

Cd-vacancy and Cd-interstitial complexes in Si and GeH. Höhler, N. Atodiresei, K. Schroeder, R. Zeller, and P. H. Dederichs
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The electrical-field gradient (EFG), measured, e.g., in perturbed angular correlation experiments, gives particularly useful information about the interaction of probe atoms like $^{111}\text{In}/^{111}\text{Cd}$ with other defects. The interpretation of the EFG is, however, a difficult task. This paper aims at understanding the interaction of Cd impurities with vacancies and interstitials in Si and Ge, which represents a controversial issue. We apply two complementary *ab initio* methods in the framework of density-functional theory, (i) the all electron Korringa-Kohn-Rostoker Green function method and (ii) the pseudopotential-plane-wave method, to search for the correct local geometry. Surprisingly we find that both in Si and Ge the substitutional Cd-vacancy complex is unstable and relaxes to a split-vacancy complex with the Cd on the bond-center site. This complex has a very small EFG, allowing a unique assignment of the small measured EFGs of 54 MHz in Ge and 28 MHz in Si. Also, for the Cd-self-interstitial complex we obtain a highly symmetrical split configuration with large EFG's, being in reasonable agreement with experiments.

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I. INTRODUCTION

The detailed understanding of the electronic structure of intrinsic defects in semiconductors is in many cases still an unresolved problem. Many different experimental methods aiming at microscopic information about intrinsic defect structures exist. The “state of the art” experiments for these kind of problems are the measurements of hyperfine interactions. One example is the perturbed angular correlation measurement (PAC) of the electric-field gradient (EFG).³⁻⁷ The EFG describes the interaction of the electrons with the electric quadrupole moment Q_{ij} of the nuclei and is given by the second derivative V_{ij} of the Coulomb potentials at the nuclear site.

Since the PAC technique itself is based on a radioactive decay, it is essential for Si and Ge host crystals to implant a proper probe atom. The transformation of implanted ^{111}In isotopes to ^{111}Cd by electron capture leaves the ^{111}Cd probe in an excited state and the subsequent decay to its ground state makes the determination of the EFG possible. That means the EFG is just measured at the Cd site and reflects the local electronic structure which again depends on the atomic environment.

Since the EFG vanishes for cubic or tetrahedral point symmetry, probe atoms such as Cd give no signal on substitutional sites. An EFG only arises due to the symmetry lowering induced by other defects. In addition the direction of the main axis of the EFG gives very clear information about the symmetry of the corresponding complexes formed. Therefore PAC measurements yield particularly useful information about the interaction of Cd probe atoms with other defects. The only disadvantage of the method is that the resulting EFG's are difficult to understand and that reliable information about the EFG and the electronic and geometrical structure of complexes can only be obtained by *ab initio* calculations.

The paper aims at understanding PAC experiments with Cd probes in Si (Refs. 4,9,10) and Ge.^{1,2,11,12} Of particular

interest is the interaction with intrinsic defects, i.e., vacancies and self-interstitials. In previous studies two complexes in Ge have been identified, both with main axis along (111) and asymmetry parameter $\eta=0$ but with very different quadrupolar coupling constants ν , i.e., $\nu_1=54$ MHz and $\nu_2=415$ MHz. Both values, which differ by an order of magnitude, were measured^{1,2} by two different groups and interpreted as Cd complexes with intrinsic defects. However the two groups disagree about the assignment of the EFG. For Feuser *et al.* ν_2 is assigned to a substitutional Cd-vacancy complex, while ν_1 should refer to an interstitial Cd atom in the vicinity of a vacancy. In contrast to this Sielemann *et al.*¹¹ assigns ν_1 to the substitutional Cd atom with a vacancy on the nearest-neighbor site and ν_2 to a substitutional Cd with a self-interstitial on a (111) oriented interstitial position. Compared to Ge, the interpretation of the measured frequencies is much more uncertain in Si.⁴

In this paper we perform *ab initio* calculations to solve this problem. Basically we can confirm the assignment of Sielemann *et al.*^{1,11,12} that the small frequency ν_1 belongs to the Cd-vacancy complex and the high frequency to the interstitial one. However in both cases the configurations are very unusual: The Cd atom sits on a bond-center position and the single vacancy as well as the interstitial are split on two neighboring sites. The existence of such an impurity-split vacancy configuration has already been suggested by Watkins¹³ for a Sn-vacancy pair in Si. In a forthcoming paper we will show that this pair configuration is also the most stable one for the vacancy complexes with other impurities such as In, Sn and Sb in Si and Ge. Therefore we expect that our results are typical for oversized impurities in group IV semiconductors.

II. THEORETICAL METHODS

All calculations are based on density-functional theory in the local-density approximation.¹⁴ Two different methods have been used to solve the Kohn-Sham equations. The first

TABLE I. Parameters used to construct the pseudopotential projectors. For the KB potentials only the cutoff radii are listed for each one-channel, for the PAW potentials the cutoff radii / reference energies (in Ry) are listed. The first line for Cd refers to eigenvalues of the bound states for the respective l -channel, the second line to the specific energies for the unbound states used to construct the second projector for each l -channel. All radii are in a_B (0.529 177 Å).

