COMMENTARY

Band anisotropy in thermoelectric materials

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Thermoelectric (TE) materials, which enable the direct conversion between heat and electricity, have attracted considerable attention due to their promising applications in refrigeration and power generation. Considering wider application scenarios and greater demand near room temperature (RT), TE materials with high performance near RT have attracted considerable research attention in the past decades. The TE performance of the material is judged by its dimensionless figure of merit $zT = S^2\sigma T/(\kappa_e+\kappa_L)$, where S, σ, T, κ_e, and κ_L are the Seebeck coefficient, the electrical conductivity, the absolute temperature, the electronic and lattice components of thermal conductivity κ, respectively. Up till now, Bi_2Te_3-based alloys are the only commercialized materials with desirable zT values near RT, while n-type Mg_3Sb_2 has recently been identified as another promising TE material with zT about 0.8 around RT. Both Bi_2Te_3 and Mg_3Sb_2 possess intrinsic low lattice thermal conductivity κ_L, which lays one of the foundations for their high TE performances.[1-4] Besides their low κ_L, their excellent electrical properties also contribute to the superior zT values.

The band structure is one of the keys to determining the zT of TE materials since S, σ, and κ_e are all related to the transport behavior of charge carriers around the Fermi level. High band degeneracy directly contributes to a higher TE performance. For instance, Bi_2Te_3 holds highly degenerated bands with N_v = 6 for both the conduction band minimum (CBM) and valence band maximum (VBM), as shown in Figure 1. As for Mg_3Sb_2, it has an N_v of 6 at CBM, but only one at the VBM. The VBM of Mg_3Sb_2 exhibits an obvious anisotropic character and sits at the center of its Brillouin zone (BZ). Band anisotropy has also been considered to be an important aspect to enhance TE performance from the theoretical view. However, experimental research on how band anisotropy influences electrical transport properties has rarely been systematically carried out, partly owing to the difficulty in growing large-size single crystals.

