Electronic structure and hyperfine interactions for deep donors and vacancies in II-VI compound semiconductors

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We present *ab initio* total-energy calculations for group-IV donors, vacancies and cation self-interstitials in cubic II-VI compound semiconductors. The calculations have been performed using the linear muffin-tin orbital method in the atomic-sphere approximation, with a particular emphasis on hyperfine and ligand hyperfine interactions. Our theoretical hyperfine interaction results for paramagnetic point defect states which transform according to the A_1 irreducible representation agree fairly well with the results obtained experimentally by electron paramagnetic resonance. There are two marked exceptions, the selenium vacancy in ZnSe and the tellurium vacancy in CdTe, for which there is an order of magnitude discrepancy. We conclude that the identification of these defects must be highly questionable. [S0163-1829(96)06228-5]

I. INTRODUCTION

The use of wide-gap II-VI compound semiconductors in optoelectronic applications has renewed the general interest in these materials, and in particular the interest in their intrinsic and extrinsic point defects. Experimentally, the number of studies has risen sharply (for a recent reviews, see Meyer and Stadler[1] and Watkins[2]). Several theoretical studies have been devoted to the most important topic of doping and self-compensation.[3–6] In these papers total energies, lattice relaxations, and impurity concentrations have been dealt with. With one exception,[7] however, hyperfine interactions (hfi) have not been calculated.

Theoretical hfi results are of utmost importance when assigning a specific atomic structure model to a point defect observed experimentally by magnetic resonance techniques like electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). Even if experimentally the hfi with an impurity nucleus and with a few ligand nuclei can be resolved, this assignment can be quite cumbersome. The hfi of the impurity nucleus in many cases reveals the chemical nature of this defect, and ligand hyperfine interactions can provide valuable information about the neighborhood of the point defect, but quite often this information is not sufficient to determine the atomic structure of a defect in a unique way.

With the progress of modern *ab initio* total-energy calculations it has become possible to reliably calculate the hfi and ligand hfi for point defects in solids.[7–9] These calculations start from a fixed microscopic structure model for which the electronic structure, total energy, and hfi matrix elements are calculated. Comparison with experimental data allows in some cases to assign this model to a specific defect observed experimentally, and to exclude alternate models. The isolated sulfur deep double donor in silicon can be taken as an example: For S_{Si}^{+} on a regular lattice site, one obtains theoretical hfi and ligand hfi data[8,9] that agree quantitatively with experimental ENDOR data of Ludwig.[10] For the alterative model which places the S atom on a tetrahedral interstitial site, the theoretical data do not agree even qualitatively with experimental data.

In this paper we shall present theoretical hfi results for simple point defects in cubic II-VI semiconductors with particular emphasis on F centers, i.e., isolated anion vacancies. These are among the most simple point defects: the paramagnetic defect state has the full cubic symmetry of the ZnS lattice, transforms according to the A_1 irreducible representation of the group T_d, and is, therefore, not subject to a Jahn-Teller distortion.

In II-VI semiconductors, however, these F centers are not frequently observed.[1] The early EPR measurement by Schneider and Räuber in 1967 (Ref. 11) identified the F center defect in ZnS which for the following 20 years and more was the only member of its class. Gorn *et al.*[12] in 1990 reported a defect in ZnSe which was identified with the anion vacancy. The experimental hfi data for this defect, however, are rather unusual and, therefore, the identification must be regarded as questionable. For the F center in CdTe, EPR (Ref. 13) and ENDOR (Ref. 14) experiments have recently been reported, which succeeded in resolving the hfi structure with 15 shells of ligands. This defect therefore appears an ideal system against which one can check theoretical hfi results.

In the course of our investigation[15] it appeared that our theoretical results for V_{Te}^{+} in CdTe do not at all agree with the experimental hfi data reported for the F center in CdTe. In order to check the validity of our theoretical results, we have investigated the hfi for deep group-IV donors and also for Zn self-interstitials, deep paramagnetic states transforming according to the A_1 irreducible representation for which experimental hfi and ligand hfi data are known.[16–18] For all these isolated point defects the hfi with the central defect nucleus and the calculated ligand hfi data agree perfectly with the experimental data.

In the next section we shall briefly describe the calculational scheme used in the course of our investigation. The results are presented and discussed in Sec. III, and summarized in a short section containing our conclusions.