Atom	pp type	Atom conf.	s channel	p channel	d channel	f channel
Ge	KB	Ground state	1.15	1.15	1.65	-
Si	KB	Ground state	1.15	1.25	1.25	-
Cd	PAW	Ground state	2.33/-0.0408	2.6/-0.1052	2.6/-0.105	-
		Ground state	2.33/-0.1	2.6 / 0.4	2.6/-0.6	2.6/-0.4

one is the pseudopotential-plane-wave (PPW) method, which has mostly been used to investigate the configuration and stability of the Cd-split vacancy and the Cd-split interstitial configurations. These configurations, as well as the relaxations of the neighboring atoms, have been recalculated by the KKR-Green function method,¹⁵⁻¹⁷ which as an all electron method allows also to calculate electric-field gradients and hyperfine fields.^{8,19,20}

The PPW method approximates the inhomogeneous system containing defect complexes by periodically arranging large supercells and uses plane waves to expand the electronic wave functions. This has the advantage that band-structure methods can be used to determine the electronic structure, and total energies and forces on the atoms can be calculated without difficulty for arbitrary arrangements of the atoms in the supercell. Our ESTCOMP-program²⁰ can handle norm-conserving Kleinman-Bylander (KB) pseudopotentials²¹ and projector-augmented (PAW)-multi-projector pseudopotentials²² used to describe the electron-ion interaction. For Si and Ge KB nonlocal pseudopotentials are used for the s , p valence electrons and the $d(l=2)$ component is used as a local potential. For Cd the $5s$, p valence electrons as well as $4d$ electrons are treated explicitly with PAW potentials and the $f(l=3)$ component is used as a local potential. Partial-core correction was used for Cd. The atomic configurations, cutoff radii and reference energies used to generate the projectors are listed in Table I. For the actual calculations we used a (111)-oriented supercell with the basis vectors $\vec{b}_1=(3/2)a(0,-1,1)$; $\vec{b}_2=(3/2)a(-1,1,0)$; $\vec{b}_3=2a(1,1,1)$ containing 108 atoms. a is the theoretical lattice constant

($10.44a_B$ for Ge and $10.25a_B$ for Si; Bohr radius $a_B=0.529\,177$ Å). The Cd complex was placed in the middle of the cell. We used C_{3v} symmetry explicitly for all configurations. A plane-wave basis set equivalent to $6 \times 6 \times 6$ Monkhost-Pack²³ \vec{k} points was used which yields three inequivalent \vec{k} points in the irreducible part of the Brillouin zone for our supercell. We used a plane-wave cutoff of 20.25 Ry, which is required for the convergence of the Cd PAW potential. The atoms belonging to the Cd complexes and their nearest neighbors were relaxed until the forces on all atoms were less than 0.1 mRy/ a_B . We checked that forces on further neighbors (which were not moved) were of the order of 1 mRy/ a_B and we estimate that the positions of all relaxed atoms were determined with an accuracy better than $0.01a_B$.

In the KKR Green function method the calculation is divided in two steps. First, the Green function of the host is determined. In a second step the host Green function is used to determine the Green function of the crystal with a single impurity by a Dyson equation. For details we refer to Ref. 24. All calculations are performed with an angular momentum cutoff of $l_{max}=4$. For the host crystal we use the local-density approximation (LDA) lattice constants²⁵ of Si ($10.21a_B$) and Ge ($10.53a_B$). A k mesh of $30 \times 30 \times 30$ \vec{k} points in the full Brillouin zone is used. We use the screened KKR formalism,^{26,27} with the tight-binding (TB)-structure constants determined from a cluster of 65 repulsive potentials of 4 Ry heights. The diamond structure is described by a unit cell with four basis sites, two for host atoms and two for vacant sites. For the Green function of the defective systems, we allow 77 potentials of the defect and the surrounding host atoms to be perturbed, which are then calculated self-consistently with proper embedding into the host crystal. All calculations include the fully anisotropic potentials in each cell and thus allow the reliable calculation of forces, lattice relaxations, and electric-field gradients. The single-particle electron density $n(\vec{r})$ can be calculated via the imaginary part of the Green function:

$$n(\vec{r}) = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{E_f} dE G(\vec{r}, \vec{r}; E). \quad (1)$$

