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A study of bistable (shallow–deep) defect systems in $\text{CdF}_2:\text{M}^{3+}$ (M: In, Ga)

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Abstract. The bistable (shallow–deep) defect systems associated with trivalent impurities (In, Ga, Y and Sc) in CdF_2 are studied. The equilibrium lattice relaxation around the defect and the wavefunction of the electron bound to the impurities are determined by minimizing the energy of the defects. The impurity–fluoride interatomic potentials determined using the electron-gas model of Gordon and Kim are used, and the defect electron is treated by the extended-ion method. In order to compare the deep and shallow states using the same discrete lattice model, a very large cluster of atoms is treated. Two groups of trivalent impurity centres are found. With In and Ga, there is a low, but clearly identified, potential barrier which separates the deep level from the shallow one. In Sc and Y, only a simple shallow level state is obtained. The analysis of the result shows that the difference is to be attributed to the short-range potential of the trivalent impurity centres. On the basis of present work, we predict that Ti^{3+} would exhibit similar bistable behaviour.

1. Introduction

Cadmium fluoride, CdF_2 , has the fluorite structure. It is composed of an FCC sublattice with a basis of three ions, Cd^{2+} at $(0, 0, 0)$ and two F^- s at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$, respectively. Thus the anions have tetrahedral coordination with the cations and form an octahedral arrangement about the body-centred interstitial site which is alternately occupied by a cation or empty. The lattice constant, a_0 , is 5.365 \AA (at 4.2 K) [1]. The pure crystal is highly insulating with a large band gap of about 7.6 eV and a resistivity of the order of $10^7 \Omega \text{ cm}^{-1}$ at room temperature [2]. CdF_2 can be doped with numerous trivalent dopants: Sc, Y and rare earth elements. In 1961 Kingsley and Prenner [3,4] discovered that when trivalent-metal-doped CdF_2 is annealed in cadmium-metal vapour, the insulating and transparent crystal becomes semiconducting and coloured, with the resistivity decreasing to $1 \Omega \text{ cm}^{-1}$. Such a conversion to the semiconducting state is attributed to the electrons which are liberated into the crystal as the interstitial fluorines diffuse to the surface to form a CdF_2 molecule with the Cd metal during the thermal annealing. At low dopant concentration, 0.1% or less, the dopant–dopant distance is much larger than the lattice constant. The lattice configuration consists of an isolated trivalent ion with an electron around it.

Most of the trivalent metals in CdF_2 produce stable shallow hydrogenic donor states [2]. However, In [5] and Ga [6] have shown unusual bistable behaviour. In room temperature absorption spectra of $\text{CdF}_2:\text{In}$ two strongly asymmetric bands are seen. One of these is in the visible light range (VIS), peaked at 3 eV, and another in the mid-infrared (mid-IR), at 0.2 eV. According to Langer *et al* [5], the 0.2 eV band indicates a weakly localized $\text{In}^{3+} + e^-$ state with a thermal ionization energy of 0.14 eV, while the 3 eV band indicates a strongly localized In^{2+} state with a thermal ionization energy of only 0.25 eV (all thermal energies

refer to 0 K), which means an enormous Stokes shift for the deeper state. The energy barrier separating the two states and leading to the metastable effects is about 0.17 eV. The absorption spectra of CdF₂:Ga has similar asymmetric bands peaked at 4 eV and 0.17 eV, respectively [6]. It is believed that Ga is a second bistable impurity centre in CdF₂, but details have not been published.

The most general framework for the theoretical description of bistability occurring in a dielectric medium has been developed by Toyozawa [7]. The main point of Toyozawa's model is that all the electron states in insulating solids are either strongly localized (self-trapping, S-type) or delocalized (free, F-type in Toyozawa's notation). In the case of an electron bound to a charged impurity, the electron always has a delocalized shallow state and in addition may have a localized deep minimum stabilized by combined action of the short-range impurity potential and the electron-phonon interaction. If the thermal ionization energies for these two states are in the same order, then they should be separated by a barrier. Bistability here is produced by the same centre in either highly localized or delocalized orbits. The discontinuity in localization results from the competition between the long-range (Coulombic) and short-range (electron-phonon coupling) forces [8].

