AFRL-AFOSR-VA-TR-2023-0086

Computationally-Guided Discovery of Semiconductors with Axis-Dependent Conduction Polarity - "Goniopolar" Materials

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10/19/2022
Final Technical Report

Air Force Research Laboratory
Air Force Office of Scientific Research
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED	
20221019	Final	START DATE 20180701	END DATE 20210630

4. TITLE AND SUBTITLE
Computationally-Guided Discovery of Semiconductors with Axis-Dependent Conduction Polarity - "Goniopolar" Materials

5a. CONTRACT NUMBER	5b. GRANT NUMBER	5c. PROGRAM ELEMENT NUMBER
	FA9550-18-1-0335	61102F
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)	10. SPONSOR/MONITOR'S ACRONYM(S)	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
Air Force Office of Scientific Research 875 N. Randolph St. Room 3112 Arlington, VA 22203	AFRL/AFOSR RTB1	AFRL-AFOSR-VA-TR-2023-0086

12. DISTRIBUTION/AVAILABILITY STATEMENT
A Distribution Unlimited: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The overall goal of this proposal is to combine theory, synthesis and property characterization to create new families of semiconducting “goniopolar” materials – materials that can
simultaneously conduct n-type and p-type carriers along orthogonal crystallographic axes. In most modern electronic materials and devices, a single material is optimized to exhibit a single
kind of electronic behavior, either metallic or semiconducting that is doped to exhibit a majority carrier type. However, many crystal lattices that feature anisotropic bonding along different directions, such as layered or chain-like frameworks can exhibit completely different band curvatures within the layer or chain axes and orthogonal to them. With the ideal band curvatures, this can lead to electron and hole mobility tensors that are orders of magnitude higher along different axes, and thus simultaneous electron and hole conduction along these orthogonal directions, when both carrier types are present. Our aims are to combine computational predictions, single crystal synthesis and axis-dependent measurements to a) Understand the origin of axis-dependent conduction polarity in Re4Si7 which is currently the only known goniopolar semiconductor as well as predict and experimentally confirm new families of b) narrow band bap goniopolar semiconductors (Egap < 0.4 eV) and wide band gap goniopolar semiconductors (Egap > 0.4 eV). We proposed to search for goniopolarity in the 1:1:1 copper group AMX compounds (i.e. CaCuP, BaCuP), the Nowotny chimney ladder
phases, and layered Zintl phase intermetallics to have 1:1:1 stoichiometry. Over the course of this project we have established the key band structure fingerprints for goniopolar materials,
more than doubled the number of known goniopolar compounds, and have demonstrated their potential in a variety of applications. These efforts are documented in 8 publications, and two
graduate student dissertations. This funding supported the training of the technical workforce leading to the graduation of two students with a PhD, and partially supported 6 other students
who will be graduating with PhD's in the coming years.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
a. REPORT U	b. ABSTRACT U	c. THIS PAGE U	UU	8

19a. NAME OF RESPONSIBLE PERSON	19b. PHONE NUMBER *(Include area code)*
ALI SAYIR	426-7236

AFOSR Final Report 8/31/2021

FA9550-18-1-0335: Computationally-Guided Discovery of Semiconductors with Axis-Dependent Conduction Polarity – "Goniopolar" Materials

PI: Joshua Goldberger;
Co-PI: Wolfgang Windl
The Ohio State University

The overall goal of this proposal is to combine theory, synthesis and property characterization to create new families of semiconducting *"goniopolar"* materials – materials that can simultaneously conduct *n*-type and *p*-type carriers along orthogonal crystallographic axes. In most modern electronic materials and devices, a single material is optimized to exhibit a single kind of electronic behavior, either metallic or semiconducting that is doped to exhibit a majority carrier type. However, many crystal lattices that feature anisotropic bonding along different directions, such as layered or chain-like frameworks can exhibit completely different band curvatures within the layer or chain axes and orthogonal to them. With the ideal band curvatures, this can lead to electron and hole mobility tensors that are orders of magnitude higher along different axes, and thus simultaneous electron and hole conduction along these orthogonal directions, when both carrier types are present. Our original aims are to combine computational predictions, single crystal synthesis and axis-dependent measurements to a) Understand the origin of axis-dependent conduction polarity in Re_4Si_7 which is currently the only known goniopolar semiconductor as well as predict and experimentally confirm new families of b) narrow band bap goniopolar semiconductors (E_{gap} < 0.4 eV) and wide band gap goniopolar semiconductors (E_{gap} > 0.4 eV). We proposed to search for goniopolarity in the 1:1:1 copper group AMX compounds (i.e. CaCuP, BaCuP), the Nowotny chimney ladder phases, and layered Zintl phase intermetallics to have 1:1:1 stoichiometry. Over the course of this project we have established the key band structure fingerprints for goniopolar materials, more than doubled the number of known goniopolar compounds, and demonstrated their potential in a variety of applications.

