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as of 13-Jan-2022

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STEM Degrees: 3 **STEM Participants:**

Major Goals: In this project, we will focus on a family of layered superatomic crystals (SACs) assembled from two-dimensional (2D) sheets of metal chalcogenide superatoms and fullerenes (e.g. C60s and C70s). We will study how structure of the layers can integrate with orientational disorder to predictably tune material properties for Army-relevant applications such as infrared (IR) detection, thermoelectric and pyroelectric energy conversion, and thermal switching. Goals include: (1) Synthesis of new layered SACs, (2) measurement of thermal transport properties in new layered SACs, and (3) simulation of thermal transport properties in new layered SACs. Due to the similarity in samples and experimental tools we have also considered layered perovskites, metal organic frameworks, covalent organic frameworks, and layered van der waals metals such as TaFeTe4.

Accomplishments: Accomplishments under the Major Goals are described in terms of the relevant publications that reference ARO support and have been released to the scientific community. These have been uploaded at the “Products” tab and are referenced in the descriptions below [].

(1) Synthesis of new layered SACs.
Several new SACs were synthesized as part of this project, creating a library built from inorganic clusters (e.g. [Co6Te8(PEt3)6][C70]2) alone or with fullerene derivatives (e.g. C60, C70) and similarly sized [JACS 2018]. Prior to our work on this project these SACs were single crystals with specified stoichiometries, but we also learned to synthesize disordered thin film “alloys” where the cluster/fullerene ratio can be continuously varied [JACS 2019]. Later we found the alloys could also be synthesized in the crystalline phase by substitution of the metal center in the inorganic cluster from Co to Cr [Nature Chemistry 2021]. in Several newly synthesized SACs (e.g. Re6Se8Cl2) are layered materials where in-plane covalent bonds and cross plane van der Waals bonds generate anisotropy of in-plane and cross-plane properties [Nano Letter 2020, JACS 2020]. Our publications, summarized below describe synthetic approaches as well as descriptions of transport properties within these materials.

(2) Measurement of thermal transport properties in new layered SACs.

In [JACS 2018] we discuss [Co6Te8(PEt3)6][C70]2, a novel superatomic crystal with two separate phase transitions that drastically transform the collective material properties. A coupled structural-electronic phase transition triggers the emergence of a new electronic band in the fullerene sublattice of the crystal, increasing its electrical conductivity by 2 orders of magnitude, while narrowing its optical gap and increasing its spin density. Independently, an order–disorder transition transforms [Co6Te8(PEt3)6][C70]2 from a phonon crystal to a phonon glass. These results introduce a family of materials in which functional phase transformations may be manipulated by varying the constituent building blocks.

In [JACS 2019] we show that electrostatic interactions between nanoscale clusters can be frustrated by using large clusters with long and flexible side-chains (i.e. using PCBM instead of C60) so that the ionic cluster pairs do not crystallize. As such, we report ionic superatomic materials that can be easily solution-processed into completely amorphous and homogeneous thin-films. These new amorphous superatomic materials show tunable compositions and new properties that are not achievable in crystals, including very high electrical conductivities of up to 300 S per meter, ultra low thermal conductivities of 0.05 W per meter per degree kelvin, and high optical transparency of up to 92%. We also demonstrate thin-film thermoelectrics with unoptimized ZT values of 0.02 based on the superatomic thin-films. Such properties are competitive to state-of-the-art materials and make superatomic materials promising as a new class of electronic and thermoelectric materials for devices.

In [Nano Letters 2020] we report the electrical and thermal transport properties of Re6Se8Cl2, a two-dimensional superatomic semiconductor. We find that this compound can be n-doped in situ through Cl dissociation, drastically altering the transport behavior from semiconducting to metallic and giving rise to superconductivity with a critical temperature of ~8 K and upper critical field exceeding 30 T. This work is the first example of superconductivity in a van der Waals superatomic crystal; more broadly, it establishes a new chemical strategy to manipulate the electronic properties of van der Waals materials with labile ligands.

In [JACS 2020] we report two new vdW materials with strongly anisotropic in-plane structures featuring stripes of metallic TaTe2 and semiconducting FeTe2, α-TaFeTe4 and β-TaFeTe4. We find that the structure of α-TaFeTe4 produces strongly anisotropic in-plane electronic transport (anisotropy ratio of up to 250%), outcompeting all other vdW metals, and demonstrate that it can be mechanically exfoliated to the two-dimensional (2D) limit. We also explore the possibility that broken inversion symmetry in β-TaFeTe4 produces Weyl points in the electronic band structure. Eight Weyl nodes slightly below the Fermi energy are computationally identified for β-TaFeTe4, indicating they may contribute to the transport behavior of this polytype. These findings identify the TaFeTe4 polytypes as an ideal platform for investigation of 2D transport anisotropy and chiral charge transport as a result of broken symmetry.

In [Nature Chemistry 2021] we report the synthesis and properties of two solid solutions in hierarchical solids that are built from atomically precise clusters. Two geometrically similar metal chalcogenide clusters, Co6Se8(PEt3)6 and Cr6Te8(PEt3)6, were combined as random substitutional mixture, in three different ratios, in a crystal lattice together with fullerenes. This does not alter the underlying crystalline structure of the [cluster][C60]2 material, but it influences its electronic and magnetic properties. All three solid solutions showed increased electrical conductivities compared with either the Co- or Cr-based parent material, substantially so for two of the Co:Cr ratios (up to 100-fold), and lowered activation barriers for electron transport. We attribute this to the existence of additional energy states arising from the materials' structural heterogeneity, which effectively narrow transport gaps.

Finally we note that novel thermal transport measurements on related materials were made using methods developed by this project. In metal-organic frameworks (MOFs) we observed reduced thermal conductivity framework due to the presence of adsorbates, which has implications for CO2 and hydrogen storage [Nature Comms, 2020]. In two-dimensional Ruddlesden-Popper phase peroviskites we observed signitures of coherent phonon transport that indicate the ability to manipulate heat using the wavelike properties of phonons [ACS Nano, 2021]. In covalent organic frameworks (COFs) we found the unusual combination of both ultra-low dielectric permeability and high thermal conductivity that could enable high power density computing [Nature Materials, 2021].

