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Reliable density functional calculations for the electronic structure of thermoelectric material ZnSb

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In this paper, we present the results of systematic test calculations for the electronic structure of thermoelectric material ZnSb using a first-principles full-potential all-electron computational method. We used a linear combination of atomic orbitals (LACO) formalism, based on density functional theory (DFT). The exchange-correlation interaction potential of the many electron system was described by using a generalized gradient approximation (GGA). We compared the calculated indirect and direct band gaps as well as the effective masses of holes and electrons in ZnSb with experimental measurement results. The calculated indirect band gap of ZnSb is 0.56 eV, which agrees very well with the experimentally measured values of 0.50 eV ∼ 0.61 eV. The calculated direct band gap at X point is 0.89 eV. The calculated effective masses of electrons and holes in ZnSb also agree with experimental data. The systematical test calculations as well as the comparisons of the calculated results with experimental measurements show that the obtained electronic structure of ZnSb would be reliable. We did not observe a major deficiency of the first-principles DFT calculation for the electronic structure of ZnSb, using full-potential all electron LACO method. The reported electronic structure of single crystal ZnSb from this work may provide a fundamental knowledge base for further research and applications for this important thermoelectric material. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5051346

I. INTRODUCTION

High-efficiency thermoelectric (TE) materials are important for power-generation devices that are designed to convert solar and waste heat, geothermal energy and other thermal energy into electrical energy. Novel thermoelectric materials can also be used in advanced solid-state refrigeration devices. To be applicable for large scale exploitation of thermoelectrics, the high-efficiency TE materials must be cheap, abundant, nontoxic and stable in applied temperature range.1 In the recent years, the promising low-cost, non-toxic intermetallic material ZnSb has been intensively investigated due to its high TE efficiency. It is one of the best thermoelectric compounds in the moderate temperature range between 400 °K and 600 °K, for which only a limited number of efficient thermoelectric materials is known.

ZnSb is a small band gap semiconductor with an orthorhombic structure. The experimentally measured indirect band gap for single crystal ZnSb by optical absorption was 0.50 eV at room temperature, 0.59 eV at 77 °K and 0.61 eV at 4.2 °K from Turner et al.,2 and 0.53 eV from Komiya et al.3 In most of the references, 0.5 eV has been considered to be a reference value for the indirect band gap of single crystal ZnSb with some uncertainties.4 Theoretically, the electronic properties of ZnSb has been studied by several research groups through first-principles as well as other calculation methods. Mikhaylushkin et al. performed first-principles calculations for the electronic structure of

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TABLE I. Previously calculated and experimentally measured indirect band gaps of single crystal ZnSb. Experimentally measured band gaps: 0.50 eV (300°K)/0.59 eV (77°K)/0.61 eV (4.2°K)/0.53 eV.

| Ab-Initio Method | Additional Correction | Band Gap (eV) |
|------------------|-----------------------|--------------|
| PAW-GGA          | No                    | 0.25         |
| PAW-GGA-PBE      | No                    | 0.05         |
| PAW-GGA          | No                    | 0.05         |
| PAW-GGA-PBE      | No                    | 0.03         |
| PAW              | HSE hybrid functional | 0.56         |
| No               | Fitted Pseudopotential method | 0.60 |
| PAW-GGA-PBE      | Modified Becke Johnson (MBJ) Potentials | 0.56 |

