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Theoretical studies on the thermopower of semiconductors and low-band-gap crystalline polymers

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A numerical procedure has been used for the prediction of the Seebeck coefficient of a crystalline material based on its electronic band structure with the goal of testing this approach on the simple polymers polythiophene and polyaminosquaraine. The investigation of several representative materials, including the crystalline solids β-Zn_4Sb_3 and $AuIn_2$ and these polymers, under ambient or external pressure conditions, indicates that Seebeck coefficients can be calculated within the rigid-band and constant-relaxation-time approximations. The results are in semiquantitative agreement with experiment and provide a basic understanding of the mechanisms for thermopower. These theoretical results together with previous similar studies show that band-structure calculations can be used to guide the rational design of high-performance thermoelectric materials. We also suggest that appropriate and specially engineered doped low-band-gap polymers may be promising candidate materials for thermoelectric applications.

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INTRODUCTION

The search for high-performance thermoelectric (TE) materials is a subject of current intense research. The performance of TE materials depends on the dimensionless figure of merit (ZT) of the material given by $ZT=(S^2\sigma T/\kappa)$ where S, T, σ, and κ are the Seebeck coefficient, absolute temperature, electrical conductivity, and total thermal conductivity, respectively.[1,2] The best materials available today for devices operating near room temperature are doped semiconductor alloys of antimony and bismuth tellurides,[3–6] which have ZT of about 1. This is a very low value since these TE devices only operate at about 10% of the Carnot-cycle efficiency. For practical purposes, a suitable high-performance TE material should have a ZT of at least 4. However, increasing ZT by a factor of 4 has remained a formidable challenge. Many approaches to enhance ZT have been explored. Among those, promising results or predictions have been reported for quantum-well structures,[7] thin film and multilayer materials,[8] crystals with complex electronic structures[9] and a class of compounds with the behavior of "electron-crystal phonon glasses," that is, materials with the electronic properties of a crystalline material and the thermal properties of a glass.[10] To advance the rational design of high-performance TE materials a fundamental understanding and theoretical prediction of the effects of the crystal and electronic structure on the thermal properties and Seebeck coefficient are necessary.

A qualitative relationship between the Seebeck coefficient of a material and its electronic band structure is well established. Within kinetic transport theory[11] it can be shown that when $kT \ll \varepsilon_f$, where ε_f is the energy at the Fermi level, $S=(\pi^2k^2T/3e)\ [d\ln(\sigma)/dE]_{E=\varepsilon_f}$ for metallic systems. The electrical conductivity is then given as $\sigma \propto [N(E)\times\langle v_f(E)^2\rangle]_{E=\varepsilon_f}$ if the electron scattering relaxation time is assumed to have no energy dependence. The Seebeck coefficient is related to the *derivatives* of the electronic density of states at the Fermi surface, $N(E)$, and the band velocity $v_f(E)$, and therefore depends on the details of the electronic band structure. The electronic band structure for almost any crystalline compound can now be obtained routinely from accurate first-principles methods.[12] There have already been several attempts to compute the Seebeck coefficient from first-principles calculations.[13–15] Although the results obtained from these calculations are not exhaustive, nevertheless from the rather limited number of comparison with experimental data, it appears that first-principles approaches can provide a (semi)quantitative prediction of the thermopower of crystalline materials.[13] More importantly, a deeper understanding of the physical basis of the Seebeck coefficient can be obtained from the analysis of the relevant band structure. The computation of the Seebeck coefficient involving the integration of the derivatives of the energy bands over the entire Fermi surface, a very large k-point set $O(N)\approx 10^4$ is needed. However, often less discussed is the accuracy of the band interpolation procedure. This is particularly important for very flat bands which are associated with high density of states and therefore large Seebeck coefficients.[16] In this paper, we describe our implementation of the calculation of the Seebeck coefficient. This method is independent of the methods and programs generating the electronic band structures. First we validate the program against the well-studied high-efficiency thermoelectric material β-Zn_4Sb_3.[13] We then investigate the interesting phenomenon of pressure-induced enhancement of the Seebeck coefficient by the electronic topological transition (ETT) or Lifshitz transition in $AuIn_2$.[17,18] Finally, we propose and demonstrate that low-band-gap semiconducting organic polymers with unique band-structure characteristics can be promising materials for high-efficiency thermoelectric materials.

