Vacancy ordering induced topological electronic transition in bulk Eu$_2$ZnSb$_2$

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Metal-semiconductor transitions from changes in edge chirality from zigzag to armchair were observed in many nanoribbon materials, especially those based on honeycomb lattices. Here, this is generalized to bulk complex Zintl semiconductors, exemplified by Eu$_2$ZnSb$_2$ where the Zn vacancy ordering plays an essential role. Five Eu$_2$ZnSb$_2$ structural models are proposed to guide transmission electron microscopy imaging. Zigzag vacancy ordering models show clear metallic behaviour, while the armchair models are semiconducting with indirect bandgaps that monotonously increase with the relative distances between neighboring ZnSb$_2$ chains. Topological electronic structure changes based on cation ordering in a Zintl compound point toward tunable and possibly switchable topological behavior, since cations in these are often mobile. Thus, their orderings can often be adjusted by temperature, minor alloying, and other approaches. We explain the electronic structure of an interesting thermoelectric and point the way to previously unidentified types of topological electronic transitions in Zintl compounds.

INTRODUCTION

The preparation and investigation of graphene (1) have led to important discoveries in layered materials, particularly the electronic and topological properties of honeycomb lattices and related two-dimensional (2D) materials. Graphene is a topological semimetal with Dirac cones at the K and K’ points of the 2D hexagonal Brillouin zone. Such 2D layered structures can be used as the basis for nanoribbons or other 1D nanostructures with properties that depend on the edge structures and symmetry. Two such structures for the honeycomb lattice were the armchair and zigzag types. An important observation was that there are frequently semiconductor-metal transitions depending on the edge shape chirality, especially between armchair and zigzag types (2–5). For example, armchair edge graphene nanoribbons presented semiconducting behavior while and zigzag type graphene nanoribbons were typically metallic in the absence of spin polarization (2, 3) and may become magnetic due to the instabilities of 1D metals (6, 7). Other examples were in layered transition-metal dichalcogenides for which zigzag nanoribbons may present metallic behavior, while the corresponding armchair nanoribbons are semiconducting, including prototypical examples of MoS$_2$ (5, 8), WS$_2$ (9), and WSe$_2$ (10). Similar behavior was found in BN, where bulk is semiconducting, as are passivated armchair nanoribbons, but passivated zigzag nanoribbons are metallic and magnetic (11). Here, we show that this edge-related behavior can also occur directly in bulk materials. Specifically, we show a bulk analogy in a complex Zintl phase compound with a nominally semiconducting composition, where the electronic behavior could be controlled by vacancy ordering.

Zintl phase compounds are of considerable interest as the thermoelectric (TE) materials for power generation and many other applications (12–17). The complex stoichiometry in these Zintl phase materials often leads to unusual bonding patterns, otherwise not typically associated with the elements. This is also associated with low thermal conductivity, while maintaining conductive networks (18). This makes these Zintl phases important TE materials. In particular, the Zn-Sb–based Zintl systems showed complicated structural behaviors as a result from their covalent bonding patterns and the overall constraints on electron counts (19, 20).

Among these Zintl phase compounds, there is a class of hexagonal layered compounds in which the polyanion substructure composed of planar or wrinkled or otherwise distorted honeycomb lattice layers. These included CaCuSb$_2$ (21), LiZnSb$_2$ (22), and AZn$_x$Sb$_2$ (A = Ca, Sr, Eu, and Yb) (23). There is also a recently found compound Eu$_2$ZnSb$_2$, which is reported to have a hexagonal structure (24) and can be modified to yield a high-performance TE material, with a respectable TE figure of merit $ZT = 1$ (25). Because of the Zintl electron counting rules, the compound has a stoichiometry that leaves half of the Zn sites in the honeycomb lattice empty. Similar patterned vacancy arrangements were also observed in Prussian blue analogs, where a very high diversity of vacancy networks is observed (26). Because of such intriguing structural and electronic complexity, the exact structures are not yet established, and consequently, the electronic structures, which underlie the high $ZT$ but depend on the crystal structure, are still unresolved.