(3) Simulation of thermal transport properties in SACs.
As part of this project we investigated thermal transport in fullerene-based SACs using molecular dynamics simulations [Nanoscale Horizons, 2020]. The temperature-dependent predictions agree with the trends of previous measurements. The thermal conductivity behavior emerges as a result of the C60 molecule rotational dynamics and orientation, which are quantified using the root mean square displacements of the carbon atoms and the relative orientations of the C60s. At low temperatures, the C60s exhibit small rotations around equilibrium positions (i.e., librations). When the librating C60s are orientationally-ordered, as in the [C60] and [Co6Se8(PEt3)6][C60]2 SACs, thermal conductivity decreases with increasing temperature, as is typical for a crystal. When the librating C60s are orientationally-disordered, however, as in the [Co6Te8(PEt3)6][C60]2 SAC, thermal conductivity is lower and temperature independent, as is typical for an amorphous solid. At higher temperatures, where the C60s in all three SACs freely-rotate and are thus dynamically disordered, thermal conductivity is temperature independent. The abrupt changes driven by the C60 dynamics suggest that fullerene-based SACs can be designed to be thermal conductivity switches based on a variety of external stimuli.

Training Opportunities: A Columbia postdoctoral fellow, Elena Meirzadeh, has developed synthesis protocols for several layered superatomic crystals including Re6Se8Cl2, Ta4S9Br8, Mo6S3Br6, and CoTeC70. Another Columbia postdoctoral fellow worked on studying the transport properties of superatomic superconductor Re6Se8Cl2. The Columbia work was performed with the help of fellowshipped student Avalon Dismukes and Jake Russell. Another Columbia postdoctoral fellow, Jingjing Yang has developed synthesis protocols for superatomic crystal thin films based on PCBM rather than C60. Their synthetic work creates the materials for property measurements at CMU.

Two graduate students at Carnegie Mellon have made significant contributions to this project. Alex Christodoulides and Matthew Bartnof learned nanofabrication skills, low temperature and low pressure techniques, and frequency domain thermoreflectance in support of the C70 SAC, PCBM SAC film, MOF, COF, and perovskite measurement. Matthew has also performed molecular dynamics simulations on C60 based superatomic crystals and covalent organic networks. A third CMU PhD student, Xiaoman Wang, performed ANSYS simulations to assess temperature in the superconductive superatomic crystals Re6Se8Cl2.

Results Dissemination: Journal Articles

(1) E. S. O'Brien, J. C. Russell, M. Bartnof, A. D. Christodoulides, K. Lee, J. A. DeGayner, D. W. Paley, A. J. H. McGaughey, W. L. Ong, J. A. Malen, X-Y. Zhu, X. Roy, Spontaneous Electronic Band Formation and Switchable Behaviors in a Phase-Rich Superatomic Crystal, Journal of the American Chemical Society 140 (46), 15601 (2018).
(2) J. Yang, B. Zhang, A. D. Christodoulides, Q. Xu, A. Zangiabadi, S. R. Peurifoy, C. K. McGinn, L. Dai, E. Meirzadeh, X. Roy, M. L. Steigerwald, I. Kymissis, J. A. Malen, C. Nuckolls, Solution Processible Superatomic Thin-Films, Journal of the American Chemical Society, 141 (28), 10967 (2019).
(3) E. J. Telford, J. C. Russell, J. R. Swann, B. Fowler, X. Wang, K. Lee, A. Zangiabadi, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Batail, X. Zhu, J. A. Malen, C. R. Dean, X. Roy, Doping-induced superconductivity in the van der Waals superatomic crystal Re6Se8Cl2. Nano Letters, 20 (3), 1718-1724 (2020)
(4) Q. Liang, M. Bartnof, Y.-L. He, J. A. Malen, and A. J. H. McGaughey, Fullerene rotational dynamics generate disordered configurations that suppress thermal conductivity in superatomic crystals. Nanoscale Horizons 5, 1524-1529 (2020). DOI: 10.1039/D0NH00358A
(5) H Babaei, ME DeCoster, M Jeong, ZM Hassan, T Islamoglu, H Baumgart, AJH McGaughey, E Redel, OK Farha, PE Hopkins, JA Malen, CE Wilmer, Observation of reduced thermal conductivity in a metal-organic framework due to the presence of adsorbates, Nature communications 11 (1), 1-8 (2020)
(6) D Saha, X Yu, Y Du, Z Guo, F Xiong, AJ Gellman, JA Malen, Enhancing Thermal Interface Conductance to Graphene Using Ni–Pd Alloy Contacts, ACS Applied Materials & Interfaces 12 (30), 34317-34322 (2020)
(7) R. A. Wiscons, Y. Cho, S. Y. Han, A. H. Dismukes, E. Meirzadeh, C. Nuckolls, T. C. Berkelbach, X. Roy, "Polytypism, Anisotropic Transport and Weyl Nodes in the van der Waals Material TaFeTe4, Journal of the American Chemical Society 143, 1, 109–113 (2021)
(8) A. D. Christodoulides, P. Guo, L. Dai, J. M. Hoffman, X. Li, X. Zuo, D. Rosenmann, A. Brumberg, M. G. Kanatzidis, R. D. Schaller, J. A. Malen, Signatures of Coherent Phonon Transport in Ultralow Thermal Conductivity Two-Dimensional Ruddlesden–Popper Phase Perovskites. ACS Nano. 15, 4165–4172 (2021).
(9) A. M. Evans, A. Giri, V. K. Sangwan, S. Xun, M. Bartnof, C. G. Torres-Castanedo, H. B. Balch, M. S. Rahn, N. P. Bradshaw, E. Vitaku, D. W. Burke, H. Li, M. J. Bedzyk, F. Wang, J.-L. Brédas, J. A. Malen, A. J. H. McGaughey, M. C. Hersam, W. R. Dichtel, P. E. Hopkins, Thermally conductive ultra-low -k dielectric layers based on two-dimensional covalent organic frameworks. Nature Materials, 1–7 (2021).
(10)J. Yang, J. C. Russell, S. Tao, M. Lessio, F. Wang, S. R. Peurifoy, A. C. Hartnett, E. A. Doud, E.S. O'Brien, N. Gadjieva, X.-Y Zhu, D. R. Reichman, A. C. Crowther, S. J. L. Billinge, X. Roy, M. L. Steigerwald, and C. Nuckolls, "Superatomic Solid Solutions", Nature Chem. 2021, 13, 607-613.
(11)J. Yang, F. Wang, F. C. Russell, T. Hochuli, X. Roy, M. Steigerwald, X.-Y. Zhu, D. W. Paley, C. Nuckolls, "Shape Matching in Superatom Chemistry and Assembly", J. Am. Chem. Soc. 2020, 142, 11993-11998.

