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Thermoelectric properties of topological insulators based on π-stacked molecular and graphene-belt systems with hydrogen bonds

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Abstract. Recently, new two-dimensional topological crystalline insulators were theoretically predicted in the family of molecular networks and graphene nanobelts. The planar structures are vertically stacked in columns formed via the π-type interactions between benzene rings. Moreover, the molecular or graphene-belt parts interact with each other via the hydrogen bonds, due to their termination with O and H. These organic materials possess flat band structures, which are characteristic for weakly interacting systems. As a consequence, the thermolectric power is high and excess that of graphene nearly four times.

1. Introduction

The thermoelectric power of materials should be high for technological applications in "green" electronics. The Seebeck effect is the electric voltage generation in a conductor under a temperature gradient, and it is used in the heat sink devices. This parameter is dependent on a slope of the energy bands. It grows for the more flat parts of the electronic structures. It is natural, thus, that the organic or nanostructure systems with weak interactions are often the high thermopower materials. The type of the chemical bonds between molecules in the organic crystals might influence the thermoelectrics. The same mechanism holds when a pressure is applied.

Recently, the molecular and graphene-belt based systems were theoretically studied for their interesting electronic structure properties, namely the topological edge states [1, 2]. Their 2D structures were built via vertical stacking, i.e. the π-type interactions, of the 1D parts. Additionally, the 1D molecular structures were obtained via hydrogen bonds which form due to the oxygen and hydrogen termination of the opposite ends of the molecules. On the other hand, the same type of O- and H-termination of the zigzag edges of the graphene nanobelts introduces the hydrogen bonds in the vertical direction, in contrast to the horizontal bonds in the molecular systems. Both types of interactions, the π-stacking and the O...H weak bonds, are very easy to tailor their strength with the applied pressure. Therefore, the band structures and thermopower are easily tunable with pressure. Another flexibility in the design is obtained via a change of an order of the carbon-rings stacking (namely AA, AB or ABC type) and an order of the vertical overlap of the O- and H-terminated edges.

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Here, a report is given on the thermopower in this interesting new family of the topological crystalline insulators. The next section describes the methods of the calculations, and the following section presents the detailed atomic structure of the systems and the calculated Seebeck constant at various modifications of the conformations.

2. Methods and computational details

Firstly, the density-functional theory (DFT) [3] calculations were done with the use of the plane-wave pseudopotential code Quantum Espresso [4]. The gradient-corrected funtional of the Perdew-Burke-Ernzerhof parametrization [5] was chosen. The ultrasoft [6] and normconserving [7] pseudopotentials were used for the atomic cores of the graphene belts and the molecular system, respectively. The plane-wave cutoffs of 30 Ry and 60 Ry were sufficient for the convergence with the ultrasoft and normconserving pseudopotentials, respectively. The uniform k-mesh of Monkhorst and Pack type [8] was used, and checked for the convergence in each direction of the calculated systems (around 8 to 12 points).

The self-consistent DFT electronic density was used for the calculations of the thermoelectric data. In this step, the maximally localized Wannier functions [9, 10] were obtained with the wannier90 code [11]. Then, the energy bands were accurately interpolated using the Hamiltonian represented in the Wannier functions. The thermoelectric parameters are defined as gradients of the energy bands, as described below. Thus, the Boltzwann code [12], which is the wannier90 postprocessing code and treats the problem in a semiclassical way, was used.

The transport distribution function (TDF) is a 3D tensor $\Sigma_{ij}(E)$ defined as a function of the energy E as follows:

$$\begin{aligned} \Sigma_{ij}(E) &= \frac{1}{V}\sum_{n,\mathbf{k}} v_i(n,\mathbf{k})v_j(n,\mathbf{k})\,\tau_{n\mathbf{k}}\,\delta(E-E_{n,\mathbf{k}}), \\ v_i(n,\mathbf{k}) &= \frac{1}{\hbar}\frac{\partial E_{n,\mathbf{k}}}{\partial k_i}, \end{aligned} \tag{1}$$

where V is the system volume, $v_i(n,\mathbf{k})$ is the band velocity, $E_{n,\mathbf{k}}$ is the band dispersion, and $\tau_{n\mathbf{k}}$ is the relaxation time dependent on the band index n and the reciprocal space $\mathbf{k}$. The TDF enters an expression for the 3D tensor of the Seebeck coefficients S_{ij}, which depends on the chemical potential μ and temperature T, and is defined as:

$$S_{ij}(\mu,T) = \frac{1}{eT}\,K_{ij,1}(\mu,T)\,K^{-1}_{ij,2}(\mu,T), \tag{2}$$

where

$$\begin{aligned} K_{ij,1}(\mu,T) &= \int_{-\infty}^{\infty} dE\,\left(-\frac{\partial f(E,\mu,T)}{\partial E}\right)\,(E-\mu)\,\Sigma_{ij}(E), \\ K_{ij,2}(\mu,T) &= \int_{-\infty}^{\infty} dE\,\left(-\frac{\partial f(E,\mu,T)}{\partial E}\right)\,\Sigma_{ij}(E). \end{aligned} \tag{3}$$

