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Ab initio study of point defects in CdF$_2$

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The plane-wave pseudopotential method is used to study point defects in CdF$_2$. We present comprehensive results for the native defects as well as for dominant impurities. In addition to F$_i$, V$_{Cd}$ and O$_F$ were found to be easily formed compensating acceptors. For In and Ga impurities the experimentally observed large Stokes shift could not be established, and the results rule out symmetric atomic relaxation as the mechanism leading to the bistable behavior. The limitations of the present approach utilizing density-functional theory and the local-density approximation in the case of ionic materials are addressed. [S0163-1829(97)05447-7]

I. INTRODUCTION

Cadmium fluoride (CdF$_2$) has recently gained growing interest due to its unusual electrical and optical properties. CdF$_2$ has a very wide band gap (over 7.8 eV) typical for insulating ionic crystals, but can be made semiconducting by doping with trivalent metal impurities.[1] Most dopants, such as Sc or Y, produce only a shallow donor state, but In or Ga related defects exhibit bistable behavior: in addition to the shallow state these impurity centers also have a deep state.[2-4] Application of ultraviolet-visible light at low temperatures results in the disappearance of the absorption peak corresponding to the deep electronic state and an infrared absorption band associated with the occupation of the metastable shallow state arises.[2-4] In other words, the electrons occupying the deep state are lifted due to photoexcitation to shallow states. At low temperatures the electrons cannot be trapped back to the deep states due to a barrier induced by different atomic configurations for the shallow and deep states. The change in the electronic occupation causes a large difference in the local refractive index, which can be used as means for holographic writing at nanoscale spatial resolution.[5]

Recent experimental work[6,7] has verified that In centers in CdF$_2$ have a negative-U character, i.e., the deep state traps two electrons. Similar metastable behavior is well known to occur in the case of DX centers in Al$_x$Ga$_{1-x}$As alloys,[8,9] where this phenomenon has as well been demonstrated to suit for optical writing.[10,11] DX-type behavior has also been observed to occur in a multitude of other III-V semiconductors, the latest example being the oxygen impurities in AlGaN alloys.[12-14]

A critical quantity for applications utilizing the bistable behavior is the annealing temperature above which the metastable occupation disappears. This temperature is typically below 100 K, as well for In in CdF$_2$ (Refs. 2,3) as for Si in Al$_x$Ga$_{1-x}$As.[8] However, for Ga-doped CdF$_2$ metastable behavior persists up to 250 K,[4,15] which is very advantageous considering the possible applications operating close to room temperature.

The aim of the present paper is to apply state-of-the-art computational methods to study point defects in CdF$_2$. We first discuss the requirements set by CdF$_2$ for the plane-wave pseudopotential (PWPP) approach, and verify that our results for the bulk material are in good agreement with the all-electron calculations performed with the full-potential linear muffin-tin orbital (FP-LMTO) method.[16] We then proceed to study native defects, for which the formation energies and ground-state atomic geometries are determined. Based on this data the donor compensation mechanism due to the presence of different acceptor defects is addressed, including the contributions from oxygen impurities occupying the fluorine atomic site. Second we concentrate on trivalent dopant impurities, for which we find evidence for the principal qualitative difference: In and Ga dopants are clearly more likely to be stabilized in the negative charge state than Y, consistent with the experimental data. However, the experimentally observed large difference in thermal and optical ionization energies (Stokes shift) is not reproduced by the present calculations for In and Ga impurities, which is discussed in detail in the context of the atomic relaxations.

One further aspect of our paper is to explore the limits of the present approach based on density-functional theory (DFT) in the local-density approximation (LDA) in the case of ionic crystals. Although this method has been successfully applied in the case of more covalently bonded systems such as Al$_x$Ga$_{1-x}$As (Ref. 9) or Al$_x$Ga$_{1-x}$N,[12,17] we find evidence that defects in ionic compounds such as CdF$_2$ present a much harder challenge for standard DFT-LDA–based methods.

II. METHOD AND BULK CALCULATIONS

Our method for solving the many-particle electron-ion problem is based on the self-consistent solution of Kohn-Sham equations in DFT utilizing the PWPP method. For the exchange-correlation term we use LDA as parametrized by Perdew and Zunger.[18]

