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Signatures of charge inhomogeneities in the infrared spectra of topological insulators Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$

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Abstract
We present the results of an infrared spectroscopy study of topological insulators Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$. Reflectance spectra of all three materials look similar, with a well defined plasma edge. However, there are some important differences. Most notably, as temperature decreases the plasma edge shifts to lower frequencies in Bi$_2$Se$_3$, whereas in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ it shifts to higher frequencies. In the loss function spectra we identify asymmetric broadening of the plasmon, and assign it to the presence of charge inhomogeneities. It remains to be seen if charge inhomogeneities are characteristic of all topological insulators, and whether they are of intrinsic or extrinsic nature.

1. Introduction
Topological insulators (TI) are novel electronic materials that behave like ordinary insulators in the bulk, but have conducting states on the surface [1, 2]. Their unusual properties are believed to originate from strong spin–orbit coupling. Conducting states on the surface are protected by time-reversal symmetry and are characterized by linear carrier dispersion, represented with Dirac cones. It has been shown that unique properties of TI stem from the fact that they have an odd number (usually one) of cones per unit cell [1, 2].

Based on recent terahertz Kerr measurements on Bi$_2$Se$_3$ [3] it was suggested that bulk charge distribution might not be uniform, and that signatures of those inhomogeneities might be observable in the infrared spectra. To address this issue we conducted a comprehensive infrared study of several ‘second generation’ TI, with the goal of probing their electrodynamic properties under identical experimental conditions. Our results reveal that charge inhomogeneities are indeed present in TI and are particularly pronounced in Bi$_2$Se$_3$. The results also confirm that IR spectroscopy can be used for detecting such inhomogeneities, in a contactless and non-destructive way.

2. Results and discussion
Single crystals of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ for this study were grown by the flux method [4, 5]. Samples with layered structure and irregular shapes were produced. Most of them had at least one naturally flat surface, with typical surface area of approximately 3 mm $\times$ 3 mm, and thickness of several millimeters. All spectroscopic measurements were performed on these flat surfaces. X-ray diffraction (XRD) spectra were taken with Cu K$\alpha$ radiation ($\lambda = 0.154 18$ nm) using a Rigaku Miniflex x-ray machine. Unit cell refinement obtained by fitting the XRD spectra using the Rietica software showed that samples were single phase and with lattice parameters consistent with previous results [6].

DC resistivity is measured using a four-point probe setup and the results are shown in figure 1(a). All three samples display characteristic metallic behavior, which correlates with behavior of carrier scattering rate $1/\tau(\omega)$ and plasma
frequency \( \omega_p \) extracted from IR spectra (see below) and shown in figures 1(b) and (c). The resistivity of Bi\(_2\)Se\(_3\) displays characteristic shape observed previously [7]. Compared to [7], both in terms of absolute values and temperature dependence, our sample is closest to sample \( v \) for which the carrier density was estimated based on Shubnikov–de Haas (SdH) measurements to be approximately 10\(^{16}\) cm\(^{-3}\). Similar to that sample, the resistivity of our sample also displays a shallow minimum around 30 K. However, our sample does not display the downturn of resistivity at high temperatures, which indicates that the carrier density is higher than 10\(^{16}\) cm\(^{-3}\), and this will indeed be revealed by our IR measurements.

The shape of resistivity of Bi\(_2\)Te\(_3\) is qualitatively similar to that of Bi\(_2\)Se\(_3\), but overall it is lower by approximately an order of magnitude. Assuming similar scattering rates, this indicates that the carrier density is higher in Bi\(_2\)Te\(_3\), consistent with IR measurements (figure 1(c)). The resistivity of Bi\(_2\)Te\(_3\) also displays a shallow, but more pronounced, minimum around 15 K. The resistivity of Sb\(_2\)Te\(_3\) is even lower, indicating even higher carrier density. This sample does not display a shallow minimum at low temperatures, similar to Bi\(_2\)Se\(_3\) samples with carrier densities higher than 10\(^{16}\) cm\(^{-3}\) [7].

Infrared spectra of Bi\(_2\)Se\(_3\), Bi\(_3\)Te\(_3\) and Sb\(_2\)Te\(_3\) are reported over a broad range of frequencies and temperatures from 300 K down to 10 K. All measurements have been performed on natural, freshly cleaved surfaces to minimize exposure to air. Reflectance spectra were collected with the electric field vector oriented along the cleaved surfaces to probe the in-plane charge dynamics. An overcoating technique, with gold or aluminum coating of the sample as reference, was used to obtain the absolute values of reflectance [8]. The results are shown in figure 2 for all three materials, and they all display a well defined plasma edge, consistent with previous reports [7, 9–11]. This characteristic shape of reflectance is a consequence of zero crossing in the real part of the dielectric function [12] that occurs at the so-called renormalized plasma frequency \( \omega_p^* \), which, on the other hand, is related to the carrier density \( n \) as:

\[
\omega_p^* = \sqrt{\frac{4 \pi n e^2}{m^* \epsilon_\infty}}.
\]