ZnSb, utilizing frozen core all-electron projected augmented wave (PAW) method and the exchange-correlation interaction potential was described by the generalized gradient approximation (GGA). They found that the valence band (composed of Zn-s, Zn-p, and Sb-p states) was separated from the conduction band by a small gap of 0.2 eV, which is 0.3 eV smaller than the experimentally measured band gap of 0.5 eV. Benson et al. calculated the electronic structure of ZnSb by using the first-principles PAW method with the exchange-correlation effects treated with GGA using the Perdew-Burke-Ernzerhof (PBE) parameterization. Their calculated electron band gap for orthorhombic ZnSb is 0.05 eV, which is too small in comparison to 0.50 eV from the experimental measurement. The first-principles GGA and GGA-PBE calculations for the electronic structure of ZnSb by Niedziolka and Jund obtained indirect band gaps of 0.05 eV and 0.03 eV, respectively. All the previous first-principles DFT calculations using GGA or GGA-PBE listed above obtained much underestimated electron band gaps for ZnSb, in comparison with the experimental one of about 0.5 eV. In order to improve the calculated band gap of ZnSb, Niedziolka and Jund utilized a Heyd-Scuseria-Ernzerhof (HSE) hybrid functional with an empirically adjustable parameter and obtained the calculated band gap of 0.56 eV. In 1978, Yamada calculated the band structure of ZnSb by using an empirical-pseudopotential method (EPM) developed by Cohen and Heine. An improved band structure (with an indirect band gap of 0.6 eV) was obtained by making the values of the pseudopotential form factors in the region of \(0.9 \leq q/2k_F \leq 1.5\) larger than those given by Cohen and Heine. He et al. performed structure optimizations for ZnSb using the PAW method with GGA-PBE functional, and then calculated the band structures with a modified version of Beck Johnson (mBJ) exchange potential, which is a kind of “hybrid” potential whose amount of “exact exchange” is given by a parameter \(c\). The obtained band gap for ZnSb from He et al. was 0.60 eV. Although the obtained band gaps of ZnSb from those improved calculations agree well with the experimental value, the methods/potentials they used, including HSE, EPM and mBJ, depend highly on some adjustable parameters. The dramatic difference between the theoretical band gaps (listed in Table I) from first-principles DFT predictions, as well as that between them and the experimental measurements, are the motivation for this work. In addition, the underestimation of the band gaps of some materials was previously blamed on the deficiency of density functional theory. Therefore, the aim of this work is re-examining the above problem by performing a systematic test for the first-principles all electron full potential calculations for the electronic structure of ZnSb, utilizing a linear combination of atomic orbitals (LCAO) method based density functional theory. The results of the test calculation showed that the calculated electron band gap for ZnSb is 0.56 eV, which agreed very well with experimental measurement data.

II. COMPUTATIONAL METHOD

In this work, we performed first-principles full-potential all electrons calculations for the electronic properties of ZnSb, based on the density functional theory (DFT). We used a linear combination of atomic orbitals (LACO) formalism and method, which has been extensively described in our previous publications. Our first-principles LCAO package was adapted from the Ames laboratory of the US Department of Energy in Iowa. We began the calculations with first-principles self-consistent computations for the atomic wave functions for Zn and Sb atoms. The radial parts of
the atomic wave functions were expanded in terms of Gaussian functions. A set of even-tempered Gaussian exponents was employed with a minimum of 0.10 and a maximum of 0.23 × 10^6 in atomic unit. For the description of Zn atomic wave functions, we used 21, 21, and 17 Gaussian functions for the s, p and d wavefunctions, respectively. For Sb atomic wave functions, we used 22, 22, and 19 Gaussian functions for the s, p and d orbitals, respectively.

The single crystal ZnSb is in space group D_{2h}^{15}, Pbca, with an orthorhombic structure. The primitive unit cell of ZnSb contains 8 formula units and 16 atoms per unit cell, with the Zn and Sb atoms both locate at the 8(c) Wyckoff positions. The lattice parameters we used are a₀=6.202 Å, b₀=7.742 Å, and c₀=8.100 Å, from experimental measurement by Carter et. al.25 In the first-principles calculations for the electronic structure of single crystal ZnSb, a nonlocal density functional potential from the generalized gradient approximation (GGA) was employed for the description of the exchange-correlation interaction of the many-body electron system.26–29 A mesh of 64 k points, with proper weights in the irreducible Brillouin zone, was used in the self-consistent iterative calculations for the electronic structure of ZnSb in orthorhombic structure. The self-consistent potentials converged to a difference around 10^-5 after about 35 iterations. The total number of iterations varies with the input potentials. To execute the ab initio self-consistent calculations, we began with a small atomic basis set that contained the minimum atomic basis set (MABS), which is the one just large enough to accommodate all the electrons in atomic or ionic species under study (e.g., see: https://www.nist.gov/image/periodic-table-2017). This is defined as Calculation 1. Then, we successively augment the initial small basis set by one atomic orbital at a time for the following self-consistent calculations, which are defined as Calculations 2, 3, . . . , n, n+1, . . . . The occupied energies from each calculation are numerically and graphically compared to the corresponding values from the calculation immediately preceding it. If the occupied energies of one calculation were lower than those from the previous one, this is an indication that the basis set used for the previous calculation was not complete for the DFT description of the system being investigated, and as a result, further calculations were deemed necessary. This process of self-consistent calculations was continued until a calculation, say N, for example, was found to have the same occupied energies as those of Calculation (N+1) that immediately followed it. The excellent superposition of the occupied bands from the two calculation was an indication that Calculation N produced the ground state energies. Calculation N+2 may be needed to confirm the attainment of the full convergence of the calculations, i.e., with respect to the numbers of iterations (self-consistency) and to the size and attendant attributes of the basis sets. Such attributes include angular symmetries inherent to the s, p, and d orbitals. Here, Calculation N is the one giving the real DFT description for the electronic structure of the material being studied, and the basis set employed in Calculation N is defined as the optimal basis set. From the test calculations for the electronic structure of single crystal ZnSb in this work, the basis set of Calculation 4 is the optimal basis set which led to the real DFT description for the electronic structure of ZnSb.

