

Density Functional Theory Calculations Establish the Experimental Evidence of the DX Center Atomic Structure in CdTe

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The In DX center and the DX -like configuration of the Cd host atom in CdTe are investigated using density functional theory. The simultaneous calculation of the atomic structure and the electric field gradient (EFG) allows one to correlate the theoretically predicted structure of the DX center with an experimental observable, namely, the EFG obtained from radioactive $^{111}\text{In}/^{111}\text{Cd}$ probe atoms in In doped CdTe. In this way, the experimental identification of the DX center structure is established.

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Exhibiting prominent metastable behavior, many donor species in semiconductors are unstable against DX center formation. The peculiar electrical and optical properties related to DX centers have attracted a great deal of interest, where most extensively the III-V compound $\text{Al}_x\text{Ga}_{1-x}\text{As}$ has been investigated [1]. Theoretical studies in the framework of density functional theory (DFT) provided an important contribution for the understanding of this type of defect [2], showing that the DX center originates from a large lattice relaxation of the substitutional donor atom, accompanied by the capture of an additional electron according to the reaction $2d^0 \rightarrow DX^- + d^+$; here, d^0 and d^+ denote the neutral and the ionized substitutional donor, respectively.

While the electrical and optical properties of the DX center are very well characterized experimentally, the model for the atomic structure is primarily based on theoretical studies. The need for direct experimental evidence of the microscopic structure was pointed out more than a decade ago [1,3], but even now only very few approaches towards a direct identification are reported: Positron annihilation spectroscopy experiments indicated positron trapping at DX centers in Cl doped CdZnTe [4]. A photoinduced lattice relaxation, observed by x-ray absorption (EXAFS) spectroscopy, has been reported for CdTe:In [5]. However, details of the local structural configuration of the DX center could be resolved in neither experiment. Motivated by the fact that nuclear hyperfine interaction studies with radioactive probe atoms are perfectly suited to study local atomic configurations in semiconductors [6], the Te DX center in AlGaAs was investigated by Bemelmans *et al.* [7] using the Mössbauer isotope $^{129\text{m}}\text{Te}$. A measured electric field gradient (EFG) was identified with a DX -like configuration of the ^{129}I daughter isotope. The authors pointed out, however, that models for the structure of the DX center could only be tested against the experimentally observed EFG tensor by performing the full electronic calculation at the probe atom. Being unfeasible at that time, these EFG calculations for DX centers are a substantial part of the present work.

Experimental EFG related to the In DX center in CdTe and ZnTe were recently obtained by means of perturbed $\gamma\gamma$ angular correlation (PAC) experiments employing radioactive ^{111}In probe atoms [8]. Experimentally, the EFG is used as a unique “fingerprint” of the observed defect, e.g., of the DX centers observed in Ref. [8], because it is very sensitive to the local atomic configuration around the probe atom [6,9]. Since, however, the EFG itself does not yield detailed information about the actual defect structure, DFT calculations are used in the present work to determine theoretically the atomic and electronic structure of the In DX center in CdTe, including the characteristic EFG. In this way, the theoretical model of the DX center structure is directly correlated with the EFG as an experimentally accessible quantity. Within this approach, the high quality of the atomic structure and EFG calculations, being a prerequisite for the present purpose, has been demonstrated in the case of the group V acceptors in CdTe [10]. Experimental literature data on In doped CdTe, obtained by conductivity measurements [11,12] and EXAFS [5], are reviewed in the context of the present DFT study, in order to obtain a consistent picture about the stability of the DX center. Furthermore, the calculated EFG are used to discriminate experimentally between different compensation mechanisms that are connected with different defect structures. The resulting identification of the compensating defects is important since the prevailing compensation mechanism in CdTe:In, limiting the achievable electron concentration to the 10^{18} cm^{-3} range, is still subject to discussion: While DX centers have been proposed on the basis of theoretical studies [13], the formation of A centers (here, $\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs) is a competing model with strong experimental evidence [14–16].

