Charge carrier thermalization in bulk and monolayer CdTe: A first principles study

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While cadmium telluride (CdTe) thin films are being used in solar cell prototyping for decades, the recent advent of two-dimensional (2D) materials challenges the fundamental limit for thickness of conventional CdTe layers. Here, we report our theoretical predictions on photocarrier dynamics in an ultimately thin (about 1 nm) CdTe slab. It corresponds to a layer that is just a single unit cell thick, when the bulk parent crystal in the zinc blende phase is cleaved along the [110] facet. Using an ab-initio method based on density functional theory (DFT) and the Boltzmann equation in the relaxation time approximation (RTA), we determine the thermalization time for charge carriers excited to a certain energy for instance through laser irradiation. Our calculations include contributions arising from all phonon branches in the first Brillouin zone (BZ), thus capturing all relevant inter- and intraband carrier transitions due to electron-phonon scattering. We find that the photocarrier thermalization time is strongly reduced, by one order of magnitude for holes and by three orders of magnitude for electrons, once the CdTe crystal is thinned down from the bulk to a monolayer. Most surprisingly, the electron thermalization time becomes independent of the electron excess energy up to about 0.5 eV, when counted from the conduction band minimum (CBM). We relate this peculiar behavior to the degenerate and nearly parabolic lowest conduction band that yields a constant density of states in the 2D limit. Our findings may be useful for designing novel CdTe-based optoelectronic devices, which employ nonequilibrium photoexcited carriers to improve the performance.

I. INTRODUCTION

Dynamics of nonequilibrium carriers in semiconductors greatly impact the performance of optoelectronic and photovoltaic devices because of the high excess energy that they can transfer [1, 2]. The phenomenon is especially interesting in low dimensional structures [3], where carriers can be extracted well before thermalization and potentially be exploited in external circuits [4]. This approach, however, requires full understanding of the excited carrier evolution on an ultrafast time scale.

In the following the term “hot carriers” may refer to electrons or holes being in or out of equilibrium. In the former case, the carriers are described by a Fermi-Dirac distribution with a temperature hotter than those of the lattice. In the strong nonequilibrium state the concept of temperature becomes meaningless, and the carriers are instead characterized by a certain excess energy. The simplest way to generate such hot carriers in a semiconductor is the interband excitation of electron-hole pairs by light absorption. The electron or hole excess energy, counted from the respective band edges, is determined by the frequency of the absorbed photons. Since we consider a single-temperature model in this work, we will use the terms “hot carriers” and “photoexcited carriers” interchangeably.

A direct bandgap facilitates the interband absorption in semiconductors, because of the vanishing momentum mismatch in optical transitions between the valence band maximum (VBM) and CBM. Group II-VI and III-V semiconductors exhibit a direct bandgap and are therefore excellent candidates to exploit interband optical transitions. One of the popular choices among this group is CdTe, being a direct-bandgap semiconductor used in electro-optic modulators and nuclear detectors [5]. Its most prevalent commercial application is in photovoltaics as a component of cadmium sulfide (CdS)-CdTe junctions [6]. State of the art CdS-CdTe solar cells have reached impressive 21% external quantum efficiency [7].

Recent progress in nanofabrication technologies has made it possible to reduce the thickness of CdTe crystals to just a few layers [8] and even to roll the layers up into nanoscrolls [9]. Atomically thin layers of other members of the group II-VI semiconductors have also been synthesized recently [8, 10]. In particular, a four-layer-thick zinc selenide (ZnSe) slab cleaved along the [110] facet of the bulk crystal has been shown to be stable [11]. Note that bulk CdTe features the same zinc blende crystal structure as ZnSe, see Fig. 1(a). Keeping in mind this tremendous progress, we anticipate fabrication of monolayer CdTe in the near future, because first principles studies suggest that this material is dynamically stable [12–14]. In this work we address what happens with the ultrafast dynamics of photoexcited carriers in CdTe films, once their thickness is reduced down to the fundamental limit of a monolayer, as shown in Fig. 1(b).

