

**Defect interactions of group-I elements in cubic II-VI compounds**V. Ostheimer,<sup>1</sup> S. Lany,<sup>1</sup> J. Hamann,<sup>1</sup> H. Wolf,<sup>1</sup> Th. Wichert,<sup>1</sup> and ISOLDE Collaboration<sup>2</sup><sup>1</sup>*Technische Physik, Universität des Saarlandes, D-66041 Saarbrücken, Germany*<sup>2</sup>*PPE ISOLDE, CERN, CH-1211 Genève, Switzerland*

(Received 27 June 2003; published 8 December 2003)

By means of perturbed  $\gamma\gamma$  angular correlation (PAC) experiments using the radioactive dopants  $^{77}\text{Br}$ ,  $^{111}\text{Ag}$ , and  $^{111}\text{In}$ , the behavior of the group-I elements Li, Cu, Ag, and Au is investigated. Group-I elements are shown to form nearest- (NN) and next-nearest-neighbor donor-acceptor pairs in the II-VI semiconductor CdTe. The simultaneous occurrence of cation vacancies indicates the transition of group-I elements from substitutional to interstitial lattice sites. In case of NN pairs, the electric-field gradients measured in the PAC experiments are compared with those obtained theoretically by density-functional theory calculations. PAC experiments performed in ZnTe and ZnSe show a similar behavior regarding the donor-acceptor pairing with group-I elements in these compounds.

DOI: 10.1103/PhysRevB.68.235206

PACS number(s): 61.72.Vv, 76.80.+y, 71.55.Gs, 71.15.Ap

**I. INTRODUCTION**

In semiconductors, the understanding of doping processes forms a key issue for the development of electronic devices. In this context, donor and acceptor atoms in II-VI compounds are subject of widespread investigations.<sup>1,2</sup> In the case of group-I elements, the interest is focused on their potential use as acceptors and on the occurrence of compensating defect reactions. The information about the behavior of group-I elements in II-VI semiconductors, however, is still rather scarce. In addition, the situation is complicated by the possibility of an unintentional incorporation of these elements, in part supported by their high diffusivity, and the problem of a unique identification of these elements. Photoluminescence experiments show that the group-I elements Li, Cu, Ag, and Au form acceptor levels in CdTe.<sup>3</sup> Since the achievable *p*-type conductivity is strongly limited, it was supposed that the elements Li and Ag are amphoteric dopants being incorporated on substitutional lattice sites as acceptors and, at the same time, on interstitial lattice sites as donors.<sup>2</sup> For Li, this behavior was confirmed by infrared absorption spectroscopy measuring localized vibrational modes (LVM's) in CdTe:Li, which showed the formation of close  $\text{Li}_{\text{Cd}}\text{-Li}_i$  pairs.<sup>4,5</sup> For the heavier group-I elements, like Ag,<sup>6,7</sup> the corresponding pairing process is believed to exist but not yet unambiguously identified. In the case of Li, also the formation of  $\text{Al}_{\text{Cd}}\text{-Li}_{\text{Cd}}$  and  $\text{In}_{\text{Cd}}\text{-Li}_{\text{Cd}}$  next-nearest-neighbor pairs was observed via their characteristic LVM's,<sup>8</sup> indicating the passivation of group-I acceptors by the interaction with different elements that act as donor atoms. By use of the radioactive donor  $^{111}\text{In}$ , perturbed  $\gamma\gamma$  angular correlation (PAC) experiments showed characteristic new electric-field gradients (EFG's) in II-VI semiconductors doped with Ag. The Ag related EFG, however, have been discussed controversially as caused by cation vacancies (for CdTe, see Ref. 9), by the donor-acceptor (*D-A*) pair formation of  $^{111}\text{In}$  and Ag (for CdTe, see Ref. 10), and by a complex involving Ag at interstitial lattice sites (for CdS, see Ref. 11). Positron annihilation spectroscopy (PAS) showed that Ag diffused into CdTe occupies substitutional Cd sites by filling up Cd vacancies ( $V_{\text{Cd}}$ ).<sup>12</sup> Finally, in emission channeling measure-

ments using the isotopes  $^{109\text{m}}\text{Ag}$  and  $^{107\text{m}}\text{Ag}$ , it was observed that implanted Ag atoms leave substitutional Cd sites above  $T=400$  K.<sup>13</sup> In general, however, there exists no comprehensive scenario concerning the behavior of group-I elements in II-VI compounds and, in particular, their interactions with other defects, up to now. In this work, the radioactive dopant atoms  $^{77}\text{Br}$ ,  $^{111}\text{Ag}$ , and  $^{111}\text{In}$  are used in order to study the incorporation of the group-I elements Li, Cu, Ag, and Au as acceptors via the formation of nearest-neighbor (NN) and next-nearest-neighbor (NNN) *D-A* pairs in CdTe and, in part, also in ZnTe and ZnSe. In addition, the existence of Cd vacancies is shown via the formation of *A* centers. In case of the formation of NN pairs in CdTe, the experimental results are complemented by theoretical calculations. Preliminary results of the experimental data were published in Refs. 10 and 14–16.

**II. EXPERIMENTAL TECHNIQUE**

For the investigation of defect structures in semiconductors on an atomic scale, the EFG measured by the perturbed  $\gamma\gamma$  angular correlation technique has turned out to be a very successful tool.<sup>17,18</sup> In this type of experiment, the EFG, which is measured via its interaction with the nuclear electric quadrupole moment of a radioactive probe atom, characterizes the defect complex which the probe atom is part of. Often, however, a unique assignment of the measured EFG to specific defect configurations is difficult to achieve solely based on the experimental sample conditions used. In order to overcome this problem, the calculation of the EFG for the supposed probe-defect configuration (here, the *D-A* pair) can be employed. In this work, the behavior of the group-I elements Li, Cu, Ag, and Au in CdTe is investigated by PAC using the probe atoms  $^{77}\text{Br}/^{77}\text{Se}$ ,  $^{111}\text{Ag}/^{111}\text{Cd}$ , and  $^{111}\text{In}/^{111}\text{Cd}$  (referring to the parent and daughter isotopes, respectively). In order to arrive at a most certain identification, *ab initio* calculations corresponding to the assigned defect configurations were performed and compared with the experimentally determined EFG. The quality of such calculations has recently been demonstrated in the case of experi-

mentally well characterized  $D$ - $A$  pairs in Si, Ge,<sup>19</sup> and CdTe.<sup>20</sup>

The group-I elements Cu, Ag, and Au were introduced into CdTe single crystals by evaporation of a 10-nm-thick layer of the respective metal onto the surface of the crystal and subsequent diffusion at 550 K (Cu), 550–700 K (Ag), and 900 K (Au) in an evacuated quartz ampoule for 30 min. In the case of Li, the crystal along with a piece of Li metal was heated for 30 min at 880 K. Stable In atoms were introduced using different techniques as described in Ref. 21. Finally, stable Br atoms were introduced by implantation at an energy of 60 keV and a dose of  $10^{14}$  cm<sup>-2</sup> at the Forschungszentrum Rossendorf (FZR, Dresden, Germany).