In order to compare the EFG obtained by DFT calculations with the EFG measured in PAC experiments using the probe atom ^{111}In , it is important to recall the process of the measurement of the EFG: First, the radioactive ^{111}In isotopes are introduced into the CdTe sample. At this stage the probe atoms are subject to compensation, i.e., DX center formation, for instance. The actual

measurement of the EFG, however, takes place following the radioactive β decay of ^{111}In at the excited $I = 5/2$ state of the ^{111}Cd daughter nucleus ($t_{1/2} = 85$ ns). Thus, a characteristic EFG due to DX center formation is only measured if the ^{111}In probe is incorporated in the strongly relaxed DX configuration *and* if there exists also a metastable DX -like configuration for the ^{111}Cd atom—labeled Cd_{DX} in the following. In order to be detectable, the Cd_{DX} configuration must be separated from the substitutional ground state by an energy barrier high enough that this configuration survives for about 500 ns. The EFG, being conventionally characterized by the largest component V_{zz} of the traceless EFG tensor V_{ii} and by the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, is experimentally measured via the quadrupole coupling constant $\nu_Q = |eQV_{zz}/h|$, where $Q = 0.83$ b is the quadrupole moment of the excited ^{111}Cd state. For a detailed description of the application of the PAC method to defect identification in semiconductors, the reader is referred to Ref. [9].

Employing the linearized augmented plane wave (LAPW) code WIEN97 [17] and supercells including 32 lattice sites, the DFT calculations in the generalized gradient approximation are performed for both the In_{DX} and the metastable Cd_{DX} configuration. While confirming the general phenomenon of a large lattice relaxation for the In_{DX} configuration reported by Park and Chadi [13], substantial differences in the actual local structure are found. For the negatively charged In_{DX}^- configuration with trigonal C_{3v} symmetry, the LAPW calculations yield a stable position of the In atom rather close to the interstitial lattice site: The In atom is displaced by 2.15 Å from the substitutional In_{Cd} site towards the $[\bar{1}\bar{1}\bar{1}]$ antibonding direction. This value is distinctly different from the 1.89 Å displacement reported in Ref. [13]. Following bond breaking, a 0.59 Å displacement of the $\text{Te}_{[111]}$ atom in the same direction is obtained as compared to only 0.15 Å reported in [13]. Also in the case of the substitutional donor In_{Cd}^+ , a pronounced difference of the bond length is found: The LAPW calculation yields a nearest neighbor (NN) distance of 2.81 Å, practically identical to the undisturbed Cd-Te bond length, compared to 3.14 Å [13]. Note that this latter result of the LAPW calculation is in excellent agreement with the EXAFS result of $d_{\text{NN}} = 2.80$ Å for substitutional In [5].

In order to calculate the Cd_{DX} configuration, the In impurity is replaced by a Cd host atom while the atomic coordinates are taken from the In_{DX}^- configuration. Maintaining the trigonal point group symmetry, the nearest local minimum in energy is then found by relaxation of all atoms in the 32 atom supercell. In the doubly charged Cd_{DX}^{2-} state [18], a metastable, DX -like configuration is found which is separated from the substitutional ground state by a barrier of a few hundred meV. Remarkably, the resulting atomic structure of this configuration is very similar to that obtained for In_{DX}^- : The relaxed Cd atom and the $\text{Te}_{[111]}$ atom are displaced by 2.20 and 0.53 Å, respectively. The local atomic structures

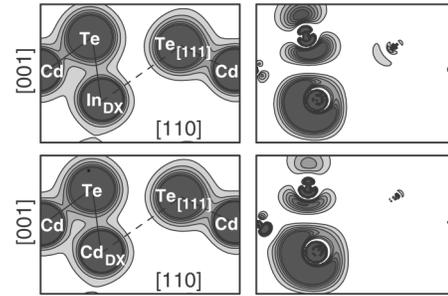


FIG. 1. Charge density contour plot for the In_{DX}^- (top) and the Cd_{DX}^{2-} (bottom) configurations. Plotted is the total valence electron density (left, contour spacing $0.1 e/\text{\AA}^3$) and charge density of the DX orbital only (right, spacing $5 \times 10^{-3} e/\text{\AA}^3$).

of both the In_{DX}^- and the Cd_{DX}^{2-} configuration are illustrated by their valence electron density contours in Fig. 1 (left). In the neutral and the singly charged states, Cd_{DX}^0 and Cd_{DX}^- , there is no barrier predicted, and the relaxation leads to the substitutional configuration. Thus, only the doubly charged configuration Cd_{DX}^{2-} is expected to be experimentally observable.