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THE CALCULATION OF ELECTRONIC TRANSPORT PROPERTIES FROM FIRST-PRINCIPLES BAND-STRUCTURE CALCULATIONS

The method for the calculation of transport properties of a crystalline solid is based on the semiclassical Boltzmann theory and has been described in detail previously.[16] In essence, in the low-magnetic-field limit, the electrical conductivity σ_0 is calculated from the energy integral[11]

$$\sigma_0(T) = \frac{e^2}{3}\int dE\, \tau(E,T)N(E)v^2(E)\left(-\frac{\partial f(E)}{\partial E}\right), \qquad (1)$$

where e, τ, f, and v represent the charge of the electron (sign is included), electronic relaxation time, Fermi distribution function, and Fermi velocity, respectively. If one assumes the relaxation time for the electron scattering processes is a constant, i.e., $\tau(E,T)=\text{const}$, which has been shown to yield reasonably good results in several materials, then the temperature dependence of $\sigma_0(T)$ can be calculated in terms of the constant relaxation time τ,

$$\frac{\sigma_0(T)}{\tau} = \frac{e^2}{3}\int dE\, N(E)v^2(E)\left(-\frac{\partial f(E)}{\partial E}\right). \qquad (2)$$

Although this relation is strictly valid for metals, it also has been applied to the study of doped semiconductors.[19] The Seebeck coefficient is calculated from the ratio of the zeroth and first moments of the electrical conductivity with respect to energy,

$$S(T) = \frac{1}{eT}\frac{I^1}{I^0}, \qquad (3)$$

where

$$I^x(T) = \int dE\, \tau(E,T)N(E)v^2(E)(E-E_F)^x\left(-\frac{\partial f(E)}{\partial E}\right). \qquad (4)$$

A product of the density of states $N(E)$ and arbitrary quantity g which has energy and k-vector dependence as in the expressions (1) and (4) can be obtained by integration on the constant energy surface S in k space.[16,20]

An accurate interpolation scheme is important for the evaluation of the derivative of very-low-energy dispersion bands (flat bands) that cross at or near the Fermi surface. In fact, as mentioned earlier, materials with high Seebeck coefficient are often associated with very high density of states near the Fermi level. In this paper, the modified Shankland-Koelling-Wood scheme[21] as described in Ref. 16 is used to obtain interpolated band-dispersion data. It has been previously shown for the calculations of the Hall coefficient[16] of cubic metals using the Shankland-Koelling-Wood interpolation[22] scheme that high-frequency oscillations in interpolated band structures due to band crossings near the Fermi surface can be suppressed by a suitable filtering technique.[16]

The band-fitting procedure[16] has been implemented in an independent package. Since the only input is the electronic band structure, this code can be used in conjunction with the WIEN97 and WIEN2K[23] full-potential linearized augmented-plane-wave (FLAPW) electronic structure code[23] or other electronic structure codes, such as the pseudopotential plane-wave code VASP.[24] The application of this method is illustrated through the calculation of the Seebeck coefficient of several materials to be discussed below.

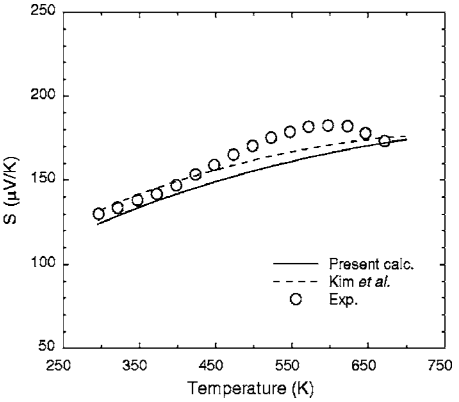


FIG. 1. Comparison of calculated Seebeck coefficient (S) of Zn_4Sb_3 with experimental data and data from a previous theoretical calculation (Ref. 13).