II. COMPUTATIONAL

In our calculation we have used a Green's-function approach in which the isolated point defect is considered as a

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severe perturbation, the range of which is limited to a rather small region in space which is embedded into an otherwise perfect crystal. Our computations are based on the linear muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA) by Gunnarsson, Jepsen, and Andersen.[19] The application of this method to the calculation of deep defects in semiconductors has been described by Refs. 20 and 9. Exchange and correlation are treated in the local-spin-density approximation of the spin-density-functional theory[21,22] (LSDA-DFT). The use of the LMTO-ASA method restricts us to consider point defects located either at the tetrahedral lattice sites or at the tetrahedral interstitial positions of the lattice and prevents any consideration of lattice relaxation.

Fundamental single particle band gaps calculated for semiconductors by means of the LSDA-DFT are known to be too small by about 0.5 eV if compared to the experimental band gaps. We have used the scissors operator technique by Baraff and Schlüter[23] (see also Ref. 20) to expand the calculated band gaps by 0.3–0.5 eV to their respective experimental values. As a side effect, the use of the scissors operator shifts the calculated electrical levels by about 0.2–0.4 eV toward higher energies.

The isotropic hyperfine interaction (Fermi contact term) for an electron with gyromagnetic ratio g_e interacting with a nucleus at the site $\mathbf{R_N}$ with gyromagnetic ratio g_N is usually taken to be given by the magnetization density at the nucleus in question, i.e., by

$$a_N = \tfrac{2}{3}\mu_0 g_e g_N \mu_N m(\mathbf{R_N}), \tag{1}$$

where μ_0 is the susceptibility constant and μ_N is the nuclear magneton. The magnetization density $m(\mathbf{r})$ is the product of Bohr's magneton, μ_B, and the difference between the electron spin densities of up- and down-spins, $n_\uparrow$ and $n_\downarrow$, respectively,

$$m(\mathbf{r}) = \mu_B[n_\uparrow(\mathbf{r}) - n_\downarrow(\mathbf{r})]. \tag{2}$$

$m(\mathbf{r})$ can be analyzed in terms of three different contributions. The first contribution arises from the paramagnetic spin of the single-particle wave function describing the deep state. This contribution actuates the magnetization of the valence states, and also a spin polarization of the impurity and ligand core states. We shall in the following present the resulting total hfi only, since for the defects studied here the contribution from the gap state is dominant.

It should be noted that for the computation of particle and spin densities in the nuclear region of heavier atoms like Ge, Sn, and Pb, it is important to take relativistic effects into account, at least by using a scalar relativistic wave equation (see, e.g., Ref. 24). For the contact interaction in a relativistic theory,[25,26] the magnetization density is not to be taken at the center of the nucleus [as indicated by Eq. (1)], where it would be divergent for s-like states, nor should it be averaged over the nuclear volume. Instead an average of the magnetization density must be performed over a sphere with a diameter equal to the Thompson radius $r_{\mathrm{Th}} = Ze^2/(2mc^2)$. For test purposes we have also performed nonrelativistic calculations and obtained isotropic hfi constants that are smaller than the corresponding results of a relativistic calculation by a factor of 1.14 for the ^{73}Ge, by 1.42 for ^{119}Sn, and by as much as a factor of 3.0 for the ^{207}Pb nuclei, respectively.

The anisotropic (dipolar) hfi is given by an integral over the magnetization density over all space,

$$(b_N)_{i,j} = \frac{\mu_0}{8\pi} g_e g_N \mu_N \int \frac{3x_i x_j - r^2\delta_{i,j}}{r^5} m(\mathbf{r}+\mathbf{R_N}) d^3r. \tag{3}$$

The integrand is strongly peaked at the nucleus and, therefore, it is sufficient in practically all cases to perform the integration over the central ASA sphere and to approximate the contributions from the other spheres, replacing the spin distribution in each of these spheres by point dipoles with a dipole moment appropriate for the integrated spin density in the spheres. The anisotropic hyperfine tensor can be diagonalized into the form

$$b_N = \begin{pmatrix} b-b' & 0 & 0 \\ 0 & b+b' & 0 \\ 0 & 0 & -2b \end{pmatrix}, \tag{4}$$

and thus can be characterized by two numbers b and b'.

