PHYSICAL REVIEW B **78**, 172105 (2008)

Bismuth-induced deep levels and carrier compensation in CdTe

Mao-Hua Du
Materials Science and Technology Division and Center for Radiation Detection Materials and Systems, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

(Received 8 September 2008; published 12 November 2008)

First-principles calculations show that Bi on Cd site in CdTe can be either a donor $\mathrm{Bi}_{\mathrm{Cd}}^{+}$ or an acceptor $\mathrm{Bi}_{\mathrm{Cd}}^{-}$, depending on the Fermi level. The $\mathrm{Bi}_{\mathrm{Cd}}^{-}$ can bind a substitutional O (O_{Te}) with large binding energy of 1.40 eV. The calculated (0/−) transition level for $\mathrm{Bi}_{\mathrm{Cd}}^{-}$-$\mathrm{O}_{\mathrm{Te}}$ complex is in good agreement with experimentally observed deep hole trapping level. Bi can also substitute Te to form an acceptor. The amphoteric nature of Bi in CdTe results in the pinning of the Fermi level and the high resistivity. The transition of the CdTe samples from semi-insulating to *p* type at high Bi doping levels is explained by the formation of secondary phase that contains Bi and Te.

DOI: 10.1103/PhysRevB.78.172105 PACS number(s): 61.72.S−, 71.55.Gs

High resistivity is an important requirement for the semiconductor radiation detectors.[1,2] Deep levels are believed to play a key role in the carrier compensation that leads to the high resistivity.[3,4] In addition, the deep levels may also be effective carrier traps and recombination centers, which have detrimental effect on the performance of the detectors. Many deep levels have been reported for CdTe-based detectors, but their identities are often controversial.[5]

Several recent experimental works show that the Bi doping at the level of $\sim 10^{17}$ cm^{-3} results in semi-insulating CdTe.[6–9] It is well known that the Cd vacancy (V_{Cd}), which is a shallow acceptor, is abundant in CdTe, typically at the concentration of $10^{16} \sim 10^{17}$ cm^{-3}.[1,2] Thus, it was suggested that the Bi occupies the Cd site ($\mathrm{Bi}_{\mathrm{Cd}}$) acting as donors that compensate V_{Cd}.[6,9] Photoinduced current transient spectroscopy (PICTS) and thermal electric effect spectroscopy (TEES) revealed a Bi-related deep level at E_V+0.73 eV, which was assigned to a deep donor level. However, the TEES shows that this deep level is a hole trap,[9] indicating that this level is actually a deep acceptor level. It is reasonable to believe that the high resistivity is due to the Bi-induced Fermi level pinning near the midgap. But as the Bi concentration [Bi] increases from 10^{17} to 10^{19} cm^{-3}, the resistivity decreases with *p*-type conductivity and, meanwhile, the deep level disappears and a new acceptor level of E_V +0.30 eV appears, which was assigned to Bi on the Te site ($\mathrm{Bi}_{\mathrm{Te}}$).[6,9,10]

