

Donor impurities and DX centers in the ionic semiconductor CdF_2 : Influence of covalency

D. E. Onopko and A. I. Ryskin

S. I. Vavilov State Optical Institute, 199034, St. Petersburg, Russia

(Received 27 September 1999)

Analysis of the electronic structure of MF_8^{6-} complexes ($M = Al, Ga, In, Sc, Y$) in the predominantly ionic semiconductor CdF_2 shows a significant increase of covalency of the chemical bond for Al, Ga, and In impurity centers as compared with a regular crystal, i.e., with a CdF_8^{6-} complex, and an increase of the ionicity of the bond for Sc and Y. As a result, an essential noncenterosymmetrical distortion of the center occurs possible for the former centers, when capturing an extra electron by the center. Two additional prerequisites for the formation of such a (DX) state of the center are the presence of both $d-d$ interactions of the impurity ion and cations and of filled atomic-type shells at the single-ionized impurity ion. The former condition is not realized for Al. For Sc and Y both breaking of the latter condition and increase of ionicity of the bond at doping inhibit formation of DX centers; these ions in CdF_2 produce only the shallow donor levels.

Recently, semiconductor CdF_2 crystals doped with column-III dopants have attracted growing interest due to both scientific and technological reasons. This crystal has the fluorite structure $O_h^5(Fm\bar{3}m)$, which may be presented as a simple cubic lattice of anions; cations occupy the body-centered positions in alternating cubes. Highly ionic CdF_2 is a dielectric with a 7.8-eV band gap and remains such at doping by column-III dopants. Compensation of donors is realized by interstitial F^- ions. Annealing of such crystals in reducing atmospheres of hydrogen or metal vapors (an additive coloration of the crystals) results in the flow of the fluorine ions from the bulk of the crystal, the charge compensation being provided by electrons coming from the surface and supplied by a reducing agent. These electrons localize at hydrogenic orbitals centered at impurity atoms (e_{hydr}) or in the conduction band and convert the crystal into a semiconducting state.¹ The “shallow” hydrogenic state has a binding energy of about 0.1 eV well above binding energies of donors in conventional semiconductors.

For the two column-III impurities, Ga and In the hydrogenic donor state is metastable, being separated from the ground (“deep”) state by a potential barrier due to large lattice relaxation in the deep state.²⁻⁶ Recently, it was shown that in this state *two* electrons are localized at the impurity.⁷⁻¹⁰ The metastable state becomes populated through the photoionization of the ground state and persists for a very long time at a sufficiently low temperature as does the photoinduced conductivity of the crystal (the persistent photo-conductivity). The change in the state of the center is accompanied by a noticeable change of the refractive index of the crystal allowing the use of CdF_2 crystals doped with Ga and In for writing reversible phase holograms that can be used in both data storage systems and real-time holography devices.¹¹⁻¹⁵

Thus, most column-III dopants M in additively colored CdF_2 crystals form two states, shallow donor states ($M^{3+} + e_{hydr}$) and ionized, electrically and optically “silent” states M^{3+} , whereas for bistable dopants a two-electron deep state is also present. One may consider this state as a single-valence state of the impurity Ga^{1+}/In^{1+} . Ga and In centers in CdF_2 are analogues of DX centers in conventional III-V

and II-VI semiconductors with essential covalency of the bond. They show typical features such as absence of a magnetic moment in the ground state, large Stokes shift, i.e., difference between optical and thermal ionization energy for this state, persistent photoconductivity, etc.

