Angle-resolved photoemission study of the high-performance low-temperature thermoelectric material CsBi$_4$Te$_6$

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We report a study of the valence-band electronic structure of the newly discovered thermoelectric material, CsBi$_4$Te$_6$, using angle-resolved photoelectron spectroscopy. This material exhibits quasi-one-dimensional behavior, which is related to its unique crystal structure. The highly anisotropic band dispersions might explain the large value of the figure of merit, $ZT$, observed in the hole-doped systems. Our experimental results are compared with a recent theoretical band-structure calculation.

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For over thirty years the narrow-gap semiconductor Bi$_2$Te$_3$ and its alloys have been the best-known room-temperature bulk thermoelectric materials. One recent approach to finding new and better thermoelectric (TE) materials is to synthesize multinary compounds using Bi$_2$Te$_3$ as a parent compound.\(^1\) CsBi$_4$Te$_6$ is a promising new TE material resulting from this approach. This material works surprisingly well at lower temperatures,\(^2\) especially in the temperature range where the Bi$_2$Te$_3$ alloys cease to be effective. The thermoelectric efficiency is intimately related to the electronic structure near the band gap. We report an angle-resolved photoemission (ARPES) study of the electronic structure of CsBi$_4$Te$_6$. A theoretical investigation of its electronic structure has been performed recently,\(^3\) and will be discussed in comparison with the experimental results presented here. Emphasis will be given to the bands near the band gap, although other valence bands will also be discussed.

Thermoelectric materials are characterized by a dimensionless figure of merit,

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

where $S$ is the thermopower, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature. A good TE material must have a high thermopower and a high thermal conductivity.\(^1\) These properties depend on the details of the electronic structure, which can be seen more clearly in another often used parameter

$$B = \gamma T^{5/2}(m_x m_y m_z)^{1/2} \frac{\mu_x}{\kappa_L},$$

which is roughly proportional to $ZT$.\(^4\) Here $m_x$, $m_y$, and $m_z$ are the effective masses in the respective directions, $\mu_x$ is the carrier mobility along the direction of the current flow (chosen as the $x$ direction), $\gamma$ is the $k$-space degeneracy of the band extrema,\(^5\) and $\kappa_L$ is the lattice thermal conductivity. A high value of $B$ and therefore $ZT$ can be achieved if the material's electronic structure possesses a high degree of $k$-space degeneracy, heavy effective masses, a high carrier mobility, and low thermal conductivity. Hicks and Dresselhaus have argued that in a highly anisotropic material, a large carrier mobility along a certain direction coupled to high effective masses in the two orthogonal directions, can lead to a large $ZT$ value.\(^4\) While this idea was originally applied to quantum well structures and quantum wires, it has now been applied to bulk materials, which are better suited for fabrication and application. ARPES is ideally suited for studying the valence-band electronic structures, as it is the most direct probe of a material’s occupied bands.\(^8\)\(^9\)

CsBi$_4$Te$_6$ has a modest room temperature $ZT$ of 0.65 (compared to optimized Bi$_2$Te$_3$ with a $ZT$ of 0.95). However, at 225 K the CsBi$_4$Te$_6$ $ZT$ increases to 0.82, which is a significant improvement over Bi$_2$Te$_3$ ($ZT \sim 0.58$) at the same temperature.\(^2\) The two materials have a roughly equivalent thermal conductivity, suggesting that the cause of the increased $ZT$ is electronic in nature.\(^2\)\(^3\) CsBi$_4$Te$_6$ is a narrow-gap semiconductor, with a gap size estimated at between 0.05 and 0.11 eV.\(^2\) The crystal structure of CsBi$_4$Te$_6$ is monoclinic, space group $C2/m$, with 88 atoms in the unit cell [see Fig. 1(a)]. The structure consists of Bi$_4$Te$_8$ laths connected via Bi-Bi bonds, forming two-dimensional slabs. Compared to other bismuth chalcogenide compounds, the Bi-Bi bonds are unique to this material. These Bi$_4$Te$_8$ slabs are each separated by a layer of Cs atoms. The crystals of this material have a needlelike morphology. The $b$ axis of the Bi$_4$Te$_8$ laths, which is normal to the plane of the paper in Fig. 1(a), is the needle growth axis and is the direction of the highest charge mobility. The Brillouin zone of the monoclinic unit cell is shown in Fig. 1(b).

