Bi$_2$Te$_3$: implications of the rhombohedral $k$-space texture on the evaluation of the in-plane/out-of-plane conductivity anisotropy

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Abstract

Different computational scheme for calculating surface integrals in anisotropic Brillouin zones are compared. An example of the transport distribution function (plasma frequency) of the thermoelectric material Bi$_2$Te$_3$ near the band edges is discussed. The layered structure of the material together with the rhombohedral symmetry causes a strong anisotropy of the transport distribution function for the directions in the basal plane (in-plane) and perpendicular to the basal plane (out-of-plane). It is shown that a thorough reciprocal space integration is necessary to reproduce the in-plane/out-of-plane anisotropy. A quantitative comparison can be made at the band edges, where the transport anisotropy is given in terms of the anisotropic mass tensor.

(Some figures may appear in colour only in the online journal)

1. Introduction

Thermoelectric materials are nowadays widely used to convert waste heat into electrical energy or for cooling purposes [1]. The main advantage of this conversion process is the absence of moving parts, or liquid or gaseous components. The efficiency of the process is rather low and is mainly determined by the dimensionless parameter

$$ZT = \frac{\sigma S^2}{\kappa},$$

called the figure of merit. It is determined by the specific conductivity $\sigma$, the thermopower $S$, the absolute temperature $T$ and the thermal conductivity $\kappa$, comprising the electronic and lattice parts $\kappa_e$ and $\kappa_L$.

New experimental techniques allow for the preparation of nanostructured and low-dimensional thermoelectric devices which are supposed to possess larger $ZT$ values [2, 3]. Values up to 2.4 are reported for multilayered Bi$_2$Te$_3$/Sb$_2$Te$_3$ systems [4, 5]. A microscopic understanding of these effects can be obtained by calculating the conductivity and power factor in the semiclassical limit exploiting the relaxation time approximation. The so-called transport distribution function has to be determined as a function of electron energy $E$ as integrals of surfaces of constant electron energy in reciprocal space [6]. If one considers an anisotropic material, like Bi$_2$Te$_3$, these quantities show a strong directional dependence, which can support the enhancement of the figure of merit in thermoelectric heterostructures. The calculation of these isoenergetic surface integrals requires a thorough integration in $k$-space. The implications of different integration schemes will be demonstrated. To this end the paper is organized as follows. We start with a derivation of the transport anisotropy near the band edges as a function of the effective mass tensor. This provides benchmark numbers at certain energies to check the numerical integration schemes. The systematic deviations of the integration schemes are related to the anisotropic structure of the reciprocal space of the rhombohedral lattice and the anisotropy of the band edges quantified by the effective masses which are discussed afterward. At the end, a simplified analytical model for a two-dimensional integration will be discussed to show the influence of the rhombohedral lattice anisotropy on the transport quantities. Results for a free electron model show a strong dependence on the procedure...
to fill the reciprocal space with tetrahedra in a way that the symmetry operations of the lattice can still be applied to reduce the numerical effort.

2. Inverse mass tensor and conductivity anisotropy at band edges

We determined the band dispersion for Bi$_2$Te$_3$ at the experimental lattice constants with the atomic positions taken from the literature [7]. The topology of the band structure and the electronic structure calculational scheme are described in detail in [8], see figure 2 for the band structure and figure 3 for the symmetry points in the rhombohedral Brillouin zone. The band structure is characterized by a sixfold-degenerate valence band maximum on the plane (100) and a twofold-degenerate conduction band minimum on the line (110). We used a fully relativistic Korringa–Kohn–Rostoker (KKR) Green’s function method based on the local density approximation of density functional theory in the atomic sphere approximation with an angular momentum cutoff of 3 [9, 10]. Assuming a constant relaxation time the energy-dependent matrix-valued transport distribution is defined as [6]

$$\sigma_{\alpha\beta}(E) = -\frac{e^2}{(2\pi)^2} \hbar \int \frac{dS}{|\mathbf{v}(k)|} v_{\alpha}(k)v_{\beta}(k),$$