The Coulomb potential can be expressed in terms of $n(\vec{r})$ and therefore the force \vec{F}^n on atom n can be derived with the use of the ‘‘ionic’’ Hellmann-Feynman theorem:²⁴

$$\vec{F}^n = Z^n \left. \frac{\delta V_{coul}}{\delta \vec{r}} \right|_{\vec{r}=\vec{R}^n} - \int d\vec{r} n_C(\vec{r} - \vec{R}^n) \frac{\delta V_{eff}}{\delta \vec{r}}, \quad (2)$$

where the first term denotes the Coulomb force of the valence electrons and of the other nuclei on the nuclear charge Z^n , while the second term gives the force on the core electrons C of atom n , evaluated by the derivative of the Kohn-Sham potential. It can be shown, that in an angular momentum expansion the force is determined via the $l=1$ component of the charge density. The tensor of the EFG is given by the second derivative of the Coulomb potential:

$$\mathbf{V}_{\alpha\beta} = \left. \left\{ \frac{\partial V_{coul}}{\partial \alpha \partial \beta} - \delta_{\alpha\beta} \frac{1}{3} \sum_{i=1}^3 \frac{\partial V_{coul}}{\partial \alpha^2} \right\} \right|_{\vec{r}=0},$$

$$\alpha, \beta = x, y, z; \quad \text{Tr } \mathbf{V}_{\alpha\beta} = 0, \quad (3)$$

where (x, y, z) denotes the coordinate system. In practical applications, since we expand all quantities in spherical harmonics, the electric-field gradient is calculated as follows:^{18,19}

$$\mathbf{V}_{\alpha\beta} = \sum_{m=-2}^2 \tilde{V}_{2,m}(0) \partial_{\alpha} \partial_{\beta} [r^2 Y_{2m}(\vec{r})],$$

$$\tilde{V}_{2,m}(0) = I_1 + I_2,$$

$$I_1 = \frac{8\pi}{5} \int_0^{R_{MT}} r'^2 \frac{n_{2m}(r')}{r'^3} dr';$$

$$I_2 = \frac{V_{2m}(R_{MT})}{R_{MT}^2} - \frac{8\pi}{5} \int_0^{R_{MT}} \frac{n_{2m}(r') r'^4}{R_{MT}^5} dr', \quad (4)$$

where $Y_{2m}(\vec{r})$ are spherical harmonics, $\tilde{V}_{2,m}(r)$ are the $l=2$ components of the Coulomb potential, and R_{MT} is the muffin-tin radius of the probe atom. Furthermore $n_{2m}(r)$ are the $l=2$ components of the radial charge density. We note that just the $l=2$ components are needed for the EFGs, while the $l=1$ components enter into the forces. Due to this, the EFG vanishes for sites with cubic or tetrahedral symmetry. For the cell division of the crystal we used a generalized Voronoi construction. The impurity cell at the bond center was constructed such that it is slightly larger than the cells of the host atoms, thus avoiding to decrease the muffin-tin radius of real atoms by more than 16%. For the energy contour in Eq. (1) all d -states are included. For the treatment of occupied states in the band gap, we have used a separate energy contour for gap energies. Since we used group theory we are able to occupy these gap states according to their symmetry, in this way avoiding to calculate the wave functions of the localized gap states.

III. Cd-SPLIT VACANCY COMPLEX

A. The substitutional Cd-vacancy complex

The starting point of our study is the substitutional Cd-vacancy complex. To our surprise this complex with the Cd on the substitutional site and the vacancy on the nearest-neighbor site is highly unstable. When fixing the Cd at the substitutional position and allowing the six host atoms to relax, the energy of the configuration for both Si and Ge hosts is more than 1 eV higher than the energy of the stable split configuration shown in Fig. 1. When the Cd atom is allowed to relax, the energy continuously lowers (without energy barrier) until the Cd reaches the stable bond-center position shown in Fig. 1. The fixed substitutional configuration is highly anisotropic and the calculations give rather high EFG's for the Cd atom, with values of about -420 to -430 MHz in Ge and -390 to -420 MHz in Si, where the spread is caused by the different charge states. However both the PPW and the KKR calculations show that this configuration is unstable and does not represent a local minimum.

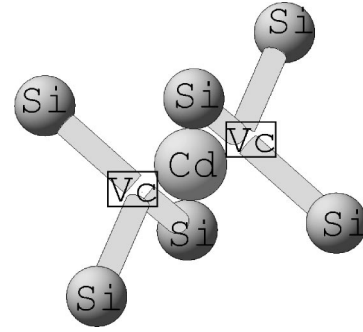


FIG. 1. The Cd-split vacancy configuration.

Thus a comparison of the EFG's with the measured frequency $\nu_2=415$ MHz in Ge is meaningless, since the configuration is not stable. Apparently the instability arises from the large size of the Cd atom, which is pushed away from the three Si or Ge neighbors into the empty space towards the vacancy and settles on the symmetrical bond-center position.

B. The divacancy in Si and Ge

Since the electronic structure of the Cd-split vacancy complex can most easily be understood by first considering the divacancy, we present in Fig. 2 the calculated density of states (DOS) of the divacancy in Si. Four different peaks can be seen: single degenerate A_{1g} and A_{2u} resonances in the valence band, and double degenerate E_g and E_u localized states in the gap. The splitting into g and u state arises from the hybridization of the A - and E -dangling-bond states of the two single vacancies into bonding and antibonding combinations. In a molecular orbital (MO) scheme the energy levels are schematically indicated in Fig. 3 on the right. In the calculation the Fermi level is situated at the maximum of the valence band E_{val} . Therefore only four of the six dangling-bond electrons can be accommodated, so that in the calculation the charge state of the divacancy is $2+$.