A band-structure calculation by Larson et al.\(^3\) examined the electronic structure of CsBi$_4$Te$_6$ and its effect on the...
that the valence bands low symmetry of the crystal structure. The calculation shows material. These bands do not become degenerate due to the G sequence of the large number of atoms per unit cell. The calculation and the spin-orbit interactions were included in a second variational procedure. The calculation predicts more than seventy valence bands within 5 eV below the valence-energy distribution curves (EDCs) taken from an n-type sample for k points along the \( \Gamma-X \) symmetry line. The photon energy was 21 eV. From the bottom to the top curve, \( k \) was scanned from the \( \Gamma \) point to the \( X \) point, and then to the \( \Gamma \) point in the next zone, by varying the analyzer angle at 2° intervals. The initial state energies were referenced to the experimental Fermi level \( (E_F) \), derived from a clean platinum foil in electrical contact with the sample. The spectra were normalized to photon flux. The inelastically scattered secondary electron background has been approximated as proportional to the total primary intensity at higher kinetic energies and subtracted from the spectra. We can identify two features, labeled \( A \) and \( B \), just below \( E_F \). These two features can be discerned more clearly in the higher resolution spectra (solid curves) shown in Fig. 2(b). Both features are intense only near the \( \Gamma \) point. Peak A appears to be nondispersive and might be an impurity state due to the n-type dopants that resides within the narrow band gap. Consequently, we assign peak \( B \) as the top valence band. It has the lowest binding energy at the \( \Gamma \) point, away from which it becomes indistinguishable from the other valence bands at higher binding energies.

The assignment of peak \( A \) as an impurity state is further supported by the comparison between the n- and p-type spectra (solid and dashed curves, respectively) shown in Fig. 2(b). In this figure, the initial energy for the n-type spectra was referenced to the experimental Fermi level; the p-type spectra were rigidly shifted toward higher binding energies by 0.05 eV. As can be seen, after this shift, the p- and n-type spectra match reasonably well except that peak \( A \) is missing in the p-type spectra immediately below \( E_F \). This is consistent with the notion that peak \( A \) is an n-type impurity state. This also indicates that the energy gap is in the order of 0.05 eV, which is comparable to the band gap determined by other experimental methods (0.05–0.1 eV) (Ref. 2) and that predicted by the band-structure calculation (0.04 eV) (Ref. 3). It is believed that the impurity states are bulk states in stead of surface states, since doping occurs throughout the bulk as

![Crystal Structure](image1.png)

**FIG. 1.** (a) The crystal structure of CsBi\textsubscript{4}Te\textsubscript{6}. The small white circles are the Te atoms; the small black circles are the Bi atoms; the larger gray circles are the Cs atoms. (b) The Brillouin zone for CsBi\textsubscript{4}Te\textsubscript{6} of the monoclinic unit cell. The three important symmetry directions are indicated.
evidenced in the thermopower measurements. Also, surface states are unlikely to occur in a quasi-one-dimensional material such as CsBi$_4$Te$_6$. Quantitative estimate of the density of the impurity states from ARPES spectra is difficult because of matrix element effects, therefore is not attempted.

The majority of the valence bands lie between 0.3 and 5 eV below $E_F$ [Fig. 2(a)]. A large number of spectral features can be observed within this energy range. As mentioned earlier, the band-structure calculation performed by Larson et al.$^3$ predicts more than seventy valence bands in this energy range. Obviously, it is impossible to identify each individual band from the spectra because of lifetime and instrument broadening. It should be noted that the inverse lifetime for states at binding energies higher than 0.5 eV could be as
large as 0.5–1.0 eV. Thus, the spectral widths in that energy range are dominated by the lifetime broadenings; improving the spectrometer energy resolution would not have resulted in more resolved spectral features. Given the large number of predicted bands and the spectral broadenings due to lifetime, it would not be meaningful to perform a spectral modeling. Therefore, instead of attempting a complete determination of the band dispersions, we simply identify a few prominent spectral features [indicated by tick marks and labeled as features A–G in Fig. 2(a)] and qualitatively trace their dispersions. At the $\Gamma$ point, approximately 0.4 eV separates peak $B$ and the next identifiable feature, $C$. Feature $C$ disperses toward higher binding energies as $k$ was scanned from $\Gamma$ to $X$. So do most of the other features. As $k$ was further scanned from $X$ to $\Gamma$ in the next zone, the dispersions are reversed as expected from symmetry. In particular, features $D$, $E$, and $F$ become degenerate at the $X$ point and disperse apart in both directions.