The structure of Ga/In centers in CdF_2 was considered in Refs. 16 and 17 using various versions of the first-principle pseudopotential technique based on the local-density approximation. It was found that the ground state of these ions, in fact, contains two electrons, however, it was impossible to establish such important characteristics of the centers as the large Stokes shifts and the barriers separating two states of the centers.¹⁶ Only the inclusion of d orbitals of the cation in the set of valence states of the crystal and taking account of the $d-d$ interactions of the impurity ion and cations leads to agreement between the experimental and calculated parameters of the centers.¹⁷

One should note that the use of such a general technique for calculation of the electronic and microscopic structure of the impurity centers does not provide a physical explanation of why a defect has exactly this structure. For this reason such calculations should be reinforced by an analysis based on a cluster approximation, which allows direct estimation of the change in the nature of the chemical bond with doping and the influence of this change on restructuring of the impurity center. Such a direct though semiquantitative approach proved useful for studies of DX centers in conventional semiconductors.¹⁸ Here, such analysis is done for column-III impurities Al, Ga, In (B subcolumn, electronic configuration $[P]ns^2(n+1)p$; P is configuration of the preceding noble-gas atom) and Sc, Y (Sc subcolumn, electronic configuration $[P]nd^1(n+1)s^2$) in CdF_2 .

For the predominantly ionic CdF_2 crystal a good approximation for the magnitudes of charges of ions are $2e$ for Cd and $-e$ for F. In the calculations of the electronic structure of CdF_8^{6-} and MF_8^{6-} ($M = Al, Ga, In, Sc, Y$) clusters we use the self-consistent X_α method of scattered waves.¹⁹ In this technique, the space occupied by a molecule or cluster is divided into three volume regions: (i) atomic spheres, i.e., volumes inside spheres surrounding every atom, (ii) interatomic volume, i.e., the volume between atomic spheres and

a large sphere, which envelopes all atomic spheres, and (iii) external volume, i.e., a volume outside the large sphere. All spheres are chosen in order that they maximally touch each other. In any of these volumes, an individual model potential is used corresponding to its manner of decomposition of the molecular orbitals. A noticeable presence of the orbital charge in atomic spheres and in inter-atomic volume testifies to the covalent nature of the bonding between the corresponding atoms realized by this orbital. Breaking of one of these two conditions shows the predominantly ionic nature of this orbital.

Interatomic distances are supposed to be equal for all these clusters.

In Table I the distribution of the charge between the three above volumes is given for upper valence levels of the CdF_8^{6-} , GaF_8^{6-} , InF_8^{6-} , ScF_8^{6-} , and YF_8^{6-} clusters. For the CdF_8^{6-} cluster the relatively small covalent component is mainly due to the interaction between 5s Cd states with the 2p states of F within $1a_{1g}$ -crystal orbital and, in lesser extent, to the $5p(\text{Cd})$ - $2p(\text{F})$ interaction ($1t_{1u}$ -crystal orbital). The 4d and 5d states of Cd, participating in e_g and t_{2g} orbitals make additional, though insignificant contribution to the covalency.

Substitution of Al, Ga, and In for Cd results in a substantial increase of the covalency of the chemical bond in the respective clusters, whereas doping by transition metals of this column (Sc, Y) increases the ionicity of the bond. Covalency is larger for Ga as compared with Al and In, whereas ionicity increases with atomic number. All these regularities are determined by the change of energies of the valence s and p orbitals of the dopants relative to Cd orbitals or, in more exact wording, by the change in the electronegativity of these atoms. In any case, the antibonding (nonbonding) $2a_{1g}$ state is occupied by only one electron (an additional valence electron of the impurity atom). This state is essentially more localized for Al, Ga, In as compared with Sc and Y.

The formation of DX centers in III-V and II-VI semiconductors is governed by covalency, which determines the orientation of interatomic bonds.^{20,21} Let us consider one possible way that the DX centers could restructure. Two electrons of a negatively charged donor center, which are superfluous for the chemical bond of the tetrahedral cluster (the lone-pair electrons), are localized at one of four bonds of the impurity with ligands. This bond breaks as a result and the Coulombic repulsion of two lone pairs (one at the impurity and the second at the ligand) causes a displacement of the impurity atom towards the nearest interstitial. Thus, the essentially nonuniform distribution of the charge of the breaking bond is the origin of the lowering the symmetry at the restructuring of the center.

