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The role of electronic and crystal structure in the effect of volumetric band convergence

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ABSTRACT

The effect of rearrangement of the electronic band structure by changing the volume of a crystalline cell was investigated by means of first-principles calculation. The corresponding effect on the thermoelectric power factor was studied in Boltzmann approximation. The separate role of electronic structure of constituent elements and crystal structure was investigated. As the example, cubic Mg_2Si and orthorhombic Sr_2Sn were considered, and vice versa, hypothetical orthorhombic Mg_2Si and cubic Sr_2Sn. We found that in all studied cases there is rearrangement of electronic bands, mostly conduction ones, with the change of volume of the cell. In all cases it may leads to the increase of power factor.

1. Introduction

Electrical energy is the most practical form of energy. Therefore, the search for effective converters of thermal, mechanical and other forms of energy into electrical is an important task. Much attention is paid to direct methods of converting thermal energy into electrical energy, which include, in particular, solid-state thermoelectric materials [1]. Such converters have a number of advantages: the absence of moving parts, reliability, compactness. The operating principle of the thermoelectric material is based on the Seebeck effect. The effectiveness of such a material is determined by a dimensionless quantity ZT, figure of merit: $ZT = \frac{S^2\sigma}{k_{el} + k_{latt}}T$, where S is the Seebeck coefficient, σ is the conductivity, k_{el} is the electronic thermal conductivity, and k_{latt} is the lattice thermal conductivity. To optimize ZT, usually one try to increase the numerator $S^2\sigma$, which is called the power factor (PF). Another approach is to lower the denominator $k_{el} + k_{latt}$, focusing on the lattice thermal conductivity [2]. Of course, all these quantities are interrelated, which makes the optimization task difficult [3].

An increase in the PF can be achieved by optimizing the electronic band structure (BS) of the material. Optimization is achieved, usually, in two ways: increasing the degeneracy of the electronic bands near Fermi level and creating gradients in the energy density of electronic states. In the first case, one try to achieve convergence of the electronic levels near the Fermi level [4–6]. In the second approach, one try to find doping, that create sharp changes in the density of electronic states [7,8].

Let us consider the first of these ways of increasing efficiency: the rearrangement of the BS. To do this is to change the cell volume, for example, by alloying. It has been shown experimentally that $Mg_2Si_{1-x}Sn_x$ compounds have a higher PF than the Mg_2Si and Mg_2Sn compounds separately [9]. Also $Mg_2Si_{1-x}Sn_x$ studied theoretically, where an increase in the power factor was observed [10,11].

Indeed, in the work [4], the change in transport properties was studied with a change in the cell volume. It was shown that an increase in cell volume leads to an increase in the PF. In particular, magnesium compounds Mg_2X (X = Si, Ge) were considered, which proved to be ones of the best in terms of the PF gain [12].

Lets focus on what role does the crystal structure and electronic structure of the valence shells of elements play in the realization of the effect. Specifically, if one change the lattice type or replace atoms in the given compound by the atoms from the same group, how BS and PF behave with the cell volume change? It is of practical importance, because the thermal conductivity of compounds with heavy atoms generally will be lower, which may lead to an improvement in the thermoelectric figure of merit.

As an example we focus on the A_2B type compounds of the elements II and IVa groups. To study the mentioned problem, the cubic Mg_2Si ($Fm\bar{3}m$) and orthorhombic Sr_2Sn (Pnma) compounds were considered. To clarify the contribution of the crystal lattice, hypothetical structures of cubic Sr_2Sn ($Fm\bar{3}m$) and orthorhombic Mg_2Si (Pnma) were studied.

2. Method of calculation

The calculations were carried out using the PAW package VASP

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Table 1
Table of parameters used in calculation.

Compound	Structure	k-points grids[a]	E_{cut}, eV
Mg_2Si	cubic	14 × 14 × 14 (44 × 44 × 44)	340
	orth.	16 × 12 × 12 (32 × 24 × 24)	380
Sr_2Sn	orth.	16 × 12 × 12 (28 × 21 × 21)	350
	cubic	14 × 14 × 14 (44 × 44 × 44)	475

[a] Top for self-consistent calculation, bottom for calculation on a densified grid.

5.4.1 [13,14]. The cubic structure of Mg_2Si ($Fm\bar{3}m$, No 225) was specified by a primitive unit cell containing three atoms with lattice parameter a = 6.338 Å [15]. To determine the structure of Sr_2Sn (Pnma, No 62), the generators of this group were used [16] and the parameters: a = 5.378 Å, b = 8.402 Å, c = 10.078 Å, x = 0.6561, z = 0.0723, obtained in the experimental and theoretically works [18,17]. The Sr_2Sn unit cell contains 12 atoms. The hypothetical cubic structure Sr_2Sn ($Fm\bar{3}m$, No 225) same as stable Mg_2Si was specified by a primitive unit cell containing three atoms. The lattice parameter a = 7.985 Å was obtained by the optimization of the structure. Then, by analogy, the hypothetical orthorhombic structure Mg_2Si (Pnma, No 62) containing 12 atoms was considered. The lattice parameters are obtained from the optimization of the structure: a = 4.378 Å, b = 7.353 Å, c = 14.144 Å. For self-consistent calculation, we used a Γ-centered grids of k-points and a cutoff energy of the basis of plane waves E_{cut} shown in Table 1.

