

Chapter 2

Properties of Bi_2Se_3 and Bi_2Te_3

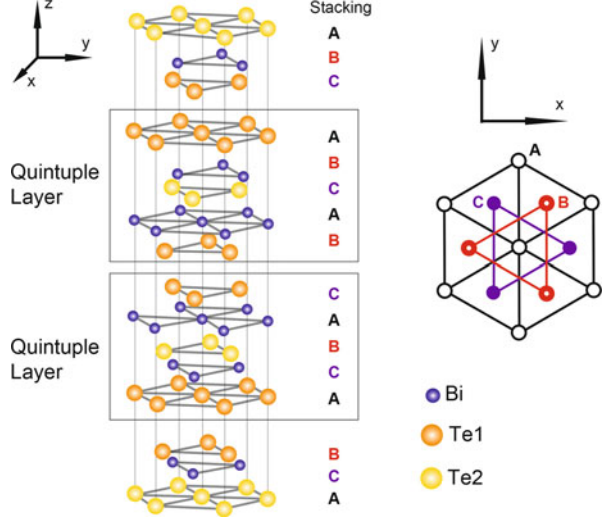
In this chapter I will present the fundamentals of the studied systems. I will begin by identifying the crystal structure of each system as well as their point and space group symmetries. From there I will move on to a review of measurements of the bulk vibrational structure using Raman, IR, and inelastic neutron scattering spectroscopies. Additionally, I will present recent ARPES measurements of the surface electronic structure that clearly indicate the presence of chiral DFQs, whose interaction with phonons is the main topic of this dissertation.

2.1 Crystal Structure

The strong 3D TIs Bi_2Se_3 and Bi_2Te_3 share the same rhombohedral structure, which is presented in Fig. 2.1. The bulk structure consists of alternating hexagonal monatomic crystal planes stacking in ABC order. Units of X-Bi-X-Bi-X (X = Se, Te) form quintuple layers (QLs): bonding between atomic planes within a QL is covalent whereas bonding between adjacent QLs is predominantly of the van der Waals type. This weak bonding between QLs allows the crystal to be easily cleaved along an inter-QL plane, a process which will be further elaborated upon in Chap. 4. The crystal structure belongs to the space group $R\bar{3}m$, while the point group contains a binary axis (with twofold rotation symmetry), a bisectrix axis (appearing in the reflection plane), and a trigonal axis (with threefold rotation symmetry).

It is convenient to work in the hexagonal basis when talking about this structure. A unit cell in the hexagonal basis contains 3 QLs and thus 15 atoms, whereas the

Fig. 2.1 Hexagonal unit cell of the Bi_2Te_3 crystal comprised of three QLs and belonging to the space group $R\bar{3}m$. Note that the Te2 layer within each QL is a center of inversion symmetry. Figure from [10]



actual primitive cell in the rhombohedral basis contains five atoms. For now I will work in the hexagonal basis and write the translation vectors as

$$\mathbf{t}_1 = a \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}, 0 \right), \quad \mathbf{t}_2 = a(0, 1, 0), \quad \mathbf{t}_3 = c(0, 0, 1) \quad (2.1)$$

where a and c are lattice constants of the hexagonal cell. Using X as the subscript to indicate the material we have, $a_{\text{Se}} = 4.14 \text{ \AA}$, $c_{\text{Se}} = 28.64 \text{ \AA}$, $a_{\text{Te}} = 4.38 \text{ \AA}$, and $c_{\text{Te}} = 30.49 \text{ \AA}$. The corresponding reciprocal lattice vectors are

$$\mathbf{G}_1 = \frac{2\pi}{a} \left(\frac{2}{\sqrt{3}}, 0, 0 \right), \quad \mathbf{G}_2 = \frac{2\pi}{a} \left(\frac{1}{\sqrt{3}}, 1, 0 \right), \quad \mathbf{G}_3 = \frac{2\pi}{c} (0, 0, 1) \quad (2.2)$$

