First-Principles Study of Structural Bistability in Ga- and In-Doped CdF_2

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We have identified the microscopic structures for the shallow and deep donor states of Ga and In donor impurities in CdF_2 through first-principles calculations. The deep state arises from a large [100]-axis atomic displacement of a donor. It has all the properties of a DX center; i.e., it is *negatively* charged and is separated from the metastable substitutional state by a large energy barrier that leads to persistent photoconductivity. [S0031-9007(98)08097-1]

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The phenomenon of bistability in which a dopant atom has both effective-mass hydrogenic ("shallow") and highly localized deep states is well known in many III-V and II-VI zinc blende semiconductors and has been extensively studied [1,2]. Surprisingly, the same type of bistability is observed in the very-large-band-gap fluorite structure compound CdF_2 when doped with Ga or In donor impurities [3–10]. Experimental data on the absence of a paramagnetic moment for the deep center [5], a quantum yield of two electrons per photon for the deep-shallow transition [6], the bimolecular nature of the shallow center thermal decay [4,6], self-compensation, a relatively large energy barrier between the shallow and deep states [6], a large Stokes shift between thermal and optical ionization energies, persistent photoconductivity [3], photoinduced lattice shrinkage [8], and recent positron annihilation measurements [11] showing an open-volume defect occurring upon DX center formation indicate that the deep center in In- and Ga-doped CdF_2 is a negative-U center with a large lattice relaxation. The bistability of Ga in CdF_2 has aroused great interest in this material as a new type of photorefractive medium [12,13]. Optical excitation of DX centers leads to a change in the refractive index that may have potential applications in high sensitivity optical recording and provides advantages as compared to a conventional nonlinear material such as $LiNbO_3$ [7].

The band gap of CdF_2 is about 7.8 eV and the bonding is highly ionic. The crystal structure is $O_h^5(Fm3m)$ cubic [14]. The F atoms, by themselves, make a simple cubic structure with a lattice constant of 2.677 Å. Cadmium atoms are located at the centers of alternate F cubes so that half the cubes are filled while the other half are empty (Fig. 1a). This leads to a structure in which each F atom is tetrahedrally bonded to four Cd atoms, while each Cd atom is bonded to *eight* F atoms. Despite its large band gap, CdF_2 can be doped n type by the incorporation of Ga or In. The shallow effective-mass state has a binding energy of about 0.1 eV and is metastable with respect to the deep donor DX state.

The DX center in zinc blende semiconductors arises mainly from large atomic displacements along antibonding directions, either at the impurity or at a nearest-neighbor cation [2,15]. In the fluorite structure, a similar lattice relaxation is inhibited by the eightfold coordination of a substitutional donor on a Cd site. Originally, Langer suggested a totally symmetric breathing mode relaxation for the deep state [3]. However, the relaxation energy and the energy barrier between the localized and the delocalized state (i.e., the electron capture barrier) were subsequently found not to be large enough to explain the high temperature persistent photoconductivity data [16]. A recent theoretical study did not reveal a more stable structure for the deep center either [17].

In this Letter we report on our investigations of the atomic structure of Al, Ga, In, and Sc donor impurities in CdF_2. We find a lattice instability for Ga and In (but not Al or Sc) atoms in CdF_2 when the donor atom undergoes a large displacement into an adjacent empty F cube. Hybridization between Cd and donor semicore d orbitals is found to be essential to the stabilization of the DX center. The structural bistability provides a microscopic explanation for persistent photoconductivity and other experimental data.

We use the first-principles pseudopotential method [18,19] based on the local density approximation (LDA) [20]. Norm-conserving nonlocal pseudopotentials [21] were generated by the scheme of Troullier and Martins [22], and a Kleinman-Bylander type of fully separable pseudopotentials was constructed [23]. We include semicore Ga-3d, Cd-4d, In-4d, and Sc-3d states as valence electrons. The inclusion of semicore d states is crucial in explaining the stability of the ground state DX configuration. An energy cutoff of 59 Ry for the plane-wave expansion was used. Total-energy minimization was achieved by an efficient Davidson-type self-consistent diagonalization method [24]. For the simulation of