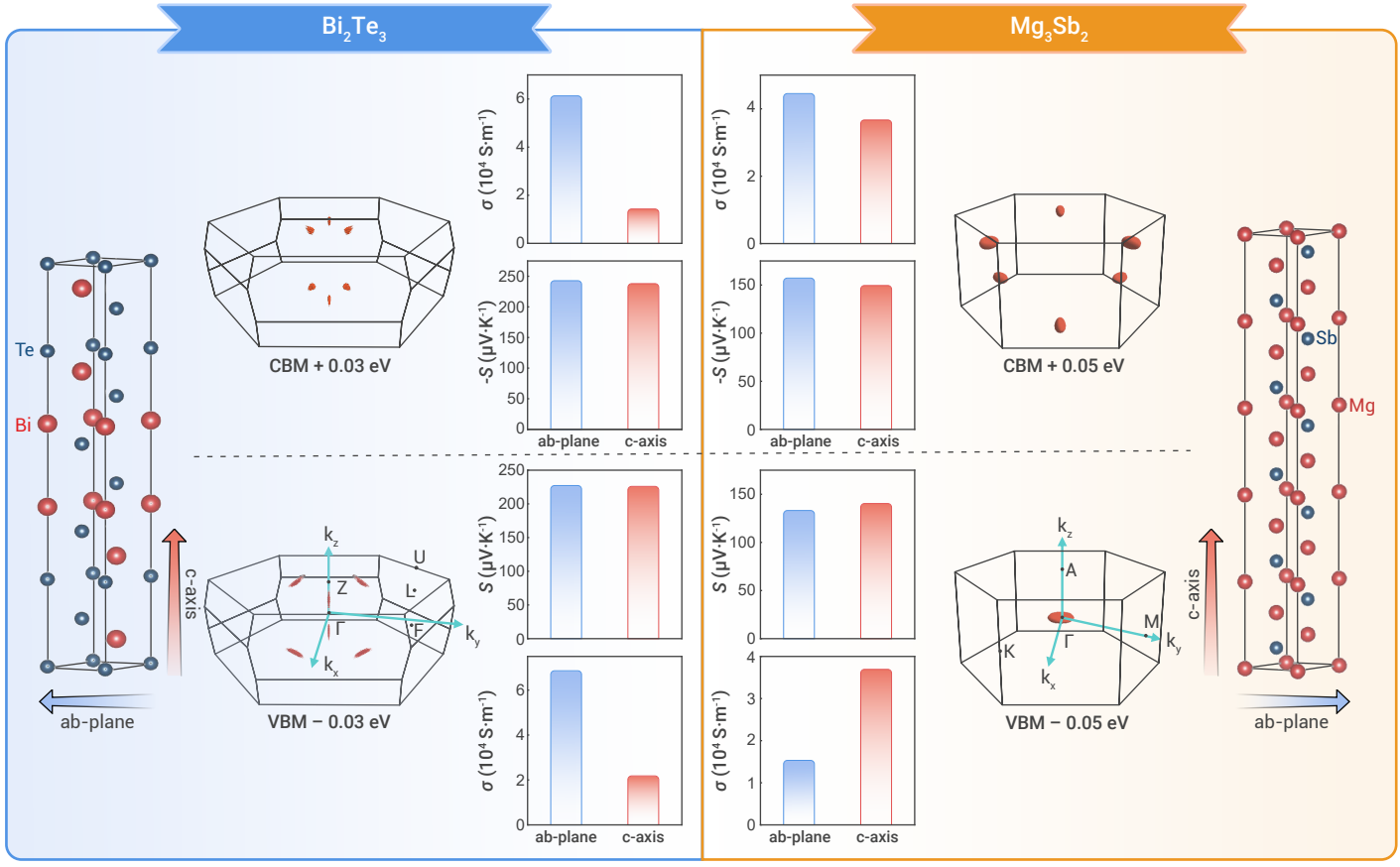

Figure 1. Crystal structures, Fermi surfaces, and electrical properties at RT for single-crystalline Bi_2Te_3 and Mg_3Sb_2. Electrical properties data are taken from the literature.[1-4]

Both Bi_2Te_3 and Mg_3Sb_2 crystallize in the non-cubic crystal structure with Bi_2Te_3 being rhombohedral and Mg_3Sb_2 trigonal (Figure 1). Their non-cubic crystal structures imply their possible anisotropic electrical transport properties. Band anisotropy describes the phenomena of a band with different band curvature along different wave vector directions. Band curvature is inversely proportional to the band effective mass m^*, and the value of anisotropic factor $K = m_{//}^*/m_{\perp}^*$ has been used to gauge the degree of the band anisotropy, where $m_{//}^*$ and $m_{\perp}^*$ are the band effective masses along the parallel and perpendicular directions, respectively. The larger the K is, the smaller the inertial effective mass $m_i^*= 3/(2/m_{\perp}^*+1/m_{//}^*)$ and the higher μ and σ are. In Bi_2Te_3, the σ along the ab-plane is much higher than that of the c-axis for both n- and p-type Bi_2Te_3,[3,4] as shown in Figure 1. This anisotropic σ

has been ascribed to the highly anisotropic Fermi surface of Bi_2Te_3. However, the complex multiply degenerated band edges at both CBM and VBM of Bi_2Te_3 make it difficult to directly reveal how the band anisotropy influences the TE transport.

Distinct from Bi_2Te_3, there is only one single hole pocket located at the center of the BZ for p-type Mg_3Sb_2, making it easy to resolve the relationship between the valley direction in the reciprocal space and the crystallographic direction in the real space. Meanwhile, the valence band of Mg_3Sb_2 displays a plate-like Fermi surface (Figure 1), and it will be an ideal paradigm to demonstrate the effects of band anisotropy on TE transport properties. As seen in Figure 1, the m^* along Γ-K and Γ-A directions is estimated to be $0.9m_e$ and $0.11m_e$, respectively, giving a K value of 8.2, resulting in an obvious anisotropy in the hole transport. That is, the σ along the ab-plane measured at RT is about 60% lower than that along the c-axis (Figure 1),[1] which is significantly different from Bi_2Te_3.

It is worth noting that the bonding strength along the c-axis is thought to be relatively weaker than that along the ab-plane in Mg_3Sb_2. The higher μ and σ along the weaker c-axis in p-type Mg_3Sb_2 seem to be unusual. The anisotropic valence band of Mg_3Sb_2 is revealed to be dominant by the p_z orbital of Sb with nearly no orbital contributions by Mg, and the dumbbell-like p_z orbital overlaps more and brings its small m^* along the c-axis, resulting in the higher μ and σ along the c-axis. There are also some other cases with the p_z orbital dominated anisotropic valence band like Mg_3Sb_2, such as $YbMg_2Sb_2$, $CaMg_2Bi_2$ and $EuMg_2Bi_2$.[1] Besides the anisotropic VBM, the CBM of Mg_3Sb_2 is mainly contributed by the s orbital of Mg, and the sphere-like s orbital leads to a weak anisotropy of σ, which is in agreement with the experiments that σ is not significantly different between the ab-plane and c-axis in n-type Mg_3Sb_2 (Figure 1).[2] Besides Mg_3Sb_2 and Bi_2Te_3, SnSe is another TE system that exhibits anisotropic transport behavior. Both p-type and n-type SnSe have lower σ along the out-of-plane direction, probably owing to the weaker interlayer bonding, while the anisotropy in n-type SnSe is weaker than that of the p-type.[5] The existence of multiple conduction bands in SnSe might be the reason why the n-type transport properties are less anisotropic.