On the basis of our electron microscopy imaging, we constructed five different Eu$_2$ZnSb$_2$ structural models to guide analysis of the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) results and their connection with electronic structure. These were different arrangements of Zn vacancies along two high symmetry directions in the ZnSb honeycomb layer, giving rise to three armchair-type models and two zigzag-type models. The electronic structures of these Eu$_2$ZnSb$_2$ vacancy ordering models were calculated using the first-principles density functional theory (DFT)–based methods including a Coulomb U for the localized Zn $d$ and Eu $f$ electrons (27, 28) and the modified Becke-Johnson potential for obtaining band structures (29). The metal-semiconductor...
transitions in the bulk Eu$_2$ZnSb$_2$ phase depended on the vacancy ordering, analogous to the different topological edge states for armchair and zigzag honeycomb lattice nanoribbons. Specifically, all the armchair-type Eu$_2$ZnSb$_2$ models were narrow bandgap semiconductors, while, conversely, the zigzag types were all metallic. In addition, we found that the bandgap of armchair-type monotonously increased with the relative distance between neighboring ZnSb$_2$ chains of the armchair type along the c axis, and, analogously, the extent of band overlapping near the Fermi level decreased as the relative distance of ZnSb$_2$ chains of zigzag type increased.

**RESULTS**

Eu$_2$ZnSb$_2$ forms a hexagonal lattice based on x-ray diffraction data (25), similar to the Bi alloy, Eu$_2$ZnSb$_{2-\delta}$Bi$_\delta$ (30). It may be viewed as being formed by removing the Zn sublattice atoms, namely, forming Zn vacancies, from the hypothetical EuZnSb. This hypothetical EuZnSb would have the space group $P6_3/mmc$ as in the ZrBeSi structure, consisting of the planar honeycomb Zn-Sb layers sandwiching the trigonal layers of Eu ions. Within the Zintl concept, Eu cations donate charge to the anionic Zn-Sb honeycomb sheets. These sheets must then have Zn vacancies to maintain the exact valence electron counts. The original crystal structure is maintained rather than forming reconstructed geometries as in Ba$_2$ZnSb$_2$ (31). From the point of view of TE performance, it is important to note that the structural complexity due to the large numbers of vacancies on the honeycomb sheets could efficiently scatter phonons, reducing the thermal conductivity and thus favoring high ZT values (25, 32–34). Moreover, the partially filled Zn sublattice can introduce additional complexity, since the Zn vacancies may not be fully random. We used the General Structure Analysis System (GSAS) program to check the structure and did Rietveld refinement based on X-ray diffraction (XRD) data and the initial structure and space group reported by Wilson and co-workers (24). The data show that our samples are in the same structure as previously reported. The Rietveld refinement shows that the Zn site has a higher mean square displacement than the other sites and that it has an occupancy very close to the expected value of 0.5 based on charge balance. We proceeded to use HAADF-STEM to elucidate the structural details related to the Zn vacancies.

The spherical aberration–corrected (Cs-corrected) HAADF-STEM images of Eu$_2$ZnSb$_2$ are shown in Fig. 1. We identified three kinds of HAADF-STEM patterns and all appeared over hundreds of square nanometers. The [100] crystal direction was chosen for observing the specific Zn vacancy patterns. The imaging contrast of HAADF-STEM was positively correlated with the atomic number (Z), approximately proportional to the 1.7 power of Z. Hence, the spots shown in HAADF-STEM from the brightest to the darkest were Eu (Z = 63), Sb (Z = 51), and Zn (Z = 30), respectively. Two possible Zn sites exist in one primitive cell. They were non-occupied, half occupied, and full occupied and clearly shown in the 10 times amplified images in the insets of Fig. 1 (A to C), respectively. In Fig. 1B, it was clear that only one Zn atom was found in each unit cell at a fixed site, indicating an alternating arrangement of the Zn-Sb layers and the Sb-only layers, namely, an alternating zinc vacancy distribution profile. Our DFT results (Fig. 2) give a metallic electronic structure for all these three models, which is in contrast with the experimental result (the experimental bandgap is 0.17 eV) (25). Therefore, here, we built five kinds of Zn-Sb chain models consistent with the actual stoichiometry. We note that some models had been constructed previously for Eu$_2$ZnSb$_{2-\delta}$Bi$_\delta$ alloys (30). These include the zigzag-stagger model and the structure shown in fig. S1 (cross-arrangement). The atomic projections along [1 0 0] crystal direction of these models is also in accord with one of the HAADF-STEM images (Fig. 1C).