CdF$_2$ has the fluorite structure, i.e., it has three atoms in the unit cell: Cd at $(0,0,0)$, one F at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ and another F at $(\frac{3}{4},\frac{3}{4},\frac{3}{4})$. This cubic structure is illustrated in Fig. 1. Both Cd and F present challenges for proper treatment in the PWPP method. The $4d$ electrons of Cd act as semicore states and reside high in the valence band close to the highest occupied states.[19,20] This is clearly illustrated in the band structure (Fig. 2) produced by the all-electron calculation utilizing the FP-LMTO method.[16] Thus the explicit treatment of the Cd $4d$ electrons as valence states in the PWPP calculation was considered essential. This assumption was further confirmed
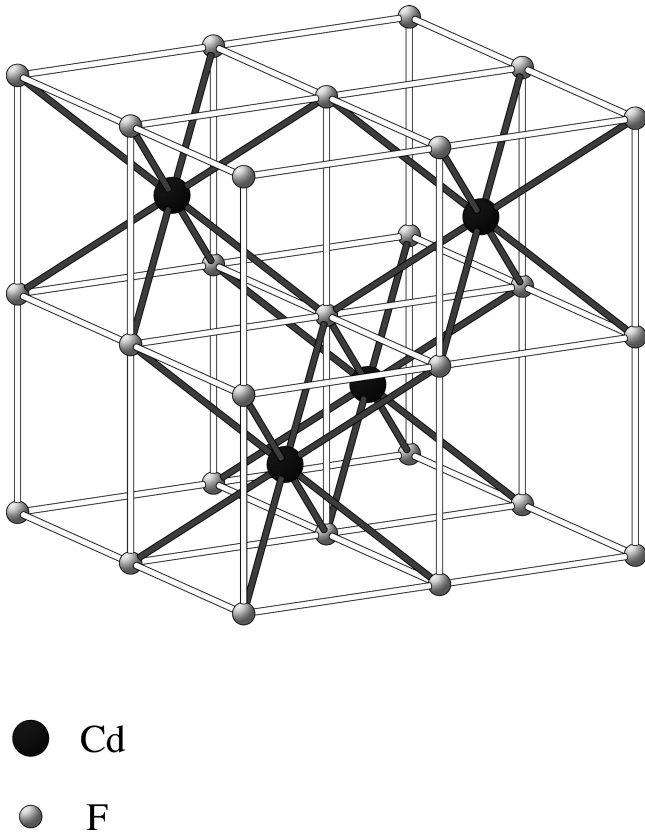
Cd

F

FIG. 1. CdF_2 exhibits the fluorite structure. Each Cd atom has eight F atoms as nearest neighbors. Correspondingly, each F atom is surrounded by a four-atom Cd tedrahedron.

by performing test calculations with Cd $4d$ states treated as core states. As a result the lattice constant was underestimated by nearly 10% with respect to the experimental value. Application of the nonlinear core-valence exchange-
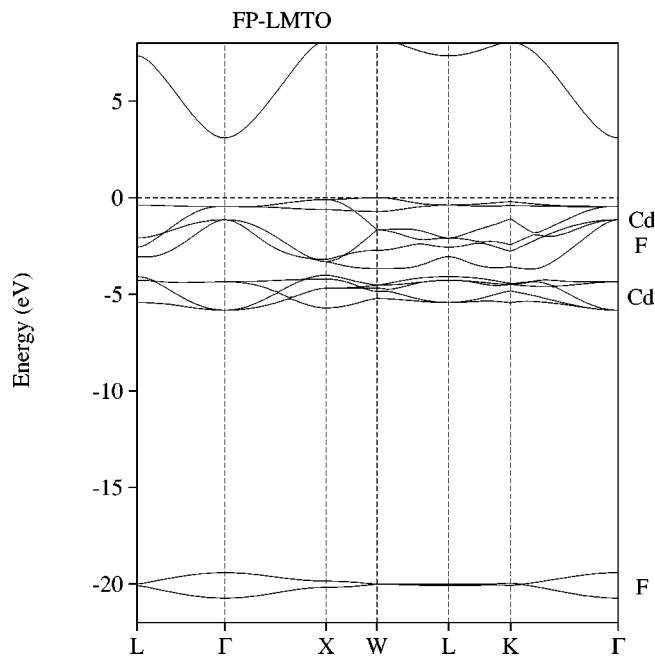

FIG. 2. Band structure for CdF_2 as calculated by the FP-LMTO method.

correlation scheme (nlcv-xc) (Ref. 21) slightly improved the situation, but the lattice constant still remained more than 5% smaller than the experimental value. In order to comply with the treatment of $4d$ electrons as valence states, soft Troullier-Martins[22] pseudopotentials were employed for Cd. The employed core radii for the s, p, and d channels were 2.4, 2.4, and 2.3 a.u., respectively, and the s component was used as the local one. With this choice of generation parameters a 44-Ry kinetic-energy cutoff was found to be adequate for well-converged results. The fluorine atoms have three occupied electronic states of which only the $1s$ was included in the core. A 44-Ry kinetic-energy cutoff was found far too low if a Troullier-Martins pseudopotential was also employed for the fluorine species. Therefore, Vanderbilt ultra-soft pseudopotentials[23] with 1.35-a.u. core radii for both s and p channels were used instead. Tests with the fluorine dimer showed that even a 30-Ry plane-wave basis would have been enough for well-converged results; thus the 44-Ry cutoff employed in the calculations involving CdF_2 guaranteed extremely good convergence with respect to fluorine-related electronic states.

