CHIN. PHYS. LETT. Vol. 34, No. 11 (2017) 117202

Predicted High Thermoelectric Performance of Quasi-Two-Dimensional Compound GeAs Using First-Principles Calculations *

Dai-Feng Zou(邹代峰)[1,2**], Chuan-Bin Yu(余传斌)[2,3], Yu-Hao Li(李宇豪)[2,3], Yun Ou(欧云)[1,2]

[1]*School of Physics and Electronic Science, Hunan University of Science and Technology, Xiangtan 411201*
[2]*Shenzhen Key Laboratory of Nanobiomechanics, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, Shenzhen 518055*
[3]*State Key Laboratory of Mechanics and Control of Mechanical Structures, Nanjing University of Aeronautics & Astronautics, Nanjing 210016*

(Received 21 August 2017)

The electronic structure of binary quasi-two-dimensional GeAs is investigated using first-principles calculations, and it is found that the anisotropic structure of the layered compound GeAs brings about the anisotropy of the transport properties. Meanwhile, the band structure of GeAs exhibits a relatively large dispersion near the valence-band maximum in the Z–V direction while it is rather flat in the Z–Γ direction, which is highly desirable for good thermoelectric performance. The calculated partial charge density distribution also reveals that GeAs possesses anisotropic electrical conductivity. Based on the semi-classical Boltzmann transport theory, the anisotropic transport properties are observed, and the optimal doping concentrations are estimated. The temperature dependence transport properties of p-type GeAs are compared with the experimental data in good agreement, and the theoretical figure-of-merit ZT has been predicted as well.

PACS: 72.20.Pa, 72.80.Ga, 31.15.A− DOI: 10.1088/0256-307X/34/11/117202

Thermoelectric materials, which can directly and reversibly convert heat into electricity, have potential applications in power generation and refrigeration.[1,2] The conversion efficiency of thermoelectric materials is described by the figure of merit, ZT, which is defined as $ZT = S^2\sigma T/(\kappa_e+\kappa_l)$, where S, σ, κ_e and κ_l are the Seebeck coefficient, electrical conductivity, and electric and lattice thermal conductivities, respectively. A good thermoelectric material must possess a high ZT value, and most of the recent efforts in ZT improvement have been concentrated around these compounds that possess an intrinsically low lattice thermal conductivity and then optimize the electronic properties $S^2\sigma$ (power factor: PF). Due to the anisotropic character, quasi low-dimensional compounds such as SnSe and BiCuSeO have recently gained attention due to their low thermal conductivities and high figures of merit.[3,4] Recently, the binary quasi-two-dimensional compound GeAs, which can possess very low lattice thermal conductivity, is also predicted as a promising thermoelectric material which is assumed to possess a comparative β value with that of SnSe.[5] On the experimental side, the thermoelectric properties of layered compound GeAs are reported by Lee *et al.*[6] Due to the high Seebeck coefficient and low thermal conductivity, the ZT value of GeAs can reach 0.35 at 660 K.[6] However, few theoretical studies have systematically investigated the thermoelectric performance properties of GeAs compounds. Therefore, it is necessary to estimate the relationship of GeAs between its electronic structure and thermoelectric properties, and to evaluate the optimal concentration for improving its thermoelectric performance.

In this Letter, the semi-classic Boltzmann transport theory is used to calculate the anisotropy of the thermoelectric performance of GeAs, and the links between the anisotropic thermoelectric properties and electronic structure are estimated, and the results are compared with the experimental dada. According to the doping dependence of electrical transport properties of GeAs, we estimate the optimal p-type doping concentrations based on the calculated maximum power factors, which can serve as a guide on how to optimize the thermoelectric properties of this compound. In addition, the theoretical figure of merit ZT has been predicted based on the optimal doping concentrations.