Such extremely thin CdTe films belong to the class of atomically thin or 2D materials such as graphene [15], transition metal dichalcogenides (TMDCs) [16], 2D oxides [17], germanane [18], and phosphorene [19]. 2D materials show properties drastically different from their bulk counterparts due to quantum confinement. For example, TMDCs demonstrate a transition from indirect to direct gap when reduced from the bulk to a monolayer, resulting in strong excitonic photoluminescence peaks [16, 20]. Interestingly, the opposite behavior of a direct to indirect bandgap can be observed in metal monochalcogenides, leading to a vanishing of the excitonic absorption in stacks that are less than 8 layers thick [21]. The peculiar optical properties make 2D materials promising for photodetection and other photonic applications [22–26].

To understand the microscopic details of hot-carrier dy-
namics in CdTe, both theoretical and experimental efforts are necessary. There are several pump-probe studies on the electron-spin relaxation in bulk CdTe, highlighting the role of photoexcited carrier density and excitation energy [27–29]. In the pump-probe studies the carriers mainly thermalize via emission of optical phonons and interactions with defects [27, 29, 30]. Although surface phonons in the group II-VI semiconductors have also been investigated [31], their role in photocarrier thermalization is still unknown. In perfect crystals the dominant mechanisms involved in hot-carrier scattering are electron-electron and electron-phonon interactions [3].

It is well established by means of ab-initio methods that the electron-phonon scattering plays a major role near the band edges [32–34]. We therefore focus on the electron-phonon scattering in this paper. In what follows we combine DFT with many-body perturbation theory to calculate band- and momentum-dependent electron-phonon scattering times over a range of temperatures. Furthermore we use the Boltzmann equation in the RTA to compute the thermalization time of photoexcited carriers with a given excess energy. Our approach highlights the effects of electron-phonon scattering, providing access to the microscopic details involved in photocarrier thermalization processes. We show that the thermalization process is qualitatively different, depending upon whether CdTe is bulk or 2D. The respective thermalization times differ by orders of magnitude and demonstrate a distinct behavior upon excess energy and temperature changes.

The paper is organized as follows. In Sec. II, we discuss the computational methods used to calculate electronic and phononic properties, electron-phonon scattering rates, and photocarrier thermalization times. In Sec. III, we explain the results obtained for bulk and monolayer CdTe. Finally, we conclude with a summary and an outlook in Sec. IV.

II. COMPUTATIONAL DETAILS

To calculate electronic and phononic structure information, we use ground-state DFT within the local density approximation (LDA) considering spin-orbit coupling and rely on the implementation in Quantum ESPRESSO [35]. We employ plane wave (PW) basis sets with a kinetic energy cutoff of 70 Ry, a charge density cutoff of 280 Ry, and Troullier-Martins pseudopotentials including a relativistic core correction that assume six valence electrons for both Cd and Te [36]. The dimensions of the unit cell and the atoms inside it are relaxed with the help of the Broyden-Fletcher-Goldfarb-Shanno algorithm for both bulk and monolayer CdTe until the net force on atoms is less than $10^{-6}$ Ry/a.u. and total energy changes are below $10^{-8}$ Ry. We separate CdTe monolayers in the out-of-plane direction through vacuum with a thickness of 18 Å to avoid spurious interlayer interactions. The electron density is calculated on a Γ-centered $k$ grid in the BZ containing $12 \times 12 \times 12$ points for bulk and $9 \times 12 \times 1$ points for monolayer CdTe. The phonon band structure is computed within density functional perturbation theory (DFPT) [37] on a Γ-centered $q$ grid of size $6 \times 6 \times 6$ for bulk and $9 \times 12 \times 1$ for monolayer CdTe.

Having determined electronic and phononic band structures, we evaluate the electronic self-energy $\Sigma_{nk}(T)$ in the lowest order of the electron-phonon interaction for a given electron band $n$, a wave vector $k$, and the temperature $T$ using the EPW code [38]. The self-energy is given as

$$
\Sigma_{nk}(T) = \sum_{m,p} \int_{BZ} \frac{d^3q}{\Omega_{BZ}} |g_{mn,p}(k, q)|^2 \left[ \frac{N_{\omega_{pq}}(T) + f_{m,k+q}^{(0)}(T)}{\epsilon_n - (\epsilon_{m,k+q} - \epsilon_p) + i\eta - \omega_{pq} V + i\eta} + \frac{N_{\omega_{pq}}(T) + 1 - f_{m,k+q}^{(0)}(T)}{\epsilon_n - (\epsilon_{m,k+q} - \epsilon_p) - \omega_{pq} V + i\eta} \right].
$$