In this Brief Report, we show that $\mathrm{Bi}_{\mathrm{Cd}}$ is a single electron donor ($\mathrm{Bi}_{\mathrm{Cd}}^{+}$) when the Fermi level ($E_F$) is low. When E_F is raised, the $\mathrm{Bi}_{\mathrm{Cd}}$ undergoes a Jahn-Teller distortion and becomes a single electron acceptor ($\mathrm{Bi}_{\mathrm{Cd}}^{-}$). In addition, we find that the $\mathrm{Bi}_{\mathrm{Cd}}^{-}$ can bind with a substitutional O (O_{Te}) with large binding energy of 1.40 eV. The calculated (0/−) level of the $\mathrm{Bi}_{\mathrm{Cd}}^{-}$-$\mathrm{O}_{\mathrm{Te}}$ complex is E_V+0.8 eV close to the experimentally observed deep acceptor level at E_V+0.73 eV.[6,9] Bi can also substitute Te as an acceptor $\mathrm{Bi}_{\mathrm{Te}}^{-}$, which is more stable than $\mathrm{Bi}_{\mathrm{Cd}}^{-}$ or $\mathrm{Bi}_{\mathrm{Cd}}^{-}$-$\mathrm{O}_{\mathrm{Te}}$ complex according to the calculations. The amphoteric nature of Bi in CdTe can pin the Fermi level and lead to high resistivity. Increasing [Bi] above 10^{18} cm^{-3} may cause the segregation of $\mathrm{Bi}_2\mathrm{Te}_3$ phase or other phases containing Bi and Te because our calculated Bi solubility at the typical growth temperature of 1100 °C is in the order of 1×10^{16} cm^{-3} when the E_F is near the midgap. The formation of the $\mathrm{Bi}_2\mathrm{Te}_3$ secondary phase may result in a relatively Te poor condition in CdTe, favoring the formation of $\mathrm{Bi}_{\mathrm{Te}}$, which is an acceptor with its acceptor level at E_V +0.3 eV. This explains the reduced resistivity with *p*-type conductivity at high Bi doping level.[6,9,10]

We performed calculations based on density-functional theory within the local-density approximation, as implemented in VASP.[11] The electron-ion interactions are described by projector augmented wave pseudopotentials.[12] The valence wave functions are expanded in a plane-wave basis with cut-off energy of 400 eV. All the calculations were preformed using 64-atom cubic cells. A $2 \times 2 \times 2$ grid was used for the *k*-point sampling of Brillouin zone. All the atoms were relaxed to minimize the Feynman-Hellmann forces to below 0.02 eV/Å. The calculated CdTe lattice constant is 6.420 Å, in good agreement with the experimental values of 6.477 Å.[13]

The defect formation energy is given by

$$\Delta H_f = \Delta E - \sum_i n_i(\mu_i + \mu_i^{\mathrm{ref}}) + q(\varepsilon_{\mathrm{VBM}} + \varepsilon_f), \qquad (1)$$

where ΔE is the energy difference between the defect-containing and defect-free supercells, and n_i is the difference in the number of atoms for the *i*th atomic species between the defect-containing and defect-free supercells. μ_i is a relative chemical potential for the *i*th atomic species referenced to μ_i^{ref}. For Cd and Te, $\mu_{\mathrm{Cd}}^{\mathrm{ref}}$ and $\mu_{\mathrm{Te}}^{\mathrm{ref}}$ are the chemical potentials in bulk Cd and bulk Te, respectively. q in Eq. (1) is the defect charge state. ε_f is the Fermi energy referenced to the valance-band maximum (VBM) $\varepsilon_{\mathrm{VBM}}$, which is taken as bulk VBM corrected by aligning the core potential of atoms (averaged within a sphere centered at the atom) far away from the defect in the defect-containing supercell with that in the defect-free supercell. If the system is under thermal equilibrium and there is no Te or Cd precipitation, we have $\mu_{\mathrm{Cd}}+\mu_{\mathrm{Te}}=\Delta H_f(\mathrm{CdTe})$ and $\Delta H_f(\mathrm{CdTe}) < \mu_{\mathrm{Te}} < 0$, where $\Delta H_f(\mathrm{CdTe})$ is the heat of formation for CdTe. $\Delta H_f(\mathrm{CdTe})$ is calculated to be −0.72 eV, in reasonable agreement with the experimental value of −0.96 eV.[13] The defect transition energy level $\varepsilon(q/q')$ is the Fermi level, ε_f in Eq. (1), at which

©2008 The American Physical Society

the formation energies of the defect at the charge states q and q' are equal to each other.