Conference Presentations

1. "Molecular Clusters: Building Blocks for Material Design", GRC on Atomically Precise Nanochemistry, Galveston TX (2/10/2020)
2. "Switchable Transport Behaviors in Phase Change Superatomic Crystals", ACS 2019, San Diego, CA (8/29/2019)
3. "Molecular Clusters as Electronic Circuit Elements", International Symposium on Clusters and Nanomaterials, Richmond, VA (11/7/2019)

4. "Thermal transport and fullerene dynamics in superatomic crystals." Alan McGaughey, Qi Liang, Wee Liat Ong, Matthew Bartnof, Ya-Ling He, Xavier Roy, Jon Malen. Invited talk given at MRS Spring 2021 Meeting, Seattle, WA, April 2021.

5. M. Bartnof, Q. Liang, and A. J. H. McGaughey, "Predicting Material Properties of Superatomic Crystals using Molecular Dynamics Simulations." MRS 2019 Fall Meeting, Boston, MA, December 2019.

6. J. A. Malen, E. O'Brien, J. Russell, M. Bartnof, A. Christodoulides, K. Lee, D. Paley, A. J. H McGaughey, W.-L. Ong, X. Zhu, and X. Roy, "Orientational disorder controls the thermal conductivity of C_70 based superatomic crystals." MRS 2019 Spring Meeting, Phoenix, AZ, April 2019.

7. M. Bartnof, A. Christodoulides, W.-L. Ong, E. O'Brien, X. Roy, A. J. H. McGaughey, and J. A. Malen, "Fullerene-based Superatomic Crystals' Thermal Transport Controlled by Orientation Disorder." ASME 2018 IMECE, Pittsburgh, PA, November 2018.

8. J. A. Malen, "How heat is transported in organic-inorganic hybrid materials including superatom crystals and

many others," Lawrence Livermore National Laboratory, March 15, 2017. ?

9. J. A. Malen, "Heat Transport: From organic-inorganic hybrid materials to high powered electronics," Northrop Grumman Next, Redondo Beach, CA, October 5, 2017

The following seminars Acknowledging ARO support were given by Xavier Roy:
1. Colorado State University- Department of Chemistry (1/24/2020)
2. University of Oregon- Department of Chemistry (11/22/19)
3. University of Pennsylvania – Department of Chemistry (4/9/19)
4. Stanford University – Department of Chemistry (4/4/19)
5. Rutgers State University – Department of Chemistry (3/12/19)
6. University of California, San Diego – Department of Chemistry (2/21/19)
7. Massachusetts Institute of Technology – Department of Chemistry (2/13/19)
8. University of Maryland – Department of Chemistry (2/7/19)
9. University of Montreal, Canada – Department of Chemistry (10/29/18)
10. Concordia University, Canada – Department of Chemistry (10/26/18)
11. New York University – Department of Chemistry (10/5/18)
12. Harvard University – Department of Chemistry (4/30/18)
13. Hamilton College – Department of Chemistry (4/20/2018)
14. Carnegie Mellon University – Department of Chemistry (4/5/2018)
15. ACS National Meeting, New Orleans (3/20/2018)
16. University of California, Santa Barbara – Department of Chemistry (12/8/2017)
17. University of California, Los Angeles – Department of Chemistry (12/6/2017)
18. California Institute of Technology – Department of Chemistry (12/4/2017)
19. University of California, Riverside – Department of Chemistry (12/1/2017)
20. Simon Fraser University – Department of Chemistry (11/16/2017)
21. University of British Columbia – Department of Chemistry (11/15/2017)
22. University of Washington, Seattle – Department of Chemistry (11/14/2017)
23. Virginia Commonwealth University – Department of Physics (11/10/2017)
24. University of Chicago – Department of Chemistry (10/20/2017)
25. Northwestern University – Materials Research Science and Engineering Center (10/10/2017)
26. University of California, Berkeley – Department of Chemistry (10/6/2017)
27. Pennsylvania State University – Department of Chemistry (9/26/2017)
28. Georgia Institute of Technology – Department of Chemistry (9/19/2017)

The following seminars Acknowledging ARO support were given by Jonathan Malen:
(1) University of Santiago de Compostela, Department of Chemistry, January 18, 2019.
(2) Rice University, Department of Mechanical Engineering, November 7, 2018.
(3) University of Illinois Urbana-Champaign, Department of Mechanical Engineering, May 11, 2018.
(4) University of Virginia, Department of Mechanical Engineering, April 28, 2021
(5) University of California, Riverside, Department of Mechanical Engineering, May 13, 2021
(6) Notre Dame University, Department of Mechanical Engineering, September 21, 2021

The following seminars Acknowledging ARO support were given by Alan McGaughey:
(1) University of Virginia, Department of Mechanical and Aerospace Engineering, October, 2020
(2) Massachusetts Institute of Technology, MIT S3TEC Seminar Series, February 9, 2018.