III. RESULTS

A. Cation vacancies

Substitutional defects in semiconductors have been interpreted successfully in terms of the defect model.[27] Therefore, we discuss the undistorted Cd vacancy in CdTe first as an example and also for further use in the discussion of the group-IV donors. Removal of a Cd atom from the lattice can be considered to be equivalent to the removal of one structural unit followed by the creation of four dangling bonds at the nearest-neighbor (nn) Te ligands. These dangling bonds are arranged as sp^3 states that transform according to the a_1 and the t_2 irreducible representations, respectively. The single-particle states, as calculated for neutral V_{Cd} in cubic CdTe, are shown in Fig. 1(a). The state transforming according to the a_1 irreducible representation forms a resonance in the upper valence band, while the t_2 state is a localized gap state which is occupied by four electrons for the vacancy in its neutral state. Due to the orbital degeneracy there will be a trigonal Jahn-Teller distortion (which is not included in our calculation) for the charge states of the vacancy (neutral and singly negative), except for the twofold negatively charged state.

The valence band, as shown schematically in Fig. 1(a), consists of three groups of bands: the lowest band is essentially due to the Te 5s states, the next group consists of the Cd 4d states and the upper group of bands which is about 5 eV wide is formed by Te 5p-like states that are hybridized with Cd 5s- and 5p-like states.

In our picture the removal of one atom followed by the formation of dangling bonds means that we also have implicitly removed one full structural unit from the otherwise undisturbed crystal. We, therefore, also find that one state transforming according to a_1 and t_2, respectively, are missing in the upper group of valence bands which are also indicated in

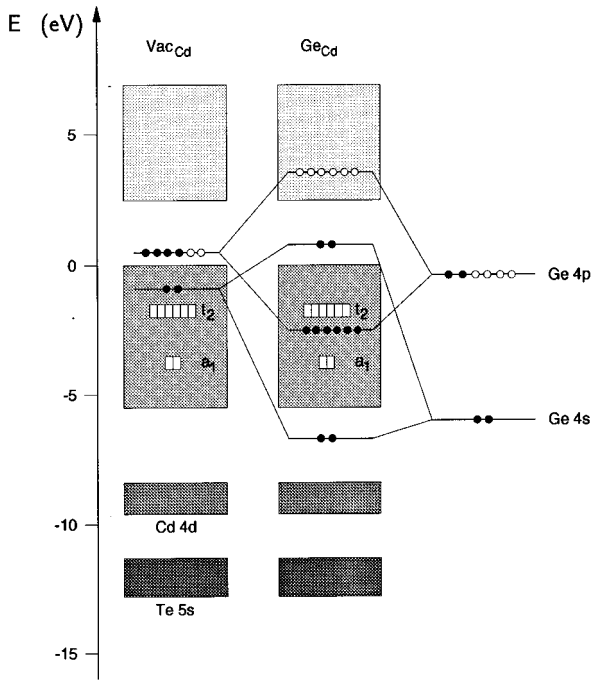

FIG. 1. Orbital model for the cation V_{Cd} vacancy in CdTe (a), the free Ge atom (c), and the Ge_{Cd} substitutional donor. Orbitals missing from the valence bands are also indicated.

Fig. 1(a). For a neutral cation vacancy we have six electrons which completely fill the a_1 states and also four out of the six t_2 states.

In Fig. 2(a) we display the spin density for the negatively charged V_{Cd}^- vacancy in the (110) plane. The spin density is strongly localized at the Te ligands, and is predominantly p like. In contrast, the vacancy in silicon (see, e.g., Bernholc *et al.*, Ref. 27, Fig. 2) is much less localized, and furthermore has predominantly sp^3 character pointing toward the vacancy site. Little spin density is found at the Cd ligands and also at the vacancy site.

In contrast to the spin density the induced particle density (i.e., the difference between the particle density of the crystal with vacancy and an undisturbed crystal) as shown in Fig. 2(b), is more extended in space: The most prominent feature is the large (negative) induced density that is due to the removal of a Cd atom when forming a vacancy. At the nearest-neighbor Te site the positive density from the occupied dangling-bond-like states dominates over the general depletion of the particle density around a vacancy.