In order to test the quality of our PWPP approach we calculated the lattice constant, bulk modulus, and band structure and compared the results with those from an all-electron calculation with the FP-LMTO method. With both methods a $4 \times 4 \times 4$ Monkhorst-Pack special k-point grid[24] was used for the reciprocal space integration, and the same LDA parametrizations were employed. The lattice constant given by our PWPP calculations was 10.11 a.u. while the FP-LMTO result was 10.03 a.u. There is some scatter in the experimental lattice constant values ranging from 10.14 a.u. to 10.20 a.u.[25,26] Thus there is good agreement between the two computational results, and the well-known LDA overbinding manifests itself in the slight underestimation with respect to experimental values. The bulk moduli given by PWPP calculation was 1.21 Mbar, in good agreement the FP-LMTO result of 1.30 Mbar. In Figs. 2 and 3 the band structures from the two calculations are compared. We find excellent agreement between the two plots verifying the reliability of our PWPP approach. The fluorine $2s$ states reside deep (about 20 eV) below the valence-band top. The Cd $4d$ derived band occurs only slightly below the uppermost valence states, which mainly have a fluorine $2p$ character, since the Cd $5s$ electrons are largely transferred to these states due to the large electronegativity of the F ions. Our calculations predict an *indirect* band gap for CdF_2: the valence-band maximum occurs at W (about 0.5 eV higher than at Γ) while the conduction band has its minimum at Γ. The obtained band structures are in good general agreement with the earlier calculations utilizing either tight-binding or empirical pseudopotential approaches.[19,20] However, a minor difference exists in whether the valence maximum occurs at W or X. The band-gap value found in our calculations with both methods applied is 2.8 eV, which is considerably lower than the experimental estimate 7.8 eV.[20] This band-gap underestimation is a well-known deficiency of the DFT-LDA calculations, and its effects on the results will be addressed below.

III. DEFECT CALCULATIONS

The defect calculations were performed with a supercell containing 48 atoms in the ideal structure. For the reciprocal
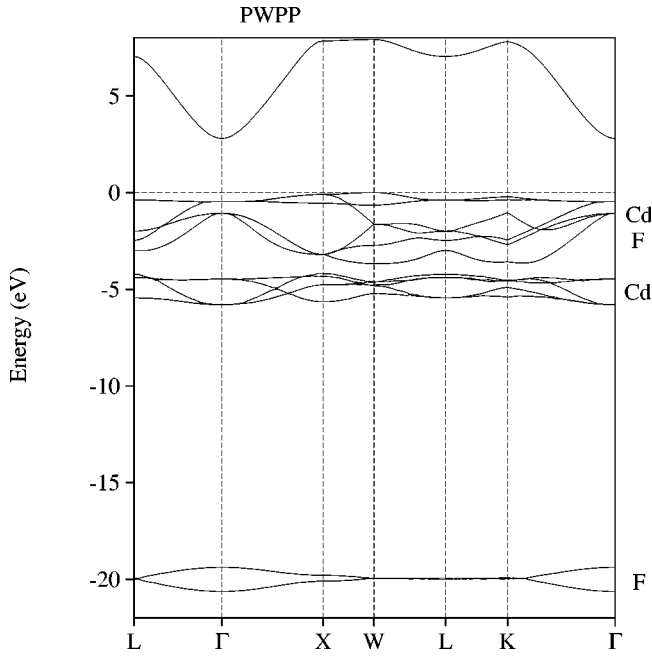
PWPP

FIG. 3. Band structure for CdF$_2$ as calculated by the PWPP method.

space integration a $2 \times 2 \times 2$ Monkhorst-Pack grid[24] was used (four k points in the case of no assumptions of symmetry). The rather extensive calculations were performed with a massively parallelized version of our PWPP code with typical processor numbers being 32 or 64. About 100 MFlops performance per processor was obtained on the Cray T3E machine with nearly ideal scaling behavior up to 128 processors.[27] In all defect calculations the atomic positions were fully relaxed without any symmetry constraints. The initial atomic positions were randomized with a maximum Cartesian amplitude of 0.25 a.u. in order to break metastable symmetries that may prevent the system from reaching the true ground-state geometry.