Note that the defect formation energy and the transition level are both determined by using the total energies calculated at special k points. Thus, for consistency, the energies of the VBM and the conduction-band minimum (CBM) for bulk CdTe were taken as averages over all special k points. This approach has been described in details in Ref. 14 and has been applied to many previous studies of defects in different systems.[4,15–19] CdTe has the zinc-blende structure. There is only one nonequivalent k point in the $2\times2\times2$ k mesh for a perfect zinc-blende structure in a 64-atom cubic supercell. The band gap at the special k point is calculated to be 1.71 eV close to the experimental band gap of 1.61 eV.[13] Therefore, no further band-gap correction was applied.

We have tested the convergence of the calculated defect formation energies with respect to the k mesh (up to a $4\times4\times4$ k mesh), the plane-wave cut-off energy (up to 500 eV), and the supercell size (up to a 216-atom supercell). Each of these convergence tests yields the formation energies that converge to within 0.1 eV. The numerical error on the defect transition level is estimated to be 0.1 eV.

For charged defects, a jellium background of opposite charge is used to neutralize the supercell. We do not apply corrections to address the electrostatic interactions between the charged defects and their periodic images because the frequently used Makov-Payne[20] correction often significantly overestimates the correction.[15] The convergence test on the supercell size suggests that the error due to the charged defects is not significant.

We first show that $\mathrm{Bi_{Cd}}$ can be either a donor or an acceptor depending on the E_F. Bi has three more valence electrons than Cd. For neutral $\mathrm{Bi_{Cd}}$ with T_d symmetry, the symmetry determines that the three extra electrons of Bi should fully occupy one a_1 level and partially occupy the higher t_2 level. The calculation shows that the a_1 level is below the VBM and the t_2 level is slightly above the CBM. Thus, the $\mathrm{Bi_{Cd}}$ can lose one electron to the conduction band and become a single electron donor. The neutral $\mathrm{Bi_{Cd}}$ is unstable against a Jahn-Teller distortion because the threefold degenerate t_2 level (not counting spin degeneracy) is occupied by only one electron. The $\mathrm{Bi_{Cd}}$ atom moves into a trigonally symmetric interstitial position (C_{3v}) as shown in Fig. 1. Consequently, the t_2 level splits into a singly occupied a_1 level inside the band gap and an empty e level above the CBM. The $\mathrm{Bi_{Cd}}(C_{3v})$ is thus a deep acceptor. The $\mathrm{Bi_{Cd}^-}$ has a fully occupied a_1 level in the band gap, corresponding to a lone pair orbital on the $\mathrm{Bi_{Cd}}$ atom. The $\mathrm{Bi_{Cd}}$ is a negative-U center and its $(+/-)$ transition level is calculated to be $E_V+1.4$ eV.

The T_d to C_{3v} distortion of $\mathrm{Bi_{Cd}}$ causes large local compressive strain, which promotes the substitution of the nearest-neighbor Te by a smaller-sized impurity. It is known that oxygen impurity usually has a concentration of $10^{16}-10^{17}$ cm^{-3}.[21,22] The much smaller size of O compared to Te causes tensile strain. Thus the binding of $\mathrm{Bi_{Cd}}(C_{3v})$ and $\mathrm{O_{Te}}$ results in large strain reduction and large binding energy.[23] Our calculated binding energy E_b between $\mathrm{Bi_{Cd}^-}$ and $\mathrm{O_{Te}}$ is 1.40 eV. Following the law of mass action, i.e., $[\mathrm{Bi_{Cd}^-}\text{-}\mathrm{O_{Te}}]=[\mathrm{Bi_{Cd}^-}][\mathrm{O_{Te}}]\exp(E_b/kT)/N$, where N is the total possible lattice sites for $\mathrm{Bi_{Cd}^-}$ or $\mathrm{O_{Te}}$, we find that practically all $\mathrm{Bi_{Cd}^-}$ shall bind with $\mathrm{O_{Te}}$ forming complexes at the typical growth temperature of 1100 °C unless $[\mathrm{Bi_{Cd}^-}]>[\mathrm{O_{Te}}]$. On the other hand, the binding energy between $\mathrm{Bi_{Cd}^+}$ and $\mathrm{O_{Te}}$ is calculated to be only 0.51 eV because without the T_d to C_{3v} distortion, the $\mathrm{Bi_{Cd}^+}$ (which is slightly larger than the Cd ion) produces small compressive strain that consequently has a small compensating effect on the large tensile strain produced by the $\mathrm{O_{Te}}$.

