The Strong Confinement Regime in HgTe Two-Dimensional Nanoplatelets

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ABSTRACT: The confinement in colloidal HgTe nanocrystals enables this material to be promising for colloidal optoelectronics over a wide range of energies, from the THz spectral range up to the visible region. Herein, using a combination of high-energy-absorption HgTe nanoplatelets and low-energy-absorption HgTe nanocrystals, we probe the optical transmission of HgTe nanoparticles over the 0.26–1.8 eV range, from 0 to 300 K temperatures and under simultaneous pressure, up to 4 GPa. While the pressure dependence of nanoplatelets follows the one observed for bulk and nanocrystals, the temperature dependence dramatically differs for nanoplatelets. The modeling of the electronic energy dispersion using up to 14-band k·p formalism suggests that the second conduction band and higher bands of HgTe play a vital role in describing and explaining the HgTe nanoparticle spectroscopies.

INTRODUCTION

In bulk semiconductors, spectral tunability relies on material alloying with a second compound. This alloying condition can become a challenge when lattice-matched thin films need to be grown on a given substrate. In nanocrystals (NCs), quantum confinement offers an alternative method to achieve spectral control. This approach is nowadays used to generate green and red light for displays1 using CdSe or InP as active materials. In such an application, the confinement-induced renormalization of the band gap corresponds to a few tens of percent. Over the past decade, infrared optoelectronics2 has also generated significant interests in the 80s–90s owing to the use of this material for IR sensing.17,18 Bulk HgTe is a vanishing band gap semiconductor with an inverted band ordering, see Figure 1.19

The electronic structure of the bulk Hg(Cd)Te attracted significant interests in the 80s–90s owing to the use of this material for IR sensing.17,18 Bulk HgTe is a vanishing band gap semiconductor with an inverted band ordering, see Figure 1.19

Recently, the material has regained some interest as the first example of a topological insulator.20 In the latter case, a barely confined quantum well of HgTe is sandwiched within a CdTe matrix and presents edge channels for transport, as the bands recover their normal ordering at the interface.21,22 For zero-dimensional (0D) NCs, the electronic spectrum has been deeply investigated using infrared spectroscopy to measure the absorption cross-section,23 or to reveal the exciton fine structure.24,25 Complementary, the electronic spectrum of weakly confined HgTe NCs has been modeled using the two-band k·p formalism24 and the tight-binding method.26,27 However, very little work has been devoted to the most strongly confined form of HgTe such as the one obtained in...
HgTe 2D NPLs where the confinement energy can be as large as 1.5 eV.

This lack appears to be detrimental since device progresses appear to be strongly correlated to a deeper understanding of the material and its electronic structure. For the sake of illustration, systematic measurements of the band alignment\(^\text{10,24,28}\) in HgTe NCs have enabled the design of unipolar barriers\(^\text{28}\) to reduce the device dark current. Alternatively, the development of HgTe-based colloidal heterostructures not only appears promising to expand the range of wavelengths to cryogenic operating conditions for IR sensors, and NCs with various conduction bands of HgTe. In practice, we grow a series of HgTe 2D NPLs where the conduction and valence (black) bands of bulk HgTe from the \((3 + 1)\) band \(k\mathbf{p}\) model.

**METHODS**

**Chemicals.** Mercury chloride (HgCl\(_2\), Strem Chemicals, 99%) and Hg(Acetate)\(_2\) (Hg(Ac)_2, Aldrich, > 99.0%); mercury compounds are highly toxic. Handle them with special care. Tellurium powder (Te, Sigma-Aldrich, 99.99%), cadmium oxide (CdO) (Aldrich 99.99%), trioctylphosphine (TOP) (Alfa, 90%), oleic acid (OA, Sigma, 90%), propionic acid (Aldrich, 99%), oleylamine (OLA, Acros, 80–90%), dodecanethiol (DDT, Sigma-Aldrich, 98%), trietylamine (TOA, Aldrich), octadecene (ODE) (Aldrich, 90%), chloroform (Carlo Erba), methanol (VWR, 98.5%), acetone (VWR rectapur), ethanol (absolute VWR), and toluene (VWR, 99.8%). All chemicals are used without further purification.

