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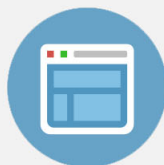
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Motivated by controversies over the identification of high frequency local vibrational modes (LMV) in CdSe doped with oxygen [G. Chen, J. S. Bhosale, I. Miotkowski, and A. K. Ramdas, Phys. Rev. Lett. **101**, 195502 (2008)], we have studied the LVM of complexes involving interstitial and substitutional O_2, H_2, and H_2O molecules in CdSe by first-principle calculations. We found that our theoretical results can account for, both quantitative and qualitatively, the unusual LVM reported by the Purdue group in oxygen doped CdSe. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4831938]

I. INTRODUCTION

CdTe and CdSe are common semiconductors used extensively in fabricating thin film solar cells.[1–3] In addition, Cd compounds have attracted attention as room temperature nuclear particle detectors.[4] Oxygen and related defects are likely to appear in both chalcogenides either during the growth stage or later in the treatment and finishing stage due to oxidization by air. Since oxygen has the same valence as Te and Se, substitutional oxygen is an isovalent impurity in chalcogenides. The non-destructive detection of these defects, especially after device fabrication, is highly desirable. Infrared absorption spectroscopy in which oxygen produces extremely sharp local vibrational modes (LVM) is one such method. The group at Purdue University has reported the LVM of oxygen in both CdTe and CdSe bulk crystals doped with oxygen.[5–7] In addition to LVM due to substitutional oxygen (O_{Te}), they also found LVMs with very high frequencies in the range of $>1000 \, cm^{-1}$.[5] In CdSe doped with oxygen (abbreviated as CdSe:O), they observed LVM with frequencies even higher than 2000 cm^{-1}.[6] The authors have assigned these high frequency modes to vibrations of complexes consisting of either O_{Te} next to a Cd vacancy (V_{Cd}) or, in case of the modes above 2000 cm^{-1}, to an "anti-site" defect: O_{Cd}. The unusually high frequencies of these LVM have stirred up controversies in the literature concerning their interpretation. Several groups[8,9] have questioned the interpretations of the Purdue group based on *ab initio* calculations of the frequencies of oxygen induced LVM in both CdTe and CdSe. One group[8,10] suggested that the $>2000 \, cm^{-1}$ high frequency modes are produced by hydrogen impurities in the samples. In response to this criticism, Chen *et al*.[7] argue that their samples were very pure and free of hydrogen contamination. Recently, Bastin *et al*.[11] have grown CdSe under exposure to both hydrogen and deuterium. These authors observed in their samples the $>2000 \, cm^{-1}$ high frequency modes reported by Chen

et al. The isotope induced shift of these modes proved conclusively that the $>2000 \, cm^{-1}$ high frequency modes in CdSe are produced by H-Se vibration. However, this identification still leaves unresolved the identification of the $\sim1100 \, cm^{-1}$ LVM in CdSe. In our previous publications,[9] we have applied *ab initio* calculations to study the vibrational frequencies and symmetries of LVM due to complexes containing oxygen molecules trapped in V_{Cd} in CdTe:O. With our model, we have not only been able to explain quantitatively the high frequencies of these modes but also qualitatively their symmetry and temperature dependence. In the present paper, we have applied our *ab initio* calculations to study oxygen and water molecules complexes in CdSe:O. With our model, we have also been able to explain quantitatively all the experimental results on the LVMs in CdSe. In particular, we have found that O_2 molecules can exist in CdSe in interstitial sites with much lower formation energy than in Cd vacancies.

The organization of this paper is as follows. In Sec. II, we will describe our theoretical approach and models. This will be followed by a description of our computation results and then by a discussion of how these results provide a framework for explaining the experimental results of the Purdue group. In the last section, we present our conclusions.