RESULTS AND DISCUSSION

We first validate the implemented method with the calculation of the Seebeck coefficient of β-Zn_4Sb_3.[13] The electrical resistivity and the thermopower of β-Zn_4Sb_3 have been measured and it has a fairly large $ZT \sim 1.3$.[25] Furthermore, its electronic structure has been investigated in detail and the thermopower calculated. Therefore this compound is a good benchmark to validate our calculations. The electronic band structure of β-Zn_4Sb_3 was calculated with WIEN2K with the generalized gradient approximation within the Perdew-Burke-Ernzerhof scheme[23] and a well-converged 2000 k-point set in the Brillouin zone (BZ), 182 in the irreducible wedge of the BZ with $RK_{max}=7$. Transport properties were calculated in an even denser 40 000 k-point set. The calculated Seebeck coefficient as a function of temperature is shown in Fig. 1. The present calculations are in good accord with previous theoretical results and agree with the experimental data particularly for $T < 400$ K. Deviation from the measured Seebeck coefficient starts around 410 K where the calculations predicted a slow monotonic increase with temperature whereas the experiment shows a maximum at $\sim$580 K and then a gradual decrease with increasing temperature. The turnover of the experimental thermopower is probably associated with the increase of electrical conductivity observed at 580 K.[26]

A more sensitive test of the numerical stability of the proposed band-fitting procedure is the calculation of the Hall coefficient. The calculation of the Hall coefficient requires the computation of the inverse mass tensor which is related to the second derivative of the Fermi surface.[16] The calculated Hall concentration as a function of energy shift relative to the Fermi level of the undoped crystal is shown in Fig. 2. The magnitude and the energy dependence of the hole concentrations are in excellent agree with previous theoretical results. For example, the small change in the curvature of the

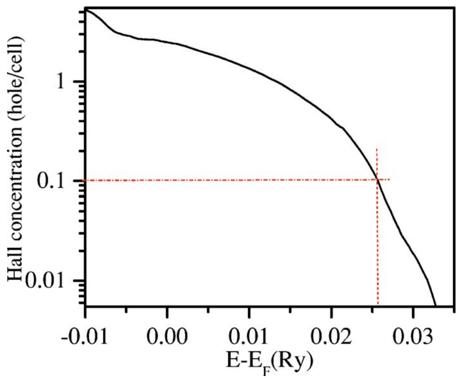
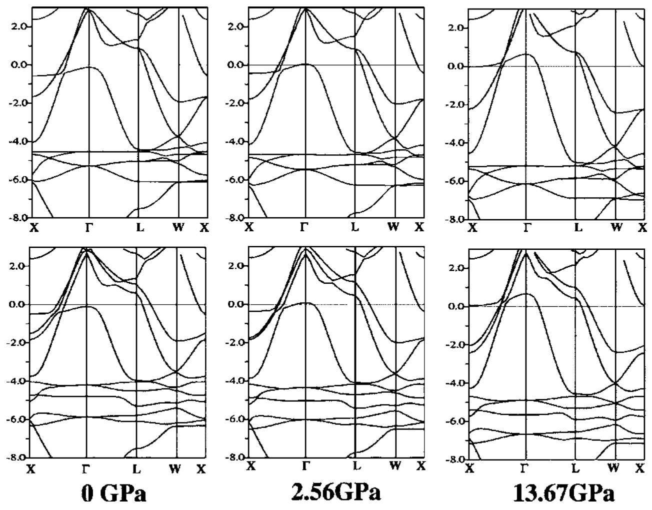


FIG. 2. (Color online) Calculated Hall concentration (electron or hole concentration) for Zn_4Sb_3. The dotted lines indicate the doping level of 0.1 hole/cell. The structure used for this calculation was identical to that of Ref. 13.

