# REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188



| 1. REPORT DATE (DD-MM-YYYY) | 2. REPORT TYPE | 3. DATES COVERED (From - To) |
|---|---|---|
| 28-09-2016 | Final Report | 1-Mar-2012 - 31-Aug-2016 |

**4. TITLE AND SUBTITLE**
Final Report: Searching For Novel Phenomena in Two-Dimensional Ferroelectrics and Multiferroics

**5a. CONTRACT NUMBER**
W911NF-12-1-0085

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**
611102

**6. AUTHORS**
Laurent Bellaiche

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

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**8. PERFORMING ORGANIZATION REPORT NUMBER**

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES)**
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

**10. SPONSOR/MONITOR'S ACRONYM(S)**
ARO

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**
60780-MS.58

**12. DISTRIBUTION AVAILIBILITY STATEMENT**
Approved for Public Release; Distribution Unlimited

**13. SUPPLEMENTARY NOTES**
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

**14. ABSTRACT**
The main objective of this proposal is to investigate various static and dynamical properties of two-dimensional ferroelectrics and multiferroics (and related materials), in general, and to discover novel phenomena of large fundamental and technological importance in these ultrathin films, in particular.

**15. SUBJECT TERMS**
ferroelectrics, multiferroics, films

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| a. REPORT | b. ABSTRACT | c. THIS PAGE | | | Laurent Bellaiche |
| UU | UU | UU | UU | | 19b. TELEPHONE NUMBER 479-575-6425 |

## Report Title

Final Report: Searching For Novel Phenomena in Two-Dimensional Ferroelectrics and Multiferroics


## ABSTRACT

The main objective of this proposal is to investigate various static and dynamical properties of two-dimensional ferroelectrics and multiferroics (and related materials), in general, and to discover novel phenomena of large fundamental and technological importance in these ultrathin films, in particular.


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## Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

### (a) Papers published in peer-reviewed journals (N/A for none)

| Received | | Paper |
|---|---|---|
| 09/28/2016 | 54 | Raymond Walter, Sergei Prokhorenko, Zhigang Gui, Yousra Nahas and L. Bellaiche. Electrical Control of Chiral Phases in ElectrotoroidicNanocomposites, Advanced Electronic Materials, (07 2015): 1500218. doi: |
| 09/28/2016 | 53 | Y. Nahas, S. Prokhorenko, L. Louis, Z. Gui, I. Kornev and L. Bellaiche. Discovery of stable skyrmionic state inferroelectric nanocomposites, Nature Communications, (05 2016): 8542. doi: |
| 09/28/2016 | 55 | Y. Nahas, S. Prokhorenko, I. Kornev and L. Bellaiche. Topological Point Defects in Relaxor Ferroelectrics, PHYSICAL REVIEW Letters, (07 2015): 127601. doi: |
| 09/28/2016 | 56 | Y. Nahas, S. Prokhorenko and L. Bellaiche. Frustration and Self-Ordering of Topological Defects in Ferroelectrics, PHYSICAL REVIEW Letters, (07 2015): 117603. doi: |
| **TOTAL:** | | **4** |

**Number of Papers published in peer-reviewed journals:**

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### (b) Papers published in non-peer-reviewed journals (N/A for none)

| Received | | Paper |
|---|---|---|
| **TOTAL:** | | |

**Number of Papers published in non peer-reviewed journals:**

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### (c) Presentations

**Number of Presentations:** 18.00

## Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

**TOTAL:**

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):**

## (d) Manuscripts

Received Paper

**TOTAL:**

**Number of Manuscripts:**

## Books

| Received | Book | |
|---|---|---|
| 09/28/2016 | 57.00 | Sergei Prosandeev, Ivan I Naumov, Huaxiang Fu, Laurent Bellaiche, Michael P.D. Campbell, Raymond G. P. McQuaid, Li-Wu Chang, Alina Schilling, Leo J. McGilly, Amit Kumar, J. Marty Gregg. , : Wiley, ( 2016) |

**TOTAL:** **1**

| Received | Book Chapter |
|---|---|

**TOTAL:**

## Patents Submitted

## Patents Awarded

## Awards

Dr Laurent Bellaiche was named the 2015 ZiQiang Professorship from Shanghai University (Shanghai, China).

## Graduate Students

| NAME | PERCENT_SUPPORTED | Discipline |
|---|---|---|
| Zhigang Gui | 1.00 | |
| **FTE Equivalent:** | **1.00** | |
| **Total Number:** | **1** | |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| Yousra Nahas | 0.75 |
| Satadeep Bhattacharjee | 0.25 |
| **FTE Equivalent:** | **1.00** |
| **Total Number:** | **2** |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|---|---|---|
| Laurent Bellaiche | 1.00 | |
| **FTE Equivalent:** | **1.00** | |
| **Total Number:** | **1** | |

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

## Names of Personnel receiving masters degrees

| NAME |
|---|
| **Total Number:** |

## Names of personnel receiving PHDs

| NAME | |
|---|---|
| Zhigang Gui | |
| **Total Number:** | **1** |

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
| --- | --- |

**FTE Equivalent:**
**Total Number:**

## Sub Contractors (DD882)

## Inventions (DD882)

## Scientific Progress

See Attachment

## Technology Transfer

Developments of novel numerical tools

## Contract Information

| | |
|---|---|
| Contract Number | W911NF-12-1-0085 |
| Title of Research | Searching For Novel Phenomena in Two-Dimensional Ferroelectrics and Multiferroics |
| Principal Investigator | Laurent Bellaiche |
| Organization | University of Arkansas |

## Technical Section

### *Technical Objectives*

The main objective of this proposal is to investigate various static and dynamical properties of two-dimensional ferroelectrics and multiferroics (and related materials), in general, and to discover novel phenomena of large fundamental and technological importance in these ultrathin films, in particular.

### *Technical Approach*

To reach our goals, we developed and used first-principles-based schemes, as well as collaborated with International scientists.

### *Progress*

The following articles have been published in the last reported period of the grant (from July 31, 2015 to August 30, 2016).

- 1) ``Discovery of stable skyrmionic state in ferroelectric nanocomposites," Y. Nahas, S. Prokhorenko, L. Louis, Z. Gui, I. Kornev and L. Bellaiche, Nature Communications 6, 8542 (2015).

Non-coplanar swirling field textures, or skyrmions, are now widely recognized as objects of both fundamental interest and technological relevance. So far, skyrmions were amply investigated in magnets, where due to the presence of chiral interactions, these topological objects were found to be intrinsically stabilized. Ferroelectrics on the other hand, lacking such chiral interactions, were somewhat left aside in this quest. Here we demonstrated, via the use of a first-principles-based framework, that skyrmionic configuration of polarization can be extrinsically stabilized in ferroelectric nanocomposites. The interplay between the considered confined geometry and the dipolar interaction underlying the ferroelectric phase instability induces skyrmionic configurations. The topological structure of the obtained electrical skyrmion can be mapped onto the topology of domain-wall junctions. Furthermore, the stabilized electrical skyrmion can be as small as a few nanometers, thus revealing prospective skyrmion-based applications of ferroelectric nanocomposites.

- 2) ``Frustration and Self-Ordering of Topological Defects in Ferroelectrics," Y. Nahas, S. Prokhorenko and L. Bellaiche, Physical Review Letters 116, 127603 (2016).