Cadmium Propionate (Cd(prop)_2). CdO (1.036 g) is mixed in 10 mL of propionic acid under Ar for 1 h. Then, the flask is opened and exposed to air, and the temperature is raised to 140°C up to the point the volume gets divided by a factor of 2. The whitish solution is precipitated by the addition of acetone. After centrifugation, the solid is dried under vacuum for 24 h.

**1 M TOP:Te Precursor.** Te powder (2.54 g) is mixed in 20 mL of TOP in a three-neck flask. The flask is kept under vacuum at room temperature for 5 min and then the temperature is raised to 100°C. Furthermore, the degassing of the flask is conducted for the next 20 min. The atmosphere is switched to Ar, and the temperature is raised to 275°C. The solution is stirred until a clear orange coloration is obtained. The flask is cooled down to room temperature, and the color switches to yellow. Finally, this solution is transferred to an Ar-filled glovebox for storage.

**Synthesis of 3 MLs CdTe NPLs with TOA.** In a three-neck flask, Cd(prop)_2 (390 mg, 1.5 mmol), oleic acid (240 \(\mu\)L, 0.75 mmol), and 30 mL of octadecene are degassed under vacuum at 90°C for 1 h. Under argon flow, TOP:Te at 1 M (300 \(\mu\)L) diluted in 1.5 mL of octadecene is swiftly injected at 210°C. After 30 min of reaction, the mixture is cooled down and 1.7 mL of oleic acid is introduced. The resulting nanoplatelets are precipitated twice with an excess of ethanol and then are redispersed in 30 mL of hexane.

**Cation Exchange for the Synthesis of 3 MLs HgTe NPLs with TOA.** In a glass tube, 2 mL of hexane and 200 \(\mu\)L of CdTe NPLs are introduced. A volume of 60 \(\mu\)L of fresh 0.1 M HgAc\(_2\) in trietylamine solution is added at room temperature. The Cd:Hg ratio is 1:2. The cation exchange is followed by absorption spectroscopy. Once the first excitonic peak has reached 824 nm, 80 \(\mu\)L of oleic acid is added to stabilize the HgTe NPLs. The excess of precursors is removed by centrifugation. The resulting NPLs are resuspended in 1 mL of toluene. Procedures for other surface chemistries on the HgTe NPL surface are given in the Supporting Information.

**HgTe NCs Synthesis with Band Edge at 4000 cm\(^{-1}\).** HgCl\(_2\) (513 mg) was added to 60 mL of oleylamine in a 100 mL round flask. The solution was placed under vacuum and heated to 110°C for 1 h. Then, the temperature is decreased to 80°C and the solution is placed in a \(N_2\) atmosphere. A volume of 1.9 mL of TOP:Te (1 M) with 10 mL of oleylamine is added to the mercury solution. The solution color gradually turns to dark brown, and the reaction is stopped after 3 min. A solution made of 1 mL of dodecanethiol and 9 mL of toluene is quickly added to quench the reaction. The nanocrystals are then precipitated with ethanol. After centrifugation, the nanocrystals are redispersed in chloroform. The washing step is repeated one more time. The solution is filtered with a 0.2 \(\mu\)m filter and redispersed in 6 mL of chloroform. Procedures for other NC sizes are given in the Supporting Information.

**Electron Microscopy.** For transmission electron microscopy (TEM) pictures, a drop of the NC solution is drop-cast onto a copper grid covered with an amorphous carbon film. The grid is degassed overnight to reduce future contamination. A JEOL 2010F is used for the acquisition of pictures and operated at 200 kV.