II. TECHNIQUES

We have applied first-principles density functional theory (DFT) to compute the total electronic energies of CdSe supercells without any defects or impurities. The computation was performed by means of two commercial softwares: VASP[12,13] and MedeA.[14] A 128-atom supercell consisting of Cd and Se atoms only is constructed by MedeA. The interactions between ions, electrons and each other are treated by the projector-augmented wave (PAW) method as implemented by VASP. The density functional

we chose was based on the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[15,16] Spin-orbit interaction was neglected since it was expected to have a small effect on the high frequency vibrational modes of interest to this paper. The plane wave cutoff energy was set to be $> 460\,\text{eV}$. The spacing between the reciprocal space vectors (**k** points) was set to be $< 2\,\text{nm}^{-1}$ in all calculations. The **k**-mesh was set to $5 \times 5 \times 5$. The calculation explored the full Brillouin zone and included an interaction range of about 1 nm. The atoms were displaced by ± 0.001 nm to determine the restoring forces for the phonon frequency calculations. As a test of these programs, we calculated the electronic band structure and phonon dispersion of pure CdSe. The lattice was allowed to relax fully and the calculated lattice constant of CdSe was found to agree with the experimental value within 1% and the band gap agrees with theoretical values obtained by similar DFT theory calculations reported previously in the literature. The phonon dispersion and density-of-states of pure CdSe were found to agree well with the experimental and theoretical results in the literature.[17,18] Our approach is essentially the same as in our previous report on the phonon frequencies of pure CdTe and of oxygen molecules in CdTe.[9,19] The same technique is now applied to the calculation of phonon modes of oxygen and water molecule related complexes in CdSe.

In calculating the LVM's involving defect complexes, a Cd or Se atom is removed from the supercell to create a vacancy. Afterwards, various oxygen containing molecules are added to these vacancies to create molecular complexes containing oxygen. The resulting supercells are allowed to relax unless stated otherwise. The symmetry of the relaxed structure is determined by MedeA. Although the concentration of defect complexes in our models is typically many orders of magnitude higher than in experimental samples, there is very little interaction between the LVM's due to their highly localized nature. The phonon frequencies are calculated by freezing the motions of all host atoms while allowing only the impurity atoms to move. The previously reported frequencies of oxygen LVM in CdTe have shown that this "frozen host atom approximation" is capable of reproducing quantitatively the experimental LVM frequencies for CdTe.[9]

In the experiment reported by the Purdue group, the samples were grown under different conditions to either promote or suppress vacancies.[6] As a result, it is likely that Cd vacancies are present in some of their samples. In fact, the authors have attributed the very high frequency modes (following their notation these modes will be referred to as the μ modes) observed in samples, where Se was added to suppress Se vacancies, to an oxygen located inside a V_{Cd} (or O_{Cd}). As pointed out by T-Thienprasert *et al.*[10] the theoretical frequencies of the LVM's of O_{Cd} (in the neutral state) are only 417 and 502 cm^{-1}, far below the experimental values. In samples, where there were additional large amount of Se to promote V_{Cd}, the Purdue group observed LVM's around 1100 cm^{-1} (these modes will be referred to as the γ modes). These γ modes were identified as vibrational modes of O_{Se}-V_{Cd} complexes. Again the identification of these modes was challenged by T-Thienprasert *et al.*[10] who showed that the theoretical values of the LVM's of this complex varies from 201 to 495 cm^{-1}.

