Polar and Magneto-Electric Properties of Anti-Ferrodistortive Ordered Jahn-Teller Distortions in a multiferoic metal-organic framework

Alessandro Stroppa
CNR-SPIN, Via Vetoio, 67100, L’Aquila-Italy
E-mail: alessandro.stroppa@spin.cnr.it

Abstract. There is great interest in hybrid organic-inorganic materials such as metal-organic frameworks (MOFs). Here, we focus on [C(NH$_2$)$_3$]Cu(HCOO)$_3$, a MOF with perovskite topology which crystallizes in polar space group Pna2$_1$. In inorganic compounds, octahedral tilting and Jahn-Teller structural distortions are usually non-polar distortions. However, in this MOF cooperative interactions between the antiferro-distortive distortions of the framework and the C(NH$_2$)$_3$ organic cation via hydrogen bonding breaks the inversion symmetry and induces a ferroelectric polarization. Our ab-initio study supports the picture of an orbital-order-induced ferroelectricity, a rare example of dipolar ordering caused by electronic degrees of freedom. Moreover, we show that the switching of polarization direction implies the reversal of the weak ferromagnetic component. These results therefore offer an important starting point for tailoring multiferoic properties in this emerging class of materials for various technological applications.

1. Introduction
Metal-organic frameworks (MOFs) are a new class of hybrid crystalline compounds comprised of extended networks formed by organic linkers and metal cations, forming porous materials at the interface between molecular coordination chemistry and materials science. They show unique properties arising from the organic-inorganic duality[1]. There have been a huge interest in these compounds not only because they show a variety of physical properties and applications, such as gas storage, gas exchange or separation, catalysis, drug delivery, optics, magnetism [2] but also for the infinite possibilities of new MOFs that can be created by varying the inorganic/organic components[3-6]. Very recently, more dense hybrid frameworks with perovskite ABX$_3$ topology have attracted much attention, for their interesting magnetic, optical, electronic and dielectric properties along with improved thermal stability[3,7,8]. These compounds provide access to more oxide-like properties and the flourishing diversity of structures and dimensionality seen in these materials has led to their growth into a major field of research[3]. The ABX$_3$ topology is ubiquitous in inorganic material science. We may think of an organic-inorganic hybrid perovskite by ideally replacing the inorganic A component with an organic cation and the inorganic X anion with an organic ligand. The ABX$_3$ structure is the basis of many transition metal oxides with important properties such as high T$_c$ superconductivity, colossal magnetoresistance,
ferroelectricity (FE), charge ordering, nonlinear optical behaviour, and so on[5]. Last but not least, multiferroicity[9].

Multiferroics (MFs) present at least two coexisting orders among the electric, magnetic and/or elastic ones. The study of multiferroic compounds has become a hot field in materials science[10-13]. The most appealing combination involves electric and magnetic orders, opening new routes to spintronic devices[11]. MFs can be divided in two main groups: those having independent electric and magnetic orders and those exhibiting a magnetoelectric (ME) coupling. The former allows, for example, the conception of a four-state memory[11-15]. Probably ME compounds are more interesting, since they may offer the possibility of controlling the magnetic ordering via an electric field and viceversa[16]. MFs are highly desirable [9] although, the coexistence of electric and magnetic orders is rare[13]. When one combines the Renaissance of Magnetoelectric MFs [16] and the Explosion of papers in MOFs[17] it is clear that MF MOFs is a newborn field of research where only a few papers have been published so far.

The very first \textit{ab-initio} study has been performed by A. Stroppa et al.[18] We have studied the compound \([\text{C(NH}_2\text{)}_3\text{]}\text{Cu[(HCOO)}_3\text{]}\), synthesized in 2009[19]. We call it Cu-MOF hereafter. We found that the Cu-MOF i) is multiferroic with a ferroelectric (FE) polarization estimated of \(0.37 \mu C/cm^2\) and it shows a weak- ferromagnetic component (weak-FM); ii) it is magnetoelectric, \textit{i.e.} the weak-FM is coupled to the FE polarization, thus allowing the electric control of magnetic properties; iii) the FE polarization is due to a peculiar interplay between Jahn-Teller (JT) distortions and organic A-group through hydrogen bondings[18]. To the best of our knowledge, this is a new and very peculiar mechanism, which demonstrates the rich field for new effects in this class of materials. We want to remark that while the \textit{ab-initio} design and characterization of multiferroic inorganic materials can be considered nowadays at a mature stage, this is certainly not true for MF MOFs.