With reference to CdF_2 , such restructuring may occur only for atoms of the B subcolumn of the column III. A comparison of distribution of the charge for the main bonding orbitals of doped III-V:IV, II-VI:III and CdF_2 :Al, CdF_2 :Ga, CdF_2 :In shows that the covalent contribution for CdF_2 :Ga is essential though it is smaller than in conventional semiconductors with DX centers. Even for CdF_2 :Al and CdF_2 :In, this component may not be neglected. Thus, the proposal for the covalent mechanism of DX center formation in CdF_2 crystals seems reasonable.

As is the case for bistable centers in conventional semiconductors, the extra two electrons of the negatively charged impurity center, superfluous for chemical bond formation, fill the corresponding antibonding orbital, which results in the break of the bonding of the central atom with one or several ligands. The character of the center's restructuring is determined by the localization of this orbital. Two main variants of the restructuring are possible. One should note that in a CdF_2 crystal, of the two electrons in every Cd-F bond, 0.25 electron is supplied by the cation and 1.75 electron by the anion. Thus, if one proposes that the antibonding orbital will be localized at bonds with four F atoms disposed at one side of the fluorine cube then, the bond of the impurity with these four ligands breaks and under the action of the Coulombic repulsion, the impurity will be pushed out along the corresponding four-fold axis into a neighboring (empty) cube [Fig. 1(a)]. Reconstructed in such a manner the defect has tetragonal symmetry. On the other hand, the localization of the antibonding orbital at one of the metal-F bonds could promote the trigonal distortion of the center, pushing out the corresponding ligand towards the interstitial void [Fig. 1(b)]. Since a single electron of the cation participates in four bonds and with allowance for the weak orientation of bonds in CdF_2 (a consequence of the high ionicity of this compound) and the unfavorable energy of an F^- ion located inside a fluorine cube, the first variant of the restructuring seems more preferable. Just this type of negatively charged center restructuring in CdF_2 :Ga/In was found in Ref. 17. Its existence was supported by recent positron annihilation studies²² showing an open-volume defect, i.e., essentially, the presence of the cation vacancy in the structure of the DX center.

In principle, such a mechanism may be applied not only to Ga and In but also to Al. For this atom, however, restructuring of the center does not lead to a sufficiently stable state (see below).

Initially, it was supposed that the ground state of the Ga/In center in CdF_2 contains a single electron, i.e., it corresponds to $\text{Ga}^{2+}/\text{In}^{2+}$ valence state of the impurity.^{3-6,23,24} The motivation for this proposal was the high ionicity of the crystal (see Ref. 24). At the shallow-to-deep state transition, at which the electron passes from shallow hydrogenic to deep atomic-like orbital, such a center undergoes the totally-symmetric relaxation of the lattice since the occurrence of a single electron at an antibonding (nonbonding) a_{1g} orbital does not create the necessary prerequisites for distortion of the impurity complex with its lowered symmetry. It is evident from the above consideration that this concept, which does not take into account an essential increase of covalency at doping by these ions, does not correspond to reality.

It was stated above that the effect of covalency is larger for CdF_2 :Ga than for CdF_2 :In. The relaxation of the interatomic distances increases further the covalency of the Ga dopant. Ionic radii of Cd^{2+} , Ga^{3+} , and In^{3+} in fluoride compounds with 8-fold coordination are respectively 1.24, 0.78, and 1.04 Å.²⁵ Thus, introduction of Ga results in essentially a larger compression of the lattice as compared with In.²⁶

The influence of the covalency induces for Ga much larger energy changes as compared with In. In fact, the binding energy of the Ga deep state equals 0.70 eV (calculated in Ref. 17) as compared with 0.25 eV (experiment,²⁷

TABLE I. Distribution of the charge at the upper valence orbitals of the AB_8^{6-} cluster for CdF_2 , $CdF_2:Ga$, $CdF_2:In$, $CdF_2:Sc$, and $CdF_2:Y$ crystals ($A = Cd, Ga, In, Sc, \text{ and } Y$, respectively, $B = F$).