Based on a simple configuration coordinate (CC) model, Langer [9] has presented a qualitative description of the lattice relaxation around the In³⁺ impurity centre in the shallow and deep levels. The CC used is an effective nearest-neighbour distance between the In³⁺ and the F⁻ ions. According to this model, a symmetric and local lattice collapse is expected in the shallower M³⁺ state due to a change of the core screening after ionization of the defect, while lattice in the deeper M²⁺ state is expected to be perturbed slightly from the perfect state.

In this paper we present a study of the structure of the M³⁺ impurity with an excited electron bound to it (with M = In, Ga, Sc and Y). The discrete structure of the lattice and detailed interaction between the excited electron and the impurity atom as well as the surrounding atoms of Cd²⁺ and F⁻ are explicitly taken into account within the approach of the extended-ion method. In order to compare the shallow and deep level states on the same footing, an identical treatment is applied to both states. The interaction of the electron with the surrounding atoms is represented as in a one-electron Hartree-Fock approach, while the lattice distortion and polarization are treated by the pair potentials and Mott-Littleton method [10]. The adiabatic potential energy is determined as a function of the CC chosen (the nearest-neighbour M³⁺-F⁻ distance) by minimizing the total energy of the defect system. The defect electron is represented by a linear combination of several floating Gaussian orbitals (FGO) which can represent both a diffuse and a compact state. As expected, one finds a strongly relaxed lattice environment associated with the shallow (diffuse electron wavefunction) level, and an almost undistorted lattice environment for the deep (compact state) level. The most significant result is that the short-range potential of the impurity atom core plays an important role in the appearance of the bistable state.

We will describe the methods used and the parameters fitted in section 2 and then present and discuss the results of our calculations in section 3.

2. Method of calculation

We calculate the total energy as a function of the positions of the ion shells. The total energy is taken to be the sum of the lattice energy, the energy of the defect electron and the polarization energy of the crystal. As our principal interest is in determining the structure, both electronic and lattice, of the defect system, we minimize the total energy with regard to the CC chosen. In this way we find either a bistable or simple stable defect level.

2.1. Energy terms

We consider the interaction of the defect with a cluster of about 1800 ions surrounding the impurity for calculating the electron energy and a cluster of about 500 ions for calculating the polarization energy. The cluster is chosen such that the energy converges in this region. We take the zero of energy to be the energy of the perfect lattice, the perfect lattice being all ions at their undisplaced positions and without the impurity.

The energy of the distorted lattice is made up of the electrostatic Coulomb energy and the short-range repulsive interaction of the ions. The Coulomb energy is calculated by interpolating the Madelung potential expressed as a series of cubic harmonics (up to the order of $L = 8$). For the short-range interactions we use a Born-Mayer potential,

$$V_{ij} = A_{ij} \exp(-r/\rho_{ij})$$

for cation-anion pairs and a Buckingham potential, which includes a van der Waals part,

$$V_{--} = A_{--} \exp(-r/\rho_{--}) - C_{--}/r^6$$

for anion-anion pairs, as the $F^- - F^-$ interaction is apparently attractive at large interionic separations [11, 12]. The short-range repulsion is obtained by summing the potentials over the nearest neighbours of the ion being moved. The method of determining the parameters A_{ij} , ρ_{ij} , A_{--} , ρ_{--} and C_{--} will be explained later.

To calculate the energy (and structure) of the defect electron, we use the extended-ion model, which is based on the one-electron Hartree-Fock approximation. Earlier a versatile version of this method [13-16] has been developed. The interaction of the electron with the deep core orbital of the lattice ions are treated with the ion-size parameters originally formulated by Bartram *et al* [17, 18] while the outer s, p and d orbitals are treated with interpolation formulae. The use of the floating 1s Gaussian orbital (FGO) makes it practical to evaluate various short-range terms (screened Coulomb, exchange and overlap integral) efficiently. It also gives us the required flexibility to place the Gaussian centres at appropriate positions in the crystal to best represent the defect electron states.

The impurity ion has a net charge of $+e$. This means that polarization effects will take on an important role in this problem, especially for the shallow state. Polarization, being complex to treat accurately, is often subject to various approximations. We calculate this energy by the Mott-Littleton method [10] including monopole-dipole and dipole-dipole terms. The polarizabilities employed are 1.8 \AA^3 for Cd^{+2} [19] and 1.04 \AA^3 for F^- [19]. The impurity polarizabilities used are 0.73, 0.55, 0.20, and 0.29 \AA^3 for In^{3+} , Y^{3+} , Ga^{3+} , and Sc^{3+} , respectively [20].