A first-principles-based effective Hamiltonian technique was used to investigate the interplay between geometrical frustration and the ordering of topological defects in a ferroelectric nanocomposite consisting

of a square array of BaTiO3 nanowires embedded in a Ba0.15Sr0.85TiO3 matrix. Different arrangements of the wires' chiralities geometrically frustrate the matrix, which in response exhibits point topological defects featuring self-assembled ordered structures spatially fluctuating down to the lowest temperatures. These fluctuations thereby endow the system with residual configurational entropy from which many properties characteristic of geometric frustration, such as the ground state degeneracy and the broadness of the dielectric response, are further found to originate.

- 3) ``Topological Point Defects in Relaxor Ferroelectrics," Y. Nahas, S. Prokhorenko, I. Kornev and L. Bellaiche, Physical Review Letters 116, 127601 (2016).

First-principles-based effective Hamiltonian simulations were used to reveal the hidden connection between topological defects (hedgehogs and antihedgehogs) and relaxor behavior. Such defects are discovered to predominantly lie at the border of polar nanoregions in both Ba.Zr0.5Ti0.5O3 (BZT) and Pb.Sc0.5Nb0.5O3 (PSN) systems, and the temperature dependency of their density allows us to distinguish between noncanonical (PSN) and canonical (BZT) relaxor behaviors (via the presence or absence of a crossing of a percolation threshold). This density also possesses an inflection point at precisely the temperature for which the dielectric response peaks. Moreover, hedgehogs and antihedgehogs are found to be mobile excitations, and the dynamical nature of their annihilation is demonstrated (using simple hydrodynamical arguments) to follows laws, such as those of Vogel-Fulcher and Arrhenius, that are characteristic of dipolar relaxation kinetics of relaxor ferroelectrics.

- 4) ``Ferroelectric Vortices and Related Configurations," Sergei Prosandeev, Ivan I Naumov, Huaxiang Fu, Laurent Bellaiche, Michael P.D. Campbell, Raymond G.P. McQuaid, Li-Wu Chang, Alina Schilling, Leo J. McGilly, Amit Kumar, J. Marty Gregg, Invited Review in Nanoscale Ferroelectrics and Multiferroics: Key Processing and Characterization Issues, and Nanoscale Effects, Volume I and II (edited by Miguel Alguero, J. Marty Gregg and Liliana Mitoseriu), 700 (2016).

An invited review article was writing on ferroelectric vortices and related configurations.

- 5) ``Electrical Control of Chiral Phases in Electrotoroidic Nanocomposites," Raymond Walter, Sergei Prokhorenko, Zhigang Gui, Yousra Nahas and L. Bellaiche, Advanced Electronic Materials 2, 1500218 (2016).

We combined Monte-Carlo (MC) and Molecular Dynamis (MD) simulations in a first-principle-based effective Hamiltonian scheme to study electrical control of chiral phases and gyrotropic response in electrotoroidic systems. MC simulations were used to study temperature evolution of system properties and provide a temperature–electric field phase diagram for a nanocomposite exhibiting several complex phenomena. These results are explained by a Landau model that includes biquadratic coupling between polarization and toroidal moment. MD simulations were used to calculate the temperature evolution of gyrotropic response at various applied DC fields and demonstrate that our system exhibits optical activity at room temperature under a certain field, even enhancing optical activity relative to lower applied fields.

Moreover, the following articles were published from March 01, 2012 to July 31, 2015 and were also previously described in previous annual reports:

- 6) ``Revisiting galvanomagnetic effects in conducting ferromagnets," R. Walter, M. Viret, Surendra Singh and L. Bellaiche, Journal of Physics: Condensed Matter, Fast Track Communications 26, 432201 (2014).

The recently proposed coupling between the angular momentum density and magnetic moments is shown to provide a straightforward alternative explanation for galvanomagnetic effects, i.e., for both anisotropic

magnetoresistance (AMR) and planar Hall effect (PHE). Such coupling naturally reproduces the general formula associated with AMR and PHE, and allows for the occurrence of so-called ``negative AMR''. This coupling also provides a unifying link between AMR, PHE and the anomalous Hall effect (AHE) since this same coupling was previously found to give rise to AHE [L. Bellaiche, W. Ren and S. Singh, Phys. Rev. B 88, 161102(R) (2013)].

- 7) ``Tuning and optimizing properties of ferroelectric films grown on a single substrate: A first-principles-based study,'' Zhigang Gui and L. Bellaiche, Physical Review B, Rapid Communications 91, 020102(R) (2015).

A first-principles-based effective Hamiltonian is used to reveal the effects of the growth direction on properties of films made of the prototype of ferroelectric materials (namely, BaTiO3) and grown on one of the most common and available substrates (that is, SrTiO3). Continuously varying the growth direction from the pseudo-cubic [001] to [110] direction, via the high-symmetry [111] direction, results in: (i) an original temperature-versus-growth angle phase diagram possessing different structural states; (ii) a tuning of the Curie temperature, Tc, by more than 450K; (iii) a minimal value of Tc being near room temperature; and (iv) optimization of important physical responses at room temperature, such as dielectric and piezoelectric coefficients, for some specific growth directions. The origins of these features are also revealed, including the finding of a law correlating Tc with the growth direction.

- 8) ``Effects of chemical and hydrostatic pressures on structural, magnetic and electronic properties of R2NiMnO6 (R=rare-earth ion) double perovskites'' Hong Jian Zhao, Xiao Qiang Liu, Xiang Ming Chen, and L. Bellaiche, Physical Review B 90, 195147 (2014).

The effects of chemical and hydrostatic pressures on structural, magnetic and electronic properties of $R_2NiMnO_6$ double perovskites, with R being a rare-earth ion, have been systematically studied by using specific first-principles calculations. These latter reproduce well the correlation between several properties (e.g., lattice parameters, Ni-O-Mn bond angles, magnetic Curie temperature and electronic band gap) and the rare-earth ionic radius (that is, the chemical pressure). They also provide novel predictions awaiting experimental confirmations, such as (i) many physical quantities responding in dramatically different manner to chemical *versus* hydrostatic pressure, unlike commonly thought in perovskites containing rare-earth ions; and (ii) the dependence of the antipolar displacements on chemical and hydrostatic pressures, which further explains why the recently predicted electrical polarization of $La_2NiMnO_6/R_2NiMnO_6$ superlattices [H. J. Zhao *et al*, Nat. Commun. **5**:4021 (2014)] can be created and controlled by playing with the rare-earth element.

- 9) ``Electronic properties of electrical vortices in ferroelectric nanocomposites from large-scale ab-initio computations,'' Zhigang Gui, Lin-Wang Wang and L. Bellaiche, Nano Letters 15, 3224 (2015).

An original ab-initio procedure is developed and applied to a ferroelectric nanocomposite, in order to reveal the effect of electrical vortices on electronic properties. Such procedure involves the combination of two large-scale numerical schemes, namely the effective Hamiltonian (to incorporate ionic degrees of freedom) and the linear-scaling three-dimensional fragment method (to treat electronic degrees of freedom). The use of such procedure sheds some light into the origin of the recently observed current that is activated at rather low voltages in systems possessing electrical vortices. It also reveals a novel electronic phenomenon, that is a systematic control of the type of the band-alignment (i.e., type-I versus-type-II) within the same material via the temperature-driven annihilation/formation of electrical topological defects.

- 10) ``Predicted pressure-induced spin and electronic transition in double perovskite R2CoMnO6 (R = rare-earth ion)," Hong Jian Zhao, Haiyang Zhou, Xiang Ming Chen, and L. Bellaiche, Journal of Physics: Condensed Matter 27 226001 (2015).

