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Symmetry breaking via hybrid improper mechanisms in molecular perovskites

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Ferroelectricity, *i.e.* the presence of a switchable electronic polarisation, is an attractive property with commercial applications; yet the realisation of ferroelectric materials can be challenging due to the requirement for a polar space group. In the well-studied perovskite oxides, polar space groups mainly arise from the off-centring of the B-site metal ion—as in $BaTiO_3$—or the presence of a stereochemically active lone pair—as in $BiFeO_3$. However, these mechanisms impose severe restrictions on the nature of the cations and hence limit the scope for the discovery of new ferroelectrics.

In light of this, hybrid improper ferroelectricity (HIF) is an attractive phenomenon as it arises from structural, rather than compositional, factors.[1] It relies on the coupling of two non-polar distortion modes, which collectively lift the global inversion symmetry and induce a polar secondary order parameter. Hence, group theory is a valuable tool for enumerating the possible coupling schemes of primary order parameters which may reasonably be expected to couple to a non-centrosymmetric mode and hence break global inversion symmetry. One of the canonical HIF materials is the Ruddlesden-Popper oxide $Ca_3Mn_2O_7$, which may be described as a layered perovskite, and its superimposed primary order parameters are the two tilt modes transforming as X_2^+ and X_3^-. However, in simple three-dimensional perovskites, hybrid improper couplings are not feasible as all tilt modes preserve the inversion centre at the B-site in the ABO_3 structure. As a result, ferroelectric bulk perovskites without layered order are rare. However, in recent years, several coordination polymers with the perovskite topology have been reported and they exhibit distortions with periodicities forbidden in inorganic perovskites, *e.g.* unconventional tilting and columnar shifts.[2]

Here, we present a group-theoretical study of hybrid improper ferroelectricity in these molecular perovskites. We identify primary order parameters that may couple to a non-centrosymmetric, and generally polar, distortion mode. Due to the larger library of symmetry-breaking distortions, molecular perovskites can adopt acentric structures even in the absence of layered order and have a higher propensity for hybrid improper ferroelectricity relative to their inorganic counterparts. Not only do our results rationalise a number of acentric compounds found in literature; it may also be used as a tool for the prediction of new, as-yet unrealised polar materials.[3]

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Crystallographic explorations into uniform distribution theory

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The crystallographic methods applied in structural chemistry for the description of crystal structures focus on a few recurring principles, among them the closest packing of spheres and space group symmetry. While the former concept is locally quantitative, e.g. by giving each atom a coordination number, it rarely offers a similar quantitative global description. The latter concept, however, while being an inherently global descriptor, is purely qualitative. For instance, every so often it happens that crystal structures, e.g. ones related by a phase transition, are very distinct in their symmetry, while being very similar in their local arrangement of atoms at the same time. In other cases, on the contrary, a point can be made for the distinction of structures, although they belong to the same family of structures sharing the same space group symmetry. Moreover, cases exist, in which the arrangement of atoms can be described in ways extending their formal space group symmetry, e.g. by algebraic relations. Thus, it appears to us, that one should search for other concepts, capable of capturing some of these 'hidden symmetries', and in a preferably quantitative and global manner. This is especially true for the description of extended solids, since qualitative and quantitative structural descriptors are well-known for molecules, for which they are successfully used in establishing structure-activity relationships. Here we report about our explorations into the realm of uniform distribution theory, in particular geometric discrepancy theory [1], applying measures for the (ir)regularity of distribution of atoms in space in an crystal chemical context. We highlight examples for the application of the star discrepancy measure in distinguishing variations of a crystal structure belonging to the same general family of structures [2], as well as relations of the diaphony measure to the description of X-ray diffraction by means of the structure factor equation [3].

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