The polarization energy is calculated in terms of the Hartree-Fock picture [21] and given by:

$$E_{\text{pol}} = - \sum_i \mathbf{E}(\mathbf{r}_i) \cdot \boldsymbol{\mu}(\mathbf{r}_i)$$

$$\boldsymbol{\mu}(\mathbf{r}_i) = \alpha_i \mathbf{E}(\mathbf{r}_i)$$

$$\mathbf{E}(\mathbf{r}_i) = \mathbf{E}_1(\mathbf{r}_i) + \mathbf{E}_{\text{dip}}(\mathbf{r}_i) \quad (\text{for 500 ions})$$

where \mathbf{E}_1 is the electric field due to the defect electron and the ions which have been explicitly relaxed (about 50), \mathbf{E}_{dip} , the electric field due to the dipoles, $\boldsymbol{\mu}(\mathbf{r}_i)$, the dipole

moment induced on the ion at r_i . They are determined self-consistently by iteration. α_i is the polarizability of ion i .

We use two diffuse and one compact Gaussian bases centred on the impurity to represent the defect electron. The optimized Gaussian damping factors ($\alpha = 0.005$ for the shallow and $\alpha = 0.08$ for the deep levels) are chosen such that the lowest energies are obtained in either the shallow (delocalized) or deep (localized) state. The surrounding shells are relaxed up to the third.

2.2. Parameters fitting

(i) *Born-Mayer pair potentials.* A major difficulty with interionic potentials is that there are no crystal data for the impurity-fluorine potential. Gordon and Kim's semiclassical treatment [22], in which the interactions between pairs of rare gas atoms and alkali halide molecules were successfully calculated in the regions both of the attractive well and of the repulsive wall at shorter distances, enables one to readily determine the repulsive energy versus distance assuming that there is no bond formation.

It has been established experimentally that the binding in CdF_2 crystal is largely ionic. In such a crystal, the ions can be considered to be free ions for the purpose of calculating the repulsive interactions between constituents. First Cd^{2+} , F^- , In^{3+} , Y^{3+} , Ga^{3+} and Sc^{3+} charge distributions were calculated with the SCF (self-consistent field) program based on the Hartree-Fock-Roothan method. Then the interionic potentials were determined with Gordon-Kim approach and fitted to the form of the Born-Mayer potential for cation-cation pairs or the Buckingham potential for anion-anion pairs. Our results are presented in table 1.

Table 1. Born-Mayer pair potential coefficients for metal-fluorine short-range interaction $V = A \exp(-r/\rho)$, and fluorine-fluorine short-range interaction $V = A \exp(-r/\rho) - C/r^6$. A , ρ and C are in atomic units.

Coefficient	$\text{Cd}^{2+}-\text{F}^-$	$\text{In}^{3+}-\text{F}^-$	$\text{Y}^{3+}-\text{F}^-$	$\text{Ga}^{3+}-\text{F}^-$	$\text{Sc}^{3+}-\text{F}^-$	F^--F^-
A (a.u.)	257.76	263.30	230.86	133.17	159.16	61.90
ρ (a.u.)	0.4641	0.4583	0.4654	0.4709	0.4605	0.5202
C (a.u.)	—	—	—	—	—	23.771

As in reference [23] it is assumed that there exists a relation between A_i and the ionic radius of trivalent ions r_i ,

$$A_i \simeq (r_i + r_{\text{F}})^{-2} \exp[(r_i + r_{\text{F}})/\rho]$$

where r_{F} is the F^- ionic radius; ρ is a constant for these trivalent ions. From figure 1, one can see that the potential curves of $\text{In}^{3+}-\text{F}^-$ and $\text{Y}^{3+}-\text{F}^-$ are almost the same, and so are those of $\text{Ga}^{3+}-\text{F}^-$ and $\text{Sc}^{3+}-\text{F}^-$. From table 1, one can see that all the impurities have similar ρ values, and In^{3+} and Y^{3+} have about the same A_i since they are of about the same size, as do Ga^{3+} and Sc^{3+} . As a test the parameters of $\text{Cd}^{2+}-\text{F}^-$ and F^--F^- listed in table 1 were used to refit the elastic constants [1] of the crystal in terms of the relations given in [11] and [24] and were found to be in acceptable agreement.