The radioactive probe atoms were introduced by ion implantation of the isotopes <sup>77</sup>Br (60 keV at ISOLDE, CERN) and <sup>111</sup>Ag (60 keV at ISOLDE, CERN, or 80 keV at the isotope separator in Bonn, Germany). Under these conditions and for the used ion doses of typically  $10^{13}$  cm<sup>-2</sup>, TRIM,<sup>22</sup> calculations yield peak concentrations of about  $10^{18}$  cm<sup>-3</sup> at a depth of about 30 nm. The <sup>111</sup>In probe atoms were introduced by diffusion from an <sup>111</sup>InCl<sub>3</sub> source at 970 K for 90 min, yielding a concentration of about  $10^{15}$  cm<sup>-3</sup> within a layer of about 10 μm below the surface.<sup>23</sup>

PAC experiments take advantage of the pair formation of the probe atoms with defects of opposite charge driven by the Coulomb attraction, which takes place in the presence of the respective radioactive parent isotopes, i.e., the donors <sup>77</sup>Br<sup>+</sup>, <sup>111</sup>In<sup>+</sup>, and the acceptor <sup>111</sup>Ag<sup>-</sup>. At the time of the radioactive  $\beta$  decay of the parent isotope, the EFG is measured via the hyperfine interaction of the electric quadrupole moment  $Q$  of the  $I=5/2$  excited state of the daughter isotope, i.e., <sup>111</sup>Cd (in the case of <sup>111</sup>Ag and <sup>111</sup>In) or <sup>77</sup>Se (in the case of <sup>77</sup>Br). In CdTe, for instance, the daughter isotope <sup>111</sup>Cd is a host atom, and the EFG thus characterizes the isolated defect which was initially trapped by the <sup>111</sup>Ag or <sup>111</sup>In atom. The daughter probe <sup>77</sup>Se, on the other hand, is an impurity being isoelectronic to Te, and the EFG consequently characterizes the complex formed by Se<sub>Te</sub> and the defect originally trapped by the <sup>77</sup>Br atom. The traceless EFG tensor is usually described by the quadrupole coupling constant  $\nu_Q = |eQV_{zz}/h|$ , the asymmetry parameter  $\eta = (V_{xx} - V_{yy})/V_{zz}$  with  $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$  and  $0 \leq \eta \leq 1$ , and the orientation of the EFG tensor with respect to the host lattice. Due to the cubic zinc-blende lattice of CdTe, ZnTe, and ZnSe, the EFG vanishes ( $V_{zz} = 0$ ) if the probe atom is incorporated on an unperturbed substitutional lattice site. Furthermore, the strength of the EFG decreases rapidly with the distance  $r$  between the probe nucleus and the generating charge distribution (e.g.,  $\nu_Q \sim r^{-3}$  in the case of a point charge generating the EFG).

The experimental PAC spectrum  $R(t)$  is described by Eq. (1). It contains the information on the strength and the symmetry of the EFG tensor by the relations  $\omega_1 \sim \nu_Q$ , and  $\omega_2/\omega_1 = g(\eta)$ , respectively;<sup>18</sup> the frequencies satisfy the relation  $\omega_3 = \omega_1 + \omega_2$ . The coefficients  $s_0^i$  and  $s_n^i$  depend strongly on the orientation of the EFG tensor with respect to the host lattice and weakly on the asymmetry parameter  $\eta$ . The parameters  $f_i$  denote the relative fractions of probe at-

oms exposed to the defect specific EFG which is characterized by the parameters  $\nu_Q^i$  and  $\eta^i$ . The parameter  $f_0$  denotes the fraction of probe atoms on unperturbed and  $f'_0$  the fraction at slightly perturbed lattice sites with cubic symmetry. A damping of the  $R(t)$  spectrum, described by the parameters  $\sigma_n$  and  $\sigma_n^i$ , occurs if the host lattice is disturbed, e.g., due to implantation damage which is not completely annealed. Finally,  $A_{22}$  describes the anisotropy of the respective  $\gamma$ - $\gamma$  correlation; it is exclusively determined by nuclear physics parameters and its effective value was  $-0.40$ ,  $-0.11$ , and  $-0.14$  for the probes <sup>77</sup>Br/<sup>77</sup>Se, <sup>111</sup>Ag/<sup>111</sup>Cd, and <sup>111</sup>In/<sup>111</sup>Cd, respectively, in the present experiments. All PAC spectra were recorded at ambient temperatures using a standard setup which consists of four  $\gamma$  detectors. The 12  $\gamma$ - $\gamma$  coincidence spectra, simultaneously recorded as a function of time  $t$  elapsed between the emission of the first and second  $\gamma$  quantum, were combined into a single time spectrum  $R(t)$ , which is described by

$$R(t) = A_{22} \left\{ f_0 + f'_0 \left[ s_0 + \sum_{n=1}^3 s_n e^{-\sigma_n t} \right] + \sum_{i=1}^3 f_i \left[ s_0^i + \sum_{n=1}^3 s_n^i e^{-\sigma_n^i t} \cos(\omega_n^i t) \right] \right\}. \quad (1)$$

The *ab initio* calculation of EFG resulting from the formation of NN donor-acceptor pairs was performed by means of the linearized augmented plane-wave method (LAPW) in the framework of density-functional theory, using the program package WIEN97.<sup>24</sup> The calculations are based on a 32-atom supercell in bcc structure containing both the probe atom and the trapped defect. If one substitutional impurity atom is part of this cluster,  $T_d$  symmetry can be assumed; in the case of a complex consisting of two impurity atoms the symmetry is lowered to  $C_{3v}$ . For a correct calculation of the EFG, the charge state of the defects and the relaxation of atoms in the supercell have to be taken into account. In the case of NN probe-defect pairs, the EFG tensor is axially symmetric ( $\eta = 0$ ) and its  $z$  principal axis is aligned along the [111] lattice direction. The calculation of defect induced EFG in semiconductors using the LAPW method is described in more detail in Refs. 20, 25, and 26. For the comparison with the experimentally determined EFG, the quadrupole moments  $Q = 0.83$  b (<sup>111</sup>Cd) and  $Q = 0.76$  b (<sup>77</sup>Se) (Refs. 27 and 28) were used to calculate  $\nu_Q$  from the theoretically determined  $V_{zz}$  values.