III. RESULTS AND DISCUSSIONS

In Table II, we listed Calculations 1 - 6 with successive addition of atomic orbitals used in our first-principles full-potential all electrons calculations. Also listed are the number of valence orbitals

| Calculation no. | Orbitals for Zn | Orbitals for Sb | No. of valence orbitals |
|-----------------|-----------------|-----------------|-------------------------|
| 1               | [Ar]3d^{10}4s^2 | [Kr]4d^{10}5s^25p^3 | 120                     |
| 2               | [Ar]5d^{10}4s^24p^6 | [Kr]4d^{10}5s^25p^3 | 144                     |
| 3               | [Ar]5d^{10}4s^24p^64d^0 | [Kr]4d^{10}5s^25p^35d^0 | 184                     |
| 4               | [Ar]5d^{10}4s^24p^64d^05s^0 | [Kr]4d^{10}5s^25p^35d^0 | 224                     |
| 5               | [Ar]5d^{10}4s^24p^64d^05s^05d^0 | [Kr]4d^{10}5s^25p^35d^0 | 232                     |
| 6               | [Ar]5d^{10}4s^24p^64d^05s^05d^0 | [Kr]4d^{10}5s^25p^35d^06s^0 | 240                     |
(or wave functions) for ZnSb in each Calculation. As we can see from Table II, we started the calculation with the small basis set, which included [Ar]3d104s2 orbitals for Zn and [Kr]4d105s25p3 orbitals for Sb, respectively. Here, [Ar] and [Kr] are the notations used in the Periodic Table of the Elements published by the National Institute of Standards and Technology (NIST), representing the core states of Zn and Sb, respectively. We then augmented the basis set for each Calculation successively by adding additional orbitals, which are marked as bold in the Table II.

