



## Viewpoint Paper

## Recent progress in calculations of electronic and transport properties of disordered thermoelectric materials



B. Wiendlocha, K. Kutorasinski, S. Kaprzyk, J. Tobola\*

AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, Al. Mickiewicza 30, 30-059 Krakow, Poland

## ARTICLE INFO

## Article history:

Received 5 March 2015

Revised 12 April 2015

Accepted 16 April 2015

Available online 28 April 2015

## Keywords:

Semiconductor compounds

Thermoelectric materials

*Ab initio* calculation

Defects in semiconductors

## ABSTRACT

Results of electronic structure calculations in disordered thermoelectric materials are presented using KKR–CPA technique. Firstly, it is applied to detect the resonant impurities in selected materials, including PbTe, where Bloch spectral functions are computed. Secondly, in combination with the Boltzmann transport theory, we discuss the effect of band convergence in  $\text{Mg}_2(\text{Si-Sn})$  and band alignment in half-Heusler  $\text{Ti}(\text{Co-Fe-Ni})\text{Sb}$ , on thermoelectric performance. Moreover, the influence of spin–orbit interaction on band features and thermopower is shown in  $\text{Mg}_2\text{X}$  ( $\text{X} = \text{Si, Ge, Sn}$ ) compounds.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Electron transport properties of crystalline systems belong to the most fascinating phenomena studied in materials science. Macroscopic quantities as electrical conductivity  $\sigma$ , thermopower  $S$ , Hall coefficient  $R_H$  or thermal conductivity  $\kappa$ , are traditionally used to probe and classify materials as metals, semimetals or semiconductors. The aforementioned quantities are also essential to determine usefulness of materials for thermoelectric (TE) applications, which is commonly expressed via dimensionless figure of merit  $zT = \frac{\sigma S^2}{\kappa} T$  at a given temperature  $T$ . The TE performance can be optimized by proper adjustment of carrier concentration  $n$  for a given temperature range. It should also be noted that theoretical description of electronic and transport properties of solid state materials has always been a difficult problem for condensed matter theory due to complexity of phenomena that should be taken into account. Electron transport behaviors are directly related to electronic states near the Fermi energy ( $E_F$ ) and searching for accurate information on  $\mathbf{k}$ -space electron features appears to be the key factor for reliable modeling, or even predicting, of TE behaviors. Fortunately, *ab initio* electronic band structure calculations combined with the Boltzmann transport theory [1–5] were established to be a quite convenient way to study electron transport in materials. In practice, it is performed via highly accurate calculation of ground state properties ( $T = 0$ ) of electrons near Fermi surface. Finite temperature effects, especially interesting in investigations of thermopower  $S(T)$  or electrical conductivity  $\sigma(T)$ , are not

explicitly taken into account in such calculations, but modifications of ground state electronic properties with temperature can be incorporated through the Fermi–Dirac distribution function  $f(E, T)$ . Furthermore, relevant processes responsible for relaxation time of electrons must also be approximated, since in general their description remains a hard task [6,7]. Actually, the constant relaxation time approach can be still regarded as a simple and reference approximation in Boltzmann transport theory. We should also bear in mind that real TE materials habitually contain different types of imperfections (alloying, impurities, vacancy, anti-site defects, etc.) that may strongly affect TE properties, in particular electron transport properties.

In this paper, recent results of electronic structure calculation as well as modeling of electron transport properties of well-known TE bulk materials are discussed. We mostly focus on (i) the problem of detection of resonant impurities and the localization of their electronic states, using doped PbTe as an example; (ii) the band convergence achieved by alloy substitution in  $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$  and its effect on thermopower and  $zT$  in function of carrier concentration and temperature; (iii) the effect of electronic band alignment in disordered half-Heusler  $\text{TiCo}_{1-x}(\text{Fe}_{0.5}\text{Ni}_{0.5})_x\text{Sb}$  alloy on thermopower. Besides, in the case of *p*-type  $\text{Mg}_2\text{X}$  ( $\text{X} = \text{Si, Ge and Sn}$ ) series of compounds, we discuss the influence of spin–orbit (S–O) interaction on TE properties, clearly evidencing that fully relativistic treatment in *ab initio* calculation may affect electron transport properties. The Korringa–Kohn–Rostoker (KKR) [8–11] method based on Green function multiple scattering theory was used to calculate electronic band structure and relevant kinetic parameters of electrons in the vicinity of  $E_F$ . Moreover, the coherent potential

