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Modelling, understanding and controlling GHz-, THz- and optical properties of ferroelectric and multiferroic materials
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``Modelling, understanding and controlling GHz-, THz- and optical properties of ferroelectric and multiferroic materials''

Laurent Bellaiche

Our main research goal is to develop and use first-principles-based schemes, and collaborate with International scientists, to understand, design and control dynamical and optical properties of ferroelectric and multiferroic materials.

The following milestones have been made during this award:

- 1) ``Subterahertz dielectric relaxation in lead-free Ba(Ti,Zr)O_3 relaxor ferroelectrics," D. Wang, A. A. Bokov, Z.-G. Ye, J. Hlinka and L. Bellaiche, Nature Communications 7, 11014 (2016).

Relaxors are complex materials with unusual properties that have been puzzling the scientific community since their discovery. The main characteristic of relaxors, that is, their dielectric relaxation, remains unclear and is still under debate. The difficulty to conduct measurements at frequencies ranging from 1 GHz to 1 THz and the challenge of developing models to capture their complex dynamical responses are among the reasons for such a situation. Here, we report first-principles-based molecular dynamic simulations of lead-free Ba.$Zr_{0.5}Ti_{0.5}O_3$, which allowed us to obtain its subterahertz dynamics. This approach reproduces the striking characteristics of relaxors including the dielectric relaxation, the constant-loss behaviour, the diffuse maximum in the temperature dependence of susceptibility, the substantial widening of dielectric spectrum on cooling and the resulting Vogel–Fulcher law. The simulations further relate such features to the decomposed dielectric responses, each associated with its own polarization mechanism, therefore, enhancing the current understanding of relaxor behaviour.

- 2) ``Driving spin excitations by hydrostatic pressure in $BiFeO_3$," J. Buhot, C. Toulouse, Y. Gallais, A. Sacuto, R. de Sousa, D. Wang, L. Bellaiche, M. Bibes, A. Barthelemy, A. Forget, D. Colson, M. Cazayous, and M-A. Measson, Physical Review Letters 115, 267204 (2015).

In collaboration with the experimental groups of Drs Cazayous (Université Paris Diderot, France) and Barthélémy and Bibes (CMRS/Thales, France), optical spectroscopy was combined with computational and theoretical techniques to show how the spin dynamics in the model multiferroic $BiFeO_3$ responds to the application of hydrostatic pressure and its corresponding series of structural phase transitions from R3c to the Pnma phases. As pressure increases, multiple spin excitations associated with noncollinear cycloidal magnetism collapse into two excitations, which show jump discontinuities at some of the ensuing crystal phase transitions. The effective Hamiltonian approach provides information on the electrical polarization and structural changes of the oxygen octahedra through the successive structural phases. The extracted parameters were then used in a Ginzburg-Landau model to reproduce the evolution with pressure of the spin wave excitations observed at low energy, and we demonstrate that the structural phases and the magnetic anisotropy drive and control the spin excitations.

- 3) ``Room-temperature paramagnetoelectric effect in magnetoelectric multiferroics $Pb(Fe_{½}Nb_{½})O_3$ and its solid solution with $PbTiO_3$,'' V. V. Laguta, A. N. Morozovska, E. A. Eliseev, I. P. Raevski, S. I. Raevskaya, E. I. Sitalo, S. A. Prosandeev, and L. Bellaiche, Journal of Materials Science 51, 5330-5342 (2016).

In collaboration with the experimental group of Dr Laguta (Institute of Physics, Czech Republic), we observed the magnetoelectric (ME) response at room temperature and above in high-resistive ceramics made of multiferroic $Pb(Fe_{½}Nb_{½})O_3$ (PFN) and PFN-based solid solution 0.91PFN-0.09$PbTiO_3$ (PFN-PT). The value of the paramagnetoelectric (PME) coefficient shows a pronounced maximum near the ferroelectric-to-paraelectric phase transition temperature, T_C, and then decreases sharply to zero for T larger than T_C. The maximal PME coefficient in PFN is about 4×10^{-18} s/A. The theoretical description of the PME effect, within the framework of a Landau theory of phase transitions allowing for realistic temperature dependences of spontaneous polarization, dielectric and magnetic susceptibilities, qualitatively reproduces well the temperature dependence of the PME coefficient. In particular, the Landau theory predicts the significant increase of the PME effect at low temperatures and near the temperature of the paraelectric-to-ferroelectric phase transition, since the PME coefficient is equal to the product of the spontaneous polarization, dielectric permittivity, square of magnetic susceptibility, and the coefficient quantifying the strength of the biquadratic ME coupling. An atomistic technique is further developed and used to further demonstrate that the PME effect can also be sensitive to the frequency of the applied magnetic field (when this frequency is of the order of GHz).