Figure 1 shows the calculated electron band structures of ZnSb along some high symmetry k points in the irreducible Brillouin zone, obtained from the successive self-consistent all electrons calculations. The Fermi energies are set to zero, at the top of the valence bands in the calculations. For the sake of a clear comparison on the band energies, especially for the occupied energies of the system, we plotted the band energies obtained from two successively calculations together in each of the panel in Figure 1. A comparison of the band energies from Calculation 1 and Calculation 2 (in Figure 1(A)) shows that after adding the 4p0 orbital of Zn to the initial small basis set, the overall occupied energies of the system were lowered down; the indirect band gap of ZnSb from Calculation 2 is obviously larger than that from Calculation 1. These differences indicated that the obtained electronic structure from Calculation 1 and 2 have not converged yet, with respect to the size of the basis set. We then augmented the basis set of Calculation 2 by adding Sb-5d0 and performed Calculation 3. The difference between the occupied energies became much smaller when we compare the calculated electron bands of Calculations 2 and 3 (as shown in Figure 1(B)). Figure 1(C) shows that the occupied and unoccupied energies from Calculations 3 and 4 are very close each other. However, a close inspection of the band structures still indicates lower occupied energies of the system when Zn 4d0 orbital was added to the basis set (i.e., Calculation 4). It is observed from Figure 1(D) that the calculated electron energy bands from Calculation 5 agree very well with those of Calculation 4. Not only the occupied bands, but also the unoccupied bands from these two successive calculations
were well superimposed. Further, Calculations 5 and 6 also showed a good superimposition on both of the occupied and unoccupied bands for ZnSb. For the purpose of simplicity, we did not list the comparison of the band structures from Calculations 5 and 6 in the figure. These test calculations show that the basis set for Calculation 4 led to converged DFT results for the electronic structure of single crystal ZnSb. This convergence, it should be noted, entails no just the convergence of iterations (i.e., self-consistency), but also the convergence of the energies with respect to the size of the basis set. The calculated direct band gap from the optimal basis sets (Calculation 4) at the X-point is 0.89 eV. The top of the valence band of ZnSb is between X and Γ, close to X-point, located at 0.75(X-Γ), where X-Γ is the distance from Γ to X points; herein, we name it as X'-point afterwards. The bottom of the conduction band of ZnSb is between Z and Γ, located at 0.20(Z-Γ), where (Z-Γ) is the distance between the Z and Γ points; we name it as Z'-point afterwards. From Figure 1, we can see that the converged calculations indicated an indirect band gap for single crystal ZnSb, which is in good agreement with the previous experimental measurements by Turner et al. and Komiya et al.2,3 The calculated indirect band gap from X' to Z' is 0.56 eV, which is in excellent agreement with the experimental values of 0.50 eV ∼ 0.61 eV, depending on measurement method and temperature.

Figure 2 shows the total electronic density of states (DOS) obtained with the calculated electronic structure from Calculation 4; the optimal basis set of Calculation 4 included the atomic orbitals of [Ar]3d104s24p04d0 of Zn and [Kr]4d105s25p35d0 of Sb, respectively. The embedded panel is the magnified DOS in an energy range of -2 eV ∼ 2 eV. Here, the Fermi level is set as the zero of energy at the top of the valence bands in the calculation. The total DOS shows a clear gap between the bottom of the conduction band and the top of the valence band, with a width of ~0.56 eV. Apparently, between -6 eV and 0, the valence band is mainly composed of three major peaks with additional fine structures. Figure 3 shows the calculated (from the optimal basis set) electronic partial DOS for Zn s and p as well as Sb s, p, and d states, respectively. The Zn 3d states are fully occupied and have no much contribution to the valence band of ZnSb in this energy range from -6 to 4 eV. It is indicated that the conduction band of ZnSb is mainly dominated by the Zn s and p and Sb s, p and d states, amongst which the Zn s and p and Sb p and d states accounts for the major contribution. Contributions from Sb-s orbitals in this energy range are also small. The valence band of the system are composed of Zn s and p, Sb s and p electrons, which agrees with the report from Mikhaylushkin et al.5 The upper part of the valence band, ranging from the top of the valence band down to about -3.0 eV, is largely the contributions of the p electrons from Zn and Sb, with a small contribution from Zn s electrons. The middle part (-4.5 eV ∼ -3.0 eV), and the lower part (-6.0 eV ∼ -4.5 eV) of the valence band are contributed from the Zn s and p and Sb p electrons, with some minor contributions from Sb s electron. It is our hope that future experimental investigations such as with X-ray photoemission spectroscopy measurements, will confirm the above features of the calculated electronic structure of ZnSb.
IN Table III, we list the calculated electronic eigen-energies of ZnSb at some high symmetry points (Z, Γ, X, S, R and Y) as well as X’ and Z’ points in the Brillouin zone, including some valence and conduction band states around the Fermi level. The listed energies are obtained from Calculation 4. As discussed above, neither the top of the valence band nor the bottom of the conduction band of ZnSb sits right at a high symmetry point. The valence band maximum is between Γ and X, very close to X, and the minimum of the conduction band is between Z and Γ, very close to Z. The calculated

TABLE III. Electronic energies (in eV) of ZnSb at some high symmetry points in the Brillouin zone, as obtained from Calculation 4 (with the optimal basis set). The zero of the energy is set at the top of the valence band, which is between Γ and X, very close to X, so we name that point as X’. The direct bandgap at X point is 0.89 eV.