The formation energy analysis for the investigated defects was performed along the standard procedure.[12] We define the formation energy of a defect in charge state q as

$$E_f(q) = E_{\text{tot}}(q) - n_{\text{Cd}}\mu_{\text{Cd}} - n_{\text{F}}\mu_{\text{F}} - n_X\mu_X + q(\mu_e + E_v), \quad (1)$$

where E_{tot} is the total energy of the supercell containing the defect. $n_{\text{Cd, F}, X}$ denotes the number of Cd, F, and possible impurity atoms of species X involved in the calculation, $\mu_{\text{Cd, F}, X}$ being the corresponding atomic chemical potential. μ_e corresponds to the electron chemical potential (Fermi-level position in the gap relative to the valence band), and E_v denotes the valence-band maximum (at W point in the case on CdF$_2$). The shift in the valence-band maximum due to defect-defect interaction was taken into account by calculating the shift between the effective potential value in the bulklike region of the defected supercell and in the same region in the ideal system.[12]

Based on Eq. (1) it possible to draw formation energy diagrams as a function of the electron chemical potential (see, e.g., Fig. 4). As a standard practice the range for the electron chemical potential is chosen to correspond to the experimental band-gap value rather than the theoretical one.
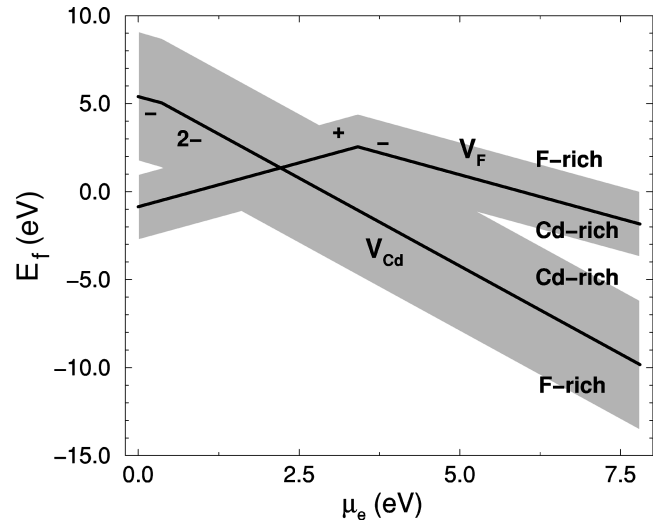

FIG. 4. Formation energies for native vacancies in CdF$_2$. The solid line illustrates the energy values obtained in stoichiometric conditions. The surrounding gray shaded area depicts the formation energy range induced by deviations from perfect stoichiometry.

This is motivated by the fact that in general the total-energy values are less influenced by the band-gap underestimation in DFT-LDA calculations than the single-particle eigenvalues. The kinks in the formation energy curves correspond to the ionization levels, i.e., the values of μ_e when the stablest charge state of a defect changes.

The gray shaded area in the plots describes the dependence of formation energies on the deviations from perfect stoichiometry in growth conditions. In Eq. (1) this is taken into account in the choice of the atomic chemical potentials; the atomic chemical potentials of both sublattice species cannot be determined simultaneously in compound materials, but in the case of CdF$_2$ they obey the relation

$$\mu_{\text{Cd}} + 2\mu_{\text{F}} = \mu_{\text{CdF}_2}^{\text{bulk}}. \quad (2)$$

Thus, for instance, the Cd-rich growth conditions can be simulated by fixing the μ_{Cd} to the value for given by calculation of elemental (hexagonal) Cd, and the value for μ_{F} is then determined from Eq. (2). Correspondingly, for F-rich conditions we have determined μ_{F} by calculating the F dimer, and successively μ_{Cd} based on Eq. (2). For native defects the formation energy difference corresponds, in principle, to the value of heat of formation. However, an important observation in the case of CdF$_2$ is that the formation energy range in the case of native defects involving the fluorine sublattice is only *half* of the value for the corresponding defects in the cadmium sublattice. This simply follows from the composition where for each Cd atoms there exist two F atoms. The experimental value for the enthalpy of formation of CdF$_2$ is -7.26 eV,[28] while our calculations give a value of -6.37 eV with the above choice of the elemental structures. In the formation energy graphs the range has been symmetrically expanded to correspond to the experimental value.

A. Native defects

As a test for the formation energies given by the method employed we have calculated the fluorine vacancy-interstitial

pair (Frenkel defect) for which the experimental estimate for the formation enthalpy is 2.1–2.8 eV.[1] Our calculations reveal that if one of the nearest fluorine atoms surrounding the fluorine interstitial site is moved to the cube center, the resulting defect pair is not stable but recombination occurs. If a fluorine atom from the second-nearest-neighbor shell is transferred into the interstitial site, the created Frenkel pair is stable with the formation energy of 1.6 eV. The formation energy for a Frenkel pair with an infinite distance is 2.0 eV assuming the singly positive charge state for the vacancy and the singly negative charge state for the interstitial (see below). This results in a value of 0.4 eV for the binding energy of a Frenkel pair at the nearest stable configuration. In general, our theoretical formation energy values are thus somewhat smaller than the experimental values. However, we emphasize that the absolute formation energy values are not important for our analysis where formation energy *differences* between various defects are the relevant quantities of interest.