### III. RESULTS

The highest sensitivity concerning the detection of substitutional group-I acceptors residing on cation sites  $M$  ( $M = \text{Cd, Zn}$ ) is obtained with the donor-probe <sup>77</sup>Br<sub>X</sub> residing on the NN anion site ( $X = \text{Te, Se}$ ). In this case, the formation of NN pairs is expected, having a higher binding energy than NNN pairs, which can be formed using the donor probe <sup>111</sup>In<sub>M</sub> residing on the NNN cation site. It should be noted that the presence of different group-I elements leads to much larger differences in the absolute values of the defect specific

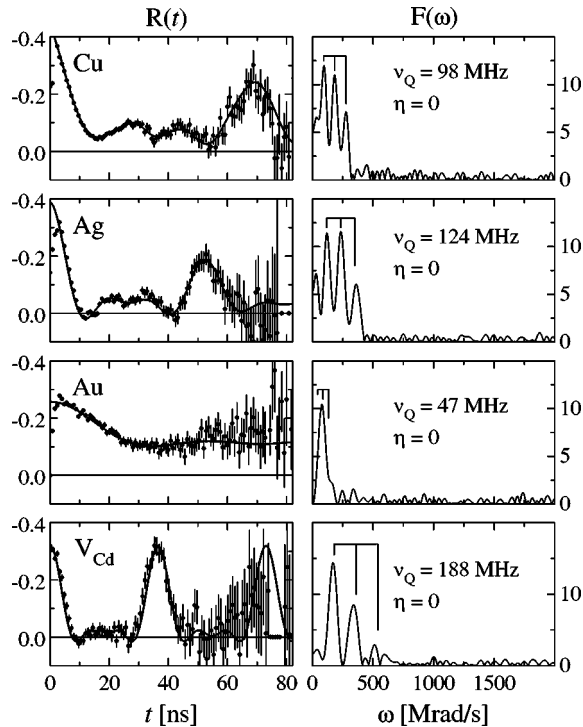


FIG. 1. PAC spectra measured with  $^{77}\text{Br}$  probe atoms in CdTe after doping with the group-I elements Cu, Ag, and Au. The bottom spectrum is obtained in the absence of doping with stable elements.

EFG's for NN pairs as compared to NNN pairs. In the following, the formation of NNN donor-acceptor pairs is investigated using the donor probe  $^{111}\text{In}_M$ . The results obtained with the probes  $^{77}\text{Br}$  and  $^{111}\text{In}$  are supplemented by investigations with the radioactive group-I probe  $^{111}\text{Ag}$ .

### A. Experiments using the probe $^{77}\text{Br}$

CdTe crystals were doped with the group-I elements before the implantation of the  $^{77}\text{Br}$  probe atoms and the PAC measurements were performed after annealing the sample at  $T_A = 550\text{--}700\text{ K}$  in order to remove the implantation induced radiation damage and to support the pairing process between probe atom and group-I element. In Fig. 1, the PAC spectra  $R(t)$  and their Fourier transforms  $F(\omega)$  clearly show triplets consisting of the quadrupole frequencies  $\omega_n$  and designating the EFG measured by the donor probe  $^{77}\text{Br}/^{77}\text{Se}$ . It is obvious that the EFG observed in CdTe crystals doped with Cu, Ag, or Au are strongly different and correlate with the presence of the respective group-I element. The EFG's are axially symmetric [ $\eta = 0.0(1)$ ] and are characterized by  $\nu_Q = 98(4)\text{ MHz}$  (Cu),  $124(4)\text{ MHz}$  (Ag), and  $47(6)\text{ MHz}$  (Au). They are not observable in crystals that are exclusively doped with  $^{77}\text{Br}$ . In this case, a different EFG [ $\nu_Q = 188(4)\text{ MHz}$ ,  $\eta = 0.0(1)$ ] is observed (Fig. 1, bottom panel), which is assigned to the formation of complexes consisting of a  $^{77}\text{Br}$  donor and an acceptorlike Cd vacancy  $V_{\text{Cd}}$  (i.e., a Br-related A center). The assignment was confirmed by EFG calculations for this defect.<sup>25</sup> Furthermore, the formation of A centers is well known from ODMR (optically detected magnetic resonance) experiments in CdTe:Br.<sup>29</sup>

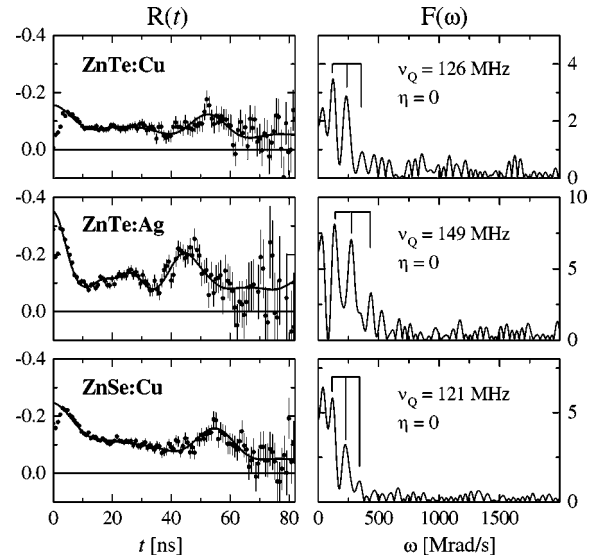


FIG. 2. PAC spectra measured with  $^{77}\text{Br}$  probe atoms in ZnTe after Cu and Ag doping, and in ZnSe after Cu doping.

Due to the relatively weak EFG in CdTe:Cu, the corresponding  $R(t)$  spectrum in Fig. 1 does not show a full modulation period within the recorded time window. Therefore a second possibility has to be taken into account for the analysis of the experimental data assuming that the probe atoms do not form NN pairs with the Au atoms but are solely located in a slightly disturbed lattice environment. Such an environment leads to a fraction  $f'_0$  with a damping  $\sigma$  in the  $R(t)$  spectrum [Eq. (1)] and the corresponding fit reproduces the data almost as well as the fit based on the axially symmetric EFG with  $\nu_Q = 47\text{ MHz}$ , which is caused by the formation of NN pairs. This ambiguity will be discussed in Sec. IV A in more detail.