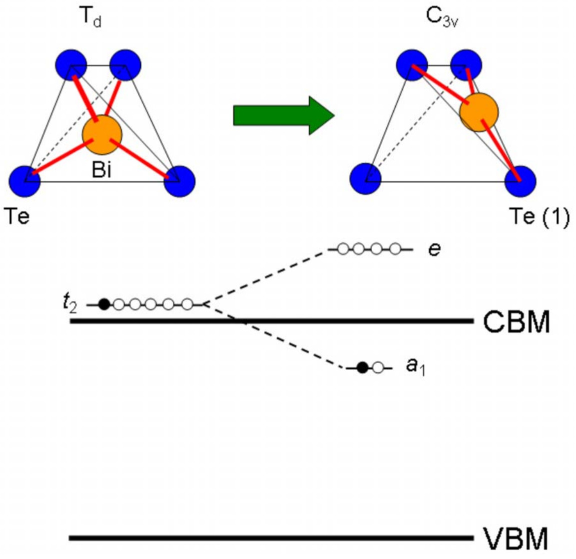

FIG. 1. (Color online) A schematic illustration of the Jahn-Teller distortion at neutral $\mathrm{Bi_{Cd}}$. The structural transformation from T_d to C_{3v} symmetry splits the t_2 level to a singly occupied a_1 level and an empty e level. The Te(1) atom may be substituted by an oxygen impurity to form a stable $\mathrm{Bi_{Cd}}$-$\mathrm{O_{Te}}$ impurity complex.

The oxygen substitution of the Te [labeled Te(1) in Fig. 1] that is the nearest neighbor to $\mathrm{Bi_{Cd}^-}$ lowers the fully occupied a_1 level from $E_V+1.5$ eV to $E_V+0.6$ eV. This is accompanied by the downward shift of the $(0/-)$ transition level. The calculated $(0/-)$ level of $\mathrm{Bi_{Cd}^-}$ is $E_V+1.1$ eV. The binding of $\mathrm{Bi_{Cd}^-}$ and $\mathrm{O_{Te}}$ lowers the $(0/-)$ level to $E_V+0.8$ eV close to the experimental value of $E_V+0.73$ eV.[9] The $\mathrm{Bi_{Cd}}$ (with or without the binding with $\mathrm{O_{Te}}$) is a DX center that transforms a donor to an acceptor through structural distortion. Thus, the $\mathrm{Bi_{Cd}}$ should exhibit persistent photoconductivity as expected for a DX center[24] and may be observed experimentally.