The ligand hyperfine interactions (hfi) calculated by us cannot be directly compared with experimental data for V_{Cd}^- because of the trigonal distortion of the vacancy. In order to obtain a rough estimate of the hfi for the distorted system we have assumed that an infinitesimal trigonal field splits the states that transform according to the t_2 irreducible representation of the group T_d into states that transform according to the e and a_1 representations of C_{3v}. This of course does not include the additional localization due to the lattice distortion, but merely fulfills symmetry requirements. Taking the a_1 state as singly occupied, we obtain the hfi results compared with experimental data in Table I for the cation vacancy in CdTe and ZnSe, respectively. The comparison shows that the dipolar interaction with the nearest-neighbor ligand on the trigonal axis (which originates from the p-like spin density) is comparable to the experimental data, whereas the contact interaction (which is due to the relatively small s-like admixture) is off by a factor of 2 (or even 6) for ZnSe (CdTe). Note that we have two sets of experimental data as the signs of the hfi have not been determined experimentally, and, therefore, the hfi parameters a and b cannot be determined uniquely.

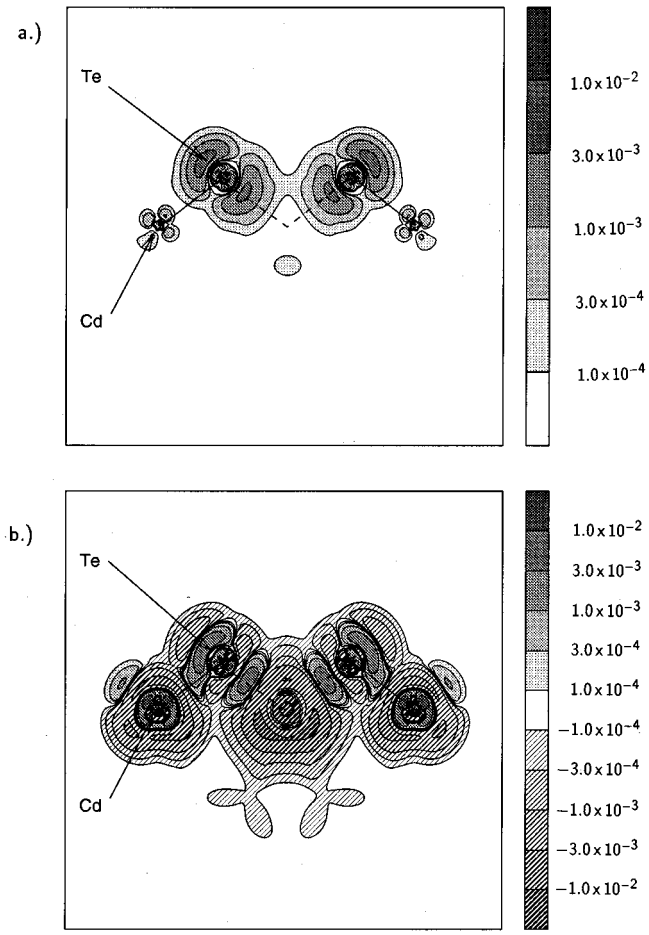

FIG. 2. Spin density (a) and induced particle density (b) of the V_{Cd}^- vacancy in CdTe plotted in a (110) plane

B. Group-IV donors on the cation site

For Ge substituting for Cd in CdTe, we show in Fig. 3(a) the spin-density distribution in the (110) plane. Figure 1(b) shows the relevant bond orbital model: the dangling bonds of the vacancy in Fig. 1(a) interact with the atomic 5s and 5p states of Ge [Fig. 1(c)] forming bonding and antibonding linear combinations [Fig. 1(b)]. Since the Ge atomic potential is more attractive than the Cd potential for which it substitutes, the bonding a_1 state is ''superdeep'' below the upper valence bands, the bonding states transforming according to t_2 are resonances in the valence bands, and the antibonding state transforming according to a_1 forms the gap state and is doubly occupied for the neutral donor and singly occupied for the donor in the paramagnetic state. As is customary with donors in the II-VI compound semiconductors we

TABLE I. Comparison of the calculated electron hyperfine interaction constants for vacancies (in MHz) with experimental data. The electron removal energies (in eV above the valence-band edge) are compared with experimental ionization energies where available.

