

## DX-centers in CdTe and ZnTe observed by locally sensitive probe atoms

S. Lany, H. Wolf and Th. Wichert

Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

### ABSTRACT

Heavily In-doped CdTe and ZnTe crystals are investigated using perturbed  $\gamma\gamma$ -angular correlation experiments. By means of characteristic electric field gradients, it is shown that in the Cd (Zn) poor regime, the compensation is governed by A-center formation. After annealing in Cd (Zn) rich atmosphere, the formation of DX-centers is observed and identified as the prevailing compensation mechanism in the Cd (Zn) rich regime.

### INTRODUCTION

In the II-VI semiconductors CdTe and ZnTe, *n*-type doping is subject to the well-known phenomenon of self-compensation: While electron concentrations in the  $10^{18} \text{ cm}^{-3}$  range have been reported in CdTe [1], it is difficult to achieve any *n*-type conductivity in ZnTe [2]. The present work focuses on the microscopic origin of the self-compensation for CdTe and ZnTe doped with Indium donors. The formation of two different compensating centers has been proposed in literature in order to explain the limited doping efficiency. The pair formation of the donor with an acceptor-like cation vacancy (A-center) has been proposed originally in Ref. [3]. In CdTe, for instance, such  $\text{In}_{\text{Cd}}\text{-V}_{\text{Cd}}$  pairs have been observed using various experimental techniques [4, 5, 6]. An alternative explanation for self-compensation is given on the basis of theoretical studies which predict the transition of a shallow donor into a DX-center, i.e. a deep, doubly occupied state induced by a large lattice relaxation [7, 8]. For In-doped CdTe, persistent photoconductivity (PPC) and metastable behavior observed in high-pressure experiments have been related in literature to the DX-center model [9, 10].

In order to identify the local structure of the In dopants, we make use of the fact that the electric field gradient (EFG) is very sensitive to the local environment about the site of a suitable probe atom. The EFG is conveniently characterized by  $V_{zz}$ , the strongest component of the traceless EFG tensor ( $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$ ), and the asymmetry parameter  $\eta = (V_{xx} - V_{yy}) / V_{zz}$ . Because of the condition  $V_{xx} + V_{yy} + V_{zz} = 0$  for a traceless tensor, the EFG vanishes at lattice sites with cubic symmetry. In the cubic zincblende structure of CdTe and ZnTe, any non-zero EFG indicates a local disturbance of the semiconductor lattice, e.g. caused by a defect. The EFG is not only sensitive to impurity atoms and native defects close to the probe atom, but also to the actual strength of the atomic relaxation around the probe [11]. Therefore, an identification of both the A-center and the DX-center is possible by means of characteristic EFG. In order to measure the EFG, we employ the perturbed  $\gamma\gamma$ -angular correlation (PAC) technique, which has proven to be very useful to investigate defects in semiconductors [12]. Thus, radioactive  $^{111}\text{In}$  probe atoms are introduced into the semiconductor crystals. By the time compensation occurs, the  $^{111}\text{In}$  atoms are incorporated in the respective centers. The actual PAC measurement, however, takes place after the radioactive  $\beta$ -decay of the parent probe  $^{111}\text{In}$  at the  $I = 5/2$  excited state of the daughter isotope  $^{111}\text{Cd}$ . The PAC experiment yields the quadrupole coupling constant  $\nu_Q$ , related to the EFG by