Supplementary investigations in ZnTe and ZnSe with the  $^{77}\text{Br}$  probe show specific EFG for the acceptors Cu and Ag in ZnTe and for Cu in ZnSe; the corresponding PAC spectra are shown in Fig. 2. The PAC results obtained with the probe atom  $^{77}\text{Br}$  in CdTe, ZnTe, and ZnSe are summarized in Table I. Like in CdTe, also in ZnTe and ZnSe an additional EFG is observed after  $^{77}\text{Br}$  implantation without any additional doping. In analogy to the interpretation for CdTe, these latter EFG's are assigned to the A center, formed by the  $^{77}\text{Br}/^{77}\text{Se}$  probe and a Zn vacancy.

### B. Experiments using the probe $^{111}\text{In}$

The experiments using the probe  $^{77}\text{Br}$  show defect structures which are directly correlated with the presence of the respective acceptors Cu, Ag, and Au. Assuming that these acceptors form NN pairs with the donor probe  $^{77}\text{Br}$ , the donor probe  $^{111}\text{In}$  might form NNN pairs with group-I acceptors as well, provided the corresponding complexes exhibit a sufficiently high binding energy. The local structure of probe atom-acceptor pairs is sketched in Fig. 3 for both the  $^{111}\text{In}$  and the  $^{77}\text{Br}$  probe. As mentioned above, due to their larger separation (see Fig. 3), the NNN pairs should give rise to

TABLE I. EFG's induced by group-I acceptors in CdTe, ZnTe, and ZnSe and measured with the PAC probe atom  $^{77}\text{Br}/^{77}\text{Se}$  ( $M=\text{Cd,Zn}$ ). The EFG's are expressed by the quadrupole coupling constant  $\nu_Q$ . All EFG's listed are axially symmetric ( $\eta=0$ ) and refer to  $T_M=295$  K. The calculated EFG's in CdTe (Ref. 25) are shown for comparison with the experimental values.

Acceptor	CdTe: $^{77}\text{Br}/^{77}\text{Se}$		ZnTe: $^{77}\text{Br}/^{77}\text{Se}$	ZnSe: $^{77}\text{Br}/^{77}\text{Se}$
	$\nu_Q$ (MHz) experiment	$\nu_Q$ (MHz) theory	$\nu_Q$ (MHz) experiment	$\nu_Q$ (MHz) experiment
$\text{Cu}_M^-$	98(4)	66	126(4)	121(4)
$\text{Ag}_M^-$	124(4)	123	149(4)	
$\text{Au}_M^-$	47(6)	20		
$\text{V}_M$	188(4)	198	245(6)	190(4)

smaller binding energies compared to the NN pairs and, at the same time, to a smaller EFG at the site of the probe atom.

Figure 4 shows PAC spectra, measured in CdTe after doping with  $^{111}\text{In}$  and diffusion of the group-I elements Au, Ag, Cu, and Li (top to bottom) at  $T_A=550\text{--}900$  K. In Ag and Au doped samples, in each case two slightly different EFG's are observed at the same time. The relative fractions of the two complexes depend on the sample treatment. In both cases, the larger of the two EFG's is identical [ $\nu_Q=60.2(5)$  MHz,  $\eta=0.17(1)$ ], is independent of the respective group-I element, and is known to be caused by the cation vacancy  $V_{\text{Cd}}$  as a consequence of the formation of  $A$  centers  $^{111}\text{In}_{\text{Cd}}V_{\text{Cd}}$ .<sup>30–33</sup> This EFG is also observable after annealing CdTe under excess Te vapor at 860 K (see Fig. 4, bottom). From the dependence of the  $A$ -center fraction on different conditions chosen for the thermal treatment, the binding energy  $E_b$  of the  $\text{In}-V_{\text{Cd}}$  pair (Refs. 10 and 33) and the migration energy  $E_m$  of the  $V_{\text{Cd}}$  defect<sup>10</sup> have been determined, previously [ $E_b=0.18(2)$  eV, and  $E_m\approx 0.8$  eV]. In contrast, the smaller, second EFG in the Ag and Au doped samples depends on the respective dopant introduced into the CdTe crystal and is characterized by  $\nu_Q=56.6(5)$  MHz,  $\eta=0.11(2)$  for Ag, and by  $\nu_Q=54.2(5)$  MHz,  $\eta=0.07(3)$  for Au (see Table II). The binding energy of the  $^{111}\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$  pair has been determined in Ref. 10 to  $E_b=0.19(2)$  eV, very close to the binding energy of the  $^{111}\text{In}_{\text{Cd}}\text{-}V_{\text{Cd}}$  pair. In the case of CdTe:Ag, additionally the orientation of the  $z$  principal axis of EFG tensor was determined to be directed approximately along the  $[111]$  crystal axis.<sup>16</sup>

In the case of CdTe:Cu, Fig. 4 shows that only a single EFG [ $\nu_Q=60.5(5)$  MHz,  $\eta=0.17(1)$ ] is observable within

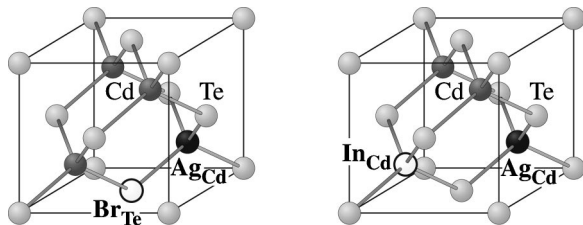


FIG. 3. Atomic configuration of NN ( $\text{Br}_{\text{Te}}\text{-Ag}_{\text{Cd}}$ ) and NNN ( $\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$ ) donor-acceptor pairs, illustrated for the CdTe lattice. In a PAC experiment, the pairs are formed with a radioactive dopant ( $^{77}\text{Br}$ ,  $^{111}\text{In}$ , or  $^{111}\text{Ag}$ ). Subsequently, the EFG is determined at the respective daughter nucleus  $^{77}\text{Se}$  or  $^{111}\text{Cd}$ .

the experimental resolution. This EFG is also known to be produced by the  $V_{\text{Cd}}$  defect just mentioned above (see Table II). Finally, in CdTe:Li the EFG measured with the probe  $^{111}\text{In}$  is not identical with but very similar to that caused by the  $V_{\text{Cd}}$  defect. It amounts to  $\nu_Q=60.1(5)$  MHz,  $\eta$