Another question concerning the band anisotropy and electronic transport is whether the band anisotropy induces anisotropic S. As shown in Figure 1, unlike the anisotropic σ, the S of Bi_2Te_3 and Mg_3Sb_2 are nearly-isotropic. No matter whether in n-type/p-type Bi_2Te_3, Mg_3Sb_2, or SnSe,[5] the S is nearly the same along both the ab-plane and c-axis at RT, which means the S does not show anisotropic character despite the materials holding the band anisotropy. This nearly-isotropic S can be understood under the single parabolic band model.[1] When the acoustic phonon scattering dominates the carrier transport, the S of a TE material can be expressed as: $S = k_B/e[2F_1(\eta)/F_0(\eta) - \eta]$, where k_B, e, $F_i(\eta)$ and η are the Boltzmann constant, the elemental charge, the Fermi integral, and the reduced Fermi level, respectively. It can be found that the S is only sensitive to η ($\eta = E_F/k_BT$) and independent of the m^*, which agrees well with the experimental results, in which the S behaves nearly isotropic along the ab-plane and c-axis in both Bi_2Te_3, Mg_3Sb_2 and along the in-plane and out-of-plane of SnSe.[1-5] In some cases, the S can show anisotropic character if there is goniopolar transport, but in most TE systems, utilizing the band anisotropy will be a feasible strategy to enhance the power factor (PF = $S^2\sigma$) due to the unchanged S but increased σ when the charge carriers transport along the light-band direction.

While band anisotropy can be utilized to enhance the PF, thermal conductivity (including κ_L and κ_e) should be taken into consideration, aiming at the improvement of zT. Both Bi_2Te_3 and Mg_3Sb_2 hold similar non-cubic crystal structures, but they show different anisotropic lattice thermal transport properties. The κ_L of Bi_2Te_3 shows a strong anisotropic character with κ_L along the ab-plane being about twice larger than that along the c-axis at RT.[3] On the contrary, the κ_L of single-crystal Mg_3Sb_2 does not display an obvious difference along different directions but still with a slightly lower κ_L along the c-axis.[2] Generally, the phonon transport is closely related to the bonding characters. The different anisotropic phonon transport in Bi_2Te_3 and Mg_3Sb_2 is caused by their different bonding anisotropies, in which Bi_2Te_3 has very weak van der Waals bonding while the bonding of Mg_3Sb_2 is slightly weak along the c-axis. This is also the case for SnSe. The bonding anisotropy results in its much lower κ_L along the out-of-plane direction than that along the in-plane direction. Besides the κ_L, the κ_e of both Bi_2Te_3, Mg_3Sb_2, and SnSe will possess the anisotropic character according to Wiedemann-Franz law ($\kappa_e = L\sigma T$, where L is Lorenz number), but κ_e is smaller compared to κ_L in the current cases.

In summary, band/bonding anisotropy can result in different anisotropic TE transport properties. For both n-type and p-type Bi_2Te_3, even though the κ_L along the c-axis is lower, they exhibit a better TE performance along the ab-plane owing to the much higher σ. In contrast, n-type Mg_3Sb_2 exhibits a nearly isotropic TE performance along both ab-plane and c-axis. Differently, the higher σ along the c-axis makes p-type Mg_3Sb_2 show a favorable zT value when the carriers transport along the weak c-axis. The situation for n-type SnSe is different from both Bi_2Te_3 and p-type Mg_3Sb_2. The much lower out-of-plane κ_L in SnSe is the leading role for determining its high TE performance direction to be along its out-of-plane direction. These results highlight the importance of understanding the relationship between band/bonding anisotropy and anisotropic TE transport for developing high-performance TE materials.

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DECLARATION OF INTERESTS

The authors declare no competing interests.