		(1,1,1) ligand		(2,2,0) ligand			
		a	b	a	b	$E^{2+/+}$	$E^{+/0}$
V_S^+ in ZnS	This work	64	4.6	1.9	1.7	0.8	2.1
	Expt.[a]	74.4	4.8			1.5[b]	
V_{Se}^+ in ZnSe	This work	68.4	4.1	14.5	8.6		
	Expt.[c]			4.2	0.0		
V_{Zn}^- in ZnSe	This work	60	−190	39	0.0		
	Expt.[d]	403	−168.4				
		368.5	−218.3				
V_{Te}^+ in ZnTe	This work	64	4	−16	−20		
V_{Te}^+ in CdTe	This work	−410	−22	−28	−20	0.67	1.27
	Expt.[e,f]	29.8	1.1	4.2	0.5		0.20
V_{Cd}^- in CdTe	This work	−170	−370	39	0.0		
	Expt.[g]	403	−116	50			
		290	−230	50			

[a]Schneider and Räuber, 1967 (Ref. 11).
[b]Leutwein, Räuber, and Schneider, 1967, (Ref. 33).
[c]Gorn *et al.*, 1990 (Ref. 12).
[d]Watkins, 1975 (Ref. 32).
[e]Meyer *et al.*, 1992 (Ref. 13).
[f]Hofmann *et al.*, 1994 (Ref. 14).
[g]Emanuelson *et al.*, 1993 (Ref. 28).

shall denote this state by Ge_{Cd}^{3+} where the upper index gives the formal oxidation state of the defect rather than its charge state.

A comparison of the spin density of Ge_{Cd}^{3+} in CdTe with the similar double donor S_{Si}^+ in silicon (here the upper index means singly positive charge state) (Fig. 6 of Ref. 27) again shows the drastic increase in state localization if one goes from silicon to the II-VI compound semiconductors. For S_{Si}^+ in silicon the cluster formed by the donor and its first shell of ligands contains about 0.2 of an electron spin only (for details, see Ref. 9). In contrast, the analogous cluster for Ge_{Cd}^{3+} in CdTe already contains 0.55 of an electron spin. The increase in localization is, however, not as pronounced if we consider the distribution of induced particle density plotted in Fig. 3(b).

For the group-IV donors in CdTe, ZnTe, and also CdTe the hfi data are compared in Table II with experimental data (for CdSe the experimental data have been taken in host material of wurtzite rather than cubic structure). All calculated data agree very closely with the experimental data (where available), which shows that the distribution of the spin density as shown in Fig. 3(a) is basically correct. The fact that the interactions with the Cd ligands are not resolved in EPR is in line with our result that the ligand hfi with these ligands is rather small. The smallness of this ligand hfi with the next-nearest neighbor, in particular of the contact term, however, is a surprising result of our calculation which deserves experimental verification. We should like to point out that, e.g., the value of $a=-1.3$ MHz for the contact hfi at the Cd (2,2,0) ligand corresponds to the s-like spin density of the fraction 10^{-4} of a spin [to be compared with the difference between calculated and experimental value at the Te(1,1,1) ligand which corresponds to 3×10^{-3} of a spin]. It would be interesting to see if calculated spin densities in the II-VI semiconductors are meaningful at ligands where the calculated spin density is that small. For interstitial Al_i^{2+} in silicon we have shown[29] that contact ligand hfi values that correspond to a fraction of 10^{-4} of a spin can still be compared with experimental data.

If we compare the contact hfi with the impurity nucleus, we observe a certain overestimate of the theoretical data for the hfi with the heaviest nucleus, ^{207}Pb, as compared to the experimental values. Further work will be necessary to clarify if this deviation is indicative of a slight systematic error of our calculations. Note, however, that the use of nonrelativistic spin densities would have led to discrepancies between experimental and theoretical data that would amount to a factor of 2.

To our knowledge there are no theoretical hfi data for point defects in II-VI compound semiconductors besides the work by Van de Walle and Blöchl,[7] on the Zn interstitial in ZnSe. We have repeated their calculation, and find essentially the same hfi interaction with the ^{67}Zn nucleus (see Table III). It is somewhat surprising that our hfi result for the ^{67}Zn(0,0,0) impurity nucleus agrees so closely with that of Ref. 7, but is distinctly different for the for the ^{77}Zn(1,1,1) ligand. A possible explanation might be that the 32-atom supercell used by Van de Walle and Blöchl is too small, because in a supercell one calculates the electronic properties of a periodic array of impurities. According to our results (in a Green's-function calculus one treats a single point defect in an otherwise perfect crystal), however, the spin density is strongly localized and, therefore, the influence of the periodic array of impurities of the supercell calculation