| Z-point | Z’ | Γ-point | X’ | X-point | S-point | R-point | Y-point |
|---------|----|---------|----|---------|---------|---------|---------|
| 3.722   | 4.207 | 3.415   | 3.483 | 3.224   | 2.608   | 3.398   | 3.443   |
| 3.722   | 3.550 | 3.275   | 3.354 | 3.224   | 2.608   | 3.398   | 3.443   |
| 3.517   | 3.430 | 3.209   | 3.205 | 2.954   | 2.608   | 3.398   | 3.275   |
| 3.517   | 3.349 | 3.107   | 3.047 | 2.954   | 2.608   | 3.398   | 3.275   |
| 2.608   | 2.675 | 3.092   | 2.426 | 2.410   | 2.242   | 2.818   | 3.117   |
| 2.608   | 2.548 | 2.883   | 2.284 | 2.410   | 2.242   | 2.818   | 3.117   |
| 1.848   | 2.036 | 2.668   | 2.247 | 2.257   | 2.242   | 2.818   | 2.273   |
| 1.848   | 1.770 | 2.423   | 2.186 | 2.257   | 2.242   | 2.818   | 2.273   |
| 1.098   | 1.262 | 2.056   | 1.750 | 1.881   | 1.299   | 1.056   | 2.226   |
| 1.098   | 1.119 | 1.838   | 1.731 | 1.881   | 1.299   | 1.056   | 2.226   |
| 0.713   | 1.048 | 1.247   | 0.982 | 0.837   | 1.299   | 1.056   | 0.761   |
| 0.713   | 0.564 | 1.139   | 0.978 | 0.837   | 1.299   | 1.056   | 0.761   |
| ~0.647  | ~0.647 | ~0.807 | 0.000 | ~0.058 | ~0.675  | ~1.052  | ~1.080  |
| ~0.647  | ~0.690 | ~0.812 | ~0.261 | ~0.058 | ~0.675  | ~1.052  | ~1.080  |
| ~1.381  | ~1.267 | ~0.981 | ~0.536 | ~0.549 | ~0.675  | ~1.052  | ~1.445  |
| ~1.381  | ~1.274 | ~1.475 | ~0.596 | ~0.549 | ~0.675  | ~1.052  | ~1.445  |
| ~1.536  | ~1.688 | ~1.573 | ~0.994 | ~1.071 | ~1.488  | ~2.280  | ~1.930  |
| ~1.536  | ~1.916 | ~1.806 | ~1.144 | ~1.071 | ~1.488  | ~2.280  | ~1.930  |
| ~2.184  | ~2.043 | ~2.073 | ~1.167 | ~1.085 | ~1.488  | ~2.280  | ~2.009  |
| ~2.184  | ~2.104 | ~2.083 | ~1.368 | ~1.085 | ~1.488  | ~2.280  | ~2.009  |
| ~2.188  | ~2.216 | ~2.200 | ~1.481 | ~1.968 | ~2.277  | ~2.340  | ~2.467  |
| ~2.188  | ~2.289 | ~2.931 | ~2.134 | ~1.968 | ~2.277  | ~2.340  | ~2.467  |
| ~2.659  | ~2.459 | ~3.046 | ~2.339 | ~2.278 | ~2.277  | ~2.340  | ~2.621  |
| ~2.659  | ~2.788 | ~3.121 | ~2.539 | ~2.278 | ~2.277  | ~2.340  | ~2.621  |
indirect band gap of ZnSb is about 0.56 eV between X’ and Z’. The direct band gap at X-point is 0.89 eV. The energies listed in Table III can be used in detailed comparisons with future experimental measurements such as X-ray and UV spectroscopic measurements.