To explain the different behavior of oxygen in CdSe as compared to CdTe, we note that they have different crystal structures. While the lattice constant of CdTe is larger than that of CdSe, the atomic planes in the latter are stacked along the c-axis of the wurtzite structure in the ABAB sequence (described as "staggered" in the literature) as shown in Fig. 3.14 of Ref. 20. Within each atomic plane the cations or anions form a hexagonal lattice. In this structure, a linear O_2 molecule can be inserted easily into the interstitial hexagonal channels in the lattice. After the starting structure has been optimized with respect to the total energy, the O_2 molecule is found to be located at the center of a hexagonal channel with its molecular axis aligned along the c-axis as shown in Fig. 1(a). As in the case of CdTe, we found that the VASP binding energy of two oxygen atoms to form a O_2 molecule in CdSe is very large ($\sim -8.8\,\text{eV}$) so it is likely that O atoms will form O_2 molecules when they can be accommodated within the lattice either at vacancies or at interstitial sites. We have, therefore, explored several possible supercell configurations containing different oxygen molecules complexes. To test the convergence of our results, we have performed calculations using supercells of increasing sizes: $Cd_{16}Se_{16}$, $Cd_{32}Se_{32}$ and $Cd_{64}Se_{64}$. From the formation energy of Cd vacancies calculated with these supercells, we
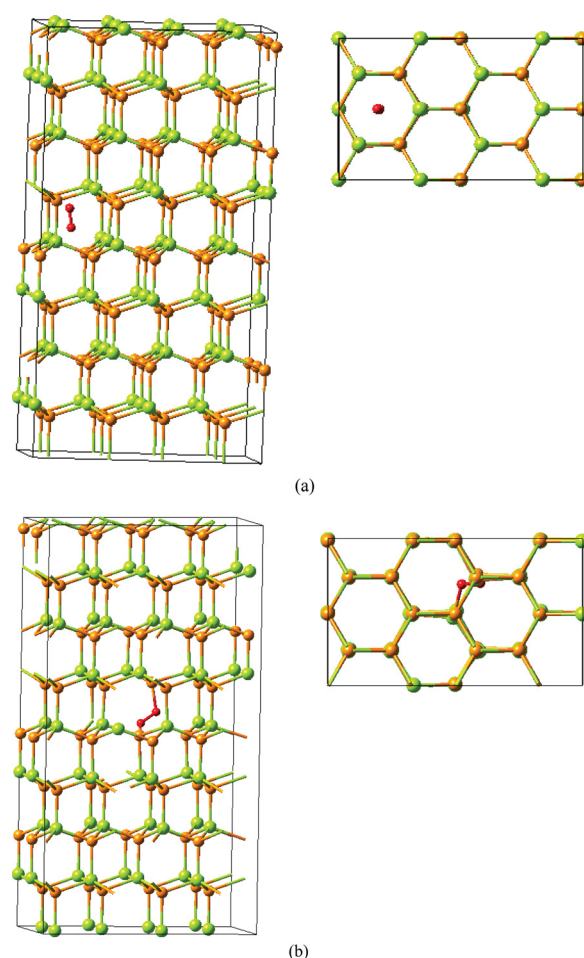

FIG. 1. The top and side view of optimized structures of oxygen molecule complexes in CdSe. (a) $Cd_{64}Se_{64}O_2$, (b) $Cd_{63}Se_{64}O_2$, Green balls represent Cd atoms while the gold balls represent Se atoms. Oxygen atoms are represented by red balls.

conclude that our computed results have converged to the bulk values within 10%.

III. MODELS AND RESULTS

In this section, we present the results of our calculations for various defect complexes in CdSe containing oxygen.

A. $Cd_{64}Se_{64}:O_2$ with O_2 at interstitial sites

The schematic structure of this defect is shown in Fig. 1(a). The formation energy of this interstitial oxygen molecule was computed to be 0.343 eV. This low formation energy shows that even without Cd vacancies O_2 molecules can be easily incorporated into interstitial sites in the wurtzite lattice. In contrast, interstitial O_2 molecule was found to be *unstable* in CdTe *without* V_{Cd}. Even in the presence of V_{Cd} the formation energy of the O_2-V_{Cd} complex in CdTe was much higher at 1.2 eV. This larger difference in formation energies of oxygen molecules inside CdTe and CdSe explains some of the differences between the IR absorption spectra of their respective oxygen doped samples. The O-O bond length of the interstitial oxygen molecule in CdSe is listed in Table I. For comparison, the O-O bond length in O_2 molecules in free space calculated with our program is also listed. From Table I, we see that the bond length is increased for O_2 molecules located inside CdSe as was found in CdTe. In CdTe, the bond length of the O_2 molecule located inside a V_{Cd} is 0.130 nm and is quite close to the bond length of the interstitial O_2 molecule in CdSe at 0.1307 nm. On the other hand, the corresponding bond length of the O_2 molecule inside the Cd vacancy in CdSe is much larger at 0.1358 nm as shown also in Table I. This result suggests that the screening of bond charges in the oxygen molecules by valence electrons in CdTe with a Cd vacancy is quite similar to that of CdSe in interstitial sites. Not too surprisingly, we found that the O-O stretching mode frequency in the two cases are also quite similar. In CdTe containing a V_{Cd} the calculated A_1 symmetry mode frequency was found to be: 1112.5 cm^{-1}.[19] The corresponding calculated value of the A_1 stretching mode (vibration along the c-axis) frequency of interstitial O_2 molecule in CdSe is: 1133.2 cm^{-1}. We note that this frequency is very close to one of the experimentally observed LMV (γ_3 for light polarized parallel to the c-axis) with a vibration frequency of 1126.33 cm^{-1}.[6] The charge difference between the two oxygen atoms is about 0.02 e in case of CdSe. This charge difference is more than a factor of 2 smaller than the value of 0.05 e found in CdTe. This difference is caused by the difference in location of the O_2