2. Structural properties and antiferro-distortive order
The compound crystallizes in the \textit{Pna2}_1 space group. The structure is shown in Figs 1,2. An important feature is the presence of JT active Cu\(^{2+}\) ions (d\(^9\) electronic configuration). The two-fold degeneracy of this configuration is removed by an octahedral structural distortion, which, in turn, introduces long and short Cu-O bonds in the \textit{ab} plan (Q\(_2\) JT mode).
The different orientations of the long Cu-O bonds on different Cu sites give rise to a characteristic Anti-Ferro-Distortive (AFD) pattern[20]: the long Cu-O bond on a Cu site is almost perpendicular to the long Cu-O bond on the neighboring Cu site in the \( ab \) plane. It is possible to introduce a function of the JT modes through the JT phase \( \phi \) which quantifies the degree of anti-ferro distortion (AFD);[15] when \( \phi \approx 4\pi/3 \) or \( 2\pi/3 \), one has a maximum distortion in the crystal, while for \( \phi \approx \pi \) one has that Cu-O long and short bonds become equal, and the AFD disappears. For details, see Ref. [20]. It must be noted that AFD modes are non-polar in standard inorganic \( ABX_3 \) compound[20]. The ground-state is antiferromagnetic, with Cu spins ferromagnetically coupled within \( ab \) plane while antiferromagnetically coupled between parallel \( ab \) planes. Note that, by introducing the spin- orbit coupling in the calculations, a weak-ferromagnetic component appears, in agreement with experiments[19]. This has important consequences for the magnetolectric behavior[18].

3. Ferroelectric order
In order to study the ferroelectric order we consider a paraelectric (centric) structure[13] in terms of which one can present the polar crystal structure as due to symmetry-lowering structural distortion from the high symmetry centric group. It is useful to introduce a parameter \( \lambda \) which is the normalized amplitude of the distortion connecting the centric to the polar structure: \( \lambda=1 \) represents the compound in the Pna\(_2\)1 space group, \( \lambda=0 \) represents the Pnna centric space group. For each \( \lambda \) between 0 and 1, one can linearly interpolate the atomic positions between the two end-points, defining a continuous path as a function of \( \lambda \), the so-called switching path. We found that the system has a FE polarization of \( P=\pm 0.37 \mu C/cm^2 \) along the polar \( c \) axis. Obviously, \( P=0 \) for \( \lambda=0 \) and \( P=P(\lambda) \) is an odd function of the polar distortion. The calculated energy behaviour reproduces the expected double-well profile characteristic of a switchable ferroelectric system[20]. Surprisingly, by monitoring the changes of \( \phi \) along the path, we have found a clear correlation between \( P=P(\lambda) \) and \( \phi(\lambda) \). In principle, one has \( \phi_{\alpha,\beta}(\lambda) \), where \( \alpha,\beta \) denotes the two
The distortion can be described by a JT coordinate vector $(Q_2, Q_3)$

$Q_2 = (l - s) / \sqrt{2}$

$Q_3 = (2m - l - s) / \sqrt{6}$

In polar coordinates:

$Q_2 = \rho \sin \varphi$

$Q_3 = \rho \cos \varphi$

$\tan \varphi = Q_2 / Q_3$

NB. $\phi = \pi$ for $l = s$

Figure 3. Jahn-Teller distortions and the description through the $Q_2$, $Q_3$ variables and Jahn-Teller phase.

Cu-sublattices in the $ab$ plane [see Fig. 3 and 4]. Each sublattice has the same orientation of the long Cu-O bonds, but the orientation “rotates” by $\pi/2$ in the neighboring Cu site (the so-called JT pseudo-rotation)[20]. One can see that $P=P(\lambda)$ and $\phi(\lambda)$ have the same behavior, thus suggesting that AFD distortions can be the source of the ferroelectric polarization. This is counterintuitive since AFD distortions are non-polar[20].

In Fig. 4 (a),(b),(c) we show the energy $E$, the polarization $P$, and the “amplitude” of the AFD distortions along the switching path. The microscopic explanation of the ferroelectric polarization is as follows: the [C(NH$_2$)$_3$]$^+$ molecular group interacts with the BX$_3$ framework through hydrogen bonding N-HO, where the H atoms belong to NH$_2$ of the [C(NH$_2$)$_3$]$^+$ group, and the O atom is bond to Cu. Both the H atoms of NH$_2$ group interact via H bond, but while at $\lambda=0$ state, the H bond strengths are the same, for $\lambda$ larger than 0, i.e. towards the ferroelectric state, the H bonding strengths become asymmetric due to the JT mode[13]; since the AFD mode controls the oxygen positions, the change of the AFD mode amplitude (changing $\phi$ along $\lambda$), induces asymmetric distortions in the NH$_2$ part of the A-group, i.e. there is an induced dipole moment which then sum up to give a finite polarization[18].