Specific first-principles calculations are performed to predict structural, magnetic and electronic properties of seven double perovskite $R_2CoMnO_6$ materials, with R being a rare-earth ion, under hydrostatic pressure. All these compounds are found to undergo a first-order transition from a high spin (HS) to low spin (LS) state at a critical pressure (whose value is dependent on the R ion). Such transition not only results in a significant volume collapse but also yields a dramatic change in electronic structure. More precisely, the HS-to-LS transition is accompanied by a transition from an insulator to a *half-metallic* state in the $R_2CoMnO_6$ compounds having the largest rare-earth ionic radius (i.e., Nd, Sm, Gd and Tb) while it induces a change from an insulator to a semiconductor having a narrow band gap for the smallest rare-earth ions (i.e., R = Dy, Ho and Er). Experiments are called for to confirm these predictions.

- 11) ``Control of ferroelectricity and magnetism in multiferroic BiFeO3 by epitaxial strain," D. Sando, A. Agbelele, C. Daumont, D. Rahmedov, W. Ren, I.C. Infante, S. Lisenkov, S. Prosandeev, S. Fusil, E. Jacquet, C. Carretero, S. Petit, M. Cazayous, J. Juraszek, J.M. Le Breton, L. Bellaiche, B. Dkhil, A. Barthelemy, M. Bibes, Philosophical Transactions of the Royal Society A 372, 20120438 (2014).

In collaboration with the experimental group from France led by Drs Barthelemy and Bibes,we review our results on the role of strain on the ferroic transition temperatures and ferroic order parameters. We found that while the Néel temperature is almost unchanged by strain, the ferroelectric Curie temperature strongly decreases as strain increases in both the tensile and compressive ranges. Also unexpected is the very weak influence of strain on the ferroelectric polarization value. Using effective Hamiltonian calculations, we showed that these peculiar behaviours arise from the competition between antiferrodistortive and polar instabilities. Finally, we presented results on the magnetic order: while the cycloidal spin modulation present in the bulk survives in weakly strained films, it is destroyed at large strain and replaced by pseudo-collinear antiferromagnetic ordering. We discussed the origin of this effect and gave perspectives for devices based on strain-engineered BiFeO3.

- 12) ``Multidomains made of different structural phases in multiferroic BiFeO3: a first-principles-based study," Dawei Wang, Ekhard K.H. Salje, Shao-Bo Mi, Chun-Lin Jia and L. Bellaiche, Physical Review B 88, 134107 (2013).

In collaboration with Dr. Dawei Wang (Xi'an, China), an effective Hamiltonian scheme was used to reveal properties of a multidomain structure in BiFeO3 consisting of alternating domains that are initially made of two different phases, namely R3c (ferroelectric with anti-phase oxygen octahedral tilting) versus Pnma (antiferroelectric with in-phase and anti-phase oxygen octahedral tiltings). These two types of domains dramatically modify their properties as a result of their cohabitation. The weak ferromagnetic vector and polarization rotate, and significantly change their magnitude, in the R3c-like region while the Pnma-like region becomes polar along the direction of domain propagation. Moreover, the domain walls possess distinct polar and oxygen octahedral tilting patterns that facilitate the transition between these two different regions. The studied multidomain is also predicted to exhibit other anomalous properties, such as its strain adopting several plateaux and steps when increasing the magnitude of an applied electric field.

- 13) ``Effect of chemical and hydrostatic pressures on structural and magnetic properties of rare-earth orthoferrites: a first-principles study," Hong Jian Zhao, Wei Ren, Yurong Yang, Xiang Ming Chen and L. Bellaiche, Journal of Physics: Condensed Matter 25, 466002 (2013).

The dependence of structural and magnetic properties of rare-earth orthoferrites (in their *Pbnm* ground state) on the rare-earth ionic radius has been systematically investigated from first principles. The effects of this ``*chemical* pressure'' on lattice constants, Fe-O bond lengths, Fe-O-Fe bond angles and Fe-O bond length splittings are all well reproduced by these *ab-initio* calculations. The simulations also offer novel predictions (on tiltings of $FeO_6$ octahedra, cation antipolar displacements and weak magnetization) to be experimentally checked. In particular, the weak ferromagnetic moment of rare-earth orthoferrites is predicted to be a linear function of the rare-earth ionic radius. Finally, the effects of applying a *hydrostatic* pressure on structural and magnetic behaviors of $SmFeO_3$ has also been studied. It is found that, unlike previously assumed, hydrostatic pressure typically generates changes in physical properties that are quantitatively and even qualitatively different from those associated with the chemical pressure.

- 14) ``Strain engineering of perovskite thin films using a single substrate," P.-E. Janolin, A.S. Anokhin, Z. Gui, V.M. Mukhortov, Yu.I. Golovko, N. Guiblin, S. Ravy, M. El Marssi, Y.I. Yuzyuk, L. Bellaiche and B. Dkhil, Journal of Physics: Condensed Matter 26, 292201 (2014).

In collaboration with the group of Dr. Brahim Dkhil (Ecole Centrale of Paris, France), we combined temperature-dependent x-ray diffraction, Raman spectroscopy and first-principles-based effective Hamiltonian calculations to show that varying the thickness of BST thin films deposited on the same single substrate (namely, MgO) enables to change not only the magnitude but also the sign of the misfit strain. Such previously overlooked control of the strain allows several properties of these films (e.g. Curie temperature, symmetry of ferroelectric phases, dielectric response) to be tuned and even optimized. Surprisingly, such desired control of the strain (and of the resulting properties) originates from an effect that is commonly believed to be detrimental to functionalities of films, namely the existence of misfit dislocations. The present study therefore provides a novel route to strain engineering, as well as leading to revisit common beliefs.

- 15) ``Coupling of the angular-momentum density with magnetic moments explains the intrinsic anomalous Hall effect," L. Bellaiche, Wei Ren and Surendra Singh, Physical Review B, Rapid Communications 88, 161102(R) (2013).

In a recent article [A. Raeliarijaona et al, Phys. Rev. Lett. 110, 137205 (2013)], we demonstrated the existence of a physical energy resulting from the coupling between the angular momentum density and magnetic moment. Here, we showed that the force associated with such energy naturally explains, in a straightforward and simple manner, the occurrence of the intrinsic anomalous Hall effect (AHE). Connections between our model and previous theories of AHE were also drawn. Our model further led to the prediction of a novel effect, namely the formation of an electric field along the direction of the magnetic field. This electric field is directly proportional to the magnetic field and to the scalar product between the components of the electric field and magnetization that are transverse to the magnetic field.

- 16) ``Novel magnetic arrangement and structural phase transition induced by spin-lattice coupling in multiferroics," Satadeep Bhattacharjee, Dovran Rahmedov, Laurent Bellaiche and Dawei Wang, MRS Communications 3, 213 (2013).

In collaboration with Dr. Dawei Wang (Xi'an, China), we used an effective Hamiltonian of mutiferroic BiFeO3 (BFO) as a toy model to explore the effect of the coefficient, C, characterizing the strength of the spin-current interaction, on physical properties. We observed that for larger C values and below a critical

temperature, the magnetic moments organize themselves in a novel cycloid which propagates along a low-symmetry direction and is associated with a structural phase transition from polar rhombohedral to a polar triclinic state. We emphasizde that both of these magnetic and structural transitions are results of a remarkable self-organization of different solutions of the spin-current model.

- 17) ``Effects of a rotating electric field on the properties of epitaxial (001) Pb(Zr,Ti)O3 ultrathin film: a first-principles-based study," David Sichuga and L. Bellaiche, Journal of Physics: Condensed Matter 26, 025302 (2014).