(1)

Here, $\omega_{pq}$ is the phonon energy for the branch $p$ with the wave vector $q$, $\epsilon_p$ is the Fermi energy set to the middle of the gap for intrinsic semiconductors, $f_{m,k}^{(0)}(T)$ and $N_{\omega_{pq}}(T)$ are the Fermi-Dirac and Bose-Einstein distributions for electrons and phonons, respectively, $\Omega_{BZ}$ is the volume of the BZ, and $\eta = 20$ meV is a small broadening parameter. A key ingredient in Eq. (1) are the electron-phonon interaction matrix elements given by [38]

$$
g_{mn,p}(k, q) = \frac{1}{\sqrt{2\omega_{pq}}} \langle m\mathbf{k} + q | \partial_{pq} V | n\mathbf{k} \rangle,
$$

(2)

where $\partial_{pq} V$ characterizes changes of the Kohn-Sham potential for displacements of nuclei through the phonon mode $pq$. In other words, the matrix elements $g_{mn,p}(k, q)$ describe the electron scattering between the initial state $|n\mathbf{k}\rangle$ and the final state $|m\mathbf{k} + q\rangle$ mediated by the phonon $pq$. The first term in
Conversely, $\Im[\Sigma_{nk}(T)]$ describes phonon absorption by an electron, the second one phonon emission. To compute $\Sigma_{nk}(T)$, we interpolate electronic wavefunctions, eigenenergies and dynamical matrices on finer $k$ and $q$ grids using Wannier function (WF) techniques, as employed in the EPW code [38–40]. We find $k$ and $q$ grid sizes of $45 \times 45 \times 45$ for bulk and $300 \times 300 \times 1$ for the monolayer to be sufficient to converge the sum in Eq. (1).

We note that in our formalism the electron-phonon couplings are assumed to be small enough such that electronic wavefunctions, eigenenergies, and dynamical matrices are basically unchanged as compared to ground-state calculations. Also, anharmonic interatomic interactions, which lead to phonon-phonon interactions and may alter scattering rates and phonon frequencies, are disregarded for simplicity [38, 41]. We assume electron and phonon baths to be at the same temperature $T$. The electron-phonon scattering time can then be determined as

$$\tau_{nk}(T) = \frac{\hbar}{2\text{Im}[\Sigma_{nk}(T)]}. \quad (3)$$

Conversely, $\Im[\Sigma_{nk}(T)]$ is proportional to the electron-phonon scattering rate $1/\tau_{nk}(T)$ and is seen to be composed of contributions originating from phonon absorption and from phonon emission in Eq. (1).

We simulate photoexcited-carrier dynamics in bulk and monolayer CdTe using the Boltzmann equation in the RTA. The initial photoexcited-carrier distribution $f_{nk}(0,T)$ is modeled as the sum of a nonequilibrium Gaussian centered at the excess energy $\zeta$ ($-\zeta$) from the band edges for electrons (holes) and the equilibrium Fermi-Dirac distribution $f_{nk}^{(0)}(T)$ at the temperature $T$ as

$$f_{nk}(0,T) = f_{nk}^{(0)}(T) - \frac{\lambda_{0}}{\sqrt{2\pi}\sigma_{e}} e^{-\frac{(\epsilon_{nk}+\zeta)^2}{2\sigma^2}}, \quad \epsilon_{nk} < \epsilon_{F},$$

$$f_{nk}(0,T) = f_{nk}^{(0)}(T) + \frac{\lambda_{0}}{\sqrt{2\pi}\sigma_{h}} e^{-\frac{(\epsilon_{nk}-\zeta)^2}{2\sigma^2}}, \quad \epsilon_{nk} \geq \epsilon_{F}. \quad (4)$$

We choose a small energy broadening $\sigma = 8.47$ meV and take the different density of states (DOS) in the conduction and valence band into account by adjusting $\lambda_{e}$ and $\lambda_{h}$ to ensure identical concentrations of photoexcited electrons and holes at $\pm \zeta$ from the CBM and VBM, respectively.