- 4) ``Photostriction in Ferroelectrics from Density Functional Theory,'' Charles Paillard, Bin Xu, Brahim Dkhil, Gregory Geneste and L. Bellaiche, Physical Review Letters 116, 247401 (2016).

An *ab initio* procedure allowing the computation of the deformation of ferroelectric-based materials under light was presented. This numerical scheme consists in structurally relaxing the system under the constraint of a fixed n_e concentration of electrons photoexcited into a specific conduction band edge state from a chosen valence band state, via the use of a constrained density functional theory method. The resulting change in lattice constant along a selected crystallographic direction is then calculated for a reasonable estimate of n_e. This method was applied to bulk multiferroic $BiFeO_3$ and predicts a photostriction effect of the same order of magnitude than the ones recently observed. A strong dependence of photostrictive response on both the reached conduction state and the crystallographic direction (along which this effect is determined) was also revealed. Furthermore, analysis of the results demonstrates that the photostriction mechanism mostly originates from the screening of the spontaneous polarization by the photoexcited electrons in combination with the inverse piezoelectric effect.

- 5) ``Simulating the radiofrequence dielectric response of relaxor ferroelectrics: a combination of Coarse-Grained Hamiltonians and Kinetic Monte Carlo,'' Gregory Geneste, L. Bellaiche and Jean-Michel Kiat, Physical Review Letters 116, 247601 (2016).

The radio-frequency dielectric response of the lead-free $Ba.Zr_{0.5}Ti_{0.5}O_3$ relaxor ferroelectric was simulated using a coarse-grained Hamiltonian. This concept, taken from real-space renormalization group theories, allowed us to depict the collective behavior of correlated local modes gathered in blocks. Free energy barriers for their thermally activated collective hopping were deduced from this ab initio–based approach, and used as input data for kinetic Monte Carlo simulations. The resulting numerical scheme allowed us to simulate the dielectric response for external field frequencies ranging from kHz up to a few tens of MHz for the first time and to demonstrate, e.g., that local (electric or elastic) random fields lead to the dielectric relaxation in the radio-frequency range that has been observed in relaxors.

- 6) ``Predicted energetics and properties of rare-earth ferrites films grown on cubic (111)- and hexagonal (0001)-oriented substrates,'' Hong Jian Zhao, Changsong Xu, Yurong Yang, Wenhui Duan, Xiang Ming Chen, and L. Bellaiche, Journal of Physics: Condensed Matter 27, 485901 (2015).

First-principles calculations were performed to compare the energetics of several phases, including hexagonal polar $P6_3cm$ and perovskite non-polar Pbnm-like states, of epitaxial $RFeO_3$ films (with R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er and Lu) grown on different cubic (1 1 1)- and hexagonal (0 0 0 1)-oriented substrates. The $P6_3cm$ phase is found to be the ground state for large enough in-plane lattice parameters in all investigated $RFeO_3$ films, and its polarization is tunable by the amount of epitaxial strain. Series of available substrates allowing the growth of hexagonal polar $RFeO_3$ films, as well as other phenomena of fundamental and technological importance (e.g., different ground states and coexistence between several phases) are also predicted.

- 7) ``Special quasirandom structures for perovskite solid solutions,'' Zhijun Jiang, Yousra Nahas, Bin Xu, Sergey Prosandeev, Dawei Wang and L. Bellaiche, Journal of Physics: Condensed Matter 28, 475901 (2016).