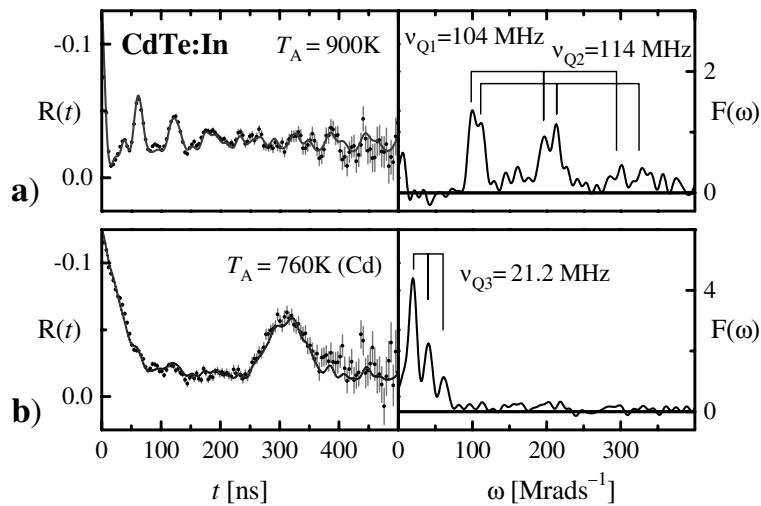
$$\nu_Q = |eQV_{zz}/h|, \quad (1)$$

along with the asymmetry parameter  $\eta$ . The component  $V_{zz}$  is calculated from  $v_Q$  using equation (1) and the quadrupole moment  $Q = 0.83$  b for  $^{111}\text{Cd}$  [13]. In order to achieve an unambiguous identification of the defects characterized by the EFG, *ab initio* electron structure calculations in the framework of density functional theory (DFT) are performed. The application of DFT to the calculation of EFG induced by defects in semiconductors is described in Ref. [11], results of such calculations for A-centers in CdTe have been published previously in Ref. [14]. The theoretical description for the Indium DX-center in CdTe will be published elsewhere [15]; here, we only briefly refer to some important results of the DFT calculations.

## RESULTS

For doping with In, a Bridgman-grown, nominally undoped CdTe crystal was annealed at 920 K for 3 days in an evacuated ampoule along with a metallic In source. The surface concentration of In after this treatment is estimated to  $1 \times 10^{20} \text{ cm}^{-3}$ , based on comparison with results reported in Ref. [16], where the diffusion of Indium in CdTe was investigated. Into this sample, radioactive  $^{111}\text{In}$  was diffused subsequently from an  $^{111}\text{InCl}_3$  source at 900 K for two hours. The concentration of  $^{111}\text{In}$  is estimated to  $5 \times 10^{16} \text{ cm}^{-3}$ , i.e. much lower than the concentration of stable In. According to this preparation, the radioactive probe atoms are regarded as representatives of all In atoms within a 2  $\mu\text{m}$  thick surface layer of almost constant In concentration. The preparation of the ZnTe sample happened in the same way, except that the metallic In source was provided in form of a thin film (25nm) evaporated onto the ZnTe surface before annealing.

Subsequent PAC measurements were performed at  $T_M = 13$  K using a closed-cycle He-cryostat in order to compare the measured EFG with the results of the DFT calculations which correspond to zero temperature. Figure 1a shows the PAC spectrum  $R(t)$  along with its Fourier transform  $F(\omega)$ , recorded directly after the diffusion of radioactive  $^{111}\text{In}$  probe atoms into the CdTe sample. The analysis of the PAC data yields two frequency triplets [cp.  $F(\omega)$  in figure 1a] each belonging to a single EFG. The observed EFG are characterized by



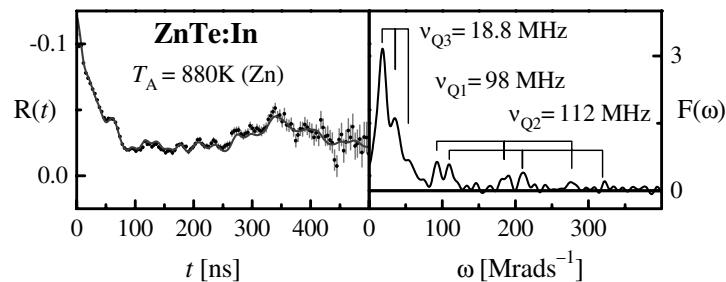
**Figure 1.** PAC spectra  $R(t)$  and  $F(\omega)$  for In-doped CdTe, measured at  $T_M = 13$  K with the PAC probe  $^{111}\text{In}/^{111}\text{Cd}$ . (a) After diffusion of In from a metallic source. (b) After subsequent annealing at 760 K under excess Cd vapor.