molecule in the two materials. In case of CdTe the O_2 molecule is located along a Cd-Te bond, while the O_2 molecule is interstitial in CdSe. Hence, the stretching mode of the interstitial O_2 molecule in CdSe is infrared-active for light polarized parallel to the c-axis. In case of CdTe, we have shown previously that the O_2 molecule can be oriented along one of the Cd-Te bonds or perpendicular to these bonds.[19] At low temperature, the vibrational frequencies of the O_2 molecule are different for these two orientations. However, at higher temperatures, the vibrational mode of the O_2 molecule can be excited causing the two O_2 molecule vibrational modes to merge into one single mode with the T_d symmetry.

B. $Cd_{63}Se_{64}:O_2$ with a O_2-V_{Cd} complex

In case of both CdTe and CdSe, the Purdue group has grown their samples under conditions which promote the production of Cd vacancies. However, in case of CdSe, we have found that the LVM of interstitial O_2 molecules can already explain their γ-modes. This result raises the question: what happens to the O_2 molecules in CdSe when V_{Cd} is present and why are their LVM's not observed experimentally. The answer to this question lies in the formation energy of the V_{Cd}-O_2 complex in CdSe. We found that its formation energy at 2.34 eV is significantly higher than that of interstitial O_2 molecule. Most of this formation energy is associated with the formation of the Cd vacancy. With our program we have found that the formation energy of Cd vacancy in CdSe is 3.41 eV. Wei *et al.* have computed the formation energies of neutral Cd vacancy in CdTe and in wurtzite CdS and obtained the values of 2.1 and 4.1 eV, respectively. The high formation energy of the V_{Cd} in CdSe relative to that of CdTe on one hand and the smaller formation energy of interstitial O_2 molecule in CdSe on the other hand explains the different behaviors of oxygen dopants in CdSe and CdTe. The structure of the O_2-V_{Cd} complex after relaxation is shown in Fig. 1(b), while the corresponding O-O bond length is listed in Table I. We note that the bond length of the substitutional O_2 molecule in CdSe is significantly increased when compared to the interstitial oxygen molecule. As a result of this larger bond length, the frequency of the O-O stretching mode decreases to 811 cm^{-1}. Furthermore, the charge difference between the two O atoms decreases by a factor of 2 to become only 0.01 e. This charge difference is about the size of the error bar in our calculation indicating that this substitutional O_2 molecule, even when it exists, is probably not IR active. Thus, it should be very difficult to observe the O_2 molecule located inside a Cd vacancy in CdSe by IR absorption.

C. $Cd_{64}Se_{63}:H_2$

Zhang *et al.*[8] noted that the very high frequencies of the μ_1 and μ_2 modes suggest a very light atom, such as hydrogen, is involved in the vibration. From their first-principle DFT calculation, they found that the vibrational frequencies of H bonded to Se inside a Cd vacancy are 2092 cm^{-1} and 2101 cm^{-1}, respectively, for the non-axial and axial H-Se bonds. These frequencies are higher than the experimental values of the μ-modes by about 100 cm^{-1}. Furthermore, the

TABLE I. The calculated oxygen molecule bond length and their vibrational frequencies inside CdSe. The corresponding bond length and frequency of a free oxygen molecule is given for comparion.