The idea of model construction can be understood as follows. The pattern of the EuZnSb projected along [100] crystal direction is shown in Fig. 3A. Two highly symmetrical ZnSb$_2$ patterns on the ZnSb plane were presented in Fig. 3 (B and B’) for zigzag type and Fig. 3 (C and C’) for armchair type. In Fig. 3A, the Eu ions (pink balls) were located at the vertices of trigonal prisms, while Zn (gray balls) and Sb (brown balls) ions were alternated at the hollow sites. The Eu trigonal layer and ZnSb honeycomb layers alternated along the c axis, and the vacancies of neighboring ZnSb layer were ordered oppositely. In Fig. 3 (B to C’), the red solid lines highlight the geometrical

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**Fig. 1.** [1 0 0] HAADF-STEM images for Eu$_2$ZnSb$_2$, showing two possible Zn sites in one primitive cell. (A) Non-occupied, (B) half occupied (24), and (C) full occupied in two Zn sites. Eu, pink; Sb, brown; Zn, gray. Ten times magnification images are presented in the insets of (A), (B), and (C), respectively.

**Fig. 2.** Calculated band structures based on three possible structures in Eu$_2$ZnSb$_2$. (A) Non-occupied in the Zn sites and (A’) its band structure. (B) Half occupied in the Zn sites and (B’) its band structure. (C) Full occupied in the Zn sites and (C’) its band structure. Eu, pink; Sb, brown; Zn, gray; Zn void, white.
patterns, in particular, the zigzag or armchair character. The removed Zn atoms (Zn vacancies) are represented by white balls. As shown within the blue dashed boxes, the Zn voids are not readily distinguished because of the overlap of Zn atoms in this projection. In describing the structure, one may view the Eu cations as a framework that stabilizes the flat ZnSb honeycomb layers.

Here, we focus on the difference between the zigzag and armchair geometries, focusing on the parallel alignment cases (figs. S2C and S3C). Other possible arrangements are presented in the supporting information (figs. S1 to S3). These models follow the possible structures discussed by Bobev and co-workers (24). The armchair-overlap (A-overlap, Fig. 4A) and armchair stagger (A-stagger, Fig. 4C) have space group $Pmc_2_1$ (26), which is also noncentrosymmetric with space group $Pm$ (6), which is the symmetry of armchair 2 (A-drift, Fig. 4B) (see details in tables S1 and S2). The zigzag-overlap (Z-overlap, Fig. 5A) and zigzag-stagger (Z-stagger, Fig. 5B) structures have space group symmetry $Pmm2$ (25), which is noncentrosymmetric due to lack of mirror symmetry in the z direction. We find only very small changes in the lattice parameter after full structural relaxation of the models, consistent with the experiment. This supports the reasonableness of these models. The static energies and the energy differences of each type are listed in table S3, showing that the semiconducting armchair-type models have lower energy. The energy differences are small in the range of 0.1 eV per atom and below, which implies that the actual patterns may potentially be controlled by achievable chemical tuning and other conditions.

