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Final Report: Ab initio design of noncentrosymmetric metals: crystal engineering in oxide heterostructures. f. Research Area 6: Physics

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W911NF-15-1-0017

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
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6. AUTHORS

5d. PROJECT NUMBER

5e. TASK NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
Northwestern University Evanston Campus
1801 Maple Avenue

Evanston, IL 60201 -3149

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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

15. SUBJECT TERMS

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a. REPORT	b. ABSTRACT	c. THIS PAGE			James Rondinelli
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RPPR Final Report
as of 08-Aug-2022

Agency Code: 21XD

Proposal Number: 66645ELPCS **Agreement Number: W911NF-15-1-0017**
INVESTIGATOR(S):

Name: James M Rondinelli
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Principal: Y

Organization: **Northwestern University Evanston Campus**
Address: 1801 Maple Avenue, Evanston, IL 602013149
Country: USA
DUNS Number: 160079455 EIN: 362167817
Report Date: 07-Apr-2022 Date Received: 05-Aug-2022
Final Report for Period Beginning 08-Dec-2014 and Ending 07-Jan-2022
Title: Ab initio design of noncentrosymmetric metals: crystal engineering in oxide heterostructures. f. Research Area 6: Physics
Begin Performance Period: 08-Dec-2014 **End Performance Period:** 07-Jan-2022
Report Term: 0-Other
Submitted By: James Rondinelli Email: jrondinelli@northwestern.edu
Phone: (847) 491-3198

STEM Degrees: **STEM Participants:**

Major Goals: At electrostatic equilibrium the net electric field inside a conductor is zero due to charge screening. Thus, free carriers within a metal should prohibit the development of acentricity. For this reason, it is unusual to find metals with a noncentrosymmetric structure (or a subclass of them dubbed polar metals). They are extremely scarce in oxides compounds. Lack of reliable crystal-chemistry guidelines and the limited understanding of the microscopic origin of inversion symmetry-lifting displacements in metals, with nontrivial interactions such as correlation and spin-orbit coupling, presents a serious challenge to their discovery and dynamical control. The main goal of this project is to formulate design strategies for the realization of noncentrosymmetric metals in transition metal oxides and routes to dynamically tune their equilibrium states. To this purpose, it is crucial to understand the driving mechanism behind the ferroelectric-like instability in polar metals. Additional project objectives include to (a) predict new metallic transition metal oxides without inversion symmetry, (b) design new multiferroics materials using polar metals, (c) identify potential applications, and (d) realize and verify the computational models and predictions through experimental collaboration.

Accomplishments: See attached PDF

RPPR Final Report
as of 08-Aug-2022

Training Opportunities: The project supported researchers with multiple levels of expertise, including graduate student (Daniel Hickox-Young) and Research Assistant Professor (Danilo Puggioni). These researchers have become proficient and fluent in performing density functional theory calculations. They have learned how to use complimentary post-processing tools to understand lattice dynamical simulations and aid in the application of group theoretical studies to explain the behavior of noncentrosymmetric metals. The scientific advances made Hickox-Young has also led to his successful completion of the PhD during this reporting period. He is now a visiting professor position at Roanoke College, Salem, VA in September 2021.

To provide professional development opportunities, all researchers supported by this award helped to prepare supplemental computational supercomputing hour, from which the results described in Section 2 (Accomplished under Goals) were in part obtained. These efforts include the submission and preparation of compute proposals to the Center for Nanoscale Materials (CNM) at Argonne National Laboratory and the Extreme Science and Engineering Discovery Environment (XSEDE), which were subsequently awarded. These computational hours complement those made available from the DOD through the HPCMP, and provide useful professional training in proposal writing.

All researchers also presented their work at the American Physical Society (APS) March Meetings in 2022 and at other scientific conferences.

Results Dissemination: Results have been disseminated in the form of peer-reviewed publications as well as oral presentations. Numerous articles have been published, with additional articles under peer-review.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: PD/PI
Participant: James Rondinelli
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Staff Scientist (doctoral level)
Participant: Danilo Puggioni
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

ARTICLES:

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.115.087202
Volume: 1.15E+002 Issue: 8.0E+000 First Page #: 87202
Date Submitted: Date Published:
Publication Location:
Article Title: Design of a Mott Multiferroic from a Nonmagnetic Polar Metal
Authors:
Keywords: Multiferroic, metal-insulator transition
Abstract: We examine the electronic properties of the newly discovered “ferroelectric metal” LiOsO3 combining density-functional and dynamical mean-field theories. We show that the material is close to a Mott transition and that electronic correlations can be tuned to engineer a Mott multiferroic state in the 1/1 superlattice of LiOsO3 and LiNbO3. We use electronic structure calculations to predict that the (LiOsO3)1/(LiNbO3)1 superlattice exhibits strong coupling between magnetic and ferroelectric degrees of freedom with a ferroelectric polarization of 41.2??? C?cm?2, Curie temperature of 927 K, and Néel temperature of 379 K. Our results support a route towards high-temperature multiferroics, i.e., driving nonmagnetic polar metals into correlated insulating magnetic states.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physics: Condensed Matter
Publication Identifier Type: DOI Publication Identifier: 10.1088/0953-8984/27/28/283202
Volume: 2.7E+001 Issue: 2.8E+001 First Page #: 283202
Date Submitted: Date Published:
Publication Location:
Article Title: Anharmonic lattice interactions in improper ferroelectrics for multiferroic design
Authors:
Keywords: ferroelectrics, improper phase transitions, anharmonic interactions, multiferroics,pseudo-Jahn-Teller
Abstract: The design and discovery of new multiferroics, or materials that display both ferroelectricity and long-range magnetic order, is of fundamental importance for new electronic technologies based on low-power consumption. Far too often, however, the mechanisms causing these properties to arise are incompatible or occur at ordering temperatures below room temperature. One design strategy which has gained considerable interest is to begin with a magnetic material, and find novel ways to induce a spontaneous electric polarization within the structure. To this end, anharmonic interactions coupling multiple lattice modes have been used to lift inversion symmetry in magnetic dielectrics. Here we provide an overview of the microscopic mechanisms by which various types of cooperative atomic displacements result in ferroelectricity through anharmonic multi-mode coupling, as well as the types of materials most conducive to these lattice instabilities. The review includes a description of the origin
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: 10.1038/ncomms7735
Volume: 6.0E+000 Issue: 0 First Page #: 6735
Date Submitted: Date Published:
Publication Location:
Article Title: Polarization screening-induced magnetic phase gradients at complex oxide interfaces
Authors:
Keywords: Magnetic transitions, multiferroics, Jahn-Teller transitions
Abstract: The design and discovery of new multiferroics, or materials that display both ferroelectricity and long-range magnetic order, is of fundamental importance for new electronic technologies based on low-power consumption. Far too often, however, the mechanisms causing these properties to arise are incompatible or occur at ordering temperatures below room temperature. One design strategy which has gained considerable interest is to begin with a magnetic material, and find novel ways to induce a spontaneous electric polarization within the structure. To this end, anharmonic interactions coupling multiple lattice modes have been used to lift inversion symmetry in magnetic dielectrics. Here we provide an overview of the microscopic mechanisms by which various types of cooperative atomic displacements result in ferroelectricity through anharmonic multi-mode coupling, as well as the types of materials most conducive to these lattice instabilities. The review includes a description of the origin
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature
Publication Identifier Type: DOI Publication Identifier: 10.1038/nature17628
Volume: 533 Issue: 7601 First Page #: 68
Date Submitted: 8/19/16 12:00AM Date Published: 4/1/16 5:00AM
Publication Location:
Article Title: Polar metals by geometric design
Authors: T. H. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. J. Ryan, Y. Choi, J.-W. Kim, J. R. Patz
Keywords: polar metals, nickelates
Abstract: Here we describe the quantum mechanical design and experimental realization of room-temperature polar metals in thin film ANiO3 perovskite nickelates using a strategy based on atomic scale control of inversion-preserving (centric) displacements. We predict with ab initio calculations that cooperative polar A cation displacements are geometrically stabilized with a nonequilibrium amplitude and tilt pattern of the corner-connected NiO6 octahedra—the structural signatures of perovskites—owing to geometric constraints imposed by the underlying substrate. Heteroepitaxial thin-films grown on LaAlO3 (111) substrates fulfil the design principles. We achieve both a conducting polar monoclinic oxide that is inaccessible in compositionally identical films grown on (001) substrates, and observe a hidden, previously unreported6–10, non-equilibrium structure in thin-film geometries. We expect that the geometric stabilization approach will provide novel avenues for realizing new materials.
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Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.93.115147
Volume: 93 Issue: 11 First Page #:
Date Submitted: 8/19/16 12:00AM Date Published: 3/1/16 6:00AM
Publication Location:
Article Title: Interplay between electron correlations and polar displacements in metallic
Authors: Gianluca Giovannetti, Danilo Puggioni, James M. Rondinelli, Massimo Capone
Keywords: polar metals, molybdates, density functional theory
Abstract: Using density functional theory and dynamical mean-field theory, we study the electronic properties of the proposed candidate polar metal SrEuMo2O6. Its electronic structure shares similarities with centrosymmetric SrMoO3 and EuMoO3, from which it may be considered an ordered derivative, but polar displacements of the divalent cations and oxide anions lift inversion symmetry mediated by an anharmonic lattice interaction in the metallic state. We find that Hund's coupling promotes the effects of electronic correlations owing to the Mo4+ d2 electronic configuration, producing a correlated metallic phase far from the Mott state. The contraindication between metallicity and polar distortions is thereby alleviated in part through the renormalized quasiparticles, which are unable to fully screen the ordered local dipoles.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Applied Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4942651
Volume: 119 Issue: 8 First Page #: 086102
Date Submitted: 8/19/16 12:00AM Date Published: 2/1/16 6:00AM
Publication Location:
Article Title: Comment on "High-pressure synthesis of orthorhombic SrIrO3 perovskite and its positive magnetoresistance" [J. Appl. Phys. 103, 103706 (2008)]
Authors: D. Puggioni, J. M. Rondinelli
Keywords: iridates; octahedral rotations
Abstract: In their article, Zhao et al. report the synthesis of SrIrO3 at high temperature and high pressure [J. Appl. Phys. 103, 103706 (2008)]. Under these conditions, the crystal structure of SrIrO3 can be stabilized as an orthorhombic perovskite with space group Pnma. They refine the lattice parameters and list the Wyckoff orbits and atomic coordinates. We believe that Zhao and coworkers made an unintentional error in reporting the crystal structure, which may adversely affect the description of the electronic structure. Indeed, we show the reported structure does not define a standard perovskite with nearly rigid IrO6 octahedral tilts and rather exhibits a structural discrepancy with respect to the equilibrium structure obtained from density functional calculations.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.93.085118
Volume: 93 Issue: 8 First Page #:
Date Submitted: 8/19/16 12:00AM Date Published: 2/1/16 12:00AM
Publication Location:
Article Title: Strain-induced nonsymmorphic symmetry breaking and removal of Dirac semimetallic nodal line in an orthoperovskite iridate
Authors: Jian Liu, D. Kriegner, L. Horak, D. Puggioni, C. Rayan Serrao, R. Chen, D. Yi, C. Frontera, V. Holy, A. V
Keywords: iridates; Dirac semimetal; density functional theory
Abstract: By using a combination of heteroepitaxial growth, structure refinement based on synchrotron x-ray diffraction, and first-principles calculations, we show that the symmetry-protected Dirac line nodes in the topological semimetallic perovskite SrIrO3 can be lifted simply by applying epitaxial constraints. In particular, the Dirac gap opens without breaking the Pbnm mirror symmetry. In virtue of a symmetry-breaking analysis, we demonstrate that the original symmetry protection is related to the n-glide operation, which can be selectively broken by different heteroepitaxial structures. This symmetry protection renders the nodal line a nonsymmorphic Dirac semimetallic state. The results highlight the vital role of crystal symmetry in spin-orbit-coupled correlated oxides and provide a foundation for experimental realization of topological insulators in iridate-based heterostructures.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Mater. Chem. C
Publication Identifier Type: DOI Publication Identifier: 10.1039/C6TC90107G
Volume: 4 Issue: 24 First Page #: 5864
Date Submitted: 8/19/16 12:00AM Date Published:
Publication Location:
Article Title: Correction: Design of noncentrosymmetric perovskites from centric and acentric basic building units
Authors: Joshua Young, Parth Lalkiya, James M. Rondinelli
Keywords: noncentrosymmetric; oxides
Abstract: This publication is a correction to another published article. It updates a typographical error in a Figure.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: J. Mater. Chem. C
