

Group V acceptors in CdTe: *Ab initio* calculation of lattice relaxation and the electric-field gradient

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Using the linearized augmented plane wave method, the self-consistent electronic structure of the group V acceptors N, P, As, and Sb in CdTe is calculated in order to derive the electric field gradient (EFG) at the neighboring Cd site. The agreement between theory and experiment is very good and, due to the high sensitivity of the EFG on the local structure, it is evidence of the accuracy of the calculated lattice relaxation. The dependence of the EFG on the charge state of the group V acceptors is discussed in terms of the calculated electronic density of states.

In semiconductors, the understanding of extrinsic and intrinsic defects is of central importance. It represents a constant driving force behind the large number of experimental investigations, collecting information about the presence as well as the opto-electrical properties of defects. The usefulness of the collected information, however, is closely related to the quality of the identification of the respective defects.¹ Here, the electric field gradient (EFG) has turned out to be a valuable tool. The EFG is measured via its interaction with the nuclear electric quadrupole moment of a suitable probe atom by different experimental techniques, such as perturbed $\gamma\gamma$ -angular correlation (PAC), Mössbauer spectroscopy, nuclear quadrupole resonance, or electron nuclear double resonance.² Each defect modifies the local electrostatic potential at the position of the probe atom in its own way and creates its own characteristic EFG. In the past, a large number of distinct EFG, caused by different types of extrinsic and intrinsic defects, were determined in elemental, binary, and ternary semiconductors.^{2,3} Because of the lack of reliable theories to calculate the EFG caused by a distinct defect, in most cases, the EFG have only been useful as ‘‘fingerprints’’ which do not tell about the microscopic structure of the defect.

A simple approach to EFG calculation is the point charge model, which is quite reasonable for highly ionic crystals, but it breaks down as covalent bonding (e.g., in semiconductors) becomes more important.⁴ Therefore, it is desirable to calculate the EFG in an *ab initio* approach. The EFG is very sensitive to the anisotropic charge distribution close to the nucleus, and for its accurate calculation the entire electronic configuration of the semiconductor, perturbed by the defect complex, has to be determined. This can be done in the framework of the density functional theory (DFT). A well-proven method to solve the DFT equations in solids is the linearized augmented plane wave (LAPW) method, implemented, for example, in the program package WIEN97,⁵ which was used in the present work. As an important characteristic of the LAPW method, the plane wave basis set is augmented by a basis in a spherical harmonics expansion within so called ‘‘muffin-tin’’ spheres. This method is described in detail in Ref. 6, and it has been employed for calculations of

EFG in undisturbed lattices with a symmetry lower than cubic, e.g., for hcp metals⁷ or various Fe compounds.⁸ In the present case, however, EFG are addressed that are caused by lattice defects, such as dopant atoms, in a lattice with cubic symmetry. In this case a supercell approach is used, in which the small unit cell is replaced by a larger one and one atom of the host lattice is replaced by the dopant. Since the computational time scales with the third power of the number of atoms per cell, the size of the supercells that can be treated within an acceptable time is very limited. The large number of atoms that have to be considered, along with the required high accuracy of the charge distribution close to the nucleus, are the reasons for the very little work performed in calculating defect induced EFG up to now. Thus, there are recent calculations using the full potential Korringa-Kohn-Rostocker method which give results for pairs consisting of a Cd atom and different group V elements in Si and Ge.⁹

In this paper, LAPW supercell calculations for the group V acceptors N, P, As, and Sb in the II–VI semiconductor CdTe are reported, and the calculated EFG are compared to PAC measurements with the radioactive probe $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ at the nearest neighbor (NN) site; first, preliminary results were published in Ref. 3. It should be noted that the pair formation of the $^{111}\text{In}/^{111}\text{Cd}$ probe with the acceptor (cf. Fig. 1) takes place with the ^{111}In donor driven by the Coulomb

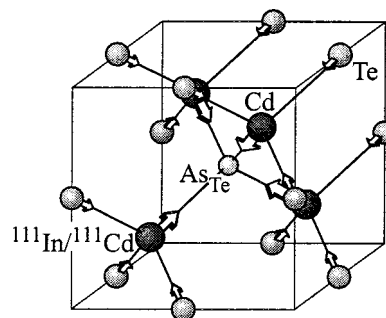


FIG. 1. Relaxation of the first and second atomic shells about the group V impurity As_{Te} in CdTe. (Note, that this figure does not show the complete 32 atomic supercell used in the present calculation).

