Supplemental Material: Infrared and Raman spectroscopy measurements of a transition in the crystal structure and a closing of the energy gap of BiTeI under pressure

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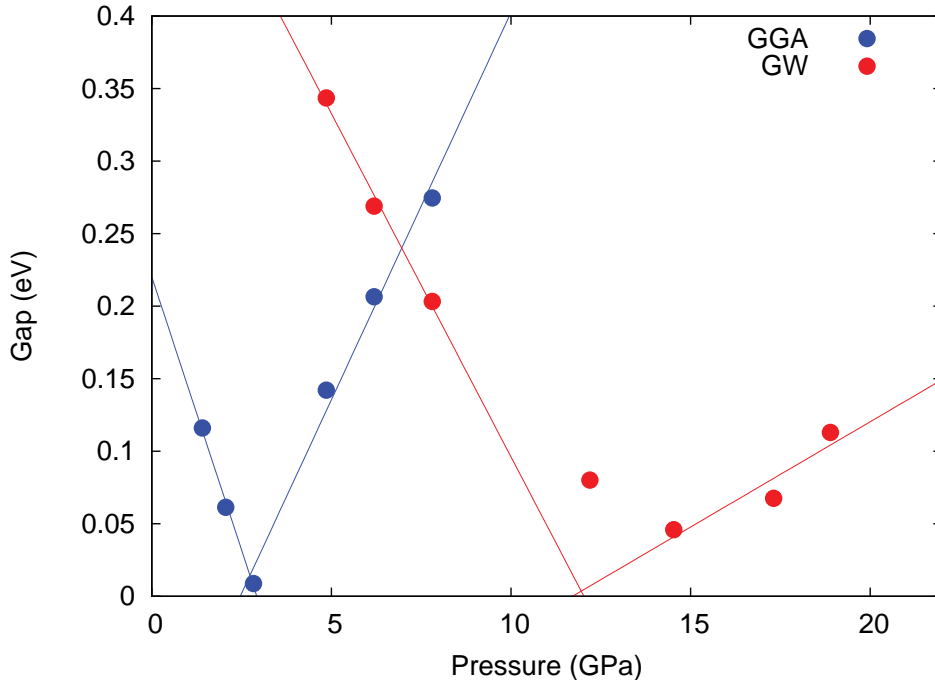
1. DFT AND GW CALCULATIONS

FIG. 1. Gap as a function of pressure for GGA and GW calculations.

The band structures of BiTeI under pressure were first calculated from density functional theory (DFT) within the generalized gradient approximation (GGA) as implemented in the QUANTUM-ESPRESSO package [1]. Spin-orbit effects were accounted for using the fully relativistic norm-conserving pseudopotentials acting on valence electron wavefunctions represented in the two-component spinor form [2].

The atomic positions and cell shape were relaxed at constant volume for a range of volume between $0.85V_0$ and $1.15V_0$, where V_0 is the experimental unit cell volume ($V_0 = 111.76\text{Å}^3$). The pressure was obtained by fitting the Murnaghan equation of state to the energy vs. volume curve. The gap as a function of the pressure is shown on Fig. 1. A closing of the gap is expected around $P_C = 2.7$GPa. A sketch of the band structure transition is shown on Fig. 2c). The closing of the gap takes place near the A point along the A→H line in the Brillouin zone.