Publication Identifier Type: DOI Publication Identifier: 10.1039/C5TC04239A
Volume: 4 Issue: 18 First Page #: 4016
Date Submitted: 8/19/16 12:00AM Date Published:
Publication Location:
Article Title: Design of noncentrosymmetric perovskites from centric and acentric basic building units
Authors: Joshua Young, Parth Lalkiya, James M. Rondinelli
Keywords: noncentrosymmetric; oxides; perovskites
Abstract: We present a detailed crystal-chemistry approach to lift inversion symmetry in inorganic crystals. Although no combinations of simple B-site ordering lifts inversion, we find that a wide variety of polar, chiral, and second harmonic active structures can be realized with A-site and mixed A- and B-site cation ordering. We then show that the ability of such combinations to lift inversion symmetry depends on whether a given rotation pattern of the octahedral units distorts the A-site environment into centric or acentric polyhedra, as well as whether the cation ordering scheme aligns them in the proper orientation. Finally, we discuss the chemical factors stabilizing the various tilt patterns and ordering schemes, such as the tolerance factor and global instability index. The guidelines described here offer new insights into this vast family of materials, and detail a useful way to think about the design of noncentrosymmetric materials from basic building units.
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Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.94.195116
Volume: 94 Issue: 19 First Page #:
Date Submitted: 8/29/17 12:00AM Date Published: 11/1/16 5:00AM
Publication Location:
Article Title: Magnetoelectric coupling in the type-I multiferroic
Authors: G. Giovannetti, D. Puggioni, P. Barone, S. Picozzi, J. M. Rondinelli, M. Capone
Keywords: Multiferroic, Magnetoelectric, Ferrate
Abstract: We investigate the electronic structure and the ferroelectric properties of the recently discovered multiferroic ScFeO3 by means of ab initio calculations. The 3d manifold of Fe in the half-filled configuration naturally favors an antiferromagnetic ordering, with a theoretical estimate of the antiferromagnetic N´eel temperature in good agreement with the experimental values. We find that the inversion symmetry breaking is driven by the off-centering of Sc atoms, which results in a large ferroelectric polarization of ?105 ?C/cm2. Surprisingly the ferroelectric polarization is sensitive to the local magnetization of the Fe atoms resulting in a large negative magnetoelectric interaction. This behavior is unexpected in type-I multiferroic materials because the magnetic and ferroelectric orders are of different origins.
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Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.97.115116
Volume: 97 Issue: 11 First Page #:
Date Submitted: 8/28/18 12:00AM Date Published: 3/1/18 12:00PM
Publication Location:
Article Title: Crystal structure stability and electronic properties of the layered nickelate
Authors: Danilo Puggioni, James M. Rondinelli
Keywords: Nickelates, metal-insulator transition, density functional theory
Abstract: We investigate the crystal structure and the electronic properties of the trilayer nickelate La4Ni3O10 by means of quantum-mechanical calculations in the framework of the density-functional theory. We find that, at low temperature, La4Ni3O10 undergoes a hitherto unreported structural phase transition and transforms to a new monoclinic P21/a phase. This phase exhibits electronic properties in agreement with recent angle-resolved photoemission spectroscopy data reported in H. Li et al., [Nat. Commun. 8, 704 (2017)] and should be considered in models focused on explaining the observed ?140 K metal-to-metal phase transition.
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Volume: 58 Issue: 12 First Page #: 2491
Date Submitted: 8/29/19 12:00AM Date Published: 8/1/18 5:00AM
Publication Location:
Article Title: Learning from Correlations Based on Local Structure: Rare-Earth Nickelates Revisited
Authors: Nicholas Wagner, Danilo Puggioni, James M. Rondinelli
Keywords: nickelates, materials informatics, correlation heat maps, metal-insulator transition
Abstract: Here we show how additional descriptive statistics and computational experiments can help researchers explicitly recognize these limitations and fill in missing gaps by constructing amplitude (a) and normalized-amplitude (n) distortion-mode–property correlation-coefficient-heat maps, aCCHMs and nCCHMs, respectively. We demonstrate this utility within the rare-earth nickelate perovskites RNiO3 (R = rare earth R \neq La), which exhibit antiferromagnetic and metal-insulator transitions with crystallographic symmetry breaking, and analyze the CCHMs obtained from experimental and first-principles derived symmetry modes. In contrast with the crystallographic trends gleaned from the reported experimental structures, the equilibrium structures obtained from density functional theory indicate that the Jahn-Teller distortion mode plays a negligible role in affecting the Neel temperature.
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Volume: 18 Issue: 5 First Page #: 3088
Date Submitted: 8/28/18 12:00AM Date Published: 4/1/18 5:00AM
Publication Location:
Article Title: Observation of Quasi-Two-Dimensional Polar Domains and Ferroelastic Switching in a Metal, Ca
Authors: Shiming Lei, Mingqiang Gu, Danilo Puggioni, Greg Stone, Jin Peng, Jianjian Ge, Yu Wang, Baoming Wa
Keywords: domain walls; Domains; ferroelastic switching; in situ TEM; polar metal
Abstract: Polar domains arise in insulating ferroelectrics when free carriers are unable to fully screen surface-bound charges. Recently discovered binary and ternary polar metals exhibit broken inversion symmetry coexisting with free electrons that might be expected to suppress the electrostatic driving force for domain formation. Contrary to this expectation, we report the first direct observation of polar domains in single crystals of the polar metal Ca3Ru2O7. By a combination of mesoscale optical second-harmonic imaging and atomic-resolution scanning transmission electron microscopy, the polar domains are found to possess a quasi-two-dimensional slab geometry with a lateral size of ?100 ?m and thickness of ?10 nm. Electronic structure calculations show that the coexistence of electronic and parity-lifting orders arise from anharmonic lattice interactions, which support 90° and 180° polar domains in a metal.
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Volume: 9 Issue: 1 First Page #:
Date Submitted: 8/28/18 12:00AM Date Published: 2/1/18 12:00AM
Publication Location:
Article Title: Tunable metal-insulator transition, Rashba effect and Weyl Fermions in a relativistic charge-ordered ferroelectric oxide
Authors: Jiangang He, Domenico Di Sante, Ronghan Li, Xing-Qiu Chen, James M. Rondinelli, Cesare Franchini
Keywords: charge order, MIT, Rashba, Dressehaus, Weyl semi metal
Abstract: Controllable metal–insulator transitions (MIT), Rashba–Dresselhaus (RD) spin splitting, and Weyl semimetals are promising schemes for realizing processing devices. Here, using first-principles calculations and symmetry analysis, we identify an electric-field tunable MIT, RD effect, and Weyl semimetal in a known, charge-ordered, and polar relativistic oxide Ag2BiO3 at room temperature. Remarkably, a centrosymmetric BiO6 octahedral-breathing distortion induces a sizable spontaneous ferroelectric polarization through Bi3+/Bi5+ charge disproportionation, which stabilizes simultaneously the insulating phase. The continuous attenuation of the Bi3+/Bi5+ disproportionation obtained by applying an external electric field reduces the band gap and RD spin splitting and drives the phase transition from a ferroelectric RD insulator to a paraelectric Dirac semimetal, through a topological Weyl semimetal intermediate state.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Materials
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevMaterials.2.114403
Volume: 2 Issue: 11 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 11/1/18 5:00AM
Publication Location:
Article Title: Design of a polar half-metallic ferromagnet with accessible and enhanced electric polarization
Authors: Danilo Puggioni, Alessandro Stroppa, James M. Rondinelli
Keywords: Half-metal; polar metal; spin filter, multiferroic
Abstract: We design a compound belonging to a class of materials designated as polar half-metallic ferromagnets, where a 100% spin polarization coexists with polar distortions that globally lift inversion symmetry. Using electronic structure calculations, we predict that the ultrashort period (LaNiO3)1/(YCrO3)1 superlattice belongs to this materials class, exhibiting an integer magnetic moment of 4 ?B. The minority channel electric polarization, as computed using Berry phase theory, is as high as ?13.0 ?Ccm?2, and we discuss experimental strategies to access the polarization. We propose that polar ferromagnetic half-metals exhibit multiferroism and can be exploited to realize nonreciprocal effects and directional anisotropy owing to the absence of both space-inversion and time-reversal symmetries.
Distribution Statement: 2-Distribution Limited to U.S. Government agencies only; report contains proprietary info
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Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: 10.1038/s41467-019-11172-2
Volume: 10 Issue: 1 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 7/1/19 5:00AM
Publication Location:
Article Title: Evidence for the weakly coupled electron mechanism in an Anderson-Blount polar metal
Authors: N. J. Laurita, A. Ron, Jun-Yi Shan, D. Puggioni, N. Z. Koocher, K. Yamaura, Y. Shi, J. M. Rondinelli, D.
Keywords: Polar metal, displacive transition, ultrafast spectroscopy