These efforts are documented in 8 publications, and two graduate student dissertations. This funding supported the training of the technical workforce leading to the graduation of two students with a PhD (Yaxian Wang and Mike Scudder), and partially supported 6 other students who will be graduating with PhD in the coming years (Karl Koster, Ryan Nelson, Andrew Ochs, Cullen Irvine, Ziling Sarah Deng, Archibald Williams).

The abstracts of the 8 publications are listed below;

1) He, B.; Wang, Y. X.; Arguilla, M. Q.; Cultrara, N. D.; Scudder, M. R.; Goldberger, J. E.; Windl, W.; Heremans, J. P. The Fermi surface geometrical origin of axis-dependent conduction polarity in layered materials. *Nat. Mater.,* **18**, 568 (2019).

Electronic materials generally exhibit a single isotropic majority carrier type, electrons or holes. Some superlattice(1,2) and hexagonal(3-5) materials exhibit opposite conduction polarities along in-plane and cross-plane directions due to multiple electron and hole bands. Here, we uncover a material genus with this behaviour that originates from the Fermi surface geometry of a single band. NaSn2As2, a layered metal, has such a Fermi surface. It displays in-plane electron and cross-plane hole conduction in thermopower and exactly the opposite polarity in the Hall effect. The small Nernst coefficient and magnetoresistance preclude multi-band transport. We label this direction-dependent carrier polarity in single-band systems 'goniopolarity'. We expect to find goniopolarity and the Fermi surface geometry that produces it in many metals and semiconductors whose electronic structure is at the boundary between two and three dimensions. Goniopolarity may enable future explorations of complex transport phenomena that lead to unprecedented device concepts.

2) Scudder, M. R.; He, B.; Wang, Y. X.; Rai, A.; Cahill, D. G.; Windl, W.; Heremans, J. P.; Goldberger, J. E. Highly efficient transverse thermoelectric devices with Re4Si7 crystals. *Energy Environ. Sci.,* **14**, 4009-4017 (2021).

The principal challenges in current thermoelectric power generation modules are the availability of stable, diffusion-resistant, lossless electrical and thermal metal-semiconductor contacts that do not degrade at the hot end nor cause reductions in device efficiency. Transverse thermoelectric devices, in which a thermal gradient in a single material induces a perpendicular voltage, promise to overcome these problems. However, the measured material transverse thermoelectric efficiencies, z(xy)T, of nearly all materials to date has been far too low to confirm these advantages in an actual device. Here, we show that single crystals of Re4Si7, an air-stable, thermally robust, layered compound, have a transverse z(xy)T of 0.7 +/- 0.15 at 980 K, a value that is on par with existing commercial longitudinal theremoelectrics today. Through constructing and characterizing a transverse power generation module, we prove that extrinsic losses through contact resistances are minimized in this geometry, and that no electrical contacts are needed at the hot side. This excellent transverse thermoelectric performance arises from the large, oppositely signed in-plane p-type and cross-plane n-type thermopowers. These large anisotropic thermopowers arise from thermal population of the highly anisotropic valence band and isotropic conduction band in this narrow gap semiconductor. Overall, this work establishes Re4Si7 as the "gold-standard" of transverse thermoelectrics, allowing future exploration of unique device architectures for waste heat recovery.

3) Wang, Y. X.; Koster, K. G.; Ochs, A. M.; Scudder, M. R.; Heremans, J. P.; Windl, W.; Goldberger, J. E. The Chemical Design Principles for Axis-Dependent Conduction Polarity. *J. Am. Chem. Soc.,* **142**, 2812-2822 (2020).