The low value of P_C predicted by GGA is due to the underestimation of the band gap inherent to the DFT methodology. For a better estimation of the band gap, we performed a GW calculation. The quasiparticle energies were evaluated within the G_0W_0 approximation
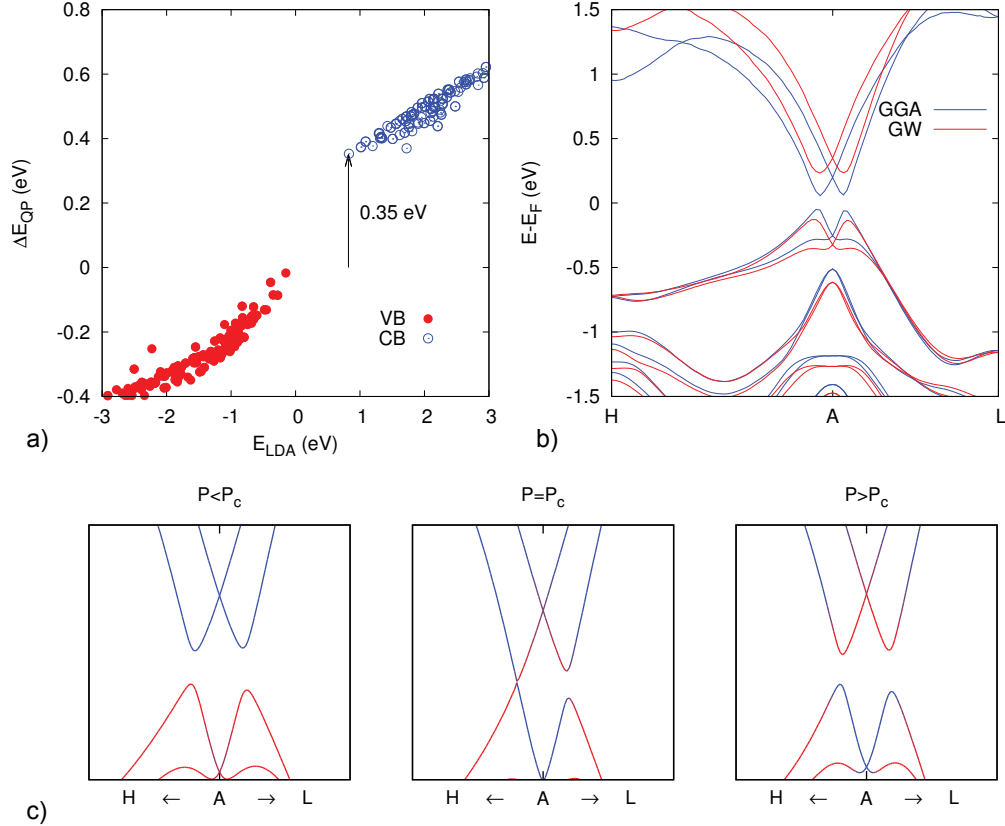
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FIG. 2. (a) Quasiparticle self-energy corrections as a function of LDA energies for bulk BiTeI, (b) GGA and GW band structure of bulk BiTeI at ambient pressure, and (c) Topological band structure transition around the critical pressure P_C. The color correspond to the weight of the state on the Bi (blue) and Te (red) atoms.

to the electron self-energy starting from non relativistic LDA results for ambient pressure BiTeI using the approach of Hybertsen and Louie [3]. This first-principles GW methodology is implemented in the BERKELEYGW code [4]. The quasiparticle self-energy correction is shown on Fig. 2a. The correction leads to an opening of the non-relativistic band gap of 0.35eV. The ambient pressure quasiparticle correction was applied to the non-relativistic GGA band structure at different volume using the scissor shift approximation. The spin-orbit effect were included as a last step by calculating the spin-orbit matrix element between the scissor-shifted Kohn-Sham GGA eigenstates following the approach of Ref. 5. The bands structure at ambient pressure obtained from this methodology is shown in Fig. 2b. The band gap as a function of the pressure from GW is shown on Fig. 1. The critical pressure within this approximation is ~ 10 GPa.
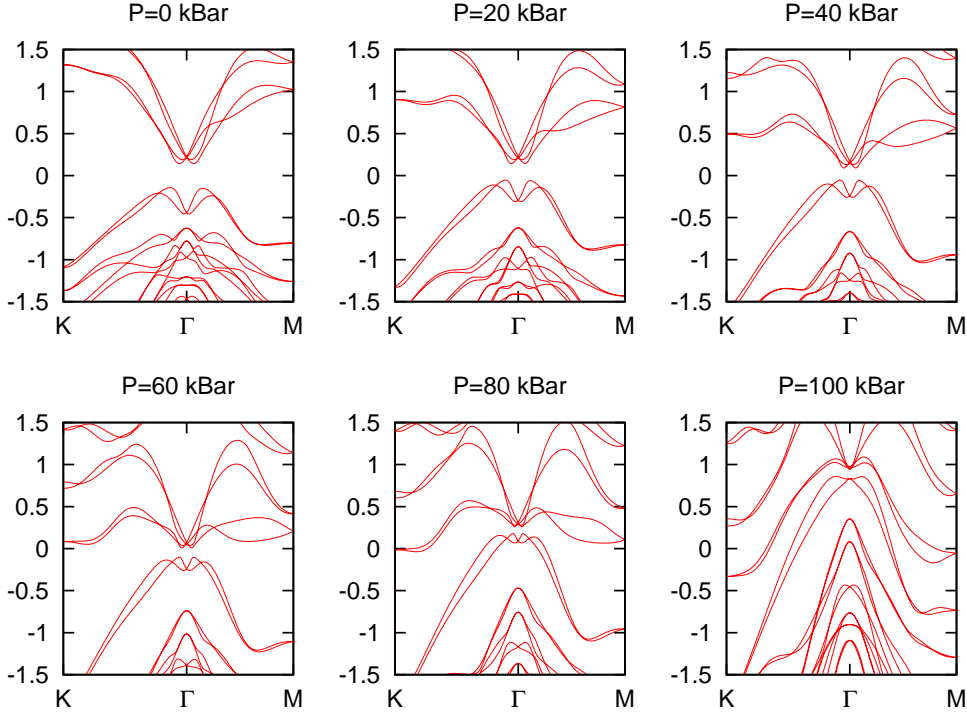
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FIG. 3. Band structure of the P6$_3$mc phase under pressure