$Pb(Zr,Ti)O_3$ ultrathin films under open-circuit electrical boundary conditions and subjected to an electric field rotating in the (-110) plane were investigated via the use of an effective Hamiltonian, for different magnitude of this field. Varying direction and magnitude of the electric field leads to specific reorganization of dipoles into original configuration states, whose microstructures and macroscopic properties were revealed. In particular, a novel (direction of the electric field – *versus* – magnitude of the electric field) phase diagram was reported here. The field-induced correlation between the polar distortions and the oxygen octahedral tilting was also discussed.

- 18) ``Effect of chemical pressure, misfit strain and hydrostatic pressure on structural and magnetic behaviors of rare-earth orthochromates," Hong Jian Zhao, Wei Ren, Xiang Ming Chen, and L. Bellaiche, Journal of Physics: Condensed Matter 25, 385604 (2013).

First-principles calculations were performed to investigate structural and magnetic behaviors of rare-earth orthochromates as a function of *"chemical"* pressure (that is, the rare-earth ionic radius), epitaxial misfit strain and hydrostatic pressure. On a structural point of view, (i) *"chemical"* pressure significantly modifies antipolar displacements, Cr-O-Cr bond angles and the resulting oxygen octahedral tiltings; (ii) hydrostatic pressure mostly changes Cr-O bond lengths; and (iii) misfit strain affects all these quantities. The correlations between magnetic properties (Néel temperature and weak ferromagnetic moments) and unit cell volume are similar when varying the misfit strain or hydrostatic pressure, but differ from those associated with the *"chemical"* pressure. Origins of such effects were also discussed.

- 19) ``Terahertz dynamics of ferroelectric vortices from first principles," Zhigang Gui and L. Bellaiche, Physical Review B 89, 064303 (2014).
A first-principles-based effective Hamiltonian is used to reveal dynamics of vortices in ferroelectrics. In addition to the ``usual" dielectric modes that are generated by the fluctuation of the electrical polarization, novel toroidic modes, resulting from the electric toroidal moment fluctuations, are also discovered in the THz regime. Such latter modes can have their own dynamics, with a resonant frequency that softens via a square-root law when the temperature approaches the critical temperature at which electric vortices form. These dynamics are also found to be governed by the fluctuation of the self-organized azimuthal component of individual electric dipoles. Toroidic modes thus behave as pendulums, in contrast to springs that represent polarization dynamics.

- 20) ``Terahertz dielectric response and coupled dynamics of ferroelectrics and multiferroics from effective Hamiltonian simulations," Dawei Wang, Jeevaka Weerasinghe, Abdullah Albarakati and L. Bellaiche, Invited Review in International Journal of Modern Physics B 27, 1330016 (2013).

In collaboration with Dr. Dawei Wang (Xi'an, China), an invited review article on dynamics of ferroelectrics and multiferroics was written.

- 21) ``Ultrafast switching of the electric polarization and magnetic chirality in BiFeO3 by an electric field," Satadeep Bhattacharjee, Dovran Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, Physical Review Letters 112, 147601(2014).

In collaboration with Dr. Iniguez from ICMAB (Barcelona, Spain), we used a first-principles-based effective Hamiltonians within molecular dynamics simulations, to discover that applying an electric field that is opposite to the initial direction of the polarization results in a switching of both the polarization and the magnetic chirality vector of multiferroic BiFeO3 at an ultrafast pace (namely of the order of picoseconds). Such double ultrafast switching may hold promise for designing various devices, and is further found to involve original intermediate magnetic states. Its origin was also revealed and discussed.

- 22) ``Quantum Anomalous Hall Effect in Graphene Proximity Coupled to an Antiferromagnetic Insulator,'' Zhenhua Qiao, Wei Ren, Hua Chen, L. Bellaiche, Zhenyu Zhang, A. H. MacDonald and Qian Niu, Physical Review Letters 112, 116404 (2014).

We proposed realizing the quantum anomalous Hall effect by proximity coupling graphene to an antiferromagnetic insulator that provides both broken time-reversal symmetry and spin-orbit coupling. We illustrated our idea by performing ab initio calculations for graphene adsorbed on the (111) surface of BiFeO**3**. In this case, we find that the proximity-induced exchange field in graphene is about 70 meV, and that a topologically nontrivial band gap is opened by Rashba spin-orbit coupling. The size of the gap depends on the separation between the graphene and the thin film substrate, which can be tuned experimentally by applying external pressure.

- 23) ``Prediction of novel interface-driven spintronic effects,'' S. Bhattacharjee, S. Singh, D. Wang, M. Viret and L. Bellaiche, Journal of Physics: Condensed Matter 26, 315008 (2014).

The recently proposed coupling between the angular momentum density and magnetic moment (Raeliarijaona et al 2013 Phys. Rev. Lett. 110 137205) is shown here to result in the prediction of (i) novel spin currents generated by an electrical current and (ii) new electrical currents induced by a spin current in systems possessing specific interfaces between two different materials. Some of these spin (electrical) currents can be reversed near the interface by reversing the applied electrical (spin) current. Similarities and differences between these novel spintronic effects and the well-known spin Hall and inverse spin Hall effects are also discussed.

- 24) ``Near room-temperature multiferroic materials with tunable ferromagnetic and electrical properties," Hong Jian Zhao, Wei Ren, Yurong Yang, Jorge Iniguez, Xiang Ming Chen and L. Bellaiche, Nature Communications 5, 4021 (2014).

The quest for multiferroic materials with ferroelectric and ferromagnetic properties at room temperature continues to be fuelled by the promise of novel devices. Moreover, being able to tune the electrical polarization and the paramagnetic-to-ferromagnetic transition temperature constitutes another current research direction of fundamental and technological importance. Here we report on the first-principles-based prediction of a specific class of materials—namely, R2NiMnO6/La2NiMnO6 superlattices where R is a rare-earth ion—that exhibit an electrical polarization and strong ferromagnetic order near room temperature, and whose electrical and ferromagnetic properties can be tuned by means of chemical pressure and/or epitaxial strain. Analysis of the first-principles results naturally explains the origins of these highly desired features.

- 25) ``Ferroelectric domains in multiferroic BiFeO3 films under epitaxial strains," Wei Ren, Yurong Yang, Oswaldo Dieguez, Jorge Iniguez, Narayani Choudhury, and L. Bellaiche, Physical Review Letters 110, 187601 (2013).

In collaboration with ICMAB (Barcelona, Spain), first-principles calculations were performed to investigate energetic and atomistic characteristics of ferroelectric domains walls (DWs) of $BiFeO_3$ (BFO) films subject to compressive strain. Significantly lower DW energies than those previously reported, and a different energetic hierarchy between the various DW types, are found for small strains. In all investigated cases (corresponding to ideal angles of 71°, 109°, and 180° formed by the domain polarizations), the DW energy reaches its maximum value for misfit strains that are around the critical strain at which the transition between the R-like and T-like phases occurs in single-domain BFO. Near these strains, several quantities depend strongly on the type of domain wall; such a distinct behavior is associated with an elastic difference and a large out-of-plane polarization at the DW in the 180° case. A further increase of the magnitude of the strain leads to (1) a change of hierarchy of the DW energies; (2) large out-of-plane polarizations inside each up and down domain; and (3) novel atomic arrangements at the domain walls. Our study can thus initiate a new research direction, namely strain engineering of domain-wall functionalities.

- 26) ``Thickness-dependent polarization of strained BiFeO3 films with constant tetragonality," J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthelemy, L. Bellaiche, and N. Barrett, Physical Review Letters 109, 267601 (2012).