$\nu_{Q1} = 104(1)$  MHz,  $\eta = 0.05(5)$  and by  $\nu_{Q2} = 114(1)$  MHz,  $\eta = 0.18(2)$ . The corresponding fractions of probe atoms are  $f_1 = 28\%$  and  $f_2 = 16\%$ , respectively. After annealing the CdTe sample for 24 h at 760 K under excess Cd conditions, these PAC signals nearly completely vanish (see figure 1b), the respective contributions account now for only  $f_1 = f_2 = 4\%$ . Instead, a new PAC signal with a coupling constant  $\nu_{Q3} = 21.2(5)$  MHz and  $\eta = 0.0(1)$  is observed. Additionally, there is a contribution from probe atoms located at substitutional lattice sites with cubic symmetry ( $\nu_{Q0} = 0$ ). The analysis of the  $R(t)$  spectrum shows that a distribution of EFG around zero with  $\delta\nu_{Q0} = 10$  MHz is present, indicating a disturbance of the Cd lattice sites which probably stems from the high doping level. The theoretical  $R(t)$  function, shown in figure 1b, accurately describes the PAC data under the condition that the fraction of probe atoms corresponding to  $\nu_{Q3}$  equals the fraction located at substitutional lattice sites ( $f_3 = f_0 = 46\%$ ). The constraint  $f_3 = f_0$  will be of importance for the discussion regarding the DX-centers, given below.

Similar to the observation in CdTe, also in ZnTe two EFG are observed after diffusion of the radioactive  $^{111}\text{In}$  atoms. Here, the EFG are characterized by  $\nu_{Q1} = 98(2)$  MHz,  $\eta = 0.0(1)$  and by  $\nu_{Q2} = 112(2)$  MHz,  $\eta = 0.19(5)$ , respectively. After annealing at 880 K under excess Zn conditions, the original fractions  $f_1$  and  $f_2$  are considerably reduced, similar as in CdTe. The  $R(t)$  and the  $F(\omega)$  spectra following this treatment are shown in figure 2. Again, a new PAC signal appears [ $\nu_{Q3} = 18.8(10)$  MHz,  $\eta = 0.0(1)$ ], and there is a disturbed contribution from substitutional lattice sites ( $\nu_{Q0} \approx 0$ ). The fit to the  $R(t)$  spectrum (see figure 2) yields  $f_1 = f_2 = 9\%$  and  $f_3 = 41\%$ , where the condition  $f_3 = f_0$  is again constrained.

## DISCUSSION

The coupling constants  $\nu_{Q1}$  and  $\nu_{Q2}$ , observed in the CdTe sample after In diffusion, are well-known [17, 18, 19] and the assignment to A-center formation has recently been confirmed by means of EFG calculation [14]. These EFG occur generally in  $n$ -doped material where the probe-vacancy complex is in a charged state after the decay of the  $^{111}\text{In}$  probe atom [19]. The presence of two EFG simultaneously observed is likely due to the possibility that two In atoms bind to  $V_{\text{Cd}}$ , i.e. the EFG of the  $(^{111}\text{Cd}-V_{\text{Cd}})^{-}$  and the  $(^{111}\text{Cd}-V_{\text{Cd}}-\text{In}_{\text{Cd}})^{-}$  complexes are measured [20]. Thus, the present experiment shows that after diffusion of In from a metallic source, the In donors are compensated by the formation of complexes with Cd vacancies, i.e. by A-centers (cp. figure 3a) [21]. The same conclusion holds for ZnTe, where the occurrence of the respective frequencies has already been assigned to A-center formation in Ref. [19]. The slightly different value of  $\nu_{Q1}$  in the present work is due to the lower measuring temperature.



**Figure 2.** PAC spectra  $R(t)$  and  $F(\omega)$  for In-doped ZnTe, measured at  $T_M = 13$  K with the PAC probe  $^{111}\text{In}/^{111}\text{Cd}$  after annealing at 880 K under excess Zn vapor.