Our electronic structure calculations show that armchair types of Eu$_2$ZnSb$_2$ are semiconductors with indirect bandgaps and similar band structure characters. The fact that armchair structures especially
A-overlap and A-stagger are the lowest energy structures consistent with the observed TE behavior of the material. The valence band maxima are located at the $\Gamma$ point, while the conduction band minima are at the Y point. The valence band near the band edge consists of three nearby bands that have predominant Sb $p$-character. The bottom of the conduction band has two bands with degeneracy at the Y point. They have more Zn character.

In addition to analogous band shape, there are two trends among the armchair type of Eu$_2$ZnSb$_2$ structure. With increase of distance between the neighbor chains, the bandgaps increase. From A-overlap to A-stagger, they are 0.30, 0.38, and 0.43 eV, respectively. Also, with inclusion of spin-orbit coupling (SOC), the bandgaps are reduced. The values with SOC are 0.18, 0.17, and 0.31 eV, respectively. These structures remain semiconducting with SOC. The band structures with SOC are shown in fig. S4. There are also distortions of the bands, as seen particularly in shifts of the second conduction band minimum.

Zigzag-type ZnSb$_2$ chain models and corresponding electronic structures are given in Fig. 5. As in the case of the armchair types, zigzag-type structures can also be characterized by the nearest neighbor chain distance, leading in this case to two distinct models. The ZnSb$_2$ honeycomb structure can be seen at an angle after rotating $120^\circ$ and is consistent with the experimental results (fig. S2).

Both the zigzag-type models present metallic properties in the absence of spin orbit. There are band crossings and overlap, leading to a band inversion around the zone center in a range of roughly 0.1 eV of the Fermi level. The details again depend on the interaction along...
the $c$ axis and differ between the two cases. There are other differences as well depending on the relative positions of the chains. These are, for example, as seen near the $S$ point. However, the band inversion persists. Notably, the bands cross linearly, so that the charge transport is donor-dominated at $k_{\parallel}$ and acceptor-dominated at $k_{\perp}$, depending on the particular Zn order, specifically on whether one has zigzag or armchair $ZnSb_2$ substructures. This is important for the TE properties since bipolar conduction associated with insufficient bandgaps is detrimental to performance, in particular, by reducing the Seebeck coefficient (40). Such a metal-insulator distinction induced by the Zn vacancy ordering in the bulk phases share the same underlying physics as those well-known topological edge states in honeycomb-structured nanoribbons. The fact that these topological electronic structure changes are based on cation ordering in a Zintl compound points toward tunable and possibly switchable topological behavior. This is because cations in such compounds are typically mobile, and thus, their orderings can often be adjusted by temperature, minor alloying, intercalations and deintercalations, and other approaches.

**MATERIALS AND METHODS**

Europium (Eu, 99.99%, chunk), zinc (Zn, 99.999%, powder), and antimony (Sb, 99.999%, shot) were weighed according to the stoichiometry of $Eu_2ZnSb_2$. The raw materials were loaded into a stainless steel jar with stainless steel balls in an argon-filled glove box and then ball-milled with liquid nitrogen. This is generally suitable for these TE materials. Four specimens were prepared to ensure consistency. The microstructures were investigated by a C$_e$-corrected electron microscope (JEM-ARM200F).

DFT calculations were performed using the Vienna ab initio simulation package (VASP) (41, 42). We used the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE). (43) with the addition of on-site Coulomb $U$ terms as below for the structure relaxations. Projected augmented wave pseudopotentials were used with a cutoff energy of 500 eV. The Brillouin zone samplings for the supercell models, including final relaxations, were done with $8 \times 4 \times 4$ Monkhorst-Pack $k$-meshes for the zigzag type and $4 \times 4 \times 4$ meshes for the armchair type, following initial relaxations with coarser $k$-meshes. These meshes were checked by calculations for different choices. A convergence criterion of $10^{-5}$ eV was used in the self-consistent total energy calculations. Geometry optimization was performed by using the conjugate gradient method, with both the crystal structures and ionic positions fully relaxed until the Hellmann-Feynman forces on all ions were lower than $10^{-3}$ eV/Å.