For electronic structural calculations of GeAs, the first-principles implemented in the Vienna *ab initio* simulation package (VASP)[7] are used with the Perdew–Burke–Ernzerhof (PBE)[8] generalized gradient approximation (GGA) and projector augment wave (PAW)[9] pseudopotentials. The cutoff energy of the plane-wave expansion is 400 eV. Atomic positions and unit cell vectors are relaxed until all the forces are below 0.03 eV/Å, and the energy convergent criterion is 10^{-6} eV per unit cell. The Brillouin zone is sampled using a Monkhorst-Pack k-point mesh ($9\times9\times8$) for GeAs.

The Seebeck coefficient S and electronic conductivity over relaxation time σ/τ are calculated using the semi-classical Boltzmann theory.[10,11] This approach has been used in the successful predication of the thermoelectric properties of many thermoelectric materials.[12–16] All the calculations of transport properties are implemented in the BoltzTraP

*Supported by the National Key Research and Development Program of China under Grant No 2016YFA0201001, the National Natural Science Foundation of China under Grant No 11627801, and the Education Bureau of Hunan Province of China under Grant No 16C0626.
**Corresponding author. Email: daifengzou@gmail.com
© 2017 Chinese Physical Society and IOP Publishing Ltd

code[17] based on the crystal structure and eigenenergies obtained from *ab initio* results. To obtain reasonable transport properties, a more dense k-mesh ($18\times18\times16$) is used for GeAs in the Monkhorst-Pack scheme, and it can guarantee convergence for determining the electrical transport properties of GeAs.

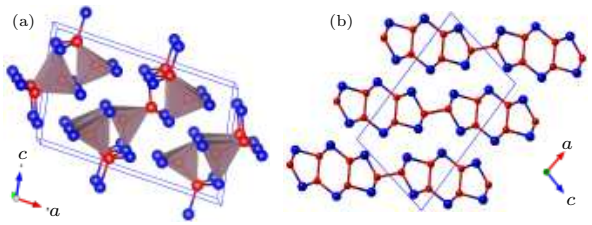

Fig. 1. Crystal structure of GeAs. Red and blue balls denote Ge and As atoms, respectively. The blue solid-line shows a unit cell. (a) Polyhedral view, and (b) ball and stick model.

The GeAs compound is crystallized in the monoclinic space group $C2/m$ in a layered crystal structure. The crystal structure of GeAs is displayed in Fig. 1(a). Within each layer, Ge-Ge pairs are surrounded by six As atoms forming a distorted trigonal antiprism. The formed Ge-As-Ge layers are stacked by weak van der Waals interactions along the orientation either parallel to or perpendicular to the c axis.[6] In the crystal structure of GeAs, each layer is terminated by As atoms shown by blue balls in Fig. 1(b), with strong covalent bonding within the layers. The ground state lattice parameters are calculated with relaxation of both atomic coordinates and lattice constants by the GGA method. The optimized a and c of GeAs in a primitive cell are calculated to be 8.0354 and 9.5879 Å, which match with the corresponding experimental values (8.0362 and 9.5127 Å).[6] There are three nonequivalent Ge atoms or As atoms in the unit cell, and each Ge atom is coordinated by three As atoms and one Ge atom while each As atom is coordinated by three Ge atoms. The shortest Ge-Ge and Ge-As bond distances found in GeAs are 2.479 and 2.471 Å, respectively, which are both much smaller than interlayer spacing (4.910 Å), and it brings about weak bonding and anisotropy which can be favorable for thermoelectric performance.

The electronic band structure of GeAs as calculated using GGA is shown in Fig. 2. It can be seen from Fig. 2(a) that the GeAs is with an indirect gap of 0.18 eV. The value is slightly higher than the optical band gap measurement of 0.65 eV, and this is because GGA often underestimates the band gaps of semiconductors.[18] To prevent bipolar transport for the transport properties calculations, an operator of scissors is used by moving the conduction band upward to match with the experimental data of band gaps, as previously reported for some semiconductors.[9,19] It is found experimentally that GeAs tends to form a p-type semiconductor,[6] and we only focus the discussion on the upper part of the valence band. It can be seen from Fig. 2(a) that the band structure exhibits a relatively large dispersion around the upper part of the valence band in the Z–V direction while it is rather flat in the Z–Γ direction. The upper valence band in the Z–Γ direction is extremely flat, suggesting that this compound possesses a narrow carrier energy distribution and large effective mass in this direction. Meanwhile, the large dispersion around the upper part of the valence band in the Z–V direction indicates that the effective mass is small in this direction. Thus the combination of flat and dispersive bands can yield a high PF since the Seebeck coefficient is proportional to the effective mass while electrical conductivity is inversely proportional to the effective mass. It has also been observed in other thermoelectric compounds that the flat-and-dispersive band structure can be beneficial for thermoelectric performance.[12,20]