In collaboration with two experimental groups from France (led by Drs Barrett and Bibes), the ferroelectric polarization of BiFeO3 films down to 3.6 nm was measured using low energy electron and photoelectron emission microscopy. The measured polarization decays strongly below a critical thickness of 5-7 nm predicted by continuous medium theory whereas the tetragonal distortion does not change. We resolved this apparent contradiction using first-principles-based effective Hamiltonian calculations. In ultrathin films, the energetics of near open circuit electrical boundary conditions, i.e. unscreened depolarizing field, drive the system through a phase transition from single out-of-plane polarization to nanoscale stripe domains. It gives rise to an average polarization close to zero as measured by the electron microscopy whilst maintaining the relatively large tetragonal distortion imposed by the non-zero polarization state of each individual domain.

- 27) ``Novel Nanoscale Twinned Phases in Perovskite Oxides," S. Prosandeev, Dawei Wang, Wei Ren, Jorge Iniguez and Laurent Bellaiche, Advanced Functional Materials 23, 234 (2013)

In collaboration with Dr Jorge Iniguez (Barcelona, Spain) and Dr. Dawei Wang (Xian, China), we used different theoretical methods to show that a complete new family of stable phases, all displaying complex and nano-twinned tilting patterns (as well as other anomalous properties), exists in multiferroic BiFeO3 and related compounds.

- 28)``Electronic transition from graphite to graphene via controlled movement of the top layer with scanning tunneling microscopy," P. Xu, Yurong Yang, D. Qi, S.D. Barber, J.K. Schoelz, M.L. Ackerman, L. Bellaiche, and P.M. Thibado, Physical Review B 86, 085428 (2012). [selected to be an Editors' Suggestion].

A series of measurements using a technique called electrostatic-manipulation scanning tunneling microscopy (EM-STM) were performed on a highly-oriented pyrolytic graphite surface. The electrostatic interaction between the STM tip and the sample can be tuned to produce both reversible and irreversible large-scale movement of the graphite surface. Under this influence, atomic-resolution STM images revealed that a continuous electronic transition from triangular symmetry, where only alternate atoms are imaged, to hexagonal symmetry can be systematically controlled. Density functional theory (DFT) calculations revealed that this transition can be related to vertical displacements of the top layer of

graphite relative to the bulk. Evidence for horizontal shifts in the top layer of graphite was also presented. Excellent agreement was found between experimental STM images and those simulated using DFT.

- 29) ``Natural optical activity and its control by electric field in electrotoroidic systems," Sergey Prosandeev, Andrei Malashevich, Zhigang Gui, Lydie Louis, Raymond Walter, Ivo Souza and L. Bellaiche, Physical Review B 87, 195111 (2013).

We proposed the existence, via analytical derivations, novel phenomenologies, and first-principles-based simulations, of a new class of materials that are not only spontaneously optically active, but also for which the sense of rotation can be switched by an electric field applied to them-- via an induced transition between the dextrorotatory and laevorotatory forms. Such systems possess electric vortices that are coupled to a spontaneous electrical polarization. Furthermore, our atomistic simulations provide a deep microscopic insight into, and understanding of, this class of naturally optically active materials.

- 30) ``Full field electron spectromicroscopy applied to ferroelectric materials," N. Barrett, J. E. Rault, J. L. Wang, C. Mathieu, A. Locatelli, T. O. Mentes, M. A. Nino, S. Fusil, M. Bibes, A. Barthelemy, D. Sando, W. Ren, S. Prosandeev, L. Bellaiche, B. Vilquin, A. Petraru, I. P. Krug, and C. M. Schneider, Review Article, Journal of Applied Physics 113, 187217 (2013).

In collaboration with Thales (France), a review article (about the application of full field electron spectromicroscopy to ferroelectric materials) was written.

- 31) ``Spin switching and magnetization reversal in single-crystal NdFeO3," Shujuan Yuan, Wei Ren, Fang Hong, Yabin Wang, Jincang Zhang, L. Bellaiche, Shixun Cao, and G. Cao, Physical Review B 87, 184405 (2013).

We reported an experimental and computational study of single-crystal $NdFeO_3$, which features two inequivalent magnetic sublattices, namely, Fe- and Nd-sublattices that are coupled in an antiparallel fashion. The work reveals that a strong interaction between 3d- and 4f-electrons of the two sublattices along with a spin-lattice coupling drives an extremely interesting magnetic state that is highly sensitive to the orientation and history of weak magnetic field. The following phenomena are particularly remarkable: **(1)** sharply contrasting magnetization, M(T), along the ***a***-and ***c***-axes; **(2)** a first-order spin switching along the ***a***-axis below 29 K when the system is *zero-field-cooled*; **(3)** a progressive magnetization reversal when the system is *field-cooled*. The intriguing magnetic behavior is captured in our first-principles density functional theory calculations.

- 32) ``Universal collaborative couplings between oxygen-octahedral rotations and anti-ferroelectric distortions in perovskites," L. Bellaiche and Jorge Iniguez, Physical Review B 88, 014104 (2013).

We identifed two elemental interatomic couplings that control the collaborative (as opposed to competing) interaction between the O6 octahedral rotations (usually called anti-ferrodistortive or AFD modes) and the anti-ferroelectric (AFE) displacement patterns of the A-site cations in oxides with the ABO3 perovskite structure. Straightforward analytical derivations allowed us to reproduce, and explain the origin of, various long-range AFE orders that have been previously found in different phases of several perovskite compounds, all possessing simple or even complex long-range AFD patterns. Our analysis also led to the prediction of original peculiar combinations of AFD and AFE orders that are awaiting to be observed.

- 33) ``Predicted Coupling of the Electromagnetic Angular Momentum Density with Magnetic Moments," Aldo Raeliarijaona, Surendra Singh, Huaxiang Fu, and L. Bellaiche, Physical Review Letters 110, 137205 (2013).

Analytical derivations were developed to demonstrate that (i) the angular moment density associated with an electromagnetic field can directly couple with magnetic moments to produce a physical energy; (ii) this direct coupling explains known, subtle phenomena, including some recently predicted in magnetoelectric materials; and (iii) this coupling also results in novel effects, such as the occurrence of a magnetic anisotropy that is driven by antiferroelectricity.

- 34) ``Field-induced Percolation of Polar Nanoregions in Relaxor Ferroelectrics," S. Prosandeev, Dawei Wang, A. R. Akbarzadeh, B. Dkhil and L. Bellaiche, Physical Review Letters 110, 207601 (2013).

In collaboration with ECP (France), A first-principles-based effective Hamiltonian was used to investigate low-temperature properties of Ba(Zr,Ti)O3 relaxor ferroelectrics under an increasing dc electric field. This complex system progressively develops an electric polarization that is highly non-linear with the dc field. This development leads to a maximum of the static dielectric response at a critical field, Eth, and involves four different field regimes. Each of these regimes is associated with its own characteristic behavior of polar nanoregions (PNRs), such as shrinking, flipping and elongation of dipoles or change in morphology. Strikingly, clusters propagating inside the whole sample, with dipoles being parallel to the field direction, begin to form at precisely the Eth critical field. Such result, and further analysis we performed, therefore reveal that field-induced percolation of PNRs is the driving mechanism for the transition from the relaxor to ferroelectric state.

-35) ``Crafting the magnonic and spintronic response of BiFeO3 films by epitaxial strain," D. Sando, A. Agbelele, D. Rahmedov, J. Liu, P. Rovillain, C. Toulouse, I.C. Infante, A.P. Pyatakov,S. Fusil, E. Jacquet, C. Carretero, C. Deranlot, S. Lisenkov, D. Wang, J.-M. Le Breton, M. Cazayous, A. Sacuto, J. Juraszek, A.K. Zvezdin, L. Bellaiche, B. Dkhil, A. Barthelemy and M. Bibes, Nature Materials, 12, 641 (2013).

