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Defect identification by means of EFG calculation

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Abstract

The electric field gradients (EFG) caused by group V acceptors, group Ib acceptors and the cadmium vacancy in CdTe are calculated using the linearised augmented plane wave method and compared to the corresponding experimental values. Experimentally, the EFG are determined by the perturbed γγ-angular correlation spectroscopy with the radioactive probe isotopes ^{111}In and ^{77}Br. Besides the chemical nature, information about the charge state and the lattice relaxation associated with each defect is obtained.

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1. Introduction

Defects in semiconductors induce characteristic electric field gradients (EFG) at neighbouring lattice sites. 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 γγ-angular correlation (PAC), Mössbauer spectroscopy, nuclear quadrupole resonance or electron nuclear double resonance. Defect-related EFG have been successfully used as 'fingerprints' of the respective defects in the past, because they are very sensitive to an anisotropic charge distribution about the probe nucleus, caused for example by a neighbouring defect [1, 2]. However, the EFG by itself does not tell much about its microscopic origin so that due to the lack of appropriate theories for predicting the EFG of a distinct defect, lots of defects, though experimentally well characterised via their EFG, have remained unidentified.

The EFG discussed in this paper are experimentally determined by PAC spectroscopy, using the radioactive PAC probe atoms ^{111}In and ^{77}Br. The investigation of defects in semiconductors using PAC spectroscopy is described in detail in Ref. [2]. In the II-VI semiconductor CdTe, both ^{111}In and ^{77}Br are donor atoms which can form close donor-acceptor (D-A) pairs with stable acceptors, driven by the Coulomb attraction of ionised donors and acceptors. The actual PAC measurement takes place after the radioactive decay of the parent probes ^{111}In and ^{77}Br at the $I = 5/2$ excited state of the daughter isotopes ^{111}Cd and ^{77}Se, respectively, and yields the quadrupole coupling constant ν_Q, related to the EFG by $\nu_Q = |eQV_{zz}/h|$, along with the asymmetry parameter $\eta = (V_{xx}-V_{yy})/V_{zz}$ ($|V_{xx}| \le |V_{yy}| \le |V_{zz}|$). The component V_{zz} is calculated from ν_Q using the quadrupole moments $Q = 0.83$ b for ^{111}Cd [3] and $Q = 0.76$ b for ^{77}Se (I=5/2) [4]. It is noted that the daughter isotope ^{111}Cd of the PAC probe ^{111}In is a host atom in CdTe, and the EFG characterises the isolated defect originally trapped at the ^{111}In donor. In the case of ^{77}Br, the daughter isotope ^{77}Se is isoelectronic to the Te host and consequently the EFG characterises the defect pair, consisting of a stable acceptor and the isoelectronic ^{77}Se isotope. Exemplified for the group V acceptor N and the group Ib acceptor Ag, the local defect structure after the radioactive decay of the employed PAC probes is sketched in Fig. 1.

By the detection of the fraction of probe atoms, which are exposed to the characteristic EFG of a distinct defect, the presence of this defect is immediately proven and, at the same time, thermodynamic parameters of the involved defects, such as binding and migration energies, can be determined. If fluctuation rates become comparable to the spin precession frequencies induced by the EFG, electronic as well as geometrical changes of the complex formed with the (daughter) probe can be observed (cf. Ref. [2]). Since this kind of information is useful only if the observed EFG is assigned to the correct defect model, the reliable EFG calculation is an appreciated complement to the PAC spectroscopy.

For more than a decade, calculations based on the density functional theory (DFT) formalism have been used for determining theoretically the properties of defects in semiconductors (e.g. Ref. [5]), but

calculations yielding also the EFG caused by impurities came up only recently [6, 7]. In the present work, the linearised augmented plane wave (LAPW) code WIEN97 [8] is employed for EFG calculation. Exchange and correlation effects are treated in the generalised gradient approximation as described in Ref. [9] being a development based on the local density approximation (LDA). The general treatment of a defect in a semiconductor host lattice within this method is performed according to Ref. [7], where a 32 atom supercell in BCC structure with T_d symmetry was used. Here, we are dealing also with cases in which two impurity atoms are introduced into the supercell and consequently the symmetry is lowered to C_{3v}.