The reciprocal space structure of Bi_2X_3 is shown in Fig. 2.2. The first bulk BZ is actually presented for the rhombohedral basis and has an interesting shape with eight hexagonal faces and six rectangular faces. The surface reciprocal lattice, which is the primary focus of this dissertation, is a 2D hexagonal lattice obtained by taking the projection of the bulk BZ along the q_z axis as shown in Fig. 2.2. The SBZ contains three high-symmetry points including $\bar{\Gamma}$ at the zone center, $\bar{M}$ at the center of the zone edge, and $\bar{K}$ at the intersection of two zone edges. It is worth noting that not all $\bar{K}$ points are equivalent because they cannot be connected directly by a reciprocal lattice vector.

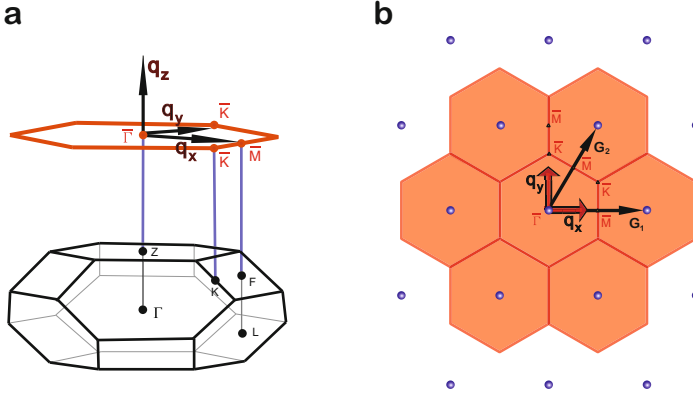


Fig. 2.2 Bulk and surface reciprocal space structure of Bi_2X_3 . Panel (a) shows the rhombohedral bulk BZ and high-symmetry points. The SBZ is represented as a projection along $\mathbf{q}_z$. The extended surface reciprocal lattice is shown in (b) depicting high-symmetry points $\bar{\Gamma}$, $\bar{M}$, and $\bar{K}$ as well as reciprocal lattice vectors $\mathbf{G}_1$ and $\mathbf{G}_2$. Figure from [10]

2.2 Bulk Vibrational Structure

At this point I will present measurements of the bulk vibrational spectra of both Bi_2Se_3 and Bi_2Te_3 . This data will allow me to fix the values of some of the empirical parameters entering the pseudocharge phonon model (to be discussed in Chap. 5) used to identify the character and symmetry of the bulk and surface phonon dispersions of the crystal. Investigations of the bulk vibrational structure have been carried out using one of the three methods: Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, and inelastic neutron scattering spectroscopy. The first two methods listed are light scattering spectroscopies and thus are only capable of providing information about optical phonon modes at the BZ center because of the low momentum transfer involved in the scattering process. Neutron scattering, on the other hand, is capable of providing detailed information of bulk phonon dispersions off the Γ point because of neutron's significant momentum owing to its finite mass.

The primitive rhombohedral cell of Bi_2X_3 contains five distinct atoms, each with three degrees of freedom. Therefore we expect a total of fifteen phonon modes at any given wave vector, three acoustic and twelve optical. The atomic displacements for these modes at the Γ point are displayed in Fig. 2.3. The modes are labeled according to their symmetry with A modes belonging to a one-dimensional irreducible representation (irrep) and E modes belonging to a two-dimensional (doubly degenerate) irrep. The subscripts u and g indicate an even or odd parity about the central atom in the primitive cell. The former are accessible by FTIR scattering whereas the latter are only accessible via Raman scattering. Since the E modes are doubly degenerate the number of unique optical phonon frequencies is reduced from twelve to eight.