The effective masses of electrons, at the bottom of the conduction band, and of holes, at the top of the valence band, are important physical quantities for investigating the electron transport properties in the materials, especially for semiconductors. Using the obtained electronic structure from Calculation 4 that has been intensively discussed above, we further calculated the effective masses of holes around the top of the valence band and of electrons around the bottom of the conduction band in ZnSb. The calculated electron (n-type) effective masses are \( m_{e}^{*} = 0.17 m_{0}, 0.12 m_{0}, \) and 0.13 \( m_{0} \), along \( a, b \) and \( c \) directions, respectively. Here \( m_{0} \) is the mass of a free electron. The calculated effective masses of holes (p-type) are \( m_{h}^{*} = 0.30 m_{0}, 0.76 m_{0}, \) and 0.13 \( m_{0} \), along \( a, b \) and \( c \) directions, respectively. The cyclotron resonance measurements on ZnSb by Stevenson in 1960, using optical excitation, reported the effective masses as 0.175 \( m_{0} \), 0.146 \( m_{0} \), and 0.146 \( m_{0} \), along \( a, b \) and \( c \) directions, respectively; though the sign of the charge of the carrier was not determined. These reported effective masses are very close to our calculated effective masses of n-type carrier (electrons). Komiya et al studied the optical and electrical transport properties of single crystal p-type ZnSb and found that the dc mobility tensor has components \( \mu_{<c>} \), \( \mu_{>c>} \), \( \mu_{b} \), indicating that \( \mu_{<c>}/m_{c} > \mu_{>c>}/m_{b} > \mu_{b}/m_{b} \), where \( \tau_{a}, \tau_{b}, \tau_{c} \) and \( m_{a}, m_{b}, m_{c} \) are the tensor components of relaxation time and effective mass of holes. These authors did not report a specific value for the hole effective mass and gave their tentative estimate as \( m_{h} \sim 0.05 m_{0} \), \( -0.6 m_{0} \), for the effective masses along \( c, b \) and \( a \) directions. These estimated relationships between the hole effective masses in different directions are close to those between our calculated ones as discussed above, i.e., \( m_{a} (0.13m_{0}) < m_{b} (0.30m_{0}) < m_{c}(0.76m_{0}) \) for holes. In these experimental studies, they used complex formulas to fit the experimental data in order to extract the effective masses of charge carriers; this procedure was complex and difficult. Our calculated effective masses of electrons and holes in ZnSb can complement experimental studies in obtaining the relevant physical quantities for this small band gap semiconductor for further research and applications. Our reported results for the electronic structure of ZnSb may stimulate further experimental investigations for the effective masses of electrons and holes in ZnSb.

In summary, we performed systematic test calculations for the electronic structure of single crystal ZnSb, using first-principles full-potential all electron LACO method, based on density functional theory. The calculated indirect and direct band gaps of ZnSb agree very well with the experimentally measured values, indicating a correct relative position of the valence bands and conduction bands in energy - momentum space for this material. The calculated effective masses of n- and p-type charge carriers in ZnSb, which were derived from the second derivatives of the calculated electron energy band dispersions with respect to the k-point in the Brillouin zone, also agree with the experimentally measured results. The first derivatives of the electron energy band dispersions with respect to the k-point around the top of the valence band and the bottom of the conduction band should be zero, which is obvious. These results may lead to a conjecture that the calculated electronic structure of thermoelectric material ZnSb from this work would be reliable as compared to experimental measurements. We did not observe a major (or large) deficiency of the first-principles DFT calculation for the electronic structure of ZnSb, using full-potential all electron LACO method. The reported

IV. CONCLUSIONS

In this work, we performed ab initio all electrons full-potential GGA calculations for the electronic structure of the thermoelectric material ZnSb. The presented results include the electronic energy bands, total and partial densities of states (DOS), and effective masses for holes and electrons for single crystal ZnSb. The calculated indirect band gap of ZnSb is 0.56 eV, which is in excellent agreement with experimental measurements. The calculated direct band gap at X-point is 0.89 eV. The calculated effective masses of electrons and holes in ZnSb also agree with experimental measurements. The calculated direct band gap at X-point is 0.89 eV. The calculated indirect and direct band gaps of ZnSb agree very well with the experimentally measured results. The first derivatives of the electron energy band dispersions with respect to the k-point around the top of the valence band and of electrons around the bottom of the conduction band should be zero, which is obvious. These results may lead to a conjecture that the calculated electronic structure of ZnSb from this work would be reliable. We did not observe a major deficiency of the first-principles DFT calculation for the electronic structure of ZnSb, using full-potential all electron LACO method. The reported
electronic structure of single crystal ZnSb may also provide a fundamental knowledge base for further research and applications for this important thermoelectric material.

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