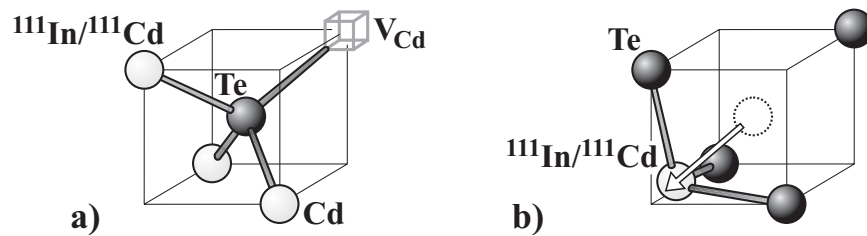
According to Ref. [1], the highest efficiency of In doping in CdTe is achieved in the Cd rich regime. Annealing of the In doped CdTe sample under Cd excess vapor, therefore, should increase the fraction of electrically active  $\text{In}_{\text{Cd}}$  donors, which could be detected in a PAC experiment by the  $\nu_{\text{Q}} = 0$  contribution from the substitutional  $^{111}\text{In}_{\text{Cd}}$  configurations. However, at an estimated In concentration of  $10^{20} \text{ cm}^{-3}$  in our sample, we expect that still practically all In atoms are compensated, since the maximum achievable doping level is limited to about  $10^{18} \text{ cm}^{-3}$  [1]. Accordingly, the observation of a non-zero EFG, characterized by  $\nu_{\text{Q}3}$ , is directly correlated to the actual compensation mechanism for the present condition of the CdTe sample. Since the radioactive  $^{111}\text{In}$  probe atoms are representatives of all In dopants, the change in the PAC spectrum due to the annealing under Cd excess (cp. figure 1a and b) shows that the compensation mechanism has changed completely: After the diffusion of Indium into the CdTe sample, the self-compensation is a consequence of A-center formation, which is experimentally revealed by the observation of the coupling constants  $\nu_{\text{Q}1}$  and  $\nu_{\text{Q}2}$ . In contrast, the A-center formation is suppressed in the Cd rich regime, and the compensation is governed by a new center which is characterized by  $\nu_{\text{Q}3}$ .

The experimental observation for ZnTe is very similar to that for CdTe, except that the formation of A-centers is not so strongly suppressed after annealing in Zn atmosphere as in CdTe. Additional experiments in CdTe show, however, that the extent to which the compensation mechanism changes from A-center formation towards the formation of the new center depends on the detailed conditions during the annealing in Cd atmosphere, i.e. most importantly, the annealing temperature. It is noted that the coupling constants  $\nu_{\text{Q}3}$  are very similar in CdTe and ZnTe indicating that the corresponding centers have a similar origin.

A possible candidate for the compensation mechanism present in the metal-rich regime is the DX-center as proposed in Ref. [8]. In the DX-center theory, the substitutional In donors are unstable against a large lattice relaxation according to the reaction ( $M = \text{Cd}, \text{Zn}$ ):



The local structure of the  $\text{In}_{\text{DX}}$  configuration is sketched in figure 3b. During the large lattice relaxation, one  $\text{In}_{\text{M}}^0$  donor captures an additional electron provided by another In donor which becomes ionized ( $\text{In}_{\text{M}}^+$ ). As a consequence of the reaction (2), the number of DX-centers equals the number of substitutional, ionized In donors in case of complete compensation. Since practically full compensation is expected at the present In concentrations, this is perfectly consistent with the experimentally observed relation  $f_3 = f_0$  for the defect fractions (see above), supporting the assignment of the coupling constant  $\nu_{\text{Q}3}$  to the DX-center.



**Figure 3.** Local structure of (a) the A-center and (b) the  $\overline{111}$  DX-center in CdTe doped with In. The arrow indicates the large lattice relaxation along the  $\overline{111}$  antibonding direction in case of the DX-center. Note that the EFG is measured at the site of the  $^{111}\text{Cd}$  daughter isotope.