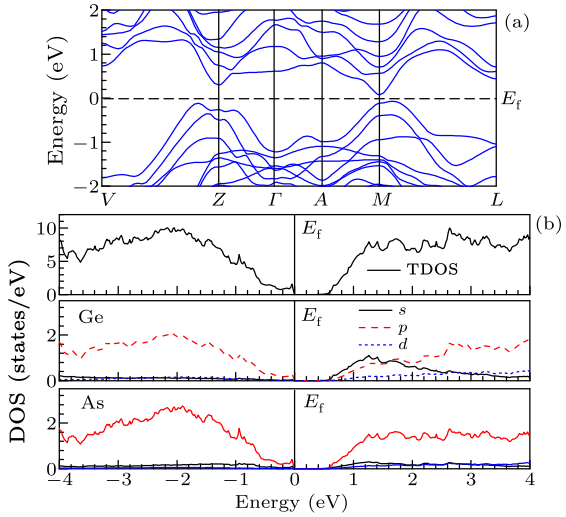

Fig. 2. (a) Calculated band structure near the Fermi energy of GeAs, and (b) density of states of GeAs. The Fermi level is set to zero.

Since the electron states around the Fermi level have an important effect on the electronic transport properties of thermoelectric materials, we plot the total and projected density of states (DOS) of GeAs in the energy interval between −4 eV and 4 eV in Fig. 2(b). From the projected DOS, we can see that the bottom of the conduction band primarily comes from 4s and 4p states of the Ge atom and the 4p state of the As atom, and the top of the valence band is mainly due to the hybridization of Ge 4p and As 4p orbitals. A previous experimental study[6] revealed that GeAs usually exhibits p-type conduction, and we will only discuss the upper part of the valence band which determines the thermoelectric properties of p-type GeAs. Based on the above results, one can obtain that the Seebeck coefficient and electrical conductivity for the p-type GeAs are primarily determined by the hybridization of Ge 4p and As 4p orbitals. Meanwhile, it is found from Fig. 2(b) that a steep change in the total DOS near the Fermi level can be a good indicator of a large Seebeck coefficient.[21,22]

To probe the nature of the bond character of Ge 4p-As 4p atoms which determine the transport properties of p-type GeAs, the partial charge density distribution is calculated. A contour plot of the par-

tial charge density on the Ge-Ge-As plane of GeAs in the upper portion of the valence bands (−2 eV–0) is plotted in Fig. 3. The partial charge density distribution shows the distribution of the electronic states in real space.[19] Based on the discussion of DOS, the energy window of −2 eV to 0 corresponds to the $4p$ Ge–$4p$ As states. As shown in Fig. 3, there is an enhanced charge density on the side of As atoms pointing to the adjacent layers in the charge density distributions, and these electronic states consist of As $4s^2$ electrons at the upper portion of the valence bands of GeAs, which form electron lone pairs. Such a charge density distribution is also observed in other ns^2-based compounds.[9,23,24] In addition, we can also see that there is a distribution of electronic states between Ge-As atoms indicating the presence of covalent bonds between Ge-As atoms, and it forms a conductive network for hole transport of GeAs. The white background means that there is no charge density distribution in this area. As shown in Fig. 3, it is clear that there is a minimum of the localized electron density distribution between adjacent layers, suggesting that there are no covalent bonds between the layers. The analysis by partial charge density distribution confirms that GeAs indeed has a layered two-dimensional conductive network with weak conductive path between the layers, that is, there exists anisotropic electric conductivity in GeAs.