Honors and Awards: 1. Xavier Roy won the NSF CAREER Award
2. Xavier Roy won the Lenfest Faculty Award
3. Jonathan Malen: Invitee: National Academy of Engineering's 2017 US Frontiers of Engineering Symposium
4. Jonathan Malen: Carnegie Mellon College of Engineering Benjamin Richard Teare Teaching Award
5. Alan McGaughey: Carnegie Mellon College of Engineering Philip L. Dowd Fellowship
6. Alan McGaughey: APS Fellow
7. Alan McGaughey: Trustee Professorship in Engineering, Carnegie Mellon University
8. Alan McGaughey: Viskantha Fellowship, Purdue University
9. Alan McGaughey: Invitational Fellowship for Research in Japan, Japan Society for the Promotion of Science

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Participant: Alexander Christodoulides
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Participant: Matthew Bartnof
Person Months Worked: 12.00 **Funding Support:**
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Participant Type: Graduate Student (research assistant)
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Person Months Worked: 12.00 **Funding Support:**
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Participant: Elena Meirzadeh
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Abstract: Atomically precise nanoscale clusters could assemble into crystalline ionic crystals akin to the atomic ionic solids through the strong electrostatic interactions between the constituent clusters. Here we show that, unlike atomic ionic solids, the electrostatic interactions between nanoscale clusters could be frustrated by using large clusters with long and flexible side-chains so that the ionic cluster pairs do not crystallize. As such, we report ionic superatomic materials that can be easily solution- processed into completely amorphous and homogeneous thin-films. These new amorphous superatomic materials show tunable compositions and new properties that are not achievable in crystals, including very high electrical conductivities of up to 300 S per meter, ultra low thermal conductivities of 0.05 W per meter per degree kelvin, and high optical transparency of up to 92%. We also demonstrate thin-film thermoelectrics with unoptimized ZT values of 0.02 based on the superatomic thin-film
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Abstract: Structural phase transitions run in families of crystalline solids. Perovskites, for example, feature a remarkable number of structural transformations that produce a wealth of exotic behaviors, including ferroelectricity, magnetoresistance, metal?insulator transitions and superconductivity. In superatomic crystals and other such materials assembled from programmable building blocks, phase transitions offer pathways to new properties that are both tunable and switchable. Here we describe [Co6Te8(PEt3)6][C70]2, a novel superatomic crystal with two separate phase transitions that drastically transform the collective material properties. A coupled structural-electronic phase transition triggers the emergence of a new electronic band in the fullerene sublattice of the crystal, increasing its electrical conductivity by 2 orders of magnitude, while narrowing its optical gap and increasing its spin density. Independently, an order?disorder transition transforms [Co6Te8(PEt3)6][C70]2 from a
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Keywords: superatomic crystal, superconductivity
Abstract: Superatomic crystals are composed of discrete modular clusters that emulate the role of atoms in traditional atomic solids1–4. Owing to their unique hierarchical structures, these materials are promising candidates to host exotic phenomena, such as superconductivity and magnetism that can be revealed through doping5–10. Low-dimensional superatomic crystals hold great promise as electronic components11,12, enabling these properties to be applied to nanocircuits, but the impact of doping in such compounds remains unexplored. Here we report the electrical transport properties of Re6Se8Cl2, a two-dimensional superatomic semiconductor13, 14. Using an in situ current annealing technique, we find that this compound can be n-doped through Cl dissociation, drastically altering the transport behaviour from semiconducting to metallic and giving rise to superconductivity below ~9 K. This work is the first example of superconductivity in a van der Waals (vdW) superatomic crystal; more broadly, it es
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Abstract: Superatomic crystals are composed of discrete modular clusters that emulate the role of atoms in traditional atomic solids. Owing to their unique hierarchical structures, these materials are promising candidates to host exotic phenomena, such as doping-induced superconductivity and magnetism. Low-dimensional superatomic crystals in particular hold great potential as electronic components in nanocircuits, but the impact of doping in such compounds remains unexplored. Here we report the electrical transport properties of Re6Se8Cl2, a two-dimensional superatomic semiconductor. We find that this compound can be n-doped in situ through Cl dissociation, drastically altering the transport behavior from semiconducting to metallic and giving rise to superconductivity with a critical temperature of ?8 K and upper critical field exceeding 30 T. This work is the first example of superconductivity in a van der Waals superatomic crystal; more broadly, it establishes a new chemical strategy to manipu
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Authors: Alexander D. Christodoulides, Peijun Guo , Lingyun Dai , Justin M. Hoffman , Xiaotong Li , Xiaobing Zuo
Keywords: thermal transport, methylammonium lead-iodide, 2D perovskites, layered materials, photovoltaics, optoelectronics.
Abstract: An emerging class of methylammonium lead iodide (MAPbI3)-based Ruddlesden–Popper (RP) phase perovskites, BA2MAn–1PbnI3n+1 (n = 1–7), exhibit enhanced stability to environmental conditions relative to MAPbI3, yet still degrade at elevated temperatures. We experimentally determine the thermal conductivities of these layered RP phases for n = 1–6, where n defines the number of repeated perovskite octahedra per layer. We measure thermal conductivities of 0.37 ± 0.13/0.12, 0.17 ± 0.08/0.07, 0.21 ± 0.05/0.04, and 0.19 ± 0.04/0.03 W/m·K in thin films of n = 1–4 and 0.08 ± 0.06/0.04, 0.06 ± 0.04/0.03, 0.06 ± 0.03/0.03, and 0.08 ± 0.07/0.04 W/m·K in single crystals of n = 3–6. With the exception of n = 1, these thermal conductivities are lower than the range of 0.34–0.50 W/m·K reported for single-crystal MAPbI3. Reduced-order lattice dynamics modeling suggests that the initially decreasing trend of thermal conductivity in similarly oriented perovskites with increasing n may result from the tran
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nature Communications
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1038/s41467-020-17822-0
Volume: 11 Issue: First Page #: 4010
Date Submitted: 1/25/21 12:00AM Date Published: 8/11/20 4:00AM
Publication Location:
Article Title: Observation of reduced thermal conductivity in a metal-organic framework due to the presence of adsorbates
Authors: Hasan Babaei, Mallory E. DeCoster, Minyoung Jeong, Zeinab M. Hassan, Timur Islamoglu, Helmut Bau
Keywords: metal-organic framework, MOF, thermal conductivity
Abstract: The thermal conductivity of fullerene-based superatomic crystals (SACs) is investigated using molecular dynamics simulations. The temperature-dependent predictions agree with the trends of previous measurements. The thermal conductivity behavior emerges as a result of the C60 molecule rotational dynamics and orientation, which are quantified using the root mean square displacements of the carbon atoms and the relative orientations of the C60s. At low temperatures, the C60s exhibit small rotations around equilibrium positions (i.e., librations). When the librating C60s are orientationally-ordered, as in the [C60] and [Co6Se8(PEt3)6][C60]2 SACs, thermal conductivity decreases with increasing temperature, as is typical for a crystal. When the librating C60s are orientationally-disordered, however, as in the [Co6Te8(PEt3)6][C60]2 SAC, thermal conductivity is lower and temperature independent, as is typical for an amorphous solid. At higher temperatures, where the C60s in all three SACs fre
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RPPR Final Report
as of 13-Jan-2022