In collaboration with different European experimental and theoretical groups (led by Drs Cazayous, Juraszek, Zvezdin, Dkhil, Barthelemy and Bibes), we showed that the bulk-like cycloidal spin modulation that exists at low compressive strain in BiFeO3 films is driven towards pseudo-collinear antiferromagnetism at high strain, both tensile and compressive. For moderate tensile strain, we also predict and observe indications of a new cycloid. Accordingly, we find that the magnonic response is entirely modified, low energy magnon modes being suppressed as strain increases. Finally, we revealed that strain progressively drives the average spin angle from in-plane to out-of-plane, a property we used to control the exchange bias and giantmagnetoresistive response of spin valves

- 36) ``Elastic excitations in BaTiO3 single crystals and ceramics: mobile domain boundaries and Polar nanoregions observed by resonant ultrasonic spectroscopy," Ekhard K.H. Salje, Michael A. Carpenter, Guillaume Nataf, Gunnar Picht, Kyle Webber, Jeevaka Weerasinghe, S. Lisenkov, and L. Bellaiche, Physical Review B 87, 014106 (2013).

In collaboration with the group led by Dr. Salje (Cambridge, UK), dynamical properties of elastic domain walls in $BaTiO_3$ were investigated using Resonance Ultrasonic Spectroscopy (RUS). The sequence of phase transitions is characterized by minima in the temperature dependence of RUS resonance frequencies and changes of Q factors (resonance damping). Damping is related to the friction of mobile twin boundaries ($90^o$ degree ferroelectric walls) and distorted polar nano regions (PNRs) in the cubic phase. Damping is largest in the tetragonal phase of ceramic materials but very low in single crystals. Damping is also small in the low temperatures phases of a ceramic sample and slightly increases with decreasing temperature in the single crystal. The phase angle between the real and imaginary part of the dynamic response function changes drastically in the cubic and tetragonal phase and remains constant in the orthorhombic phase. Other phases show a moderate dependence of the phase angle on temperature

showing systematic changes of twin microstructures. Mobile twin boundaries (or sections of twin boundaries such as kinks inside twin walls) contribute strongly to the energy dissipation of the forced oscillation while the reduction in effective modulus due to relaxing twin domains is weak. Single crystals and ceramics show strong precursor softening in the cubic phase related to polar nano regions. The effective modulus decreases when the transition point of the cubic-tetragonal transformation is approached from above. The precursor softening follows very similar temperature dependences as recent results from Brillouin scattering. Between the Burns temperature (≈586K) and $T_c$ at 405K, we found a good fit of the squared RUS frequency to a Vogel-Fulcher process with an activation energy of ca. 0.2 eV. Finally, some first-principles-based effective Hamiltonian computations were carried out in $BaTiO_3$ monodomains to explain some of these observations in terms of the dynamics of the soft mode and central mode.

- 37) ``Understanding and Revisiting Properties of EuTiO3 Bulk Material and Films from First Principles," Yurong Yang, Wei Ren, Dawei Wang and L. Bellaiche, Physical Review Letters 109, 267602 (2012).

In collaboration with Dr. Dawei Wang (Xi'an, China), *ab-initio* computations were performed to investigate properties of bulks and epitaxial films made of EuTiO3 (ETO). A whole family of nanoscale twinned phases, that present complex oxygen octahedra tilting (OOT) and unusual antiferroelectricity, were found to be degenerate in energy with simpler phases (all possessing typical antiphase OOT) in ETO bulks. Such degeneracy provides a successful explanation of recently observed anomalous phenomena, such as the change of diffraction spectra over a long time period or the dramatic difference between short-range and average crystallographic structures. The calculations also led to revisiting the phase diagram of ETO films, since many previously overlooked equilibrium phases (all exhibiting either complex or simple OOT) are found, depending on the sign and magnitude of the epitaxial strain.

- 38) ``Effect of the central mode on the dielectric tunability of ferroelectrics near room temperature: A first-principle-based study," Jeevaka Weerasinghe, Dawei Wang and L. Bellaiche, Journal of Physics Condensed Matter, Fast Track Communication 25, 252202 (2013) [also selected for inclusion in IOP Select].

First-principles-based effective Hamiltonian molecular dynamics simulations were performed to investigate GHz-THz dynamical properties of bulk and epitaxially strained film made of SrTiO3 near room temperature. Our simulations confirmed the huge dielectric tunability recently observed in films. Moreover, universal phenomenological laws, with bulk-like parameters, were found to describe reasonably well the dielectric tunability-versus-dc electric field curves in both systems at low and high electric fields, except for the sole case of the STO film in the low-field regime. Such deviation originates from the presence of a central mode in this low-dimensional system. A revised equation, arising from an original analysis of the simulations, was proposed for modeling this latter situation.

- 39) ``Epitaxial short-period PbTiO3/BiFeO3 superlattices studied by first-principles calculations," Yurong Yang, Massimiliano Stengel, Wei Ren, X. H. Yan and L. Bellaiche, Physical Review B 86, 144114 (2012).

In collaboration with Dr. Massimiliano Stengel (ICMAB, Spain), first-principles calculations were used to predict properties of (001) epitaxial, short-period PbTiO3/BiFeO3 superlattices (SL) as a function of the in-plane lattice constant. These heterostructures exhibit original phenomena, such as three strain-driven isostructural phase transitions (two being of first-order and one being of second-order); five equilibrium phases that all differ in symmetry from those found in the pure PbTiO3 (PTO) and BiFeO3 (BFO) films; and the presence of significant oxygen octahedra tiltings in the PTO layers of the superlattice within a broad range of epitaxial strain values. All these unusual features can be understood

from (i) the knowledge of the corresponding phases in the pure PTO and BFO films; (ii) the requirement that the out-of-plane component of the ``formal'' polarization (including ferroelectric and compositional dipoles) be homogeneous inside the superlattice; and (iii) the competition between polarization and oxygen octahedral tilting, in presence of electrostatic couplings and interfacial proximity effects.

- 40) ``Emergence of central mode in the paraelectric phase of ferroelectric perovskites,'' J. Weerasinghe, L. Bellaiche, T. Ostapchuk, P. Kuzel, C. Kadlec, S. Lisenkov, I. Ponomareva, and J. Hlinka, MRS communications 3, 41 (2013).

In collaboration with the experimental group of Dr. Hlinka (Prague, Czech Republic), THz-range dielectric spectroscopy and first-principle-based effective-Hamiltonian molecular dynamics simulations were employed to elucidate the dielectric response in the paraelectric phase of (Ba,Sr)TiO3 solid solutions. Analysis of the resulting dielectric spectra suggests the existence of a crossover between two different regimes: a higher-temperature regime governed by the soft mode only versus a lower-temperature regime exhibiting a coupled soft mode/central mode dynamics. Interestingly, a single phenomenological coupling model can be used to adjust the THz dielectric response in the entire range of the paraelectric phase (i.e., even at high temperature). We conclude that the central peak is associated with thermally activated processes, and that it cannot be discerned anymore in the dielectric spectra when the rate of these thermally activated processes exceeds certain characteristic frequency of the system.

- 41) ``Study of strain effect on in-plane polarization in epitaxial BiFeO3 thin films using planar electrodes,'' Zuhuang Chen, Xi Zou, Wei Ren, Lu You, Chuanwei Huang, Yurong Yang, Ping Yang, Junling Wang, Thirumany Sritharan, L. Bellaiche, and Lang Chen, Physical Review B 86, 235125 (2012).