The dispersions of the selected spectral features in Fig. 2(a) are plotted as crosses in Fig. 3(a) where the results of the band-structure calculation by Larson et al.\textsuperscript{3} are also shown (small symbols). The observed dispersions are qualitatively consistent with the general dispersion trend in the calculated bands. In particular, both the experiment and calculation find that the top valence band along $\Gamma$-$X$ has a maximum at the $\Gamma$ point. Some differences can be observed. For instance, in the observed spectra, the second highest valence band $C$ is separated from the top valence band $B$ by approximately 0.4 eV at the $\Gamma$ point, whereas the theory predicts a separation of only 0.2 eV. Also, peak $B$ is seen to disperse by as much as 0.8 eV from $\Gamma$ to $X$ whereas the theory predicts a dispersion of only 0.6 eV.

Figure 4(a) shows EDCs taken from an $n$-type sample for $k$-points along the $\Gamma$-$V$ symmetry line. The Brillouin zone is very short in this direction. The $\Gamma$-$V$ distance corresponds to approximately 1.7° angular difference at $hv=21$ eV, which is roughly the size of our angular resolution. The spectra shown were taken at 1° intervals. The spectral features show changes in relative intensity because of matrix element effects, but significant dispersion is not apparent. Peaks $A$
and $B$ can be seen near $E_F$ and they do not disperse in this direction. This was confirmed in the higher resolution spectra taken at 0.5° intervals (not shown). Figure 4(b) shows EDCs taken from an $n$-type sample for $k$-points along the $\Gamma$-$Z$ symmetry line. Momentum $k$ was varied by varying the photon energy in the normal emission geometry. The Brillouin zone is also short in this direction. The $\Gamma$-to-$Z$ distance corresponds to approximately 4 eV difference in photon energy. The spectra shown were taken at 1 eV intervals. Peaks $A$ and $B$ can also be seen and they do not disperse in this direction.

The lack of dispersion in the top valence band along $\Gamma$-$V$ and $\Gamma$-$Z$ indicates heavy carrier effective masses in these two directions. Some small dispersions can be seen in the higher binding energy bands along $\Gamma$-$Z$ (e.g., roughly 0.5 eV in feature $F$), though, overall, not as much as seen along $\Gamma$-$X$.

Compared to the calculated band dispersions [Fig. 3(b)], the observed bands along $\Gamma$-$Z$ are flatter than predicted. In particular, the calculation shows the top valence band to disperse about 0.3 eV from $\Gamma$ to $Z$. The measured spectra show

FIG. 4. EDCs for an $n$-type CsBi$_4$Te$_6$ sample taken along (a) $\Gamma$-$V$ and (b) $\Gamma$-$Z$. The energy is referenced to the experimental Fermi level derived from a clean platinum foil in electrical contact with the sample.
no discernable dispersions within the experimental resolution
\(\Delta E = 0.046 \text{ eV}, \ \Delta k = 0.07 \text{ Å}^{-1} \) along \( \Gamma - V \) and \( \Delta k = 0.03 \text{ Å}^{-1} \) along \( \Gamma - Z \). It is important to note here that while our \( k \) resolution along \( \Gamma - Z \) is more than adequate to map the predicted dispersions in this direction, our \( k \) resolution along \( \Gamma - V \) is larger than the \( \Gamma \)-to-\( V \) line (~0.06 Å\(^{-1}\)). This implies that each spectrum averages over the entire \( \Gamma - V \) line and the peaks might be broadened by the finite dispersions in this direction. From the widths of peaks \( A \) and \( B \) (full width at half maximum 0.05 eV and 0.15 eV, respectively), we can put an upper limit to the amount of dispersion. Higher momentum and energy resolution measurements are required in order to determine the detailed band dispersions in this direction.

To summarize, we studied the valence-band dispersions in CsBi\(_4\)Te\(_6\) using ARPES. High-resolution spectra indicate that the valence-band maximum is located at the \( \Gamma \) point consistent with the band-structure calculation result. We also find that the electronic structure is quasi-one-dimensional in that band dispersions are much stronger in the \( \Gamma \)-\( X \) direction than in the other two orthogonal directions. In particular, the highest valence band is very flat along \( \Gamma \)-\( V \) and \( \Gamma \)-\( Z \), indicating heavy carrier effective masses in these two directions. These results provide support for the postulate that the large anisotropy in the carrier effective masses is the reason for the large value of \( ZT \) observed in hole-doped CsBi\(_4\)Te\(_6\). By comparing the spectra measured from \( n \)- and \( p \)-type samples, we estimate a band gap of approximately 0.05 eV, which is comparable to the value observed in other experiments,\(^2\) and that predicted by band-structure calculation.\(^3\)

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5. The degree of \( k \)-space degeneracy here refers to the number of equivalent locations in the three-dimensional Brillouin zone due to symmetry.