Structure	Oxygen bond length (in units of 0.1 nm)	Phonon frequency in THz (in 1000 cm^{-1} inside parenthesis)
O_2 Molecule in free space	1.251	46.414 (1.5482)
$Cd_{64}Se_{64}O_2$	1.307	33.972 (1.1332)
$Cd_{63}Se_{64}O_2$	1.358	24.338 (0.81182)

TABLE II. Calculated bond lengths and vibrational frequencies of the H-Se bonds when H_2 passivates a Cd vacancy in CdSe.

Structure	Axial H-Se bond length (0.1 nm)	Non-axial H-Se bond length (0.1 nm)	Frequency of H-Se stretch in mode in THz (or cm^{-1})
One H-Se bond is axial	1.491	1.490	67.434 (2248,‖c-axis) 67.536 (2251, Perpendicular to c-axis)
Both H-Se bonds are non-axial		1.490	58.576 (1953)
			63.208 (2107)

experimental axial mode (corresponding to E‖c) has a lower frequency rather than the other way around. With our software and approximations, we have obtained the axial and non-axial modes frequencies as: 2248 and 2251 cm^{-1}, respectively. Thus our results (summarized in Table II) are qualitatively similar to those of Zhang *et al.* although our vibrational frequencies are higher than their values by about 150 cm^{-1}. The H-Se bond lengths in the two H-Se bonds are both 0.149 nm, but the distance between the two H atoms is much larger at 0.256 nm. These results suggest that inside CdSe, the H_2 molecule will dissociate into two H atoms to passivate the Se dangling bonds. This dissociation explains the experimental observation that in substituting H_2 with a HD mixture, there is no evidence of the existence of a HSe-DSe complex.[11] We have also computed the formation energy when both H-Se bonds are non-axial. The formation energy of this complex is smaller, by about 4 meV, than that of the complex in which one H-Se is axial and one non-axial. Since this difference is within our error bar we cannot draw any conclusion concerning the stability of the two complexes from our calculation. The computed LVM frequencies for the two non-axial H-Se complex are shown in Table II. These results are substantially different from the experimental observations. This suggests that the non-axial H-Se complex is not energetically favorable.

D. Vibration of Cd$_{64}$Se$_{63}$:H$_2$O (H$_2$O molecule substituting for Se)

The Purdue group has pointed that they have paid special attention to the purity of source materials and that contamination by hydrogen molecule is very unlikely.[7] We agree that contamination in the form of H_2 is probably very unlikely given the high temperature growth environment. However, contamination by hydrogen in the form of H_2O is possible given the ubiquitous nature of moisture. To explore

TABLE III. Calculated bond lengths and vibrational frequencies of the Water Molecule both as an isolated molecule and when located inside a Selenium Vacancy or Cadmium Vacancy in CdSe.

Structure	H-O Bond length (0.1 nm)	H-O-H Bond angle (°)	Frequency of OH Stretch in THz (or cm^{-1})
Isolated H_2O molecule	0.973	104.5	114.344 (3811)
			110.891 (3696)
H_2O molecule in V_{Se}	0.986, 1.016	103.7	85.703 (2857)
			67.355 (2245)
H_2O molecule in V_{Cd}	1.056, 1.057	104.2	66.401 (2213)
			69.876 (2329)

this possibility, we first calculate the bond lengths and vibrational frequencies of an isolated H_2O molecule. Our results are summarized in Table III. We notice that for a free water molecule, the two OH bonds are, in principle, identical and, therefore, the OH bond stretching mode is doubly degenerate. In our $T = 0$ K calculation, a slight asymmetry is produced in the two modes because the water crystallizes into ice at low temperature. The calculated frequencies are very high and consistent with the experimental frequencies of the OH stretching mode reported in the literature at low T. We consider next the model in which a water molecule is located inside a Se vacancy in CdSe. The calculated OH vibration frequencies are shown in Table III and are substantially higher than the experimental LMV frequencies. In addition, we find that the displacement of Cd atoms surrounding the Se vacancy lowers the symmetry of the water molecule environment. As a result, the frequencies of the two OH stretching modes in the water molecule differ by as much as 600 cm^{-1}. Figures 2(a) and 2(b) show the schematic location of the water molecule inside the Se vacancy.