In the above formulae, the function $f(E,\mu,T)$ is the Fermi-Dirac distribution and e is the electron charge. It is important to note that the Seebeck coefficients are independent on the relaxation time, which was fixed for 10 fs for the TDF calculations. The k-mesh for the bands interpolation and gradients was 1000 points for each periodic direction of the systems.

3. Results

3.1. Molecular topological insulators

The molecular system built on phenalene derivatives has been shown to possess the edge states which enable us to classify this material as a weak topological crystalline insulator [1].

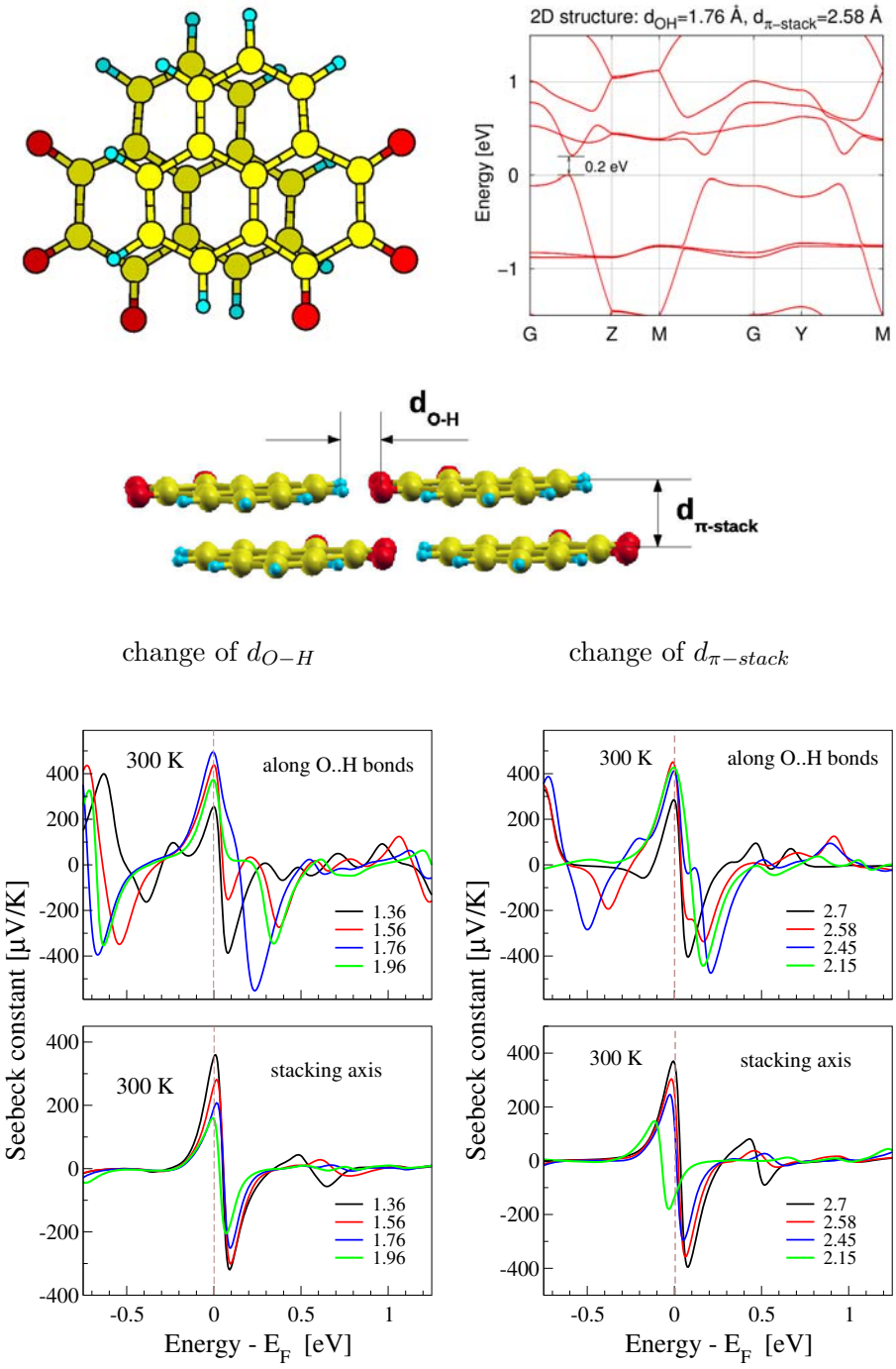

Figure 1. The atomic structure and bandlines of molecular topological system. The Seebeck constant is calculated for the molecular structures at various intermolecular distances in $\mathring{A}$ units.