Abstract: Over 50 years ago, Anderson and Blount proposed that ferroelectric-like structural phase transitions may occur in metals, despite the expected screening of the Coulomb interactions that often drive polar transitions. Recently, theoretical treatments have suggested that such transitions require the itinerant electrons be decoupled from the soft transverse optical phonons responsible for polar order. However, this decoupled electron mechanism (DEM) has yet to be experimentally observed. Here we utilize ultrafast spectroscopy to uncover evidence of the DEM in LiOsO3, the first known band metal to undergo a thermally driven polar phase transition (Tc ? 140 K). We demonstrate that intra-band photo-carriers relax by selectively coupling to only a subset of the phonon spectrum, leaving as much as 60% of the lattice heat capacity decoupled. This decoupled heat capacity is shown to be consistent with a previously undetected and partially displacive TO polar mode, indicating the DEM in LiOsO3.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemistry of Materials
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemmater.9b00385
Volume: 31 Issue: 9 First Page #: 3083
Date Submitted: 8/29/19 12:00AM Date Published: 4/1/19 5:00AM
Publication Location:
Article Title: MnBi2: A Metastable High-Pressure Phase in the Mn-Bi System
Authors: James P. S. Walsh, Samantha M. Clarke, Danilo Puggioni, Alexandra D. Tamerius, Yue Meng, James M
Keywords: magnetism, high-pressure, intermetallic
Abstract: Permanent magnetism underpins a wide range of applications including wind energy harvesting and electric powered vehicles, where magnets are a critical component of the generators and motors inherent to these technologies. Materials that fuse a large magnetic response with a high coercivity (i.e., resistance to demagnetization) display permanent magnetism. One approach toward creating novel permanent magnets is by bringing together atoms that are spin-bearing, featuring large magnetic moments, with atoms possessing significant orbital angular momentum, to induce a high coercivity. Herein, we report the discovery of the metastable MnBi2, a previously unknown binary phase in the Mn?Bi system, which we synthesized above pressures of 8.3(1) GPa. Preliminary calculations on this phase indicate it may be a permanent magnet with a magnetic anisotropy of 0.205 MJ/m3 in favor of the ?100? magnetization direction at 0 K.
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Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.99.155111
Volume: 99 Issue: 15 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 4/1/19 5:00AM
Publication Location:
Article Title: Ultrafast quasiparticle dynamics in the correlated semimetal
Authors: Yakun Yuan, Peter Kissin, Danilo Puggioni, Kevin Cremin, Shiming Lei, Yu Wang, Zhiqiang Mao, James
Keywords: polar metals, ultrafast pump-probe, semimetal, ruthenate
Abstract: The correlated polar semimetal Ca3Ru2O7 exhibits a rich phase diagram including two magnetic transitions(TN = 56 K and TC = 48 K) with the appearance of an insulating-like pseudogap (at TC). In addition, there is a crossover back to metallic behavior at T ? = 30 K, the origin of which is still under debate. We utilized ultrafast optical-pump optical-probe spectroscopy to investigate quasiparticle dynamics as a function of temperature in this enigmatic quantum material. We identify two dynamical processes, both of which are influenced by the onset of the pseudogap. This includes electron-phonon relaxation and, below TC, the onset of a phonon bottleneck hindering the relaxation of quasiparticles across the pseudogap. Our results highlight the value of low-fluence ultrafast optics as a sensitive probe of low-energy electronic structure, thermodynamic parameters, and transport properties of Ruddlesden-Popper ruthenates.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Materials
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevMaterials.3.064411
Volume: 3 Issue: 6 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 6/1/19 5:00AM
Publication Location:
Article Title: High-pressure synthesis of the BiVO3 perovskite
Authors: R. A. Klein, A. B. Altman, R. J. Saballos, J. P. S. Walsh, A. D. Tamerius, Y. Meng, D. Puggioni, S. D. Ja
Keywords: vanadate; perovskite, antiferromagnetic, metallic
Abstract: We report the high-pressure, high-temperature synthesis of BiVO3, a cubic perovskite that thus far has remained inaccessible under ambient pressure conditions. We created this material at ?25 GPa and 1500 K in a laser-heated diamond-anvil cell and recovered it to ambient pressure and temperature. Our synthetic approach circumvents the oxidative chemistry that, at ambient pressures, previously rendered the cubic BiVO3 perovskite inaccessible. We find through density-functional theory calculations that this material is a unique metallic and antiferromagnetic transition-metal oxide.
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Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.99.224411
Volume: 99 Issue: 22 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 6/1/19 5:00AM
Publication Location:
Article Title: Comprehensive magnetic phase diagrams of the polar metal Ca3(Ru0.95Fe0.05)O7
Authors: Shiming Lei, Shalinee Chikara, Danilo Puggioni, Jin Peng, Mengze Zhu, Mingqiang Gu, Weiwei Zhao, Y
Keywords: polar metal, magnetism, SHG, high-magnetic field
Abstract: Polar metals exist as a rather unique class of materials as they combine two seemingly mutually exclusive properties (polar order and metallicity) in one system. So far only a few polar metals have been unambiguously identified; the magnetic ones are exceptionally rare. Here we investigate a 5% Fe-doped polar metal Ca3Ru2O7, via electrical transport, magnetization, microstrain, and optical second-harmonic generation measurements. We report the full magnetic phase diagrams (in the field-temperature space) for magnetic field H||a and H||b, which exhibit distinct field-dependent magnetizations behavior. In particular, for H||a we found a ferromagnetic incommensurate spin structure, which is absent in the pure Ca3Ru2O7. We propose a microscopic spin model to understand this behavior, highlighting the role of Fe doping in tipping the delicate balance of the underlying exchange-interaction energy in this system.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Applied Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5049607
Volume: 124 Issue: 17 First Page #: 174102
Date Submitted: 8/29/19 12:00AM Date Published: 11/1/18 5:00AM
Publication Location:
Article Title: Polar metals as electrodes to suppress the critical-thickness limit in ferroelectric nanocapacitors
Authors: Danilo Puggioni, Gianluca Giovannetti, James M. Rondinelli
Keywords: nanocapacitors, ferroelectrics, electrodes, polar metals
Abstract: Here, we show how to overcome the critical thickness limit imposed on ferroelectricity by utilizing electrodes formed from a novel class of materials known as polar metals. Electronic structure calculations on symmetric polar-metal electrode/FE capacitor structures demonstrate that electric polarizations persist to the sub-nanometer scale with the thickness approaching zero when a component of the polar axis in the electrode is perpendicular to the electrode/insulator interface, i.e., aligned along the direction of the polar displacements in the ferroelectric. Our results reveal the importance of interfacial dipolar coherency in sustaining the polarization, which provides a platform for atomic structure-based design of functions that deteriorate in reduced dimensions.
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Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.99.014105
Volume: 99 Issue: 1 First Page #:
Date Submitted: 8/29/19 12:00AM Date Published: 1/1/19 6:00AM
Publication Location:
Article Title: Atomic and electronic structure of domains walls in a polar metal
Authors: Greg Stone, Danilo Puggioni, Shiming Lei, Mingqiang Gu, Ke Wang, Yu Wang, Jianjian Ge, Xue-Zeng L
Keywords: polar metal, domain walls, improper ferroelectric
Abstract: Polar metals counterintuitively bring two well-known phenomena into coexistence, namely, bulk polar displacements, and an electronic Fermi surface giving rise to metallic conduction. However, little is known about the polar domains or domain walls in such materials. Using atomic resolution electron microscopy imaging combined with first principles density functional theory, we show that uncharged head-to-tail walls, and “charged” head-to-head and tail-to-tail walls can exist in the bulk of such crystals of polar metals Ca3Ru2O7, where both structural changes at the wall as well as electrostatic considerations define the wall nature. Significant built-in potentials of 30–170 meV are predicted at such walls.
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Journal: Applied Physics Letters
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5042769
Volume: 113 Issue: 12 First Page #: 122906
Date Submitted: 8/29/19 12:00AM Date Published: 9/1/18 5:00AM
Publication Location:
Article Title: Linear and nonlinear optical probe of the ferroelectric-like phase transition in a polar metal, LiOsO
Authors: Haricharan Padmanabhan, Yoonsang Park, Danilo Puggioni, Yakun Yuan, Yanwei Cao, Lev Gasparov,
Keywords: optical properties, polar metal, SHG, osmate
Abstract: LiOsO3 is one of the first materials identified as a “polar metal,” a class of materials that are simultaneously noncentrosymmetric and metallic. In this work, the linear and nonlinear optical susceptibility of LiOsO3 is studied by means of ellipsometry and optical second harmonic generation (SHG). Strong optical birefringence is observed using spectroscopic ellipsometry. The nonlinear optical susceptibility extracted from SHG polarimetry reveals that the tensor components are of the same magnitude as in the isostructural insulator LiNbO3, except the component along the polar axis d33 is suppressed by an order of magnitude. Temperature-dependent SHG measurements in combination with Raman spectroscopy indicate a continuous order-disorder type polar phase transition at 140K. Linear and nonlinear optical microscopy measurements reveal 109¬/71¬ ferroelastic domain walls, like in other trigonal ferroelectrics. No 180 degree polar domain walls are observed across the transition