E. Vibration of Cd$_{63}$Se$_{64}$:H$_2$O (H$_2$O molecule substituting for Cd)

Finally, we consider the possibility that the water molecule is located inside a Cd vacancy rather than in Se vacancy, since the Purdue group observed the μ-modes only in samples grown under conditions favorable for the formation of Cd vacancies. In these samples, they found that the environment of the complex responsible for the μ-modes is the same as Cd. The frequencies of the OH stretching modes when the water molecule is located inside the Cd vacancy are shown in Table III. The agreement between our results and the experimentally observed LVM frequency is improved. Furthermore, the difference in the frequencies of the two stretching modes is significantly reduced. However, the difference between these calculated mode frequencies and the experimental value is still much larger than that for the H-Se stretching modes.

IV. DISCUSSIONS

The Purdue group has, however, found that when Cd vacancies are introduced during growth, very high frequency (>1000 cm^{-1}) LVM are produced in both CdTe and CdSe. Some of the modes in these two chalcogenides exhibit considerable similarities. For example, both kinds of samples exhibit high frequencies modes around 1100 cm^{-1}. This has led the Purdue group to identify these modes as due to the vibrations of V_{Cd}-O complexes. But they also found
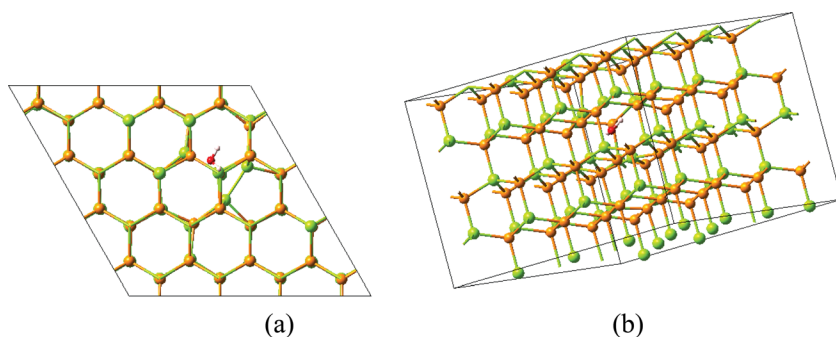
FIG. 2. Schematic plots of the water molecule inside a Se vacancy in CdSe. (a) top view along the c-axis and (b) a slightly tilted side view. Green balls represent Cd atoms while the gold balls represent Se atoms. Oxygen and hydrogen atoms are represented, respectively, by red and white balls.

significant differences between the two chalcogenides. For example, in CdSe grown under conditions favoring the introduction of V_{Cd} they observe LVM modes with frequencies above $2000\,cm^{-1}$. The Purdue group proposed that these very high frequency LVMs are due to oxygen replacing Cd in CdSe. However, they were not able to explain *quantitatively* the very high frequencies of these local modes. Based on our first-principle calculation, we have now found that the LVM with frequencies around $1100\ cm^{-1}$ in both chalcogenides are due to vibration of O_2 molecules. The difference in behavior between CdTe and CdSe comes from the formation energy of the substitutional O_2 molecule in the two materials. The high formation energy of the Cd vacancy in CdSe makes substitutional O_2 molecule unlikely in CdSe. However, it is possible to accommodate the O_2 molecules in *interstitial* sites in the wurtzite structure with quite low formation energy. As a result the O_2 molecules can be introduced into CdSe even under growth conditions not favoring Cd vacancies. When CdSe is grown under conditions favorable for Cd vacancies, the resultant vacancies turn out to be passivated by hydrogen as demonstrated convincingly by the recent work of Bastin *et al.*[11] The source of this hydrogen contamination is controversial. According to the Purdue group, they have taken all the necessary precautions to avoid contamination. Since hydrogen is highly explosive it is unlikely that the Purdue group will keep a source of hydrogen near their growth furnace. We suggest that the source of the hydrogen contamination may come from water vapor instead since water is much more common than hydrogen in the everyday environment. However, we have found that the calculated OH vibrational frequencies of substitutional water molecules in CdSe, whether replacing Cd or Se, are too high to explain the experimental results. We propose that the water molecules probably dissociate into hydrogen and oxygen inside CdSe under the high temperature crystal growth environment. We have computed the formation energy of the hydroden passivated Cd vacancy in CdSe and found it to be rather low at $1.76\,eV$. On the other hand, the formation energy of the Cd vacancy containing a H_2O molecule in CdSe is much higher at $3.12\,eV$. When these formation energies are compared with the value of $3.41\,eV$ for the Cd vacancy, it is clear that hydrogen passivated Cd vacancy will be the dominant defect in CdSe when Cd vacancies coexist with water molecules. This proposal is supported by the good quantitative agreement between the computed vibrational frequencies of the H-Se bonds in CdSe and the experimentally observed frequencies of the μ-modes. The fact that