Figure 2 shows the formation energies of $\mathrm{Bi_{Cd}^+}$, $\mathrm{Bi_{Cd}^-}$, and $\mathrm{Bi_{Te}}$ at Te-rich limit. The Bi chemical potential μ_{Bi} should satisfy the relation of $2\mu_{\mathrm{Bi}}+3\mu_{\mathrm{Te}}<\Delta H_f(\mathrm{Bi_2Te_3})$, where $\Delta H_f(\mathrm{Bi_2Te_3})$ is the heat of formation for $\mathrm{Bi_2Te_3}$ calculated to be -1.07 eV. This ensures that no phase segregation of $\mathrm{Bi_2Te_3}$ occurs. The energies shown in Fig. 2 correspond to the upper bound of μ_{Bi} equal to $[\Delta H_f(\mathrm{Bi_2Te_3})-3\mu_{\mathrm{Te}}]/2$. The $\mathrm{Bi_{Te}^-}$ is found to be more stable than the $\mathrm{Bi_{Cd}^-}$. The formation energy of $\mathrm{Bi_{Cd}^-}$-$\mathrm{O_{Te}}$ depends on the O chemical potential μ_{O}. If we choose the upper bound of μ_{O} that satisfies $\mu_{\mathrm{Cd}}+\mu_{\mathrm{O}}=\Delta H_f(\mathrm{CdO})$, we obtain the formation energy of $\mathrm{O_{Te}}$ as 1.21 eV. The 1.40 eV binding energy between $\mathrm{Bi_{Cd}^-}$ and $\mathrm{O_{Te}}$ thus lowers the formation energy of $\mathrm{Bi_{Cd}^-}$-$\mathrm{O_{Te}}$ by 0.19 eV compared to that for $\mathrm{Bi_{Cd}^-}$. The resulted formation energy of $\mathrm{Bi_{Cd}^-}$-$\mathrm{O_{Te}}$ is still 0.31 eV higher than that of $\mathrm{Bi_{Te}^-}$. The am-

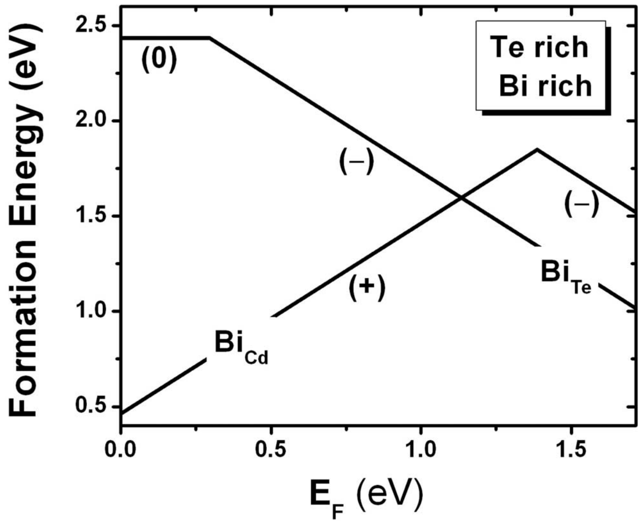

FIG. 2. Calculated formation energies for $\mathrm{Bi}_{\mathrm{Cd}}$ and $\mathrm{Bi}_{\mathrm{Te}}$ in CdTe as a function of electron Fermi energy at Te-rich limit. The slope of an energy line indicates the charge state of the defect, as shown in the figure. The transition levels are given by the Fermi energy at which the slope changes.

photeric nature of Bi in CdTe can pin the E_F at the value at which the formation energies of $\mathrm{Bi}_{\mathrm{Cd}}^{+}$ is equal to that of $\mathrm{Bi}_{\mathrm{Te}}^{-}$. This E_F pinning level is calculated to be $E_V+1.1$ eV at the Te-rich limit. The $\mathrm{Bi}_{\mathrm{Te}}^{-}$ has a calculated $(0/-)$ transition level at $E_V+0.3$ eV, in agreement with previous calculation.[25] A level at $E_V+0.30$ eV has also been observed experimentally.[8,9] However, it is unclear why this level is only observed in p-type CdTe with $[\mu_{\mathrm{Bi}}]\sim 7-8\times 10^{18}$ cm^{-3} but not in the semi-insulating CdTe with $[\mu_{\mathrm{Bi}}]\sim 10^{17}$ cm^{-3}.[8,9]