Crystal	Γ	$-\epsilon, Ry$	q_A	q_B	q_{II}	q_{III}
CdF_2	$2a_{1g}$	0.056				
	$3t_{2g}$	0.372	0.094	0.800	0.060	0.045
	$1e_u$	0.379	0.0	0.903	0.097	0.0
	$1a_{2u}$	0.391	0.011	0.871	0.062	0.056
	$1t_{1g}$	0.391	0.003	0.882	0.114	0.001
	$2t_{1u}$	0.414	0.008	0.831	0.120	0.041
	$2t_{2g}$	0.436	0.033	0.814	0.149	0.004
	$1t_{2u}$	0.468	0.002	0.791	0.181	0.026
	$2e_g$	0.478	0.066	0.715	0.192	0.026
	$1t_{1u}$	0.482	0.034	0.781	0.162	0.023
	$1a_{1g}$	0.536	0.115	0.702	0.163	0.020
	$1e_g(4dCd)$	0.707	0.909	0.037	0.053	0.001
	$1t_{2g}(4dCd)$	0.717	0.868	0.093	0.037	0.002
$CdF_2:Ga$	$3a_{1g}$	0.028				
	$2a_{1g}$	0.138	0.364	0.299	0.132	0.205
	$1e_u$	0.400	0.0	0.904	0.096	0.0
	$1a_{2u}$	0.410	0.010	0.875	0.061	0.054
	$1t_{1g}$	0.412	0.004	0.881	0.113	0.002
	$3t_{2g}$	0.420	0.009	0.860	0.084	0.047
	$2t_{1u}$	0.436	0.008	0.832	0.124	0.036
	$2t_{2g}$	0.472	0.011	0.842	0.147	0.0
	$1t_{2u}$	0.487	0.002	0.795	0.178	0.025
	$2e_g$	0.513	0.006	0.751	0.217	0.026
	$1t_{1u}$	0.516	0.060	0.757	0.161	0.022
	$1a_{1g}$	0.630	0.295	0.521	0.172	0.012
	$1t_{2g}(3dGa)$	1.315	0.991	0.006	0.003	0.0
$1e_g(3dGa)$	1.316	0.995	0.0	0.005	0.0	
$CdF_2:In$	$3a_{1g}$	0.011				
	$2a_{1g}$	0.119	0.144	0.128	0.244	0.484
	$1e_u$	0.459	0.0	0.903	0.097	0.0
	$1a_{2u}$	0.471	0.012	0.876	0.062	0.050
	$1t_{1g}$	0.471	0.002	0.885	0.112	0.001
	$3t_{2g}$	0.472	0.014	0.864	0.078	0.044
	$2t_{1u}$	0.495	0.008	0.836	0.123	0.033
	$2t_{2g}$	0.527	0.012	0.839	0.149	0.0
	$1t_{2u}$	0.547	0.003	0.796	0.178	0.023
	$2e_g$	0.569	0.007	0.755	0.214	0.024
	$1t_{1u}$	0.573	0.051	0.766	0.162	0.021
	$1a_{1g}$	0.662	0.202	0.606	0.178	0.014
	$1t_{2g}(4dIn)$	1.366	0.971	0.018	0.011	0.0
$1e_g(4dIn)$	1.370	0.983	0.001	0.016	0.0	
$CdF_2:Sc$	$3t_{1u}$	0.052				
	$2a_{1g}$	0.106	0.008	0.028	0.251	0.713
	$1e_u$	0.491	0.0	0.904	0.096	0.0
	$1a_{2u}$	0.500	0.011	0.879	0.061	0.049
	$1t_{1g}$	0.502	0.003	0.884	0.112	0.001
	$2t_{2g}$	0.520	0.024	0.839	0.103	0.034
	$2t_{1u}$	0.521	0.008	0.847	0.109	0.036
	$1t_{2u}$	0.577	0.002	0.798	0.177	0.023
	$1t_{1u}$	0.578	0.023	0.801	0.157	0.019
	$1t_{2g}$	0.585	0.076	0.786	0.134	0.004
	$1a_{1g}$	0.609	0.061	0.775	0.144	0.020
	$1e_g$	0.612	0.028	0.728	0.222	0.022
	$CdF_2:Y$	$3t_{1u}$	0.055			

TABLE I. (Continued).

