Symmetry analysis: exploring structural subtleties of complex materials

Understanding the relationships between crystal structure and physical properties is one of the biggest challenges in functional materials, especially in view of engineering new compounds. This is very much so in the case of the "multiferroics", materials that exhibit more than one type of "ferroic" (or anti-ferroic) order *e.g.* ferromagnetism, ferroelectricity, etc. In such materials, the possibility of controlling an electric polarization by applying a magnetic field or, inversely, of controlling magnetization with an electric field could have considerable applications, for example in data storage devices. Since symmetry puts strong constraints on the existence and nature of the various ferroic orders, the use of the technique called "symmetry analysis" is a must for understanding the properties of these complex materials.

Very often, a crystal structure can be considered pseudo-symmetric with respect to some configuration of higher symmetry, denoted as its parent structure. The observed structure can then be described as the parent crystal structure plus a static, symmetry-breaking structural distortion. The distortion relating the two structures may be quite complex but can be decomposed into contributions from different modes, with symmetries given by the irreducible representations of the parent space group. Modes are collective, correlated, atomic displacements fulfilling specific symmetry properties. Depending on the amplitudes of the modes, by describing a structure in terms of symmetry modes one can discriminate between the modes which are fundamental for the stability of the low symmetry phase and those which are marginal. Such a description introduces a physical hierarchy among the structural parameters; this is the purpose of the so-called "symmetry-mode analysis" method.
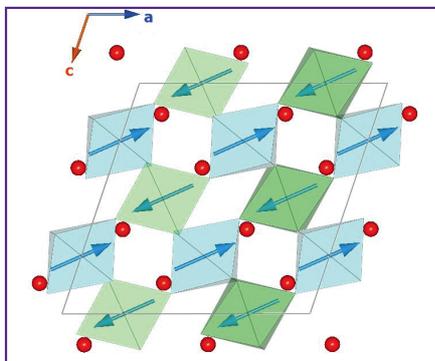

Figure 2 : (a) The distortion mode responsible for the antiferroelectricity of $BiCrO_3$: blue arrows are directions of displacements of the O^{2-} ions , red arrows are displacement directions for Bi^{3+} ions.

(b) The antiferroelectric arrangement of the eight Bismuth ions, within the unit cell (cf. Fig.1), as deduced by symmetry analysis. Arrows represent local electric dipoles resulting from the relative displacement of each Bi^{3+} ion (red spheres) within its cage of twelve O^{2-} ions (not shown).

Fig.1: The highly distorted crystal structure of Bismuth Chromate $BiCrO_3$. The orientations of the Cr^{3+} spins (arrows), responsible for the compound's antiferromagnetism, are shown within their coordination octahedra (green and blue figures; the O^{2-} anions, not shown, occupy the 6 vertices). Red spheres are Bi^{3+} ions.

We have successfully applied this method of analysis to Bismuth Chromate $BiCrO_3$. The compound was synthesized under high pressure and temperature at the Institut NEEL and studied by X-Ray Diffraction (for the crystal structure) and by neutron diffraction (for the magnetic structure). The structure of $BiCrO_3$, see Fig 1, is a distorted form of the classic, cubic, "perovskite" structure. It combines the "lone-pair" ion Bi^{3+}, which favours a non-centrosymmetric structural distortion and thus can induce electric polarization, and a transition-metal ion with a partially filled 3d-electron shell, Cr^{3+}, which can generate magnetism.

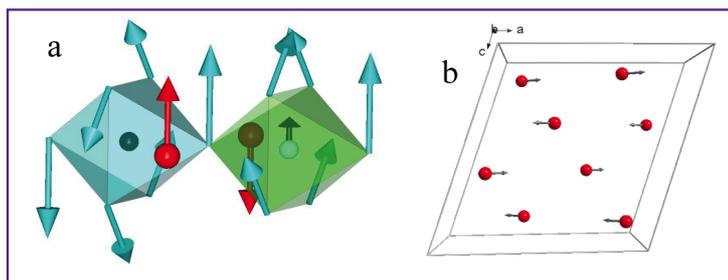Indeed $BiCrO_3$ is clearly antiferromagnetic, below a Néel temperature $T_N = 109$ K. However, its ferroelectric properties are very controversial. Whereas dielectric measurements seem to indicate the existence of a ferroelectric polarization, the compound is found to crystallize in a centro-symmetric space group, incompatible with ferroelectricity.

Symmetry-mode analysis allowed us to decompose the highly distorted crystal structure of $BiCrO_3$ in terms of six distortion modes with respect to the ideal cubic perovskite structure. The six distinct distortion components have different importance for the material's properties. One of the two major modes is very specific to Bi-based perovskites: it involves displacements of Bi, Cr, and a complex distortion of the oxygen octahedra (Fig.2a). The respective displacement of the Bi^{3+} cation within its cage of twelve O^{2-} anions is about 0.4 Å, giving rise to a local electric dipole. But, the analysis shows that in the unit cell, the eight local electric dipoles are oriented in opposite directions (Fig. 2b). Thus, the total dipole moment is zero within the cell, as follows from the inversion centre in the space group. This mode is therefore responsible for the very complex and specific antiferroelectric arrangement in $BiCrO_3$.

In conclusion, the symmetry-mode analysis is a very powerful method that allows one to hierarchize the distortion modes and to identify those modes which stabilize the various distorted structures of a crystal. Symmetry analysis can be applied either a posteriori to analyse a given distorted structure, or a priori to parametrize a structure to be determined. This method gives very useful physical insight into the structure and can be applied to many different material systems.

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