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Applied Materials and Interfaces
Publication Identifier Type: DOI Publication Identifier: https://doi.org/10.1021/acsami.0c06953
Volume: 12 Issue: 30 First Page #: 34317
Date Submitted: 1/25/21 12:00AM Date Published: 7/1/20 4:00AM
Publication Location:
Article Title: Enhancing Thermal Interface Conductance to Graphene Using Ni-Pd Alloy Contacts
Authors: Dipanjan Saha, Xiaoxiao Yu, Yanhao Du, Zhitao Guo, Feng Xiong, Andrew Gellman, Jonathan A Malen
Keywords: 2D materials, thermoreflectance, alloy thin films, spinodal decomposition, miscibility gap, TEM images
Abstract: The thermal conductivity of fullerene-based superatomic crystals (SACs) is investigated using molecular dynamics simulations. The temperature-dependent predictions agree with the trends of previous measurements. The thermal conductivity behavior emerges as a result of the C60 molecule rotational dynamics and orientation, which are quantified using the root mean square displacements of the carbon atoms and the relative orientations of the C60s. At low temperatures, the C60s exhibit small rotations around equilibrium positions (i.e., librations). When the librating C60s are orientationally-ordered, as in the [C60] and [Co6Se8(PEt3)6][C60]2 SACs, thermal conductivity decreases with increasing temperature, as is typical for a crystal. When the librating C60s are orientationally-disordered, however, as in the [Co6Te8(PEt3)6][C60]2 SAC, thermal conductivity is lower and temperature independent, as is typical for an amorphous solid. At higher temperatures, where the C60s in all three SACs fre
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Nanoscale Horizons
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0NH00358A
Volume: 5 Issue: First Page #: 1524
Date Submitted: 1/25/21 12:00AM Date Published: 9/4/20 4:00AM
Publication Location:
Article Title: Fullerene rotational dynamics generate disordered configurations that suppress thermal conductivity in superatomic crystals
Authors: Qi Liang, Matthew Bartnof, Ya-Ling He, Jonathan A. Malen, and Alan J. H. McGaughey
Keywords: superatomic crystal, libration, rotational dynamics, thermal conductivity
Abstract: The thermal conductivity of fullerene-based superatomic crystals (SACs) is investigated using molecular dynamics simulations. The temperature-dependent predictions agree with the trends of previous measurements. The thermal conductivity behavior emerges as a result of the C60 molecule rotational dynamics and orientation, which are quantified using the root mean square displacements of the carbon atoms and the relative orientations of the C60s. At low temperatures, the C60s exhibit small rotations around equilibrium positions (i.e., librations). When the librating C60s are orientationally-ordered, as in the [C60] and [Co6Se8(PEt3)6][C60]2 SACs, thermal conductivity decreases with increasing temperature, as is typical for a crystal. When the librating C60s are orientationally-disordered, however, as in the [Co6Te8(PEt3)6][C60]2 SAC, thermal conductivity is lower and temperature independent, as is typical for an amorphous solid. At higher temperatures, where the C60s in all three SACs fre
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.0c11674
Volume: 143 Issue: 1 First Page #: 109
Date Submitted: 1/25/21 12:00AM Date Published: 12/24/20 5:00AM
Publication Location:
Article Title: Polytypism, Anisotropic Transport, and Weyl Nodes in the van der Waals Metal TaFeTe
Authors: Ren A. Wiscons, Yeongsu Cho, Sae Young Han, Avalon H. Dismukes, Elena Meirzadeh, Colin Nuckolls
Keywords: Band structure,Crystal structure,Magnetic properties,Charge transport,Electrical transport
Abstract: The thermal conductivity of fullerene-based superatomic crystals (SACs) is investigated using molecular dynamics simulations. The temperature-dependent predictions agree with the trends of previous measurements. The thermal conductivity behavior emerges as a result of the C60 molecule rotational dynamics and orientation, which are quantified using the root mean square displacements of the carbon atoms and the relative orientations of the C60s. At low temperatures, the C60s exhibit small rotations around equilibrium positions (i.e., librations). When the librating C60s are orientationally-ordered, as in the [C60] and [Co6Se8(PEt3) 6][C60]2 SACs, thermal conductivity decreases with increasing temperature, as is typical for a crystal. When the librating C60s are orientationally-disordered, however, as in the [Co6Te8(PEt3)6][C60]2 SAC, thermal conductivity is lower and temperature independent, as is typical for an amorphous solid. At higher temperatures, where the C60s in all three SACs fre
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Journal: Nature Materials
Publication Identifier Type: DOI Publication Identifier: 10.1038/s41563-021-00934-3
Volume: 20 Issue: 8 First Page #: 1142
Date Submitted: 10/20/21 12:00AM Date Published: 3/1/21 5:00AM
Publication Location:
Article Title: Thermally conductive ultra-low-k dielectric layers based on two-dimensional covalent organic frameworks
Authors: Austin M. Evans, Ashutosh Giri, Vinod K. Sangwan, Sangni Xun, Matthew Bartnof, Carlos G. Torres-Cas
Keywords: phonon
Abstract: As the features of microprocessors are miniaturized, low-dielectric-constant (low-k) materials are necessary to limit electronic crosstalk, charge build-up, and signal propagation delay. However, all known low-k dielectrics exhibit low thermal conductivities, which complicate heat dissipation in high-power-density chips. Two-dimensional (2D) covalent organic frameworks (COFs) combine immense permanent porosities, which lead to low dielectric permittivities, and periodic layered structures, which grant relatively high thermal conductivities. However, conventional synthetic routes produce 2D COFs that are unsuitable for the evaluation of these properties and integration into devices. Here, we report the fabrication of high-quality COF thin films, which enable thermoreflectance and impedance spectroscopy measurements. These measurements reveal that 2D COFs have high thermal conductivities (1?W?m?1 K?1) with ultra-low dielectric permittivities (k?=?1.6). These results show that oriented, l
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Volume: 13 Issue: 6 First Page #: 607
Date Submitted: 10/26/21 12:00AM Date Published: 4/1/21 8:00AM
Publication Location:
Article Title: Superatomic solid solutions
Authors: Jingjing Yang, Jake C. Russell, Songsheng Tao, Martina Lessio, Feifan Wang, Alaina C. Hartnett, Samu
Keywords: superatom
Abstract: In atomic solids, substitutional doping of atoms into the lattice of a material to form solid solutions is one of the most powerful approaches to modulating its properties and has led to the discovery of various metal alloys and semiconductors. Herein we have prepared solid solutions in hierarchical solids that are built from atomically precise clusters. Two geometrically similar metal chalcogenide clusters, Co6Se8(PEt3)6 and Cr6Te8 (PEt3)6, were combined as random substitutional mixture, in three different ratios, in a crystal lattice together with fullerenes. This does not alter the underlying crystalline structure of the [cluster][C60]2 material, but it influences its electronic and magnetic properties. All three solid solutions showed increased electrical conductivities compared with either the Co- or Cr-based parent material, substantially so for two of the Co:Cr ratios (up to 100-fold), and lowered activation barriers for electron transport. We attribute this to the existence of a
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Journal: Journal of the American Chemical Society
Publication Identifier Type: DOI Publication Identifier: 10.1021/jacs.0c04321
Volume: 142 Issue: 28 First Page #: 11993
Date Submitted: 10/26/21 12:00AM Date Published: 6/1/20 4:00AM
Publication Location:
Article Title: Shape Matching in Superatom Chemistry and Assembly
Authors: Jingjing Yang, Feifan Wang, Jake C. Russell, Taylor J. Hochuli, Xavier Roy, Michael L. Steigerwald, Xia
Keywords: superatom
Abstract: Creating structures with superatomic nanoclusters rather than atoms offers the possibility of new hierarchical solids with collective properties. The variability of chemical compositions, sizes, and shapes of these superatomic building blocks provides great opportunities to access unknown assemblies. Herein we explore this concept by using geometrically anisotropic superatomic nanoclusters as building blocks. We reveal a series of novel superatomic architectures that are built from rod-shaped Co12Se16(PEt3)10 and C140 nanoclusters. More importantly, these assemblies show nonclose packings that afford voids to accommodate solvent molecules as a result of the shape anisotropy of the constituent building blocks. These intercalated small molecules act as “crystal modulators” to modulate the solid-state structures and properties. As a result, we are able to tune the crystal packings and optical gaps of the solids and see the moment when electrical conduction is “turned on”. Our results demo
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Acknowledged Federal Support: **Y**