(1)

with $\alpha$, $\beta$ the Cartesian coordinates, $k$ a combined index of reciprocal space vector $\mathbf{k}$ and band index $\nu$, $\epsilon(k)$ the band energy and $v_{\nu}(k)$ the group velocity in the direction $\alpha$. To obtain the anisotropy $\sigma_{\|}/\sigma_{\perp}$, we assume in the vicinity of the band edges parabolic bands in an anisotropic effective mass model. The inverse mass tensor $\mathbf{M}$ close to the band edges is diagonalized in the form

$$\mathbf{M} = \mathbf{m}^{-1} = \text{diag}(M_1, M_2, M_3),$$

with eigenvectors

$$\vec{c}_i = c_{ix} \hat{e}_x + c_{iy} \hat{e}_y + c_{iz} \hat{e}_z \quad (i = 1 \cdots 3),$$

(2)

the inverse masses $M_i = 1/m_i$ and $\hat{e}_i$ the basis vectors of the Cartesian coordinate system. The transport distribution for the anisotropic effective mass model along the main axes $\vec{c}_i$ of the effective mass ellipsoid are proportional to

$$\sigma_{ii} \propto \sqrt{m_1m_2m_3} / m_i,$$

(3)

$$m = \sqrt{m_1m_2m_3},$$

(4)

where the masses have to be chosen positive for both the valence band maximum and the conduction band minimum.

The following expressions for the in-plane and cross-plane conductivities project the mass tensor of general orientation given by equation (2) to the Cartesian coordinates:

$$\sigma_{xx} \propto \epsilon_{x}^2 M_{x},$$

$$\sigma_{xy} \propto (c_{x1}^2 M_{1} + (c_{x2})^2 M_{2} + (c_{x3})^2 M_{3})$$

$$\sigma_{yy} \propto (c_{y1}^2 M_{1} + (c_{y2})^2 M_{2} + (c_{y3})^2 M_{3})$$

$$\sigma_{zz} \propto (c_{z1}^2 M_{1} + (c_{z2})^2 M_{2} + (c_{z3})^2 M_{3}),$$

(5)

Due to the space group $D_3^5h$ ($R3m$) the considered band extrema are two- and sixfold-degenerate. In the case of the rhombohedral lattice this summation leads to equal contributions $\sigma_{xx}$ and $\sigma_{yy}$ and keeps the $\sigma_{zz}$ unchanged. The in-plane transport distribution is given for symmetry reasons by $\sigma_{||} = (\sigma_{xx} + \sigma_{yy})/2$ and the cross-plane component by $\sigma_{\perp} = \sigma_{zz}$. In the following the term $\sigma_{||}$ will be used synonymously for the in-plane component $\sigma_{||}$, so the anisotropy is denoted as $\sigma_{xx}/\sigma_{zz}$.

The mass tensor in Bi$_2$Te$_3$ is parameterized close to the band edges using the calculated band structure on a very dense mesh in k-space corresponding to 400 points along a reciprocal lattice vector to obtain convergence concerning the position of the extremum and the inverse mass tensor. The values for the valence and the conduction band are summarized in tables 1 and 2 [8].

| Table 1. Inverse effective mass tensor eigenvalues $M_i$ and eigenvectors $\vec{c}_i$ at the valence band maximum (VBM). |
|---|---|---|---|
| VBM | $M_i$ | $c_{ix}$ | $c_{iy}$ | $c_{iz}$ |
| 1  | −41.3 | 0.5000 | −0.8660 | 0.0000 |
| 2  | −7.42  | 0.6000 | 0.3463  | 0.7212  |
| 3  | −5.07  | 0.6246 | 0.3606  | −0.6927 |

| Table 2. Inverse effective mass tensor eigenvalues $M_i$ and eigenvectors $\vec{c}_i$ at the conduction band minimum (CBM). |
|---|---|---|---|
| CBM | $M_i$ | $c_{ix}$ | $c_{iy}$ | $c_{iz}$ |
| 1  | 5.62  | 1  | 0  | 0 |
| 2  | 6.52  | 0  | 1  | 0 |
| 3  | 1.20  | 0  | 0  | 1 |

The position $\vec{q}_S$ of the sixfold-degenerate valence band maximum in units of inverse Bohr radii is $0.372 199, 0.644 655, -0.029 9675$ on the plane (110). The effective mass ellipsoid is very anisotropic. The angle $\phi$ of the long axis of the ellipsoid with the $(xy)$ basal plane is 43.8°, which is in good agreement with other calculations and experiments, which show quite a spread [11–13]. The transport anisotropy ratio determined by the effective mass tensor for hole states close to the valence band maximum accounts for $\sigma_{xx}/\sigma_{zz} = 5.40$.