C. Cd-split vacancy complex

The local DOS (LDOS) at the Cd bond-center site of the Cd-split vacancy complex is shown in Fig. 4, both for Si and

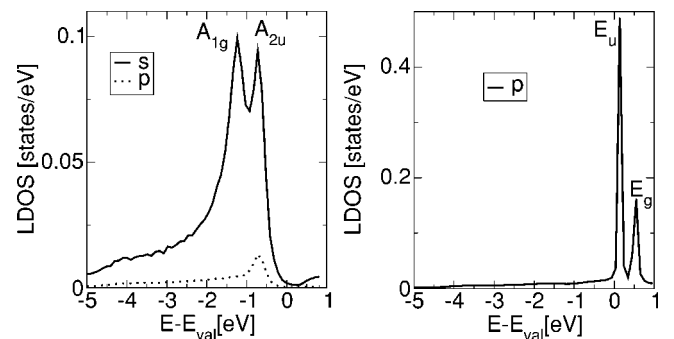


FIG. 2. Local density of states (LDOS) for the divacancy²⁺ in Si. Shown are the major local l -contributions on a vacancy site: s and p for the A_{1g} and A_{2u} subspaces (left), and p for the E_u and E_g subspaces (right). The other l channels contribute less than 10% over the entire energy range.

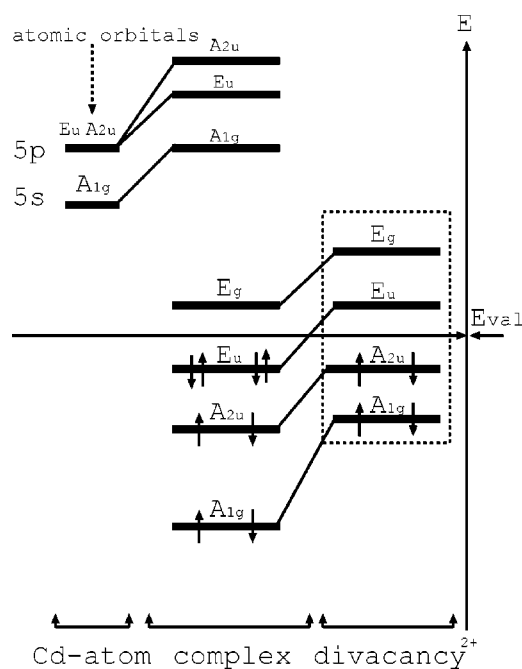


FIG. 3. Schematic tight-binding scheme of energy levels to explain the electronic structure of the Cd-split vacancy complex in Si and Ge. Included are the $5s$, $5p$ levels of the Cd atom and the dangling-bond states of the divacancy in its $2+$ state. From left to right: the single Cd-atom, the Cd-split vacancy complex, and the divacancy $^{2+}$.

Ge. Since this complex preserves the point symmetry D_{3d} of the divacancy and since the Cd $5s$ and $5p$ states are well above the Fermi level, the decomposition and level structure of the divacancy DOS are basically preserved. As indicated by the MO level scheme in the center of Fig. 3, by hybridization between the states of the Cd and of the divacancy the divacancy levels are pushed to lower energies and the Cd states to higher energies. The self-consistent calculations yield the E_u state as a resonance at the top of the valence band, in agreement with the level scheme assumed for the split complex in Fig. 3. In this configuration eight electrons are accommodated in the single degenerate A_{1g} and A_{2u} states and the double degenerate E_u state. These eight electrons just correspond to the six electrons of the dangling bonds of the divacancy and the two electrons of Cd, so that the calculations yield the neutral charge state, as long as the E_g level in the gap remains unoccupied. The d states of Cd are located around -8.5 eV and, while included in the calculations, are basically localized and of minor importance for the electronic structure and the EFG.

As Fig. 1 shows, the Cd atom has in its nearest coordination shell six host atoms at a distance at 1.26 times the nearest-neighbor distance (if lattice relaxations are neglected; see below). Therefore the hybridization between the Cd $5sp$ states and the divacancy states is rather weak, so that the occupied A_{1g} , A_{2u} , and E_u states contain locally only relatively small admixtures of these Cd states, leading to a charge of only 1.0 electrons (in the case of Ge; for Si: 0.9 electrons) in the Cd sphere, which has about the same size as the Si or Ge spheres. Therefore we can understand the elec-