Special quasirandom structures (SQS) were generated for disordered $(A'_{1-x}A_x)BX_3$ and $A(B'_{1-x}B_x)X_3$ perovskite solid solutions, with x = 1/2 as well as 1/3 and 2/3. These SQS configurations were obtained by imposing that the so-called Cowley parameters are as close to zero as possible for the three nearest neighboring shells. Moreover, these SQS configurations are slightly larger in size than those available in the literature for x = 1/2, mostly because of the current capabilities of atomistic techniques. They are used here within effective Hamiltonian schemes to predict various properties, which are then compared to those associated with large random supercells, in a variety of compounds, namely $(Ba_{1-x}Sr_x)TiO_3$, $Pb(Zr_{1-x}Ti_x)O_3$, $Pb(Sc_{0.5}Nb_{0.})O_3$, $Ba(Zr_{1-x}Ti_x)O_3$, $Pb(Mg_{1/3}Nb_{2/3})O_3$ and $(Bi_{1-x}Nd_x)FeO_3$. It is found that these SQS configurations can reproduce many properties of large random supercells of most of these disordered perovskite alloys, below some finite material-dependent temperature. Examples of these properties are electrical polarization, anti-phase and in-phase octahedral tiltings, antipolar motions, antiferromagnetism, strain, piezoelectric coefficients, dielectric response, specific heat and even the formation of polar nanoregions (PNRs) in some relaxors. Some limitations of these SQS configurations were also pointed out and explained.

- 8) ``Pinched hysteresis loop in defect-free ferroelectric materials,'' Bin Xu, Charles Paillard, Brahim Dkhil, and L. Bellaiche, PHYSICAL REVIEW B 94, 140101(R) (2016).

In addition to the single polarization-versus-electric field hysteresis loop that is characteristic of ferroelectrics and the double hysteresis loop that is known to occur in antiferroelectrics, a third kind of polarization-versus-electric field function has been reported in several systems. This third kind is commonly termed the “pinched” loop due to its unusual shape, and is typically believed to originate from the pinning of domain walls interacting with defects. Here, using an atomistic effective Hamiltonian scheme, we demonstrate that such a belief has to be broadened since our simulations also yield pinched loops in defect-free ferroelectric materials, as a result of the occurrence of intermediate modulated phases exhibiting an inhomogeneous dipolar pattern leading to the coexistence of both ferroelectric and antiferroelectric orders.

- 9) ``Pressure-Induced Multiferroics via Pseudo Jahn–Teller Effects and Novel Couplings,'' Changsong Xu, Yang Li, Bin Xu, Jorge Íñiguez, Wenhui Duan, and Laurent Bellaiche, Adv. Funct. Mater. 2017, 1604513.

Multiferroic materials are currently attracting a lot of interest because of the cross-coupling between their electrical and magnetic properties, which has the potential to lead to novel devices. There is a relatively small number of multiferroics and, hence, various strategies have been proposed to design materials possessing both ordered electric and magnetic dipoles. However, one strategy that has been scarcely investigated so far is the application of hydrostatic pressure because such external factor has the tendency to suppress, rather than enhance or create, electrical polarization. Here, first-principles calculations are used to demonstrate that hydrostatic pressure can, in fact, stabilize a novel polar and magnetic – and thus multiferroic – phase; the occurrence of such a phase seems very general, as it is found in many presently investigated R MnO3 compounds, where R is a rare-earth ion. The predicted structure features original pseudo Jahn–Teller effects that induce a spontaneous electrical polarization via a previously unknown structural coupling of a rather convenient form. Such a discovery opens a new route to create multiferroics and tunable electronic devices.

- 10) ``Properties of rare-earth iron garnets from first principles,'' Ryan Nakamoto, Bin Xu, Changsong Xu, Hu Xu and L. Bellaiche, PHYSICAL REVIEW B 95, 024434 (2017).

Structural and magnetic properties of rare-earth iron garnets (RIG), which contain 160 atoms per unit cell, are systematically investigated for rare-earth elements varying from La to Lu (and including Y), by performing spin polarized density-functional calculations. The effects of 4f electrons (as core or as valence electrons) on the lattice constant, internal coordinates, and bond lengths are found to be rather small, with these predicted structural properties agreeing rather well with available experiments. On the other hand, treating such electrons as valence electrons is essential to interpret the total magnetization measured in some RIG at low temperature, the different orientation and magnitude of the magnetizations that Fe and rare-earth ions can adopt and to also explain why some RIG have a compensation temperature while others do not. The magnetic exchange couplings and orbital-projected density of states are also reported for two representative materials, namely $Gd_3Fe_5O_{12}$ and $Nd_3Fe_5O_{12}$, when accounting for their 4f electrons.

