Structural transition and collapse of the gap in BiTeI under pressure

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BiTeI is a giant Rashba spin splitting system, in which a non-centrosymmetric topological phase has recently been suggested to appear under high pressure. We investigated the optical properties of this compound, reflectivity and transmission, under pressures up to 15 GPa. The semiconducting gap collapses above \( p \sim 9 \) GPa and does not reopen up to at least 15 GPa. The plasma edge, associated with intrinsically doped charge carriers, is smeared out through a phase transition at 9 GPa. Using high pressure Raman spectroscopy, we follow the vibrational modes of BiTeI and show that a structural transition occurs at 9 GPa. The closing of the band gap is caused by a change of symmetry, which possibly precludes the high-pressure topological phase.

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Interest in the non-centrosymmetric semiconductor BiTeI surged when it was found that this compound hosts the largest known Rashba spin splitting in bulk form \([1, 3]\). While this material is structurally related to the recently discovered bismuth chalcogenide topological insulators \([4, 5]\), its band topology is trivial with Chern number equal to zero. Recent first-principles band structure calculations suggested that BiTeI undergoes a transition to the topological insulating phase under pressure \([6]\), through which BiTeI would become the first example of non-centrosymmetric topological insulator. Moreover, such a band-structure topology change realizes a remarkable example of topological phase transition. While several examples of topological phase transitions occurring upon varying chemical composition have been reported in the literature \([2, 4]\), the pressure-induced transition in BiTeI would present the advantage of being controllable and reversible.

Optical conductivity is well suited to probe the band structure of BiTeI under pressure. In this Letter, we determine the high pressure optical properties by measuring transmission and reflectivity of BiTeI up to 15 GPa. We follow the optical gap under pressure and find that it decreases monotonically until 9 GPa. At this pressure the plasma edge associated with the doped carriers is strongly broadened. Above this pressure the gap collapses and does not reopen up to the highest pressure reached. The high pressure phase appears to be metallic. Using Raman spectroscopy, we observe several vibrational modes that disappear or appear at 9 GPa, which shows that a structural transition occurs at this pressure and leads to a change in the band structure.

Single crystals of BiTeI were grown by the floating zone method, starting from the stoichiometric ratio of metallic bismuth, tellurium and bismuth iodide. The unit cell of BiTeI is composed of triple layers, Te–Bi–I, which are stacked along the polar \( c \)-axis \([1]\). The triple layers are bound by a weak van der Waals interaction. The structure is described by the non-centrosymmetric space group \( P3m1 \).

At ambient pressure, the reflectance was measured at a near-normal angle of incidence on a freshly-cleaved surface for light polarized in the \( a-b \) planes, from 25 meV to 0.9 eV using an \textit{in situ} evaporation technique. The complex dielectric function and the optical conductivity were obtained by Kramers-Kronig transformation of the reflectivity, supported by spectroscopic ellipsometry data from 0.6 eV to 5.6 eV. Knowing the optical constants of diamond, we converted the vacuum-sample reflectivity to one at the diamond-sample interface, \( R_{sd} \). Transmission was measured through a flake of BiTeI using an infrared microscope. Optical data at high pressure were acquired up to 15 GPa with a diamond anvil cell (DAC) placed in the focus provided by the IR synchrotron beamline of the SLS \([10, 11]\). Reflectivity was determined in the frequency range from 60 meV to 1 eV for a dense set of pressures. The intensity of radiation reflected from the diamond to sample interface was normalized by the intensity from the interface between the diamond and the metallic (Cu-Be alloy) DAC gasket. The reflectivity ratios measured in the DAC were calibrated against \( R_{sd} \) obtained from the absolute reflectivity measured outside the cell. In order to calculate the complex dielectric function \( \epsilon(\omega) \) the reflectivity data were fitted for all pressures to a Drude-Lorentz expression. A sufficiently large number of oscillators (variational dielectric function \([12]\) was used so as to reproduce all fine details of the reflectivity spectra. Transmission was measured from 80 meV to 1 eV for a fine mesh of pressure points. Raman spectra at high pressure were recorded using the same DAC up to 15 GPa, with daphne oil 7375 as pressure medium and a home-made micro Raman spectrometer as described previously \([10]\).