(ii) *Extended-ion parameters.* In the present system, there are several ions whose parameters have never been evaluated before. They are Cd^{2+} , In^{3+} , Ga^{3+} , Y^{3+} and Sc^{3+} . The deep core parameters and extended-ion parameters are determined in the same way as developed by Song *et al* [25]. There are three kinds of terms for the most outer-shell

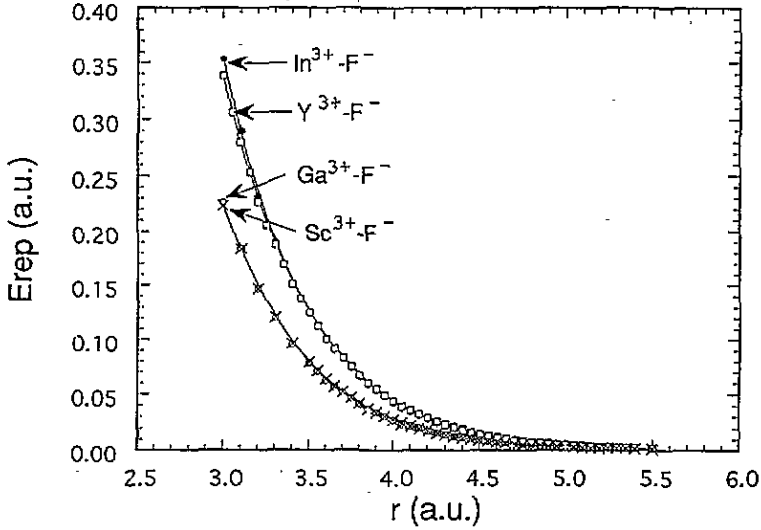


Figure 1. Interionic potentials of $M^{3+}-F^-$ ($M = \text{In, Ga, Y}$ and Sc) calculated with the electron gas model of Gordon and Kim [22]. ●: $\text{In}^{3+}-\text{F}^-$; ○: $\text{Ga}^{3+}-\text{F}^-$; □: $\text{Y}^{3+}-\text{F}^-$; ×: $\text{Sc}^{3+}-\text{F}^-$.

electrons of ions: overlap integral, screened Coulomb and exchange potentials. In previous works, only s and p shells needed to be included in the outershells. However, in this work the 4d shell is the highest occupied energy level for Cd^{2+} and In^{3+} , and 3d for Ga^{3+} . We have to calculate the three terms of the d shells exactly. Analytical expressions are derived for calculating the overlap and the screened Coulomb terms by using wavefunctions in Gaussian bases, which have been fitted from our own SCF calculations. Instead of the exact expression which is too complex for a d orbital, the Slater approximation,

$$E_{\text{ex}} \approx 3(3/8\pi)^{1/3}[\rho(r)]^{1/3} \quad (\text{in Hartree})$$

is employed to calculate the exchange energy of d orbital. Here $\rho(r)$ is the charge density.

In order to test the quality of the present extended-ion approximation we have evaluated the energies of the three lowest excited states for Cd^{2+} , In^{3+} , Y^{3+} , Ga^{3+} and Sc^{3+} by using about eight FGO bases. Results are listed in table 2 and are compared with experimental data. There is quite good agreement, and it is certainly satisfactory to study defects in solids.

3. Results and discussion

In this work we have studied the structure of the impurity states in $\text{CdF}_2:\text{M}^{3+}$ (where $M = \text{In, Ga, Sc}$ and Y). We have found a bistable defect system for In and Ga and a single shallow level system for Sc and Y in agreement with experimental observations. The calculated adiabatic potential energy is shown for the four impurities in figures 2 and 3. Here the CC is the nearest $\text{M}^{3+}-\text{F}^-$ distance. We will discuss in the following the characteristic aspects of both the deep and shallow levels, and analyse the mechanism which leads to either the bistable or the single-level system.

In all four M^{3+} studies, a shallow level with a very diffuse wavefunction (the Gaussian damping factor $\alpha = 0.005$ (in a.u.) of $\exp(-\alpha r^2)$ has the largest weight) appears.