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Volume: 2 Issue: 3 First Page #: 033174
Date Submitted: 8/26/20 12:00AM Date Published: 7/1/20 5:00AM
Publication Location:
Article Title: Evidence for an extended critical fluctuation region above the polar ordering transition in LiOsO3
Authors: Jun-Yi Shan, A. de la Torre, N. J. Laurita, L. Zhao, C. D. Dashwood, D. Puggioni, C. X. Wang, K. Yamau
Keywords: polar metal, fluctuations, SHG
Abstract: Metallic LiOsO3 undergoes a continuous ferroelectric-like structural phase transition below Tc = 140 K torealize a polar metal. To understand the microscopic interactions that drive this transition, we study its critical behavior above Tc via electromechanical coupling—distortions of the lattice induced by short-range dipole-dipole correlations arising from Li off-center displacements. By mapping the full angular distribution of second harmonic electric-quadrupole radiation from LiOsO3 and performing a simplified hyper-polarizable bond model analysis, we uncover subtle symmetry-preserving lattice distortions over a broad temperature range extending from Tc up to around 230 K, characterized by nonuniform changes in the short and long Li-O bond lengths. Such an extended region of critical fluctuations may explain anomalous features reported in specific heat and Raman scattering data and suggests the presence of competing interactions must be treated.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Research
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevResearch.2.023141
Volume: 2 Issue: 2 First Page #:
Date Submitted: 8/26/20 12:00AM Date Published: 5/1/20 5:00AM
Publication Location:
Article Title: Cooperative interactions govern the fermiology of the polar metal Ca3Ru2O7
Authors: Danilo Puggioni, M. Horio, J. Chang, James M. Rondinelli
Keywords: polar metal, Lifshitz transition, ruthenates
Abstract: Here we perform both first-principles calculations with static correlations and angle-resolved photoelectron spectroscopy experiments to construct a complete model of Ca3Ru2O7, reconciling inconsistencies among interpretations of electrical transport, thermopower measurements, and momentum- and energy-resolved band dispersions. The solution relies on treating the interplay among Coulomb repulsion, magnetic ordering, spin-orbit interactions, and the RuO6 octahedral degrees of freedom on equal footing. For temperatures 30 < T < 48K, we propose weak electron-electron interactions produce a symmetry-preserving metal-semimetal transition withWeyl nodes in proximity to the Fermi level, whereas an orthorhombic Pn21a structure emerges for T < 30K, exhibiting charge- and spin-density waves from enhanced Coulombic interactions.
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Journal: Chemistry of Materials
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemmater.9b02466
Volume: 31 Issue: 18 First Page #: 7626
Date Submitted: 8/26/20 12:00AM Date Published: 8/1/19 10:00AM
Publication Location:
Article Title: Covalency-driven Structural Evolution in the Polar Pyrochlore Series Cd2Nb2O7-xSx
Authors: Geneva Laurita, Daniel Hickox-Young, Samra Husremovic, Jun Li, Arthur W. Sleight, Robin Macaluso, J
Keywords: pyrochlore, polar displacements, anion substitution
Abstract: Here, we investigate the effect of varying degrees of covalency in the pyrochlore lattice through a detailed structural and lattice dynamical analysis of the pyrochlore oxysulfide series Cd2Nb2O7?xSx above and below the ferroelectric transition temperatures (TC) using synchrotron X-ray diffraction and first principles calculations. All compositions exhibit the cubic Fd3?m pyrochlore aristotype above TC, whereas the amplitude and character of various structural distortions are found to be composition-dependent below TC. For x = 0, large Cd and Nb cation displacements occur to produce the polar Ima2 structure accompanied by a change in translational symmetry. Our symmetry and lattice dynamical calculations indicate that Cd2Nb2O7 undergoes a proper ferroelectric transition through TC.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.102.014108
Volume: 102 Issue: 1 First Page #:
Date Submitted: 8/26/20 12:00AM Date Published: 7/1/20 5:00AM
Publication Location:
Article Title: Persistent polar distortions from covalent interactions in doped BaTiO3
Authors: Daniel Hickox-Young, Danilo Puggioni, James M. Rondinelli
Keywords: second-order Jahn-Teller effect, polar metal, perovskite
Abstract: Here, we perform a first-principles analysis of the evolution in the polar distortions in perovskite BaTiO3 under electrostatic doping to ascertain the dependencies of acentricity and electrical conductivity at the microscopic level. We focus on the role of local off-centering displacements, driven by the second-order Jahn-Teller effect, rather than discussing bulk homogeneous and cooperative lifting of inversion symmetry, which relies on long-range Coulombic interactions.We show that n-type doping disrupts the Ti-O covalent bond and advocate for using chemical bonding arguments as a framework for understanding the interplay between local distortions and free charge carriers rather than solely principles of dielectric screening in metals.
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Journal: Physical Review Materials
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Volume: 3 Issue: 9 First Page #:
Date Submitted: 8/26/20 12:00AM Date Published: 9/1/19 5:00AM
Publication Location:
Article Title: Uncorrelated Bi off-centering and the insulator-to-metal transition in ruthenium A2Ru2O7 pyrochlores
Authors: Geneva Laurita, Danilo Puggioni, Daniel Hickox-Young, James M. Rondinelli, Michael W. Gaultois, Kath
Keywords: metal-insulator transition, polar displacements, pyrochlore
Abstract: Here we study the roleof disorder in the form of cation off-centering on the compositionally-controlled insulator-to-metal transition in the solid solution oxide pyrochlore (Pr1?xBix)2Ru2O7. Prior work has established site disorder by the Bi3+ cations shifting incoherently away from their ideal crystallographic site in the Bi end-member pyrochlore as a consequence of stereochemical activity of the lone pair of electrons. However, less is known about the consequences of such off-centering in solid solutions and its role in determining the electronic ground state. Here we demonstrate through total scattering studies that even a small substitution of Bi on the pyrochlore A site leads to site disorder that enhances the average effective size of the A-site cation. Density functional calculations suggest the combination of primary and secondary (due to size) electronic effects of the lone pair-driven incoherent cation displacements drive the solid solution into a metallic state.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.125.077202
Volume: 125 Issue: 7 First Page #:
Date Submitted: 8/26/20 12:00AM Date Published: 8/1/20 5:00AM
Publication Location:
Article Title: Pressure-Induced Collapse of Magnetic Order in Jarosite
Authors: Ryan?A. Klein, James P.?S. Walsh, Samantha?M. Clarke, Zhenxian Liu, E. Ercan Alp, W
Keywords: jarosite, kagome, magnetism
Abstract: We report a pressure-induced phase transition in the frustrated kagome material jarosite at ?45 GPa, which leads to the disappearance of magnetic order.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemical Science
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0SC01994A
Volume: 11 Issue: 23 First Page #: 5922
Date Submitted: 8/26/20 12:00AM Date Published:
Publication Location:
Article Title: Synthetic investigation of competing magnetic interactions in 2D metal-chloranilate radical frameworks
Authors: Kelsey A. Collins, Richard J. Saballos, Majed S. Fataftah, Danilo Puggioni, James M. Rondinelli, Danna
Keywords: MOFs, kagome, spin frustration
Abstract: Herein, we describe the synthesis and magnetic characterization of a new 2,5-dihydroxy-1,4-benzoquinone based material, (NMe2H2)3.5Ga2(C6O4Cl2)3 (1), which features radical-based electronic spins on the sites of a kagom´e lattice, a geometric lattice known to engender exotic electronic properties. Vibrational and electronic spectroscopies, in combination with magnetic susceptibility measurements, revealed 1 exhibits mixed valency between the radical-bearing trianionic and diamagnetic tetraanionic oxidation states of the ligand. This unpaired electron density on the ligand forms a partially occupied kagom´e lattice where approximately 85% of the lattice sites are occupied with an S=1/2 spin.
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Journal: Inorganic Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.inorgchem.9b01785
Volume: 58 Issue: 22 First Page #: 14939
Date Submitted: 8/26/20 12:00AM Date Published: 10/1/19 5:00AM
Publication Location:
Article Title: Viewpoint: Atomic-Scale Design Protocols toward Energy, Electronic, Catalysis, and Sensing Applications
Authors: Florian Belviso, Victor E. P. Claerbout, Aleix Comas-Vives, Naresh S. Dalal, Feng-Ren Fan, Alessio Filip
Keywords: complex oxides, phase transitions, energy materials
Abstract: Nanostructured materials are essential building blocks for the fabrication of new devices for energy harvesting/storage, sensing, catalysis, magnetic, and optoelectronic applications. However, because of the increase of technological needs, it is essential to identify new functional materials and improve the properties of existing ones. The objective of this Viewpoint is to examine the state of the art of atomic-scale simulative and experimental protocols aimed to the design of novel functional nanostructured materials, and to present new perspectives in the relative fields. This is the result of the debates of Symposium I “Atomic-scale design protocols towards energy, electronic, catalysis, and sensing applications,” which took place within the 2018 European Materials Research Society fall meeting.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.123.236402