Reflectance and transmission data are shown in Fig. 1a...
at ambient pressure and room temperature. A sharp plasma edge appears in the reflectance at 0.15 eV, and near 0.4 eV a kink is observed. Transmission through a 6 μm thick flake of BiTeI in the MIR range displays a maximum around 0.45 eV, which matches the frequency of the kink in the reflectivity. Another small peak in the transmission is observed at 0.15 eV and concurs with the plasma edge in the reflectance. $R_{sd}$ is the reflectivity expected for the diamond-sample interface, showing similar features as the reflectivity with a plasma edge at the same position.

The real part of the optical conductivity $\sigma_1(\omega)$ shown in Fig. 1 is gapped below $\sim 0.5$ eV, which is just above the energy of the maximum in transmission. Simultaneously, a Drude contribution emerges below 0.1 eV which agrees with the metallic behavior of the resistivity as well as with the previous optical studies [13-15]. This metallicity contribution is very likely due to the impurity doping and a slight off-stoichiometry, particularly of iodine because of its high fugacity. We attribute the fine structures in the optical conductivity to the interband transitions $\alpha$ and $\beta$, and the onset of absorption (gap edge) $\gamma$, as sketched in the insets of Fig. 1. [13-15].

The band structure and the interband transitions are expected to be strongly influenced by pressure [6]. Indeed, we observe significant pressure induced changes in the optical properties. Fig. 2a shows the reflectivity as a function of photon energy for various pressures. The reflectivity is measured at a sample-diamond interface, and the levels may be compared to the $R_{sd}$ shown in Fig. 1. Numerous features can be distinguished in the pressure-dependent reflectivity. The lowest pressure curves contain Fabry-Perot resonances at frequencies just below the gap onset, due to the small sample thickness and the sample transparence. Reflectivity in Fig. 2a has a sharp plasma edge at 0.15 eV, consistent with Fig. 1a. Very little change is observed up to 7 GPa, and the plasma edge remains at the same energy. There is, however, a gradual increase of the reflectivity level at frequencies above the plasma edge, and a decrease of the level below the plasma edge. Above ~7 GPa, the plasma edge suddenly begins to shift towards lower energies, and at 8.5 GPa it starts to gradually smooth out. Above 9.5 GPa, the plasma edge progressively disappears, and the reflectivity level now increases across the entire photon energy region. For the highest pressure reached no plasma edge is observed, but the reflectivity has an upturn towards low energies suggesting a metallic state. Overall, the reflectivity experiences a dramatic pressure-induced change in the studied energy range.

The real part of the optical conductivity $\sigma_1(\omega)$ obtained from the complex dielectric function $\epsilon(\omega)$ is shown in Fig. 2b [14]. In the low-pressure regime (below 8.5 GPa), the Drude contribution persists almost unchanged, and the high-frequency $\sigma_1$ indicates a gradual shift of the absorption edge towards lower energies. This means that below 0.2 eV there is little change in $\sigma_1(\omega)$, whereas above 0.35 eV $\sigma_1(\omega)$ increases as the gapped states become filled. As the absorption edge shifts, the dip in $\sigma_1(\omega)$ at 0.45 eV gradually disappears with increasing pressure. Above 8.5 GPa, the Drude contribution disappears from our energy window and $\sigma_1(\omega)$ becomes rather flat below 0.2 eV. It is around this pressure that the slope of $\sigma_1(\omega)$ changes sign at low energies, from negative to positive. As the pressure increases further, the gap edge shifts more rapidly to lower energies. By 12 GPa, the low energy states (below 0.2 eV) have been filled and the gap tends toward very low energies. At the highest reached pressures, the gap in $\sigma_1(\omega)$ appears to be zero or very small. There are two clear limiting cases for the optical gap. At zero pressure, the gap is finite ($\sim 0.5$ GPa), and at 15 GPa the conductivity is not gapped at room temperature. Between these two limits we cannot attach a precise value to the gap because it is not accompanied by a clear spectroscopic feature.