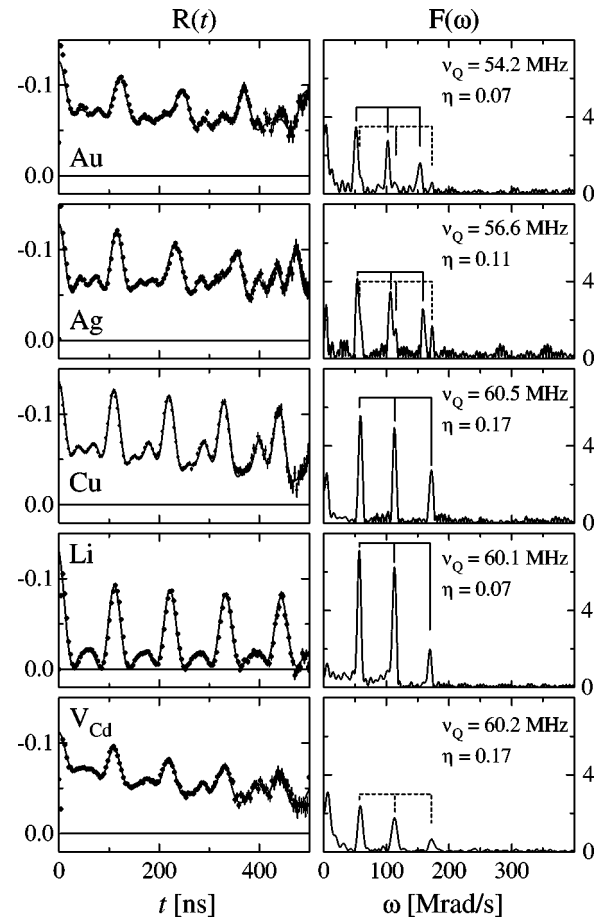


FIG. 4. PAC spectra of CdTe crystals, diffused with  $^{111}\text{In}$  and different group-I elements. After annealing CdTe under Te excess vapor, the PAC spectrum shows the EFG of the  $A$  center  $^{111}\text{In}_{\text{Cd}}V_{\text{Cd}}$  (bottom panel). The same defect complex (indicated by dashed lines) is observed in CdTe:Au and CdTe:Ag together with  $^{111}\text{In}_{\text{Cd}}\text{-Au}_{\text{Cd}}$  and  $^{111}\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$  pairs. In CdTe:Cu the same EFG as for the  $A$  center is observed. In CdTe:Li the asymmetry of the EFG significantly differs from that of the  $A$  center, indicating the formation of  $^{111}\text{In}_{\text{Cd}}\text{-Li}_{\text{Cd}}$  pairs.

TABLE II. EFG's induced by group-I acceptors in CdTe, ZnTe, and ZnSe and measured with the PAC probe atom  $^{111}\text{In}/^{111}\text{Cd}$ . It holds  $T_M=295$  K for all measurements with the exception of ZnTe:Ag ( $T_M=77$  K).

Acceptor	CdTe: $^{111}\text{In}/^{111}\text{Cd}$		ZnTe: $^{111}\text{In}/^{111}\text{Cd}$		ZnSe: $^{111}\text{In}/^{111}\text{Cd}$	
	$\nu_Q$ (MHz)	$\eta$	$\nu_Q$ (MHz)	$\eta$	$\nu_Q$ (MHz)	$\eta$
$\text{Li}_M^-$	60.1(5)	0.07(3)	59.2(5)	0.08(3)	72.4(5)	0.08(3)
$\text{Cu}_M^-$	60.5(5)	0.17(1)			70.3(5)	0.11(2)
$\text{Ag}_M^-$	56.6(5)	0.11(2)	58.5(10)	0.05(5)	69.8(5)	0.09(3)
$\text{Au}_M^-$	54.2(5)	0.07(3)				
$\text{V}_M$	60.2(5)	0.17(1)	60.0(10)	0.15(5)	71.9(5)	0.05(3)

$=0.07(3)$  and the EFG differs from that known for  $V_{\text{Cd}}$  only by the different asymmetry parameter  $\eta$ . However, this small difference is of experimental significance as is also reflected by the different shapes of the modulations at long delay times in the corresponding  $R(t)$  spectra shown in Fig. 4. (Note that the evolution of the different shapes at long delay times is caused by the different frequency ratios  $\omega_2/\omega_1$ , which are directly related to the respective  $\eta$  values of the two different EFG tensors.<sup>18</sup>)

In ZnTe and ZnSe doped with  $^{111}\text{In}$  probe atoms, a defect induced EFG is observed after doping with the group-I acceptors Li and Ag in ZnTe and after doping with Li, Cu, and Ag in ZnSe (Table II). The PAC spectra measured in Ag doped ZnTe and ZnSe are shown in Fig. 5. For the sake of completeness, the EFG corresponding to the  $A$  centers ( $^{111}\text{In}_{\text{Zn}}-V_{\text{Zn}}$ ), occurring in ZnTe and ZnSe after thermal treatment in a chalcogen rich atmosphere<sup>32</sup> also are listed in Table II. It is noted that in these compounds the quadrupole coupling constants for  $V_{\text{Zn}}$  and those ones occurring after group-I doping are distributed in an interval of only 2 MHz width, which is even narrower than in case of CdTe. Accordingly, a unique distinction between the different PAC signals is at the limit of experimental resolution.

### C. Experiments using the probe $^{111}\text{Ag}$

In case of the group-I element Ag, the results presented so far were complemented by studying the pair formation with

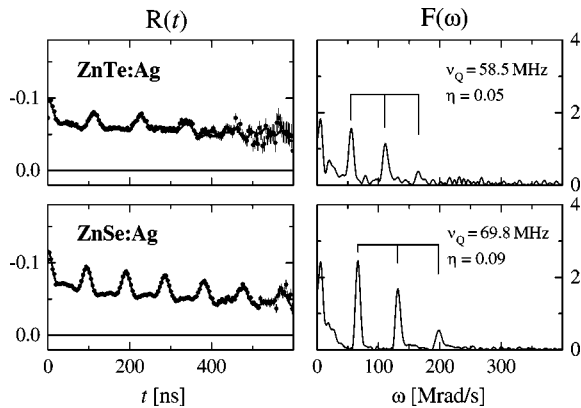


FIG. 5. PAC spectra measured with  $^{111}\text{In}$  probe atoms in ZnTe and ZnSe after Ag doping.

the stable donor atoms Br and In from the point of view of the Ag acceptor by employing the acceptor probe  $^{111}\text{Ag}$ . The PAC experiments in CdTe crystals, which were doped with stable Br and radioactive  $^{111}\text{Ag}$ , yield an axially symmetric EFG ( $\eta=0$ ) with  $\nu_Q=259(5)$  MHz.<sup>15</sup> In CdTe doped with In and  $^{111}\text{Ag}$  a characteristic EFG with  $\nu_Q=62(3)$  MHz and  $\eta=0$  is observed.<sup>14</sup> Similarly, in the other II-VI semiconductors In-correlated defect structures were observed: PAC experiments in ZnTe:In and ZnSe:In using the probe  $^{111}\text{Ag}$  showed EFG's which are not observed in crystals doped exclusively with  $^{111}\text{Ag}$ . Therefore it can be assumed that the observed defect complexes are induced by In doping. The corresponding EFG's measured with the probe  $^{111}\text{Ag}$  are listed in Table III.