The time evolution of the electronic occupation $f_{nk}(t,T)$ within the RTA is calculated separately for electrons and holes. It is given as

$$\frac{df_{nk}(t,T)}{dt} = -\frac{f_{nk}(t,T) - f_{nk}^{(0)}(T)}{\tau_{nk}(T)} \quad (5)$$

with the solution

$$f_{nk}(t,T) = f_{nk}^{(0)}(T) + e^{-\frac{1}{\tau_{nk}(T)}} \left[ f_{nk}(0,T) - f_{nk}^{(0)}(T) \right]. \quad (6)$$

Here, $f_{nk}^{(0)}(T)$ is the Fermi-Dirac distribution at $t \to \infty$ with the quasi-Fermi level corresponding to the same number of photoexcited carriers as at $t = 0$. Equation (6) is only valid for weak excitations, when RTA applies [42]. The intermediate relaxation steps are omitted within RTA, and the photoexcited carriers for a given $(n,k)$ relax directly to equilibrium with the rate $1/\tau_{nk}(T) \propto \Im[\Sigma_{nk}(T)].$

We define the thermalization time $\tau_{\text{th}}$ as

$$P(\zeta, t = \tau_{\text{th}}, T) = \frac{1}{e^\zeta} \quad (7)$$

with the population

$$P(E, t, T) = \sum_{nk} \delta(E - \epsilon_{nk}) \times \begin{cases} 1 - f_{nk}(t,T), & E < \epsilon_{F}, \\ f_{nk}(t,T), & E \geq \epsilon_{F}. \end{cases} \quad (8)$$

In our numerical calculations, we approximate the delta function in Eq. (8) by a narrow Gaussian with a width of 20 meV. We focus on excitations above the quasi-Fermi levels, so that the finite width does not affect $\tau_{\text{th}}.$

## III. Results

Bulk CdTe possesses the zinc blende structure with a relaxed lattice constant of $[a] = 6.42$ Å, see Fig. 1(a), and shows Cd-Te bonds of mixed covalent-ionic character with lengths of $2.87$ Å, in good agreement with experimental values [43]. All the facets except [110] exhibit a polar surface and are therefore unstable [44]. This is the reason, why we cleave CdTe along the [110] facet to obtain a stable monolayer. As shown in Fig. 1(b)-(c), the monolayer unit cell consists of 8 atoms: 4 Cd, 4 Te, and each Cd atom is bonded to three Te atoms and vice versa. Due to the energy optimization of the unit cell, exterior Cd atoms are pulled into the layer, resulting in a rippled surface. We find lattice parameters of monolayer CdTe to be

![Figure 2. Electronic band structure calculated using plane wave (PW) and Wannier function (WF) basis sets for (a) bulk and (b) monolayer CdTe. The corresponding DOS is shown in arbitrary units to the right of the band structure. Phononic band structure for (c) bulk and (d) monolayer CdTe.](image)
layer is two-fold degenerate, but the degeneracy is quickly down from the VBM by about 0.8 eV. The VBM of the mono-fold degenerate, and the spin-orbit split-off band is shifted modes with the highest longitudinal-optical mode energy of atoms in the unit cell, gives rise to 3 acoustical and 21 optical

determined by both carrier types. For electrons and holes, the electron-phonon scatter-
ing increases in efficiency at higher temperatures because the number of phonons increases, facilitating phonon absorption by both carrier types.

Figure 3(b) shows $\text{Im}[\Sigma_{nk}(T)]$ for monolayer CdTe. It keeps a constant value from 1.07 eV up to 1.5 eV and then abruptly increases due to the local minimum in the conduction band around the $Y$ point. In the case of holes, $\text{Im}[\Sigma_{nk}(T)]$ remains constant from $-1.07$ eV down to $-1.2$ eV and then also increases due to the second VBM at the $\Gamma$ point. The band structure becomes increasingly complex at higher excitation energies away from the band edges, and multiple extrema in the electronic band structure give rise to several peaks in $\text{Im}[\Sigma_{nk}(T)]$ for electrons and holes.