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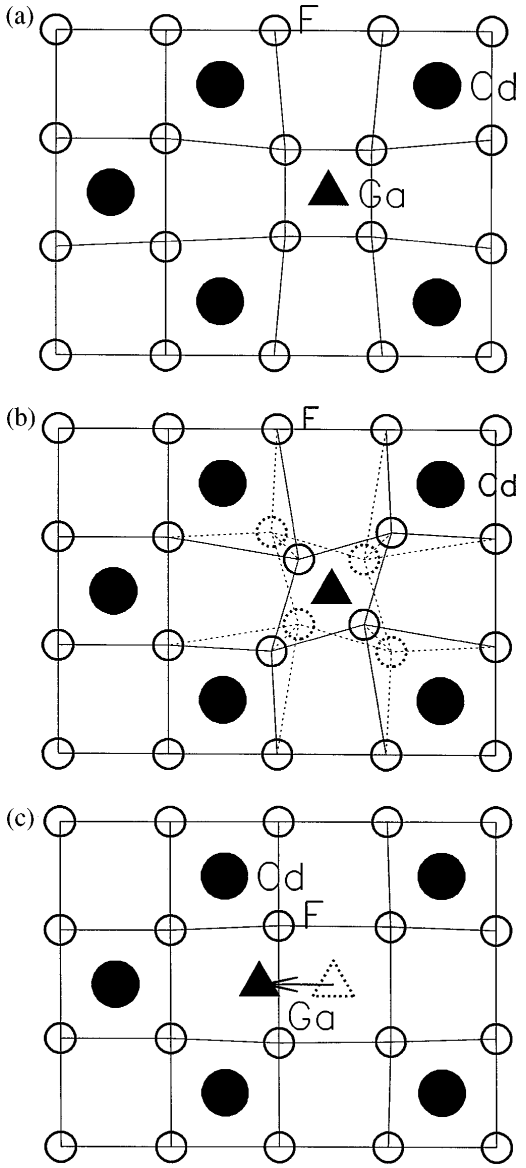

FIG. 1. In the ideal CdF_2 structure, the fluorine atoms form a simple cubic structure with the cations occupying the centers of alternate cubes. A schematic atomic structure for the substitutional donor state D^{+}_{sym} of CdF_2:Ga is shown in (a). The lattice relaxation is caused by the smaller ionic radius of Ga as compared to Cd. For Ga (but not In) the state in (a) is metastable with respect to the tetrahedrally distorted D_{T_d} state shown in (b). The dotted circles denote Cd atoms in a different plane. The lines joining the atoms are drawn to show the strains induced by the Ga impurity. The displacement of Ga to a neighboring empty cell as depicted in (c) results in the formation of a *DX* center.

defects, we used a bcc supercell with 48 atoms per cell and a $1/4(1,1,1)$ special k point for Brillouin zone summations [25].

The calculated lattice constant of 5.354 Å for CdF_2 is in good agreement with the experimental value of 5.356 Å and with other calculations [17,26]. The theoretically determined bulk modulus of 1.27 Mbar is also consistent with previous results of 1.2–1.3 Mbar [17]. The calculated band gap of 2.85 eV is significantly underestimated from the experimental value of 7.8 eV [26] because of the well-known deficiency of the LDA method in describing excited states.

For the positive substitutional donor state of Ga-doped CdF_2, the two structures with the lowest energies are shown in Figs. 1a and 1b. In the "conventional" high symmetry D^{+}_{sym} state shown in Fig. 1a, the neighboring eight F atoms are all equidistant from the donor impurity atom, with a dopant-F distance of 2.11 Å for Ga and 2.23 Å for In. These are about 5%–10% shorter than the ideal Cd-F separation of 2.318 Å. In the other structure $D^{+}_{T_d}$, shown in Fig. 1b, four F atoms surrounding impurity are relaxed inward while the remaining four F atoms are relaxed slightly outward in a tetrahedrally symmetric mode. In the $D^{+}_{T_d}$, the distances between Ga and F atoms are calculated to be 1.93 Å for the "short bonds" and 2.41 Å for the "long bonds." The $D^{+}_{T_d}$ structure is found to occur only for Ga where it is 0.1 eV more stable than the D^{+}_{sym} state. The small ionic radius of Ga compared to Cd results in a large lattice strain for the D^{+}_{sym} state which raises its energy. The strain is much smaller for In thereby making the D^{+}_{sym} state the lowest energy state. In the neutral charge state, the symmetric D^{0}_{sym} configuration is found to be most stable for both Ga and In. The D_{T_d} structure is unstable in either neutral or negative charge states.