Hall concentration–Fermi energy shift plot near –0.005 Ry is reproduced. Moreover, the calculated Fermi-energy shift of 0.026 Ry corresponding to a 0.1 hole/cell doping is also in substantial agreement with the previous value of ~0.025 Ry.[13]

ENHANCEMENT OF THE THERMOPOWER OF $AuIn_2$ BY ELECTRONIC TOPOLOGICAL TRANSITION

The motivation behind the pressure-tuning approach to guide the search for improved thermoelectric materials is the anticipation that the application of pressure to a crystal with complex band structure may change the electronic properties that affect the thermopower.[27] There have been some notable successes with this method. For example, it was reported recently that at room temperature when *p*-doped $Sb_{1.5}Bi_{0.5}Te_3$ was compressed to 2 GPa, the observed figure of merit (*ZT*) was almost double that under ambient pressure.[28] Another system where the thermopower has shown large variation with pressure is the simple $AuIn_2$ alloy.[17] It was reported that the thermopower of $AuIn_2$ increases monotonically and reaches a maximum at 2 GPa and then decreases with increasing pressure in the 2–4 GPa pressure range. Incidentally, the electrical conductivity also shows a departure from the low-pressure linear trend at 2 GPa. This interesting behavior has been attributed to an electronic transition in this pressure range. A theoretical linear combination of muffin-tin orbital[17] and FLAPW calculations[18] has been performed to characterize the electronic band structure. It was found that at around 4 GPa, the electronic band along $X \rightarrow \Gamma \rightarrow L$, initially below the Fermi level in the low-pressure structures, crosses the Fermi surface and creates a hole around Γ.[17,18] The change in the electronic structure, however, is apparently not accompanied by a structural transformation. This phenomenon is known as an ETT transition. This suggestion was confirmed from a recent investigation of the equation of state obtained from x-ray diffraction.[18] From the analysis of the measured *P-V* curve a change of slope of the universal equation of state was observed at 3.8 GPa. Our objective here is to study how changes in the topology of the Fermi surface affect the Seebeck coefficient of this material.



0 GPa **2.56GPa** **13.67GPa**

FIG. 3. Electronic band structure (energy in eV) for face-centered-cubic $AuIn_2$ (Ref. 17) at selected pressures calculated with (lower panel) and without (upper panel) spin-orbit interactions.

The computational procedure and parameters for $AuIn_2$ are similar to those of β-Zn_4Sb_3 but with the RK_{max} increased to 8. In view of the potential effects of spin-orbit (SO) coupling on the band structure and therefore on the calculated quantities for alloys composed of heavy elements, these effects were included in the calculations using a perturbative scheme.[29] Convergence of the total energies with the size of *k*-point sampling was carefully monitored (up to 5000 *k* points). A series of calculations were performed at different volumes. The volumes and calculated energies are then fitted with the Murnaghan equation of state. Without the consideration of spin-orbital coupling, the derived equilibrium cell constant is 6.689 Å with a bulk modulus (B_0) of 55 GPa and $B_0'=5.2$. Including spin-orbit coupling, the calculated constant is 6.660 Å with a bulk modulus (B_0) of 58 GPa and $B_0'=6.0$. The theoretical values are in substantial agreement with the unit cell of 6.507 Å and B_0 of 50 GPa (with B_0' fixed at 4) derived from a x-ray diffraction study.[17]

The calculated band structures of $AuIn_2$ with and without spin-orbit interactions at several selected volumes are shown in Fig. 3. The present results confirm previous calculations that the energy band along $X \rightarrow \Gamma \rightarrow L$ moves closer to the Fermi level as the volume is reduced (pressure is increased). The ETT phase transition, estimated when the energy band touches the Fermi surface, is ~3 GPa. No apparent differences are observed between the energy band profiles with and without SO coupling at and near the Fermi level. The only noticeable difference is that the degeneracy of the highly dispersed electronic band along $X \rightarrow \Gamma$ that crosses the Fermi level has been lifted somewhat via spin-orbit interactions.