To obtain transport coefficients semiclassical Boltzmann theory was used, as implemented in BoltzTraP code [19]. Densified grids of k-points were used to calculate transport properties shown in Table 1. Note that we calculate the reduced power factor $\frac{S^2\sigma}{\tau}$, when τ is the relaxation time. In general, the relaxation time depend on temperature, chemical potential and crystal structure which could change the shape of the curves of the obtained dependencies. We assume that the relaxation time qualitatively behaves closely for all crystal structures of the same material. In the follow by PF we mean the reduced power factor.

3. Results and discussion

3.1. Mg_2Si in the cubic structure of $Fm\bar{3}m$

The effect of band convergence in cubic Mg_2Si with volume change is well-studied [4,20]. Our results are very close, so we present BS and PF in the supplementary material. With the increase of volume of the cell, two lowest bands at point X converge (Fig. S1), leading to the increase in PF (Fig. S2a–b).

3.2. Sr_2Sn in the orthorhombic structure of Pnma

The band structures of orthorhombic Sr_2Sn is shown in Fig. 1a. As the cell volume increases, the C1 and C2 conduction bands converge, as well as C1 and C3. There are also changes in the position of other conduction bands. The valence band, however, remains almost unchanged. The energy difference between these bands as function of the relative cell volume, is presented in Fig. 1b. The most significant convergence of the bands is observed near the minimum of the conduction band, as well as in the cubic Mg_2Si (Fig. 1b).

The PF as function of the chemical potential at a fixed temperature is presented in Fig. 2a–b. As the cell volume increases, the maximum value of the PF increases. The peak value of the PF is shown in Table 2. The largest effect is observed for the conduction bands, which is associated with a significant change of their position. It should be noted, that at given value of the chemical potential (relate to the concentration of carriers), the PF can even decrease, for example, for the p-type. This suggests that it is necessary to optimize not only the electronic structure, but also the carrier concentration, to get a maximum benefit.

The obtained result illustrates that the BS rearrangement effect is observed near the edge of the conduction band not only in the cubic structure of magnesium compounds, but also in the orthorhombic structure of Sr_2Sn and also leads to an increase in the PF.

3.3. Sr_2Sn in the cubic structure $Fm\bar{3}m$

Taking into account the previous result, one can make the assumption that the effect, observed near the conduction band minimum, is determined mainly by the electronic structure. In A_2B type stable compounds of the elements II and IVa groups there are two types of lattice: cubic and orthorhombic. It is interesting to see how the effect under investigation will behave in the considered compound if one change the lattice type. To do this, we first consider the hypothetical cubic structure of Sr_2Sn of the space group $Fm\bar{3}m$. The calculated enthalpy of formation of this structure is H_{form}(cubic Sr_2Sn) = −0.6 eV/atom, for the orthorhombic structure H_{form}(orth. Sr_2Sn) = −0.63 eV/atom. The difference from the ground state is ΔH_{form} = 0.03 eV/atom.

The calculated band structures are shown in Fig. 3a. It can be seen that near the minimum of the conduction band, the convergence of the bands (C3 and C2 bands at the point X) is not as pronounced as in the previous case. However, band C1 at the point Γ significantly changes its

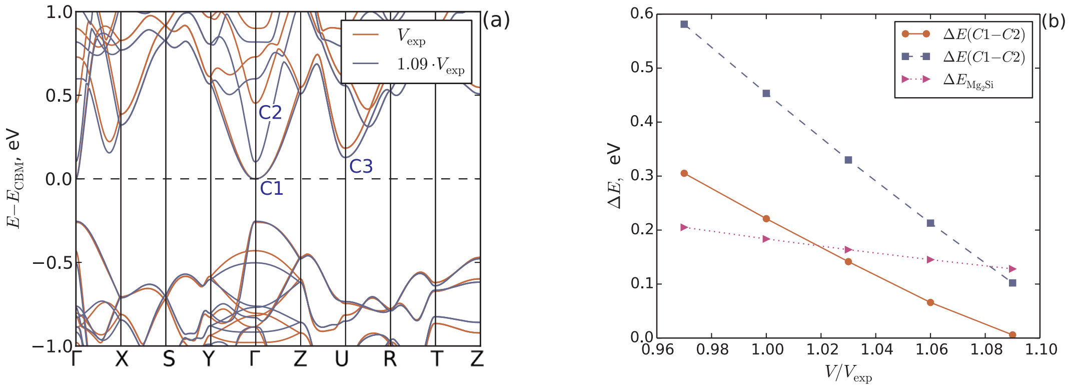

Fig. 1. (a) Band structure of orthorhombic Sr_2Sn for different cell volumes: experimental and increased by 9 vol.% of the experimental. In the figure, C1 and C2 is the first and second lowest conduction bands at the point Γ, respectively. C3 is the lowest conduction band at the point U; (b) dependence of the energy difference between the bands indicated on the band structure, on the relative volume of the cell. Also, for comparison, the dependence of the energy difference between of two lowest conduction bands at the point X (Fig. S1) of the cubic Mg_2Si is presented.

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