A NOVEL CRYSTAL STRUCTURE WITH SPIN-PROTECTED SURFACE ELECTRONIC CONDUCTION

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Allocation: Illinois/40 Knh
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EXECUTIVE SUMMARY

Newly discovered nanostructures can fill the need for materials in energy and optoelectronic technologies. Using a kinetically driven method of nanostructure synthesis, the research team accesses novel crystal structures of ionic semiconductors.

For example, the group synthesized mercury selenide (HgSe) nanocrystals with a wurtzite structure quite unlike the natural zincblende form. The scientists computed the bulk band structure of the wurtzite form, which showed a finite band-gap and band inversion—prerequisites for a 3D topological insulator (TI) property. To determine if wurtzite HgSe is indeed a 3D TI, the team needed to elucidate the surface electronic structure. Using the current allocation, the researchers determined band structures of wurtzite HgSe slabs with specific surface facets. These computations showed the spin-protected nature of surface states in wurtzite HgSe, allowing its conclusive designation as a 3D TI. Spin-protection allows resistanceless electron transport along the surface. Thus, the newly discovered HgSe crystal structure can lead to logic devices capable of operating efficiently with minimal heat dissipation.

RESEARCH CHALLENGE

Engineered nanocrystals are often utilized for making new functional electronic and optical materials such as superionic solids and battery electrodes. The research team 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. Further, computational electronic structure investigations allow the researchers to explore the properties of these new, unconventional materials. In addition, the team is also elucidating chemical trends in heterostructures and alloys and developing solid-state principles from these trends. The results from these 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 calculations spanning a range of physicochemical parameters. As opposed to a single large and expensive calculation, this 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. When solid-state principles such as those resulting from this project become known, the rate at which new materials can be discovered or designed will be greatly expedited, because the community is no longer limited to a time- and energy-consuming trial-and-error approach.

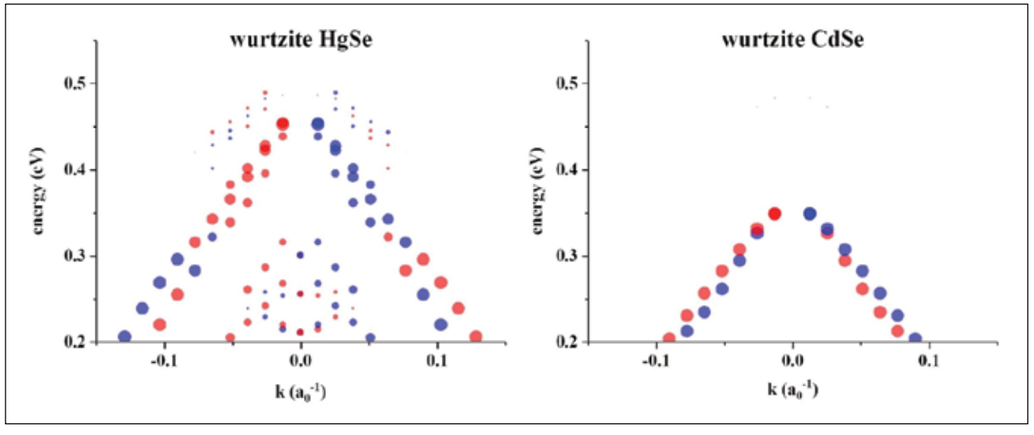

Figure 1: Calculated valence band structure of the (001) surface facet of a wurtzite HgSe (left) and CdSe (right) slab. Spins of opposite sign are distinguished by the color (red or blue). The size of the dots in the plot represents the electronic character contribution from the top (001) surface of the slab. The wurtzite HgSe surface band structure shows the presence of spin-protected surface states, as manifested by the states of opposite spin segregating on either side of the Γ-point (k = 0). In contrast, in wurtzite CdSe, such a demarcation is not seen between states of opposite spin.

METHODS & CODES

The research group used the open source Quantum Espresso software suite [1] to run density functional theory calculations of the electronic band structure. To study the effects of chemical composition, crystal structure, and crystallite size on the electronic properties, numerous calculations must be run. Each calculation is distinguished from the others by the crystal structure, chemical formula, or crystallite size. Through analysis of orbital energies, electronic character (orbital and spin), and band structures, the nature of surface electronic states and topology can be determined.

RESULTS & IMPACT

Prior electronic structure calculations by the research team demonstrated that bond elongation in a novel wurtzite polymorph of mercury selenide (HgSe) and mercury–cadmium selenide ($Hg_xCd_{1-x}Se$) is responsible for the opening of a band gap. Combined with the inverted band structure of HgSe, it was thought that these polymorphs would exhibit 3D topological insulator (TI) behavior [2]. Three-dimensional 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. For this reason, 3D TIs are of interest as components of energy-efficient logic devices that can operate at high capacity with minimal heat dissipation. While the team's past work suggested the possibility of the wurtzite phase being a 3D TI, a definitive conclusion was not possible without information on the surface electronic states.

Therefore, the researchers went beyond band structure calculations of bulk HgSe and CdSe crystals to slab geometries with well-defined exposed surface facets. As compared to electronic structure calculations of fully periodic bulk crystals, calculations of slab geometries are more expensive; but the latter system allows access to information of surface electronic states, which is missing in bulk crystal calculations.

The most recent spin-resolved calculations of the surface band structures of faceted slabs have shown the existence of spin-protected electronic states on a wurtzite HgSe surface (Fig. 1). Spin protection, however, is missing from analogous wurtzite CdSe surfaces. These calculations now provide a firm basis for designating wurtzite HgSe as a 3D TI material.

In addition, the research team performed all-atom calculations of nanocrystals. While computationally expensive, this work was undertaken to understand how crystallite size and nanoscale confinement influence surface electronic structure and topology. Unlike slab geometries, which are periodic in the *x* and *y* directions, the nanocrystal geometries are finite in all dimensions. Nanocrystals of wurtzite-structure HgSe and CdSe of different size (2 nm, 2.5 nm, and 3 nm) were studied. The team identified nanocrystal surface states based on the spatial character of the electronic states. This systematic set of calculations shows that surface states have a much richer character in these nanoscale-confined geometries as compared to that in the bulk.

WHY BLUE WATERS

Single calculations of a slab and even all-atom calculations of a nanocrystal may be accomplished using computational resources other than Blue Waters. However, a large number of single calculations of these geometries with varying elemental composition and crystal dimensions are required for the research team's study of size effects and chemical trends. The computational expense of such an effort would be prohibitive 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.

PUBLICATIONS & DATA SETS

D. D. Torres, P. Banerjee, S. Pamidighantam, and P. K. Jain, "A non-natural wurtzite polymorph of HgSe: A potential 3D topological insulator," *Chem. Mater.*, vol. 29, no. 15, pp. 6356–6366, 2017.

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