- 11) ``Intrinsic polarization switching mechanisms in $BiFeO_3$,'' Bin Xu, Vincent Garcia, Stephane Fusil, Manuel Bibes, and L. Bellaiche, PHYSICAL REVIEW B 95, 104104 (2017).

In collaboration with the experimental group of Manuel Bibes (CNRS-Thales, France), A first-principles-based effective Hamiltonian technique was used to investigate the polarization switching mechanisms in two polymorphic phases of $BiFeO_3$ having no defects. The switching mechanism is homogeneous for any switching field in the rhombohedral phase, while in the supertetragonal phase it changes from the classical nucleation and domain-wall motion to nucleation-limited switching with virtually no propagation, and then to homogeneous switching with increasing electric field. The first two inhomogeneous switching mechanisms of the supertetragonal phase of BiFeO3 are thus intrinsic in nature, and can be well described by the classical and nucleation-limited switching models, respectively. The reason behind their absence in the rhombohedral phase is also indicated. Moreover, the field-induced changes of switching mechanism within the supertetragonal phase are further elucidated from an energetic point of view.

- 12) ``Creating a low-symmetry insulating, ferroelectric, and antiferromagnetic material from a high-symmetrical metallic ferromagnet via defect engineering: The case of LaBaCo2O5+δ compounds,'' Yurong Yang, Chunrui Ma, Ming Liu, Hong Jian Zhao, Yuan Lin, Chonglin Chen and L. Bellaiche, PHYSICAL REVIEW B 95, 165132 (2017)

In collaboration with the experimental group of Dr. Chen (San Antonio, Texas), first-principles calculations were performed to investigate the properties of defect-free LaBaCo2O6 materials as well as LaBaCo2O5 films possessing ordered oxygen vacancy structures. These calculations predict that the defect-free LaBaCo2O6 crystallizes in a tetragonal state with an axial ratio smaller than unity, and is metallic and ferromagnetic as consistent with the literature. In contrast, the LaBaCo2O5 film adopts a low-symmetry monoclinic state having an axial ratio larger than 1, is insulating and even ferroelectric, as well as exhibits a G-type antiferromagnetic ordering. Our calculations further reveal the origin of these defect-induced changes in properties. Moreover, further experiments we conducted demonstrate the possibility to grow highly epitaxial LaBaCo2O5 films with ordered oxygen vacancies, via reduction treatments, and confirm some of our predictions. These findings can open a new avenue for the design and synthesis of multiferroics via defect engineering.

- 13) ``Designing lead-free antiferroelectrics for energy storage,'' Bin Xu, Jorge Iniguez and L. Bellaiche, NATURE COMMUNICATIONS 8:15682 (2017).

Dielectric capacitors, although presenting faster charging/discharging rates and better stability compared with supercapacitors or batteries, are limited in applications due to their low energy density. Antiferroelectric (AFE) compounds, however, show great promise due to their atypical polarization-versus-electric field curves. Here we report our first-principles-based theoretical predictions that Bi1_xRxFeO3 systems (R being a lanthanide, Nd in this work) can potentially allow high energy densities (100–150 J cm_3) and efficiencies (80–88%) for electric fields that may be within the range of feasibility upon experimental advances (2–3MVcm_1). In addition, a simple model is derived to describe the energy density and efficiency of a general AFE material, providing a framework to assess the effect on the storage properties of variations in doping, electric field magnitude and direction, epitaxial strain, temperature and so on, which can facilitate future search of AFE materials for energy storage.

- 14) ``Photostrictive Two-Dimensional Materials in the Monochalcogenide Family,'' Raad Haleoot, Charles Paillard, Thaneshwor P. Kaloni, Mehrshad Mehboudi, Bin Xu, L. Bellaiche, and Salvador Barraza-Lopez, PHYSICAL REVIEW LETTERS 118, 227401 (2017)

Photostriction is predicted for group-IV monochalcogenide monolayers, two-dimensional ferroelectrics with rectangular unit cells (the lattice vector a1 is larger than a2) and an intrinsic dipole moment parallel to a1. Photostriction is found to be related to the structural change induced by a screened electric polarization (i.e., a converse piezoelectric effect) in photoexcited electronic states with either px or py (in-plane) orbital symmetry that leads to a compression of a1 and a comparatively smaller increase of a2 for a reduced unit cell area. The structural change documented here is 10 times larger than that observed in BiFeO3, making monochalcogenide monolayers an ultimate platform for this effect. This structural modification should be observable under experimentally feasible densities of photexcited carriers on samples that have been grown already, having a potential usefulness for light-induced, remote mechano-optoelectronic applications.