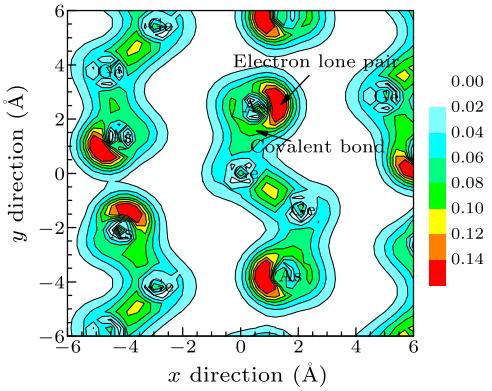

Fig. 3. Calculated partial charge density in the upper portion of the valence bands (−2–0 eV) of GeAs on the Ge-Ge-As plane. The Fermi level is set to zero. The charge density is in units of e/Å^3.

As mentioned previously, layered materials can exhibit anisotropy transport properties. The anisotropy transport properties of GeAs are calculated based on the calculated electronic structure using the Boltzmann theory. It is found that GeAs tends to form p-type semiconductors in experimental work,[6] and a hole-doped case is only considered in the following thermoelectric properties. The electronic transport properties of p-type GeAs as a function of carrier concentration at 800 K are shown in Figs. 4(a)–4(c). As can be seen in Fig. 4(a), there is a slight anisotropy of the Seebeck coefficient S of GeAs, where the values of S along the zz direction are less than the xx and yy directions when the carrier concentration is below 2×10^{20} cm^{-3}, and the behavior reverses at a high carrier concentration. Meanwhile, it can be observed that there are moderate values of S at middle carrier concentrations: the Seebeck coefficient S with $p = 1 \times 10^{20}$ cm^{-3} along xx, yy and zz directions are 204 μV/K, 200 μV/K and 191 μV/K, respectively. These values are higher than the data of layered Sb_2Te_3 while lower than layered SnSe,[3,25] indicating that GeAs can show better thermoelectric performance when it possesses high electrical conductivity and low thermal conductivity.

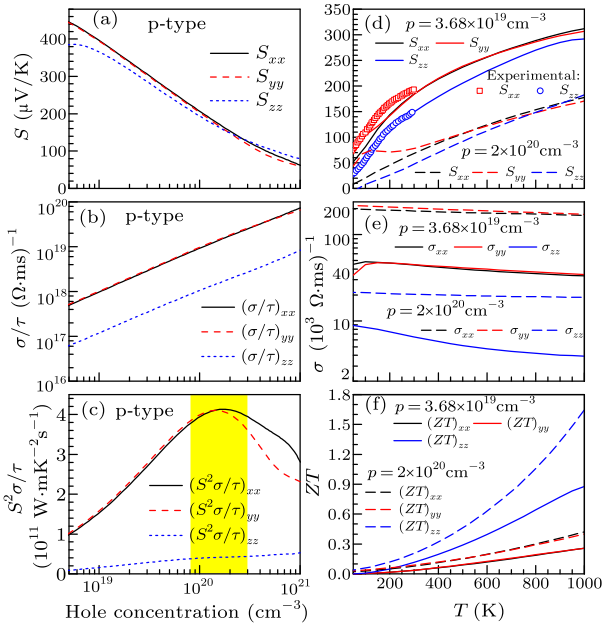

Fig. 4. Calculated thermoelectric properties as a function of carrier concentration along three axes at 800 K: (a) Seebeck coefficient, (b) electrical conductivity with respect to relaxation time, and (c) power factors versus relaxation time. The range of optimum doping concentrations is denoted with yellow. Calculated thermoelectric properties of GeAs along three axes as a function of temperature: (d) Seebeck coefficient, (e) electrical conductivity and (f) figure of merit. These data represented by dots are the experimental measurements taken from Ref. [6].