Volume: 123 Issue: 23 First Page #:
Date Submitted: 8/26/20 12:00AM Date Published: 12/1/19 6:00AM
Publication Location:
Article Title: Design of Heteroanionic MoON Exhibiting a Peierls Metal-Insulator Transition
Authors: Nathan J. Szymanski, Lauren N. Walters, Danilo Puggioni, James M. Rondinelli
Keywords: metal-insulator transition, polar metal, rutile
Abstract: Using a first-principles approach, we design the heteroanionic oxynitride MoON to exhibit a first-order isosymmetric thermally activated Peierls-type metal-insulator transition (MIT). We identify a ground state insulating phase (?-MoON) with monoclinic Pc symmetry and a metastable high temperature metallic phase (?-MoON) of equivalent symmetry. We find that ordered fac-MoO3N3 octahedra with edge and corner connectivity stabilize the twisted Mo-Mo dimers present in the ? phase, which activate the MIT through electron localization within the 4d a1g manifold. By analyzing the temperature dependence of the soft zone-boundary instability driving the MIT, we estimate an ordering temperature TMIT ? 900 K. Our work shows that electronic transitions can be designed by exploiting multiple anions, and heteroanionic materials could offer new insights into the microscopic electron-lattice interactions governing unresolved transitions in homoanionic oxides.
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Publication Identifier Type: DOI Publication Identifier: 10.1126/science.aax9753
Volume: 368 Issue: 6486 First Page #: 71
Date Submitted: 8/26/20 12:00AM Date Published: 4/1/20 5:00AM
Publication Location:
Article Title: Extreme tensile strain states in La0.7Ca0.3MnO3 membranes
Authors: Seung Sae Hong, Mingqiang Gu, Manish Verma, Varun Harbola, Bai Yang Wang, Di Lu, Arturas Vailion
Keywords: oxide membranes, magnetic transition, perovskite
Abstract: A defining feature of emergent phenomena in complex oxides is the competition and cooperation between ground states. In manganites, the balance between metallic and insulating phases can be tuned by the lattice; extending the range of lattice control would enhance the ability to access other phases. We stabilized uniform extreme tensile strain in nanoscale La0.7Ca0.3MnO3 membranes, exceeding 8% uniaxially and 5% biaxially. Uniaxial and biaxial strain suppresses the ferromagnetic metal at distinctly different strain values, inducing an insulator that can be extinguished by a magnetic field. Electronic structure calculations indicate that the insulator consists of charge-ordered Mn4+ and Mn3+ with staggered strain-enhanced Jahn-Teller distortions within the plane. This highly tunable strained membrane approach provides a broad opportunity to design and manipulate correlated electron states
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Journal: Physical Review B
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Volume: 102 Issue: 23 First Page #:
Date Submitted: 8/27/21 12:00AM Date Published: 12/1/20 6:00AM
Publication Location:
Article Title: Ferri-chiral compounds with potentially switchable Dresselhaus spin splitting
Authors: Pu Huang, Zhiguo Xia, Xiaoqing Gao, James M. Rondinelli, Xiuwen Zhang, Han Zhang, Kenneth R. Poe
Keywords: chiral materials, cuprate, Dresselhaus spin texture
Abstract: Spin splitting of energy bands can be induced by relativistic spin-orbit interactions in materials without inversion symmetry. Here we find a type of ferri-chiral materials with an alternative type of Dresselhaus symmetry, referred to as D-1B, exhibiting crystal class constraints similar to D-1A (all dipoles add up to zero), but unlike D-1A, at least one polar site is occupied. The spin splitting is associated with the crystalline chirality, which in principle could be reversed upon a change in chirality. Focusing on alkali metal chalcogenides, we identify NaCu5S3 in the nonenantiomorphic ferri-chiral structure, which exhibits CuS3 chiral units differing in the magnitude of their Cu displacements. Our electronic structure calculations demonstrate it exhibits D-1B spin splitting as well as a ferri-chiral phase transition, revealing spin splitting interdependent on chirality.
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Volume: 3 Issue: 4 First Page #: 1211
Date Submitted: 8/27/21 12:00AM Date Published: 10/1/20 5:00AM
Publication Location:
Article Title: Discovery Principles and Materials for Symmetry-Protected Persistent Spin Textures with Long Spin Lifetimes
Authors: Xue-Zeng Lu, James M. Rondinelli
Keywords: spin textures, ferroelectrics, oxides
Abstract: Persistent spin textures (PSTs) in solid-state materials arise from a uni-directional spin-orbit field in momentum space and offer a route to deliver the necessary long carrier spin lifetimes utilized in future quantum microelectronic devices. Nonetheless, few bulk materials host PSTs owing to crystal symmetry and chemical requirements, with even fewer experimentally demonstrated examples. This scarcity makes both PST materials discovery and performance assessment challenging. Here, we demonstrate that bulk PSTs exist in the family of layered A3B2O7 oxides and that a persistent spin helix (PSH) occurs over a large region of the Brillouin zone—a feature essential to experimental realization. By solving the spin-diffusion equations in the strong coupling limit and using the PST performance criteria we formulate, we find that the spin lifetime of the PSH is ~63 ns in Sr3Hf2O7—substantially larger than that predicted and demonstrated experimentally in GaAs/AlGaAs quantum wells.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Chemistry of Materials
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.chemmater.1c00540
Volume: 33 Issue: 13 First Page #: 4936
Date Submitted: 8/27/21 12:00AM Date Published: 6/1/21 5:00AM
Publication Location:
Article Title: Polar Ferromagnetic Metal by Intercalation of Metal–Amine Complexes
Authors: Huafei Zheng, Brandon C. Wilfong, Daniel Hickox-Young, James M. Rondinelli, Peter Y. Zavalij, Efrain E
Keywords: polar ferromagnetic metal, intercalation chemistry, 2D materials
Abstract: The metal?amine complex Co(en)3, where en = ethylenediamine, intercalates between layers of cobalt sulfide(CoS) to form a polar, ferromagnetic metal. We solve the structure of the hybrid compound [Co(en)3](CoS)12·en in the polar group Pca21 with lattice parameters a = 14.778(3) Å, b = 11.066(3) Å, and c = 20.095(5) Å using single-crystal X-ray diffraction. The [Co(en)3]2+ complexes order between CoS layers and break their inherent fourfold symmetry. Moreover, the chiral Co(en)3 complexes hydrogen bond to the terminal sulfides of the layers and break inversion symmetry, thereby inducing a polar state. From 1.8 to 300 K, the title compound displays metallic electrical resistivity and an anomaly at 43 K. Through magnetization measurements, we find that Co(en)3 exhibits spontaneous ferromagnetic order below 43 K. First-principles calculations reproduce the ferromagnetic structure and illustrate decoupling between the conducting electrons and the inversion-lifting distortion.
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Volume: 103 Issue: 16 First Page #:
Date Submitted: 8/27/21 12:00AM Date Published: 4/1/21 5:00AM
Publication Location:
Article Title: Comprehensive anisotropic linear optical properties of the Weyl semimetals TaAs and NbAs
Authors: Rui Zu, Mingqiang Gu, Lujin Min, Chaowei Hu, Ni Ni, Zhiqiang Mao, James M. Rondinelli, Venkatraman
Keywords: Weyl semimetal, Optical Properties
Abstract: TaAs and NbAs are two of the earliest identified Weyl semimetals that possess many intriguing optical properties, such as chirality-dependent optical excitations and giant second harmonic generation (SHG). Linear and nonlinear optics have been employed as tools to probe the Weyl physics in these crystals. Here, we extend these studies to address two important aspects: determining the complete anisotropic dielectric response and exploring if and how they can reveal essential Weyl physics. We determine the complete anisotropic dielectric functions of TaAs and NbAs by combining spectroscopic ellipsometry and density functional theory (DFT). We suggest that strong optical resonances from trivial bands are the likely origin of the large optical SHG previously reported at these energies.
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Journal: Nature Communications
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Volume: 13 Issue: 1 First Page #:
Date Submitted: 8/5/22 12:00AM Date Published: 4/1/22 5:00AM
Publication Location:
Article Title: Interlayer magnetophononic coupling in MnBi2Te4
Authors: Hari Padmanabhan, Maxwell Poore, Peter K. Kim, Nathan Z. Koocher, Vladimir A. Stoica, Danilo Puggic
Keywords: magnetophononic coupling,
Abstract: The emergence of magnetism in quantum materials creates a platform to realize spin-based applications in spintronics, magnetic memory, and quantum information science. A key to unlocking new functionalities in these materials is the discovery of tunable coupling between spins and other microscopic degrees of freedom. We present evidence for interlayer magnetophononic coupling in the layered magnetic topological insulator MnBi2Te4. Employing magneto-Raman spectroscopy, we observe anomalies in phonon scattering intensities across magnetic field-driven phase transitions, despite the absence of discernible static structural changes. This behavior is a consequence of a magnetophononic wave-mixing process that allows for the excitation of zone-boundary phonons that are otherwise ‘forbidden’ by momentum conservation. Our microscopic model based on density functional theory calculations reveals that this phenomenon can be attributed to phonons modulating the interlayer exchange coupling.
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DISSERTATIONS:

Publication Type: Thesis or Dissertation
Institution: Drexel University
Date Received: 19-Aug-2016 Completion Date: 4/1/16 10:37PM
Title: First Principles Design of Non-Centrosymmetric Metal Oxides
Authors: Joshua Young
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Publication Type: Thesis or Dissertation
Institution: Northwestern University
Date Received: 27-Aug-2021 Completion Date: 8/9/21 1:41PM
Title: Materials and Models for Coexisting Metallic Conductivity and Broken Inversion Symmetry
Authors: Daniel Hickox-Young
Acknowledged Federal Support: **Y**

PATENTS:

Intellectual Property Type: Patent Date Received: **29-Aug-2017**
Patent Title: Noncentrosymmetric Metal Electrodes for Ferroic Devices
Patent Abstract: A ferroelectric heterostructure may comprise a ferroelectric layer comprising a ferroelectric mate
Patent Number: 15/666,856
Patent Country: USA
Application Date: 02-Aug-2017 Application Status: 1
Date Issued:

Partners

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I certify that the information in the report is complete and accurate:
Signature: James Rondinelli
Signature Date: 8/5/22 6:10PM

MAJOR ACCOMPLISHMENTS

Major goals in this period are enumerated next and discussed below:

A. Harmonizing acentricity and metallicity in theory, simulation, and experiment with a lexicon for polar metals.
B. Transforming a strain-stabilized ferroelectric into an intrinsic polar metal with light.
C. Time-reversal symmetry breaking in a strongly polar metal by design.

A. Harmonizing acentricity and metallicity in theory, simulation, and experiment with a lexicon for polar metals. The concept of crystalline metals without inversion symmetry, specifically those that lift parity symmetry to support a polar crystal structure, has been frequently attributed to a concise 1965 Letter by Blount and Anderson titled "Symmetry Considerations on Martensitic Transformations: 'Ferroelectric' Metals." What is less well appreciated is that Blount and Anderson's article focuses on how a nominally first-order ferroelastic transition, observed at the time in the metallic silicide V_3Si, could exhibit second-order character, presumably attributed to a displacive component akin to the paraelectric-to-ferroelectric transition found in insulating compounds which exhibit a well-defined electric polarization below a critical temperature. At the time nearly all martensitic (ferroelastic) transformations in metals exhibited strong first-order character; yet, V_3Si exhibited second-order behavior. The continuous response was rationalized by inferring that the symmetry-break should be like that found in second-order displacive ferroelectrics, hence the quotes around "ferroelectric" in the title. Blount and Anderson did not suppose that "ferroelectric" metals would possess a switchable polarization. Gauss's Law dictates that no electric field may exist within a metal, so the atomic structure of a polar metal should be immune to perturbation via external applied electric field. Ironically, for years this same physical law seemed to imply that polar metals shouldn't exist at all. In prototypical ferroelectrics like $BaTiO_3$ it was shown that the polar displacement was stabilized by long-range dipole-dipole interactions. In the presence of free charge carriers, such interactions would be completely screened, favoring the centrosymmetric structure. In the decades following Anderson and Blount's prediction, it appeared that Gauss's Law would prevail over the synthesis of a polar metal. There were a couple of candidates in the 2000's which combined polar order and metallicity via compositional ordering, but it was not until 2013 that Shi et al. showed a displacive polar transition in the metal $LiOsO_3$. Their work demonstrated that a "ferroelectric"-like transition need not rely on long-range interactions, but may derive from local structural effects (geometrically-driven Li displacement in the case of $LiOsO_3$).

During the rapid increase in scholarship, diverse methods of combining these previously contraindicated properties have been proposed and executed, ranging from degenerately doped ferroelectrics to metals with hybrid improper polar distortions to two-dimensional thin films and interfaces. Accompanying these materials are a variety of terms. Polar, ferroelectric, "ferroelectric," ferroelectric-like, and native ferroelectric qualifiers that have been used to describe metallic systems with broken inversion symmetry. Furthermore, many so-called "ferroelectric metals" either push the boundaries of what may be called 'metallic' or do not exhibit a switchable polarization. Given the advances in dielectric, modern polarization, and soft-mode theories, we find that the ferroelectric-like designation and its derivatives are cumbersome and nonessential descriptions, obfuscating the physics displayed by very different (and yet, equally interesting) classes of materials. In addition, we note that both experimental and computational approaches to studying these materials have at times been abused. Computationally, the background-charge approach to electrostatic doping simulations fails to model reality in multiple underappreciated ways. Meanwhile, in experiments, the application of ferroelectric characterization techniques to materials that are not formally ferroelectrics both erodes the key differences separating metals from dielectrics and can lead to misinterpretations of measured dielectric polarizations, e.g., electric polarization hysteresis.

In the last period, we developed meaningful atomic and electronic structure descriptions to distinguish materials based on conductivity and symmetry considerations. We have prepared a manuscript highlighting the ways in which the assumptions of the popular background-charge approach to electrostatic doping simulations do not always resemble experiments. This leads to a discussion of the tensions between theory and experiment, as exemplified by both the various methods for combining polar order and metallicity and the shortcomings of our current terminology. Finally, we presented a survey of materials known to combine conductivity with broken inversion, suggesting new terminology and

classification based on clearly defined class descriptors. A research paper in which we report our ideas and opinions on polar metals is under preparation and will be submitted as soon as possible.