The DFT + $U$ method with spin polarization was used to represent the localized nature of the Eu $f$ states ($U = 10$ eV) and Zn $d$ states ($U = 4$ eV) to obtain bandgaps. The combination of $U$ and spin polarization yields a fully polarized half-filled Eu $4f$ shell with $f$ states away from the band edges allowing analysis of the band structure. We find only modest spin splitting of the states at the band edges, at most 0.073 eV, and generally considerably less. The use of a Hubbard $U$ for Zn is to shift the occupied Zn $d$ states to higher binding energy. This is done to correct known self-interaction errors, as has been discussed in the case of ZnO, for example, (44, 45). The lower value of $U$ used here as compared to oxides is to reflect the better screening that can be expected in Zn-Sb compounds, which are more covalent than oxides. After the geometry optimizations were done, we performed additional modified Becke-Johnson potential calculations, in combination with DFT + $U$, for the band structures. This method generally provides semiconductor bandgaps in accord with experiment. The effects of SOC were investigated in the calculations. A high symmetry path was obtained by connecting the following points in the Brillouin zone of the orthorhombic system: $\Gamma (0, 0, 0)$, $X (0.5, 0, 0)$, $S (0.5, 0.5, 0)$, $Y (0.5, 0.5, 0.5)$, $\Gamma (0, 0, 0)$, $Z (0, 0, 0.5)$, $U (0.5, 0.5, 0.5)$, $R (0.5, 0.5, 0.5)$, $T (0.0, 0.5, 0.5)$, and $Z (0, 0, 0.5)$, using the Visualization for Electronic and Structural Analysis (VESTA) software (46).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/6/eabd6162/DC1

**REFERENCES AND NOTES**

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorenko, A. A. Firsov, Electric field effect in atomically thin carbon films, Science 306, 666–669 (2004).
13. Y.-W. Son, M. L. Cohen, S. G. Louie, Energy gaps in graphene nanoribbons. Phys. Rev. Lett. 97, 216803 (2006).

14. Y.-W. Son, M. L. Cohen, S. G. Louie, Half-metallic graphene nanoribbons. Nature 444, 347–349 (2006).

15. R.-L. Chu, G.-B. Liu, W. Yao, X. Xu, D. Xiao, C. Zhang, Spin-orbit-coupled quantum wires and Majorana fermions on zigzag edges of monolayer transition-metal dichalcogenides. Phys. Rev. B 89, 155317 (2014).

16. F. Ouyang, X. Ni, Z. Yang, Y. Chen, X. Zheng, X. Xiong, Effects of edge hydrogenation on structural stability, electronic, and magnetic properties of WS 2 nanoribbons. Appl. Phys. Lett. 114, 213107 (2015).

17. M. Shahbazizadeh, Linear giant Stark effect in WSe 2 nanoribbons. Physica B Condens. Matter 545, 159–166 (2018).

18. W. Chen, Y. Li, G. Yu, C.-Z. Li, S. B. Zhang, Z. Zhou, Z. Chen, Hydrogenation: A simple approach to realize semiconductor–metal–metal transition in boron nitride nanoribbons. J. Am. Chem. Soc. 132, 1699–1705 (2010).

19. S. M. Kauzlarich, S. R. Brown, G. J. Snyder, Zintl phases for thermoelectric devices. Dalton Trans., 2009–2107 (2007).

20. J. Shuai, J. Mao, S. Song, Q. Zhang, G. Chen, Z. Ren, Recent progress and future challenges on thermoelectric Zintl materials. Mater. Today Phys. 1, 74–95 (2017).

21. S.-J. Kim, M. G. Kanatzidis, A Unique Framework in BaGa 2 Sb 2: A new zintl phase with large tunnels. Inorg. Chem. 40, 3781–3785 (2001).