In this expression \( m^* \) is the carrier effective mass and \( \epsilon_\infty \) is the high-frequency dielectric function. The position of the edge progressively shifts from approximately 190 cm\(^{-1}\) in Bi\(_2\)Se\(_3\), to 735 cm\(^{-1}\) in Bi\(_2\)Te\(_3\), to 1045 cm\(^{-1}\) in Sb\(_2\)Te\(_3\). We note that the plasma edge in Bi\(_2\)Se\(_3\) is somewhat higher than for sample \( iv \) in [7] (approximately 160 cm\(^{-1}\)), but lower than in [9] (approximately 400 cm\(^{-1}\)) and [10] (approximately 500 cm\(^{-1}\)).
and Sb fit the spectra with the Drude–Lorentz model [12, 14, 15]:

\[ \sigma(\omega) = \sigma_{\infty} - \frac{o_p^2}{\omega^2 + i\gamma\omega} + \sum_{i=1}^{N} \frac{o_{p,i}^2}{o_{\omega,i}^2 - \omega^2 - i\gamma\omega}, \]  

where the second term is the Drude contribution due to free charge carriers, whereas the last term is due to finite frequency excitations, such as phonons and interband transitions. Since no phonons could be identified in the spectra of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ only the first two terms in equation (2) are used. The fitting was done over the 35–2500 cm$^{-1}$ range, using the program ReFFIT [16]. Examples of the best fits at 10 K are shown with gray lines in figure 2.

From the best fits we extract the plasma frequency of charge carriers $\omega_p$, as well as the carrier scattering rate $\gamma$. Obtained values for all three compounds are shown in figures 1(b) and (c). As can be seen, the scattering rate monotonically decreases with temperature in all three compounds and this explains the metallic behavior observed in resistivity (figure 1(a)). The plasma frequency on the other hand decreases by approximately 10% in Bi$_2$Se$_3$ between room temperature and 10 K, but increases by 15% in Bi$_2$Te$_3$ and by almost 20% in Sb$_2$Te$_3$, consistent with the observed temperature dependence of the plasmon (figure 2). We speculate that observed opposite trends in the temperature dependence of $\omega_p$ might be related to different type of charge carriers present. Namely, it has been known that charge carriers in Bi$_2$Se$_3$ are electron-like [7], whereas in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ they are predominantly hole-like [17, 18].

From the plasma frequency $\omega_p$ one can in principle calculate carrier density, if their effective mass is known (equation (1)). In [7] the effective mass of charge carriers was determined for Bi$_2$Se$_3$ based on SdH measurements, and the value of $m^* = 0.15 m_0$ was obtained. Assuming the same value for all three compounds$^5$, and using a three-dimensional free electron gas model [19], we extract the carrier density of 1.1 $\times$ 10$^{16}$ cm$^{-3}$ for Bi$_2$Se$_3$, 6.9 $\times$ 10$^{15}$ cm$^{-3}$ for Bi$_2$Te$_3$ and 1.1 $\times$ 10$^{20}$ cm$^{-3}$ for Sb$_2$Te$_3$.

Figure 3 displays the far-IR optical conductivity $\sigma_1(\omega)$ of Bi$_2$Se$_3$ on semi-log scale. The spectra reveal two phonon modes at all temperatures. However the 65 cm$^{-1}$ mode displays considerable asymmetry and no good fits could be obtained with a Lorentzian. Following LaForge et al [9] we fit this mode with the Fano model, and the results of the fits are shown with gray lines in figure 3. At higher temperatures (300 and 200 K) the best fits yield for the Fano parameter $q$ large values (typically $q \approx -30$) which indicates that there is very little asymmetry. On the other hand at low temperatures (77 and 10 K) the value of the Fano parameter is approximately $-15$, in agreement with LaForge et al [9].

Phonon asymmetry is commonly observed in systems with correlated electrons and is usually assigned to coupling of these modes to collective electron excitations. In the case of Bi$_2$Se$_3$ it was argued that the 65 cm$^{-1}$ mode is coupled to the plasmon at higher energies (figure 4 bellow), yielding negative values of Fano parameter $q$. We also note that the positions ($\omega_0$ in equation (2)) of both two phonon modes display small temperature dependences, although in different directions: 65 cm$^{-1}$ mode softens slightly as temperature decreases, whereas the 133 cm$^{-1}$ mode hardens.

Plasmon is a longitudinal mode and the real part of the optical conductivity $\sigma_1(\omega)$ does not couple to it. Instead, the

As temperature decreases the plasma edge sharpens in all three materials. In addition, these shifts are not in the same direction in all three compounds. In Bi$_2$Se$_3$ the plasma minimum shifts to lower frequencies (softens), whereas in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ it shifts to higher frequencies (hardens) as temperature decreases. The softening of the plasmon in Bi$_2$Se$_3$ was observed in both [7, 9] but was not discussed.