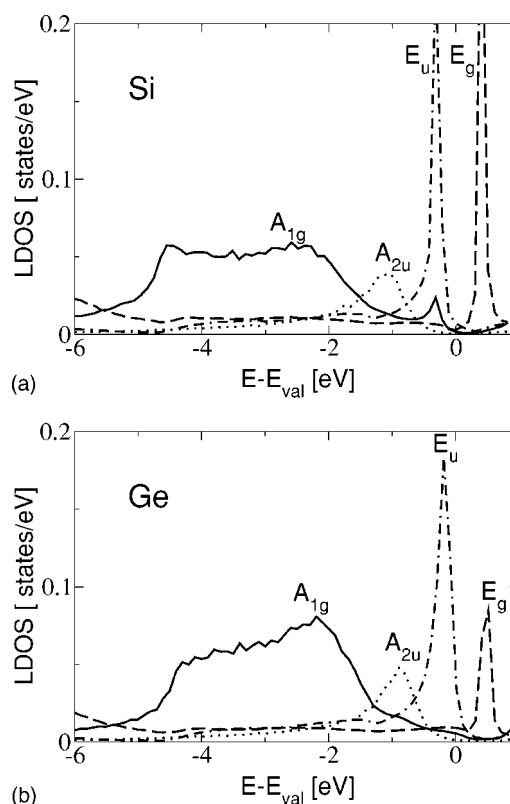


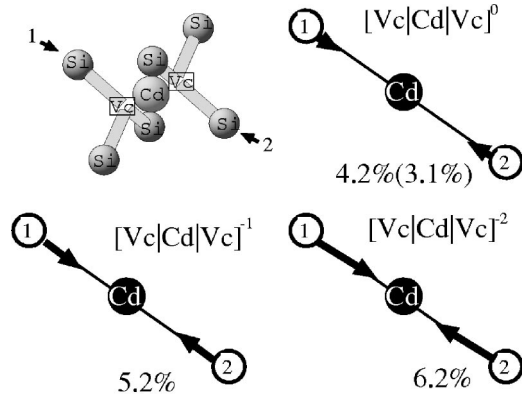
FIG. 4. LDOS projected on the irreducible subspaces of the D_{3d} group at the Cd site (bc) for the Cd-split vacancy in Si (above) and Ge (below). The nearest neighbors are fixed on ideal lattice positions.

tronic structure in a simple picture in real space, by considering the Cd as a "naked" Cd^{2+} ion embedded at the bond-center position into the divacancy. The strongly attractive Cd^{2+} potential lowers all divacancy states, but preferentially, and in first-order perturbation theory only, the A_{1g} level which has the full D_{3d} symmetry of the defect. Due to this, the A_{1g} state is stronger localized at the Cd site than the other states and shows up more prominently in the LDOS of Cd. The LDOS for the Si and Ge hosts are qualitatively and quantitatively very similar.

The different charge states $[CdV]^{1-}$, $[CdV]^{2-}$, ..., of the Cd-split vacancy complex are obtained by occupying the double degenerate E_g state in the gap. The $[CdV]^{1-}$ state is magnetic and exhibits a small moment about $0.02 \mu_B$ at the Cd site, both in Si and Ge. Since the total moment is $1 \mu_B$, this shows the large spatial extent of the E_g state.

D. Lattice relaxations

Figure 5 shows the calculated lattice relaxations of the six nearest-neighbor Si-atoms around the Cd atoms, while the table gives the calculated values for the case of Ge. All relaxations are given in percentages of the nearest-neighbor (NN) distance of the host crystal. First, we see that in the case of the neutral complexes the KKR values agree well with the PPW ones. The small differences arise from the different ways used to describe the electron-ion interaction



Defect	KKR [% NN]	PPW [% NN]
$[V Cd V]^0$ in Ge	6.6	6.0
$[V Cd V]^{-1}$ in Ge	7.5	
$[V Cd V]^{2-}$ in Ge	8.5	

FIG. 5. Relaxations of the six nearest neighbors of the Cd-atom, Cd-split vacancy complex in the figure for the Si host, in the table for the Ge host. Besides the KKR values for the neutral configuration also the PPW values are given.

(pseudopotentials for the PPW and all electron in KKR) and the slightly different lattice constants. They are of the same order of magnitude as typical differences in other instances, e.g., for the relaxations of the near surface atoms of Cu surfaces. Second, we notice that the relaxations point toward the Cd atom and increase by about 1% with increasing total charge of the complex. Both facts are consequences of the electrostatic interaction, i.e., the Cd^{2+} ion attracts the dangling-bond electrons of the Si or Ge neighbors and the attraction increases with increasing charge in the extended E_g states. Third, the relaxations in Ge are larger than the relaxations in Si, which is a consequence of the 3% larger lattice constant of Ge as compared to Si (theoretical values), so that the local distances are very similar in both hosts. Despite the sizeable relaxations the final distances are still very large, the strength of the hybridization is still weak and the LDOS's are hardly changed by relaxations.

E. Charge anisotropy and EFGs

As stressed in the Introduction the EFG is determined by the anisotropy of the charge density at the Cd site, more correctly by the $l=2$ components of the (lm) -projected charge density $n_{2m}(r)$. Such $l=2$ components arise from the anisotropy of the p - and the d -charge densities, since mixed $s-d$ or $p-f$ terms are very small. In a good approximation the EFG is therefore determined by the anisotropy of the local p and d charge^{18,19}

$$V_{zz} = a \Delta N_p + b \Delta N_d, \quad (5)$$

where ΔN_p and ΔN_d are the anisotropic p and d charges, which for the considered symmetry and z axis in (111) direction are given by

TABLE II. Calculated EFG and hyperfine fields (HF) on fully relaxed positions for the Cd-split vacancy in Si and Ge for different charge states (0, 1-, 2-). We used $Q=0.83$ barn for Cd. Experimental values (EXP) are taken from Refs. 1 and 9.