In Fig. 4 the formation energies and ionization levels for native vacancies are presented. V_{Cd} is found to be an effective acceptor that principally traps two electrons when the Fermi level resides below midgap. The eight fluorine atoms surrounding the vacant Cd site are found to relax 7% outwards in the singly and doubly negative charge states. At high Fermi-level positions we find even the possibility for additional trapping of two electrons corresponding thus to the 4− charge state. The (2−/4−) ionization level is found at about $E_v + 4$ eV. However, an accurate position for this ionization level is difficult to obtain in the present calculations since V_{Cd}^{4-} induces a doubly occupied electron level close to the conduction band; due to the too small theoretical band gap the distance of this upper-gap electron level is underestimated from the valence-band maximum acting as the reference point, and therefore the formation energy for this kind of defect experiences a tendency towards a too small value. For the first two charge states possessing electron levels close to the valence band the total energies are obviously much less influenced by the actual value of the band gap.

V_F is predicted to have an amphoteric character by our calculations: it acts as a donor at low Fermi-level positions, but above midgap it can trap two more electrons corresponding to the single negative charge state. The anion vacancies have a well-known ability to trap an electron in ionic crystals (*F* centers),[1] in good agreement with our result.

The vacant fluorine site is surrounded in the ideal lattice by four Cd atoms forming an tetrahedron. The next-nearest neighbor shell is formed by six fluorine atoms which are 15% farther. Interestingly, in the singly positive charge state we find that the nearest-neighbor Cd atoms relax outwards while the next-nearest fluorine atoms relax inwards. Finally at equilibrium both four Cd atoms and six F atoms are at an equal distance from the vacant site, which is calculated to be 1.07 times the ideal nearest-neighbor bond length. In the singly negative charge state this phenomenon is removed and the nearest Cd atoms move only two percent outward from their ideal sites while the F atoms reside at 1.12 times the nearest-neighbor distance from the vacancy center (about 3% inward relaxation compared with the ideal configuration).

Figure 5 represents the results for Cd and F interstitials. For Cd_i we investigated several atomic configurations. The
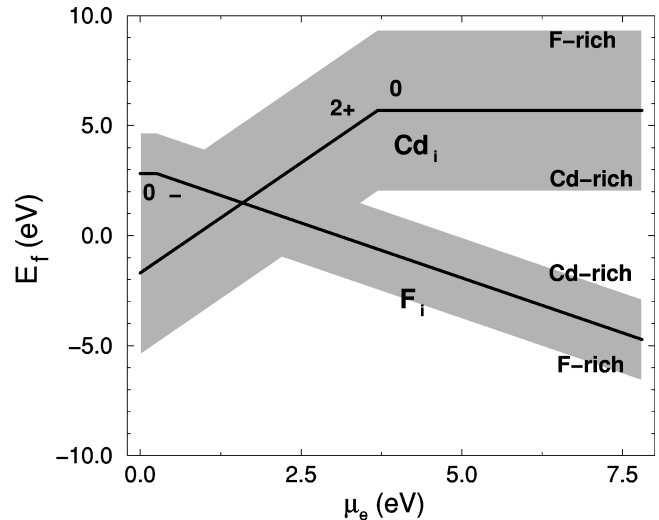

FIG. 5. Formation energies for interstitial atoms in CdF_2. The solid line illustrates the formation energy values obtained in stoichiometric conditions. The surrounding gray shaded area depicts the energy range induced by deviations from perfect stoichiometry.

simple cube-center interstitial position (surrounded by eight F atoms) was found to be the most favorable. In the doubly positive charge state the nearest F atoms relax two percent inwards while in the neutral charge state the relaxation has the same magnitude but opposite direction. The relatively high formation energy values found for the Cd interstitial suggest that it is not a dominant defect in CdF_2.

The donor compensation in CdF_2 is traditionally believed to be caused by interstitial fluorine ions,[1] and our calculations indeed predict F_i to be a very efficient compensation acceptor as shown in Fig. 5. The dominant charge state is found to be the singly negative one, in which the F atom persists at the cube-center interstitial position in good agreement with the experimental data.[1] The surrounding eight F atoms relax 5% outwards in the singly negative charge state. At high Fermi-level positions we find evidence for the stabilization of the triply negative charge state. The (1−/3−) ionization level occurs at about $E_v + 4$ eV, but is likely to be influenced by the band-gap underestimation due to similar reasons as for V_{Cd}^{4-}.