Transmission, shown in Fig. 2b, features a sharp peak at 0.46 eV at low pressure, just below the band gap. It agrees with the ambient pressure transmission shown in Fig. 1. The position of the transmission maximum redshifts with pressure and diminishes in intensity. This decrease in the maximum intensity is particularly sharp at 3 GPa. Above 9 GPa, the monotonic decrease is replaced by an abrupt collapse of the peak at 10 GPa. The collapse of the transmission peak above 9 GPa suggests...
that a phase transition is taking place at this pressure, involving a strong reduction of the band gap. This is in agreement with the reflectivity and the optical conductivity, which indicate that above 9 GPa the gap starts to collapse.

Fig. 2 shows $\sigma_1$ as a function of pressure, for a series of photon energies ranging from 0.07 eV to 0.7 eV. Common to all the curves is a sharp kink at $p \sim 9$ GPa. This confirms that at 9 GPa a phase transition takes place which influences the electronic structure. Above 9 GPa, $\sigma_1(p)$ steeply increases in the whole energy range.

One of the most striking aspects of the presented data is the abrupt disappearance of the plasma edge for $p \approx 9$ GPa in the reflectivity. The sharp low-pressure plasma edge originates in a well defined Drude peak in $\sigma_1(\omega)$, which suggests a coherent charge transport in the low pressure phase ($p < 8.5$ GPa). To better illustrate the pressure dependence of the plasma frequency, Fig. 2e and 2f show the loss function, $-\text{Im}(1/\varepsilon)$. A maximum in the loss function corresponds to the screened plasma frequency. At ambient pressure we observe one such mode at 0.13 eV and associate it with the intraband plasmon. This plasmon mode widens with pressure and slightly bends towards lower energies above 3 GPa, with no appreciable pressure dependence up to 9 GPa. The loss function remaining constant means that the spectral weight of the Drude contribution does not change much. However, at 9 GPa the peak in the loss function suddenly vanishes. When the plasmon peak dramatically disappears, this is not because the free carriers disappear. There still has to be a Drude contribution at highest pressures, since the reflectivity has clear Hagen-Rubens upturns at low energies. Instead, the conductivity $\sigma_1(\omega)$ increases above 9 GPa and this sudden increase in the conductivity produces very strong damping. The plasmon thus becomes overdamped by background conductivity and appears washed out. High pressure pushes the interband transitions close to zero energy, and above 9 GPa they become strongly mixed with the tail of the Drude peak. It is at this point that the system changes from a doped semiconductor into an overdamped semimetal.

To gain better understanding of the transition at 9 GPa, we supplement the infrared study with the pressure effects on the optical phonons using Raman spec-

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FIG. 2. (Color online) (a) Reflectivity as a function of incident photon energy, shown for different pressures at room temperature. Inset shows a sketch of the sample environment within the diamond anvil pressure cell. (b) The frequency dependence of the real part of the optical conductivity, $\sigma_1(\omega)$, at different pressures, determined from the above reflectance series. Thin black line shows the ambient pressure $\sigma_1(\omega)$. (c) Transmission at room temperature through a $\sim 5\mu$m thick sample, shown as a color map in function of pressure and incident light energy. (d) The pressure dependence of $\sigma_1$, at different photon energies. (e) and (f) The loss function, $-\text{Im}(1/\varepsilon)$, shown as a function of pressure and phonon energy. In all panels, the data taken between 0.22 and 0.33 eV are not shown due to strong diamond absorption lines.
FIG. 3. (Color online) (a) Raman spectra of BiTeI taken at a series of different pressures from 7 GPa to 15 GPa in a diamond anvil cell. Open symbols mark mode positions. (b) The pressure dependence or Raman mode frequencies below and above the phase transition at 9 GPa (white circles). The color background represents mode intensity.