Fig. 2.3 Diagram depicting the atomic displacements of the five atoms in the primitive cell of Bi_2X_3 for optical phonon modes at the bulk BZ center. The modes are divided into distinct types: non-degenerate A_u and doubly degenerate E_u modes accessible by FTIR scattering and non-degenerate A_g and doubly degenerate E_g modes accessible by Raman scattering. Image taken from Ref. [1]

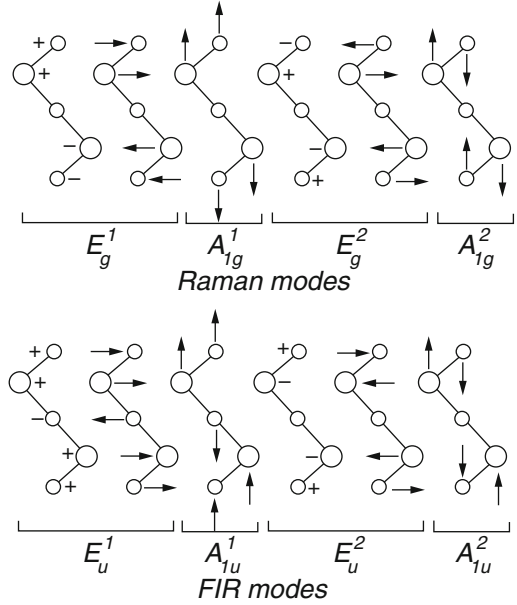


Table 2.1 Experimental values of the optical phonon frequencies of Bi_2Se_3 and Bi_2Te_3 at Γ . Data taken from [1]

Bi_2Se_3		Bi_2Te_3	
Mode	Frequency (cm^{-1})	Mode	Frequency (cm^{-1})
A_{1g}^1	72	A_{1g}^1	62.5
A_{1g}^2	174.5	A_{1g}^2	134
E_g^1	N/A	E_g^1	N/A
E_g^2	131.5	E_g^2	103
A_{1u}^1	N/A	A_{1u}^1	94
A_{1u}^2	N/A	A_{1u}^2	120
E_u^1	65	E_u^1	50
E_u^2	129	E_u^2	95

Studies of the bulk vibrational structure of Bi_2Se_3 are actually relatively few in number. To the best of my knowledge, no group has ever performed neutron scattering spectroscopy on these samples. Thus we are limited to results from studies using FTIR and Raman spectroscopy [1]. In their study, Richter and company were able to successfully observe only five of the eight unique optical modes at the Γ point. Their measured values can be found in Table 2.1.

In the case of the Bi_2Te_3 all three spectroscopies have been performed by various groups [1–4]. We thus have more complete description of the bulk vibrational

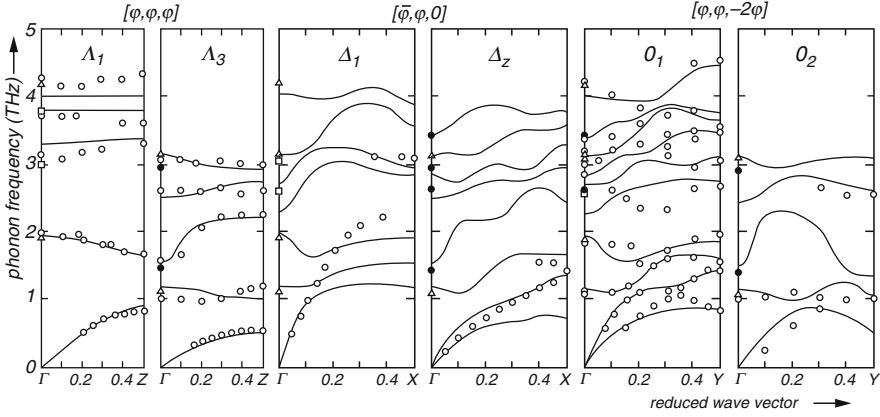


Fig. 2.4 Measurements of the bulk phonon dispersion of Bi_2Te_3 . *Open circles* denote neutron data, *open squares* and *closed circles* correspond to FTIR data, and *open triangles* signify Raman data. The *solid lines* represent calculations based on a shell model for the phonon frequencies. Results are shown for the three distinct high-symmetry directions (Λ , Δ , and Σ) in the bulk BZ. Image taken from Ref. [2]

structure of this crystal. The data from FTIR and Raman spectroscopies can be found in Table 2.1. One will notice that all mode frequencies are smaller than their Bi_2Se_3 counterparts, consistent with heavier mass of Te when compared to Se. Neutron scattering data for this crystal is available in Fig. 2.4. Dispersions along three high-symmetry directions are shown, with two panels for each direction corresponding to distinct symmetry classes. This data will be fit in Chap. 5 to obtain values for the bulk force constant parameters appearing in our pseudocharge phonon model.