Host crystal	Si	Ge	Si	Ge
	EFG [MHz]	EFG [MHz]	HF [kG]	HF [kG]
$[V Cd V]^0$	-6.97	-32.69		
$[V Cd V]^{-1}$	-27.99	-55.69	21.8	8.5
$[V Cd V]^{2-}$	-49.47	-79.64		
EXP	± 28.00	± 54.00		

$$\Delta N_p = \int_0^{E_F} dE' \left[\frac{1}{2} [n_{p_x}(E') + n_{p_y}(E')] - n_{p_z}(E') \right]$$

$$\Delta N_d = \int_0^{E_F} dE' \left[n_{d_{x^2-y^2}}(E') + n_{d_{xy}}(E') - \frac{1}{2} [n_{d_{xz}}(E') + n_{d_{yz}}(E')] - n_{d_{z^2}}(E') \right]. \quad (6)$$

The positive constants a and b in Eq. (6) are matrix elements of $1/r^3$ with normalized p and d wave functions at E_F .

We can now analyze the anisotropic charges in terms of the contributions from the different irreducible contributions A_{1g} , A_{2u} , E_u , and E_g to the local Cd DOS as given in Fig. 4. The A_{1g} subspace only contains the local s and d_{z^2} contributions, the subspace A_{2u} only the p_z , the E_u subspace the p_x and p_y , and the E_g state the local d_{xy} , $d_{x^2-y^2}$, d_{xz} and d_{yz} contributions.

In the neutral state $[CdV]^0$ the E_g state is not occupied and we find negative electric-field gradients. The contribution ΔN_p is negative, since the E_u state cannot overcome the negative n_{p_z} contribution of A_{2u} and ΔN_d is negative due to the $n_{d_{z^2}}$ contribution from A_{1g} . When one then populates the E_g state, we find that the contributions from $d_{x^2-y^2}$ and d_{xy} are very small, so that additional negative contributions from d_{xz} and d_{yz} are expected for the charged configurations.

The calculated values for the relaxed configurations are given in Table II. First, we would like to point out that the displacements of the NN atoms play only a minor role, which is not surprising in view of the small changes found in the LDOS. Second, we observe that for the charged defects the EFG's in Si and Ge increase for each electron added in the E_g state by about 20 MHz, more correctly about 21 in Si and 23 in Ge. This is a consequence of the fact that the E_g state is very extended: For each electron added to the complex the local charge of Cd increases only by 0.05 electrons, which represents a weak perturbation. Finally we find that the EFG of the singly charged configuration $[CdV]^{-1}$ agrees both in Si and Ge very well with the measured values. Note that experimentally the sign of the EFG cannot be determined. We consider the close agreement as a confirmation that the Cd-split vacancy complex is the most stable Cd-vacancy complex and that the measurements refer to the negatively charged $[CdV]^{-1}$ complex. This is in agreement

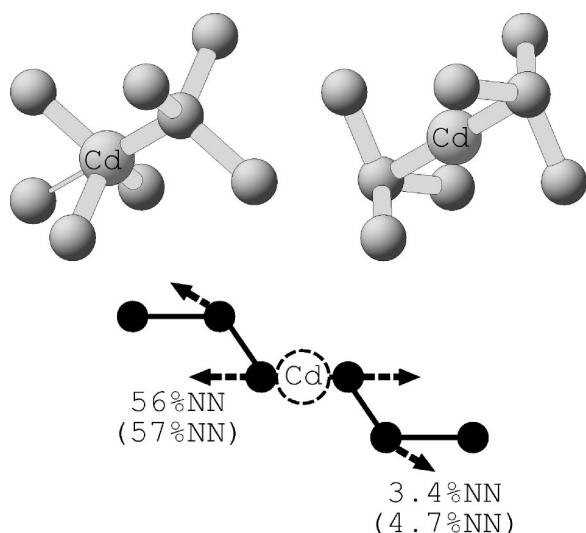


FIG. 6. The Cd-self-interstitial complex with Cd on the substitutional site (above left) leads after relaxation to the symmetrical complex with Cd on the bond center and the two host atoms shifted half way between the substitutional and interstitial positions (above right). The lower figure gives the calculated displacements of the neighbors from the ideal positions in percent of the nearest-neighbor distance for the Ge host. In brackets the results of the PPW calculation are given.

with Haesslein *et al.*,¹ who assigned the frequency $\nu_1 = \pm 54$ MHz in Ge to a Cd-vacancy complex in the charge state 1-. As mentioned earlier already, in this configuration the complex is magnetic and for the Cd atom our calculations predict a small hyperfine field of 21.8 kG in Si and 8.5 kG in Ge. Up to now these hyperfine fields have not been measured. In summary we find that the small EFG's measured are a typical feature of the Cd-split vacancy configuration, in which the Cd atom is far away from the nearest neighbors so that the hybridization is very small, much smaller than for the strongly anisotropic (but unstable) substitutional configuration, yielding EFG's of around 400 MHz. Partly the geometrical structure also helps, since the Cd atoms and the six neighbors form a distorted octahedron. For an ideal octahedron the EFG would vanish due to symmetry.