**Infrared Spectroscopy as a Function of Temperature.** The solution of the nanocrystal is drop-cast onto a double side polished Si wafer for the sample in the mid-infrared and onto a CaF\(_2\) substrate for the sample in the near-infrared. The
Table 1. Values of the Simple (3 + 1) and the 14-Band Model Parameters Used to Describe the Confinement, Temperature, and Pressure Dependences
d
<table>
<thead>
<tr>
<th>parameter</th>
<th>simple (3 + 1)-band model value</th>
<th>14-band k.p model value</th>
<th>reference</th>
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<tr>
<td>( E^0 )</td>
<td>0.31 eV</td>
<td>0.375 eV</td>
<td>0.303 eV in ref 55.</td>
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<td>simulated ( E^0(k = 0) )</td>
<td>0.365 eV</td>
<td>3.35 eV</td>
<td>4.11 eV (QSGW) and 3.07 eV (LDA) in ref 51.</td>
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<tr>
<td>( E^C )</td>
<td>4 eV</td>
<td>2.5 eV</td>
<td>fitted, 24.8 eV in ref 55.</td>
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<tr>
<td>simulated ( E^C(k = 0) )</td>
<td>2.78 eV</td>
<td>10 eV</td>
<td>fitted</td>
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<tr>
<td>( E_F )</td>
<td>25 eV</td>
<td>30 eV</td>
<td>fitted</td>
</tr>
<tr>
<td>( E_V )</td>
<td>15 eV</td>
<td>20 eV</td>
<td>fitted</td>
</tr>
<tr>
<td>( \delta E^C/\delta T )</td>
<td>from ( E^C(T, P) ), typically ( \approx -0.61 ) meV/K(^{-1})</td>
<td>from ( E^C(T, P) ) plus a constant 0.1 meV.K(^{-1}), typically ( \approx -0.51 ) meV.K(^{-1})</td>
<td>see ( E^C(T, P) ) formula in Supporting Information</td>
</tr>
<tr>
<td>( \delta E_p/\delta T )</td>
<td>( -2.4 ) meV.K(^{-1})</td>
<td>( -3 ) meV.K(^{-1})</td>
<td>fitted</td>
</tr>
<tr>
<td>( \delta E_p/\delta P )</td>
<td>( -85 ) meV/GPa</td>
<td>( -95 ) meV/GPa</td>
<td>fitted</td>
</tr>
<tr>
<td>( \delta E_p/\delta P )</td>
<td>( +220 ) meV/GPa</td>
<td>( +600 ) meV/GPa</td>
<td>fitted</td>
</tr>
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</table>

| a HgTe nanoparticle lattice parameter | 0.6465 nm | 0.6500 nm | ref 34 at 300 K |
| a HgTe nanoparticle lattice parameter |          |          | from measurement on NPLs at 300 K, Figure S6c |
| \( B_0 \)                            | 30 GPa                           |            | from measurement on NPLs at 300 K, Figure S6c |
| \( \delta B_0/\delta P \)            | \(-1.5\)                         |            | fitted        |
| \( m^*_L \)                          | 0.013 \( m_0 \)                  | 0.013 \( m_0 \)        | output        |
| \( m^*_H \)                          | 0.33 \( m_0 \)                   | 0.69 \( m_0 \)         | output        |
| spin-orbit coupling \( \Delta \)     | n.a.                             | 0.5 eV      | 0.775 eV (hQSGW) in ref 51. |
| simulated spin-orbit coupling at \( k = 0 \) | n.a. | 0.732 eV | 1.08 eV in ref 51. |
| \( \Delta_C \)                       | n.a.                             | 1 eV        | 1.06 eV (QSGW) 1.17 eV (LDA) in ref 51. |
| simulated spin-orbit coupling at \( k = 0 \) | n.a. | 0.768 eV | fitted |
| \( \Delta' \)                        | n.a.                             | \(-1.5\) eV | fitted |

a.n.a. means nonapplicable.

The latter is used in a transmission configuration with two ZnSe windows. The cryostat is then introduced into the Fourier transform infrared spectrometer (FTIR, Thermo Fischer iS50). Two sources have been used: a white light in the near-infrared and a globar in the mid-infrared. Two beam splitters have been used: a CaF\(_2\) beam splitter in the near-infrared and an extended KBr one in the mid-infrared. Two detectors have been used: an InGaAs sensor in the near-infrared and an extended KBr one in the mid-infrared. Two detectors have been used: an InGaAs sensor in the near-infrared and an extended KBr one in the mid-infrared. Two detectors have been used: an InGaAs sensor in the near-infrared and a DTGS one in the mid-infrared. In all the cases, the background is made at room temperature using the same optical configuration but without sample onto the substrate. Spectra are acquired with a 4 cm\(^{-1}\) resolution and typically averaged 100 times.