Applying Kramers–Kronig transformation on the raw reflectance spectra we calculate other optical functions, such as the optical conductivity $\sigma(\omega) = \sigma_1(\omega) + i\sigma_2(\omega)$, and the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The real part of optical conductivity $\sigma_1(\omega)$ is particularly useful because it reveals the presence of transverse modes in solids. The optical conductivity of all three compounds display a well defined Drude-like mode, followed by contributions from interband transitions at higher energies. IR active phonon modes are also identified in the spectra of Bi$_2$Se$_3$ at 65 and 133 cm$^{-1}$ (figure 3), in agreement with previous measurements [9, 7, 10, 13]. Interestingly no phonon modes are observed in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ down to the lowest measured temperature. One can argue that the phonons are better screened because the latter two compounds are more conducting, i.e. their carrier density is higher.

To gain better understanding of the electronic properties we fit the spectra with the Drude–Lorentz model [12, 14, 15]:

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{o_p^2}{\omega^2 + i\gamma\omega} + \sum_{i=1}^{N} \frac{o_{p,i}^2}{o_{\omega,i}^2 - \omega^2 - i\gamma\omega},$$  

where $\omega_p$ and $\gamma$ are the plasma frequency and the scattering rate, respectively. The number of terms $N$ is chosen based on the quality of the fit. In Bi$_2$Se$_3$ and Sb$_2$Te$_3$ the first two terms are sufficient, whereas in Bi$_2$Te$_3$ three terms are needed. The fitting was done over the 35–2500 cm$^{-1}$ range, using the program ReFFIT [16]. Examples of the best fits at 10 K are shown with gray lines in figure 2.

From the best fits we extract the plasma frequency of charge carriers $\omega_p$, as well as the carrier scattering rate $\gamma$. Obtained values for all three compounds are shown in figures 1(b) and (c). As can be seen, the scattering rate monotonically decreases with temperature in all three compounds and this explains the metallic behavior observed in resistivity (figure 1(a)). The plasma frequency on the other hand decreases by approximately 10% in Bi$_2$Se$_3$ between room temperature and 10 K, but increases by 15% in Bi$_2$Te$_3$ and by almost 20% in Sb$_2$Te$_3$, consistent with the observed temperature dependence of the plasmon (figure 2). We speculate that observed opposite trends in the temperature dependence of $\omega_p$ might be related to different type of charge carriers present. Namely, it has been known that charge carriers in Bi$_2$Se$_3$ are electron-like [7], whereas in Bi$_2$Te$_3$ and Sb$_2$Te$_3$ they are predominantly hole-like [17, 18].

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Plasmon is a longitudinal mode and the real part of the optical conductivity $\sigma_1(\omega)$ does not couple to it. Instead, the

The values of other fitting parameters (at 10 K) from equation (2), not shown in figure 1, are as follows: for Bi$_2$Se$_3$ $\varepsilon_{\infty} = 9$, $\omega_p, \gamma = 64$ cm$^{-1}$, $\omega_p, \gamma = 632$ cm$^{-1}$ and $\gamma_p = 3$ cm$^{-1}$, for Bi$_2$Te$_3$ $\varepsilon_{\infty} = 64$, and for Sb$_2$Te$_3$ $\varepsilon_{\infty} = 42$.

The assumption that the effective mass is the same in all three compounds is questionable, but since the actual measurements on Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are not available, we are forced to use it.
in figure 4 we display the loss function \( \text{Im}[1/\varepsilon(\omega)] \) for all three samples. The loss function reveals the presence of longitudinal modes, such as plasmons, in the optical spectra. As can be seen from figure 4 the plasmon is temperature dependent in all three compounds, but as anticipated from the raw reflectance data in Bi\(_2\)Se\(_3\) it shifts to higher frequencies. We also note considerable asymmetry in the shape of the peak, which might indicate the presence of charge inhomogeneities. Gray lines are fits to the Drude–Lorentz model (equation (2)).

The above calculations imply presence of charge inhomogeneities, especially in Bi\(_2\)Se\(_3\), but based on these calculations one cannot distinguish if the inhomogeneities are intrinsic to topological insulators\(^6\), or if they are due to sample imperfections, such as impurities, defects, disorder etc. Recent tunneling measurements [25, 26] indicate that surface charge distribution is fairly uniform. However, IR measurements primarily probe bulk carriers, whose properties can be quite different from those on the surface. Terahertz Kerr measurements on Bi\(_2\)Se\(_3\) [3], which first suggested the existence of charge inhomogeneities, could not elucidate the true nature of these inhomogeneities either. Alternative approaches might be needed to address this important question.

3. Summary

In summary, we presented IR spectra of three ‘second generation’ topological insulators Bi\(_2\)Se\(_3\), Bi\(_2\)Te\(_3\) and Sb\(_2\)Te\(_3\). The spectra reveal peculiar temperature dependence of...
Figure 5. Histogram representation of the distribution function of plasma frequencies $\rho(\omega_p)$, shown as a function of normalized plasma frequency $\omega_p/\omega_0$ (bottom axes), as well as carrier density $n$ (top axes). The distribution function of plasma frequencies $\rho(\omega_p)$ was calculated from the loss function data at 10 K (figure 4). For the purpose of comparison, the distribution functions are normalized to their maximum values.

the plasmon in the three compounds. The analysis of the loss function spectra reveals the presence of charge inhomogeneities, most notably in Bi$_2$Se$_3$. Further studies will be needed to check if they are characteristic of all topological insulators, and if they are of intrinsic or extrinsic nature.

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