2. Donor-acceptor pairs with ^{111}In in CdTe

For the D-A pairing of ^{111}In donors with group V acceptors in CdTe, the experimental EFG obtained by PAC are compared to the calculated EFG in Table 1 [10, 7]. Here, the use of T_d symmetry in the calculation implies $\eta = 0$. The LAPW calculations yield excellent agreement of the EFG at a nearest neighbour (NN) Cd site with the experimental data in the case of the ionised group V acceptors [7]. Structural relaxation (cf. Fig. 1a) is found to be crucial for an accurate EFG calculation: The relaxation of the NN-Cd atoms towards the group V acceptor by 1% of the undisturbed Cd-Te bondlength increases the calculated EFG by about 10^{21}V/m^2, i.e. by about of 10%. Regarding the strong relaxation of more than 20% for the N acceptor (cf. Table 1), it is clear that without taking into account relaxation a calculated EFG is meaningless. The high accuracy of the calculated EFG gives also evidence of the accuracy of the calculated lattice relaxation in the context of the high sensitivity of the EFG to the local structure. The occurrence of a second EFG, experimentally observed after As and additional Li doping, is interpreted in terms of the neutral As acceptor As^0 [7]. The agreement with the calculated value for As^0 shows that the calculation of EFG for non-ionised acceptor states can be reliable even for the rather small cell size of 32 atoms, where the spatial expansion of the bound hole exceeds the size of the supercell. Thus, in cases where the EFG depends significantly on the charge state of the defect, the EFG calculation can be used to determine the actual charge state observed in an experiment.

3. Donor-acceptor pairs with ^{77}Br in CdTe

The implantation of the radioactive ^{77}Br isotopes into CdTe crystals was performed at the ISOLDE mass separator at CERN (Geneva, CH). The experimental results obtained for the D-A pairs of ^{77}Br donors with stable group Ib elements are briefly summarised in Table 2. A more detailed discussion of the experiments is given Ref. [11]. Due to the relatively weak EFG for the Au acceptor, the corresponding experimental data is difficult to interpret in a unique way. The assumption that the ^{77}Se probes are located in a disturbed lattice environment, would be also consistent with the PAC spectra observed after Au doping. Thus, the value for the Au acceptor given in Table 2 is obtained by assuming an axially symmetric EFG tensor, as it is measured for the Cu and Ag acceptors. Attributed to the $^{77}Se_{Te}$-Au_{Cd} configuration, the EFG is unexpectedly small for a NN pair if it is compared to the EFG for the Cu and Ag acceptors or, for example, with the EFG for the group V acceptors (Table 1). It rather has a strength that is typical for cases where the probe and the trapped defect form more distant next nearest neighbour (NNN) pairs [2]. Thus, based solely on experimental observations, the interpretation of the PAC data obtained with the ^{77}Br probe is particularly difficult regarding Au doped CdTe crystals, and support from theoretical tools is highly appreciated.

After implantation of ^{77}Br into undoped CdTe samples, an EFG, characterised by $\nu_Q = 188(4)$ MHz, $\eta = 0.0(1)$ is observed [11]. Based on the annealing behaviour under Cd vapour pressure, this EFG is interpreted with the formation of bromine A-centres, i.e. close pairs of ^{77}Br donors with the acceptor-like cadmium vacancy. The theoretical determination of EFG is particularly interesting in the case of intrinsic defects, such as the present example of V_{Cd} in CdTe, because here the defect identification is generally more difficult than in the previous examples where the ^{77}Br donors form D-A pairs with deliberately introduced dopants.

As mentioned above, the calculation of the EFG at a Se_{Te} site in CdTe, induced by a neighbouring group Ib acceptor, requires that two impurity atoms are introduced into the supercell used for the LAPW calculation, leading to a C_{3v} symmetry. Compared to the T_d symmetry, the calculation becomes more demanding: First, less symmetry operations can be exploited in order to reduce the computational effort. Second, there are more degrees of freedom for structural relaxation (cf. Fig. 1b) so that finding the equilibrium positions of the atoms in the supercell becomes a lengthy task. Including relaxation of all atoms in the supercell, the calculated EFG for the ionised group Ib acceptors, i.e. Cu_{Cd}^-, Ag_{Cd}^- and Au_{Cd}^-, and for the ionised cadmium vacancy V_{Cd}^{--} are compared to the experimental data in Table 2. Here, the use of C_{3v} symmetry in the calculation implies $\eta = 0$. The detailed results for the relaxation of the ^{77}Se probe, the group Ib acceptor, and the neighbouring atoms – i.e. all atomic positions shown in Fig. 1b – are listed separately in Table 3. For the Ag acceptor and the cadmium vacancy, the EFG calculation reaches the high degree of agreement as in the case of the group V acceptors. For the Cu and Au acceptor the calculated EFG differ from the experimental values by about $1.5 \cdot 10^{21} V/m^2$, but are still close enough to confirm the proposed defect model, i.e. $^{77}Se_{Te}$-Cu_{Cd} and $^{77}Se_{Te}$-Au_{Cd} complexes. (Note that absolute differences between calculated and experimental EFG should be regarded rather than relative ones, because V_{zz} can assume negative and positive values including zero.) In particular, the unusually low magnitude of the EFG the Au acceptor is causing at a NN site, is clearly reproduced. For the neutral state of the group Ib acceptors the EFG is calculated to be more positive by up to $2.5 \cdot 10^{21} V/m^2$, yielding less agreement with the experimental data. Consequently, the measured EFG are attributed to the ionised state, in accordance with the observation for the group V acceptors [7]. In contrast, the calculated EFG for the neutral and the singly charged Cd vacancy do not differ much from the value for V_{Cd}^{--} ($-9.6 \cdot 10^{21} V/m^2$ and $-9.1 \cdot 10^{21} V/m^2$ for V_{Cd}^0 and V_{Cd}^-), so that the EFG calculation supports the identification of V_{Cd} but the assignment of the measured EFG to a specific charge state can not be made definitively. It is noted, that the trigonal symmetry used for the calculation of the Se_{Te}-V_{Cd} defect complex in principle allows the Jahn-Teller relaxation expected for V_{Cd}^0 and V_{Cd}^-. However, the LAPW calculations give no indication for a Jahn-Teller effect. The properties of both the anion and cation vacancy in CdTe are discussed in detail in a parallel paper [12].