B. Transforming a strain-stabilized ferroelectric into an intrinsic polar metal with light. We explored the effects of chemical and photodoping in the strain-induced multiferroic $EuTiO_3$ grown on $DyScO_3$ substrates. The polar order was probed experimentally using second harmonic generation (SHG) and modeled using ab initio calculations. At low photodoping concentrations, we observed a reduction in SHG signal, indicating a destructive coupling between charge carriers and polar order in accordance with our simulations and expectations for a second-order Jahn-Teller driven ferroelectric. However, under increased photodoping the reduction in SHG plateaus at 84% of its original magnitude, indicating resilience of the polar order in the presence of a high concentration of delocalized electrons. This behavior stands in contrast with our first principles simulations, indicating that $EuTiO_3$ undergoes a transition from ferroelectric to polar metallic character under photodoping. We suggest several hypotheses for the mechanism behind this change in distortion character. A manuscript reporting these findings is under consideration by *Physical Review Letters.*

C. Time-reversal symmetry breaking in a strongly polar metal by design. Polar metals, with a combination of conflicting polarization and metallicity, have recently garnered increased interest because of their promising functionalities. Adding magnetism into this unique state would offer exciting opportunities to obtain exotic quantum states, analogous to magnetoelectric multiferroics with coupled polarization and magnetization. However, such an intrinsic ferromagnetic polar metallic state remains elusive, especially in correlated electron materials. We reported the experimental realization of coexisting ferromagnetism, polarity, and metallicity in a new quasi-two-dimensional 3*d* transition metal oxide $Ca_3Co_3O_8$. Structural oxygen vacancies order to form a periodic stacking of oxygen tetrahedral monolayers alternating with octahedral bilayers. The ferromagnetic metallic state is confined within the quasi-two-dimensional CoO_6 octahedral layers, while the broken inversion symmetry arises simultaneously from Co displacements, amplified by the onset of magnetism. The dual absence of spatial-inversion and time-reversal symmetries, as well as their strong coupling, produce an intrinsic magnetochiral anisotropy with exotic magnetic field-free nonreciprocal electrical resistivity, which we show is tunable through flexoelectric coupling with applied stresses. We also observed an extraordinarily robust topological Hall effect that persists over a broad temperature-field phase space arising from dipolar-induced Rashba spin-orbit coupling. Our work provides a rich platform to couple polar and magnetic states and defines a novel design strategy to access new correlated oxides with rich properties through ordered oxygen vacancies. The manuscript is under consideration by *Nature*.

OTHER ACCOMPLISHMENTS

1. Interlayer magnetophononic coupling in $MnBi_2Te_4$. The emergence of magnetism in quantum materials creates a platform to realize spin-based applications in spintronics, magnetic memory, and quantum information science. A key to unlocking new functionalities in these materials is the discovery of tunable coupling between spins and other microscopic degrees of freedom. We present evidence for inter-layer magnetophononic coupling in the layered magnetic topological insulator $MnBi_2Te_4$. We employ magneto-Raman spectroscopy to observe anomalies in phonon scattering intensities across magnetic field-driven phase transitions despite the absence of discernible static structural changes. This behavior is a consequence of a magnetophononic wave-mixing process that allows for the excitation of zone-boundary phonons that are otherwise 'forbidden' by momentum conservation. Our microscopic model based on density functional theory calculations reveals that this phenomenon can be attributed to phonons modulating the inter-layer exchange coupling. Moreover, signatures of magnetophononic coupling are also observed in the time domain through the ultrafast excitation and detection of coherent phonons across magnetic transitions. In light of the intimate connection between magnetism and topology in $MnBi_2Te_4$, the magnetophononic coupling represents an important step towards coherent on-demand manipulation of magnetic topological phases. These results are published in *Nat Commun* **13,** 1929 (2022) [https://www.nature.com/articles/s41467-022-29545-5].

2. Large Itinerant Electron Exchange Coupling in the Magnetic Topological Insulator $MnBi_2Te_4$. Magnetism in topological materials creates phases exhibiting quantized transport phenomena with applications in spintronics and quantum information. The emergence of such phases relies on strong interaction between localized spins and itinerant states comprising the topological bands, and the subsequent formation of an exchange gap. However, this interaction has never been measured in any intrinsic magnetic topological material. Using a multimodal approach, this exchange interaction is measured in $MnBi_2Te_4$, the first realized intrinsic magnetic topological insulator. Interrogating nonequilibrium spin dynamics, itinerant bands are found to exhibit a strong exchange coupling to localized Mn spins. Momentum-resolved ultrafast electron scattering, and magneto-optic measurements reveal that itinerant spins disorder via electron-phonon scattering at picosecond timescales. Localized Mn spins, probed by resonant X-ray scattering, disorder concurrently with itinerant spins, despite being energetically decoupled from the initial excitation. Modeling the results using atomistic simulations, the exchange coupling between localized and itinerant spins is estimated to be >100 times larger than superexchange interactions. This implies an exchange gap of >25 meV should occur in the topological surface states. By directly quantifying local-itinerant exchange coupling, this work validates the materials-by-design strategy of utilizing localized magnetic order to create and manipulate magnetic topological phases, from static to ultrafast timescales. The manuscript is under consideration by *Advanced Materials* and the preprint is available on arXiv at https://arxiv.org/abs/2204.04791.

3. Quantized non-Abelian, Berry's flux and higher-order topology of Na_3Bi. Recent theoretical works on effective, four-band models of three-dimensional, Dirac semimetals suggest the generic planes in momentum space, orthogonal to the direction of nodal separation, and lying between two Dirac points are higher-order topological insulators, supporting gapped, edge-states. Furthermore, the second homotopy classification of four-band models shows the higher-order topological insulators support quantized, non-Abelian Berry's flux and the Dirac points are monopoles of SO(5) Berry's connections. Due to the lack of suitable computational scheme, such bulk topological properties are yet to be determined from the ab initio band structures of Dirac materials. In this work, we report first, comprehensive topological classification of ab initio band structures of Na_3Bi, by computing Wilson loops of non-Abelian, Berry's connections for several, Kramers-degenerate bands. Our work shows the quantized, non-Abelian, Berry's flux can be used as a stable, bulk invariant for describing higher-order topology and topological phase transitions. A manuscript reporting these findings is under preparation and the initial preprint is available on arXiv at https://doi.org/10.48550/arXiv.2102.06207.

4. Topology of three-dimensional Dirac semimetals and generalized quantum spin Hall systems without gapless edge modes. Usually, the quantum spin Hall states are expected to possess gapless, helical edge modes. Are there clean, non-interacting, quantum spin Hall states without gapless, edge modes? We show the generic, n-fold-symmetric, momentum planes of three-dimensional, stable Dirac semi-metals, which are orthogonal to the direction of nodal separation are examples of such generalized quantum spin Hall systems. We demonstrate that the planes lying between two Dirac points and the celebrated Bernevig-Zhang-Hughes model support identical quantized, non-Abelian Berry flux of magnitude 2π. Consequently, both systems exhibit spin-charge separation in response to electromagnetic π-flux vortex. The Dirac points are identified as the unit-strength, monopoles of $SO(5)$ Berry connection, describing topological quantum phase transitions between generalized, quantum spin Hall and trivial insulators. Our work identifies precise bulk invariant and quantized response of Dirac semimetals and shows that many two-dimensional higher-order topological insulators can be understood as generalized quantum spin Hall systems, possessing gapped edge states. This work is under consideration by *Physical Review Letters* and the preprint is available on arXiv at https://arxiv.org/abs/2012.12906.