- 15) ``Rules and mechanisms governing octahedral tilts in perovskites under pressure,'' H. J. Xiang, Mael Guennou, Jorge Íñiguez, Jens Kreisel and L. Bellaiche, PHYSICAL REVIEW B 96, 054102 (2017)

The rotation of octahedra (octahedral tilting) is common in ABO3 perovskites and relevant to many physical phenomena, ranging from electronic and magnetic properties, metal-insulator transitions to improper ferroelectricity. Hydrostatic pressure is an efficient way to tune and control octahedral tiltings. However, the pressure behavior of such tiltings can dramatically differ from one material to another, with the origins of such differences remaining controversial. In this paper, we discover several new mechanisms and formulate a set of simple rules that allow us to understand how pressure affects oxygen octahedral tiltings via the use and analysis of first-principles results for a variety of compounds. Besides the known A-O interactions, we reveal that the interactions between specific B ions and oxygen ions contribute to the tilting instability. We explain the previously reported trend that the derivative of the oxygen octahedral tilting with respect to pressure (dR/dP) usually decreases with both the tolerance factor and the ionization state of the A ion by illustrating the key role of A-O interactions and their change under pressure. Furthermore, three new mechanisms/rules are discovered, namely that (i) the octahedral rotations in ABO3 perovskites with empty low-lying d states on the B site are greatly enhanced by pressure, in order to lower the electronic kinetic energy; (ii) dR/dP is enhanced when the system possesses weak tilt instabilities, and (iii) for the most common phase exhibited by perovskites—the orthorhombic Pbnm state—the in-phase and antiphase octahedral rotations are not automatically both suppressed or both enhanced by the application of pressure because of a trilinear coupling between these two rotation types and an antipolar mode involving the A ions. We further predict that the polarization associated with the so-called hybrid improper ferroelectricity could be manipulated by hydrostatic pressure by indirectly controlling the amplitude of octahedral rotations.

- 16) ``Improper ferroelectricity at antiferromagnetic domain walls of perovskite oxides,'' Yali Yang, Hongjun Xiang, Hongjian Zhao, Alessandro Stroppa, Jincang Zhang, Shixun Cao, Jorge Íñiguez, L. Bellaiche, and Wei Ren, PHYSICAL REVIEW B 96, 104431 (2017)

First-principles calculations are performed on magnetic multidomain structures in the SmFeO3 rare-earth orthoferrite compound. We focus on the magnetic symmetry breaking at (001)-oriented antiphase domain walls,treating magnetism in the simplest (collinear) approximation without any relativistic (spin-orbit coupling) effects. We found that the number of FeO2 layers inside the domains determines the electrical nature of the whole system: multidomains with odd number of layers are paraelectric, while multidomains with even number of layers possess an electric polarization aligned along b axis and a resulting multiferroic Pmc21 ground state. Our ab initio data and model for ferroelectricity induced by spin order reveal that this polarization is of the improper type and originates from an exchange striction mechanism that drives a polar displacement of the oxygen ions located at the magnetic domain walls. Additional calculations ratify that this effect is general among magnetic perovskites with an orthorhombic SmFeO3-like structure.

- 17) ``Giant Resistive Switching in Mixed Phase BiFeO3 via phase population control," D. Edwards, N. Browne, K. Holsgrove, A. B. Naden, S. O. Sayedaghaee, B. Xu, S. Prosandeev, D. Wang, D. Mazumdar, M. Duchamp, A. Gupta, S.V. Kalinin, M.A. Arredondo, R. G. P. McQuaid, L. Bellaiche, J. M. Gregg and A. Kumar, Nanoscale 10, 17629 (2018).

Highly-strained coherent interfaces, between rhombohedral-like (R) and tetragonal-like (T) phases in BiFeO3 thin films, often show enhanced electrical conductivity in comparison to non-interfacial regions. In principle, changing the population and distribution of these interfaces should therefore allow different resistance states to be created. However, doing this controllably has been challenging to date. Here, we show that local thin film phase microstructures (and hence R–T interface densities) can be changed in a thermodynamically predictable way (predictions made using atomistic simulations) by applying different combinations of mechanical stress and electric field. We use both pressure and electric field to reversibly generate metastable changes in microstructure that result in very large changes of resistance of up to 108%, comparable to those seen in Tunnelling Electro-Resistance (TER) devices.