2.3 Electronic Structure

One of the most interesting aspects of the topological insulators Bi_2Se_3 and Bi_2Te_3 is their unique electronic structure. Both materials exhibit semiconducting behavior, with bulk band gaps of approximately 300 meV in the case of Bi_2Se_3 and 100–150 meV for Bi_2Te_3 . Both possess an inverted band structure owing to the presence of strong spin-orbit coupling resulting from the large Bi mass. This, along with the inversion symmetry of the bulk crystal, guarantees a non-trivial $\mathbb{Z}_2$ as mentioned in Chap. 1 making both strong 3D topological insulators. The surfaces of the crystal are thus host to metallic DFQ surface states protected by TRI which serve to close the bulk band gap and usher in the change in $\mathbb{Z}_2$ occurring at the crystal/vacuum interface.

Because electronic transport experiments have difficulty distinguishing surface state contributions to the conductivity from imperfections of the bulk crystal (including Se and Te vacancies), experimental verification of said surface states has largely been carried out using ARPES. Numerous studies of the surface band structure have confirmed the existence of a single, linearly dispersive Dirac cone

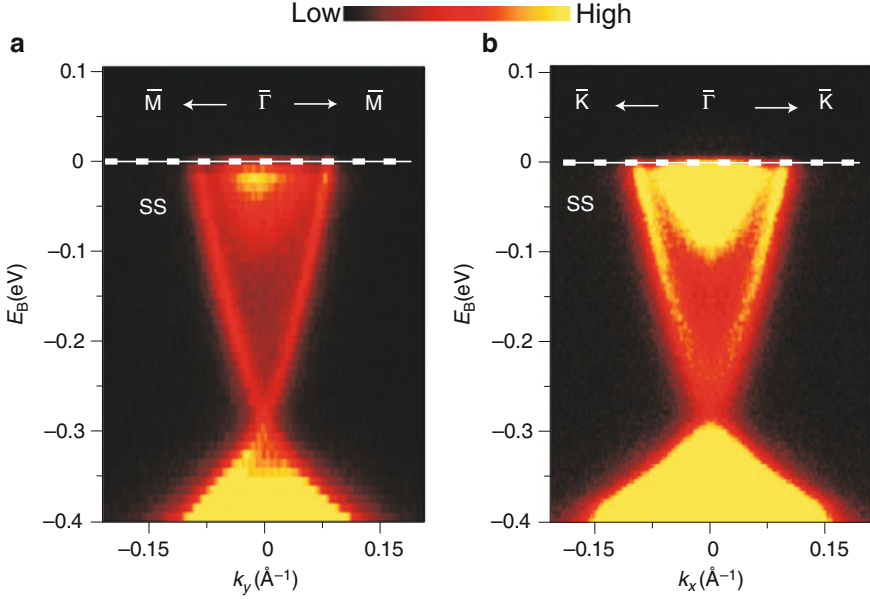
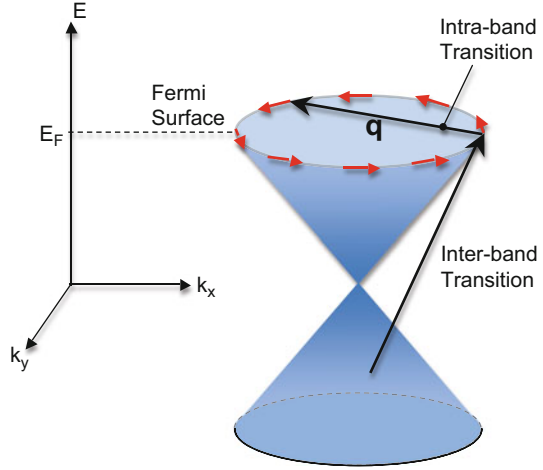