Though very useful for the interpretation of the experimental data, the EFG calculations yield somewhat lower agreement with experiment for the group Ib acceptors compared to the group V acceptors. This is probably a consequence of the LDA used in DFT calculations, which does not exactly describe the *d* electrons of the group Ib elements. In Fig. 2a, the calculated electronic density of states (DOS) for a supercell containing a Se_{Te}-Cu_{Cd} pair is shown, and the predominant character of the wavefunctions in the different sections of the spectrum is indicated. In IIb-VI compounds, the outer cation *d* electrons (e.g. the Cd-4*d* electrons in CdTe) interact with the anion *p* states making up the upper part of the valence band [13]. The *d* states of the group Ib elements in CdTe are more loosely bound than the Cd-*d* states and lie in an energy region which coincides with the energetic position of the Se-*p* states. This is clearly visible in Fig. 2b and Fig. 2c, where the site projected and angular momentum decomposed DOS is plotted for Cu-*d* and Se-*p* states. The smaller energy separation between the Cu-*d* and the Se-*p* states compared to the Cd-*d* and the Te-*p* states leads to a stronger interaction, where the Se-p_z orbital (directed towards Cu_{Cd}) is affected rather than the Se-p_x and Se-p_y orbitals due to symmetry. It is well known that the LDA underestimates the binding energy of the cation *d* electrons (cf. e.g. [13]) and a similar effect can be expected for the outer *d* electrons of the group Ib acceptors. This means, however, that the coupling between the Se-*p* states and e.g. the Cu-*d* states is not estimated exactly and an error can be introduced in the calculated EFG, because of the anisotropic influence of the Cu-*d* electrons from point of view of the Se atom. This argument holds for all three group Ib acceptors, so that the exact agreement with the experimental value for the Ag acceptor seems to be rather fortuitous. In general, it should be emphasised that the EFG calculations have proven to be very helpful for defect identification even in the case of the group Ib acceptors in

CdTe, which is a rather difficult case for EFG calculations based on the DFT-LDA formalism due to the energetically high lying *d* orbitals.

4. Summary and outlook

LAPW calculations are presented for isolated group V acceptors and for defect complexes consisting of a group Ib acceptor and a Se neighbour in the II-VI semiconductor CdTe. The theoretically determined EFG are used to support the identification of defects. In particular for the Au acceptor, where the experimental situation is ambiguous, a clear interpretation is achieved only by support of the EFG calculation. Furthermore, the assignment of an experimentally observed EFG to the Cd vacancy is confirmed by means of the LAPW calculations. Future work will focus on cases where the PAC probe and the investigated defect are next nearest neighbours, on self compensation mechanisms such as DX an AX centre formation, and on defects in other II-VI semiconductors than CdTe, such as ZnSe.

In general, it has been shown that by comparing the experimentally and theoretically determined, defect related EFG information is obtained about the chemical nature, the charge state, and the lattice relaxation associated with each defect. This is the more important as for more than 50 defect complexes, studied in different semiconductors, experimental EFG are available.