The recent discovery that specific materials can simultaneously exhibit n-type conduction and p-type conduction along different directions of the single crystal has the potential to impact a broad range of electronic and energy-harvesting technologies. Here, we establish the chemical design principles for creating materials with this behavior. First, we define the single-carrier and multicarrier mechanisms for axis-dependent conduction polarity and their identifying band structure fingerprints. We show using first-principles predictions that the AMX (A = Ca, Sr, Ba; M = Cu, Ag, Au; X = P, As, Sb) compounds consisting of MX honeycomb layers separated by A cations can exhibit p-type conduction in-plane and n-type conduction cross-plane via either mechanism depending on the doping level. We build up the band structure of BaCuAs using a molecular orbital approach to illustrate the structural origins of the two different mechanisms for axis-dependent conduction polarity. In total, this work shows this phenomenon can be quite prevalent in layered materials and reveals how to identify prospective materials.

4) Ochs, A. M.; Gorai, P.; Wang, Y. X.; Scudder, M. R.; Koster, K.; Moore, C. E.; Stevanovic, V.; Heremans, J. P.; Windl, W.; Toberer, E. S.; Goldberger, J. E. Computationally Guided Discovery of Axis-Dependent Conduction Polarity in NaSnAs Crystals. *Chem. Mat.,* **33**, 946-951 (2021).

Most electronic materials exhibit a single dominant charge carrier type, either holes or electrons, along all crystallographic directions. However, there are a small number of compounds, mostly metals, that exhibit simultaneous p-type and n-type conduction behavior along different crystallographic directions. We demonstrate that the experimental discovery of semiconductors with this axis-dependent conduction polarity can be facilitated by identifying a large anisotropy of either the electron or hole effective masses (m^*) or both, providing the electron and hole masses dominate along different crystallographic directions. We calculated the layered semiconductor NaSnAs to have a lower electron m^* in-plane than the cross-plane and a very large hole m^* in-plane and small hole m^* cross-plane. We established the growth of >3 mm-sized NaSnAs crystals via Sn flux and confirmed the band gap to be 0.65 eV, in agreement with theory. NaSnAs exhibits p-type thermopowers cross-plane and n-type thermopowers in-plane, confirming that the large anisotropy in the effective mass at the band edges is an excellent indicator for axis-dependent conduction polarity. Overall, this work shows that the discovery of semiconductors with such a phenomenon can be accelerated by computationally evaluating the anisotropic curvatures of the band edges, paving the way for their future discovery and application.

5) Koster, K. G.; Wang, Y. X.; Scudder, M. R.; Moore, C. E.; Windl, W.; Goldberger, J. E. Synthesis and characterization of a new family of layered PbxSn4-xAs3 alloys. *J. Mater. Chem. C,* **9**, 6477-6483 (2021).

Layered two-dimensional (2D) materials have attracted considerable interest for their exotic and anisotropic electronic behavior. One such material, Sn4As3, bears a resemblance in both structure and elemental composition to two other Sn- and As-containing layered materials that have recently demonstrated axis-dependent conduction polarity: NaSn2As2 and NaSnAs. Here, a new family of Pb-alloyed PbxSn4-xAs3 crystals was synthesized and the axis-dependent electronic and thermoelectric properties were evaluated. Up to one full equivalent of Pb could be alloyed into PbxSn4-xAs3 ($0 < x < 1.06$) before phase separation occurred. We establish the structural changes and the trends in the Raman spectra with increasing Pb substitution. These materials all exhibit metallic temperature-dependent resistivities and positive thermopowers along the in-plane and cross-plane directions. The absence of axis-dependent conduction polarity in these SnAs-layered materials is consistent with theoretical predictions, and illustrates that precise control over the atomic and electronic structure and doping is essential for realizing this phenomenon in new materials.

6) Redemann, B. W. Y.; Scudder, M. R.; Weber, D.; Wang, Y. X.; Windl, W.; Goldberger, J. E. Synthesis, structural, and electronic properties of Sr1-xCaxPdAs. *Inorg. Chem. Front.,* **7**, 2833-2839 (2020).