In collaboration with the experimental group of Dr. Lang Chen (Singapore), a *planar electrode* device was used to directly measure the in-plane polarization-electric field (P-E) hysteresis loops in ultrathin strained films. We used BiFeO3 (BFO) as a model system and measured P-E loops not only in the rhombohedral-like (R-like) BFO thin films but also in largely strained BFO films exhibiting the pure tetragonal-like (T-like) phase. The exact magnitude and direction of the spontaneous polarization vector of the T-like phase was also deduced. It was shown that the polarization vector in the R-like phase of BiFeO3 is constrained to lie within the (1-10) plane and rotates from the [111] towards [001] pseudo-cubic direction when the compressive strain is increased from zero. At high misfit strains such as -4.4%, the pure T-like phase is obtained and its polarization vector is constrained to lie in the (010) plane with a significantly large in-plane component. First-principle calculations were carried out in parallel, and provided a good agreement with the experimental results.

- 42) ``Revisiting properties of ferroelectric and multiferroic thin films under tensile strain from first principles,'' Yurong Yang, Wei Ren, Massimiliano Stengel, X. H. Yan and L. Bellaiche, Physical Review Letters 109, 057602 (2012).

In collaboration with ICMAB (Barcelona, Spain), first-principles calculations were performed to revisit properties of (001) epitaxial BiFeO3 (BFO) and PbTiO3 thin films under tensile strain. While these two films possess different ground states when experiencing no misfit strain, they both exhibit the same, previously unknown phase for tensile strains above 5% at T=0K. This novel state is of orthorhombic Pmc2_1 symmetry, and is macroscopically characterized by a large in-plane polarization coexisting with oxygen octahedra tilting in-phase about the out-of-plane direction. On a microscopic point of view, this Pmc2_1 state exhibits short atomic bonds and zig-zag cation displacement patterns, unlike conventional ferroelectric phases and typical domains. Such unusual inhomogeneous patterns originate from the coexistence of polar and antiferroelectric distortions having the same magnitude, and lead BFO films to

be the first known material for which orbital ordering coexists with a large polarization. Furthermore, this Pmc2_1 state is also found in other perovskite films under tensile strain, which emphasizes its generality.

- 43) ``Novel complex phenomena in ferroelectric nanocomposites," Lydie Louis, Igor Kornev, Gregory Geneste, Brahim Dkhil and L. Bellaiche, Journal of Physics Condensed Matter, Fast Track Communication 24, 402201(2012) [also selected for inclusion in IOP Select].

In collaboration with Ecole Centrale of Paris (ECP), a first-principles-based effective Hamiltonian was used to investigate finite-temperature properties of ferroelectric nanocomposites made of periodic arrays of ferroelectric nanowires embedded in a matrix formed by another ferroelectric material. Novel transitions and features related to flux-closure configurations were found. Examples include (i) a vortex core transition, that is characterized by the change of the vortices core from being axisymmetric to exhibiting a ``broken-symmetry"; (ii) translational mode of the vortex cores; (iii) striking zigzag dipolar chains along the vortex core axis; and (iv) phase-locking of ferroelectric vortices accompanied by ferroelectric antivortices. These complex phenomena were all found to coexist with a spontaneous electrical polarization aligned along the normal of the plane containing the vortices.

- 44) ``Atomistic Molecular Dynamic Simulations of Multiferroics," Dawei Wang, Jeevaka Weerasinghe and L. Bellaiche, Physical Review Letters 109, 067203 (2012).

In collaboration with Dr. Dawei Wang (Xian, China), A first-principles-based approach was developed to simulate dynamical properties, including complex permittivity and permeability in the GHz-THz range, of multiferroics at finite temperatures. It includes both structural degrees of freedom and magnetic moments as dynamic variables in Newtonian and Landau-Lifshitz-Gilbert (LLG) equations within molecular dynamics, respectively, with the couplings between these variables being incorporated. The use of a damping coefficient and of the fluctuation field in the LLG equations is required to obtain equilibrated magnetic properties at any temperature. No electromagnon is found in the spin-canted structure of of BiFeO3. On the other hand, two magnons with very different frequencies are predicted via the use of this method. The smallest-in-frequency magnon corresponds to oscillations of the weak ferromagnetic vector in the basal plane being perpendicular to the polarization, while the second magnon corresponds to magnetic dipoles going in-and-out of this basal plane. The large value of the frequency of this second magnon is caused by static couplings between magnetic dipoles with electric dipoles and oxygen octahedra tiltings.

- 45) ``Giant direct magnetoelectric effect in strained multiferroic heterostructures," P.-E. Janolin, N. A. Pertsev, D. Sichuga and L. Bellaiche, Physical Review B, Rapid Communications, 85, 140401 (2012).

In collaboration with Dr. Janolin (Ecole Centrale of Paris, France), the direct magnetoelectric (ME) effect mediated by lattice strains induced in a ferroelectric film by a ferromagnetic substrate was evaluated using first-principles-based calculations. To that end, the strain sensitivity of ferroelectric polarization and the film permittivity were calculated as a function of the in-plane biaxial strain for Pb(Zr0.52Ti0.48)O3 films under various depolarizing fields. It was found that the ME voltage coefficient varies nonmonotonically with this strain and may reach giant values exceeding 100 V cm−1 Oe−1 over a strain range that can be controlled through the electrical boundary conditions.

- 46) ``Finite-temperature flexoelectricity in ferroelectric thin films from first principles," I. Ponomareva, A.K. Tagantsev and L. Bellaiche, Physical Review B 85, 104101 (2012).

A first-principles-based effective Hamiltonian technique is developed to study flexoelectricity in (Ba0.5Sr0.5)TiO3 thin films of different thicknesses in their paraelectric phase. The magnitude but also sign of individual components of the flexoelectric tensor are reported, which provides answers to existing

controversies. The use of this numerical tool also allows to show that flexoelectric coefficients depend strongly on the film's thickness and temperature. Such dependence is explained using the relationship between the flexoelectric coefficients and the dielectric susceptibility.

- 47) ``A simple law governing coupled magnetic orders in perovskites," L. Bellaiche, Zhigang Gui and Igor A. Kornev, Journal of Physics Condensed Matter, Fast Track Communication 24, 312201(2012)

An energetic expression containing four different macroscopic terms is proposed to explain and understand coupled magnetic orders (and the directions of the simultaneously-occurring ferromagnetic and/or antiferromagnetic vectors) in terms of anti-phase and/or in-phase oxygen octahedra tiltings, in magnetic and multiferroic perovksites. This expression is derived from a suggested simple microscopic formula, and takes its root in the Dzyaloshinsky-Moriya interaction. Comparison with data available in the literature and with first-principles calculations we further conduct here confirm the validity of such simple and general law for any tested structural paraelectric and even ferroelectric phase, and for any chosen direction of any selected primary magnetic vector.

- 48) ``Strain dependence of polarization and piezoelectric response in epitaxial BiFeO3 thin films," C. Daumont, W. Ren, I.C. Infante, S. Lisenkov, J. Allibe, C. Carretero, S. Fusil, E. Jacquet, T. Bouvet, F. Bouamrane, S. Prosandeev, G. Geneste, B. Dkhil, L. Bellaiche, A. Barthelemy and M. Bibes, Journal of Physics Condensed Matter, Fast Track Communication 24, 162202 (2012).