The Seebeck coefficients calculated as a function of pressure at 300 K are shown in Fig 4. The theoretical trend in the variation of the Seebeck coefficient or thermoelectric power (TEP) with pressure is in qualitative agreement with experiment. In the experiment, it was observed that the TEP increases linearly from 2.4 μV/K at ambient pressure to 6.5 μV/K at ~2 GPa. The error associated with the experi-

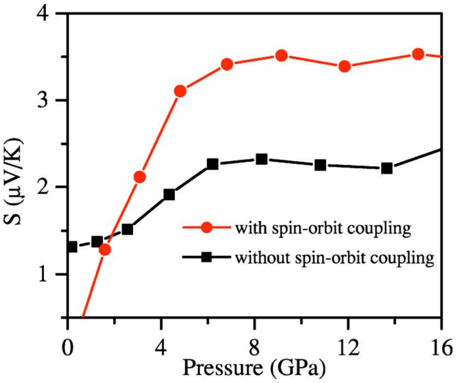


FIG. 4. (Color online) Calculated Seebeck coefficient (S) as a function of pressure for $AuIn_2$ with and without spin-orbit interactions.

mental measurements was not reported. The computed TEP without SO coupling approximately increases from 1.25 $\mu V/K$ and reaches a plateau from 5 to 12 GPa with a weak maximum of 2.30 $\mu V/K$ at $\sim$8 GPa. The computed values for the Seebeck coefficient are slightly lower than observed in the experiment. The computed TEP including SO coupling also shows a similar profile. In this case, as in the experiment, the calculated Seebeck coefficient increases almost linearly at ambient pressure to a maximum of about 3.6 $\mu V/K$. Furthermore, the magnitude of the calculated Seebeck coefficient within the SO approximation is evidently in better agreement with experiment. The small discrepancy between the calculated TEP with and without SO coupling can be traced back to the sensitivity of the Seebeck coefficient to the details of the electronic band structure, and in particular, to the curvature of the band structure near the Fermi surface. Even though the appearance of the band structures is grossly similar there are subtle differences that affect the calculated quantities. The increase of the calculated TEP as a function of pressure can be largely attributed to the increasing importance of the relatively flat energy band along $X \rightarrow \Gamma \rightarrow L$ as it approaches and finally crosses the Fermi level. Inspection of the integrals (1) and (2) shows that the Seebeck coefficient is strongly dependent on the density of states of the bands only close to the Fermi surface since these bands are weighted heavily by the derivative of the Fermi function. When the flat energy band along $X \rightarrow \Gamma \rightarrow L$ approaches the Fermi level, a second flat band along $X \rightarrow \Gamma$ follows closely. The *energy gap* between the two bands is slightly smaller in the calculation including SO than in that without SO coupling. The relative contribution of the first and second bands determines the presence of a plateau region in the TEP. In passing, it is interesting to comment on the increased electrical conductivity after the ETT. After the ETT, the highest-energy band along $X \rightarrow \Gamma \rightarrow L$ crosses the Fermi level with large slope (i.e., it is highly dispersive). Therefore, the electron effective mass associated with this band becomes smaller and therefore enhances the electrical conductivity. The calculations show that the anomaly in the TEP is the result of the interplay of several electronic bands close to the Fermi level and need not simply be due to the passage of a single electronic band through the Fermi level. Consequently, the occurrence of an anomaly in the TEP does not necessarily correspond exactly to the pressure at the ETT. In summary, the theoretical calculations reproduced the salient features of the TEP profile observed in $AuIn_2$.

