Determination of the valence band dispersions for Bi$_2$Se$_3$ using angle resolved photoemission

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The valence band dispersions for Bi$_2$Se$_3$ have been determined using angle resolved photoelectron spectroscopy. The experimentally determined band dispersions are compared with theoretical band structure calculations. In general, good agreement between experiment and theory was found. However, energy bands in the $\Gamma$-Z direction are significantly flatter than those predicted by theory.


INTRODUCTION

The study and synthesis of new thermoelectric (TE) materials has experienced a revival within the last decade. Many new directions for materials synthesis are being followed which have found promising new materials.$^{1,2}$ Most good bulk TE materials are narrow gap semiconductors which have a combination of high electrical conductivity, high thermopower, and low thermal conductivity.$^{2,3}$ These properties depend strongly on aspects of the electronic structure such as the size of the band gap, the degree of $k$-space degeneracy$^4$ of the conduction and valence band extrema, and their associated effective masses. Angle resolved photoelectron spectroscopy (ARPES) is ideal to study several of these properties as it is the most direct experimental probe of the occupied bands.

Bi$_2$Te$_3$ and its alloys are the best room temperature bulk thermoelectric materials found to date ($ZT \sim 0.95$).$^{2,3}$ Bi$_2$Se$_3$, which is isostructural to Bi$_2$Te$_3$, has a small thermopower $S \sim 10 \, \mu\text{V K}^{-1}$, compared to that of Bi$_2$Te$_3$, $S \sim 260 \, \mu\text{V K}^{-1}$. In an effort to understand why Bi$_2$Se$_3$ has such low thermopower measurements when compared to Bi$_2$Te$_3$, several band structure calculations have been performed recently.$^{7,8}$ Larson et al.$^7$ performed a calculation using the full-potential linearized augmented plan wave method within the local density approximation. Mishra et al.$^8$ performed a calculation using the linearized muffin-tin orbitals in the atomic sphere approximation method. The two calculations produced qualitatively consistent results. They find that the spin-orbit interaction has very little effect for Bi$_2$Se$_3$. They find a gap size that is in agreement with previous experiments ($\sim 0.32$ in the calculation$^7$ and $\sim 0.35$ eV previously measured).$^{9}$ They also find the conduction band minimum and the valence band maximum to occur at $\Gamma$, which are nondegenerate in $k$ space. We carried out an experimental study of the electronic structure of Bi$_2$Se$_3$ using ARPES. Results are compared with theoretical calculations.

Bi$_2$Se$_3$ is a narrow gap semiconductor with an indirect gap of approximately 0.3 eV.$^6$ The crystal structure is rhombohedral with the space group $D_{3d}^1(R3m)$ with five atoms in the unit cell. The structure can be visualized as quintuple-layer leaves stacked along the $c$ axis in the unit cell [Fig. 1(a)] with Van der Waals bonding between the leaves. The five individual atomic layers occur in the sequence Se(1)–Bi–Se(2)–Bi–Se(1) where the Se(1) and Se(2) are non-equivalent selinium sites.$^9$ The Brillouin zone is shown in Fig. 1(b).

EXPERIMENTAL DETAILS

The $n$-type Bi$_2$Se$_3$ crystals were grown by slow cooling of a molten Bi/Se mixture. The doping in these systems is substitutional in nature; excess selenium atoms substitute for bismuth atoms in the structure, introducing some disorder into the lattice.$^{10}$ The type of doping was confirmed by thermopower measurements. ARPES measurements were carried out at the Synchrotron Radiation Center in Stoughton, Wisconsin, on the Ames-Montana ERG-Seya beam line. A movable 50 mm radius hemispherical analyzer with an angular acceptance of $\pm 1^\circ$ was used. The energy resolution was 0.1 eV for all spectra. The crystals were oriented using x-ray Laue diffraction prior to being mounted in the chamber. Orientation was then confirmed by symmetry in the spectra. The crystals were cleaved in an ultrahigh vacuum ($\sim 3 \times 10^{-11}$ Torr) to obtain clean surfaces. Spectra were taken at 20 K, obtained using a closed cycle helium refrigerator, to reduce thermal broadening in the spectra.

RESULTS AND DISCUSSION

Energy distribution curves (EDCs) for $n$-type Bi$_2$Se$_3$ taken at normal emission with varied photon energies are shown in Fig. 2. The corresponding $k$ points are along the
The binding energies are referenced to the experimentally determined valence band maximum ($E_{\text{VBM}}$), which will be described later. The spectra were taken at 1 eV intervals and are stacked vertically for clarity. The spectra have been normalized to the photon flux. They show a remarkably low secondary background.

In these spectra, a total of ten bands can be identified, labeled 0–9, and are indicated by the arrows. The experimental Fermi level lies just above band 0. The spectral intensities are highly photon energy dependent which is most likely due to matrix element effects. There is also some dispersion in the features. The band dispersion in this direction is generally on the order of 100–200 meV, and can be seen more clearly in Figs. 3(b) and 3(c). Shown in Fig. 3(b) is an intensity plot of the second derivatives of the EDCs with respect to energy as a function of energy and $k$ plotted in a linear gray scale with dark corresponding to high intensity. The dark areas correspond to the energy bands. The intensity plot gives a direct qualitative and objective view of the band dispersion. Figure 3(c) is a plot of the band dispersions extracted from the spectra by modeling the spectra with Lorentzian peaks convoluted with instrument function. The bands are labeled 0–9, and are indicated by filled circles whose size is approximately the size of the energy resolution. Figure 3(c) complements the intensity plot in Fig. 3(b). From these two figures, we see that bands 1–9 are not entirely flat along this direction.
In Figs. 3(b) and 3(c), we identified band 0 as an impurity band lying above the valence band maximum, and bands 1–9 as the valence bands. There are several reasons for this assignment. First, band 0 is very flat along $\Gamma-Z$ (its dispersion is less than 0.03 eV) and is pinned at the experimental Fermi level. This suggests that it is an impurity band. Second, the sample is $n$ doped, therefore the impurity band should lie above the VBM. Third, the separation between bands 0 and 1 is approximately 0.38 eV, which is comparable to the band gap of this material measured by other experimental methods. Last, with this band assignment, a good correspondence between the observed and calculated bands can be found, as will be discussed below.