**X-ray Diffraction under Pressure.** Experiments were carried out using a membrane diamond anvil cell equipped with Boehler-type anvils with 500 \( \mu \)m cuvettes. A stainless-steel gasket with a thickness of 200 \( \mu \)m is indented down to 50 \( \mu \)m. A 150 \( \mu \)m hole is then drilled by electroerosion. The gasket is placed on the top of one of the DAC diamonds, and the gasket hole is filled with NaCl. After introducing a ruby crystal, the DAC is closed under gentle pressure until the salt forms a clear window. A drop of a diluted suspension of NCs in toluene is then added and dried on top of the NaCl window to form a dry and uniform film of NCs. The DAC is then closed and introduced in a Cassegrain microscope. The pressure is generated by means of a metallic membrane inflated with He gas. The in situ pressure is monitored by the ruby luminescence technique. A 532 nm laser is shone through one of the Cassegrain objectives and focused on the ruby crystal embedded in the cell. Ruby photoluminescence is collected and sent to an Ocean Optics spectrometer, showing a characteristic doublet around 694 nm at ambient pressure. This photoluminescence is fitted, and the pressure is computed using the main peak position. Once the pressure is stabilized, an infrared absorbance spectrum is acquired using a Thermo Fisher Nicolet iS50 FTIR with a globar source, a quartz beam splitter, and a silicon detector in a transmission configuration. This operation is repeated for various pressure values from 0 GPa to 4 GPa. When the maximum pressure is reached, the membrane is deflated and several spectra are acquired to check the reversibility of the pressure effect.
Hamiltonian matrices $3 \times 3$ and $14 \times 14$ k.p $H(k, T, P)$ are processed symbolically and diagonalized numerically for each couple of temperature and pressure $(T, P)$ using the parameters in Table 1.Bulk material energy dispersion diagrams $E(k)$ are calculated using the wave vector $k$ as a free-varying independence variable. On the contrary, spectroscopic energies of the form $E(T, P)$ are extracted by modifying $k$, with the following procedure. Since thermal dilation or pressure contraction occurs, the nanoparticles are implicitly labeled by their discretized wave vector $k_0 = 2\pi/L_0$ in $(0 K, 0 \text{ GPa})$ conditions. Based on the starting energy $E_{\text{Start}}$ in the starting conditions $(T_{\text{Start}}, P_{\text{Start}})$, the dispersion relation $E(k)$ is first inverted giving out a reference wave vector $k_{\text{Start}}$. This $k_{\text{Start}}$ wavevector is then dilated or contracted back to $(0 K, 0 \text{ GPa})$ conditions following equation S6b, thus giving the $k_0$ wavevector labeling the nanoparticle. The temperature $T$ and pressure $P$ are then freely scanned. For each $(T, P)$, the norm of the discretized wave vector $k_0$ is changed into $k(k_0, T, P)$ according to the dilation or contraction of the lattice parameter. The k.p matrix is finally numerically evaluated at this altered wave vector $k$, and the eigen energies are reported against $T$ and/or $P$.

**RESULTS AND DISCUSSION**

**From Weak to Strong Confinement in HgTe Nanocrystals.** We grow a series of HgTe NCs with various sizes to widely tune the confinement energy. As a strongly confined form of HgTe, 2D NPLs are grown. The HgTe NPLs are obtained using a two-step approach where CdTe NPLs are first synthesized, see Figure S1. The NPLs are 3 monolayers thick (three planes of Te surrounded by four planes of Cd) corresponding to a thickness of 1.1 nm. Those NPLs are then exposed to a bulky Hg precursor (Hg-amine complexes), which transforms them into pure HgTe NPLs due to cation exchange. Given that CdTe (0.648 nm) and HgTe (0.646 nm) have similar lattice parameters (0.3% difference), the final thickness of the HgTe NPL is 1.1 nm, which is confirmed by the fact that the two types of material present similar X-ray diffractogram, see Figure S2.