## IV. DISCUSSION

The results obtained with three probe atoms, complemented by the calculated EFG's for NN pairs in CdTe, provide a comprehensive basis for a safe identification of defect structures formed by group-I elements and, thereby, deliver information about the behavior of group-I elements in CdTe, ZnTe, and ZnSe. Thus the defect scenario observed with one probe can be verified with help of the information delivered by the other probe atoms and by the LAPW calculations. Thereby, the discussion of calculated EFG's will be restricted to the NN configuration because the calculations are not yet accurate enough to discriminate the nearly identical EFG's caused by different group-I elements in the case of the NNN configuration (see Sec. IV B). Concerning EFG calculations for the  $^{111}\text{In}-V_{\text{Cd}}$  pair in CdTe, the interested reader is referred to a previous publication.<sup>34</sup>

### A. Probe atom $^{77}\text{Br}$

Based on the experimental conditions, the EFG's measured in CdTe:Cu and CdTe:Ag are supposed to be caused by substitutional Cu and Ag atoms, respectively. In case of CdTe:Au the measured EFG is too small for observing a full modulation period in the PAC time spectrum so that its relationship to a well defined  $D-A$  complex remains doubtful. However, the remaining uncertainty in the interpretation of the PAC data was resolved by LAPW calculations. The calculation of the EFG that are caused by singly negatively charged group-I acceptors at their NN  $\text{Se}_{\text{Te}}$  sites yield  $\nu_Q$

TABLE III. EFG's induced by the donors In and Br in CdTe, ZnTe, and ZnSe and measured with the PAC probe atom  $^{111}\text{Ag}/^{111}\text{Cd}$  at  $T_M=295$  K.

Donor	CdTe: $^{111}\text{Ag}/^{111}\text{Cd}$		ZnTe: $^{111}\text{Ag}/^{111}\text{Cd}$		ZnSe: $^{111}\text{Ag}/^{111}\text{Cd}$	
	$\nu_Q$ (MHz)	$\eta$	$\nu_Q$ (MHz)	$\eta$	$\nu_Q$ (MHz)	$\eta$
$\text{Br}_{\text{Te}}^+$	259(5)	0.0(2)				
$\text{In}_{\text{Te}}^+$	62(3)	0.0(2)	62(1)	0.0(1)	78(2)	0.20(5)

= 66 MHz for  $\text{Cu}_{\text{Cd}}^-$ ,  $\nu_Q=123$  MHz for  $\text{Ag}_{\text{Cd}}^-$ , and  $\nu_Q=20$  MHz for  $\text{Au}_{\text{Cd}}^-$ ,<sup>25</sup> being close to the respective experimental values (see Table I). Considering the doping conditions and the good reproduction of the experimentally observed EFG's by theory, the defects corresponding to the PAC spectra shown in Fig. 1 are attributed to the substitutional, singly negatively charged group-I acceptors  $\text{Cu}_{\text{Cd}}^-$ ,  $\text{Ag}_{\text{Cd}}^-$ , and  $\text{Au}_{\text{Cd}}^-$  that form NN donor-acceptor pairs with the probe atom  $^{77}\text{Br}$  as is shown for the case of Ag in Fig. 3 (left). Since the experimental findings for Cu and Ag doped ZnTe and for Cu doped ZnSe are similar to those in CdTe, the observed EFG's are attributed to the analogous defect complexes formed with  $\text{Cu}_{\text{Zn}}^-$  and  $\text{Ag}_{\text{Zn}}^-$  acceptors (see Table I).

### B. Probe atom $^{111}\text{In}$

The EFG's observed after Ag and Au doping are supposed to be caused by  $\text{Ag}_{\text{Cd}}$  and  $\text{Au}_{\text{Cd}}$  acceptors, respectively. This assumption is confirmed by the above-mentioned formation of Br-acceptor pairs, which shows that substitutional group-I acceptors can be trapped by donors in CdTe. As a result of the NNN position of the probe atom  $^{111}\text{In}_{\text{Cd}}$  to the group-I acceptors, the nearest-neighbor shell about the probe, on which the EFG depends most sensitively, consists exclusively of Te atoms and is identical for the different acceptors (see Fig. 3, right-hand side). Accordingly, the identical nearest-neighbor shell in case of the NNN probe-defect pairs is the reason for the close similarity of the EFG caused by the different group-I acceptors (see Table II). In case of the NN pairs, such as the *D-A* pairs of the group-I acceptors with the  $^{77}\text{Br}$  probe (see Table I) as well as the pairs of group-V acceptors with the  $^{111}\text{In}$  probe,<sup>35</sup> the differences of the EFG's with regard to the respective acceptor species are much more pronounced. Since the influence of the acceptor impurity in case of the NNN pair is mediated by the Te atom neighboring both the probe and the acceptor, it is also understandable that the orientation of the EFG tensor is along the [111] direction rather than along the [110] symmetry axis of the probe-defect pair. A similar effect was reported in Ref. 36 for In-vacancy pairs in HgCdTe. The measured [111] orientation of the EFG tensor for the group-I acceptor Ag is also reproduced by the EFG calculations,<sup>26</sup> which yield only 2° deviation from the [111] lattice direction.

An EFG, measured with  $^{111}\text{In}$  and related to Ag doping, has also been reported for the II-VI semiconductor CdS.<sup>11</sup> Like in CdTe, this EFG is similar in its strength compared to the EFG caused by  $V_{\text{Cd}}$  in CdS. Based on this similarity,

the Ag related EFG has been attributed to a larger  $^{111}\text{In}_{\text{Cd}}-V_{\text{Cd}}-\text{Ag}_i$  configuration, where the interstitial Ag atom is relatively distant from the  $^{111}\text{In}$  probe.<sup>11</sup> In the light of the observation of substitutional group-I acceptors in CdTe by  $^{77}\text{Br}$  probe atoms (e.g.,  $^{77}\text{Br}_{\text{Te}}-\text{Ag}_{\text{Cd}}$  pairs) and the confirmation of this configuration by means of EFG calculation, however, we tend to ascribe the similarity between the *A*-center EFG and the EFG related to group-I acceptors to the reduced sensitivity of the EFG in the case of the NNN probe-defect configuration, mentioned above. A further, more direct argument against the formation of an  $^{111}\text{In}_{\text{Cd}}-V_{\text{Cd}}-\text{Ag}_i$  cluster with Ag at an interstitial lattice site is the observation of  $^{111}\text{Ag}-\text{In}$  pairs, which will be discussed below.