Comparison of the electronic structure of In_{DX}^- and Cd_{DX}^{2-} reveals the close relation between both configurations (Fig. 2). As a reference, the electronic spectrum, i.e., the density of states (DOS), of the undisturbed CdTe semiconductor host is displayed in Fig. 2(a). The site projected, angular momentum decomposed DOS of In_{DX}^- [Fig. 2(b)] is dominated by two mainly s -like defect orbitals within the valence band region and in the band gap (labeled In- $s1$ and In- $s2$). The actual DX state, In- $s2$, with its Kohn-Sham eigenvalue located about 0.5 eV above the valence band maximum (VBM), is fully occupied in the negatively charged In_{DX}^- state. Very similar to In_{DX}^- , also the Cd_{DX}^{2-} state exhibits two dominantly s -like states (Cd- $s1$ and Cd- $s2$) at somewhat higher energies compared to the respective In states [Fig. 2(c)]. The similarity of the In_{DX}^- and the Cd_{DX}^{2-} configurations is also reflected by the charge density emerging from the

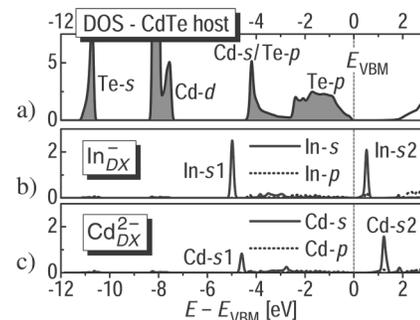


FIG. 2. (a) Energy spectrum (DOS in electrons per elementary cell) for the CdTe host lattice; occupied states are shaded. (b),(c) Local DOS (electrons per atomic site) in a supercell calculation for In_{DX}^- and Cd_{DX}^{2-} , decomposed into s and p contributions. For the given charge states, the $s2$ orbital is the highest occupied state in either case.

Kohn-Sham orbital of the DX state, shown in Fig. 1 (right): In both cases, the occupied In- s_2 and Cd- s_2 states form a charge buildup at the antibonding region of the displaced atom. This charge creates the energy barrier that prevents spontaneous relaxation from the DX to the substitutional configuration. Hence, the similarity of the In- s_2 and the Cd- s_2 state is essential for the possibility to observe the In_{DX}^- via the Cd_{DX}^{2-} configuration in a PAC experiment, thereby giving direct experimental evidence of the In DX center.