Partners

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Colin Nuckolls (Columbia University), Richard Schaller (Argonne National Lab), Peijun Guo (Yale University), Patricl

I certify that the information in the report is complete and accurate:
Signature: Jonathan A Malen
Signature Date: 1/11/22 6:17PM

W911NF1710397 : Physical Behavior of Layered Superatomic Crystals

Reporting Period: SEP 30, 2017 to JUN 29, 2021

Date Received:

Submitter: Jonathan Malen

Distribution Statement: Approved for public release; distribution is unlimited.

Major Goals

In this project, we will focus on a family of layered superatomic crystals (SACs) assembled from two-dimensional (2D) sheets of metal chalcogenide superatoms and fullerenes (e.g. C60s and C70s). We will study how structure of the layers can integrate with orientational disorder to predictably tune material properties for Army-relevant applications such as infrared (IR) detection, thermoelectric and pyroelectric energy conversion, and thermal switching. Goals include: (1) Synthesis of new layered SACs, (2) measurement of thermal transport properties in new layered SACs, and (3) simulation of thermal transport properties in new layered SACs. Due to the similarity in samples and experimental tools we have also considered layered perovskites, metal organic frameworks, covalent organic frameworks, and layered van der waals metals such as TaFeTe4.

Accomplishments Under Goals

Accomplishments under the Major Goals are described in terms of the relevant publications that reference ARO support and have been released to the scientific community. These have been uploaded at the “Products” tab. (1) Synthesis of new layered SACs. As part of this project new SACs were synthesized as described in the articles "Spontaneous Electronic Band Formation and Switchable Behaviors in a Phase-Rich Superatomic Crystal" (JACS, 2018), "Solution-Processable Superatomic Thin-Films" (JACS, 2019), “Doping-induced superconductivity in the van der Waals superatomic crystal Re6Se8Cl2” (Nano Letters 2020), and “Polytypism, Anisotropic Transport and Weyl Nodes in the van der Waals Material TaFeTe4” (JACS, 2021).

(2) Measurement of thermal transport properties in new layered SACs. As part of this project novel measurements of the thermal transport properties of layered SACs are described in "Spontaneous Electronic Band Formation and Switchable Behaviors in a Phase-Rich Superatomic Crystal" (JACS, 2018), "Solution-Processable Superatomic Thin-Films" (JACS, 2019), and “Doping-induced superconductivity in the van der Waals superatomic crystal Re6Se8Cl2” (Nano Letters 2020). Novel measurements on related materials using methods developed by this project are described in “Observation of reduced thermal conductivity in a metal-organic framework due to the presence of adsorbates” (Nature Comms, 2020), “Signatures of Coherent Phonon Transport in Ultralow Thermal Conductivity Two-Dimensional Ruddlesden–Popper Phase Perovskites” (ACS Nano, 2021), and “Thermally conductive ultra-low -k dielectric layers based on two-dimensional covalent organic frameworks” (Nature Materials, 2021).