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Tables

Table 1. Experimental EFG, calculated EFG, and calculated relaxation of the NN-Cd shell for the group V acceptors in CdTe. The EFG refer to the NN-Cd site and to the ionised acceptor (e.g. N_{Te}^{-}). The experimental EFG obtained with the ^{111}In PAC probe is axially symmetric ($\eta = 0$) in all cases, as expected for the tetrahedral symmetry of the defect. Relaxation values are given in percent of the NN distance in CdTe (2.81 Å) and refer to the atomic movement indicated by the arrows in Fig. 1a.

acceptor	experiment [10]	theory [7]	
	V_{zz} [10^{21}V/m^2]	V_{zz} [10^{21}V/m^2]	d_{NN} [%]
N_{Te}^{-}	±13.95(5)	–13.7	21.7
P_{Te}^{-}	±10.56(9)	–11.2	11.0
As_{Te}^{-}	±9.27(5)	–9.5	8.3
Sb_{Te}^{-}	±7.62(5)	–8.1	3.3

Table 2. Experimental and calculated EFG for group Ib acceptors and V_{Cd}. The EFG refer to the NN-Se_{Te} site and to the ionised state of the defect. The experimental EFG obtained with the ^{77}Br PAC probe is axially symmetric ($\eta = 0$) in all cases.

acceptor	experiment	theory
	V_{zz} [10^{21}V/m^2]	V_{zz} [10^{21}V/m^2]
Cu_{Cd}^{-}	±5.3(2)	–3.6
Ag_{Cd}^{-}	±6.7(2)	–6.7
Au_{Cd}^{-}	±2.6(3)	–1.1
V_{Cd}^{--}	±10.2(2)	–10.8

Table 3. Calculated relaxation of the local environment about the group Ib acceptors and V_{Cd}. Values are given in percent of the NN distance in CdTe (2.81 Å) and refer to the relaxations indicated by the arrows along the Te-Ag-Se-Cd chain in Fig. 1b.

	Te	Acceptor	Se	Cd
Cu_{Cd}–Se_{Te}	8.7	4.9	7.6	8.0
Ag_{Cd}–Se_{Te}	3.2	5.4	0.6	6.0
Au_{Cd}–Se_{Te}	3.9	4.6	1.4	6.2
V_{Cd}–Se_{Te}	13.4	–	8.6	9.3

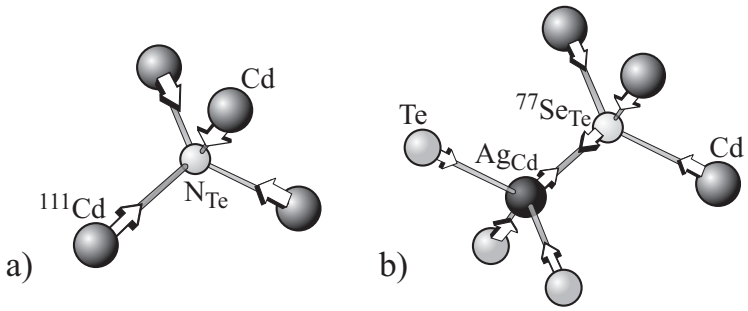

Fig. 1. Local defect structure after the radioactive decay of the parent PAC probe. (a) N acceptor trapped at a ^{111}In donor which decays to ^{111}Cd (tetrahedral symmetry). (b) Ag acceptor trapped at a ^{77}Br donor which decays to ^{77}Se (trigonal symmetry). Arrows indicate structural relaxation.

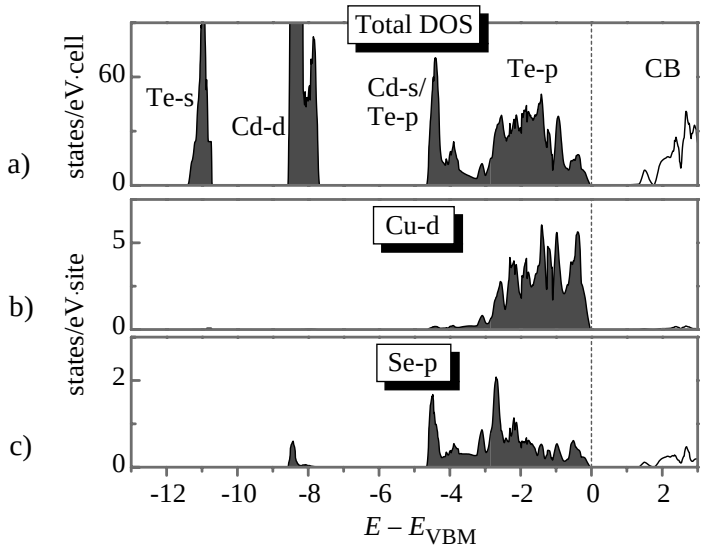

Fig. 2. (a) Total DOS for a CdTe 32 atom supercell containing a Cu_{Cd}-Se pair. The dominant characters of the wavefunctions are indicated. (b) Site projected DOS for Cu_{Cd}, *d* (*l* = 2) contribution. (c) Site projected DOS for Se_{Te}, *p* (*l* = 1) contribution.