Discovery of helical order of electric dipoles: completing the analogy between ordering of electric and magnetic dipoles

A study initiated by Alexei A. Belik (Principal Researcher, MANA) and performed in collaboration with researchers from ISIS Facility (UK), University College London (UK), and Oxford University (UK) has led to the discovery of helical order of electric dipoles in the solid state. The results have been published in the renowned journal Science.

An *electric dipole* deals with the separation of the positive and negative charges found in any electromagnetic system. The magnetic analogue, the *magnetic dipole*, is associated with a fundamental quantum property - the spin of elementary particles. Long-range ordering of electric and magnetic dipoles are one of the driving forces of phase transitions in solid-state materials, and such transitions produce many technologically important functional properties such as *magnetic* and *ferroelectric memory elements*.

Despite fundamentally different physical origins, there appears a remarkable analogy between the spontaneous ordering of electric and magnetic dipoles. Simple orders give rise to ferroelectric/ferromagnetic and antiferroelectric/antiferromagnetic materials. On the other hand, competing magnetic exchange interactions can lead to helical ordering of magnetic dipoles, where the spins of neighboring magnetic moments arrange themselves in a spiral or helical pattern. Helical magnetism leads to complex phenomena such as *spin-induced multiferroicity* and *magnetic skyrmions*, which to date do not have electric dipole counterparts.
Multiferroics are defined as materials that exhibit more than one of the ferroic properties in the same phase. They have potential for applications as actuators, switches, magnetic field sensors and new types of electronic memory devices.
Skyrmions are named for British nuclear physicist Tony Skyrme, who first proposed their existence. They can be described as a swirling quasi-particle, a knot of twisting field lines, or a subatomic hurricane.

In the present study, published 61 years after the discovery of helical magnetism, the authors describe the first example of helical ordering of electric dipoles in a crystalline material synthesized at the National Institute for Materials Science, thus completing the analogy between ordering of electric and magnetic dipoles in the solid state.

The discovery was made through a combination of cutting-edge experimental techniques. The $BiCu_{0.1}Mn_{6.9}O_{12}$ samples were synthesized under high-pressure (6 GPa) and high-temperature (1100^{o} C) conditions at the National Institute for Materials Science (NIMS), Tsukuba, Japan. The helical ordering of electric dipoles was established by the careful structural analysis (involving 4-dimensional crystallography) of time-of-flight neutron diffraction data obtained with the WISH instrument at ISIS Facility, the UK Neutron and Muon Source.

The authors demonstrate that the helical ordering of electric dipoles occurred due to the microscopic competition between two instabilities inherent to the crystal structure of $BiCu_xMn_{7-x}O_{12}$. The stereochemical activity of Bi lone-pair electrons favor a conventional, collinear ferroelectric or antiferroelectric state, while electrons localized on Mn atoms favor a complex ordering of the orbitals in which they reside. The helical ordering of electric dipoles then emerges as a delicate balance between lone-pair and orbital ordering, which is finely tuned by modifying the concentration of Cu substituted for Mn. It is noteworthy that the competition between magnetic instabilities gives rise to non-collinear magnetic states. Indeed, the present study indicates that well established principles of magnetism can now be adopted to explain emergent phenomena in dielectric materials, such as the complex microscopic nature of ferroelectric domain walls.