When an  $^{111}\text{In}/^{111}\text{Cd}$  probe atom initially forms a DX configuration, i.e.  $^{111}\text{In}_{\text{DX}}^-$ , the situation directly after the radioactive decay is that of a strongly relaxed  $^{111}\text{Cd}$  lattice atom in CdTe, or, in case of ZnTe, that of a relaxed isoelectronic  $^{111}\text{Cd}$  impurity. This configuration essentially represents a Frenkel pair (cp. figure 3b), which should return into the substitutional ground state after some time. Since for the actual EFG measurement, the behavior of the probe atom within about 500 ns after the elemental transmutation is relevant, the assignment of the coupling constant  $\nu_{\text{Q}3}$  to the DX-center can only be correct, if there is an appreciable energy barrier between the relaxed configuration of the  $^{111}\text{Cd}$  atom, labeled  $\text{Cd}_{\text{DX}}$ , and the substitutional ground state. We performed *ab initio* DFT calculations for the  $\text{In}_{\text{DX}}$  and the  $\text{Cd}_{\text{DX}}$  configurations [15]. Both in CdTe and ZnTe, a metastable configuration is found for the doubly charged  $\text{Cd}_{\text{DX}}^{--}$  state, which has an atomic and electronic structure very similar to the  $\text{In}_{\text{DX}}^-$  state and is separated from the substitutional configuration by an energy barrier. The formation of the  $^{111}\text{Cd}_{\text{DX}}^{--}$  state after the decay of an  $^{111}\text{In}_{\text{DX}}^-$  configuration is expected if the occupation of the electronic orbital corresponding to the DX state is not influenced by the radioactive decay. In CdTe, the calculated EFG at the  $^{111}\text{Cd}_{\text{DX}}^{--}$  site is  $V_{zz} = -8 \text{ V}/\text{\AA}^2$  which is in very good agreement with the experimental EFG  $|V_{zz}| = 10.6 \text{ V}/\text{\AA}^2$ , calculated from the coupling constant  $\nu_{\text{Q}3}$  using equation (1). Also for ZnTe, the calculated EFG  $V_{zz} = -9 \text{ V}/\text{\AA}^2$  agrees perfectly with the PAC data ( $|V_{zz}| = 9.2 \text{ V}/\text{\AA}^2$ ). According to the EFG calculation, the  $\text{In}_{\text{DX}}^-$  configuration in CdTe induces EFG at surrounding Cd sites that are much stronger than the relatively weak EFG of the  $\text{Cd}_{\text{DX}}^{--}$  configuration itself. Taking into account the high In concentration of  $10^{20} \text{ cm}^{-3}$  present in the experiment, this effect very well explains the distribution of EFG around zero observed for the contribution from substitutional probe atoms.

It is noted that the quadrupole coupling constant measured with the probe  $^{111}\text{In}/^{111}\text{Cd}$  in elemental Indium metal [22] is of comparable magnitude as  $\nu_{\text{Q}3}$ , observed in the present experiment. In order to avoid misinterpretation, we measured the EFG of elemental In at the same temperature  $T_{\text{M}} = 13 \text{ K}$  as for the experiments in CdTe and ZnTe. Since the resulting coupling constant  $\nu_{\text{Q}} = 25.0(5) \text{ MHz}$  is distinctly different from  $\nu_{\text{Q}3}$  measured in the semiconductor crystals, the observation of In precipitates is excluded. In early PAC experiments performed for In-doped CdTe [17], a coupling constant  $\nu_{\text{Q}} = 16 \text{ MHz}$  was measured at room temperature after Cd annealing. Because of the similarity to the EFG of In metal,  $\nu_{\text{Q}} = 17 \text{ MHz}$  at 295 K, the authors interpreted this observation with In precipitation. Considering the similarity of the sample treatment, however, it seems likely that the observed coupling constant has the same origin as  $\nu_{\text{Q}3}$  in the present work (note, the different values are due to different measuring temperatures). By the time the experiments in Ref. [17] were performed, the DX-center model for Indium in CdTe was not established. Now, in the light of the present results, and in particular due to the support by DFT calculations, we strongly tend to interpret the EFG observed after annealing under Cd or Zn excess with the compensation of In donors by DX-center formation.

## CONCLUSIONS

By means of PAC experiments employing the  $^{111}\text{In}/^{111}\text{Cd}$  probe, we have observed two different compensation mechanisms for In donors in CdTe and ZnTe. In the Cd (Zn) poor regime, as present after diffusion of metallic Indium from the surface, compensation is caused by A-center formation. In the Cd (Zn) rich regime, the prevailing compensation mechanism is the formation of DX-centers. With support from DFT calculations, the experiments described in this

work give direct evidence of Indium DX-centers in CdTe and ZnTe, based on the observation of a characteristic EFG which is measured by means of locally sensitive probe atoms.

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