troscopy. The symmetry analysis gives four zone-center vibrational modes, with the irreducible vibrational representation \( \Gamma = 2A_1 + 2E \). All of them are both Raman and infrared active because of the lack of inversion symmetry, and have been observed at ambient pressure [17] [18]. Fig. 3 shows the Raman spectra measured from 7 GPa to 15 GPa, in the energy range from 65 to 200 cm\(^{-1}\). Besides the expected blueshift of the Raman modes under pressure, an important effect is observed above 9 GPa. While four modes can be distinguished at 7 GPa, six modes are seen at 9 GPa. The discontinuities in several vibrational frequencies near \( p \sim 9 \) GPa confirm the phase transition observed in the optical properties. The appearance of new vibrational lattice modes points to a change of symmetry and shows that the sudden change of optical properties at \( p \sim 9 \) GPa is accompanied by a structural transition. The mode observed at 170 cm\(^{-1}\) for 7 GPa may be assigned to the \( A_1 \) symmetry. It disappears above 11 GPa at 182.7 cm\(^{-1}\). The \( A_1 \) mode involves ionic motion [17] along the c-axis, which is expected to be most affected by external pressure. In contrast, the modes seen at 70 an 120 cm\(^{-1}\) for 7 GPa are \( E \) modes involving in-plane atomic motion. Consequently these modes are not equally influenced by pressure.

Bahramy et al. predicted that pressure causes reduction of the band gap of the topologically trivial BiTeI [6]. As pressure reaches its critical value \( p_c \), the gap closes developing a Weyl semimetal phase, and its further increase reopens the gap resulting in a topological insulator phase characterized by a band-inversion feature. The first-principles calculations performed at the DFT-GGA level of theory estimate the critical pressure \( p_c \) to be in the range 1.7–4.1 GPa [6]. However, it was shown recently that the inclusion of many-body quasiparticle corrections calculated within the GW approximation results in a significant increase of the band gap of BiTeI bringing it in close agreement with the experimental value \( E_g = 0.38 \) eV [19]. Such an increase of the electronic band gap in the topologically trivial regime would effectively result in a positive shift of \( p_c \) [20]. Our GW calculations estimate \( p_c = 12 \) GPa [21], i.e. the structural phase transition takes place before the predicted topological phase transition and precludes its observation.

Our optical data show that the band gap continually decreases from ambient pressure to 9 GPa, followed by a phase transition which causes the gap to collapse. At room temperature, the gap is effectively closed above 9 GPa. The Raman spectra show that this phase transition is not only electronic, but also structural. Although our optical and Raman data do not exclude the topological surface states at high pressures [6], our observation with Raman spectroscopy of the structural phase transition suggests an alternative scenario where the gap closes due to changes of crystal symmetry.

To summarize, we have determined the pressure dependence of the optical properties and Raman vibrational modes of BiTeI, under pressures up to 15 GPa. The reflectivity and transmission show dramatic changes under pressure. Below 9 GPa the band gap monotonically decreases and the optical conductivity increases. At 9 GPa the gap starts to collapse as the interband transitions are pushed to very low energies, leading to a strong increase in the optical conductivity. As a result, the interband plasmon becomes overdamped above 9 GPa. The transmission data demonstrate clear evidence of a phase transition at 9 GPa, corroborated by the pressure-dependent Raman spectra which show that this transition is structural. The closure of the gap at pressures above 9 GPa is accompanied by a change of symmetry. Our study shows that the structural transition possibly prevents the predicted topological high-pressure phase in BiTeI from occurring.

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Note added - While finishing this manuscript, we became aware of the work of X. Xi et al [22], who similarly used optical spectroscopy under high pressure to study BiTeI.
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