Layered honeycomb intermetallic phases have attracted considerable research interest due to the wide array of exciting physical properties inherent in these materials. Here, we follow the evolution in structure and electronic properties of a relatively unexplored material system, Sr1-xCaxPdAs, as the hexagonal PdAs honeycomb layer in SrPdAs distorts into the orthorhombic CaPdAs structure. The Sr-rich compounds (x= 0 to 1/3) form symmetric, hexagonal honeycomb PdAs layers, whereas in the Ca-rich region (x= 1/2 to 1) the PdAs layers distort into an orthorhombic structure featuring long and short Pd-Pd distances. This distortion occurs when the average Pd-Pd distance falls below 4.21 angstrom. All compounds are observed to exhibit metallic temperature-dependent resistivity trends. There are no apparent discontinuities indicative of metal-to-insulator transitions and the room temperature resistivity values range from 18 to 180 m omega cm. In total, this work maps out the structural and electronic phase diagram of Sr1-xCaxPdAs compounds.

7) Gray, M. B.; McClure, E. T.; Holzapfel, N. P.; Evaristo, F. P.; Windl, W.; Woodward, P. M. Exploring the AgSb1-xBixI4 phase diagram: Thermochromism in layered CdCl2-type semiconductors. *J. Solid State Chem.,* **297**, 7 (2021).

AgSbI4 and several AgSb1-xBixI4 compositions have been synthesized via solid state reactions. Both end members and all intermediate compositions crystallize with the CdCl2 structure type (space group = R (3) over barm) and a random distribution of the Ag+ and Sb3+/Bi3+ cations. Hypothetical cation ordered structures have been generated and their stabilities evaluated with density functional theory. This analysis suggests that while charge balanced layers are strongly favored, the long-range interactions that favor ordered stacking of layers are too weak to produce three-dimensional cation ordering. The colors of these materials change noticeably when heated, signaling a large thermochromic effect. For example, the band gap of AgSb0.25Bi0.75I4 changes from 1.68 eV at room temperature to 1.55 eV at 150 degrees C. This thermochromic shift in band gap is larger than comparable diamond-like semiconductors, such as CdTe. VASP calculations and molecular dynamics simulations indicate the large thermochromic effect is primarily caused by significant electron-phonon coupling.

8) Shcherbakov, D.; Stepanov, P.; Memaran, S.; Wang, Y. X.; Xin, Y.; Yang, J. W.; Wei, K. Y.; Baumbach, R.; Zheng, W. K.; Watanabe, K.; Taniguchi, T.; Bockrath, M.; Smirnov, D.; Siegrist, T.; Windl, W.; Balicas, L.; Lau, C. N. Layer- and gate-tunable spin-orbit coupling in a high-mobility few-layer semiconductor. *Sci. Adv.,* **7**, 6 (2021).

Spin-orbit coupling (SOC) is a relativistic effect, where an electron moving in an electric field experiences an effective magnetic field in its rest frame. In crystals without inversion symmetry, it lifts the spin degeneracy and leads to many magnetic, spintronic, and topological phenomena and applications. In bulk materials, SOC strength is a constant. Here, we demonstrate SOC and intrinsic spin splitting in atomically thin InSe, which can be modified over a broad range. From quantum oscillations, we establish that the SOC parameter a is thickness dependent; it can be continuously modulated by an out-of-plane electric field, achieving intrinsic spin splitting tunable between 0 and 20 meV. Unexpectedly, alpha could be enhanced by an order of magnitude in some devices, suggesting that SOC can be further manipulated. Our work highlights the extraordinary tunability of SOC in 2D materials, which can be harnessed for in operando spintronic and topological devices and applications.

The abstracts for the two PhD Disserations are below;

Materials with Axis-Dependent Conduction Polarity and their Application in Transverse Thermoelectric Devices