The lateral extension of the particles is large and can reach several hundreds of nanometers according to electronic microscopy, see Figure 2a and Figures S3–S5. Due to the thickness, the material is strongly confined along the <001> crystal direction, and the band edge absorption appears around 900 nm ($\approx 11,000 \text{ cm}^{-1}$ or $\approx 1.4 \text{ eV at room temperature}$), see Figure 2c. It has been demonstrated that the exact value of the band-edge energy can be further tuned with the capping ligands, which also take part in the effective delocalization length. This enables a fine-tuning of the confinement energy while keeping the inorganic core unchanged.

In addition, we grow a series of HgTe NCs with room-temperature band edge between 9000 cm$^{-1}$ (1.11 eV) and 2000 cm$^{-1}$ (248 meV), see Figure 2b,c and Figure S6. The syntheses follow the procedure of Keuleyan et al. (for large NCs) and Geiregat et al. (for the smallest NCs). The combination of the HgTe NPLs and NCs allows us to tune the confinement energies over more than a factor of 5, from strongly to weakly confined materials as we switch from NPLs to NCs.

**Effect of Temperature on the Infrared Absorption.** We then probe the effect of temperature on the IR spectrum of the materials, see the spectra given in Figure 3a–c and Figures S8 and S9. The temperature dependence of the material is dramatically influenced by the material confinement, as shown in Figure 3a–c. For large (i.e., weakly confined) HgTe NCs (Figure 3c), the $E_g$ confinement energy redshifts as the temperature is lowered, corresponding to a positive value for $dE_g/dT$. This behavior is similar to the one observed in bulk HgTe, but it is opposite to the trend observed for wider band gap II–VI semiconductors such as CdTe or CdSe.
where whatever the particle size, only negative values have been observed for $dE_\text{G}/dT$. In NCs, such positive value for $dE_\text{G}/dT$ has been observed for lead halide perovskites$^{42}$ or large PbS NCs.$^{39}$ Nevertheless, as the confinement increases, we observe a reduction of the value of $dE_\text{G}/dT$ (Figure 3b) and surprisingly even an inversion of its sign in the case of NPLs (Figure 3a).

This change of sign for $dE_\text{G}/dT$ excludes that the observed shifts may result solely from a thermal dilation or contraction of the nanoparticles, the size of which will itself tune the confinement. In addition, this contribution of temperature has been found to be quantitatively weak (few μeV.K$^{-1}$) due to the very small thermal dilation, see Figure S11b. Note that the dimensionality does not seem to be a driving parameter for the magnitude of $dE_\text{G}/dT$ since NCs (0D) and NPLs (2D) with the same $E_\text{G}$ confinement energy present similar values for $dE_\text{G}/dT$, see circles and triangles in Figure 3d. A similar trend for $dE_\text{G}/dT$ (reduction of the amplitude and change of sign) as a function of the inverse of the particle size was observed in the case of PbS NCs. By excluding other possibilities, the band gap shift with temperature was finally attributed to a size-dependent electron–phonon coupling.$^{23,43}$

**Effect of Pressure on the Infrared Absorption.**

Similarly, we measured the pressure dependence of the band gap for the HgTe NPLs at various fixed temperatures. Note that for HgTe NCs, the pressure dependence of the band gap was already reported in ref 44, at room temperature. This is why the effect of pressure is discussed in the case of NPLs here. In practice, the sample is loaded in a diamond anvil cell together with NaCl, which is used as an infrared transparent pressure transmission medium. A ruby is also loaded in the cell and used to determine the applied pressure, see Figure 4a for a scheme of the experiment and the Supporting Information for details. All the reported observations appear to be fully reversible in the targeted range of pressure (i.e., zero pressure spectrum is recovered after pressure release). On the other hand, the process is strongly hysteretic: the full release of pressure is required to recover the initial spectrum.