THERMOPOWER OF DOPED LOW-BAND-GAP POLYMERS

Apart from the Seebeck coefficient, the electrical and thermal conductivity are two important parameters governing the thermoelectric efficiency of a material. For crystalline materials, in general the thermal conductivity is expected to be fairly high. Furthermore, the thermal conductivity increases with decreasing temperature. This behavior is in contrast to that of amorphous solids where the thermal conductivity is often very low and decreases with decreasing temperature.[30] Recently, it was shown that crystalline materials with localized low-frequency vibrations can be very efficient in reducing the thermal conductivity.[31,32] Several classes of compounds possessing this unique property, such as the skutterides[33] and the metal-doped semiconductor clathrates,[14] have been studied extensively. A class of compounds that have inherently low thermal conductivity are organic polymers. Some of the polymers can be doped to become good electrical conductors. The thermopower of many conducting polymers has already been studied in the past but the results have been disappointing.[34,35] Furthermore, organic polymers usually have fairly low melting points and become unstable at moderately high temperature (e.g., 300 °C) and are often not suitable for processing. Therefore, organic polymers were deemed not to be suitable thermoelectric materials. However, polymers have some attractive features that are absent in semiconductor solids. Compared to inorganic solids, apart from the very low thermal conductivity, conducting on semiconducting polymers with desirable electronic band structure favoring high thermopower, in principle, can be designed and perhaps synthesized. Several recent advance have helped to revive the interest in studying polymers for thermoelectric applications. The successful synthesis of low-band-gap polymers and new doping schemes may allow more controllable adjustment of the electric conductivity. Furthermore, polymers composed of N and S atoms forming the backbone and with complex substituting side groups have helped to enhance the thermal stability.[36,37]

It is often difficult to find materials that have reasonably high electrical conductivity and high Seebeck coefficient at the same time. An important exception is a recent report showing that p-doped $CsBi_4Te_6$ may be a promising highly efficient thermoelectric material at low temperature ($<$300 K).[9] Theoretical calculations revealed that $CsBi_4Te_6$ is a small-band-gap semiconductor.[38] The electronic band structure near the Fermi level was shown to be very complex with a combination of highly dispersive and nondispersive (flat) electronic bands. These are characteristic features for high Seebeck coefficient (flat bands) and high electrical conductivity (dispersive band). This explanation is not unlike the "two-band" scenario[39] proposed for the skutterides and for some high-T_c inorganic superconductors.[40] In this model, a

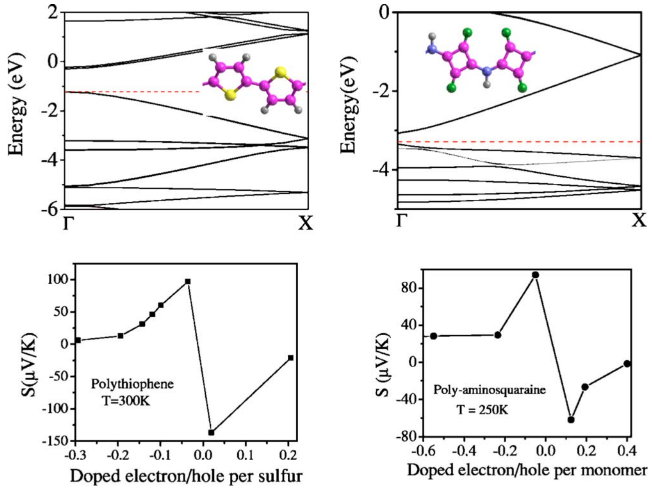


FIG. 5. (Color online) Calculated Seebeck coefficient (S) for polythiophene (left) and polyaminosquarine (right). Isolated planar polymer chains were used for this calculation.

