GA

# ATOMISTIC MODELING OF TRANSFORMATIONS IN NANOCRYSTALS

**Allocation:** Exploratory/30 Kwh
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## EXECUTIVE SUMMARY

Discovery of materials drives renewable energy and optoelectronic technologies. While using an unconventional method of nanostructure synthesis in our lab, we encountered a novel form of mercury–cadmium selenide. The wurtzite structure of this crystal distinguishes it from the natural zincblende phase. The properties of the material were unknown, motivating our computational investigations of its electronic structure. These computations revealed how subtle differences in crystallographic symmetry combine with the relativistic nature of electrons to result in novel behavior. Natural mercury selenide is a zero-band-gap semimetal. However, the wurtzite form has a band gap and is a three-dimensional topological insulator, expected to exhibit spin-protected conduction on the surface, while being electrically insulating in the bulk, a property useful for next-generation logic devices and the discovery of exotic quasi-particles. The study also elucidates how crystal structure and chemical composition can be paired to tune relativistic effects and topology of electron motion.

## RESEARCH CHALLENGE

Engineered nanocrystals are often utilized for making new functional electronic and optical materials such as superionic solids and battery electrodes. Our laboratory makes use of unconventional methods that enable manipulation of the chemical composition and crystal structure of nanocrystals. These techniques often produce novel compositions and crystal phases that are often not found in the bulk phase diagram. Computational electronic structure investigations are allowing us to explore the properties of these new, unconventional materials that have been created for the first time. Alongside, we are also elucidating chemical trends in heterostructures and alloys and developing solid-state physics principles from these trends. The results from our investigations will enable the rational design of new phases and compositions with targeted applications for resolving longstanding challenges of energy storage and device efficiency.

With advances in nanotechnology and chemical synthesis, materials are becoming ever more complex. Computations can uncover chemical principles that will ultimately allow prediction of the properties of tomorrow's indispensable materials, an existing Grand Challenge. However, these studies require extensive calculation spanning a range of physicochemical parameters. As opposed to a single large and expensive calculation, our work requires a library of moderately expensive calculations. The net cost for generating such a library of data is feasible only with a resource such as Blue Waters, with considerable payoff for future scientific advances. Dissemination of solid-state physics principles, like those resulting from our project, will accelerate the discovery and design of new materials through systematic exploration, supplanting time- and energy-consuming trial-and-error pursuits.

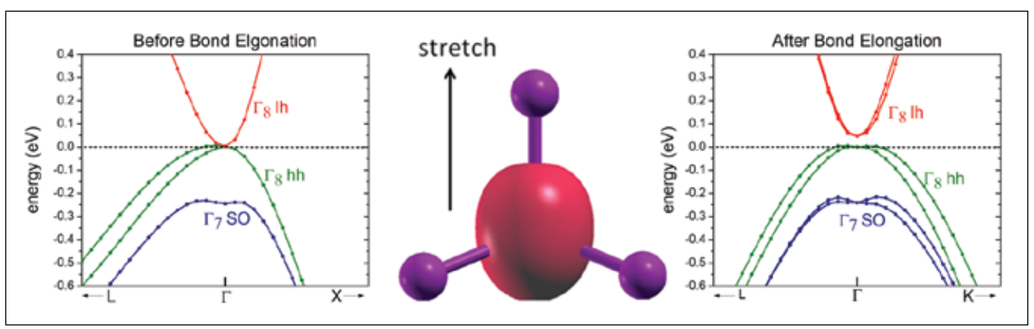


Figure 1: In the novel wurtzite form of HgSe, uniaxial elongation of Hg–Se bonds results in the opening of a band gap between the highest energy valence (green curve) and lowest energy conduction (red curve) bands. Hg atoms are shown in purple and the electron density is shown in red.



## METHODS & CODES

We used the open source Quantum Espresso software suite [1] to run our electronic structure calculations. In order to study the effects of chemical composition and structure on the alloy's electronic properties, numerous calculations were run. Each calculation is distinguished from the others in the crystal geometry, chemical formula, or both. Comparisons of energies, electron distribution, and band structure across all the calculations allowed us to make predictions about novel behavior of the wurtzite polymorph of the alloy and also understand the role of relativistic effects and symmetry breaking.