TABLE I. Comparison of experimental and calculated EFG (V_{zz} in 10^{21} V/m²) that are caused by different group V acceptors (A). Experimentally, the sign of V_{zz} is not accessible. The EFG refer to the NN Cd site (see Fig. 1). The experimental values are measured at 295 K (Ref. 11). The theoretical values are calculated for the two charge states A^- and A^0 .

CdTe:A	Experiment	Theory	
		A^-	A^0
CdTe:N	$\pm 13.95(5)$	-13.7	-13.4
CdTe:P	$\pm 10.56(9)$	-11.2	-10.0
CdTe:As	$\pm 9.27(5)$	-9.5	-7.7
CdTe:Sb	$\pm 7.62(5)$	-8.1	-5.3

attraction between the ionized donor and acceptor. After the β decay of ^{111}In to ^{111}Cd , the EFG is measured at the daughter isotope ^{111}Cd , and it is the element ^{111}Cd that governs the observed EFG, rather than ^{111}In .¹⁰ For each group V acceptor, the PAC measurements yield a characteristic EFG tensor V_{ij} . It is specified by the quadrupole coupling constant $\nu_Q = eQV_{zz}/h$, the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ (with $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$), and the orientation of the EFG tensor. The measured coupling constants at 295 K are $\nu_Q = 280, 212, 186,$ and 153 MHz for N, P, As, and Sb, respectively.¹¹ Using $Q = 0.83b$ for the nuclear quadrupole moment of the isomeric $I = \frac{5}{2}$ state of ^{111}Cd ,¹² the corresponding largest components V_{zz} of the EFG tensor are listed in Table I. In all cases, the EFG tensor is axially symmetric, i.e., $\eta = 0$, and the orientation of its symmetry axis is along a $\langle 111 \rangle$ lattice direction. Based on systematic doping experiments and the symmetry properties of the EFG, in Ref. 11 the assignment to NN $^{111}\text{Cd}-A_{\text{Te}}$ pairs was made (the symbol A is used for the group V acceptors throughout this work). Because of a presumably high degree of compensation, these EFG probably correspond to the ionized state of the group V acceptors.

For the LAPW calculations, the zinc-blende lattice of CdTe ($a_0 = 6.48$ Å for the primitive unit cell¹³) is constructed by use of a $2 \times 2 \times 2$ supercell in BCC structure, resulting in a basis of 32 atoms ($\text{Cd}_{16}\text{Te}_{15}A_{\text{Te}}$). For a first application to the EFG calculation, the choice of the CdTe matrix takes advantage of the fact that the $^{111}\text{In}/^{111}\text{Cd}$ probe is a host atom at the time of the EFG measurement: only one atom in the supercell has to be replaced (A_{Te}), and the T_d point-group symmetry can be used with respect to the acceptor (cf. Fig. 1). Due to the high symmetry, considerable computational time is saved and there are less degrees of freedom for structural relaxation. The assumption of T_d symmetry is justified by the experimental findings, namely, the asymmetry parameter $\eta = 0$ of the EFG and its orientation along the $\langle 111 \rangle$ lattice direction. With regard to the actual calculations, the following issues are mentioned: The muffin-tin radius of the host atoms times the largest reciprocal lattice vector in plane wave expansion yields $RK_{\text{max}} = 7.2$ —this parameter is often used as a measure for the size and quality of the basis set in LAPW calculations.⁶ The \mathbf{k} mesh in the full Brillouin zone (BZ) consists of 125 points, which are reduced to 10 \mathbf{k} points in the irreducible wedge of the BZ. The generalized gradient approximation as described by Perdew and

TABLE II. Relaxation of NN and NNN atoms of different group V elements (A) from the regular lattice sites (in percent of the bond length 2.81 Å of CdTe), along with the resulting Cd-A distance. The values refer to the negative acceptor A^- . The Cd-A distance for the neutral acceptor A^0 is slightly larger (by a maximum of 0.03 Å for Sb and approximately zero for N).

CdTe:A	NN-Cd [%]	NNN-Te [%]	Cd-A distance [Å]
CdTe:N	21.7	4.3	2.20
CdTe:P	11.0	2.0	2.50
CdTe:As	8.3	1.3	2.57
CdTe:Sb	3.3	0.4	2.71

co-workers¹⁴ is used to treat exchange and correlation effects. The technique of calculating the EFG within the LAPW code is described in Ref. 15, for instance.