Crystal	Γ	$-\epsilon, \text{Ry}$	q_A	q_B	q_{II}	q_{III}
	$2a_{1g}$	0.110	0.004	0.027	0.265	0.704
	$1e_u$	0.501	0.0	0.903	0.097	0.0
	$1a_{2u}$	0.513	0.014	0.876	0.062	0.048
	$1t_{1g}$	0.513	0.004	0.881	0.114	0.001
	$2t_{2g}$	0.526	0.014	0.851	0.095	0.040
	$2t_{1u}$	0.530	0.016	0.845	0.104	0.035
	$1t_{2u}$	0.572	0.018	0.805	0.161	0.016
	$1t_{1u}$	0.589	0.003	0.794	0.180	0.023
	$1t_{2g}$	0.598	0.055	0.801	0.140	0.004
	$1a_{1g}$	0.598	0.042	0.803	0.133	0.022
	$1e_g$	0.625	0.021	0.729	0.228	0.022

Note to Table I. Here, Γ is irreducible representation, by which transforms the corresponding orbital; ϵ is energy of the orbital; q_A , q_B , q_{II} , and q_{III} are portion of an orbital charge in the central atomic sphere of the cluster, in ligand spheres, in inter-atomic volume, and in external volume, respectively (for any orbital $\sum q_i = 1$; $i = \text{I, II, III}$, $q_I = q_A + q_B$).

calculated¹⁷) for the In deep state. The Stokes shifts for Ga and In are ~ 3 and ~ 2 eV, respectively,²⁴ whereas the barrier heights are ~ 1 eV for Ga and 0.1 eV for In.⁷

Covalency and "size" effects also influence the positively charged (ionized) Ga center. Unlike the In ionized center, Ga center has two states: one with cubic symmetry (the metastable state) and tetrahedral symmetry (the ground

state).¹⁷ The latter is 0.1 eV more stable than the former. The tetrahedrally distorted ground state of Ga occurs because of the tendency of B subcolumn atoms to pass into an sp^3 -hybridized state. In fact, the bond of ionized Ga atom with eight F atoms involves 16 electrons. Due to above tendency, electron density at four Ga-F bonds increases and corresponding F atoms approach Ga, whereas the decrease of the electron density at other four bonds results in the repulsion of four atoms from Ga (Fig. 2). The relatively small size of Ga is favorable for such a restructuring of the center. Due to smaller covalency and larger size of the impurity ion, the restructuring was not found for the ionized In center.

Accordingly to Ref. 17, an important factor for stabilization of the DX center in CdF_2 is the d - d interactions of the impurity with nearest Cd atoms. Due to the absence of d electrons in Al, this impurity does not form DX centers in CdF_2 . However, an interaction of filled d -shells of Ga/In and Cd atoms without noticeable addition of some excited states does not allow essential increase of energy of the bond. Thus, admixing of these states is necessary. One may propose that among these states excited d -states of impurity atom and cations will dominate.