To analyze the photocarrier thermalization time, we set the reference level for the excess energy of hot holes and electrons to the valence and conduction band edges, respectively. Figure 4 shows the evolution of the hot-carrier population, start-

Figure 4. Temporal evolution of hole (left column) and electron (right column) populations, calculated separately using the Boltzmann equation in the RTA for (a)-(b) bulk and (c)-(d) monolayer CdTe at $T = 10$ K. The initial carrier excess energy, counted from the respective band edges, is 0.2 eV. Initial and final populations correspond to photocarrier densities of $10^{17}$ cm$^{-3}$ for bulk and of $10^{11}$ cm$^{-2}$ for monolayer CdTe. The color scale indicates the time evolution (red for early, blue for late times). Note that the Gaussian shape of the thermalized population is a consequence of our choice to represent the delta function in Eq. (8) by a Gaussian.

\[ |a| = 6.20 \text{ Å}, |b| = 4.48 \text{ Å}, \text{ and Cd-Te bond lengths to vary in the interval of 2.72 to 2.83 Å, in agreement with a previous DFT study of monolayer CdTe [45].} \]

Figure 2(a)-(b) shows the electronic band structures for bulk and monolayer CdTe along with the corresponding DOS. Both materials exhibit a direct bandgap with the VBM and CBM located in the center of the BZ, i.e. at the $\Gamma$ point. As visible in Fig. 2(a), the bulk valence band at the $\Gamma$ point is four-fold degenerate, and the spin-orbit split-off band is shifted down from the VBM by about 0.8 eV. The VBM of the monolayer is two-fold degenerate, but the degeneracy is quickly lifted away from the $\Gamma$ point, see Fig. 2(b). We construct WFs from the PW basis, and the excellent match between WF-interpolated and PW-derived band structures demonstrates the quality of the WFs. DFT in the LDA is not able to predict the bandgap values reliably, and more advanced methods are required for this purpose like DFT with hybrid exchange-correlation functionals or the GW approximation. We compute DFT bandgap values for bulk and monolayer CdTe of 0.18 and 1.2 eV, respectively. To correct the bandgaps, we perform a rigid shift of occupied and unoccupied electronic bands to match with the experimental value of 1.5 eV for bulk and with calculations using the Heyd–Scuseria–Ernzerhof (HSE) functional of 2.13 eV for monolayer CdTe [45, 46]. While the shift modifies the electronic gap sizes visible in Figs. 2(a)-(b) and 3, the temporal dynamics studied in Figs. 4 and 5 are not affected by this choice. Since the electronic bandgap is much larger than maximum phonon frequencies, see Fig. 2, electrons and holes thermalize separately in our model.

The phonon spectra of bulk CdTe are well studied, and our result in Fig. 2(c) matches well with the phonon band structure calculated previously [47]. Monolayer CdTe, featuring 8 atoms in the unit cell, gives rise to 3 acoustical and 21 optical modes with the highest longitudinal-optical mode energy of 23 meV reached between the $\Gamma$ and X points, see Fig. 2(d). This agrees with the DFT results of Ref. 45. Positive frequencies throughout the BZ ensure the dynamical stability of monolayer CdTe.

Figure 3(a) shows the imaginary part of the self-energy $\text{Im}[\Sigma_{nk}(T)]$ for bulk CdTe as a function of energy at different temperatures. The imaginary part of the electronic self-energy exhibits small values from 0.75 eV up to 1.75 eV because of the two-fold spin-degeneracy in the conduction band, preclud-

Figure 3. Imaginary part of the electron-phonon self-energy in Eq. (1) as a function of energy at different temperatures, and the carrier DOS for (a) bulk and (b) monolayer CdTe.
Figure 5. Thermalization time for holes (left column) and electrons (right column) as a function of temperature over a range of initial excess energies for (a)-(b) bulk and (c)-(d) monolayer CdTe.

IV. CONCLUSIONS AND OUTLOOK

We have studied the carrier thermalization in bulk and monolayer CdTe within a range of up to 0.8 eV away from the band edges. At low temperature, the photoexcited carriers in bulk CdTe thermalize on a 0.1–100 ps timescale, whereas in monolayer CdTe this process completes within 10–100 fs. Increased temperatures generally reduce the thermalization time. Our observations are consistent with the current understanding that reduced dimensionality leads to faster carrier thermalization [3]. The thermalization time also depends on the excitation energy and is, in general, substantially reduced, if the carriers are excited far away from the band edges. Our most unexpected observation is that the photoexcited electrons in monolayer CdTe comprise an exception from this rule: Their thermalization time does not depend on excess energy up to about 0.5 eV. We attribute the behavior to a parabolic conduction band that forms in the monolayer and whose band minimum is well separated from the other conduction bands.