Fig. 2.5 ARPES data illustrating the presence of a single, linearly dispersive Dirac cone on the surface of Bi_2Se_3 centered at the $\bar{\Gamma}$ point. The surface states appear as two branches emanating from the Dirac point at -300 meV and continuing upward to the Fermi level. Contributions from the filled bulk valence band and partially filled bulk conduction appear as bright patches of *yellow* over a range of crystal momentum. Image taken from Ref. [5]

centered about the $\bar{\Gamma}$ point in the SBZ for both materials. Example ARPES data for Bi_2Se_3 can be seen in Fig. 2.5. Whereas the Dirac cone is isotropic in Bi_2Se_3 , the Fermi velocity modulates slightly depending on the crystal momentum direction in the case of Bi_2Te_3 . This gives rise to a warping effect which gives the Fermi surface a star-like shape at energies high relative to the Dirac point in contrast to Bi_2Se_3 where the Fermi surface remains nearly circular for all energies within the bulk band gap.

In both materials the metallic surface states are also spin-polarized [6, 7], again owing to the significant spin-orbit interaction. Specifically, the spin of the electronic state is always locked perpendicular to the crystal momentum and lies in the surface plane (see Fig. 2.6). Thus, these materials have a definite chirality to their surface electronic states because of the spin modulation that occurs when traversing the curve in 2D reciprocal space defined by the Fermi surface. Interestingly enough, this leads to a non-trivial Berry's phase [8, 9] of π when an electronic state is taken about the Fermi surface, which is related to their topological character. This is quite different from a non-magnetic metal wherein each state at any given crystal momentum possesses a two-fold spin degeneracy. Hence, in some ways the surface of a topological insulator can be viewed as half of a non-magnetic metal, with only a single spin species occurring at a given crystal momentum.

Fig. 2.6 Schematic diagram of the idealized Dirac cone electronic structure present on the surfaces of Bi_2Se_3 and Bi_2Te_3 . The spin texture of the Fermi surface is shown by the *red arrows*. A hypothetical low-energy scattering event involving momentum transfer $\mathbf{q}$ (perhaps from a phonon) is shown. Inter-band transitions involving higher energy are also possible. Figure from [10]



The spin-momentum locking in the surface states of topological insulators has interesting consequences. First and foremost, states on opposite sides of the Fermi surface which are propagating in opposite directions (owing to the reversed sign of the group velocity upon the substitution $\mathbf{k} \rightarrow -\mathbf{k}$) cannot backscatter into each other in the absence of magnetic perturbations. This is because such a scattering event would necessarily require flipping the spin. More generally speaking, backscattering of the electronic states on the surfaces of these materials is suppressed in the presence of time-reversal invariant perturbations. Without backscattering, the DFQs on the surface are immune to localization, a trait that has profound implications for electronic transport and potential device applications. Second, because states with opposite group velocity have opposite spin but the same charge, one can theoretically produce a net spin current without a net movement of charge by simply populating states with opposite crystal momentum simultaneously. This is quite similar to what happens in the QSHE except that here the transport takes place in a 2D plane where the Fermi surface contains a continuum of electronic states rather than a 1D edge where the Fermi surface is simply two points in reciprocal space. For these reasons, TIs are garnering interest as potential materials to be used in emerging spintronic technologies. However, to truly be effective, scattering of DFQs from time reversal invariant perturbations (phonons, crystal vacancies, grain boundaries, etc.) should also be small. Otherwise, although exact localization may not occur, the favorable transport characteristics on a macroscopic scale could be adversely affected. As such, the present study sets out to determine the nature and degree of DFQ-phonon coupling on the surfaces of TIs using helium atom surface scattering spectroscopy.

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