- 18) ``Polarization switching in the PbMg1/3Nb2/3O3 relaxor ferroelectric: An atomistic effective Hamiltonian study," Sergey Prosandeev, Bin Xu and L. Bellaiche, Physical Review B 98, 024105 (2018).

An atomistic effective Hamiltonian technique is employed to investigate the polarization switching mechanism of the (metastable but long-living) ferroelectric state of PbMg1/3Nb2/3O3 relaxor ferroelectric, resulting from the application of a dc electric field along the [-1-1-1] direction—that is, opposite to the initial polarization. It is predicted that such switching is of inhomogeneous type. It involves the creation of intermediate short-range ordered, relaxor-like phases in between long-range ordered states inside which an infinite cluster exists and has dipoles near either the initial polarization direction (for shorter times) or the field's direction (for longer times). In contrast, dipoles belonging to finite clusters or being isolated can deviate away from [111] and [-1-1-1], and, in fact, rotate in average from [111] to [-1-1-1] when time increases. Such rotations govern the reversal of the polarization from [111] to [-1-1-1] occurring within the intermediate relaxor-like states' region, while always resulting in the overall cancellation of any Cartesian component of the polarization that is perpendicular to [111]. These rotations occurring at the atomic scale also naturally imply that some fundamental assumptions of the original nucleation-limited-switching (NLS) model are not valid, despite the fact that we numerically further find that the whole temporal behavior of the macroscopic polarization can be well fitted by the general formula associated with NLS. In other words, we have stumbled into a novel switching or at least a switching that should be denoted as a generalized NLS model. Finally, three different electric-field regimes are predicted, with each of them having its own dependency of the switching time on the magnitude of the applied electric field and only one of them obeying the Merz's law. The existence of these three regimes is explained in terms of specific microscopic features.

- 19) ``Understanding and revisiting the most complex perovskite system via atomistic simulations," Yali Yang, Bin Xu, Changsong Xu, Wei Ren and L. Bellaiche, Physical Review B 97, 174106 (2018).

A first-principles-based effective Hamiltonian is developed and used, along with direct ab initio techniques, to investigate finite-temperature properties of the system commonly coined the most complex perovskite, that is NaNbO3. Such simulations successfully reproduce the existence of seven different phases in its phase diagram. The decomposition of the total energy of this effective Hamiltonian into different terms, altogether with the values of the parameters associated with these terms, also allow us to shed some light into puzzling features of such a compound. Examples include revealing the microscopic reasons of why R3c is its ground state and why it solely adopts in-phase tiltings at high temperatures versus complex nanotwins for intermediate temperatures. The results of the computations also call for a revisiting of the so-called P, R, and S states, in the sense that an unexpected and previously overlooked inhomogeneous electrical polarization is numerically found in the P state while complex tiltings associated with the simultaneous condensation of several k points are predicted for the controversial R and S phases.

- 20) ``Designing switchable near room-temperature multiferroics via the discovery of a novel magneto-electric coupling," J.S. Feng, Ke Xu, Laurent Bellaiche and H.J. Xiang, New Journal of Physics 20, 053025 (2018).

Magnetoelectric (ME) coupling is the key ingredient for realizing the cross-control of magnetism and ferroelectricity in multiferroics. However, multiferroics are not only rare, especially at room temperature, in nature but also the overwhelming majority of known multiferroics do not exhibit highly-desired switching of the direction of magnetization when the polarization is reversed by an electric field. Here, we report group theory analysis and ab initio calculations demonstrating, and revealing the origin of, the existence of a novel form ofMEcoupling term in a specific class of materials that does allow such switching. This term naturally explains the previously observed electric field control of magnetism in the first known multiferroics, i.e., the Ni–X boracite family. It is also presently used to design a switchable near room-temperature multiferroic (namely, LaSrMnOsO6 perovskite) having rather large ferroelectric polarization and spontaneous magnetization, as well as strong ME coupling.