Other than Ga and In, only Tl could be a candidate for

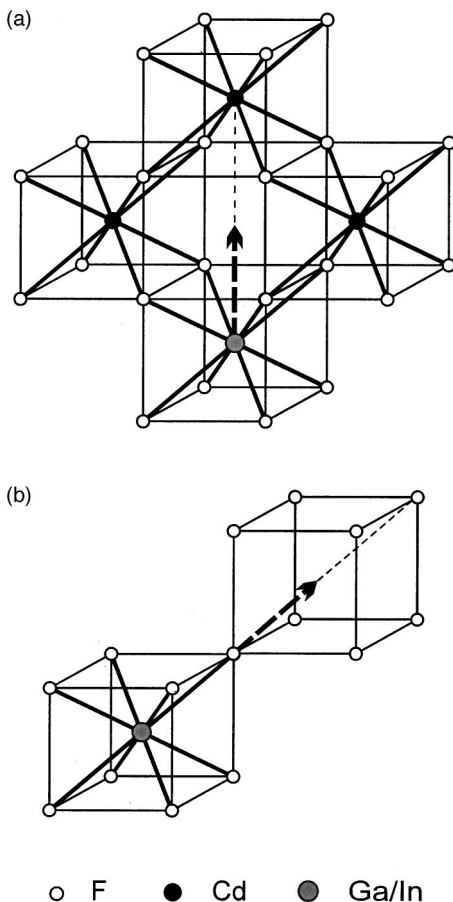


FIG. 1. Two possible lattice distortions for the DX center in CdF_2 :Ga/In with displacement of Ga/In (a) along the $\langle 100 \rangle$ direction and (b) along the $\langle 111 \rangle$ direction.

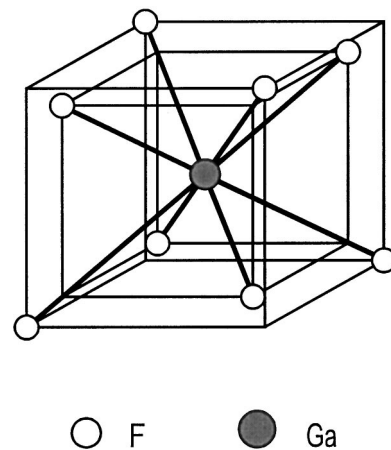


FIG. 2. Symmetric lattice relaxation associated with the ground state of the Ga^{3+} center in CdF_2 .

DX center formation among the elements of the B subcolumn of the column III. According to the above consideration, high ionicity of the chemical bond in Sc and Y centers prevents them from the essential nontotallysymmetric distortion of structure accompanying *DX* center formation. *DX* formation is probably also hampered by the absence in $\text{Sc}^{1+}/\text{Y}^{1+}$ ions of closed shell analogues to the s^2 -shell of $\text{Ga}^{1+}/\text{In}^{1+}$, which should decrease the energy of the single-valence state and thus stabilize it. These reasons allow formation of only shallow donor states by Sc and Y ions in CdF_2 . In this connection, it would be interesting to investigate possible formation of *DX* centers in CdF_2 by column-I elements Cu, Ag, and Au [electronic configuration $[P]nd^{10}(n+1)s^1$], the electronegativity of which is comparable with those of Ga

and In and which have closed shells in the single-valence state.

Thus, this consideration shows the determinative role of covalency in the formation of *DX* centers in CdF_2 doped with column-III elements. The mechanism of the change of the impurity center's structure for ionic CdF_2 crystal is similar to conventional III-V and II-VI semiconductors in its main features. Distinctive features of the former crystal are the importance of *d-d* interactions of impurity and lattice cations and, probably, the presence of filled atomiclike shells at the single-ionized impurity ion.

The authors are indebted for financial support to the "Fundamental Spectroscopy" program of the Ministry of Science and Technology.