In the experiments at In doped CdTe ($c_{\text{In}} \approx 10^{20} \text{ cm}^{-3}$), two completely different EFG signatures were observed by PAC depending on the annealing conditions of the sample [8]. Here, the investigation of heavily doped CdTe was motivated by reports that in weakly to moderately In doped CdTe the shallow In_{Cd} donor state is stable, and the DX center is not observed at ambient pressure [19]. After vacuum annealing, the PAC measurement at 13 K yields two EFG, characterized by $\nu_{Q1} = 104 \text{ MHz}$, $\eta = 0.05$ and $\nu_{Q2} = 114 \text{ MHz}$, $\eta = 0.18$. The occurrence of these EFG in heavily In doped CdTe is well known and has been assigned to In donor compensation by A center formation [14]. This assignment is confirmed by means of DFT calculations which show that the observed EFG correspond to charged states of the In probe atom-vacancy complex [20]. After annealing the CdTe sample for 24 h at 760 K under excess Cd conditions, these vacancy related EFG signals nearly completely vanish, and a new, much weaker EFG with the coupling constant $\nu_{Q3} = 21.2(5) \text{ MHz}$ and $\eta = 0.0(1)$ is observed [8]. The EFG corresponding to ν_{Q3} , $|V_{zz}| = 10.6 \text{ V/\AA}^2$, agrees very well with the present result $V_{zz} = -8 \text{ V/\AA}^2$, calculated for the Cd_{DX}^{2-} configuration, and is, therefore, interpreted with the DX center. Even though the sign of the EFG is not determined in experiment, V_{zz} can, in principle, assume both positive and negative values. Compared to other defect induced EFG (see, e.g., Refs. [6,9]), the absolute value $|V_{zz}|$ is rather small in the present case. Therefore, the actual agreement of the calculated and the measured EFG is even better than indicated by their *relative* difference. The agreement in terms of the *absolute* difference is at least as good as in the showcase EFG calculations [10]. Recalling that the EFG is very sensitive to the actual strength of atomic relaxations (cf. Ref. [10]), the excellent agreement of the measured and the calculated EFG not only supports the identification of the observed EFG with DX center formation, but also gives evidence that the atomic structure of the DX center is correctly described by the theoretical model. Strictly speaking, the measured EFG characterizes the Cd_{DX}^{2-} configuration. However, due to the pathway used experimentally to create the Cd_{DX}^{2-} state, i.e., via the In_{DX}^- configuration, the structural model for the In DX center is confirmed by the present results, too.

The fraction of probe atoms of about 50% belonging to the EFG of the DX center implies almost complete compensation [8]. Thus, the change of the PAC signals after

annealing the CdTe crystal in Cd vapor is indicative of the change from A center compensation in the Cd poor regime to DX center compensation in the Cd rich regime. Both mechanisms are identified by means of the corresponding theoretically and experimentally determined EFG. Whether A center or DX center compensation is prevailing is obviously determined by the stoichiometry of the CdTe crystal, as indicated by the respective experimental conditions.

With regard to the possibility to observe a photoinduced configuration change directly in a PAC experiment, the stability of the In DX center in CdTe is addressed. According to experimental results from literature, the configuration coordinate diagram (CCD) for the In DX center is qualitatively different in the low and high doping regimes: As shown in experiments with In concentrations up to $c_{\text{In}} \leq 2 \times 10^{18} \text{ cm}^{-3}$, the DX center is less stable than the substitutional In_{Cd} state by $E_{DX} = 0.22 \text{ eV}$ [11]. Here, a barrier of $E_{\text{em}} = 0.26 \text{ eV}$ was reported for the emission of electrons from the DX state. On the other hand, in heavily doped CdTe polycrystalline films ($c_{\text{In}} \approx 10^{21} \text{ cm}^{-3}$), an emission barrier of $E_{\text{em}} = 0.42 \text{ eV}$, along with a barrier $E_c = 0.23 \text{ eV}$ for carrier capture after photoexcitation, was observed [12]. Given the values for E_{DX} and the barrier energies, reported in Refs. [11,12], the CCD corresponding to the reaction path $d^+ + 2e \leftrightarrow DX^-$ is sketched in Fig. 3 [21]. It shows that the energy of the In_{Cd} configuration is higher by $\Delta E = 0.41 \text{ eV}$ in the heavy doping regime, and the DX state forms the ground state only in case of high In concentration.

In the following, the relation between the stability of the DX center and the doping level is discussed, and the DFT calculations along with the mentioned literature data are used to derive an estimate of the number of In atoms that can be driven from the DX to the substitutional configuration by photoexcitation. In an illumination experiment at low temperature, the photoexcitation of electrons in the DX level results in a configuration change towards the substitutional donor. During this process, two electrons are transferred to the conduction band, leading