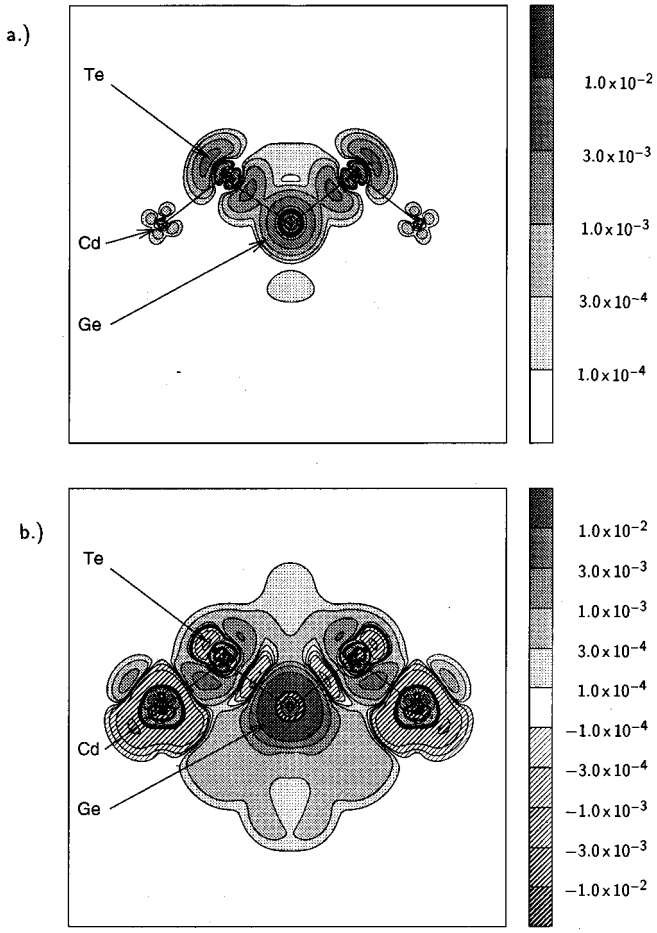

FIG. 3. Spin density (a) and induced particle density (b) of the Ge_{Cd}^{3+} deep donor in CdTe plotted in a (110) plane.

appears to be of no importance. Van de Walle and Blöchl[7] report that the lattice relaxation (which is ignored in our calculation) has a larger influence on the anisotropic hfi with the ^{77}Zn(1,1,1) nucleus. The largest discrepancy between the calculations, however, is found for the isotropic part.

C. Anion vacancies

When we started our investigation of hyperfine interactions for defects in II-VI compound semiconductors, our first impurity was the simplest possible species, the anion vacancy. This vacancy can be understood with the model presented in Fig. 1(a), with the distinction that the potential of the anion is by far more attractive than that of the cation and, therefore, vacancy levels due to a missing anion are shifted to higher energies as compared to vacancy levels of a cation. The removal of a neutral anion atom removes six electrons from the system, and also eight valence-band states. The neutral anion vacancy will, therefore, have two electrons in the state transforming according to the a_1 irreducible representation, and the t_2 states left unoccupied. The positive charge state of the anion vacancy will thus be paramagnetic, and transform according to the A_1 irreducible representation.

In Table I we compare our ligand hfi data for the V_S^+ vacancy in ZnS with the EPR data obtained in 1967 by Schneider and Räuber.[11] For the hfi with the ^{67}Zn nucleus we find excellent agreement for both the contact and the dipolar interactions. The hfi with the ^{33}S ligands is not resolved experimentally, which is consistent with the small values obtained theoretically for the hfi with these nuclei and also with the small natural abundance of ^{33}S.

