $J = -0.042(2) \text{ cm}^{-1}$ , the Hamiltonian being defined as  $H = -J\mathbf{S}_A \cdot \mathbf{S}_B$ ] in contrast with the intramolecular ferromagnetic coupling which occurs in **1** and **3** [ $J = +0.037(3)$  (**1**) and  $+0.057(3) \text{ cm}^{-1}$  (**3**)]. The magneto-structural data of **1–3** indicates a suitable relation between the magnetic coupling between two gadolinium(III) ions and the geometrical parameters at the  $\mu\text{O}(1):\kappa^2\text{O}(1)\text{O}(2)$  bridge.

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

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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 counterions, 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 quantitative 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 sidone 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 rule”; in the latter case it helped to reveal the interactions that are responsible for this [3].

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

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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

devices and sensors, etc. In order to effectively control the processing, structure and performance of these nano-materials, there is a priority on the development of robust non-destructive techniques for imaging nano-particles. The destructive and generally two-dimensional nature of electron microscopy often limits the nano-particle imaging to qualitative or semi-quantitative analysis. X-ray small-angle scattering can estimate the average scale of nano-particles over a large area/volume without destroying the specimen, however it does not resolve the shape of the particles. Here we show that x-ray diffraction intensity collected as a multi-dimensional function of scattering angle can be treated to reconstruct the three-dimensional (3D) shape of an average nano-particle with a spatial resolution of a few nanometres.

Our results demonstrate that this approach to x-ray diffraction data analysis provides the potential for 3D non-destructive analysis [1]. The methodology is based on the measurement of a high angular resolution x-ray Fraunhofer diffraction patterns with further application of a phase-retrieval formalism. The advantage of experimental data collection in momentum transfer (angular) space is that the diffraction pattern of the object is not susceptible to any of its linear translation and, consequently, the intensity distribution measured as a function of the angular direction in reciprocal space does not require coherent radiation and/or extraordinary stability of the radiation source and/or sample. The non-destructive nature of the technique renders it perfect for *in-situ* studies of nucleation and growth of nanoparticles in engineered nanocomposites [2]. The possibility of using incoherent x-ray sources allows the method to be implemented in any laboratory [1]. The only principal restriction on achievable resolution is the physical limit of the order of sub-nanometer.

We present results relative to ~50 nm diameter nano-particles dispersed in a polymer matrix with a spatial resolution of 2 nm, 50-350 nm intermetallic nanoparticles in ultra-strong Al-Cu alloys with a spatial resolution of 5-8 nm, and ~10 nm diameter carbon nanotubes with spatial resolution of 1 nm. Unlike a microscopy technique, the method to be presented does not allow one to distinguish the shape and size of individual nanoparticles within a distribution. This limits the application of the method to studies of structures with mono-dispersed nanoparticles. However, this very same limitation is a significant advantage of the method for materials science as it does allow non-destructive, *in-situ* analysis over large volumes (several mm<sup>3</sup>) of material, with determination of the modal shape-size of the dispersed particles and a close evaluation of the distribution of particle sizes [3].

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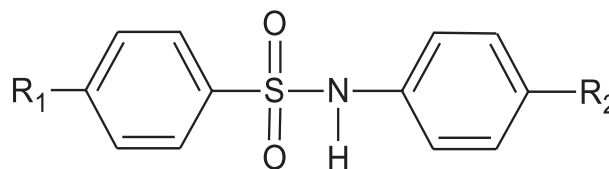
### Can heats of sublimation and melting points of organic crystals be predicted?

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The accurate calculation of the lattice energies of small organic molecules has only recently become possible as a result of developments in Density Functional Theory (DFT), including the introduction of several methods for the incorporation of non-local dispersive interactions. Much has been done to verify these developments using very accurate molecular calculations, but few publications address the validity of these methodologies for organic molecular crystals [1]. The

experimental heats of sublimation of 33 compounds will be compared with the lattice energy predictions of some of the latest solid state DFT methods. In particular, methods incorporating a dispersive correction through a damped molecular mechanics type interaction [2] (DFT(D)), will be compared with new approaches incorporating dispersive interactions as part of the functional [3]. A method incorporating dispersion as part of the functional will be shown to perform slightly better than the best DFT(D) method.

The possible prediction of melting point from knowledge of molecular structure alone has intriguing possibilities and many quantitative structure property relationships (QSPRs) [4] have been developed to allow the prediction of melting point with varying degrees of success. There is a rule of thumb that relates trends in melting points to lattice energies and, using one of the solid state DFT methods used in the study of heats of sublimation, accurate lattice energy calculations are performed on a series of 4,4'-disubstituted benzenesulfonamidobenzenes. Experimental crystal structures and melting points are available for 100 compounds with the generic molecular structure shown in the Figure. [5]. The substituents considered include Br, CF<sub>3</sub>, Me, Cl, CN, F, H, I, NO<sub>2</sub> and MeO. Solid state DFT calculations are used to optimise the geometry and unit cell of all the observed crystal structures. A comparison of the deviations between the experimental and calculated geometries allows the accuracy of the geometrical predictions of the method to be assessed. The minimised lattice energies are then used to establish correlations with the observed melting points. Preliminary results indicate that there is a significant correlation for an isostructural subset of the molecules.



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### An entire class of new compounds forming polar crystals

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In a polar crystal there is a direction which is not transformed in the opposite direction by any symmetry operation of the crystal class; that direction is the polar axis of the crystal. Centrosymmetric crystals are not polar, because the center of symmetry transforms any direction in the opposite one. However, only 10, out of the 21 crystal classes lacking the center of symmetry, are polar. In spite of their rarity, polar structures are very interesting. In fact, several functional properties requested in materials for advanced applications (piezoelectricity, pyroelectricity, ferroelectricity, second harmonic generation, electrooptic response) are only allowed or they are enhanced in polar structures.

Many strategies used for increasing the probability of getting a polar crystal are based on overriding dipole-dipole interactions and include