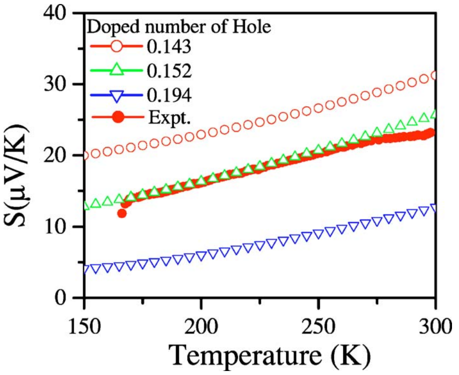


FIG. 6. (Color online) A comparison of experimental and calculated Seebeck coefficients of polythiophene at several doping concentrations (number of holes per S atom) from 150 to 300 K.

dispersive band that crosses the Fermi level gives the metallic character [high electron or hole velocity, v in Eq. (1)] while a flat band [high electron density of states $N(\varepsilon)$ in Eq. (1)] interacts strongly with particular lattice vibrations in inorganic superconductors and is responsible for the large electron-phonon coupling or high Seebeck coefficient in high-performance thermoelectric materials. It is conceivable that polymers with these unique features in the band structure already exist or can be synthesized. A potential difficulty with theoretical investigations on the electronic structure of polymers is that some of the properties may not be adequately or appropriately described from an electronic band point of view. To this end, we investigate the properties of doped polythiophene where the Seebeck coefficient has been reported.

The structure of the polythiophene polymer is shown in Fig. 5. The internal structural parameters of the polymer are fully optimized and the electronic band structure is obtained from pseudopotential plane-wave calculations employing an ultrasoft Vanderbilt pseudopotential and a generalized gradient scheme.[24] The calculations show that polythiophene has a very simple band structure and is a semiconductor with a band gap of 0.9 eV. The neutral polythiophene is an electrical insulator. Electrical conductivity, however, can be created by doping with electron-donating (n-doped) or electron-withdrawing (p-doped) agents. If the doping level is not too high (e.g., $<1-5$ %), it is reasonable to assume that the structure of the doped polymer does not change from the neutral structure; thus the electronic structure of the doped polymer may be approximated by the rigid-band model. Seebeck coefficients at 300 K for p- and n-doped polythiophene are calculated as described above and the results are shown in Fig. 5. The highest filled and lowest empty electronic bands are composed of primarily S $3p$ orbitals which interact appreciably with the π system of the polymer backbone. Inspection of the band structure shows that except very close to the zone center, where the density of states is high, the band dispersions are considerable. Experimentally,[41] p-doped polythiophenes with PF_6^- were found to have a reasonably high conductivity of $\sim 10^2-10^3$ Ω^{-1} cm^{-1} depending on the concentration and method of doping. Therefore, it is not surprising that except for extremely low doping levels the calculated Seebeck coefficients are very low. The calculated Seebeck coefficient of ~ 20 μV/K corresponding to the doping levels of $\sim 0.14-0.15$ hole/monomer unit compare favorably with the experimental value of 22 μV/K on a sample of $FeCl_3$-doped polythiophene.[42] In Fig. 6, the calculated Seebeck coefficient as a function of temperature with several doping concentrations is compared with experimental measurements.[42] Although the oxidation level for the polythiophene sample has not been characterized, the calculated doping concentration is not unreasonable as the doping level of polythiophene can be adjusted from 0.02 to 0.3 hole/monomer unit using different oxidizing agents.[43] Moreover, the very high Seebeck coefficient predicted of ~ 100 μV/K for p doping and -140 μV/K for n doping, which correspond to very low dopant concentrations of 0.04 hole/monomer unit and 0.02 e/monomer unit, respectively may not be unrealistic as these doping levels are in principle within the practical limits.