For the V_{Te}^+ vacancy in CdTe there are EPR measurements of the ligand hfi[13] and also ENDOR data,[14] which should provide us with a very detailed picture of the spin-density distribution. A comparison of the theoretical and experimental results for the first two ligand shells (many more have been resolved experimentally) which have been calculated by us and are listed in Table I is extremely unsatisfactory: There is an order of magnitude discrepancy for all ligand hyperfine interactions for which a comparison is possible. This is quite unexpected, as for all the other defects, which transform according to A_1 (donors, the Zn self-interstitial), the calculation of the ligand hfi did not present any special difficulty. We therefore suspect that the experimental identification of the V_{Te}^+ in CdTe is incorrect. This suspicion is corroborated by the observation that the ligand hfi with all 15 ligand shells observed experimentally accounts for only 0.041 electron spin. Figure 4 shows a plot of the spin density of V_{Te}^+ in the (110) plane. According to our calculation, there is about 0.2 of an electron spin localized in the ASA sphere that contains the vacancy. This is comparable with the localization of about 22 % obtained for the V_S^+ vacancy in ZnS for which the calculated hfi agrees with the experimental data. In contrast, the ENDOR data require that 0.96 of an electron spin is located at the vacancy site. We are not aware of a single isolated point defect in a semiconductor other than an f-transition element for which such a strong localization has been reported. Note also that the discrepancy between experimental and theoretical ionization energies (see Table I) disappears if both energies refer to different defects.

A different problem is apparently present for the V_{Se}^+ vacancy in ZnSe when we compare our theoretical results listed in Table I with experimental EPR data by Gorn *et al.*:[12] The experimentalists did not observe the ligand hfi with the ^{67}Zn(1,1,1) ligand which, according to our calculation should be much larger than the ligand hfi with two ^{77}Se shells. Gorn *et al.* find that the hfi with ^{77}Se(2,2,0) is isotropic, and with 4.2 MHz much smaller that the the ligand hfi with some more distant ^{77}Se ligand shell, for which a = 32.7 MHz and $b = 6.3$ MHz are reported. This is certainly not compatible with our results. Again we do not have a sound proposal as to the nature of the center observed experimentally. The case should be checked experimentally, in particular the ligand hfi with the ^{67}Zn(1,1,1) nuclei which are missing in the experiment.

IV. CONCLUSIONS

We have shown with the help of *ab initio* self-consistent computations that the hyperfine and ligand hyperfine interactions of donors and cation self-interstitials in II-VI compound semiconductors can be calculated and compared with experimental data. We find that for the hfi with the donor nuclei our calculated results agree with the experimental data to within a few percent for the lighter ^{73}Ge and ^{67}Zn nuclei. For the heavier ^{119}Sn, and in particular the ^{207}Pb nuclei, our results systematically deviate from the experimental data (by

TABLE II. Comparison of the calculated electron hyperfine interaction constants for deep donors (in MHz) with experimental data. The electron removal energies (in eV above the valence band edge) are compared with experimental ionization energies where available.

		donor(0,0,0)	anion(1,1,1)		cation(2,2,0)			$E^{4+/3+}$	$E^{3+/2+}$
		a	a	b	a	b	b′		
	ZnTe								
$^{73}Ge^{3+}_{Cd}$	This work	−664	−400	−155	1	−0.3	0.08	1.09	2.04
	Expt.	657.0[a]	496.0[a]	193.0[a]				1.10[b]	
$^{119}Sn^{3+}_{Cd}$	This work	−14 600	−540	−120	1.1	−0.3	0.09		
	Expt.	12 270.0[a]	516.0[a]	213.0[a]					
$^{207}Pb^{3+}_{Cd}$	This work	24 300	−560	−150	1.2	−0.3	0.03		
	Expt.	15 500.0[a]	354.0[a]	210.0[a]				1.20[b]	
	CdTe								
$^{73}Ge^{3+}_{Cd}$	This work	−580	−350	−180	−1.3	1	1	0.77	1.06
	Expt.	615.0[c]	543.0[c]	159.0[c]				1.10 [d]	
$^{119}Sn^{3+}_{Cd}$	This work	−13 800	−690	−170	−12	−1	0.9		
	Expt.	11 800.0[c]	570.0[c]	195.0[c]					
$^{207}Pb^{3+}_{Cd}$	This work	17 800	−380	−170	−8	1	0.9	1.4	
	Expt.	14 650.0[c]	379.0[c]	169.0[c]					
	CdSe								
$^{73}Ge^{3+}_{Cd}$	This work	−750	120	75	16	−1.1	1	1.05	1.5
	Expt.	792.0[e]							
$^{119}Sn^{3+}_{Cd}$	This work	−16 000	234	64	16	−1.1	1.0	1.47	1.89
	Expt.	13 590.0[e]							
$^{207}Pb^{3+}_{Cd}$	This work	23 900	291	72	2.6	−1.0	0.8	1.89	

[a]Hausmann and Roll, 1988 (Ref. 16).
[b]Suto and Aoki, 1968 (Ref. 30).
[c]Brunthaler *et al.*, 1985 (Ref. 17).
[d]Brunthaler *et al.*, 1984 (Ref. 31).
[e]Schultes *et al.*, 1988 for CdSe in a wurtzite structure (Ref. 18).

more than 20% for hfi with ^{207}Pb). This deviation may be indicative of a systematic error when applying the analysis of Bluegel *et al.*[25] to the heaviest nuclei.