The donor level of D^{+}_{sym} for Ga is found to be 0.22 eV *deeper* than that of $D^{+}_{T_d}$. The D^{+}_{sym} state can capture a free electron [4,7,10] and transform into a D^{0}_{sym}. A second electron capture is found to lead to a *metastable* D^{-}_{sym} state with large outward relaxations of the nearest-neighbor F atoms. For D^{-}_{sym}, the Ga-F and In-F separations are calculated to be 2.31 and 2.43 Å, respectively, about 0.2 Å larger than those for the D^{+}_{sym} state. The donor level of D^{-}_{sym} is about 0.5 eV (for In) and 0.26 eV (for Ga) deeper as compared to the corresponding ones for D^{+}_{sym}. We calculate the energy barrier between D^{-} and D^{+}_{sym} states to be less than 0.1 eV. These two states are not suitable candidates, therefore, for explaining persistent photoconductivity at a high temperature of 250 K.

The most important result of our study is the identification of the most stable state of donor impurities in CdF_2. In this deep donor *DX* state a donor impurity undergoes a large lattice relaxation along a [100] axis (Fig. 1c) and moves into a nearby empty cube of F atoms. The distortion leads to a larger contiguous open void consistent with positron annihilation results on *DX* center formation [11]. The displacements for Ga and In impurities are 1.82 and 1.84 Å, respectively, from the on-site positions, or about 70% of the F-cube dimension of 2.677 Å. The state with large lattice relaxation is found to be stable only in a negative charge state, indicating that Ga and In atoms in CdF_2 form negative-U systems. The *DX* state is highly localized as can be seen from Fig. 2a which shows the electron density contours of the highest occupied state (lying within the band gap of CdF_2) for Ga:*DX*. We find that

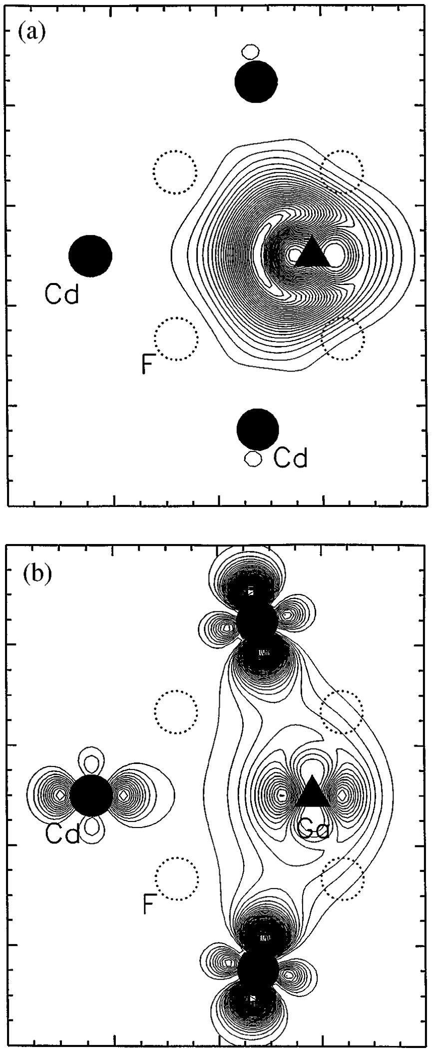

FIG. 2. Electronic charge density contours of (a) the deep donor Ga:DX state lying in the band gap and (b) an occupied localized state showing the interaction between Cd-d and Ga-d orbitals. The dotted circles denote F atoms on planes above and below the plane of Cd atoms.

when the charge state of the DX-like atomic configuration is changed to neutral or positive (e.g., through photoexcitation) the center becomes unstable and the donor atom returns to its "normal" substitutional position. This behavior is at the root of persistent photoconductivity and a quantum yield of two [6]. We have also examined the possibility of bistability for Sc and Al impurities for which no persistent photoconductivity has been seen and find that the state with large lattice relaxation is not stable for either of these impurities.

From the results of our calculations we suggest that d-d interactions between the d electrons of an impurity and those of host Cd atoms play an essential role in bistability. The Cd-d state lies about 4 eV below the valence-band maximum at the Γ point while the Ga-d and the hybridized d-d states lie, respectively, about 11 and 5.5 eV below it. As the electron density contours for this state in Fig. 2b show, the d-d interaction provides an attractive interaction between impurity and host Cd atoms which stabilizes the structure with large lattice relaxation. We believe this is the main reason why the DX center is not (theoretically) stable for impurities such as Al or Sc. Aluminum has no d electrons and Sc has only a single d electron. We also find that the DX state is unstable in CaF_2:Ga, and this can also be explained by the fact that *calcium* atoms have no d orbitals. To further demonstrate the importance of d states, we have tested the stabilization of the structure with large lattice relaxation by using the partial-core correction technique for creating the atomic pseudopotentials for Ga-d states [27]. Here, the d states are not explicitly included in the calculation and no d-d hybridization takes place. We find that the DX center is unstable in this case even though the effects of the d states on other valence electrons are partially included. This is consistent with previous results [17], where no bistability could be found when the Ga-3d states were treated by the partial-core correction method.