Table 2. Free ion levels (in eV). Calculated values are from the present method.

$\text{Cd}^{2+}[\text{Kr}]4d^{10}$	State	5s	5p	6s
	Exp. (eV)	-16.90	-11.12	-6.61
	Calc. (eV)	-16.46	-11.21	-6.20
$\text{In}^{3+}[\text{Kr}]4d^{10}$	State	5s	5p	6s
	Exp. (eV)	-28.03	-20.40	-12.30
	Calc. (eV)	-28.06	-20.25	-11.69
$\text{Ga}^{3+}[\text{Ar}]3d^{10}$	State	4s	4p	5s
	Exp. (eV)	-30.70	-22.41	-13.25
	Calc. (eV)	-30.91	-22.74	-12.52
$\text{Y}^{3+}[\text{Kr}]4p^6$	State	4d	5s	5p
	Exp. (eV)	-20.5	-19.57	-15.17
	Calc. (eV)	^a	-19.53	-14.92
$\text{Sc}^{3+}[\text{Ar}]3p^6$	State	3d	4s	4p
	Exp. (eV)	-24.75	-21.58	-16.99
	Calc. (eV)	^a	-21.20	-16.57

^a Bases ($\alpha \geq 0.3$) which are too compact for the method [16] employed here are needed to calculate 4d(Y) and 3d(Sc) levels.

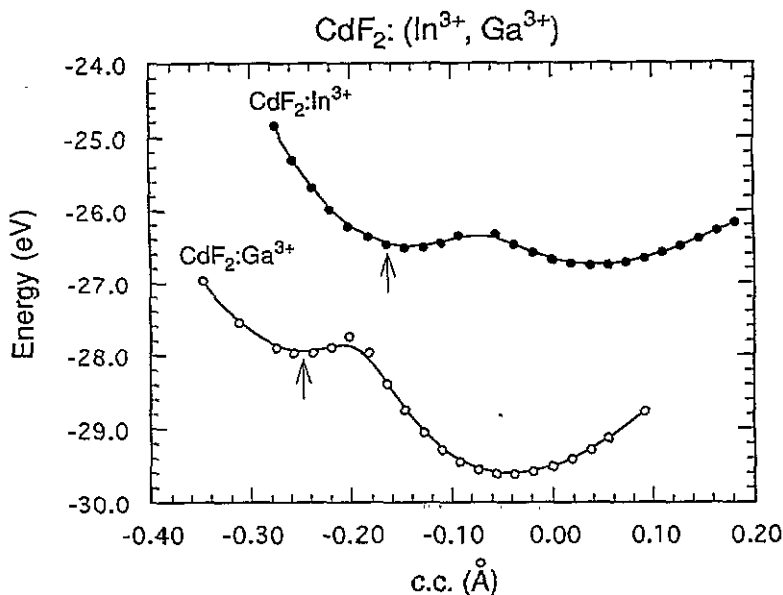


Figure 2. Potential energy curve for $\text{CdF}_2:(\text{In}^{3+}, \text{Ga}^{3+})$. Total energy of the system as a function of nearest $\text{M}^{3+}-\text{F}^-$ distance (cc). The arrows indicate the ionization limit. By measuring the distortion from this point, it can be seen that a large relaxation is associated with the deep level.

Ordinarily, one represents such a level within the effective mass approximation (EMA). As we intended to compare the two levels within the same approach with details of the structure, we had to apply the same extended-ion method. With the shallow state, a large number of