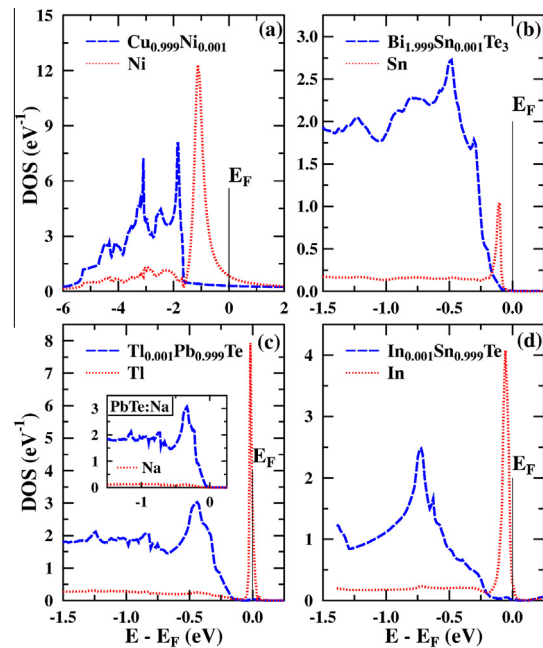
\* Corresponding author.

E-mail address: [tobola@ftj.agh.edu.pl](mailto:tobola@ftj.agh.edu.pl) (J. Tobola).

approximation (CPA) [8–10] was employed to account for chemical disorder effects on electronic structure in two aspects. Firstly, densities of states (DOS) of impurities placed in host material are calculated to verify their resonant-like or conventional-like character, and so-called Bloch spectral functions (BSF) [10,12,13] are analyzed to see how they modify the electronic bands. Secondly, complex energy electronic band structure [14–16] and resulting velocities and life-times of electrons are calculated in disordered alloys to derive electron transport quantities depending on temperature and carrier concentration.

**Resonant levels** Resonant levels (RLs), called also virtual bound states [17,18] are formed by certain impurity atoms in semiconductors (or metals), at energies, where in the absence of neighboring atoms a real bound state would be formed [19]. A manifestation of a resonant state is a sharp peak of the impurity's density of electronic states at the resonance energy, thus resonant impurities, at proper concentrations, may significantly modify the host material's band structure. As a consequence, such a system does not follow the rigid band model, where presence of impurity atoms shifts the Fermi level only. The canonical examples of resonant impurities are transition metal atoms placed in noble metals, like Cu–Ni alloy (constantan), the high-thermopower reference metallic alloy and material for thermocouples. Recently, the resonant impurities attracted much attention among thermoelectric community, as they may improve thermoelectric performance (especially thermopower) of the materials, used in thermoelectric power generators and cooling devices [18]. Examples of such cases are: PbTe:Ti [20] also alloyed with Si [21], Se and S [22], SnTe:In [23] or Bi<sub>2</sub>Te<sub>3</sub>:Sn [24]. However, there are several important questions frequently raised in connection with resonant impurities: How can we classify whether the selected impurity is, or is not, a resonant one? If the resonant impurity atom creates a sharp peak in the DOS, does it form a narrow impurity band? The second question is especially important, since if the impurity would form a narrow impurity band in semiconductor, such a band generally would not contribute much to the thermopower of the system, and in extreme cases, completely flat impurity band would lead to localization of the charge (effective mass becomes infinite). Recent works [25–27] shed some new light on those questions and we will try to answer them here.