To understand pressure-induced change in the infrared spectrum, it is first necessary to determine if the changes are the result of a structural phase transition. Bulk HgTe crystallizes in the cubic zinc blende structure at ambient pressure and undergoes several phase changes as pressure is increased. For bulk material, the cinnabar phase appears around 1.4 GPa.$^{45,46}$ Under NC form, the zinc-blende phase remains stable up to higher pressures.$^{44}$ In the range between 3 and 5 GPa, we can notice the presence of both zinc-blende and the cinnabar phase (Figure S7). It is, however, unclear if the two phases exist within the same NPL or if the signal is associated with different particles. In the zinc-blende phase, we identify a decrease in the lattice parameter with initial pressure ($\Delta a/\Delta P \approx 7$ pm/GPa), which corresponds to a bulk modulus of 30 GPa for the HgTe NPLs. This value is similar to the one measured for the HgTe NCs$^{46}$ (33 GPa), which was relatively close to the one of the bulk (34 GPa)$^{47}$.

The $E_\text{G}$ confinement energy appears to be dependent on the applied pressure, see Figures 4b,c, and 6c and Figure S10. The confinement energy gradually increases with pressure corresponding to a positive value for $dE_\text{G}/dP$. This is similar to what has been measured for HgTe NCs$^{44}$ and wider band gap II-VI semiconductor quantum dots such as CdSe$^{48}$ and core-shells made of CdSe/ZnS.$^{49,50}$ Applying pressure in the range of existence of the zinc-blende phase can lead to a shift of the confinement energy up to 300 meV, which is far more than the shift induced by cooling the sample from room temperature to cryogenic conditions ($\approx$5 meV). This order of magnitude is partially expected from the lattice parameter change under pressure around 6% as shown in Figure S7c and estimated around only 0.08% over 300 K temperature range as shown in Figure S11b. Above 4 GPa, no excitonic feature is identified. This observation is correlated to the disappearance of the zinc-blende phase under similar pressure, see Figure S7.

**Multiband k.p Modelling.**

In order to address the striking temperature and pressure dependence of the spectra observed in Figure 3 and 4, we model the nanoparticle energies using multiband k.p simulations. HgTe dispersion appears to be nonparabolic$^{56,51}$ and the effective mass approximation (1 band model) is only valid over 1% of the Brillouin zone. For the wavevectors far away from the Γ point, the dispersion becomes first linear and then slightly bends down for wavevectors corresponding to the confinement of NPLs (confinement energy above 1 eV). More bands need to be included in the k.p model to obtain an accurate description of the dispersion relation.

When a detailed description of the valence band is required, an 8-band k.p model describing the $\Gamma_6$, $\Gamma_7$, and $\Gamma_8$ bands and their degeneracy is used.$^{52,53}$ It has been estimated that the 8-band k.p model correctly described the Brillouin zone over 8% of it, corresponding to energies significantly smaller than the NPL ones that are around 1.1–1.8 eV.$^{52}$ While the effective mass approximation describes only the very bottom parabolic part of the light hole like ($\Gamma_6$) band, the inclusion of an...
additional conduction band is critical to capture the linear dispersion occurring at larger wavevectors and higher energies.

In HgTe, contrary to PbS, the hole and electron effective masses strongly differ, the valence band mass being more than 10 times the conduction band mass. Therefore, the confinement is mostly the result of the conduction band and the latter is the one requiring the most accuracy. In the Supporting Information (Figures S14–S17), we provide a 14-band $k.p$ model, which includes the minimum amount of bands to properly take into account additional conduction bands.54 This 14-band model aims at supporting a simpler $(3 + 1)$ effective bands model later described in the main text. This simple model provides the driving concepts leading to the realistic calculated 14-band structure. The $14$-band model includes notably the spin-orbit coupling, disregarded in the simplified model, and all relevant interactions. Note that Coulombic renormalization of the band gap has been neglected since these effects have been found to be small in the case of HgTe NCs.26 Even though the conclusions are qualitatively the same using each version of the model, the complete version may somewhat blur the message with a large amount of involved parameters. This is why, in the following text, we describe a simplified approach. We use a $(3 + 1)$ band one-dimensional $k.p$-like model, referred to as the simple model and described in the Supporting Information. Its illustrative role is to be tractable and to account for all the experimental features with a minimal set of necessary ingredients, as defined and shown in Figure 1. The associated parameters are given in Table 1.