- ¹J. D. Kingsley and J. S. Prener, *Phys. Rev. Lett.* **8**, 315 (1962).
- ²P. F. Weller, *J. Inorg. Nucl. Chem.* **40**, 1545 (1965).
- ³F. Trautweiler, R. Moser, and R. P. Khoshla, *J. Phys. Chem. Solids* **29**, 1869 (1968); R. P. Khoshla, *Phys. Rev.* **183**, 695 (1968).
- ⁴T. H. Lee and F. Moser, *Phys. Rev. B* **3**, 347 (1971).
- ⁵I. Kunze and W. Ulrici, *Phys. Status Solidi B* **55**, 567 (1973).
- ⁶J. E. Dmochowski, W. Jantsch, D. Dobosz, and J. M. Langer, *Acta Phys. Pol. A* **73**, 247 (1988).
- ⁷A. S. Shcheulin, A. I. Ryskin, K. Swiatek, and J. M. Langer, *Phys. Lett. A* **222**, 107 (1996).
- ⁸S. A. Kazanskii, A. I. Ryskin, and V. V. Romanov, *Appl. Phys. Lett.* **70**, 1272 (1997); *Phys. Solid State* **39**, 1067 (1997).
- ⁹A. I. Ryskin and P. P. Fedorov, *Phys. Solid State* **39**, 943 (1997).
- ¹⁰A. I. Ryskin, A. S. Shcheulin, and D. E. Onopko, *Phys. Rev. Lett.* **80**, 2949 (1998); A. S. Shcheulin, A. I. Ryskin, and D. E. Onopko, *Phys. Solid State* **39**, 1906 (1997).
- ¹¹A. I. Ryskin, A. S. Shcheulin, B. Koziarska, J. M. Langer, A. Suchocki, I. I. Buchinskaya, P. P. Fedorov, and B. P. Sobolev, *Appl. Phys. Lett.* **67**, 31 (1995).
- ¹²B. Koziarska, J. M. Langer, A. I. Ryskin, A. S. Shcheulin, and A. Suchocki, *Mater. Sci. Forum* **196-201**, 1103 (1995); *Acta Phys. Pol. A* **88**, 1010 (1995).
- ¹³A. Suchocki, B. Koziarska, T. Langer, and J. M. Langer, *Appl. Phys. Lett.* **70**, 22 (1997).
- ¹⁴A. S. Scheulin, E. V. Miloglyadov, A. I. Ryskin, D. I. Staselko, I. I. Buchinskaya, P. P. Fedorov, and B. P. Sobolev, *Opt. Spectrosc.* **84**, 461 (1998).
- ¹⁵A. I. Ryskin, A. S. Shcheulin, E. V. Miloglyadov, R. A. Linke, I. Redmond, I. I. Buchinskaya, P. P. Fedorov, and B. P. Sobolev, *J. Appl. Phys.* **83**, 2215 (1998).
- ¹⁶T. Mattila, S. Poykko, and R. M. Nieminen, *Phys. Rev. B* **56**, 15665 (1997).
- ¹⁷C. H. Park and D. J. Chadi, *Phys. Rev. Lett.* **82**, 113 (1999).
- ¹⁸D. E. Onopko and A. I. Ryskin, *Phys. Lett. A* **208**, 244 (1995); D. E. Onopko, and Bagzaev, A. I. Ryskin, *Semiconductors* **31**, 1310 (1997).
- ¹⁹K. H. Johnson, *Adv. Quantum Chem.* **7**, 143 (1973).
- ²⁰J. Dabrowski and M. Scheffler, *Mater. Sci. Forum* **83-87**, 735 (1992).
- ²¹D. J. Chadi and K. J. Chang, *Phys. Rev. B* **39**, 10 063 (1989).
- ²²J. Nissila, K. Saarinen, P. Hautajarvi, A. Suchocki, and J. M. Langer, *Phys. Rev. Lett.* **82**, 3276 (1999).
- ²³U. Piekara, J. M. Langer, and B. Krukowska-Fulde, *Solid State Commun.* **23**, 577 (1977); J. M. Langer, U. Ognowska, and B. Iller, *Inst. Phys. Conf. Ser.* **43**, 277 (1979); J. M. Langer, *Lecture Notes in Physics* (Springer, NY, 1980), Vol. 122, p. 123; *Radiat. Eff.* **72**, 55 (1983); J. M. Dmochowski, J. M. Langer, Z. Kalinski, and W. Jantsch, *Phys. Rev. Lett.* **56**, 1735 (1986).
- ²⁴J. M. Langer, *Rev. Solid State Sci.* **4**, 297 (1990).
- ²⁵R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **32**, 751 (1976).
- ²⁶At the same time, one should note that accordingly to Ref. 17, displacement of the impurity ion from the initial substitutional position at the deep center formation is nearly equal for these two dopants (1.82 Å for Ga and 1.84 Å for In).
- ²⁷T. Gessmann, K. G. Lynn, D. E. Onopko, and A. I. Ryskin (unpublished).