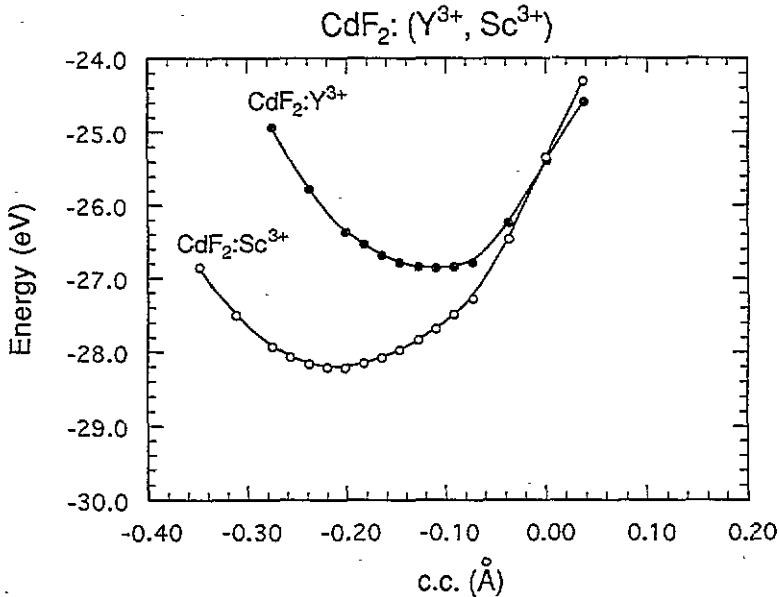


Figure 3. Potential energy curve for $\text{CdF}_2:(\text{Y}^{3+}, \text{Sc}^{3+})$. Total energy of the system as a function of nearest $\text{M}^{3+}-\text{F}^-$ distance (cc).

atoms which surround the trivalent impurity are subject to partly unscreened Coulomb field. This has been treated, as described above by the Mott-Littleton method. Typically, we found the electronic polarization energy of about -1.1 eV. The lattice 'collapses' toward the impurity atom by about 0.15 Å (for the first shell F^-) due to the Coulomb attraction.

We noted some difference from the picture given by the conventional EMA. For example, we do not notice a simple chemical shift among the four impurities. However, there is some affinity between In and Y, and also between Ga and Sc. This can be seen in figures 2 and 3. There are factors which go beyond the conventional EMA in the present study. First there is the pair potential for $\text{M}^{3+}-\text{F}^-$ which we determined separately for each of the four dopant atoms with the Gordon-Kim approach. The short-range extended-ion parameters, which is represented by the central cell correction in EMA, and the electronic polarization are also different. Although the shallow level wavefunctions are diffuse in all cases, they differ in detail when the eigenvectors are examined.

With In and Ga replacing a host Cd atom, we obtained beside the shallow level, one deeper level with a compact wavefunction (also s-like). Corresponding to the deep level, the lattice relaxation is almost negligible. The lattice responds as it would to a In^{2+} (or Ga^{2+}) ion. The electronic polarization, which is treated by the Mott-Littleton approach, is also quite small, ~ -0.1 eV. The electronic energy of the s-like electron is about -8 eV which is to be compared with the -28 eV in the free atomic state. This rise in energy is principally due to the lattice Madelung energy (which is ~ 20 eV at the cation site). Table 3 shows some characteristic data, such as the spatial extension of the electron wavefunction (α of $\exp(-\alpha r^2)$ with the largest weight), the relaxation of the $\text{M}^{3+}-\text{F}^-$ separation, electronic polarization energy, the lattice distortion energy and the total energy of the system, corresponding to the shallow and deep levels in $\text{CdF}_2:\text{In}$, Ga.

A potential barrier between the shallow and deep levels is seen in both $\text{CdF}_2:\text{In}$ and $\text{CdF}_2:\text{Ga}$. It seems rather low, although it is not possible to attach great confidence to the

Table 3. Characteristic data of the adiabatic potential energy of the bistable system $\text{CdF}_2:\text{M}^{3+}$ ($\text{M} = \text{In}, \text{Ga}$). S for shallow and D for deep.

	cc	(Å)	Energy Terms (eV)					Eigenvector $\{C_i\}$ of: $\sum C_i e^{-\alpha_i r^2}$ $\alpha_1 = 0.005 \alpha_2 = 0.08$	
			coul.	rep.	elec.	pol.	total	C_1	C_2
In	S	-0.16	-24.11	1.397	-2.720	-1.079	-26.52	1.348	0.306
	D	0.04	-19.12	0.165	-7.715	-0.091	-26.76	-0.263	-1.632
Ga	S	-0.28	-25.32	1.480	-2.720	-1.410	-27.97	1.368	0.227
	D	-0.04	-20.36	0.007	-9.069	-0.190	-29.61	-0.380	-1.980

value obtained (~ 0.1 eV). On the other hand, the energy difference between the shallow and deep levels is found to be about 0.2 eV in $\text{CdF}_2:\text{In}$ from figure 2. This value is in qualitative agreement with the one reported in [5]: 0.11 eV. In the case of $\text{CdF}_2:\text{Ga}$, there is no reported experimental value available. However, the energy difference obtained from figure 2 seems too large. Although we were successful in reproducing the observed trend in the four trivalent impurities regarding the presence of deep levels, our predicted energy difference between the shallow and deep levels is not in quantitative agreement with the experimental data. This may be attributable at least in part to the difficulty of studying a shallow centre with the atomistic discrete defect approach.