The $(3 + 1)$ band model accounts for the two bands with $\Gamma_8$ symmetry at $k = 0$ (called HH and LH in Figure 1) which are the bands around the Fermi level and involved in the absorption. We also include the $\Gamma_6$ valence band and a second conduction band. The introduction of this effective high-energy band in the conduction band is central to accurately describe the bending of the LH band occurring at large wavevectors.

All the experimental data are then accounted from the variation with temperature and pressure of only two bulk band gap energies: $E_g(T,P)$ and $E_{gc}(T,P)$. As these gaps will be affected by pressure and temperature, the band curvature will be modified (through the $E_g$ and $E_{gc}$ parameters coupling the bands), unveiling the effect of pressure and temperature in the presence of confinement (i.e., away from the $\Gamma$ point). The strong confinement in the HgTe nanoparticles is modeled by the discretization of the $k \rightarrow$ wavevector in the reciprocal space, typically at $k = \pm \frac{\pi}{a}$ along [001], where $L$ is the size of the nanoparticle, accounting for the contraction and thermal dilation of the nanoparticle with pressure and temperature, respectively.

Figures 5a and 6a, respectively, show the effects of temperature and pressure on the relation dispersion. When temperature or pressure increases, the band gaps $E_g$ and $E_{gc}$ are altered as shown in Figure S11c. The effect on the LH band effective mass $m_{LH}^{*}$ defined at small $k$, is given by:

$$E_{LH}(k, T, P) \approx \left(1 + \frac{E_p}{E_g(T, P)} - \frac{E_{pcp}}{E_{gc}(T, P)}\right)\frac{\hbar^2 k^2}{2m_{LH}^*}$$

Figure 5. Modeling the temperature effect of the dispersion relation. (a) Effect of temperature on $E(k)$ when the two band gaps $E_g$ and $E_{gc}$ vary. The gray arrows correspond to typical confinement energies for the NCs (1.5 eV) and for NCs (0.5 eV). (b) Experimental normalized shift of the band gap as a function of temperature for different 10 K sizes of HgTe NCs and 3 ML HgTe NPLs with different surface chemistries. (c) Simulated normalized shift of the confinement energy $E_{gc}$ as a function of temperature for different sizes of HgTe NCs and 3 ML HgTe NPLs with different surface chemistries.

Figure 6. Modeling the pressure effect of the dispersion relation. (a) Effect of pressure on the conduction and valence bands. The gray arrows correspond to typical confinement energies for the NPLs (1.5 eV) and for NCs (0.5 eV). (b) Simulated confinement energy variation over $\Delta P = 4$ GPa pressure difference for 3 temperatures. The light orange dot is the experimental measurement around 150 K. The two red squares are the measurements from Ref 44 at 300 K. (c) Experimental confinement energy $E_{gc}$ shifts as a function of an applied hydrostatic pressure for HgTe NPLs for three different temperatures. (d) Simulated confinement energy $E_{gc}$ shifts as a function of an applied pressure for HgTe NPLs from 0 to 300 K. The indicated slope corresponds to 0 K.
As seen in eq 1, these variations lead to a competition between the two gaps $E_g(T,P)$ and $E_{gc}(T,P)$ in the alteration of $E_{LH}(k)$ relation dispersion.

At low energy (i.e., small $k$, see the left arrow in the dispersion relation), the dispersion is ruled by the $m^*_{gh}$ effective mass reduction. The energy blueshift as shown in Figure 5a for temperature, and Figure 6a for pressure is the result of the drastic reduction of $E_g$ from 0.31 eV at 0 K down to 0.12 eV at room temperature. $E_g$ being one order of magnitude smaller than $E_{gc}$, and $\partial E_g/\partial T/E_g$ and $\partial E_{gc}/\partial T/E_{gc}$ partial derivatives being comparable, the effective mass is essentially governed by $E_g$ (i.e., the second conduction band plays no role in the vicinity of the $\Gamma$ point). The same rule of thumb holds for pressure.