Table 2 summarizes the effective mass tensor at the twofold-degenerate conduction band minimum with the position $\vec{q}_S$ in units of inverse Bohr radii $(0, 0, 0.0552)$, which is about one-third of the line (110). The transport anisotropy is $\sigma_{xx}/\sigma_{zz} = 4.67$.

With these values the convergence of the transport distribution given by equation (1) determined by interpolation schemes in the Brillouin zone for energies close to the band edges can be quantified. Using the calculated band structures and the derived effective mass tensors we obtain an anisotropy $\sigma_{xx}/\sigma_{zz}$ of 5.40 and 4.67 at the valence and conduction band edge, respectively. These values are marked by dots in figures 1 and 2. As can be seen from these figures, the effective mass approximation holds in different energy ranges. They amount for hole doping to about $5 \times 10^{20}$ cm$^{-3}$ (figure 1) and for electron doping to $3 \times 10^{19}$ cm$^{-3}$ only (figure 2).
3. Conductivity anisotropy: comparison of different interpolation scheme

The transport distribution $\sigma(E)$ of Bi$_2$Te$_3$ is calculated by two methods. The main distinction is the determination of the group velocities $\vec{v}(k)$.

The tetrahedron method divides the irreducible part of the Brillouin zone (BZ) into disjoint tetrahedra. The group velocity is obtained by a linear interpolation of the band energies at the four corner points and approximates $\vec{v}(k)$ in the volume of the tetrahedron [14]. The second method determines the velocities as derivatives along the lines of the Blöchl mesh [15] in the whole Brillouin zone. The directions of these lines are parallel to the reciprocal space vectors and so the anisotropy of the real lattice is reflected in these vectors. For Bi$_2$Te$_3$ with a large ratio $c_{\text{hex}}/a_{\text{hex}}$ of 6.95 [7] the real-space unit cell is very prolonged and the reciprocal lattice vectors are quite close to the $(xy)$ basal plane with an angle $\theta' = 118.05^\circ$ between them very close to the maximum value of 120$^\circ$. Projecting back these so-called mesh velocities to the Cartesian components quite large errors occur in the resulting velocities as discussed below. The results of the integration of equation (1) using both interpolations schemes and different densities of $k$-points are compared in figures 1 and 2.

We start the discussion with the valence band maximum because the principal axes of the mass tensor are directed along arbitrary axes. The left-hand panel of figure 1 shows the parabolic dispersion along the three principal axes with the very different effective masses, spreading by a factor of about 80. The right-hand panel summarizes the anisotropy ratios $\sigma_{xx}/\sigma_{zz}$ as a function of energy. It is obvious that both interpolation schemes give systematic deviations from the expected values. For very large $k$-mesh densities defined by 384 mesh points along a reciprocal lattice vector the results converge to the correct value at the band edge. The necessary densities of $k$-points are very demanding for realistic band structure calculations with some atoms in the unit cell. The tetrahedron method overestimates systematically the anisotropy ratio, whereas the mesh velocity method underestimates the values. This behavior will be discussed below for a simpler two-dimensional lattice and the found trends are confirmed.

A similar behavior is obtained for the conduction band minimum as shown in figure 2. Here, a second challenge appears with a local maximum of the conduction band at the $\Gamma$-point very close in energy to the conduction band minimum. In addition, a large transport anisotropy is obtained due to the occurrence of saddle points in the band structure, as discussed elsewhere [8].
The obtained anisotropies for the transport distribution can be strongly influenced by the k-mesh density, especially close to the band edges. Taking the converged transport distributions $\sigma(E)$ we obtained for small p-doping an anisotropy of about 6, and for small n-doping an anisotropy of about 9 [16]. The influence of k-mesh convergence is much more pronounced for small temperatures. At typical application temperatures of Bi$_2$Te$_3$ of about 300 K this effect is quite weak. These anisotropies are about a factor of 2 larger than found in experiment [17] and other calculations [18–20]. As is obvious, the interpolation of the velocities deviates strongly from the correct values for k-points close to the band extremum. The directions of the reciprocal basis vector mainly scan along the (xy) plane. If the anisotropy of the band dispersion $\epsilon(k)$ is very strong as in the case considered, the mesh velocities tend to equalize the in-plane and out-of-plane components of the velocity $v_{x,y} \approx v_z$ which leads to an anisotropy closer to unity. This can be seen in figures 1 and 2 by the curves labeled ‘mesh’. This effect is most pronounced close to the band edges.