The atomic structure and the energy bands calculated for chosen intermolecular distances are presented in Figure 1. The Seebeck constant as a function of the chemical potential is also presented in Figure 1 for two periodic directions of the system: the stacking axis (Z cartesian coordinate) and the O..H-bonds axis (Y coordinate). The temperature was chosen for 300 K and

the intermolecular distances were varied in the stacking and planar directions. The maxima and minima of the Seebeck constant as a function of the chemical potential move near the Fermi level with a change of the $d_{\pi-stack}$ and $d_{O..H}$ parameters. This is due to a change of the band gap. The band structures of all geometric cases were published in the supporting information of Ref. [1]. The thermopower at the top of the valence band excess for some intermolecular distances even 400 μV/K. This is a value four times larger than this parameter calculated for graphene [13], and also larger than the Seebeck constant obtained by other authors for the τ-type organic superconductors [14].

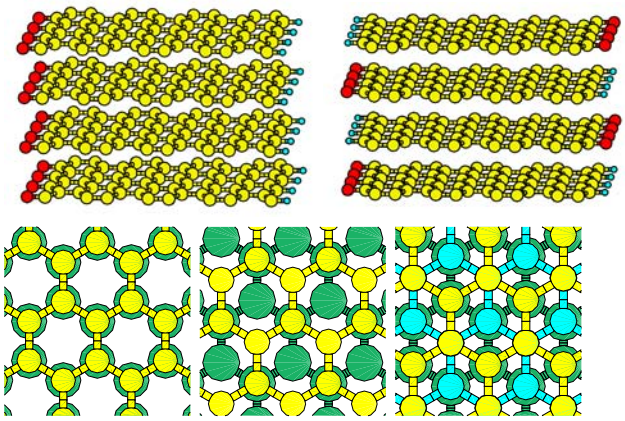

Figure 2. The atomic structure of stacked graphene belts - the order of stakicking of the zigzag O-edge (on-top or reversed) and the order of the carbon-rings stacking (AA, AB and ABC type).

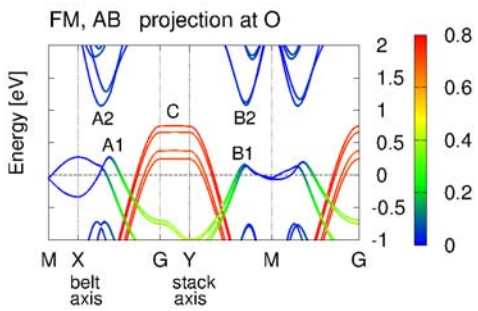

Figure 3. The schematic band structure of the stacked graphene belts. Color projection means the contribution of O-localized Wannier functions in the Bloch function.

3.2. Graphene-belt based topological insulators

Graphene has too small bands splitting due to the spin-orbit coupling to be a "classical" topological insulator. However, some graphene based systems were theoretically predicted to be the crystalline topological insulators [15, 16, 17]. Recently, it has been found that the graphene nanobelts, which are O- and H-terminated at the zigzag edge and stacked in the AB-type order (similar to graphite), are 2D quantum Hall materials [2].

The atomic structure and stacking orders are presented in Figure 2. The carbon rings can be stacked in AA, AB and ABC type. While the zigzag edges are O- and H-terminated on the opposite sides of the belt. These belts are stacked with O-edge on-top of the O-edge of the neighbor, or in the reversed order with H-edge between two O-edges. Moreover, these systems are magnetic with the spin moments localized mainly at oxygens. The coupling between these local moments might be ferro- (FM) or antiferromagnetic (AF). The Fermi level lays around 0.8 eV below the top of the valence band, because these belts are naturally p-type semiconductors due to the asymmetric termination of the edges.