Our discovery might help to exploit higher excess energies in CdTe-based optoelectronic and photovoltaic devices. Indeed, one of the promising strategies for increasing the amount of work done per absorbed photon is speeding up the photocarrier extraction into the external electrical circuit [4]. The carriers are then collected, while they are still hot or even out of thermal equilibrium. The saved excess energy can then be utilized for increasing the photovoltage. 2D materials might offer unprecedented opportunities along this path: Their thickness is so small that the photoexcited carriers could be extracted well before they thermalize and reach ambient temperature by means of phonon emission. The mechanism has recently been studied in a graphene-based van der Waals heterostructure [49]. However, the photocarrier thermalization time usually drops substantially with increasing excess energy, as one can see in Fig. 5(a)-(c). This is also true for other popular 2D semiconductors, including MoS$_2$ or WSe$_2$. Once the photocarrier thermalization becomes faster than the extraction, the excess energy is wasted as heat in terms of lattice vibrations, no matter how high it was initially. Our main result, shown in Fig. 5(d), thus suggests that monolayer CdTe could be used to circumvent this problem. Integrating a CdTe monolayer into a thin heterostructure might allow to extract a significant amount of photocarrier excess energy even though the extraction time may be rather long (hundreds of femtoseconds). Last but not least, CdTe is an established material in photovoltaic applications, offering a wide range of technological benefits such as low cost, commercial availability and scalability for streamline production. Our fundamental study could therefore be helpful for designing new optoelectronic components with improved efficiency in the near future.
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[1] J. Shah, *Hot Carriers in Semiconductor Nanostructures* (Academic Press, San Diego, 1992).
[2] P. Würfel, “Solar energy conversion with hot electrons from impact ionisation,” *Sol. Energy Mater. Sol. Cells* **46**, 43 (1997).
[3] B. K. Ridley, “Hot electrons in low-dimensional structures,” *Rep. Prog. Phys.* **54**, 169 (1991).
[4] W. A. Tisdale, K. J. Williams, B. A. Timp, D. J. Norris, E. S. Aydil, and X.-Y. Zhu, “Hot-electron transfer from semiconductor nanocrystals,” *Science* **328**, 1543 (2010).
[5] F. V. Wald, “Applications of CdTe: A review,” *Rev. Phys. Appl.* **12**, 277 (1977).
[6] J. Britt and C. Ferekides, “Thin-film CdS/CdTe solar cell with 15.8% efficiency,” *Appl. Phys. Lett.* **62**, 2851 (1993).
[7] M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, “Solar cell efficiency tables (version 48),” *Prog. Photovoltaics* **24**, 905 (2016).
[8] S. Ithurria, M. D. Tessier, B. Mahler, R. P. S. M. Lobo, B. Dubertret, and A. L. Efros, “Colloidal nanodetectors with two-dimensional electronic structure,” *Nat. Mater.* **10**, 936 (2011).
[9] R. B. Vasiliev, E. P. Lazareva, D. A. Karlova, A. V. Garshiev, Y. Yao, T. Kuroda, A. M. Gaskov, and K. Sakoda, “Spontaneous folding of CdTe nanosheets induced by ligand exchange,” *Chem. Mater.* **30**, 1710 (2018).
[10] J. S. Son, X.-D. Wen, J. Joo, J. Chae, S.-I. Baek, K. Park, J. H. Kim, K. An, J. H. Yu, S. G. Kwon, S.-H. Choi, Z. Wang, Y.-W. Kim, Y. Kuk, R. Hoffmann, and T. Hyeon, “Large-scale soft colloidal template synthesis of 1.4 nm thick CdSe nanosheets,” *Angew. Chem., Int. Ed. Engl.* **48**, 6861 (2009).
[11] P. Heeyeon, C. Haegeun, and K. Woong, “Synthesis of ultrathin wurtzite ZnSe nanosheets,” *Mater. Lett.* **99**, 172 (2013).
[12] H. Zheng, X.-B. Li, N.-K. Chen, S.-Y. Xie, W. Q. Tian, Y. Chen, H. Xia, S. B. Zhang, and H.-B. Sun, “Monolayer 2D-VI semiconductors: A first-principles prediction,” *Phys. Rev. B* **92**, 115307 (2015).