If the E_F can be pinned by the amphoteric Bi in CdTe, further increasing [Bi] is not expected to move the E_F. But it was found that increasing [Bi] from 10^{17} to 10^{19} cm^{-3} turns the CdTe from semi-insulating to p type.[8,9] This may be explained by the formation of the secondary phase that consists of Bi and Te, such as $\mathrm{Bi}_2\mathrm{Te}_3$. Due to the high vapor pressure of Cd compared to Te, the growth condition of CdTe is normally Te rich. At the Te-rich and Bi-rich limits, the total [Bi] or the Bi solubility is calculated to be 4.4×10^{16} cm^{-3}, assuming that the E_F is pinned at $E_V+1.1$ eV (corresponding to the formation energy of 1.6 eV) and that the growth temperature is 1100 °C. Note that in our calculations, the upper bound of the Bi chemical potential corresponds to segregation of the $\mathrm{Bi}_2\mathrm{Te}_3$ phase. Therefore, further increasing [Bi] should cause the formation of the secondary phase that consists of Bi and Te, in consistence with the experimentally observed phase segregation in the CdTe samples with [Bi] $>1\times 10^{18}$ cm^{-3}.[7] If the starting material is stoichiometric, such phase segregation may have the effect of creating large number of Te vacancies that leads to relatively Te-poor condition. Consequently, the $\mathrm{Bi}_{\mathrm{Te}}$ formation energy is lowered relative to that of $\mathrm{Bi}_{\mathrm{Cd}}$. At the Te-poor limit, the E_F pinning level is lowered to $E_V+0.4$ eV. The exact Te chemical potential is unknown. But the qualitative theoretical picture of increasing $[\mathrm{Bi}_{\mathrm{Te}}]$ relative to $[\mathrm{Bi}_{\mathrm{Cd}}]$ when the total [Bi] is much higher than 1×10^{17} cm^{-3} is consistent with the experimental findings that (1) the acceptor level at $E_V+0.30$ eV (assigned to $\mathrm{Bi}_{\mathrm{Te}}$) appears with the vanishing deep acceptor level at $E_V+0.73$ eV (assigned to $\mathrm{Bi}_{\mathrm{Cd}}$) and that (2) the CdTe is turned from semi-insulating to p type at high [Bi].[8,9]

In summary, we have studied the formation energies and gap states induced by Bi and Bi-related defect complexes in CdTe. We find that $\mathrm{Bi}_{\mathrm{Cd}}$ is a negative-U center, which can be stable as either $\mathrm{Bi}_{\mathrm{Cd}}^{+}$ or $\mathrm{Bi}_{\mathrm{Cd}}^{-}$ depending on the Fermi level. The $\mathrm{Bi}_{\mathrm{Cd}}^{-}$ is stabilized by a Jahn-Teller distortion and can further bind with an O_{Te} with large binding energy of 1.40 eV. The calculated $(0/-)$ transition level of $E_V+0.8$ eV for the $\mathrm{Bi}_{\mathrm{Cd}}^{-}$-$\mathrm{O}_{\mathrm{Te}}$ is close to the experimentally observed acceptor level of $E_V+0.73$ eV. Similar Jahn-Teller distortion may also be expected for other group-V impurities substituting Cd. Our calculations further show that the donor $\mathrm{Bi}_{\mathrm{Cd}}^{+}$ and the acceptor $\mathrm{Bi}_{\mathrm{Te}}^{-}$ can pin the Fermi level near the midgap, leading to the high resistivity of CdTe. However, too much Bi doping in CdTe causes the formation of the secondary phase that consists of Bi and Te. Such phase segregation creates Te vacancies, favoring the formation of $\mathrm{Bi}_{\mathrm{Te}}$ over $\mathrm{Bi}_{\mathrm{Cd}}$. This may explain the transition of CdTe from semi-insulating to p type with increasing [Bi].

The author thanks D. J. Singh for helpful discussions. This work was supported by the U.S. DOE Office of Nonproliferation Research and Development NA22.

---

[1] T. E. Schlesinger, J. E. Toney, H. Yoon, E. Y. Lee, B. A. Brunett, L. Franks, and R. B. James, Mater. Sci. Eng., R. **32**, 103 (2001).