IV. Cd-INTERSTITIAL COMPLEX

The Cd-self-interstitial complex is a possible candidate for the large EFG of $\nu_2 = 415$ MHz measured by two groups^{1,2} in Ge. In our electronic structure calculations we have first studied the interstitial-Cd complex shown in Fig. 6 (upper left): a self-interstitial on a tetrahedral site adjacent to a substitutional Cd impurity. To our surprise we find again, that this configuration is very unstable, exhibiting a large force of about $100 \text{ mRyd}/a_B$ on the Cd atom. By relaxing this configuration the three adjacent atoms in (111) direction, i.e., the self-interstitial, the Cd atom and the NN host atom in (111) direction move more or less uniformly until the Cd atom settles in the bond-center position and the two host

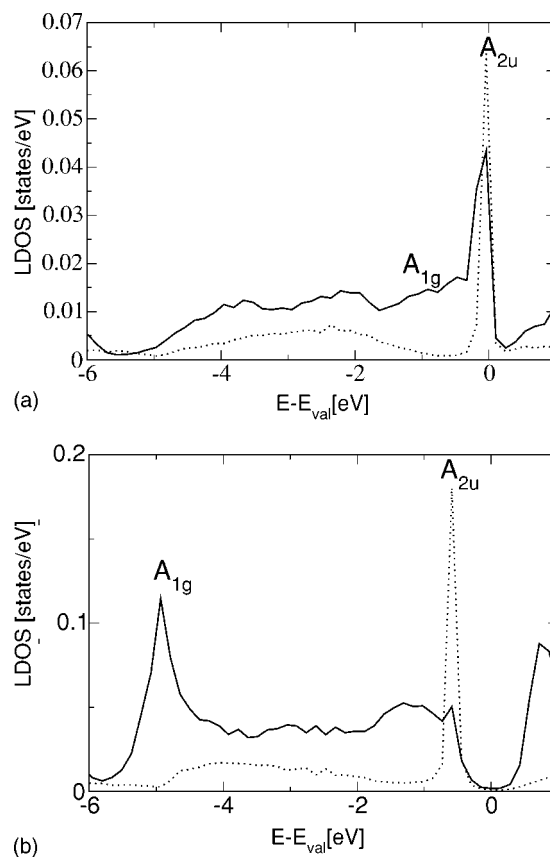


FIG. 7. LDOS in the bond-center cell for the cases that it is unoccupied by the Cd impurity (upper figure, a) and that it is occupied by Cd (lower figure, b). The position of all other atoms are the same in both figures as given for the split configuration in Fig. 6 (upper right).

atoms about halfway between the interstitial and the substitutional positions. Therefore we refer to this as the Cd-split interstitial configuration, which is highly symmetric (D_{3d} symmetry). It is shown in Fig. 6 (upper right), together with the exact positions of the neighboring atoms [Fig. 6 (bottom)].

The electronic structure of this complex can again be understood by considering the Cd atom as a Cd^{2+} ion. Figure 7 shows the LDOS in the cell of the Cd atom for this configuration, in Fig. 7(a) without the presence of the Cd atom and in Fig. 7(b) in the presence of the Cd. Only the LDOS in the A_{1g} and A_{2u} subspaces are shown, since the local E_u and E_g contributions are small and not of relevance for the EFG. These states are mostly localized at the two interstitials and the six neighboring host atoms.

For the two shifted host atoms without Cd, we see in Fig. 7(a) two sharp peaks of A_{1g} and A_{2u} symmetry at E_F . These are symmetric and antisymmetric combinations of p_z dangling-bond states of the two split atoms, pointing into the interstitial region. A contour plot in the x - z plane of the DOS of these states is shown in Fig. 8(a). Since the two dangling-bond states do practically not overlap, the A_{1g} and A_{2u} states are nearly degenerate. By inserting the Cd^{2+} ion, the bonding A_{1g} state is shifted to lower energies and becomes more lo-