A quantitative comparison of the accuracy of the mesh velocities in given in figure 4. To compare the mesh velocities with the exact values we have chosen the Z line and consider the $v_z$ component of the velocity $v_z(k_z)$. The minimum of the energy dispersion is the global minimum of the conduction band. A local maximum appears at the Z-point. For sparse k-mesh densities a strong deviation of the mesh velocities have to be stated. To reproduce the point of inflection of the band dispersion by the sign change in the velocity a very dense mesh is necessary. The velocity in the $z$ direction is overestimated by this method, if the velocities in the (xy) directions are larger than in the $z$ direction, as illustrated in figure 3 and typical for Bi$_2$Te$_3$ in both the valence and conduction bands. As a result the transport anisotropy $\sigma_{xx}/\sigma_{zz}$, which is de facto the ratio of the velocities squared, is shifted to unity. An increase of the anisotropy toward 1 is expected for the opposite case with larger velocities along the $z$ direction than along the (xy) directions.

4. Interpolation schemes: tetrahedron versus mesh velocities

4.1. Mesh velocity method

In the following the implications of different interpolation schemes for the group velocity are discussed. We start with the discussion of the so-called mesh velocities. They are determined by a numerical derivative of the band dispersion along the directions of the reciprocal lattice vectors which span the Blöchl mesh. The Cartesian components of the velocities are obtained by a non-orthogonal transformation. If the angles between the basis vectors are very large (the maximum is 120°) small errors can be largely enhanced. This appears especially at band structures with a strong anisotropy between directions in the (xy) plane and the $z$ direction.

Figure 3 shows schematically the band dispersion of Bi$_2$Te$_3$ close to the conduction band minimum by isoenergetic lines. The Brillouin zone is shown in reduced size but the angles correspond to the considered case of Bi$_2$Te$_3$. As is obvious, the interpolation of the velocities deviates strongly from the correct values for k-points close to the band extremum. The directions of the reciprocal basis vector mainly scan along the (xy) plane. If the anisotropy of the band dispersion $\epsilon(k)$ is very strong as in the case considered, the mesh velocities tend to equalize the in-plane and out-of-plane components of the velocity $v_{x,y} \approx v_z$ which leads to an anisotropy closer to unity. This can be seen in figures 1 and 2 by the curves labeled ‘mesh’. This effect is most pronounced close to the band edges.

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4.2. Tetrahedron method

The capability of the tetrahedron method to calculate the anisotropy of the transport distribution will be evaluated for a free-electron model to easily compare with the analytical result. We will consider the integration in the rhombohedral Brillouin zone and for a two-dimensional k-space; the latter
allows for an analytical evaluation. For the two-dimensional mesh the two cases of linear and quadratic interpolation of the velocities are considered. The results for a free-electron dispersion with two different arrangements of tetrahedra in the irreducible part of the rhombohedral Brillouin zone will be compared.

The regular filling of the two-dimensional lattice is characterized by the angle $\alpha$ between the border line of the triangles $S_1$ and $S_2$ and the basal $(xy)$-plane, see figure 5. Depending on the interpolation method the velocities have to be determined for the triangles $S_1$ and $S_2$ with a linear scheme and can be determined at the points A, B and C with a quadratic interpolation scheme. The second task requires the knowledge of the energy dispersion $\epsilon(k)$ at additional points on the edges. Solving the linear set of equations for the Cartesian components of the velocities $\vec{v}_1$ and $\vec{v}_2$ for a free-electron dispersion, one finds both velocities equally pointing in the same direction along the borderline of the two triangles: $\vec{v}_1 \parallel \vec{v}_2 \parallel (\cos \alpha, \sin \alpha)$. So, the anisotropy of the transport distribution $\sigma_{xx}/\sigma_{zz}$ is just given by the ratio of the components $v_x$ and $v_z$ squared:

$$\sigma_{xx}/\sigma_{zz} = \frac{\cos^2 \alpha}{\sin^2 \alpha} = \frac{1}{\tan^2 \alpha}. \quad (6)$$