- 21) ``Cooperative Couplings between Octahedral Rotations and Ferroelectricity in Perovskites and Related Materials," Teng Gu, Timothy Scarbrough, Yurong Yang, Jorge Iniguez, L. Bellaiche, and H. J. Xiang, Physical Review Letters 120, 197602 (2018).

The structure of ABO3 perovskites is dominated by two types of unstable modes, namely, the oxygen octahedral rotation (AFD) and ferroelectric (FE) mode. It is generally believed that such AFD and FE modes tend to compete and suppress each other. Here we use first-principles methods to show that a dual nature of the FE-AFD coupling, which turns from competitive to cooperative as the AFD mode strengthens, occurs in numerous perovskite oxides.We provide a unified model of such a dual interaction by introducing novel high-order coupling terms and explain the atomistic origin of the resulting new form of ferroelectricity in terms of universal steric mechanisms. We also predict that such a novel form of ferroelectricity leads to atypical behaviors, such as an enhancement of all the three Cartesian components of the electric polarization under hydrostatic pressure and compressive epitaxial strain.

- 22) ``Meta-screening and permanence of polar distortions in metallized ferroelectrics," Hong Jian Zhao, Alessio Filippetti, Carlos Escorihuela-Sayalero, Pietro Delugas, Enric Canadell, L. Bellaiche, Vincenzo Fiorentini and Jorge Iniguez, Physical Review B 97, 054107 (2018).

Ferroelectric materials are characterized by a spontaneous polar distortion. The behavior of such distortion in the presence of free charge is the key to the physics of metallized ferroelectrics in particular, and of structurally polar metals more generally. Using first-principles simulations, here we show that a polar distortion resists metallization and the attendant suppression of long-range dipolar interactions in the vast majority of a sample of 11 representative ferroelectrics. We identify a meta-screening effect, occurring in the doped compounds as a consequence of the charge rearrangements associated to electrostatic screening, as the main factor determining the survival of a noncentrosymmetric phase. Our findings advance greatly our understanding of the essentials of structurally polar metals, and offer guidelines on the behavior of ferroelectrics upon field-effect charge injection or proximity to conductive device elements.

- 23) ``Photostriction and elasto-optic response in multiferroics and ferroelectrics from first principles," Yurong Yang, Charles Paillard, Bin Xu, and L. Bellaiche, Invited Topical Review, Journal of Physics: Condensed Matter 30, 073001 (2018).

This work reviews a series of recent first-principles studies devoted to the description of the interaction of light and strain in ferroelectric and multiferroic materials. Specifically, the modelling schemes used in these works to describe the so-called photostriction and elasto-optic effects are presented, in addition to the results and analysis provided by these ab initio calculations. In particular, the large importance of the piezoelectric effect in the polar direction in the photostriction of ferroelectric materials is stressed. Similarly, the occurrence of low-symmetry phases in lead titanate thin films under tensile strain is demonstrated to result in large elasto-optic constants. In addition, first-principle calculations allow to gain microscopic knowledge of subtle effects, for instance in the case of photostriction, where the deformation potential effect in directions perpendicular to the polar axis is shown to be almost as significant as the piezoelectric effect. As a result, the numerical methods presented here could propel the design of efficient opto-mechanical devices.

- 24) ``Novel multiferroic phases and phenomena in epitaxial (111) BiFeO3 films," Changsong Xu, Hongjun Xiang and L. Bellaiche, Advanced Electronic Materials 3, 1700332 (2017).

Multiferroics are attracting much interest because they simultaneously possess ordered electric and magnetic dipoles. In particular, numerous recent studies are devoted to find novel multiferroic phases, as, for example evidenced by the flurry of activities that accompanied the discovery of the so-called T-phase in BiFeO3 systems, when these latter are made in forms of (001) epitaxial films and subject to high-enough compressive strains. Here it is predicted, via the combined use of a genetic algorithm and first-principles calculations, that novel multiferroic phases, as well as new phenomena, can also occur in epitaxial BiFeO3 films, but when grown along the less conventional [111] direction and when experiencing large enough tensile strains. One example includes the hexagonal YMnO3 -type P63cm phase, that exhibits an anomalous behavior for its out-of-plane electric polarization and that can also undergo magnetic transitions when varying the tensile strain. Another striking example is the emergence of an unusual crystal structure of triclinic symmetry, that possesses controllable polarization’s direction as well as magnetic spiral structures whose characteristics (e.g., periodicity and propagation direction) can be altered by epitaxial strain. Such findings may open new ways to design multiferroics and novel devices exploiting their cross-coupling between electric and magnetic properties.