(3) Simulation of thermal transport properties in new layered SACs. As part of this project novel simulations of thermal transport in SACs are described in “Fullerene rotational dynamics generate disordered configurations that suppress thermal conductivity in superatomic crystals” (Nanoscale Horizons, 2020).

Plans Next Period

Results Dissemination

Journal Articles (1) E. S. O'Brien, J. C. Russell, M. Bartnof, A. D. Christodoulides, K. Lee, J. A. DeGayner, D. W. Paley, A. J. H. McGaughey, W. L. Ong, J. A. Malen, X-Y. Zhu, X. Roy, Spontaneous Electronic Band Formation and Switchable Behaviors in a Phase-Rich Superatomic Crystal, Journal of the American Chemical Society 140 (46), 15601 (2018). (2) J. Yang, B. Zhang, A. D. Christodoulides, Q. Xu, A. Zangiabadi, S. R. Peurifoy, C. K. McGinn, L. Dai, E. Meirzadeh, X. Roy, M. L. Steigerwald, I. Kymissis, J. A. Malen, C. Nuckolls, Solution Processible Superatomic Thin-Films, Journal of the American Chemical Society, 141 (28), 10967 (2019). (3) E. J. Telford, J. C. Russell, J. R. Swann, B. Fowler, X. Wang, K. Lee, A. Zangiabadi, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Batail, X. Zhu, J. A. Malen, C. R. Dean, X. Roy, Doping-induced superconductivity in the van der Waals superatomic crystal Re6Se8Cl2. Nano Letters, 20 (3), 1718-1724 (2020) (4) Q. Liang, M. Bartnof, Y.-L. He, J. A. Malen, and A. J. H. McGaughey, Fullerene rotational dynamics generate disordered configurations that suppress thermal conductivity in superatomic crystals. Nanoscale Horizons 5, 1524-1529 (2020). DOI: 10.1039/D0NH00358A (5) H Babaei, ME DeCoster, M Jeong, ZM Hassan, T Islamoglu, H Baumgart, AJH McGaughey, E Redel, OK Farha, PE Hopkins, JA Malen, CE Wilmer, Observation of reduced thermal conductivity in a metal-organic framework due to the presence of adsorbates, Nature communications 11 (1), 1-8 (2020) (6) D Saha, X Yu, Y Du, Z Guo, F Xiong, AJ Gellman, JA Malen, Enhancing Thermal Interface Conductance to Graphene Using Ni–Pd Alloy Contacts, ACS Applied Materials & Interfaces 12 (30), 34317-34322 (2020) (7) R. A. Wiscons, Y. Cho, S. Y. Han, A. H. Dismukes, E. Meirzadeh, C. Nuckolls, T. C. Berkelbach, X. Roy, "Polytypism, Anisotropic Transport and Weyl Nodes in the van der Waals Material TaFeTe4, Journal of the American Chemical Society 143, 1, 109–113 (2021) (8) A. D. Christodoulides, P. Guo, L. Dai, J. M. Hoffman, X. Li, X. Zuo, D. Rosenmann, A. Brumberg, M. G. Kanatzidis, R. D. Schaller, J. A. Malen, Signatures of Coherent Phonon Transport in Ultralow Thermal Conductivity Two-Dimensional Ruddlesden–Popper Phase Perovskites. ACS Nano. 15, 4165–4172 (2021). (9) A. M. Evans, A. Giri, V. K. Sangwan, S. Xun, M. Bartnof, C. G. Torres-Castanedo, H. B. Balch, M. S. Rahn, N. P. Bradshaw, E. Vitaku, D. W. Burke, H. Li, M. J. Bedzyk, F. Wang, J.-L. Brédas, J. A. Malen, A. J. H. McGaughey, M. C. Hersam, W. R. Dichtel, P. E. Hopkins, Thermally conductive ultra-low -k dielectric layers based on two-dimensional covalent organic frameworks. Nature Materials, 1–7 (2021). (10) J. Yang, J. C. Russell, S. Tao, M. Lessio, F. Wang, S. R. Peurifoy, A. C. Hartnett, E. A. Doud, E.S. O'Brien, N. Gadjieva, X.-Y Zhu, D. R. Reichman, A. C. Crowther, S. J. L. Billinge, X. Roy, M. L. Steigerwald, and C. Nuckolls, "Superatomic Solid Solutions", Nature Chem. 2021, 13, 607-613. (11) J. Yang, F. Wang, F. C. Russell, T. Hochuli, X. Roy, M. Steigerwald, X.-Y. Zhu, D. W. Paley, C. Nuckolls, "Shape Matching in Superatom Chemistry and Assembly", J. Am. Chem. Soc. 2020, 142, 11993-11998.

Conference Presentations 1. "Molecular Clusters: Building Blocks for Material Design", GRC on Atomically Precise Nanochemistry, Galveston TX (2/10/2020) 2. "Switchable Transport Behaviors in Phase Change Superatomic Crystals", ACS 2019, San Diego, CA (8/29/2019) 3. "Molecular Clusters as Electronic Circuit Elements", International Symposium on Clusters and Nanomaterials, Richmond, VA (11/7/2019)

4. "Thermal transport and fullerene dynamics in superatomic crystals." Alan McGaughey, Qi Liang, Wee Liat Ong, Matthew Bartnof, Ya-Ling He, Xavier Roy, Jon Malen. Invited talk given at MRS Spring 2021 Meeting, Seattle, WA, April 2021.

5. M. Bartnof, Q. Liang, and A. J. H. McGaughey, "Predicting Material Properties of Superatomic

Crystals using Molecular Dynamics Simulations." MRS 2019 Fall Meeting, Boston, MA, December 2019.

6. J. A. Malen, E. O'Brien, J. Russell, M. Bartnof, A. Christodoulides, K. Lee, D. Paley, A. J. H McGaughey, W.-L. Ong, X. Zhu, and X. Roy, "Orientational disorder controls the thermal conductivity of C_70 based superatomic crystals." MRS 2019 Spring Meeting, Phoenix, AZ, April 2019.