We also find a fair agreement between our theoretical results and experimental literature data for the ligand hyperfine interactions with the anion (1,1,1) ligands. To our knowledge ligand hyperfine data for interactions with nuclei from more extended shells are available for CdS in wurtzite structure only.[18]

For cation vacancies the comparison of our results with experimental data is impeded by the fact that we ignore the trigonal Jahn-Teller distortion present for the paramagnetic state of these defects. If we simulate the symmetry lowering due to this trigonal distortion by forcing the defect state to

TABLE III. Comarison of the calculated electron hyperfine interaction constants for the tetrahedral Zn_i^+ self-interstitial (in MHz) with results from a supercell calculation (Ref. 7) and with experimental data (Ref. 34).

	a	*a*	*b*	*a*	*b*	*b′*
	^{67} Zn_i^+ (0,0,0)	^{77} Se (1,1,1)		^{67} Zn (2,0,0)		
^{67} Zn_i^+ (0,0,0) on T_d^{Se} site						
This work	1067	355	17.1	6.2	−0.14	0.034
Van de Walle and Blöchl	1078	736	11	10		
Expt.	1089	481	16.8			
	^{67} Zn_i^+ (0,0,0)	^{67} Zn (1,1,1)		^{77} Se (2,0,0)		
^{67} Zn_i^+ (0,0,0) on T_d^{Zn} site						
This work	1739	−1.8	2.0	227	20.1	0.1
Van de Walle and Blöchl	1252	≈ 0		354		

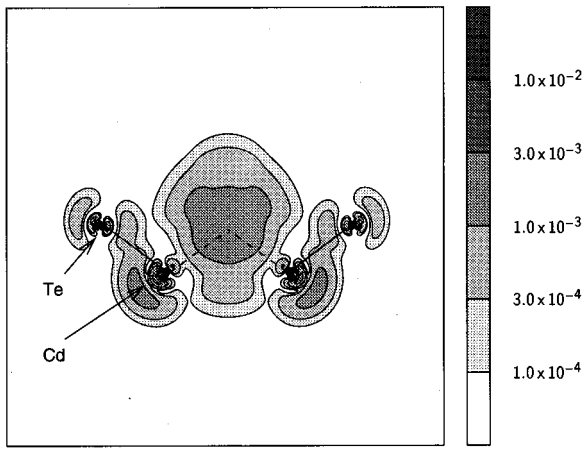

FIG. 4. Spin density of the V_{Te}^{+} vacancy in CdTe plotted in a (110) plane.

transform according to the A_1 irreducible representation of group C_{3v}, we obtain results that are of the same order of magnitude as the experimental data.

For the anion vacancies the ground state transforms according to A_1 of the group T_d and, therefore, there will be no symmetry-lowering distortion. Again we expect and find near-perfect agreement of our theoretical hfi results with data from previous EPR experiments (Schneider and Räuber, 1967, Ref. 11). There is, however, not even an order of magnitude agreement of our results with experimental EPR (Ref. 13) and ENDOR (Ref. 14) data for the defect identified as V_{Te}^{+} in CdTe. From our experience presented in this paper, that for defect states transforming according to the A_1 irreducible representation the ligand hyperfine interactions calculated for the unrelaxed defect agrees with experimental data, this discrepancy is unexpected. We therefore conclude that the theoretical work has treated a defect that is not comparable to the defect seen in the experiment. We thus strongly suspect that the defect identification in the EPR and ENDOR experiments is incorrect. A comparison of our results for the F center in ZnSe with experimental data also indicated that the identification of this defect is doubtful. We conclude in fact that F centers are a very rare species in semiconductors: besides the well-identified F center in ZnS, there seems to be no other candidate which could be identified beyond doubt.

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