When the formation energies are compared between Figs. 4 and 5, it can be seen that V_{Cd} is even slightly more favorable acceptor than F_i. Therefore, our results firmly suggest that metal vacancies should be further investigated as an alternative source for donor compensation.

Concerning the antisite defects in CdF_2 we believe that the highly ionic bonding does not favor antisite-type defects and therefore these defects do not play a dominant role in this type of materials with fluorite structure. Support for this assumption was provided by a calculation where the positions of Cd and F atoms were interchanged. The formation energy for such a double antisite defect was found to be over 11 eV, which is a very high value compared, e.g., with the analogous defect in GaAs where the formation energy is less than 3 eV according to our calculation (atoms were not allowed to relax in either calculation).

We have also made calculations for the V_k center (a hole trapped between two anions) in CdF_2. However, the decreased bond length between the two fluorine atoms along
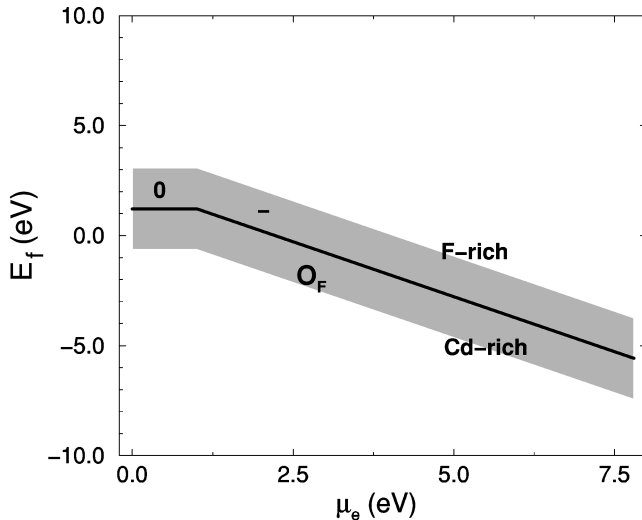
FIG. 6. Formation energy for O$_F$ defect in CdF$_2$. The solid line illustrates the energy values obtained in stoichiometric conditions. The surrounding gray shaded area depicts the energy range induced by deviations from perfect stoichiometry.
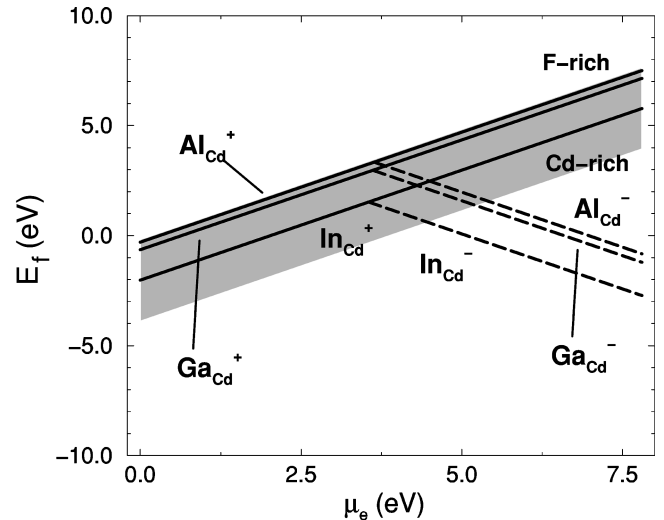

FIG. 7. Formation energies for substitutional In, Ga, and Al, defects in CdF$_2$. The results obtained for the negative charge state are depicted by the dashed lines reflecting the uncertainties due to the band-gap underestimation (see text). The gray shaded area describing the stoichiometry range is drawn only in the case of In for clarity.

[100] axis could not be stabilized, but the atoms relaxed back to their ideal positions. We further conducted an identical calculation in CaF$_2$, in which the existence of V_k centers is experimentally well established,[1] but the hole localization could neither be observed. We believe that this problem could be related to an inaccurate description of the exchange interaction in the DFT-LDA method applied.

B. Impurities

The behavior of O, In, Ga, Al, and Y impurity species was investigated. For In we used a similar Troullier-Martins pseudopotential[22] as for Cd treating the In $4d$ states in valence. When substituting In for Cd the In $4d$ states were found to produce a degenerate level about 11 eV below the valence-band maximum. Comparing with Fig. 3 it is evident that the In $4d$ induced levels thus reside separated from the Cd $4d$ and F $2s$ bands. Similarly a test calculation treating the Ga $3d$ levels in valence revealed that these levels are separated by more than 5 eV from the nearest Cd $4d$ band. However, the treatment of Ga $3d$ states in valence would require a much larger kinetic-energy cutoff than the In $4d$ states in properly converged calculations. Therefore, we decided to treat the Ga $3d$ states as part of the core in the extensive defect calculations, but taking their effect into account using the nlcv-xc scheme.[21] Due to the wide separation from other bands we believe our approach to be accurate. For Ga as well for Al and Y we used the Hamann-type[29] pseudopotential generation scheme. For oxygen we applied the Vanderbilt-type[23] ultrasoft pseudopotential.