Detection of the resonant level is possible in the first principles calculations of the density of states of the doped material. The most convenient method for such calculations is KKR–CPA, since very small amounts of the impurity (typically we use 0.1%, which is in practice close to the single impurity limit, where CPA is exact [19]) may be calculated. Such a small amount of impurity atoms allows to detect the very sharp partial impurity DOS peaks, confirming the resonant behavior, which for higher concentrations (typically calculated using supercell technique) is less evident due to enhanced hybridization effects. Examples are presented in Figure 1: (a) Ni in Cu, one of the first known “resonant” metallic alloys, where for larger Ni concentrations a “bump” in DOS just below  $E_F$  is formed<sup>1</sup>; (b) Sn in Bi<sub>2</sub>Te<sub>3</sub>, (c) Tl in PbTe, and (d) In in SnTe. Note, that (b) confirms theoretically the resonant behavior of Sn in Bi<sub>2</sub>Te<sub>3</sub> for the first time, also CPA results for SnTe:In were not presented before. DOSes presented in Figure 1 were obtained using KKR–CPA implementation described in Refs. [8,9,11,30]. In all examples in Figure 1, sharp and narrow DOS peaks on the impurity atoms are found. Note the differences in orbital character of the resonances in the aforementioned cases, in metallic Ni:Cu, resonance comes from the 3d electrons of Ni, and appearance of resonances connected to, relatively localized, 3d orbitals could be expected.



**Figure 1.** KKR–CPA densities of states of “resonant” systems: (a) Ni in Cu; (b) Sn in Bi<sub>2</sub>Te<sub>3</sub>; (c) Tl in PbTe; (d) In in SnTe. In all cases, impurity concentration is equal to 0.1%. The partial impurity DOS, marked with red dotted lines, is given per one impurity atom. Blue dashed lines are total densities of states per formula unit. Inset in (c) shows DOS of Na<sub>0.001</sub>Pb<sub>0.999</sub>Te (blue dashed line), where Na partial DOS (red dotted line) shows typical, rigid-band like and non-resonant behavior. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

In the other cases, where the host system is intrinsically a semiconductor, the resonances come from the *s* orbitals of the impurity electrons, which in other cases would contribute to the free-electron-like states, thus formation of these resonances, characterized with narrow DOS peaks, may be considered as unusual. As a contrasting example, DOS of Na in PbTe is plotted in the inset of Figure 1(c). Small partial impurity states on Na are equally distributed in the valence band of PbTe, showing typical rigid-band-like behavior, without any DOS peaks. Note also, that not only the element is important for the formation of RL, but also the site, which it occupies, if the host system is a compound. As is shown in Ref. [27], Ag might have formed resonant state in Mg<sub>2</sub>Sn, if it had replaced Mg atoms, whereas on Sn site it behaved as regular, rigid-band-like impurity.

The DOS analysis shows us, whether the selected impurity may form a resonant level in our system. It does not, however, answer the questions on the formation of impurity band and charge localization. To analyze this issue, we use the Bloch spectral density functions  $A^B(\mathbf{k}, E)$  (BSF), which are a generalization of the dispersion relations for the disordered solid [10,12,13]. For the ordered crystal,  $A^B(\mathbf{k}, E)$  at selected  $\mathbf{k}$  is a delta function of energy, being non-zero only for  $(\mathbf{k}, E)$  points, where electron in band  $\nu$  has an energy eigenvalue  $E_{\nu, \mathbf{k}} : A^B(\mathbf{k}, E) = \sum_{\nu} \delta(E - E_{\nu, \mathbf{k}})$ . In other words, the set of BSFs describe here the dispersion relation  $E(\mathbf{k})$ . For alloys or doped semiconductors, electronic bands are smeared, and when electron scattering is not very strong,  $A^B(\mathbf{k}, E)$  takes the form of the Lorentz function, where the peak of BSF gives the position to the center of the band  $E_{\nu, \mathbf{k}}$ , and full width at half maximum (FWHM) value  $\Gamma$  corresponds to the life time of the electronic state [31],  $\tau = \hbar/\Gamma$ . In such a case, we can define virtual or complex energy bands [14–16] (see, next paragraph), where the real part of energy corresponds to the band center and imaginary part to the life time, and  $\Gamma = 2 \text{Im}(E)$ . However, for the system with resonant impurities, spectral functions become very broad and

<sup>1</sup> It is worth mentioning here, that explanation of the Cu–Ni photoemission spectra was one of the first successes of CPA, see Refs. [19,28,29].

Download English Version:

<https://daneshyari.com/en/article/1498112>

Download Persian Version:

<https://daneshyari.com/article/1498112>

[Daneshyari.com](https://daneshyari.com)