We have estimated the change in lattice constant with doping. Using a 42 atom supercell with one In atom per cell, we find the equilibrium lattice constants for DX^- and $D^+_{\rm sym}$ states to be 5.42 and 5.34 Å, respectively, giving an average value of 5.38 Å when they occur in equal densities. For the neutral $D^0_{\rm sym}$ state, the lattice constant is calculated to be 5.36 Å. The host lattice constant (with no impurities) is calculated to be 5.354 Å. The difference of 0.02 Å between the lattice constants for $D^0_{\rm sym}$ and $D^+_{\rm sym} + DX^-$ states indicates that a measurable lattice shrinkage should occur when DX centers are photoexcited and all In atoms are converted into $D^0_{\rm sym}$, or possibly into $D^+_{\rm sym}$ states. Our theoretical results are consistent with and explain the experimental data of Suchocki *et al.* on photoinduced lattice shrinkage resulting from deep to shallow center transitions in CdF_2:In. To estimate the energetics of DX center formation, we examine the following negative-U reaction for donor impurities in CdF_2,

$$2D^0 \rightarrow D^+ + DX^-, \tag{1}$$

where D represents a substitutional impurity, DX denotes its highly off-center geometry, and the superscripts denote charge states. As noted above the D^0 state has cubic symmetry whereas the D^+ state (for Ga) has tetrahedral symmetry. It is difficult to estimate the reaction energy reliably because of the limitations of the LDA approach in estimating the band gap. The main source of uncertainty is the underestimation of the energy of the $D^0_{\rm sym}$ state. In our calculations, we have used a "scissor operator" to correct the band gap and the total energy of this state. Recent quasiparticle calculations [28] on various semiconductors indicate that the deviations of the estimated energy levels between LDA and accurate GW calculations are proportional to the separation of the respective bands from the intrinsic Fermi energy. The energy band gap of CdF_2 is underestimated by 4.9 eV in our calculations. We apply the scissor operator shifting the conduction band edge upward by 2.4 eV and the valence band edge downward by 2.5 eV. With these corrections, the *DX* binding energy is estimated to be 0.25 eV for In and 0.70 eV for Ga. The experimental value of the binding energy is 0.25 eV for In:*DX* [3]. The greater stability of Ga:*DX* relative to In:*DX* is consistent with experimental data [4,9]. Coulombic interactions between DX^- and D^+ centers contribute to the stability of *DX* centers. At an effective doping level of $10^{18}/\mathrm{cm}^3$, the Madelung energy per *DX* center is estimated to be 0.08 eV for an ordered array that would maximize the Coulombic energy.

In the transition from the substitutional state into the *DX* state, the energy level of the donor state drops by 1.39 eV for Ga and 1.45 eV for In. This drop is the source of the large Stokes shift between the thermal and optical ionization energies of the *DX* center. The thermal ionization energy is a measure of the total-energy difference between the substitutional and *DX* states. Experimentally, the optical ionization energy for the In-*DX* is measured to be about 2 eV, and for Ga-*DX* it is larger than 3 eV [3].

We have calculated the energy barrier between the substitutional shallow donor state and the deep donor state in CdF_2. The barrier for electron capture into *DX* is experimentally estimated to be about 1 eV for Ga:*DX* and 0.1 eV for In:*DX* [3,4,6]. From our calculations, the energy barrier is about 1.0 eV for Ga, in agreement with experimental data [7].

In summary, we have identified the *DX* state of Ga and In donor impurities in CdF_2. The *DX* state has a structure with large lattice relaxation in which a donor impurity is displaced along a [100] axis into an empty cube of F atoms. The *DX* center is stable only in a negative charge state and hybridization between impurity-*d* and Cd-*d* electrons is found to play an indispensable role in stabilizing it. The proposed *DX* state explains the major experimental observations on the properties of deep centers in CdF_2 [3–6,9,10,29].

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