In the case of impurities the choice of the atomic chemical potentials in Eq. (1) becomes even more complicated. The procedure applied here is analogous with our previous work:[12] the most stringent condition for the impurity chemical potential arises from a compound that it forms with one of the major constituents, i.e., either Cd or F. In our case the relevant compounds were found to be CdO, InF$_3$, GaF$_3$, and AlF$_3$.[26]

Figure 6 shows that oxygen is easily incorporated into the fluorine atomic site and that it acts as an efficient acceptor. Therefore, we suggest that oxygen is likely to contribute to the donor compensation in doped samples in addition to V_{Cd} and F$_i$. The four Cd atoms surrounding the oxygen atom relax inwards by two percent in the neutral charge state and by 6% in the singly negative charge state.

The results for In, Ga, and Al impurities at Cd atomic site shown in Fig. 7 reveal that these defects exhibit two charge states: the singly positive and singly negative one. The $(+/-)$ ionization level is found to occur near midgap. However, the highest occupied electron level for the negative charge state resides close to the conduction band and, therefore, the position of the ionization level is subject to inaccuracies due to the underestimation in the band-gap value. A negative-U nature for these donors is predicted to occur since the total energy of the neutral defect was in all cases found higher than for the singly positive of negative charge states. This is in agreement with recent experimental data for In-doped samples.[6,7]

For Y$_{Cd}$ we found that it only exists in the singly positive charge state. The singly negative charge state was not stabilized, but the eigenvalues associated with the uppermost electron level were clearly above the conduction-band edge. This result agrees with the experimental observation that dopants such as Sc or Y act as simple shallow donors without the ability to trap extra electrons associated with the deep state.[1]

The eight fluorine atoms surrounding the In$_{Cd}$ defect relax symmetrically 4% inwards in the singly positive charge state while in the negative charge state they remain nearly at the ideal geometry. In contrast, for Ga and Al impurities a symmetry lowering lattice relaxation occurs. Four of the nearest F atoms relax strongly (24%) inwards forming a tetrahedron surrounding the dopant atom. Three of the remaining four fluorine atoms experience a trend for outward relaxation with

roughly equal magnitude (10%), while one fluorine atom deviates in all cases from this behavior by showing a few percent inward relaxation.

The symmetric relaxation modes found for In correlate rather well with the semiempirical calculations by Cai and Song.[30] However, the symmetry lowering relaxation observed for Ga impurities has not been reported before. Whether this relaxation behavior is connected to the high annealing temperature (250 K) of the deep electron state after photoexcitation in the case of Ga doping,[4] remains unclear at this point.

In the case of Al impurities our results also deviate from the ones presented recently by Fu and Song[31] who find a qualitatively different behavior between Al and Ga dopants while our calculations predict a nearly analogous behavior. We therefore suggest that also Al should be experimentally tested as a possible bistable center in CdF_2. Following the trend in the annealing temperature after photoexcitation in the case of In and Ga (Refs. 2–4) one could speculate that Al could facilitate an even higher annealing temperature.

IV. DISCUSSION

Doping of CdF_2 with In results in photoabsorption at two very distinct energy scales. The absorption peak associated with the deep electron state is centered at 3.2 eV, while the shallow state leads to infrared absorption at about 0.2 eV.[3,6] The absorption edge for the deep state occurs at 1.9 eV, which thus corresponds to the optical ionization energy, i.e., photon energy required to lift electrons from the deep state to conduction band. The thermal ionization energy for the deep state in only 0.25 eV. Thus In-induced defects in CdF_2 exhibit an exceptionally large Stokes shift, i.e., the difference between optical and thermal ionization energies is over 1.6 eV. Similar behavior is found to characterize Ga-related defects in CdF_2 as well.[4]

The large Stokes shift is commonly associated with lattice relaxation, i.e., the equilibrium atomic configurations for the deep and shallow states differ significantly. During thermal ionization the system follows an adiabatic path from the deep to shallow configuration, while in the case of optical ionization the electrons occupying the deep level can be thought to be shifted instantaneously to the conduction band and the atomic relaxation to the new equilibrium configuration occurs at a much larger time scale via phonon emission. We have estimated these Franck-Condon shifts for isolated In and Ga impurities based on total-energy differences,[32] but all the calculated shifts were below 0.5 eV, which is in clear contrast with the much larger experimental value. In addition, the highest single-particle eigenvalues in the negative charge state were found to occur only 0.2–0.3 eV below the conduction-band edge, which are considerably smaller values than the experimentally observed optical transition energies, even when taking the notable DFT-LDA underestimate in the band-gap value into account.