[2] M. Fiederle, V. Babentsov, J. Franc, A. Fauler, and J.-P. Konrath, Cryst. Res. Technol. **38**, 588 (2003).

[3] M. Fiederle, C. Eiche, M. Salk, R. Schwarz, K. W. Benz, W. Stadler, D. M. Hofmann, and B. K. Meyer, J. Appl. Phys. **84**, 6689 (1998).

[4] M.-H. Du, H. Takenaka, and D. J. Singh, Phys. Rev. B **77**, 094122 (2008).

[5] X. Mathew, Sol. Energy Mater. Sol. Cells **76**, 225 (2003).

[6] E. Saucedo, L. Fornaro, N. V. Sochinskii, A. Cuña, V. Corregidor, D. Granados, and E. Diéguez, IEEE Trans. Nucl. Sci. **51**, 3105 (2004).

[7] E. Saucedo, O. Martínez, C. M. Ruiz, O. Vigil-Galán, I. Benito, L. Fornaro, N. V. Sochinskii, and E. Diéguez, J. Cryst. Growth **291**, 416 (2006).

[8] E. Saucedo, C. M. Ruiz, V. Bermúdez, E. Diéguez, E. Gombia, Z. Zappettini, A. Baraldi, and N. V. Sochinskii, J. Appl. Phys. **100**, 104901 (2006).

[9] E. Saucedo, J. Franc, H. Elhadidy, P. Horodysky, C. M. Ruiz, V. Bermúdez, and N. V. Sochinskii, J. Appl. Phys. **103**, 094901 (2008).

[10] C. M. Ruiz, O. Vigil, E. Saucedo, G. Contreras-Puente, and V. Bermúdez, J. Phys.: Condens. Matter **18**, 7163 (2006).

[11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

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

[13] *CRC Handbook of Chemistry and Physics*, 88th ed., edited by D. R. Lide (CRC, Boca Raton, FL/Taylor & Francis, Lodon).

[14] S. B. Zhang, J. Phys.: Condens. Matter **14**, R881 (2002).

[15] D. Segev and S.-H. Wei, Phys. Rev. Lett. **91**, 126406 (2003).

[16] A. Janotti, S.-H. Wei, and S. B. Zhang, Appl. Phys. Lett. **83**, 3522 (2003).

[17] S. Limpijumnong, S. B. Zhang, S.-H. Wei, and C. H. Park, Phys. Rev. Lett. **92**, 155504 (2004).

[18] C. G. Van de Walle, S. Limpijumnong, and J. Neugebauer, Phys. Rev. B **63**, 245205 (2001).

[19] M.-H. Du, H. M. Branz, R. S. Crandall, and S. B. Zhang, Phys. Rev. Lett. **97**, 256602 (2006).

[20] G. Makov and M. C. Payne, Phys. Rev. B **51**, 4014 (1995).

[21] N. Krsmanovic, K. G. Lynn, M. H. Weber, R. Tjossem, Th. Gessmann, Cs. Szeles, E. E. Eissler, J. P. Flint, and H. L. Glass, Phys. Rev. B **62**, R16279 (2000).

[22] S. A. Awadalla, A. W. Hunt, K. G. Lynn, H. Glass, C. Szeles, and S.-H. Wei, Phys. Rev. B **69**, 075210 (2004).

[23] In $\mathrm{Bi}_{\mathrm{Cd}}^{-}$-$\mathrm{O}_{\mathrm{Te}}$, the $\mathrm{Bi}_{\mathrm{Cd}}$ relaxes toward the interstitial position and makes a new bond with a Cd atom, which in turn breaks the bond with O_{Te}, such that the O_{Te} is three-fold coordinated and the $\mathrm{Bi}_{\mathrm{Cd}}$ is four-fold coordinated.

[24] P. M. Mooney, J. Appl. Phys. **67**, R1 (1990).

[25] S.-H. Wei and S. B. Zhang, Phys. Rev. B **66**, 155211 (2002).