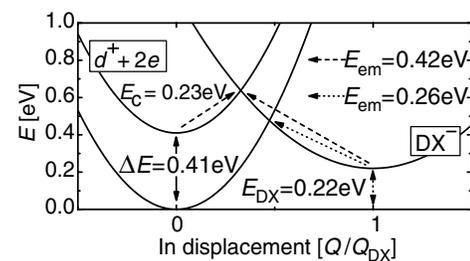


FIG. 3. Schematic configuration coordinate diagram for the In DX center in CdTe. $Q = 0$ refers to the substitutional position In_{Cd} ; $Q = Q_{DX}$ refers to the large lattice relaxation in the DX state. Barrier energies and E_{DX} taken from literature are indicated [11,12]. Dotted (dashed) arrows and the lower (higher) $d^+ + 2e$ branch refer to a moderate (heavy) doping regime [Ref. [11] (Ref. [12])].

to persistent photoconductivity. The higher energy of the $d^+ + 2e$ branch (cf. Fig. 3) in the heavy doping regime is easily understood if one regards that, due to the shallow effective electron mass in CdTe ($m_e^*/m_e \approx 0.1$), the donor wave functions of the In_{Cd} donor start to overlap at electron concentrations of about $c_e \approx 10^{18} \text{ cm}^{-3}$ (semiconductor-metal transition). Accordingly, the Fermi energy rises above the conduction band minimum (CBM) at higher electron concentrations (Moss-Burstein shift), increasing the energy of the $d^+ + 2e$ state by roughly $\Delta E = 2(E_F - E_{\text{CBM}})$. During illumination, not all DX centers can be transformed because the substitutional configuration becomes energetically too unfavorable at a certain concentration of electrons in the CB.

From the conduction band DOS, calculated for a CdTe elementary cell, it is estimated that an electron concentration of $c_e = 8 \times 10^{18} \text{ cm}^{-3}$ already leads to $\Delta E = 0.41 \text{ eV}$ [22], the energy shift deduced from literature data. Hence, it is concluded that despite the high In concentration $c_{\text{In}} \approx 10^{21} \text{ cm}^{-3}$ present in the experiments of Ref. [12] only about $4 \times 10^{18} \text{ cm}^{-3}$ DX centers were photoexcited to the substitutional configuration. This result indicates that the maximum concentration of In atoms, for which the transition from the DX to the substitutional state can be induced by illumination, stays generally below 10^{19} cm^{-3} . Taking into account the sensitivity of the PAC method, the illumination effect should be directly observable by the associated change in the EFG for In concentrations not exceeding 10^{20} cm^{-3} .

Regarding the EXAFS experiments in CdTe:In with 6 at. % In content [5], it is noted that the reported change of the mean coordination number, deduced from the increase of the EXAFS amplitude upon illumination, would imply that several 10^{20} cm^{-3} In atoms switch from the DX to the substitutional configuration. This would lead to a carrier concentration of $c_e \approx 10^{21} \text{ cm}^{-3}$, a number which seems implausibly high according to the above discussion. However, the In DX center induces considerable lattice strain in its environment, which is also reflected by strong EFG at Cd lattice sites in the vicinity of the In_{DX}^- configuration (up to $|V_{zz}| = 70 \text{ V/\AA}^2$). Thus, even the presence of only a small number of DX centers (e.g., a few 10^{18} cm^{-3}) would be sufficient to reduce the EXAFS amplitude significantly, which is restored when these DX centers are transformed to In_{Cd} donors after illumination. Thereby, the effect of illumination on the EXAFS accounts not so much for a change of the mean coordination number, but mainly for the reduction of lattice strain. Contrary to the experimental conditions reported in Refs. [8,12], the preparation technique for the CdTe samples used in the EXAFS experiment does not provide for Cd excess conditions [23]. Thus, based on the PAC data in the Cd poor regime, it is suggested that, apart from substitutional In_{Cd} donors, mainly $\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$ pairs were observed in the EXAFS study.

In conclusion, we used the simultaneous calculation of lattice relaxation and the associated EFG to establish the

experimental evidence for the theoretically predicted atomic structure of the DX center. By taking into account the available experimental data along with the present results, a consistent picture for the stability of the In DX center in CdTe is derived.

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