22. W. Liu, J. Hu, S. Zhang, M. Deng, C.-G. Han, Y. Liu, New trends, strategies and opportunities in thermoelectric materials: A perspective. Mater. Today Phys. 1, 50–60 (2017).

23. L. Liu, J. Mao, S. Peng, B. Zhou, W. Gao, J. Sui, Y. Pei, Z. Ren, Tellurium doped n-type Zintl Z 2 Sb, Sb 2 thermoelectric materials: Balance between carrier-scattering mechanism and bipolar effect. Mater. Today Phys. 2, 54–61 (2017).

24. T. Calleit, J.-P. Fleural, A. Borschhevsky, Preparation and thermoelectric properties of semiconducting ZnS 2, ZnS. J. Phys. Chem. Solids 58, 1119–1125 (1997).

25. H. Tamaki, H. K. Sato, T. Kanno, Isotropic conduction network and defect chemistry in Mg 1+y Sb 2+δ, based layered zintl compounds with high thermoelectric performance. Adv. Mater. 28, 10182–10187 (2016).

26. X. He, Y. Fu, D. J. Singh, L. Zhang, Stability, electronic structures and thermoelectric properties of binary Zn–Sb materials. J. Mater. Chem. C 4, 11305–11312 (2016).

27. G. J. Snyder, M. Christensen, E. Nishibori, T. Calleit, B. B. Iversen, Disordered zinc in ZnS 2, Sb 2 with phonon and glass–crystal-electronic thermoelectric properties. Nat. Mater. 3, 458–463 (2004).

28. J. Wang, X.-C. Liu, S.-Q. Xia, X.-T. Tao, Ca, RE-Ag 3 Sb [RE = La, Ce, Pr, Nd, Sm; 0 ≤ x ≤ 1; 0 ≤ y ≤ 1]: Interesting structural transformation and enhanced high-temperature thermoelectric performance. J. Am. Chem. Soc. 135, 11840–11848 (2013).

29. G. K. H. Madsen, Automated search for new thermoelectric materials: The case of LiZnSb. J. Am. Chem. Soc. 128, 12140–12146 (2006).

30. G. S. Pomrehn, A. Zevaklin, W. G. Zeier, A. van de Walle, G. J. Snyder, Defect-controlled electronic properties in A-Zn,Sb(Zintl phases. Angew. Chem. Int. Ed. 53, 3422–3426 (2014).

31. D. K. Wilson, B. Sarapov, S. Babov, Synthesis, crystal structures and properties of the Zintl phases SrZnP, SrZnSb, A 2ZnSb, and A 2ZnBi (A = Sr and Eu). Zeitschrift für anorganische und allgemeine Chemie 637, 2018–2025 (2011).

32. C. Chen, W. Xue, S. Li, Z. Zhang, X. Li, W. Wang, Y. Liu, J. Sui, X. Liu, F. Cao, Z. Ren, C.-W. Chu, Y. Wang, Q. Zhang, Zintl-phase E 2 ZnSb; A promising thermoelectric material with ultralow thermal conductivity. Proc. Natl. Acad. Sci. U.S.A. 116, 2831 (2019).

33. A. Simonov, T. De Baerdemaecker, H. L. B. Boström, M. L. R. Gómez, H. J. Gray, D. Chemysnych, A. Bosak, H.-B. Burgi, A. L. Goodwin, Hidden diversity of vacancy networks in Prussian blue analogues. Nature 578, 256–260 (2020).

34. V. I. Anisimov, F. Aryasetiawan, A. L. I. Lichtenstein, First-principles calculations of the electronic structure and spectra of strongly correlated systems: The LDA+U method. J. Phys. Condens. Matter. 7, 967 (1997).

35. A. I. Lichtenstein, V. I. Anisimov, I. Zaanen, Density-functional theory and strong interactions: Orbital ordering in Mott-Hubbard insulators. Phys. Rev. B 52, R5467–R5470 (1995).

36. F. Tran, P. Blaha, Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential. Phys. Rev. Lett. 102, 226401 (2009).
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