[13] J. Wang, J. Meng, Q. Li, and J. Yang, “Single-layer cadmium chalcogenides: promising visible-light driven photocatalysts for water splitting,” *Phys. Chem. Chem. Phys.* **18**, 17029 (2016).
[14] E. Unsal, R. T. Senger, and H. Sahin, “Stable monolayer α-phase of CdTe: strain-dependent properties,” *J. Mater. Chem. C* **5**, 12249 (2017).
[15] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films,” *Science* **306**, 666 (2004).
[16] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, “Atomically thin MoS 2 : A new direct-gap semiconductor,” *Phys. Rev. Lett.* **105**, 136805 (2010).
[17] M. Osada and T. Sasaki, “Two-dimensional dielectric nanosheets: Novel nanoelectronics from nanocrystal building blocks,” *Adv. Mater.* **24**, 210 (2012).
[18] E. Bianco, S. Butler, S. Jiang, O. D. Restrepo, W. Windl, and J. E. Goldberger, “Stability and exfoliation of germanane: A germanium graphene analogue,” *ACS Nano* **7**, 4414 (2013).
[19] H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek, and P. D. Ye, “Phosphorene: An unexplored 2d semiconductor with a high hole mobility,” *ACS Nano* **8**, 4033 (2014).
[20] G. Eda, H. Yamaguchi, D. Voiry, T. Fujita, M. Chen, and M. Chhowalla, “Photoluminescence from chemically exfoliated MoS 2 ,” *Nano Lett.* **11**, 5111 (2011).
[21] A. Budweg, D. Yadav, A. Grupp, A. Leitenstorfer, M. Trushin, F. Pauly, and D. Brida, “Control of excitonic absorption by thickness variation in few-layer gase,” *Phys. Rev. B* **100**, 045404 (2019).
[22] Q. H. Wang, X. Karant-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, “Electronics and optoelectronics of two-dimensional transition metal dichalcogenides,” *Nat. Nanotechnol.* **7**, 699 (2012).
[23] F. Bonaccorzo, Z. Sun, T. Hasan, and A. C. Ferrari, “Graphene photonics and optoelectronics,” *Nat. Photonics* **4**, 611 (2010).
[24] X. Li, D. Xie, H. Park, M. Zhu, T. H. Zeng, K. Wang, J. Wei, D. Wu, J. Kong, and H. Zhu, “Ion doping of graphene for high-efficiency heterojunction solar cells,” *Nanoscale* **5**, 1945 (2013).
[25] M. Bernardi, M. Palummo, and J. C. Grossman, “Extraordinary sunlight absorption and one nanometer thick photovoltaics using two-dimensional monolayer materials,” *Nano Lett.* **13**, 3664 (2013).
[26] M. Shanmugam, C. A. Durcan, and B. Yu, “Layered semiconductor molybdenum disulfide nanomembrane based Schottky-barrier solar cells,” *Nanoscale* **4**, 7399 (2012).
[27] H. Ma, Z. Jin, G. Ma, W. Liu, and S. H. Tang, “Photon energy and carrier density dependence of spin dynamics in bulk CdTe crystal at room temperature,” *Appl. Phys. Lett.* **94**, 241112 (2009).
[28] P. Nahálová, P. Němec, D. Sprinzl, E. Belas, P. Horodysky, J. Franc, P. Hliden, and P. Malý, “Spin dynamics in bulk CdTe at room temperature,” *Mater. Sci. Eng., B* **126**, 143 (2006).
[29] H. Ma and J. Leng, “Ultrafast electron spin dynamics in bulk CdTe investigated by femtosecond pump-probe reflection spectroscopy,” *Phys. Lett. A* **377**, 1974 (2013).
[30] X. He, N. Punpongjaroen, C. Wu, I. A. Davydov, and D.-S. Yang, “Ultrafast carrier dynamics of CdTe: Surface effects,” *J. Phys. Chem. C* **120**, 9350 (2016).
[31] H. M. Tütüncü, R. Miotto, and G. P. Srivastava, “Phonons on II-VI (110) semiconductor surfaces,” *Phys. Rev. B* **62**, 15797 (2000).
[32] C. J. Ciccarino, T. Christensen, R. Sundaraman, and P. Narang, “Dynamics and spin-valley locking effects in monolayer transition metal dichalcogenides,” *Nano Lett.* **18**, 5709 (2018).
[33] M. Bernardi, D. Vigil-Fowler, L. Lischner, J. B. Neaton, and S. G. Louie, “Ab-Initio study of hot carriers in the first picosec-
ond after sunlight absorption in silicon,” Phys. Rev. Lett. 112, 257402 (2014).