7. M. Bartnof, A. Christodoulides, W.-L. Ong, E. O'Brien, X. Roy, A. J. H. McGaughey, and J. A. Malen, "Fullerene-based Superatomic Crystals' Thermal Transport Controlled by Orientation Disorder." ASME 2018 IMECE, Pittsburgh, PA, November 2018.

8. J. A. Malen, "How heat is transported in organic-inorganic hybrid materials including superatom crystals and many others," Lawrence Livermore National Laboratory, March 15, 2017. ?

9. J. A. Malen, "Heat Transport: From organic-inorganic hybrid materials to high powered electronics," Northrop Grumman Next, Redondo Beach, CA, October 5, 2017

The following seminars Acknowledging ARO support were given by Xavier Roy: 1. Colorado State University- Department of Chemistry (1/24/2020) 2. University of Oregon- Department of Chemistry (11/22/19) 3. University of Pennsylvania – Department of Chemistry (4/9/19) 4. Stanford University – Department of Chemistry (4/4/19) 5. Rutgers State University – Department of Chemistry (3/12/19) 6. University of California, San Diego – Department of Chemistry (2/21/19) 7. Massachusetts Institute of Technology – Department of Chemistry (2/13/19) 8. University of Maryland – Department of Chemistry (2/7/19) 9. University of Montreal, Canada – Department of Chemistry (10/29/18) 10. Concordia University, Canada – Department of Chemistry (10/26/18) 11. New York University – Department of Chemistry (10/5/18) 12. Harvard University – Department of Chemistry (4/30/18) 13. Hamilton College – Department of Chemistry (4/20/2018) 14. Carnegie Mellon University – Department of Chemistry (4/5/2018) 15. ACS National Meeting, New Orleans (3/20/2018) 16. University of California, Santa Barbara – Department of Chemistry (12/8/2017) 17. University of California, Los Angeles – Department of Chemistry (12/6/2017) 18. California Institute of Technology – Department of Chemistry (12/4/2017) 19. University of California, Riverside – Department of Chemistry (12/1/2017) 20. Simon Fraser University – Department of Chemistry (11/16/2017) 21. University of British Columbia – Department of Chemistry (11/15/2017) 22. University of Washington, Seattle – Department of Chemistry (11/14/2017) 23. Virginia Commonwealth University – Department of Physics (11/10/2017) 24. University of Chicago – Department of Chemistry (10/20/2017) 25. Northwestern University – Materials Research Science and Engineering Center (10/10/2017) 26. University of California, Berkeley – Department of Chemistry (10/6/2017) 27. Pennsylvania State University – Department of Chemistry (9/26/2017) 28. Georgia Institute of Technology – Department of Chemistry (9/19/2017)

The following seminars Acknowledging ARO support were given by Jonathan Malen: (1) University of Santiago de Compostela, Department of Chemistry, January 18, 2019. (2) Rice University, Department of Mechanical Engineering, November 7, 2018. (3) University of Illinois Urbana-Champaign, Department of Mechanical Engineering, May 11, 2018. (4) University of Virginia, Department of Mechanical Engineering, April 28, 2021 (5) University of California, Riverside, Department of Mechanical Engineering, May 13, 2021 (6) Notre Dame University, Department of Mechanical Engineering, September 21, 2021 The following seminars Acknowledging ARO support were given by Alan McGaughey: (1) University of Virginia, Department of Mechanical and Aerospace Engineering, October, 2020 (2) Massachusetts Institute of Technology, MIT S3TEC Seminar Series, February 9, 2018.

Honors and Awards

1. Xavier Roy won the NSF CAREER Award 2. Xavier Roy won the Lenfest Faculty Award 3. Jonathan Malen: Invitee: National Academy of Engineering's 2017 US Frontiers of Engineering Symposium 4. Jonathan Malen: Carnegie Mellon College of Engineering Benjamin Richard Teare Teaching Award 5. Alan McGaughey: Carnegie Mellon College of Engineering Philip L. Dowd Fellowship 6. Alan McGaughey: APS Fellow 7. Alan McGaughey: Trustee Professorship in Engineering, Carnegie Mellon University 8. Alan McGaughey: Viskantha Fellowship, Purdue University 9. Alan McGaughey: Invitational Fellowship for Research in Japan, Japan Society for the Promotion of Science

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Training Opportunities

A Columbia postdoctoral fellow, Elena Meirzadeh, has developed synthesis protocols for several layered superatomic crystals including Re6Se8Cl2, Ta4S9Br8, Mo6S3Br6, and CoTeC70. Another Columbia postdoctoral fellow worked on studying the transport properties of superatomic superconductor Re6Se8Cl2. The Columbia work was performed with the help of fellowshipped student Avalon Dismukes and Jake Russell. Another Columbia postdoctoral fellow, Jingjing Yang has developed synthesis protocols for superatomic crystal thin films based on PCBM rather than C60. Their synthetic work creates the materials for property measurements at CMU.

Two graduate students at Carnegie Mellon have made significant contributions to this project. Alex Christodoulides and Matthew Bartnof learned nanofabrication skills, low temperature and low pressure techniques, and frequency domain thermoreflectance in support of the C70 SAC, PCBM SAC film, MOF, COF, and perovskite measurement. Matthew has also performed molecular dynamics simulations on C60 based superatomic crystals and covalent organic networks. A third CMU PhD student, Xiaoman Wang, performed ANSYS simulations to assess temperature in the superconductive superatomic crystals Re6Se8Cl2.

Technology Transfer

Nothing to Report

Participants

Name	Role	Person Months
McGaughey, Alan	Co PD/PI	3
Roy, Xavier	Co PD/PI	2
Bartnof, Matthew	Graduate Student (research assistant)	12
Christodoulides, Alexander	Graduate Student (research assistant)	15
Liang, Qi	Graduate Student (research assistant)	12
Malen, Jonathan	PD/PI	3
Meirzadeh, Elena	Postdoctoral (scholar, fellow or other postdoctoral position)	15

Telford, Evan	Postdoctoral (scholar, fellow or other postdoctoral position)	12