Relaxation of the atoms from their original lattice positions alters the EFG significantly: With respect to the probe atom ^{111}Cd , being the nearest neighbor to the acceptor atom, the EFG is proportional to the anisotropy of the charge density. Furthermore, the actual distance of each of the nearest neighbors of the probe atom influences the charge distribution within the covalent Cd-Te and Cd- A_{Te} bonds. Hence, taking into account the structural relaxation of the neighboring atoms is crucial for the quality of an EFG calculation. A change by 1% in the length of the Cd- A_{Te} bond relative to the bond length of the undisturbed lattice yields a change in the calculation EFG by about 10^{21} V/m² (approximately $\Delta\nu_Q = 20$ MHz). In the present work, the positions of all atoms up to the next nearest neighbor (NNN) shell with respect to the group V impurity are adjusted until the calculated forces are below 0.02 eV/Å. In this way, the relaxations of all NN atoms with respect to the ^{111}Cd probe are taken into account (cf. Fig. 1). For all group V elements, the amount of relaxation decreases rapidly from the NN to the NNN shell (Table II). Allowing for a relaxation of the third shell, which is still entirely contained within the supercell, leads to only minor changes of the results.

In the calculated band structure for the neutral acceptor A^0 , the Fermi level does not lie within the band gap, but it bisects the valence band. The density of states (DOS) integrated from the Fermi level to the valence band edge accommodates one electron. Accordingly, these empty states are identified with the acceptor hole. The negatively charged acceptor state A^- is then calculated by filling these states. In order to retain charge neutrality, the additional electron is compensated by a positive background charge, which is achieved by omitting the $\mathbf{k} = 0$ contribution in the Fourier expansion of the potential. The EFG of both charge states calculated at the NN Cd atom are compared to the experimental data in Table I. The absolute values of V_{zz} obtained for the ionized group V acceptors ($\text{Cd}_{16}\text{Te}_{15}A_{\text{Te}}^-$) are in very good agreement with the experimental data. This supports the negative charge state of the group V acceptors to be observed in the experiment. Since the calculated values correspond to zero temperature, and the experimental values increase by about 3% at 4 K, the agreement with the experiment is still better than indicated by Table I [e.g., the EFG of the $^{111}\text{Cd}-\text{P}$ pair is $10.56(9)10^{21}$ V/m² at 295 K and $10.91(9)10^{21}$ V/m² at 4 K]. From the calculations it is found

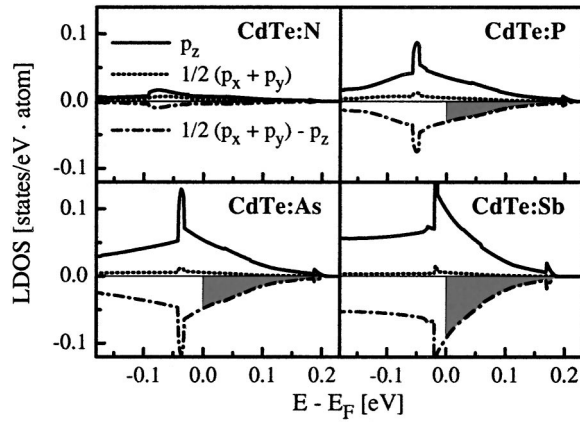


FIG. 2. LDOS at the NN Cd site in the vicinity of the valence band edge (A^0). The anisotropy of the p -LDOS is shown by the difference $[\frac{1}{2}(p_x + p_y) - p_z]$. The anisotropic part of the LDOS that gives an additional contribution to the EFG in the negative charge state (A^-) of the group V impurity is shaded.

that the EFG are mainly caused by the anisotropy of the charge density very close to the nucleus of the probe atom: integration of the charge confined within a sphere with radius of $\frac{1}{10}$ of the NN distance determines the value of the EFG almost completely; a similar observation is reported in Ref. 9.

Table I shows that the influence of the actual charge state of the acceptor on the value of the calculated EFG is most pronounced in the case of Sb and almost negligible in the case of N. In order to understand the quite different dependence of the EFG at the Cd site on the charge state of the group V acceptors, an analysis of the properties of the electron band structure is made for the investigated group V elements. Inside the muffin-tin sphere, the calculated total DOS can be decomposed into contributions from the different angular momenta. It has to be noted that this site-projected local density of states (LDOS) depends to some extent on the choice of the respective sphere radius. It is well known that the valence band maximum in common II–VI semiconductors is mainly derived from the p states of the group VI atoms (see, e.g., Ref. 16); i.e., the bands in the vicinity of the valence band maximum (VBM) have strong Te- p character. In this energy region, however, there is an additional LDOS contribution at the acceptor site that is small for N but strongly increasing with the atomic number Z of the acceptor. The acceptor hole, which is energetically localized at the VBM, is consequently more centered at the acceptor site for higher Z . This behavior is consistent with the experimental observation that the ionization energies of the group V acceptors increase with increasing Z .¹³ Due to the covalent interaction of the acceptors with the neighboring Cd atoms there is also an additional LDOS at the NN Cd site. This affects only the Cd- p_z orbital, denoting the direction of the Cd-A bond as z . In Fig. 2, the Cd- p_z LDOS is compared with the Cd- $p_{x/y}$ LDOS, and the anisotropy is visualized by the difference $[\frac{1}{2}(p_x + p_y) - p_z]$. In the negative acceptor state, the originally empty states up to the valence band edge become occupied, and the additionally occupied anisotropic part of the LDOS (shaded area in Fig. 2) leads to an additional contribution to the EFG. Since this part is increasing