In the case of CdTe:Cu, within the experimental resolution exclusively the same EFG [ $\nu_Q=60.5(5)$  MHz,  $\eta=0.17(1)$ ] is observed as known for  $V_{\text{Cd}}$  (see Table II). Consequently, there are two possible interpretations for this EFG: (i) Under the chosen experimental conditions, the diffusion of Cu exclusively leads to the formation of Cd vacancies  $V_{\text{Cd}}$  forming pairs with the  $^{111}\text{In}$  probe atoms. (ii) Cu acceptors form *D-A* pairs with  $^{111}\text{In}$  atoms and the resulting EFG cannot be distinguished experimentally from that of the cation vacancy  $V_{\text{Cd}}$ . If existing, a simultaneous formation of  $\text{In}_{\text{Cd}}-\text{Cu}_{\text{Cd}}$  and  $\text{In}_{\text{Cd}}-V_{\text{Cd}}$  pairs cannot be resolved by PAC, in this case. Taking into account the results obtained with the probe  $^{77}\text{Br}$ , which show that ionized  $\text{Cu}_{\text{Cd}}^-$  acceptors should exist, along with the results obtained with the probe  $^{111}\text{In}$ , which show that *A* centers are observed together with  $^{111}\text{In}_{\text{Cd}}-\text{Ag}_{\text{Cd}}$  and  $^{111}\text{In}_{\text{Cd}}-\text{Au}_{\text{Cd}}$  pairs, case (a) is not favored. The experimental results can be explained consistently assuming case (b), stating that  $^{111}\text{In}_{\text{Cd}}-V_{\text{Cd}}$  and  $^{111}\text{In}_{\text{Cd}}-\text{Cu}_{\text{Cd}}$  give rise to almost the same EFG at the site of the  $^{111}\text{Cd}$  probe atom. It is suggested that both defect complexes are observed simultaneously in CdTe after diffusion of Cu, as in the case of CdTe:Ag and CdTe:Au. Finally, it can also be excluded that the EFG assigned to the  $V_{\text{Cd}}$  defect rather belongs to the Cu acceptor. In this case, no  $\text{In}_{\text{Cd}}-V_{\text{Cd}}$  pairs would have been observed by PAC, up to now, which would be in strong contrast to the experimental conditions and the very detailed identification of  $\text{In}_{\text{Cd}}-V_{\text{Cd}}$  pairs in CdTe by ODMR.<sup>29</sup>

Because of the different asymmetry parameter, the EFG measured with the probe  $^{111}\text{In}$  in CdTe:Li ( $\nu_Q=60.1$  MHz,  $\eta=0.07$ ) indicates that at least a significant fraction of the probe atoms is located in a defect complex other than the *A* center. Since in infrared absorption measurements  $\text{In}_{\text{Cd}}-\text{Li}_{\text{Cd}}$  pairs are detected via their LVM's,<sup>8</sup> and taking into account the PAC data for Ag and Au, it is suggested that the new

defect complex observed by PAC is identical to the  $^{111}\text{In}_{\text{Cd}}\text{-Li}_{\text{Cd}}$  pair. As discussed above, the formation of  $A$  centers is directly observable in  $\text{CdTe:Ag}$  and  $\text{CdTe:Au}$  due to the distinctly different EFG tensor; therefore it is possible that also in  $\text{CdTe:Li}$  crystals  $A$  centers have been formed besides the  $^{111}\text{In}_{\text{Cd}}\text{-Li}_{\text{Cd}}$  pairs. In this case, a superposition of two EFG's with nearly the same strength but somewhat different asymmetry parameters ( $\eta=0.17$  and  $\eta=0.07$ , respectively) causes a PAC signal which can be fitted with an average asymmetry parameter determined by the relative fractions of the respective defect complexes. In the literature, the EFG measured after diffusion of Li has originally been attributed exclusively to the  $A$ -center complex.<sup>52</sup> The comprehensive knowledge on NNN pairs involving different group-I elements and a new, more detailed analysis of the EFG parameters observed for  $\text{CdTe:Li}$  in measurements with high statistical quality gives rise for correcting this earlier interpretation.

In context with the results obtained for  $\text{CdTe}$ , the corresponding  $D$ - $A$  pairs  $^{111}\text{In}_{\text{Zn}}\text{-}A_{\text{Zn}}$  ( $A$ =group-I acceptor) in  $\text{ZnTe}$  and  $\text{ZnSe}$  are suggested to exist in principle, too. Due to the very similar quadrupole frequencies measured in each compound, however, the different  $D$ - $A$  pairs cannot always be characterized unambiguously by a specific EFG (see Table II). In  $\text{ZnSe}$ , for instance, the EFG observed after Cu and Ag doping, and the EFG caused by Li and  $V_{\text{Zn}}$ , respectively, are identical within the experimental resolution. In  $\text{ZnTe}$ , the EFG of the  $A$  center can be distinguished from the Li and Ag related EFG due to the different asymmetry parameters.

### C. Probe atom $^{111}\text{Ag}$

Here, the group-I element is represented by the probe atom  $^{111}\text{Ag}$  itself. Thus this probe atom offers the possibility of directly examining the formation of  $D$ - $A$  pairs involving the group-I acceptor Ag, which is proposed to occur on the basis of experiments with the donor probes  $^{77}\text{Br}$  and  $^{111}\text{In}$ . For the isolated  $\text{Br}_{\text{Te}}^+$  donor in  $\text{CdTe}$ , the calculated EFG at the NN Cd site corresponds to  $\nu_{\text{Q}}=267$  MHz ( $\eta=0$ ).<sup>26</sup> This result is in good agreement with the experimental PAC data obtained with the  $^{111}\text{Ag}$  probe in  $\text{CdTe:Br}$  yielding  $\nu_{\text{Q}}=259$  MHz ( $\eta=0$ ) (see Table III). The measured EFG is therefore attributed to the  $^{111}\text{Cd}\text{-Br}_{\text{Te}}^+$  configuration. It is pointed out that the formation of the  $\text{Ag}_{\text{Cd}}\text{-Br}_{\text{Te}}$  donor-acceptor complex is observed by means of both the  $^{111}\text{Ag}$  and the  $^{77}\text{Br}$  PAC probe in combination with doping by stable Br and Ag atoms, respectively. And in both cases, the assignment of the observed EFG to the respective  $D$ - $A$  pair has been confirmed by EFG calculations.