In Figs. 3(b) and 3(c), we see that band 1 is more dispersive than band 0, with a local maximum at the $\Gamma$ point. It turns out that this is also the absolute VBM, and is therefore taken as the energy reference for all spectra. This band disperses $\sim$0.2 eV to a minimum at the $Z$ critical point. Band 1 is also well separated from the remaining valence bands; at the $\Gamma$ point, band 2 lies at more than 0.6 eV below band 1. The remaining valence bands 3–9 each disperse less than 0.2 eV along $\Gamma-Z$, and are relatively flat.

Shown in Fig. 3(a) are the band calculation results for intrinsic Bi$_2$Se$_3$ along $\Gamma-Z$ by Larson et al.\textsuperscript{7} Within 3.5 eV below $E_{\text{VBM}}$, they find nine valence bands. The top valence band has a maximum at the $\Gamma$ point, dispersing $\sim$0.4 eV to a minimum at $Z$. This band has a slightly higher binding energy and is also more dispersive than its observed counterpart, but the dispersion has the same qualitative trend. The second valence band is separated from the top valence band by $\sim$0.5 eV and is much less dispersive than the top valence band. The remaining valence bands predicted by theory are at least twice as dispersive as those observed experimentally, indicating that the material is more anisotropic than predicted.

Off-normal emission spectra of $n$-type Bi$_2$Se$_3$, taken along the $Z-F$ symmetry line (at $k$ points shown in the inset), are shown in Fig. 4. The binding energies are once more referenced to $E_{\text{VBM}}$. Ten bands, labeled 0–9, are identified in the spectra at the $Z$ point. In these spectra we can clearly see that band 0 exists only at the $Z$ point. A small remnant shoulder appears at the $k$ point just adjacent to $Z$, possibly indicating the presence of a band just above the Fermi level. The valence bands are highly dispersive in this direction.

Figures 5(a), 5(b), and 5(c) show the theoretical band structure, intensity map of the second derivative of the measured spectra, and the band dispersions extracted from the spectra by modeling, seen along the $Z-F$ symmetry line. The energy reference is $E_{\text{VBM}}$. Band 0, labeled in Fig. 5(c), exists only at the $Z$ point, separated from the valence bands by approximately 0.4 eV. The top valence band (band 1) has a local maximum along this symmetry line, at $\sim$10% $ZF$ from $Z$, with a secondary maximum at $\sim$45° $ZF$ from $Z$. Overall, the valence bands in this direction are fairly dispersive, on the order of 0.5–1 eV. However, due to the complex nature of the band structure, it is impossible to trace the dispersion of each individual band.

In Fig. 5(a), the band structure calculations also show a highly dispersive and complex electronic structure. Nine total bands are predicted along the $Z-F$ symmetry line within 3 eV of $E_{\text{VBM}}$. The top valence band disperses a total of $\sim$1 eV, moving to a local maximum at $\sim$35% $ZF$. Many of the

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**FIG. 4.** EDCs for an $n$-type Bi$_2$Se$_3$ sample taken along $Z-F$ (off-normal emission). The corresponding $k$ points are shown in the inset. The energy is referenced to the VBM.

**FIG. 5.** (a) Band dispersions along $Z-F$ from band structure calculation by Larson et al. (Ref. 7). (b) The intensity plot of the second derivatives of the EDCs ($\partial^2I/\partial E^2$) as a function of energy and $k$. (c) Band dispersions extracted from the measured spectra by modeling.
higher binding energy bands disperse more than 2 eV along the $Z$--$F$ line. Much like the dispersion along the $\Gamma$--$Z$ line, there is less dispersion seen in the experimentally observed bands than in the theoretical predictions.

Shown in Figs. 6(a), 6(b), and 6(c) are the spectra taken along the $\Gamma$--$a$--$U$, $\Gamma$--$F$, and $\Gamma$--$L$ symmetry lines, respectively. Similar to the dispersions seen along the $Z$--$F$ direction, the spectra show many dispersive features. The spectral features along the $\Gamma$--$L$ line [Fig. 6(c)] are especially well defined. Band 0 shows intensity only at the $\Gamma$ point. The remaining valence bands disperse toward higher binding energies as we move away from the $\Gamma$ point, where a local maximum exists in the top valence band.

SUMMARY

In summary, ARPES experiments have been carried out on n-type Bi$_2$Se$_3$. There is very good agreement between the theoretical calculations and the valence bands seen in the ARPS spectra. It was found that the valence band maximum is located at the $\Gamma$ point and therefore is nondegenerate. Although the bands along the $\Gamma$--$Z$ line are relatively flat, there is a measurable dispersion in those bands. The low k-space degeneracy of the VBM and the lesser degree of anisotropy may account for these materials poor TE properties as compared to that of Bi$_2$Te$_3$.

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4The degree of k-space degeneracy here refers to the number of equivalent locations in the three-dimensional Brillouin zone due to symmetry.
10It has been shown in Bi$_2$Te$_3$ that the doping is substitutional: S. N. Chizhevskaya and L. E. Shelimova, Inorg. Mater. (Transl. of Neorg. Mater.) 31, 1083 (1995) and is assumed to be so in Bi$_2$Se$_3$.