In collaboration with the groups of Drs. Agnes Barthelemy (Thales, France) and Brahim Dkhil (Ecole Centrale of Partis, France), studies on epitaxial BiFeO3 films were performed. Epitaxial strain has recently emerged as a powerful means to engineer the properties of ferroelectric thin films, for instance to enhance the ferroelectric Curie temperature (TC) in BaTiO3. However, in multiferroic BiFeO3 thin films an unanticipated strain-driven decrease of TC was reported and ascribed to the peculiar competition between polar and antiferrodistortive instabilities. Here, we reported a systematic characterization of the room-temperature ferroelectric and piezoelectric properties for strain levels ranging between -2.5% and +1%. We found that polarization and the piezoelectric coefficient increase by about 20% and 250%, respectively, in this strain range. These trends were well reproduced by first-principles-based techniques.

- 49) ``Finite-Temperature Properties of Ba(Zr,Ti)O3 Relaxors From First Principles" A. R. Akbarzadeh, S. Prosandeev, Eric J. Walter, A. Al-Barakaty and L. Bellaiche, Physical Review Letters 108, 257601 (2012).

A first-principles-based technique is developed to investigate properties of Ba(Zr,Ti)O3 relaxor ferroelectrics as a function of temperature. The use of this scheme provides answers to important, unresolved and/or controversial questions, such as: what do the different critical temperatures usually found in relaxors correspond to? Do polar nanoregions really exist in relaxors? If yes, do they only form inside chemically-ordered regions? Is it necessary that antiferroelectricity develops in order for the relaxor behavior to occur? Are random fields and random strains really the mechanisms responsible for relaxor behavior? If not, what are these mechanisms? These ab-initio-based calculations also lead to a deep microscopic insight into relaxors.

- 50) ``Domain evolution in epitaxial (001) Pb(Zr,Ti)O3 ultrathin films under an electric field applied along the [111] direction," D. Sichuga and L. Bellaiche, Physical Review B 85, 214111 (2012).

The multidomain structure evolution in $Pb(Zr,Ti)O_3$ ultrathin films subject to an electric field applied along the pseudo-cubic [111] direction is investigated via the use of an effective Hamiltonian. Varying the magnitude of this electric field (that possesses both in-plane and out-of-plane components) leads to the formation of five different states, whose microstructures and

properties are revealed here. Such variation also makes the polarization changing not only in magnitude but also in direction. The field-induced correlation between the polar distortions and the oxygen octahedral tilting is also discussed as an important factor affecting the polarization.

- 51) ``Ab initio study of the factors affecting the ground state of rare-earth nickelates," Sergey Prosandeev, L. Bellaiche, and Jorge Iniguez, Physical Review B 85, 214431 (2012).

In collaboration with Dr Jorge Iniguez (Barcelona, Spain), we have used first-principles methods to investigate the factors that control the ground state of rare-earth nickelates, studying in detail the case of NdNiO3. Our results suggest a complex phase diagram, with the bulk compounds standing on the edge of various instabilities that can be triggered by both electronic (e.g., changes in the Coulomb repulsion) and structural (e.g., epitaxial mismatch) means. In particular, we reveal that several phase transitions can be induced by epitaxial strain in thin films, and predict that a continuous transformation between insulating spin-density-wave- and metallic spin-spiral-like solutions occurs at moderate values of the in-plane mismatch. Our results provide a coherent picture of structural and electronic effects in nickelates, and have implications for current experimental and theoretical work on these compounds.

- 52) ``New Scanning Tunneling Microscopy Technique Enables Systematic Study of the Unique Electronic Transition from Graphite to Graphene," P. Xu, Yurong Yang, S.D. Barber, J.K. Schoelz, D. Qi, M.L. Ackerman, L. Bellaiche, P.M. Thibado, Carbon 50, 4633 (2012).

A series of measurements using a novel technique called electrostatic-manipulation scanning tunneling microscopy were performed on a highly-oriented pyrolytic graphite (HOPG) surface. The electrostatic interaction between the STM tip and the sample can be tuned to produce both reversible and irreversible large-scale vertical movement of the HOPG surface. Under this influence, atomic-resolution STM images reveal that a continuous electronic reconstruction transition from a triangular symmetry, where only alternate atoms are imaged, to a honeycomb structure can be systematically controlled. First-principles calculations reveal that this transition can be related to vertical displacements of the top layer of graphite relative to the bulk. Detailed analysis of the band structure predicts that a transition from parabolic to linear bands occurs after a 0.09 nm displacement of the top layer.

- 53) ``A pathway between Bernal and rhombohedral stacked graphene layers with scanning tunneling microscopy," P. Xu, Yurong Yang, D. Qi, S. D. Barber, M. L. Ackerman, J. K. Schoelz, T. B. Bothwell, Salvador Barraza-Lopez, L. Bellaiche, and P. M. Thibado, Applied Physics Letters 100, 201601 (2012).

Horizontal shifts in the top layer of highly oriented pyrolytic graphite, induced by a scanning tunneling microscope (STM) tip, are presented. Excellent agreement is found between STM images and those simulated using density functional theory. First-principle calculations identify that the low-energy barrier direction of the top layer displacement is toward a structure where none of the carbon pz orbitals overlap, while the high-energy barrier direction is toward AA stacking. Each directional shift yields a real-space surface charge density similar to graphene; however, the low-energy barrier direction requires only one bond length to convert ABA (Bernal) to ABC (rhombohedral).

- 54) ``Magnetic cycloid of BiFeO3 from atomistic simulations," D. Rahmedov, Dawei Wang, Jorge Iniguez and L. Bellaiche, Physical Review Letters 109, 037207 (2012).

An effective Hamiltonian is developed to investigate the magnetic cycloid of the BiFeO3 (BFO) multiferroic. This approach reproduces many complex features of this cycloid, such as its plane of rotation containing the polarization and the newly discovered spin density waves resulting from the canting of magnetic dipoles out of this cycloidal plane. It also suggests that the energetic origin of the cycloid can be thought of in terms of the converse spin-current model, and reveals the mechanisms

responsible for the spin density waves. Finally, this atomistic scheme resolves an ongoing controversy about the cycloid anharmonicity, and revisits a recent misconception about the relationship between out-of-plane spin-density waves and the weak magnetization associated with the spin-canted structure of BFO.

- 55) ``Atomic control of strain in freestanding graphene,'' P. Xu, Y. Yang, S.D. Barber, M.L. Ackerman, J.K. Schoelz, D. Qi, Igor A. Kornev, L. Dong, L. Bellaiche, Salvador Barraza-Lopez and P.M. Thibado, Physical Review B, Rapid Communications, 85, 121406 (2012).

In this study, we describe an experimental approach based on constant-current scanning tunneling spectroscopy to controllably and reversibly pull freestanding graphene membranes up to 35 nm from their equilibrium height. In addition, we present scanning tunneling microscopy (STM) images of freestanding graphene membranes with atomic resolution. Atomic-scale corrugation amplitudes 20 times larger than the STM electronic corrugation for graphene on a substrate were observed. The freestanding graphene membrane responds to a local attractive force created at the STM tip as a highly conductive yet flexible grounding plane with an elastic restoring force. We indicate possible applications of our method in the controlled creation of pseudomagnetic fields by strain on single-layer graphene.

**Students degrees:**

- Zhigang Gui, Ph.D. of Physics, Spring 2015, ``Static and Dynamical Properties of Ferroelectrics and Related Materials in Bulk and Nanostructure Forms.''

**Honors:**

- Dr Laurent Bellaiche was named the 2015 ZiQiang Professorship from Shanghai University (Shanghai, China).