The electrical conductivity with respect to relaxation time σ/τ of p-type GeAs along the three directions as a function of carrier concentration at 800 K are shown in Fig. 4(b). Compared with the anisotropy of the Seebeck coefficient, the electrical conductivity anisotropy is found to be larger. Both $(\sigma/\tau)_{xx}$ and $(\sigma/\tau)_{yy}$ are almost one order higher than the values of the $(\sigma/\tau)_{zz}$ throughout the whole concentration range. Such a significant anisotropy of σ/τ was observed in other layered thermoelectric materials.[12,14,26] The anisotropy of σ/τ is due to the weak covalent bonding nature along the layer direction compared with the other two axes, and this result also agrees well with the charge density of GeAs discussed above.

The ability of a thermoelectric material to produce useful electrical power is quantified by its power factor $S^2\sigma/\tau$, and we further estimate the power factor of GeAs. The calculated power factors with respect to relaxation time $S^2\sigma/\tau$ of GeAs as a function of carrier concentration at 800 K are shown in Fig. 4(c).

As shown in Fig. 4(c), the values along the xx and yy directions are much greater than those along the zz direction. This phenomenon agrees reasonably well with the magnitude of Seebeck and electrical conductivity in xx, yy and zz directions. Meanwhile, there are peak values of power factors along the xx and yy directions within the considered doping level range for GeAs, suggesting that the thermoelectric performance of GeAs can be optimized by appropriate doping concentrations. The optimum doping concentrations of p-type GeAs are in the range of $8.0 \times 10^{19}\,\mathrm{cm}^{-3}$–$2.0 \times 10^{20}\,\mathrm{cm}^{-3}$.

To assess the reliability of our calculations and to further investigate the thermoelectric performance of GeAs at the optimum doping concentrations, the thermoelectric properties of p-type GeAs along three axes as a function of temperature are shown in Figs. 4(d)–4(f). It should be noted that the thermoelectric properties of the given carrier concentration ($2.0 \times 10^{20}\,\mathrm{cm}^{-3}$) are also plotted in Figs. 4(d)–4(f). In Fig. 4(d), it is found that the calculated temperature-dependent S values of p-type GeAs agree well with those observed in experiments. Within the constant relaxation time (τ) approximation in the framework of the Boltzmann transport equation, the electrical conductivity (σ) is expressed in the form of the ratio σ/τ. However, it is difficult to determine the relaxation time due to its dependence on both temperature and concentration. Here we set the relaxation time τ as 10 fs, which has been used as an approximate constant relaxation time in some recent studies.[27–30] The calculated electrical conductivities of p-type GeAs along the xx, yy and zz directions are shown in Fig. 4(e). From Fig. 4(e), we can see that the electrical conductivity of GeAs decreases with increasing temperature and it exhibits a metal-like behavior. As expected from the crystal structure, GeAs exhibits anisotropic thermal conductivity when measured along the layers and across the layers. It was reported that the thermal conductivity along the layers is 33.2 times higher than the value perpendicular to the layers.[6] Here we choose κ to be 12.6 W/mK and 0.38 W/mK, which are thermal conductivity of GeAs along the layers and perpendicular to the layers, respectively.[6] The calculated ZT values as a function of temperature are shown in Fig. 4(f). The anisotropy of the Seebeck coefficient, electrical conductivity and thermal conductivity in GeAs compounds will inevitably result in the anisotropy of ZT. Indeed, the values of ZT exhibit a strong anisotropy for GeAs: the values along the zz direction are much greater than those along the xx and yy directions, and this is because of the low electrical conductivity coupled with low thermal conductivity for GeAs along the zz direction. As for the undoped GeAs ($p = 3.68 \times 10^{19}\,\mathrm{cm}^{-3}$), the ZT values of ZT along xx, yy and zz directions reach 0.135, 0.141 and 0.5 at 650 K, respectively. The average figure-of-merit ZT is defined as 1/3 of the trace of the figure of merit tensor, and it enables the comparison of our results with the polycrystalline samples. The calculated average figure of merit ZT is 0.258, which is very close to the experimental data (0.35 at 660 K), indicating the validity of the current model. Combining the optimum doping concentration ($p = 2 \times 10^{20}\,\mathrm{cm}^{-3}$), the largest ZT values of 1.64 along the zz direction and 0.41 and 0.39 along the xx and yy directions for the p-type materials at 1000 K have been predicted, suggesting that GeAs is a promising layered compound for high temperature thermoelectric applications.