Michael Richard Scudder, 2021

Most electronic materials exhibit a single type of conduction polarity, either holes (p-type) or electrons (n-type), along their principle axes. In the introductory chapter, we establish an overview of the chemical design principles for creating materials that can simultaneously exhibit n-type conduction and p-type conduction along different directions of the single crystal. Materials that exhibit such behavior have the potential to impact a broad range of electronic and energy-harvesting technologies. We show using first-principles predictions that the AMX (A = Ca, Sr, Ba; M = Cu, Ag, Au; X = P, As, Sb) compounds consisting of MX honeycomb layers separated by A cations can exhibit p-type conduction in-plane and n-type conduction cross-plane via either mechanism depending on the doping level. In Chapter 2, we uncover a new material genus with this behavior, now originating from the Fermi surface topology of a single band. $NaSn_2As_2$, a layered metal, has a Fermi surface with this topology. This direction-dependent carrier polarity, which we label *goniopolarity*, and this Fermi surface topology, are expected in many metals and semiconductors whose electronic structure is at the boundary between two and three dimensions. In Chapter 3, we show that Re_4Si_7, which has the largest axis-dependent conduction anisotropy to date, can be implemented in transverse thermoelectric devices. Thermoelectric devices directly convert heat to electrical power using a p-type and n-type semiconductor connected thermally in parallel and electrically in series and represent a green energy source for waste heat recovery. The principal challenges in current thermoelectric power generation modules is the availability of stable, diffusion-resistant, lossless electrical and thermal metal-semiconductor contacts that do not degrade at the hot end nor cause reductions in device efficiency. Transverse thermoelectric devices, in which a thermal gradient in a single material induces a perpendicular voltage, promise to overcome these problems. However, the measured material transverse thermoelectric efficiencies, $z_{xy}T$, of nearly all materials to date has been far too low to confirm these advantages in an actual device. Here, we show that single crystals of Re_4Si_7, an air-stable, thermally robust, layered compound, have a transverse $z_{xy}T$ of 0.7±0.15 at 980 K, a value that is on par with existing commercial longitudinal thermoelectrics today. Through constructing and characterizing a transverse power generation module, we prove that extrinsic losses through contact resistances are minimized in this geometry, and that no electrical contacts are needed at the hot side. Finally, in Chapter 4 we further investigate the performance of Re_4Si_7 transverse power generators difference device geometries. We focus on the the effect of heat distribution throughout the sample through construction of adiabatic and isothermal transverse power generators. This work will help inform future device fabrication of these modules.

Functional Properties in Novel 2D and Layered Materials

Yaxian Wang, 2019

Novel two dimensional (2D) materials have been receiving increasing attention due to various exotic properties such as massless fermions, versatile gap engineering, topological edge states and superconductivity. With that, they are currently becoming one of the most import families of quantum materials and feature very high potential to be the basis for a manifold of disruptive technologies within the realm of functional materials. Density Functional Theory (DFT) has been playing an essential role in understanding their fundamental properties and discovering new candidate materials for a wide range of applications. Here, we used DFT to study the structural, electronic, optical and transport properties of a large variety of novel 2D and layered materials. After a high-level overview, we will first discuss structural defects in hydrogen and methyl terminated germanene. There, we will show why random twisting, which is a rotation between neighboring layers, is limited to small angles in germananes and results in turbostratic disorder, which is confirmed by electron diffraction. Twisting has recently been shown to have surprising results on band structures and transport properties, which is rationalized by our results for charge redistribution between Ge atoms and terminating hydrogen atoms in a turbostratically twisted structure. Band structures are also a_ected by point defects such as vacancies or residual intercalation atoms from the synthesis process, especially in the form of deep level defect states in the band gap, which are validated by cathodoluminescene and surface photovoltage spectroscopy, for which we discuss the role of DFT in analyzing experimental spectra. Such an approach can also be applied to the analysis of experimental Raman spectra of lattice vibrations, as we demonstrate for the example of CrI3, the first reported single layer 2D magnetic semiconductor. In the effort of seeking electric field tuning of band gaps in semiconductors, we propose and study atomically thin InSe two dimensional layers. InSe shows a direct to indirect gap transition going from bulk to confined two dimensional structure. The band gap and e_ective mass in its conduction band minimum shows strong dependence to layer thickness and external electric field perpendicular to the plane. This offers promising application in 2D field effect transistors (FETs).

Next, we discovered the concept of axis dependent conduction polarity, or `goniopolarity', which our theoretical work has helped to establish following directionally dependent sign changes in the measured thermopower of NaSn2As2, an exfoliatable vdW Zintl phase. We introduce a theory that shows that open Fermi surfaces with concave/convex shapes along orthogonal crystallographic axis can produce single-band goniopolarity, which we then expand to a tightbinding model that better identi_es the roles of the atomic orbitals for goniopolarity. Furthermore, by a systematic study of prototypical AMX compounds where two mechanisms, (e.g. pxn and goniopolar) of axis-dependent polarity are achieved, we further build up reliable chemical design principles for the chemistry community. The concept of goniopolarity challenges the traditional view of charge polarity as an exclusive property in semiconductors as well as the

traditional neglect of hole-like conduction in metals and provides an exciting new playing field for electronic device concepts.