2. BAND STRUCTURE OF THE HIGH PRESSURE PHASE

Since the optical properties of BiTeI progress gradually through the crystallographic phase transition (see Fig. 2 in main text), our hypothesis is that the high pressure phase is structurally close to the ambient pressure phase. A possible candidate for the high pressure phase is the structure of the chemically related compound BiTeCl (space group $P6_3mc$ with 6 atoms per unit cell). This structure correspond to a doubling of the cell in the direction perpendicular to the layers and differs from the ambient pressure phase by the stacking of the two BiTeI layers. We calculated the band structure of this phase at different pressure within the LDA approximation (Fig. 3). The results show that in this phase the gap also decreases gradually as a function of pressure. However, in contrast with the ambient pressure phase, the $P6_3mc$ phase terminates in a topologically trivial metallic state. Thus no gap reopening or topological phase transition is expected. This is consistent with the gradual closing of the gap observed in experiment.

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3. TRANSMISSION

Fig. 4 presents transmission data down to 0.07 eV. The optical conductivity is given to a good approximation by $-\log(T(\omega))$, which is shown in Fig. 4a. Clearly the γ feature remains close to its ambient value of ~ 0.4 eV even up to 9 GPa (blue curves), indicating a gradual evolution of the gap as a function of pressure in this pressure range. The lower pressure $p < 9$ GPa data displayed in Fig. 4b shows no increase of transmission at low energy up to 9 GPa where all curves are superposed.
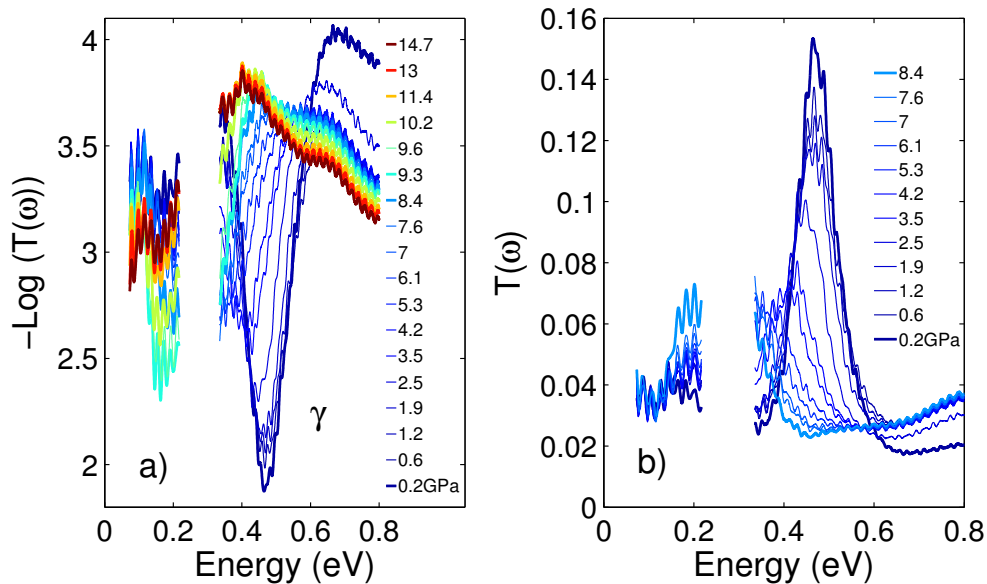

FIG. 4. Transmission data. a) Conductivity for all pressures and b) Transmission for $p < 9$ GPa. Color code matches the one used in Fig. 2b of the manuscript.

[1] Giannozzi, P. *et al.* "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials", *J. Phys.: Condens. Matter* **21**, 395502 (2009).

[2] Dal Corso, A. & Mosca Conte, A. "Spin-orbit coupling with ultrasoft pseudopotentials: Application to Au and Pt", *Phys. Rev. B* **71**, 115106 (2005).

[3] Hybertsen, M.S. & Louie, G. "Electron correlation in semiconductors and insulators: Band gaps and quasiparticle energies", *Phys. Rev. B* **34**, 5390 (1986).

[4] Deslippe, J. *et al.* "BerkeleyGW: A Massively Parallel Computer Package for the Calculation of the Quasiparticle and Optical Properties of Materials and Nanostructures", *Comput. Phys. Commun.* **183**, 1269 (2012).

[5] Hybertsen, M.S. & Louie, G. "Spin-orbit splitting in semiconductors and insulators from the ab initio pseudopotential", *Phys. Rev. B* **34**, 2920 (1986).