However, at high energies (i.e., high $k$, see the right arrow in the dispersion relation), the parabolic eq 1 ceases to be valid. When temperature increases, the second conduction band counteracts $m^*_{gh}$ reduction. As a result of the shrinking of $E_{gc}$, the second conduction band becomes closer to the LH band and repels it downward as seen in Figure 5a. In other words, the second conduction band is responsible for the sublinear relation dispersion observed at large $k$ and leads to an inversion of the conduction energy variation with a simulated redshift of the $E_g$ confinement energy.

Using the (3 + 1) band model and $-2.4$ meV·K$^{-1}$ value for $\frac{\partial E_{gc}}{\partial T}$ the experimental temperature dependence of the band gap (Figure 5b) is reproduced, as shown in Figure 5c. With low $T = 10$ K, the blueshift ($E_g(T)/E_g(low\ T) > 1$) at small energies is due to the shrinking of the $E_g$ band gap. However, at large energies, $E_{gc}$ also shrinks and the closer second conduction band pushes the first one downward, leading to a redshift ($E_g(T)/E_g(low\ T) < 1$). This interpretation is further analyzed quantitatively by plotting the simulated slopes $\frac{\Delta E_c}{\Delta T}$ as a function of the confinement energy of the particles, see the dashed green line in Figure 3d. We see that the model appears in fair agreement with the observed slopes over the whole range of experimental energies supporting the interpretation of the shrinking of the two gap energies.

Regarding the pressure dependence, the observed energy shifts with hydrostatic pressure present an average slope $\frac{\Delta E_g}{\Delta P} \approx 100$ meV/GPa in the case of NPLs (Figures 4b, 6c, and Figure S10) which has to be compared with the value of $\approx 60$ meV/GPa for the nanocrystals 44(Figure 4c and Figure S13). Contrary to the case of temperature, the confinement only quantitatively affects the pressure dependence of the confinement energy. This result contrasts to CdSe where the size dependence of the $\frac{\Delta E_c}{\Delta P}$ parameter has been found to be larger with an increase of $\frac{\Delta E_c}{\Delta P}$ from 40 to 80 meV/GPa as the size changes by only a factor of 2.48

Under increasing pressure, the second conduction band goes away from the first one. Pressure simply pushes $E_g$ confinement energy even higher, see Figure 6a. In this case, due to pressure, the second conduction band adds an additional contribution to the one of $E_g$ to the observed blueshift of the confinement energy $E_{gc}$.

Using $-85$ meV/GPa and $+220$ meV/GPa, respectively, for $\partial E_g/\partial P$ and $\partial E_{gc}/\partial P$, the $(3 + 1)$ bands model can reproduce the pressure dependence of the confinement energy of the NPLs, see Figure 6c and d. Also note that using the temperature dependence determined previously, it is possible to reproduce the weak temperature dependence of the pressure potential $dE_g/dP$ of the confinement energy in the case of NPLs, see the four simulated temperatures in Figure 6d, while capturing the moderate confinement dependence as depicted in Figure 6b and Figure S13a.

In all, though both temperature and pressure alter the bulk band gaps $E_g$ and $E_{gc}$, only blue shifts are observed with increasing pressure, while increasing temperature also shows red shifts. We thus conclude that the unusual change of the optical gap with temperature and its change of sign reflects the bulk material electronic structure and that phonon does not have to be invoked.43

### CONCLUSIONS

In conclusion, we have shown that the strong confinement in NPLs causes a nonlinear dispersion of high energy state energies in the electronic structure of HgTe nanoparticles. Measurements of the temperature dependence of the optical band gap appears as a direct probe of the dispersion relation. We found that a single parameter set in the $(3 + 1)$ effective band model can account for all the observed features in energy, temperature, and pressure, providing that the relative proximity of the second conduction band of HgTe is included. We show that the second conduction band appears as a paramount ingredient for absorption energies above $\approx 0.5–1$ eV to describe realistically the energies and electronic states of strongly confined HgTe nanoparticles.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c07533.

Material synthesis, material characterization, X-ray diffraction measurement under pressure, raw spectrum of material temperature and pressure dependence and additional information regarding the $(3 + 1)$-band $k.p$-like and 14 band $k.p$ models (PDF)

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