- 25) ``Revisiting spin cycloids in multiferroic BiFeO3,'' Bin Xu, Bertrand Dupé, Changsong Xu, Hongjun Xiang and L. Bellaiche, PHYSICAL REVIEW B 98, 184420 (2018)

We revisited the inverse spin current model that has been previously used to explain the existence of magnetic cycloids in bulk multiferroic BiFeO3. Using a first-principles-based effective Hamiltonian method, and in combination with Monte Carlo simulations, we predict a magnetic phase diagram as a function of first- and second-nearest-neighbor interaction strength in the spin current model and show that, in contrast with previous understanding, both first and second nearest neighbors have to be taken into account to be in accordance with experimental findings, including the existence of type-1 and type-2 cycloids with, respectively, [1-10] and [11-2] propagation directions, and the cycloid-to-antiferromagnetic transition under magnetic field. Other previously unknown magnetic arrangements are found in this phase diagram. The microscopic origins of all its magnetic phases are further explained in terms of the coexistence of single solutions of the spin current model having different weights (in magnitude and even sign).

- 26) ``Symmetry Modulation and Enhanced Multiferroic Characteristics in Bi1-xNdxFeO3 Ceramics,'' Jing Chen, Bin Xu, Xiao Qiang Liu, Ting Ting Gao, Laurent Bellaiche and Xiang Ming Chen, Adv. Funct. Mater., 1806399 (2018).

BiFeO3 is recognized as the most important room temperature single-phase multiferroic material. However, the weak magnetoelectric (ME) coupling remains as a key issue, which obstructs its applications. Since the magnetoelectric coupling in BiFeO3 is essentially hindered by the cycloidal spin structure, here efforts to improve the magnetoelectric coupling by destroying the cycloidal state and switching to the weak ferromagnetic state through symmetry modulation are reported. The structure is tuned from polar R3c to polar Pna21, and finally to nonpolar Pbnm by forming Bi1-xNdx FeO3 solid solutions, where two morphotropic phase boundaries (MPBs) are detected. Greatly enhanced ferroelectric polarization is obtained together with the desired weak ferromagnetic characteristics in Bi1-x Ndx FeO3 ceramics at the compositions near MPBs. The change of magnetic state from antiferromagnetic (cycloidal state) to ferromagnetic (canted antiferromagnetic) is confirmed by the observation of magnetic domains using magnetic force microscopy. More interestingly, combining experiments and first-principles-based simulations, an electric field-induced structural and magnetic transition from Pna21 back to R3c is demonstrated, providing a great opportunity for electric field-controlled magnetism, and this transition is shown to be reversible with additional thermal treatment.

27) ``Novel Dynamical Magnetoelectric Effects in Multiferroic BiFeO3,'' S. Omid Sayedaghaee, Bin Xu, Sergey Prosandeev, Charles Paillard, and L. Bellaiche, PHYSICAL REVIEW LETTERS 122, 097601 (2019)

An atomistic effective Hamiltonian scheme is employed within molecular dynamics simulations to investigate how the electrical polarization and magnetization of the multiferroic BiFeO3 respond to time-dependent ac magnetic fields of various frequencies, as well as to reveal the frequency dependency of the dynamical (quadratic) magnetoelectric coefficient. We found the occurrence of vibrations having phonon frequencies in both the time dependency of the electrical polarization and magnetization (for any applied ac frequency), therefore making such vibrations of electromagnonic nature, when the homogeneous strain of the system is frozen (case 1). Moreover, the quadratic magnetoelectric coupling constant is monotonic and almost dispersionless in the sub-THz range in this case 1. In contrast, when the homogeneous strain can fully relax (case 2), two additional low-frequency and strain-mediated oscillations emerge in the time-dependent behavior of the polarization and magnetization, which result in resonances in the quadratic magnetoelectric coefficient. Such additional oscillations consist of a mixing between acoustic phonons, optical phonons, and magnons, and reflect the existence of a new quasiparticle that can be coined an “electroacoustic magnon.” This latter finding can prompt experimentalists to shape their samples to take advantage of, and tune, the magnetostrictive-induced mechanical resonance frequency, in order to achieve large dynamical magnetoelectric couplings.

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