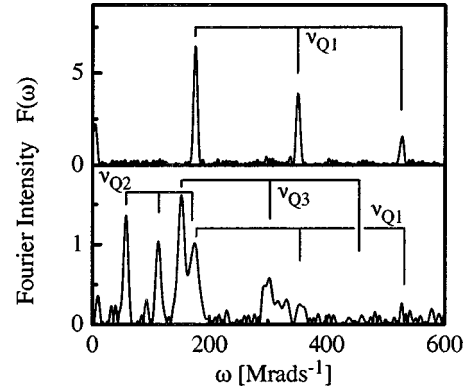


FIG. 3. Fourier spectra $F(\omega)$ of two PAC experiments performed at the probe $^{111}\text{In}/^{111}\text{Cd}$ in CdTe: (top) after doping with As and (bottom) after additional doping with Li (see text).

from N to Sb, the different sensitivity of the EFG at the Cd site on the two charge states is understandable.

Stimulated by the calculated EFG in Table I, the possible formation of a neutral acceptor state A^0 was studied by PAC measurements at a sample that was doped with As and subsequently with Li acceptors. After As doping, the PAC data in Fig. 3 (top panel) shows the known frequency triplet which belongs to the EFG caused by the $^{111}\text{Cd}\text{-As}^-$ pair ($\nu_{Q1} = 186$ MHz, at 295 K). Following additional Li doping, however, three different EFG are detected (Fig. 3, bottom panel): The first EFG still indicates the presence of $^{111}\text{Cd}\text{-As}^-$ pairs ($\nu_{Q1} = 188$ MHz, at 77 K). The second one is known to be related to the Li doping process ($\nu_{Q2} = 60$ MHz, cf. Ref. 3). The third EFG, corresponding to $\nu_{Q3} = 161$ MHz or $V_{zz} = 8.0(1)10^{21}$ V/m², is new and agrees well with the calculated EFG $V_{zz} = 7.7 \times 10^{21}$ V/m² for the neutral state of the As acceptor (cf. Table I). Since the Li acceptor [$E_A = 58$ meV (Ref. 13)] is shallower than the As acceptor [$E_A = 92$ meV (Ref. 13)], it is ionized by compensating donors with a higher probability than the As acceptor. Furthermore, the p -type conductivity should be enhanced by the Li doping in general. For these reasons, it seems to be likely that the As acceptors exist in the neutral charge state As^0 besides the ionized state As^- , and the EFG corresponding to ν_{Q3} is proposed to be assigned to the neutral As^0 acceptor. Thus, despite the use of a rather small cell size that could in principle artificially influence the EFG in the neutral state A^0 , the agreement of the calculated EFG with the PAC data is excellent for both charge states of the As acceptor.

Since the EFG strongly depends on the local structure about the probe atom, the PAC data yield valuable information on the reliability of the calculated lattice relaxation. Thus, from the sensitivity of the EFG to the $^{111}\text{Cd}\text{-A}$ distance and the accuracy of the experimental EFG, the accuracy of the calculated lattice relaxation in Table II can be estimated to 0.01 Å. Experimentally, the distance between NN atoms is directly accessible by EXAFS spectroscopy; e.g., there exist experimental data for Cl in ZnSe and ZnTe.¹⁷ This method is not sensitive to impurity concentrations well below 10^{19} cm⁻³, whereas a concentration in the range 10^{16} to 10^{17} cm⁻³ is still sufficient for PAC experiments.

Summarizing, the presented LAPW calculations of the defect induced EFG reveal a convincing agreement between

theory and experiment and, at the same time, yield quantitative information on the lattice relaxation about the different group V elements in CdTe. It is obvious that this type of calculation is applicable also to more complex defect scenarios, in which more than one host atom is replaced by a defect (e.g., if the probe atom itself is not a host atom). Thus, the present results show that the unique identification of the

numerous defects that were already well characterized by their specific EFG in the past should be possible with help of *ab initio* calculations.

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