Experimentally it is well established that the deep and shallow electronic states induced by In and Ga impurities are separated by an energy barrier that can be overcome by increasing the vibronic energy of the ions (system temperature). However, our calculations do not reveal the presence of such a barrier in the case of isolated In or Ga impurities. If two electrons were added to the system in the equilibrium atomic configuration of the singly positive charge state, the system relaxed to the configuration reported for the negative charge state.

The above observations regarding the small Stokes shift and lack of energy barrier lead us to search for alternative equilibrium configurations for isolated In and Ga donors. Motivated by the clear symmetry lowering distortion observed, e.g., for the Si donor in the deep state in AlAs (Ref. 9) and recently documented for O in AlN,[12,17] we have investigated the possibility for similar behavior in CdF_2. In and Ga impurities in the singly negative charge state were displaced along the [100] axis through the plane formed by four F atoms. However, after full atomic relaxation they returned to the configurations reported above. Similarly, if a nearest-neighbor fluorine atom was displaced along the [111] direction, no (meta)stable configuration could be found. Furthermore, we have examined a group of defect complexes such as $In_{Cd}V_F$ and $In_{Cd}F_i$, but the preliminary results did not reveal any promising candidates that would produce the observed Stokes shift and vibronic barrier.

Facing the above-mentioned problems when comparing to experimental data in the case of bistable defects, we finally address the possible limitations set by the calculational method applied. It is naturally possible that DFT-LDA method is incapable of describing correctly the deep state associated with a substitutional In or Ga atom. However, based on our experience of the deep states in other semiconducting materials this does not seem very likely. We rather believe that, despite our attempts, we have not been able to find the correct initial guess leading to a lower symmetry atomic configuration of the deep state or the effects seen in experiments are due to defect complexes not included in our preliminary studies.

In order to test the applicability of more advanced methods, we have made tests with the generalized gradient approximation (GGA).[33] However, the band gap as well as the results for the dopant impurities were hardly affected. Furthermore, we investigated the usefulness of the local mass approximation (LMA).[34] However, tests for bulk CdF_2 indicated only a minor improvement in the band-gap value. The equilibrium lattice constant was overestimated by nearly 2% compared with the experimental value, while the bulk modulus decreased by approximately 25% when compared to the values obtained in LDA calculations. Based on these observations LMA does not seem to provide any considerable improvement over LDA in ionic materials such as CdF_2 and, therefore, we did not proceed with any defect calculations utilizing LMA.

In general, it is evident that defects in CdF_2 provide an excellent test bench for more advanced methods. For example, the screened-exchange-LDA method[35–37] is very promising, but due to the heavy computational cost induced by the explicit orbital dependence reliable defect calculations have not been performed thus far. On the other hand, application of the self-interaction correction (SIC) in an approximative way utilizing SIC-constructed pseudopotentials has been shown to produce considerable improvement in the band structure of many materials (e.g., ZnO) with a similar ionic character to CdF_2.[38] Implementation of this method,

which causes only a minor increasement in the computational burden, is underway.

V. CONCLUSIONS

In this work we have applied the PWPP method to calculate defect properties in CdF$_2$. The PWPP results for bulk CdF$_2$ were compared with the data from FP-LMTO calculations and excellent agreement was found. However, the band-gap value was notably underestimated in both calculations, which is a typical drawback in the DFT-LDA–based methods.

As a general observation, the formation energies found for most defects in the present study were found to be rather low. This suggests that the fluorite lattice in CdF$_2$ often contains high defect concentrations, which is in agreement with the experimental observations.[1]

Based on the defect calculations we identified three effective acceptors, V$_{Cd}$, F$_i$, and O$_F$. The results thus suggest that cation vacancies and oxygen impurities should also be considered as a source of donor compensation, in addition to the traditionally accepted assumption of compensation due to fluorine interstitials.[1] Fluorine vacancy was found to act as a donor when the Fermi level is below midgap, but electron trapping to the vacancy becomes favorable at higher Fermi-level positions.

The calculations performed for the trivalent dopant impurities verified the experimentally observed qualitative difference: In and Ga (as well as Al) were found to be stabilized in two charge states, while Y acted only as a shallow donor unable to trap extra electrons. However, the calculated properties of the isolated In and Ga defects in the shallow and deep state cannot explain the experimentally observed large difference between the thermal and optical ionization energies (Stokes shift) or the energy barrier between the ground-state configurations of the two states. Thus our results suggest further computational and experimental studies to be carried out in order to determine conclusively the true atomic geometries associated with the bistable behavior.

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