The interactions along the stacking axis are very weak, and these systems have a flat band structure in this direction. Moreover, the mentioned bands flattening is energetically located near the valence band top. The schematic picture of the band structure is presented in Figure 3. The Wannier-functions analysis shows that the Bloch functions of the flat regions are mainly built with the oxygen-localized contributions. The flattening of the bandlines gives a mathematical reason for the large Seebeck constant. This observation was made for doped graphene and generalized for all systems with the similar bands [18]. Therefore, we can expect a

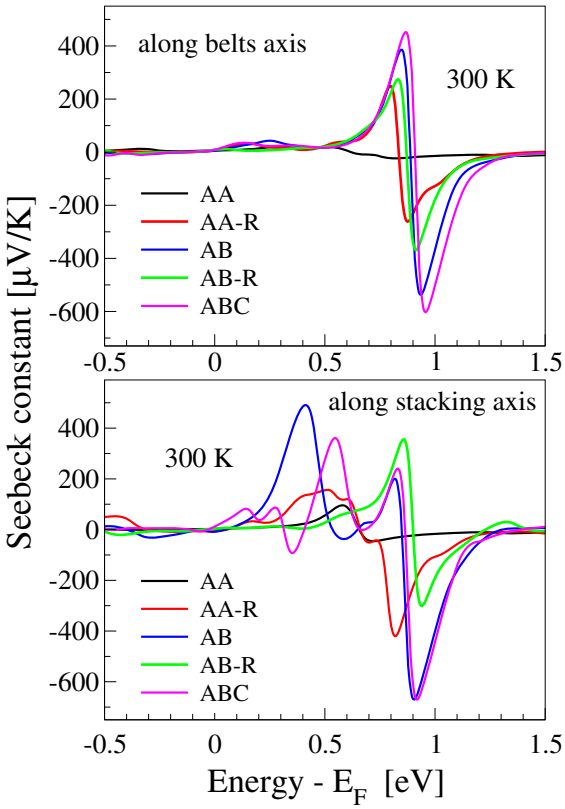

Figure 4. The Seebeck constant calculated for the ferromagnetic phase of various stacks.

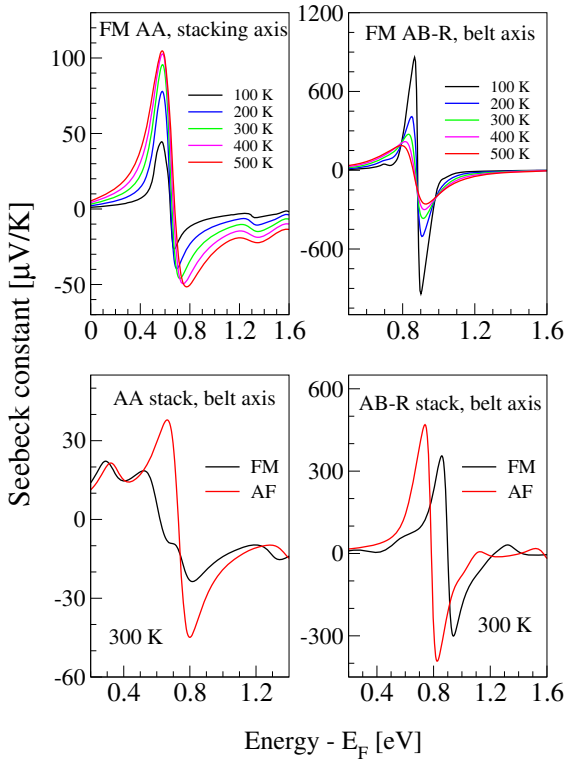

Figure 5. The temperature dependence and magnetic-phase impact on the thermoelectrics of the stacked graphene belts.

high thermopower in the described systems too. The band structures of all belts configurations are presented in the supporting information. The Seebeck constant as a function of the chemical potential is presented for the studied systems in Figure 4. The dependence of thermopower on temperature and magnetic coupling is presented for two chosen stackings in Figure 5.

For some configurations, the top of the valence band is dominated by the carbon-rings contributions to the Bloch functions. For the other cases, the flat oxygen-dominated bandlines move towards the top of the valence manifold. Some systems, namely the AA-stacked and AA-stacked reversed belts in both magnetic states, are metallic either by a "classical" bandgap closure or via the indirect negative band gap. They possess much lower Seebeck constant in comparison to the rest of the systems. Additionally, the temperature dependence of the thermopower is increasing with temperature for the metallic cases, while it is standard (decreasing with T) for the semiconducting (gapped) systems. The AB-stacked and ABC-stacked systems possess more than one flat region in their band structures. This fact has a fingerprint in the multiple peaks curvature of the thermopower function. The graphene nanobelts, similarly to the molecular topological crystalline insulators, are high thermopower materials with the maximal values of the Seebeck constant also excessing 400 μV/K at room temperature.

4. Conclusions

The topological insulators are potential materials for future electronic devices. The newly proposed topological crystalline insulators, which were found by theoretical modeling with the DFT

and tight-binding approaches, are built of light atoms only (C, O, H). They contain molecules or graphene nanobelts interacting via the π-stacking and hydrogen bonds [1, 2]. Their thermoelectric power is high - four times larger than that of graphene [13]. This is due to the weak intermolecular interactions, and - as a consequence - the flat electronic bands [18].

Acknowledgments
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