## RESULTS & IMPACT

Our electronic structure calculations demonstrated that bond elongation in a novel polymorph of HgSe and $Hg_xCd_{1-x}Se$ alloys is responsible for the opening of a band gap (Fig. 1). The presence of this band gap is of significance because it, when combined with the inverted nature of bands in HgSe, qualifies these materials as potential three-dimensional (3D) topological insulators (TIs). 3D TIs are of interest because electrons at their surface states are spin-protected from back scattering. This protection allows 3D TI materials to conduct electrons along their surface without resistance, that is, with minimal loss of energy as wasteful heat. For this reason, 3D TIs are garnering interest as components of energy-efficient logic devices that can operate at high capacity while simultaneously not contributing to the generation of heat. Such devices would reduce the need for coolants and could permit the design of more powerful supercomputers by overcoming problems caused by overheating. TI materials are also expected to harbor exotic quasi-particle states of importance in particle physics. However, only a handful of TI materials have been identified, and through our contribution we are adding this alloy system to the list of 3D TIs. In addition, our work unveils crystallographic anisotropy as a powerful synthetic handle for tuning band topology.

Our study further contributed two new principles governing band structure and topology in $Hg_xCd_{1-x}Se$ and similar alloys of a strongly relativistic and a weakly relativistic metal. The first of these new insights involves the effect of mixing electron character (Fig. 2a–2c). HgSe and CdSe have different energy ordering of their bands; the band order is inverted in HgSe with respect to the conventional CdSe case. This inversion is due to the greater relativistic mass of the Hg valence "s" electrons resulting in the contraction and energetic downshift of their orbitals. Thus, in $Hg_xCd_{1-x}Se$ alloys, wherein the electronic character of the two metals is mixed, the energy of the "s"-like band, the resulting band ordering, and the band gap depend on the relative abundance of Hg and Cd. At compositions of the wurtzite alloy, where the "s"-like band of spherical symmetry becomes close to the valence band edge, the light hole and heavy hole energies become less sensitive to crystallographic anisotropy. As a result, a smaller gap is exhibited between these two bands, negating the effect of the symmetry breaking caused by crystalline anisotropy. The second finding relates to the effect of a layered structure of the crystal (Fig. 2d). Ordering of the two metals $Hg^{2+}$ and $Cd^{2+}$ in alternate layers mimics the effect of crystallographic anisotropy and provides a second means by which a band gap can be opened. These principals gained from our study translate readily to existing TI systems and also enable the design of new alloys with TI behavior.

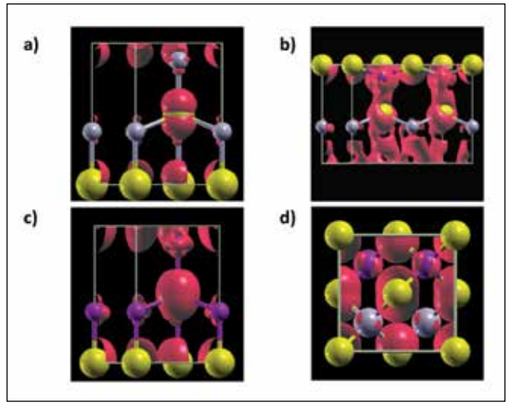


Figure 2: Electron density (red) maps elucidating trends in $Hg_xCd_{1-x}Se$ (Hg, purple; Cd: grey; Se: yellow). Unlike CdSe (a) and HgSe (c), alloys (b) show significant mixing of the states, which weakens the effect of bond elongation. (d) Creation of alternating Cd and Hg layers has a similar effect as bond elongation.

## WHY BLUE WATERS

Calculations of crystal surfaces and nanocrystals may be accomplished on computational resources other than Blue Waters. However, a large number of single calculations of these structures with varying elemental composition is required to study chemical trends. The computational expense of such an effort would be prohibitive for us were it not for a Blue Waters allocation. Furthermore, the specialized hardware of Blue Waters allows the Quantum Espresso code to run even more efficiently. This is because Quantum Espresso's parallelization schemes involve sizable and frequent communication among CPUs, which rely on the speed of the Blue Waters communication hardware. Furthermore, our ability to work with Sudhakar Pamidighantam of NCSA as a co-PI has allowed us to greatly expedite code preparation and troubleshooting with use of the SeaGrid portal [2].

## PUBLICATIONS AND DATA SETS

Dumett Torres, D., P. Banerjee, S. Pamidighantam, and P. K. Jain, A Non-Natural Wurtzite Polymorph of HgSe: A Potential 3D Topological Insulator, submitted to *Chem. Mater* (2017).