In  $\text{CdTe}$  doped with  $^{111}\text{Ag}$  probe atoms and stable In donors, a characteristic EFG with  $\nu_{\text{Q}}=62$  (3) MHz and  $\eta=0$  is measured.<sup>14,15</sup> Thus the formation of the  $D$ - $A$  complex  $\text{Ag}_{\text{Cd}}\text{-In}_{\text{Cd}}$  is also observed by the PAC probe  $^{111}\text{Ag}$  and the interpretation of the PAC data obtained with  $^{111}\text{In}$ , i.e., the formation of  $^{111}\text{In}_{\text{Cd}}\text{-Ag}_{\text{Cd}}$  pairs is confirmed (see Sec. IV B). In the case of the experiments with the  $^{111}\text{Ag}$  probe in  $\text{ZnTe:In}$  and  $\text{ZnSe:In}$ , again characteristic EFG's are observed that can be assigned to the respective  $^{111}\text{Ag}_{\text{Zn}}\text{-In}_{\text{Zn}}$

pairs (see Table III). Thus in all investigated II-VI semiconductors, the In-Ag pair formation has been confirmed by means of probe isotopes of both constituents, i.e., by  $^{111}\text{In}$  and  $^{111}\text{Ag}$ .

### D. Interaction with cation vacancies

The simultaneous observation of substitutional group-I acceptors and Cd vacancies (see Fig. 4 for Ag and Au doped samples) along with the discussion of the results for Cu and Li suggests that vacancies are formed as a consequence of the doping with group-I elements via the defect reaction



The fraction of group-I acceptor atoms  $A_{\text{Cd}}$  that leaves the substitutional lattice site transforms into interstitial donors  $A_{\text{i}}$ , which electrically compensate a part of the remaining substitutional acceptor atoms as was also proposed on the basis of photoluminescence experiments.<sup>6,7</sup> The generated Cd vacancies are detected by trapping at the donor  $^{111}\text{In}_{\text{Cd}}$ , forming  $A$  centers. Consequently,  $^{111}\text{In}_{\text{Cd}}\text{-}A_{\text{Cd}}$  and  $^{111}\text{In}_{\text{Cd}}\text{-}V_{\text{Cd}}$  pairs are simultaneously observable as shown in Fig. 4. In PAS experiments, the *inverse* reaction of Eq. (2) has been reported after diffusing Ag atoms into  $\text{CdTe}$  samples at room temperature.<sup>12</sup> Taking into account the doping conditions in the present work ( $T_{\text{A}} \geq 550$  K), the PAC results complement the picture derived from the PAS data. At the same time, both experiments are consistent with the emission channeling results from Ref. 13 showing that substitutional Ag acceptors leave the lattice site above 400 K. In contrast to  $^{111}\text{In}$ , using the probe  $^{77}\text{Br}$  a simultaneous existence of  $^{77}\text{Br}_{\text{Te}}\text{-}V_{\text{Cd}}$  and  $^{77}\text{Br}_{\text{Te}}\text{-}A_{\text{Cd}}$  pairs was not observed at similar experimental conditions. An explanation may be found by a higher binding energy of the  $^{77}\text{Br}_{\text{Te}}\text{-}A_{\text{Cd}}$  complex as compared to the  $A$ -center  $\text{Br}_{\text{Te}}\text{-}V_{\text{Cd}}$ .

Based on experiments with the probe  $^{111}\text{In}$ , it was proposed by Reislöhner *et al.*<sup>9</sup> that in  $\text{CdTe:Ag}$  the EFG characterized by  $\nu_{\text{Q}}=56.6$  MHz and  $\eta=0.11$  is also caused by  $V_{\text{Cd}}$ , in addition to the well-known EFG of  $\nu_{\text{Q}}=60.2$  MHz and  $\eta=0.17$ . The present results obtained with the probe atoms  $^{111}\text{In}$  and  $^{111}\text{Ag}$ , however, clearly contradict this interpretation by showing the formation of In-Ag pairs in  $\text{CdTe}$  using both probe atoms, whereby the  $^{111}\text{In}\text{-Ag}$  pair is characterized by  $\nu_{\text{Q}}=56.6$  MHz and  $\eta=0.11$ .

### V. SUMMARY

In the II-VI semiconductors  $\text{CdTe}$ ,  $\text{ZnTe}$ , and  $\text{ZnSe}$ , a large number of different donor-acceptor complexes involving group-I acceptors have been identified by their characteristic EFG's. In particular, it has been shown that the group-I elements Cu, Ag, Au form NN as well as NNN pairs with donor atoms. Whereas in the case of NN pairs different defects give rise to easily resolvable, significantly different EFG's, this is obviously not the case for NNN pairs: The EFG's, caused in  $\text{CdTe}$  by the different group-I acceptors or  $V_{\text{Cd}}$  at the NNN site of an  $^{111}\text{Cd}$  nucleus, give rise to  $\nu_{\text{Q}}$  values within the narrow interval between 54 and 60 MHz. In contrast, the EFG's at the  $^{111}\text{Cd}$  site, caused by different group-V elements in an NN configuration, are distributed

over a range of more than 100 MHz.<sup>35</sup> By using the experimental results obtained by the three probe atoms <sup>77</sup>Br, <sup>111</sup>Ag, and <sup>111</sup>In it is also possible to resolve some confusions with regard to the interpretation of defect related EFG's which arose in the past as a consequence of the close and possibly unexpected similarities of EFG's characterizing the formation of different NNN pairs in these materials.

Besides the bare identification of the defect related EFG's, valuable information about the behavior of the group-I acceptors has been obtained: The amphoteric character of the group-I elements according to the defect reaction in Eq. (2) has been confirmed and additional parameters such as binding and migration energies have been determined. Finally, it should be noted that the present work constitutes the first comprehensive study about NNN donor-acceptor pairs at all, irrespective of first preliminary data about the In<sub>Cd</sub>-Au<sub>Cd</sub> and In<sub>Cd</sub>-Ag<sub>Cd</sub> pairs in CdTe and the simultaneous formation of V<sub>Cd</sub> published previously.<sup>10,14-16</sup> By far the most PAC studies regarding *D-A* pairs in semiconductors have concerned

substitutional NN pairs or complexes of substitutional probe atoms with nearby interstitial defects. The present paper comprises the results obtained by PAC experiments using the probe atoms <sup>77</sup>Br, <sup>111</sup>Ag, and <sup>111</sup>In in the II-VI semiconductors CdTe, ZnTe, and ZnSe. As a valuable tool that became recently available, the density-functional theory based EFG calculation leads to a substantial improvement regarding the reliability of the identification of defect complexes in semiconductors.

## ACKNOWLEDGMENTS

It is a pleasure to thank the team of the Isotopenseparator at the University Bonn and the Forschungszentrum Rossendorf for their generous experimental help. The financial support of the Bundesministerium für Bildung und Forschung (BMBF) under Contract No. 03WI5SAA is gratefully acknowledged.

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