[34] M. Bernardi, D. Vigil-Fowler, C. S. Ong, J. B. Neaton, and S. G. Louie, “Ab-initio study of hot electrons in GaAs,” Proc. Natl. Acad. Sci. 112, 5291 (2015).

[35] P. Giannozzi, S. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, “QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials,” J. Phys.: Condens. Matter 21, 395502 (2009).

[36] N. Troullier and J. L. Martins, “Efficient pseudopotentials for plane-wave calculations,” Phys. Rev. B 43, 1993 (1991).

[37] S. Baroni, S. de Gironcoli, A. D. Corso, and P. Giannozzi, “Phonons and related crystal properties from density-functional perturbation theory,” Rev. Mod. Phys. 73, 515 (2001).

[38] S. Ponce, E. R. Margine, C. Verdi, and F. Giustino, “EPW: Electron-phonon coupling, transport and superconducting properties using maximally localized Wannier functions,” Comput. Phys. Commun. 209, 116 (2016).

[39] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, “An updated version of Wannier90: A tool for obtaining maximally-localised Wannier functions,” Comput. Phys. Commun. 185, 2309 (2014).

[40] N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, “Maximally localized Wannier functions: Theory and applications,” Rev. Mod. Phys. 84, 1419 (2012).

[41] F. Giustino, “Electron-phonon interactions from first principles,” Rev. Mod. Phys. 89, 015003 (2017).

[42] M. Lundstrom, Fundamentals of carrier transport, 2nd ed. (Cambridge University Press, Cambridge, 2000).

[43] R. J. Nelmes and M. I. McMahon, Semiconductors and Semimetals, Vol. 54 (Academic Press, San Diego, 1998) pp. 145–246.

[44] Y. Sun, Z. Sun, S. Gao, H. Cheng, Q. Liu, J. Piao, T. Yao, C. Wu, S. Hu, S. Wei, and Y. Xie, “Fabrication of flexible and freestanding zinc chalcogenide single layers,” Nat. Commun. 3, 1057 (2012).

[45] F. Iyikanet, B. Akbali, J. Kang, T. Senger, Y. Selamet, and H. Sahin, “Stable ultra-thin CdTe crystal: A robust direct gap semiconductor,” J. Phys.: Condens. Matter 29, 485302 (2017).

[46] S. Lalitha, S. Zh. Karazhanov, P. Ravindran, S. Senthilarasu, R. Sathyamoorthy, and J. Janabergenov, “Electronic structure, structural and optical properties of thermally evaporated CdTe thin films,” Phys. B (Amsterdam, Neth.) 387, 227 (2007).

[47] A. D. Corso, S. Baroni, R. Resta, and S. de Gironcoli, “Ab-initio calculation of phonon dispersions in II-VI semiconductors,” Phys. Rev. B 47, 3588 (1993).

[48] P. Ščajev, S. Miasojedovas, A. Mekys, D. Kuciauskas, K. G. Lynn, S. K. Swain, and K. Jarašiūnas, “Excitation-dependent carrier lifetime and diffusion length in bulk CdTe determined by time-resolved optical pump-probe techniques,” J. Appl. Phys. 123, 025704 (2018).

[49] Q. Ma, T. I. Andersen, N. L. Nair, N. M. Gabor, M. Massicotte, C. H. Lui, A. F. Young, W. Fang, K. Watanabe, T. Taniguchi, J. Kong, N. Gedik, F. H. L. Koppens, and P. Jarillo-Herrero, “Tuning ultrafast electron thermalization pathways in a van der Waals heterostructure,” Nat. Phys. 12, 455 (2016).