We note that the reasonable agreement between theory and experiment is not just a coincidence. To investigate this further, we have carried out a detailed series of quantum chemistry and plane-wave pseudopotential calculations to characterize the role of doping and the possible resultant polaron contributions to the results. We find that at very dilute p-doping levels, as in the situation studied here, the electronic structures are not modified significantly and the current approximation holds well. This obervation is surprising and in contrast to results for polyacetylene, where polarons form readily upon doping, particularly with n doping. The reason for the difference in behavior between polythiophene and polyacetylene is that the more flexible chain structure in the latter material promotes bond alternation. In polythiophene, however, the polymer framework is much more rigid and the electron delocalization is largely preserved upon low doping, thus reducing the influence of polarons and maintaining the band structure. The theoretical results are in substantial agreement with an experimental photoelectron study of polythiophene which shows that the valence-band structure did not change appreciable with dilute p doping.[44] The results of this detailed study will be published later. The theoretical results obtained here show that band-structure calculations are very useful tools to investigate the thermoelectric properties of conducting polymers.

As noted earlier, a good candidate material with high thermopower should possess both localized nondispersive bands with high electronic density of states and highly dispersive bands for electron mobility. In principle, this characteristic can be incorporated into a polymer structure. Taking the example of polythiophene, a suitable polymer needs both interacting and noninteracting lone-pair bands in the structure. To illustrate this design concept, we studied a hypothetical polymer polyaminoquaraine,[45] which has both oxygen and nitrogen atoms in the structure.

The crystal and molecular structure of the polyaminoquaraine polymer was fully optimized with the pseudopotential plane-wave method as used for polythiophene.[24] The electronic band structure at the optimized geometry was computed and depicted in Fig. 5. As expected the highest occupied oxygen lone-pair orbital (first electronic band at the zone center Γ) is slightly more dispersive and crosses the more localized lone-pair band of the N atoms.[45] The electronic density of states at the top of the valence band is very high. This electronic structure profile satisfies the main criteria for high-performance thermoelectric materials. The transport properties of this polymer and the effects of doping have been examined and the results are summarized in Fig. 5. The Seebeck coefficient is strongly dependent on the level of p doping (removing electrons) as indicated by the energy shift relative to the highest occupied level of the neutral polymer. A maximum in the Seebeck coefficient of $\sim 96\ \mu\text{V/K}$ is predicted at a removal of 0.05 e/monomer unit. The p doping may be achieved by doping the polymer with I_3^- or SbI_3. It is unlikely, however, that the polyaminoquaraine polymer will be stable and can be synthesized. The calculations reported here, however, support the proposal that polymers with band-structure characteristics unique to the enhancement of the thermopower can in principle be designed in a rational manner.

In passing, relevant and important polymers for thermoelectric application are carbon nanotubes. The electronic band structure of carbon nanotubes consists of localized bands with very high electronic density of states. It is also well known that doped nanotubes are highly conducting. Particularly useful are the semiconducting carbon nanotubes with oxygen molecules physically absorbed. For example, the [8,0] nanotube is a low-band-gap semiconductor and the occupied bands are strongly dispersive. Previous theoretical calculations[46] have shown that upon oxygen adsorption, a localized oxygen lone-pair band is created near the Fermi level. This situation is very similar to the polyaminoquaraine polymer described above. Therefore, carbon nanotubes with oxygen physically absorbed can be good candidate materials for high-performance thermoelectrics.

CONCLUSIONS

In this paper we applied a numerical procedure[16] for the prediction of the Seebeck coefficient of a crystalline material based on its electronic band structure with the goal of testing this approach on the simple polymers polythiophene and polyaminosquaraine. Through the investigation of several representative materials, including the crystalline solids β-Zn_4Sb_3 and AuIn_2 and these polymers under ambient or external pressure conditions, it is shown that Seebeck coefficients can be calculated within the rigid-band and constant-relaxation-time approximations. The results are in semiquantitative agreement with experiments and contribute to the understanding of the mechanisms for thermopower. The theoretical results presented here together with previous similar studies show that band-structure calculations can be used to guide the rational design of high-performance thermoelectric materials. We finally suggest that appropriate and specially engineered doped low-band-gap polymers can also be promising candidate materials.

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