For the given $c/a$ ratio of Bi$_2$Te$_3$ the angle $\alpha$ is about $23^\circ$ which results in an anisotropy value of 5.8 which is much too large in comparison with the expected ratio of unity. Improving the interpolation scheme of the velocity to second order the velocities $\vec{v}_A$, $\vec{v}_B$ and $\vec{v}_C$ are determined correctly and the error of the transport distribution function is mainly determined by the approximation of the Fermi surface (a line in the two-dimensional case) by the two line segments $a_1$ and $a_2$. Due to the canceling of prefactors in the ratio $\sigma_{xx}/\sigma_{zz}$ it is sufficient to consider the sum of the segment lengths $|a_1|$ and $|a_2|$ times the square of the corresponding velocity components of $\vec{v}_A$ and $\vec{v}_B$ for area $S_1$, and $\vec{v}_B$ and $\vec{v}_C$ for area $S_2$, see equation (1):

$$\sigma_{xx} \propto \cos^2 \alpha \sqrt{(1 - \sin^2 \alpha)^2 + \cos^2 \alpha}$$
$$+ (1 + \cos^2 \alpha) \sqrt{1 - \cos^2 \alpha} \frac{\sin^2 \alpha}{\sin^2 \alpha}$$
$$\begin{cases} \propto \cos^2 \alpha \sqrt{2 - 2 \sin \alpha} \\
+ (1 + \cos^2 \alpha) \sqrt{2 - 2 \cos \alpha} \end{cases} \quad (7)$$

$$\begin{cases} \sigma_{zz} \propto \sin^2 \alpha \sqrt{2 - 2 \sin \alpha} \\
+ (1 + \sin^2 \alpha) \sqrt{2 - 2 \cos \alpha}. \end{cases} \quad (8)$$

From these expressions the ratio $\sigma_{xx}/\sigma_{zz}$ is evaluated and shown as (thicker) blue lines in figure 6 together with the values obtained by the linear velocity interpolation as (thinner) red lines. The linear scheme shows strong deviations especially for very anisotropic lattices with small or large angles $\alpha$. This error is much reduced by the second-order interpolation scheme with a maximum error of about 30%.

Performing these procedures in a three-dimensional lattice requires the set-up of a $k$-point mesh filling the irreducible part of the Brillouin zone and allowing for a disjunct tetrahedron arrangement. Two filling schemes are evaluated, which are based on cubes (in a given basis) which are filled with six tetrahedra each if completely inside the irreducible part, otherwise they are partially used to fill the irreducible part. The first one is based on cubes with the main axes directed along the $\langle 111 \rangle$ reciprocal lattice directions. The results for the anisotropy $\sigma_{xx}/\sigma_{zz}$ with a linear and a quadratic velocity interpolation are shown as crosses and plus signs in...
the upper panel of figure 6, respectively. To define a similar angle $\alpha$ characterizing the anisotropy of the rhombohedral reciprocal lattice as in the two-dimensional case we have chosen the angle $(\pi - \angle(\vec{g}_1, \vec{g}_2 + \vec{g}_3))/2$. This is $90^\circ$ minus half the angle between the reciprocal lattice vector $\vec{g}_1$ and the plane $(\vec{g}_2, \vec{g}_3)$. This ensures the isotropic simple cubic lattice to be characterized by an angle $\pi/4$.

The second filling scheme uses the (001) directions as a basis. The results are shown in the lower panel of figure 6. The results of the two-dimensional model can be partially reproduced, especially the case of an isotropic lattice at an angle of $45^\circ$. On average the deviations are larger for the linear interpolation scheme in comparison to the quadratic one as expected from the two-dimensional model.

The results in figure 6 are evaluated for energies very close to the free-electron band minimum. In these cases the isoennergetic surface is approximated by a few trigonal elements only and the largest anisotropies caused by the interpolation errors of velocities and surface areas are expected. For larger energies these discrepancies disappear quickly. The discussed deficiencies of the interpolation schemes in $k$-space are restricted to energies close to band extrema, which appear in transport properties of medium-doped semiconductors. In cases of very small doping the application of an anisotropic effective mass model seems to be more advantageous.

5. Conclusions

By means of model and realistic band structure calculations for crystals with rhombohedral symmetry we have shown that the determination of the transport distribution function requires very dense meshes in $k$-space. Two different methods to determine the group velocities are evaluated. It is found that they underestimate and overestimate the transport anisotropy in a systematic manner. For very prolonged unit cells the anisotropy in $k$-space requires a thorough check of the convergence with respect to $k$-space density.

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