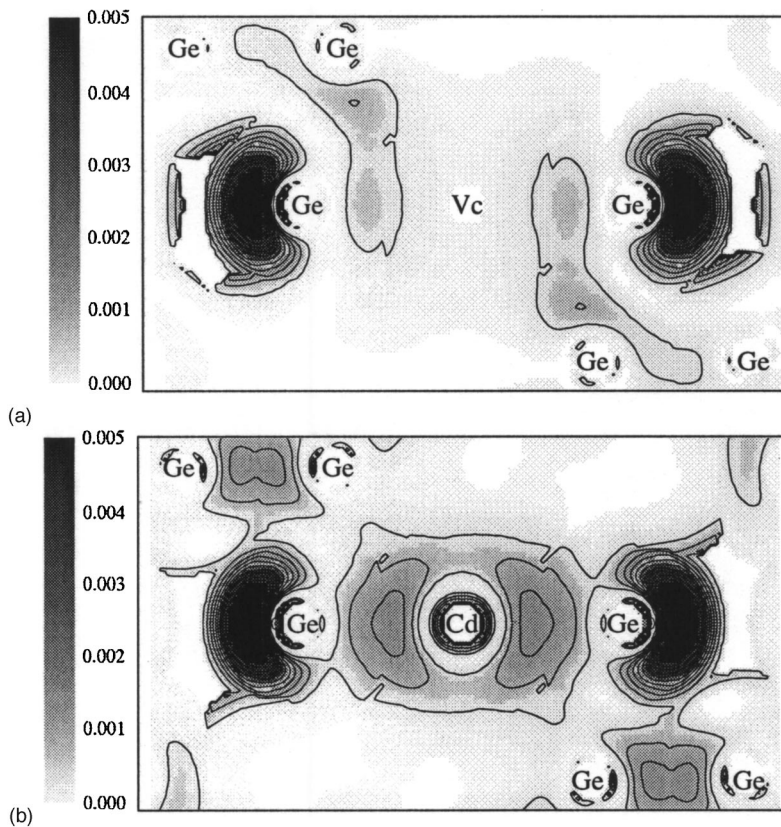


FIG. 8. A contour plot in the xz plane of the A_{2u} state close to the Fermi energy (see Fig. 7) for the Cd-split interstitial complex: Fig. 8(a) (upper panel) in the absence of the Cd impurity, Fig. 8(b) (lower panel) in the presence of the Cd on the bond-center position.

calized at the Cd site, while the A_u states is only slightly shifted to lower energies [Fig. 7(b)]. Both the A_{1g} and A_{2u} states are fully occupied yielding a neutral configuration. The contour plot of the A state close to E_F , being dominated by the A_{2u} state, shows Cd- p_z orbitals forming a bridge between the two dangling-bond states, with a nodal plane perpendicular to the z axis [Fig. 8(b)].

The calculated EFG of the Cd-split interstitial complex is quite large, i.e., -395 MHz in Ge and -345 MHz in Si. The strong anisotropy arises from the two split interstitial atoms. The major contribution to the EFG arises from the p_z orbital in the A_{2u} state, shown in the contour plot of [Fig. 8(b)]; in addition small contributions come from p_x and p_y orbitals belonging to E_u states. The A_{1g} state gives nearly no contribution, since the dominant s state is isotropic and the d_{z^2} admixture is small. The calculated EFG of -395 MHz for the Cd-split interstitial in Ge is in good agreement with the observed frequency^{1,2} $\nu_2 = \pm 415$ MHz, which has been assigned by Haesslein *et al.*¹ to a Cd interstitial, but by Feuser *et al.*² to a Cd-vacancy complex. The calculated value of -345 MHz for the interstitial complex in Si is more difficult to compare with the experimental data, which have been reviewed by Wichert *et al.*⁴ From our calculations we can exclude the axial symmetric and $\langle 111 \rangle$ oriented complex $De3$ with ± 448 MHz; moreover we can also exclude the defects $De2$ since it is not axial symmetric, and $De1$ since it refers to the Cd-split vacancy complex. A good match is only obtained with the unidentified defect $X2$ with ± 334 MHz, being axial symmetric and $\langle 111 \rangle$ oriented.

V. SUMMARY

In this paper we have investigated the electronic and geometrical structure of complexes of the radioactive probe atom Cd with intrinsic defects in Si and Ge. In particular we have calculated the electric-field gradient (EFG) of the Cd probe atom in these complexes, with the aim of assigning measured EFG frequencies to calculated defect complexes. The calculations are based on density-functional theory in the local-density approximation and apply the full-potential KKR Green's function method as well as the pseudopotential-plane-wave method. Both methods give nearly identical results for the atomic configurations.

The most simple complex, a substitutional Cd-atom adjacent to a vacancy on a nearest neighbor site, is found to be unstable and to relax into a Cd-split vacancy configuration: the Cd-atom sits on the bond-centered site, with the vacancy split into two half vacancies on the neighboring substitutional sites. As seen from the Cd atom, this complex is very isotropic and results in a rather small EFG. The values for the single negatively charged complex, i.e., -55.7 MHz in Ge and -28 MHz in Si, are in excellent agreement with measured EFG's (± 54 MHz in Ge and ± 28 MHz in Si) and also the charge state agrees with conclusions of Haesslein *et al.*¹ This close agreement confirms the existence of the calculated Cd-split vacancy configuration with very small EFG. By investigating the most simple complex of a Cd atom with an interstitial, i.e., a substitutional Cd atom with a self-interstitial on the adjacent tetrahedral site, we find that this complex is also unstable and decays spontaneously into a Cd

atom on the bond-center position and the two host atoms shifted from the substitutional site half way to the tetrahedral position, thus forming a Cd-split interstitial complex aligned in $\langle 111 \rangle$ -direction. For Ge the calculated EFG's of -415 MHz agrees well with the experimental value of ± 395 MHz assigned by Haesslein *et al.* to a Cd-interstitial complex. The experimental situation in Si is not so clear.

These unusual split configurations are typical for intrinsic complexes with oversized impurities, as we will demonstrate

in a future paper for a series of vacancy complexes with oversized and "normal" impurities.

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