In summary, we have systematically investigated the electronic structure and anisotropic thermoelectric properties of GeAs using first-principles calculations and the semi-classical Boltzmann transport theory. It is observed that the layered structure of the GeAs compound can bring out the anisotropy of transport coefficients. Meanwhile, it is found that the band structure exhibits relatively large dispersion near the valence-band maximum in the Z–V direction while rather flat in the Z–Γ direction, which leads to relatively high Seebeck coefficient and conductivity. The analysis of the density of states indicates that the upper part of the valence band near the Fermi level consists of Ge 4p-As 4p atoms. The calculated partial charge density distribution reveals that GeAs possesses anisotropic electrical conductivity. Based on the calculated power factors as a function of carrier concentration, the optimal doping concentrations are found in the range of $8.0 \times 10^{19}\,\mathrm{cm}^{-3}$–$2.0 \times 10^{20}\,\mathrm{cm}^{-3}$. The theoretical figure-of-merit ZT of p-type GeAs has been assessed, and a high ZT value of 1.64 along the zz direction at 1000 K can be obtained, indicating that layered GeAs would have promising prospects for high temperature thermoelectric applications.

References

[1] Bell L E 2008 *Science* **321** 1457
[2] Gaultois M W et al 2013 *Chem. Mater.* **25** 2911
[3] Zhao L D et al 2014 *Nature* **508** 373
[4] Li J et al 2012 *Energy Environ. Sci.* **5** 8543
[5] Gorai P et al 2016 *J. Mater. Chem.* A **4** 11110
[6] Lee K et al 2016 *Chem. Mater.* **28** 2776
[7] Kresse G and Furthmüller J 1996 *Phys. Rev.* B **54** 11169
[8] Perdew J P et al 1996 *Phys. Rev. Lett.* **77** 3865
[9] Blöchl P E 1994 *Phys. Rev.* B **50** 17953
[10] Scheidemantel T J et al 2003 *Phys. Rev.* B **68** 125210
[11] Ong K P et al 2011 *Phys. Rev.* B **83** 115110
[12] Zou D et al 2013 *J. Mater. Chem.* A **1** 8888
[13] Ali R et al 2014 *Chin. Phys. Lett.* **31** 047102
[14] Zou D et al 2016 *J. Alloys Compd.* **686** 571
[15] Guo H H et al 2014 *Chin. Phys.* B **23** 017201
[16] Kaur K and Kumar R 2016 *Chin. Phys.* B **25** 056401
[17] Madsen G K H and Singh D J 2006 *Comput. Phys. Commun.* **175** 67
[18] Aulbur W G et al 2012 *Solid State Phys.* **54** 1
[19] Xi L et al 2012 *Phys. Rev.* B **86** 155201
[20] Bilc D I et al 2015 *Phys. Rev. Lett.* **114** 136601
[21] Lee M S et al 2011 *Phys. Rev.* B **83** 085204
[22] Singh D J and Mazin I 1997 *Phys. Rev.* B **56** R1650
[23] Joshi R K et al 2005 *Physica* E **25** 374
[24] Watson G W 2001 *J. Chem. Phys.* **114** 758
[25] Ivanova L et al 1999 *Inorg. Mater.* **35** 34
[26] Gudelli V K et al 2016 *J. Phys.: Condens. Matter* **28** 025502
[27] Wang F Q et al 2015 *Nanoscale* **7** 15962
[28] He J G et al 2016 *Phys. Rev. Lett.* **117** 046602
[29] Gandi A N et al 2016 *Chem. Mater.* **28** 1647
[30] Kumar S and Schwingenschlögl U 2016 *Phys. Rev.* B **94** 035405