4. Conclusions

We have shown that the Cu-MOF, belonging to the metal-organic framework family with ABX$_3$ topology, shows a rich and fascinating physics. Our study supports the following picture: i) It is ferroelectric with an estimated polarization of 0.37 $\mu$C/cm$^2$. ii) The origin of the ferroelectricity is very intriguing: non-polar structural distortions (i.e. antiferro-distortions) give rise to a loss of inversion symmetry, paving the way for the appearance of polarization; note that this mechanism is not found in classical ABX$_3$ inorganic compounds. iii) Hydrogen bonding plays a major role in coupling the nonpolar distortions acting in the BX$_3$ framework with the organic cation. iv) A weak ferromagnetic component is allowed and it is coupled to the ferroelectricity: by using this very rare property, it would be possible to control the polarization by an applied magnetic field, and vice versa. This is called magnetoelectricity. This feature has not been discussed here, but we refer to Ref. [20] for more details.
Figure 4. (a) Energy profile, (b) ferroelectric polarization and (c) Jahn-Teller $\phi$ phases along the switching path. In (c) the orbital ordering underlying the antiferro-distortive ordering is also shown.
4.1. Acknowledgments

This research was funded by the European Research Council under the European Community, 7th Framework Programme (2007-2013)/ERC Grant Agreement no. 203523 won by Dr. S. Picozzi. Computational support by CASPUR Supercomputing Center in Rome through Standard HPC Grant 2011 is gratefully acknowledged. A.S. wishes to express his special thanks to Prof. I. Bersuker for interesting discussions about the Jahn-Teller physics and for the invitation to the XXIst International Symposium on the Jahn-Teller Effect. Interesting discussions with Dr. P. Barone and Prof. J. M. Perez-Mato are also acknowledged. All the calculations have been done by using the VASP package[21]. Figures were plotted using the VESTA package[22] For the symmetry analysis we used the tools of the Bilbao Crystallographic server[23], in particular the PSEUDOSYMMETRY[24] and AMPLIMODES crystallographic softwares[25].

5. References

[1] Yaghi O M, O’Keeffe M, Ockwig N W, Chae H K, Eddaoudi M and Kim J 2003 Nature 423 705
[2] Féréy G and Cheetham A K 1999 Science 283 1125
[3] C N R Rao C N R, Cheetham A K and Thirumurugan A 2008 J. Phys.: Condens. Matter 20 083202
[4] Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O’Keeffe M and Yaghi O M 2002 Science 295 469
[5] Green M A 2010 Nat. Mat. 9 539
[6] 2009 Chem. Soc. Rev. 38 1201
[7] Jain P, Dalal N S, Toby B H, Kroto H W and Cheetham A K 2008 J. Am. Chem. Soc. 130 10450
[8] Clausen H F, Poulsen R D, Bond A D, Chevallier M A S and Iversen B B 2005 J. Solid State Chem. 178 3342
[9] Tokura Y and Nagaosa N 2000 Science 288 389
[10] Ramesh R and Spaldin N A 2007 Nat. Mater. 6 21
[11] Chu Y H, Martin L W, Holcomb M B, Gajek M, Han S J, He Q, Balke N, Yang C H, Lee D, Hu W, Zhan Q, Yang P L, Fraile-Rodriguez A, Scholl A, Wang S X and Ramesh R 2008 Nat. Mater. 7 478
[12] Cheong S W and Mostovoy M 2007 Nat. Mater. 6 13
[13] Hill N A 2000 J. Phys. Chem. B 104 6694
[14] Khomskii D I 2001 Bull. Am. Phys. Soc. C 21 002
[15] Bersuker I B 2012 Phys. Rev. Lett. 108 137202
[16] Spaldin N A and Fiebig M 2005 Science 309 391
[17] G. Féréy 2008 Chem. Soc. Rev. 37 191
[18] Stroppa A, Jain P, Barone P, Marsman M, Perez-Mato J M, Cheetham A K, Kroto H W, Picozzi S 2011 Angew. Chemie Int. Ed. 50 5847
[19] Hu K L, Kurmoo M, Wang Z M and Gao S 2009 Chem. Eur. J. 15 12050
[20] Bersuker I B 2006 The Jahn-Teller Effect (Cambridge University Press, Cambridge)
[21] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[22] Momma K and Izumi F 2008 J. Appl. Crystallogr. 41 653
[23] http://www.cryst.ehu.es/
[24] Kroumova E, Aroyo M I, Perez-Mato J M, Ivantchev S, Igartua J M, Wondratschek H J. 2001 Appl. Crystallogr. 34 783
[25] Orozcoa D, Capillas C, Aroyo M I and Perez-Mato J M 2009 J. Appl. Crystallogr. 42 820