We now discuss the factors which contribute to the appearance of the deep level, such as in In and Ga, but not in Sc and Y. It seems reasonable to associate the deep level with the highest s-like level of the free M^{2+} ion. From table 2, these are the $5s(\text{In}^{2+})$, $4s(\text{Ga}^{2+})$, $5s(\text{Y}^{2+})$ and $4s(\text{Sc}^{2+})$ levels. For the first two, In and Ga, the binding energies are 28.0 eV and 30.7 eV, respectively [26]. As a rough estimate, these values can be reduced by 20.3 eV with the repulsive Madelung potential of the ionic lattice. The resulting energies can be compared to the purely electronic energies of the deep level which are ($-$) 7.7 eV and ($-$) 9.1 eV, respectively. Applying the same argument to the cases of Sc and Y, one finds from table 2 that the electron energies in the lattice would be about zero. It seems reasonable therefore to argue that the deep level does not show up in the cases of Sc and Y due to this internal difference of the two groups of trivalent atoms. Based on the argument just shown, we predict that Tl^{3+} would show a deep level, besides the shallow donor level. Indeed, the binding energy of the 6s electron in free Tl^{2+} is about 29.8 eV, close to those in In and Ga. After correcting for the Madelung potential, a deep level would result comparable to that observed in In and Ga. As we will discuss below, this can be interpreted as the effect of the short-range potential produced by the impurity atom in the context of the extrinsic self-trapping, proposed by Shinozuka and Toyozawa [7].

According to the fundamental studies of Shinozuka and Toyozawa [7], the self-trapping of carriers in a deformable medium of 3D is characterized with the existence of both free (F) and self-trapped (S) states which are separated by a potential barrier. In the present system involving an impurity centre, the F and S states refer to diffuse (EMA) and very compact states. Toyozawa named such cases as the 'extrinsic self-trapping' to distinguish it from self-trapping in a pure crystal. The basic idea is that a constructive addition of both the short-range impurity potential and the electron-phonon interaction leads to the realization of a deep state in a system where such a deep state would not occur with only one element at a time. Due to the charged nature of the impurity, there is a stronger lattice relaxation in the shallow (F) state and practically none for the deep (S) state. We consider this reversal

of the lattice relaxation not essential in considering the present system as an example of the extrinsic self-trapping, as did also Dmochowski *et al* [5].

Using the effective mass approximation, combined with the Fröhlich Hamiltonian to represent the electron–phonon coupling, Bednarek and Adamowski have studied the In and Y centres in CdF₂ [27, 28]. They fitted certain parameters, such as the central cell correction and the non-parabolicity of the band, to experimental data of donor ionization energy. They plotted the energy of the system as a function of the decay constant of the exponential wavefunction of the donor state. They obtained two minima for In and only one for Y. Although there are some similar aspects between this work and the present work, it is not clear in the continuum work which factor determines the bistable behaviour, and therefore a direct comparison is not straightforward.

We mention here briefly other well-known bistable defect systems. The DX centres [9] observed with various donors in III–IV semiconductors (e.s. AlGaAs or GaAs under pressure) and the E2L centres [29] in GaAs are such examples. It is believed that most donors in III–IV compounds exhibit the usual shallow donor level and also a deeper level, separated by a small potential barrier. Recent first-principles calculations on Si in GaAs, based on the super-cell (or large unit cell) method [30], show that in the charged state (D⁻), the deeper level is associated with a large lattice distortion of lowered symmetry. When the highly covalent system is compared with the present system of trivalent impurity centres in CdF₂, some differences appear. In the present work, we noted that both the shallow and deep levels occupy the same symmetry. There is no pseudo-Jahn–Teller effect involved with the deeper level, as in the case with the DX centre.

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