our computed frequencies of the H-Se bonds is higher than both the theoretical results of Zhang *et al.* and the experimental results is presumably due to our "frozen host atom approximation."

V. CONCLUSIONS

Using first-principle DFT calculations, we have explained both quantitatively and qualitatively the origin of the high frequency LVMs reported in CdSe by the Purdue group. When a high concentration of oxygen is introduced into CdSe, the oxygen form molecules in interstitial sites at the center of hexagons in the wurtzite lattice. When large amount of Cd vacancies are introduced together with oxygen during growth, these vacancies are passivated by hydrogen as demonstrated by recent isotope doping experiments. We have proposed that the source of hydrogen is due to the dissociation of water molecules introduced into CdSe as contamination during growth.

ACKNOWLEDGMENTS

[1]M. A. Green, K. Emery, Y. Hishikawa, W. Warta, and E. D. Dunlop, Prog. Photovoltaics **19**, 565 (2011).
[2]M. A. Green, J. Mater. Sci.: Mater. Electron. **18**, S15 (2007).
[3]M. Korkusinski, O. Voznyy, and P. Hawrylak, Phys. Rev. B **82**, 245304 (2010).
[4]A. Owens, J. Synchrotron Radiat. **13**, 143 (2006); A. Owens and A. Peacock, Nucl. Instrum. Methods Phys. Res. A **531**, 18 (2004).
[5]G. Chen, I. Miotkowski, S. Rodriguez, and A. K. Ramdas, Phys. Rev. B **75**, 125204 (2007).
[6]G. Chen, J. S. Bhosale, I. Miotkowski, and A. K. Ramdas, Phys. Rev. Lett. **101**, 195502 (2008).
[7]G. Chen, J. S. Bhosale, I. Miotkowski, and A. K. Ramdas, Phys. Rev. Lett. **102**, 209602 (2009).
[8]L. Zhang, J. T-Thienprasert, M. H. Du, D. J. Singh, and S. Limpijumnong, Phys. Rev. Lett. **102**, 209601 (2009).

[9]W. Cheng, L. Liu, P. Y. Yu, Z. X. Ma, and S. S. Mao, Ann. Phys. (Berlin) **523**, 129 (2011).

[10]J. T-Thienprasert, S. Limpijumnong, M. H. Du, and D. J. Singh, Physica B **407**, 2841 (2012).

[11]D. Bastin, E. V. Lavrov, and J. Weber, Phys. Rev. B **85**, 195204 (2012).

[12]P. E. Blochl, Phys. Rev. B **50**, 17953 (1994).

[13]G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[14]MedeA is a trade mark of materials design.

[15]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[16]J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **78**, 1396 (1997).

[17]A. Debernardi, N. M. Pyka, A. Göbel, T. Ruf, R. Lauck, S. Kramp, and M. Cardona, Solid State Commun. **103**, 297 (1997).

[18]F. Widulle, S. Kramp, N. M. Pyka, A. Göbel, T. Ruf, A. Debernardi, R. Lauck, and M. Cardona, Physica B **263–264**, 448 (1999).

[19]W. Cheng, L. Liu, P. Y. Yu, Z. X. Ma, and S. S. Mao, AIP Conf. Proc. **1399**, 85 (2011).

[20]P. Y. Yu and M. Cardona, *Fundamental of Semiconductors: Physics and Materials Properties*, 4th ed. (Springer-Verlag, Berlin, 2010).