PAC Study of the Acceptor Li in II-VI Semiconductors

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Abstract

For the II-VI semiconductors CdS, ZnS, and CdTe the state of Li atoms was investigated using the donor ^{111}In as radioactive probe atom for perturbed angular correlation (PAC) experiments. From the absence of In_M^+-Li_M^- pairing and the simultaneous formation of In_M^+-V_M^{--} pairs which was observed in all these semiconductors it is concluded that Li is incorporated rather interstitially as Li_i^+ accompanied by a vacancy V_M^{--} than substitutionally on the group II site as an acceptor Li_M^-.

1. Introduction

Detailed information on the atomic configuration of dopant atoms is much less available for II-VI semiconductors than for elemental or III-V semiconductors. But, in II-VI semiconductors doping, in particular *p*-doping, poses a crucial problem because of the strong interaction of the dopant atoms with intrinsic defects leading to self-compensation phenomena[1]. Since Li introduced on the group-II site is regarded as a promising candidate for *p*-doping of II-VI semiconductors we have begun an investigation of the incorporation of Li into II-VI compounds on an atomic scale. Li atoms that occupy the site of the group II element and act as an acceptor should form coulombic bound pairs with the donors that are also present in the crystal. Such a pairing is easily detectable by the perturbed angular correlation technique (PAC) using the radioactive donor ^{111}In as a probe atom as has been successfully proven for Si, Ge and several III-V semiconductors[2,3]. In contrast, PAC studies of defects in II-VI semiconductors are just at their beginning, e.g. in ^{111}In doped ZnO[4,5], CdTe[6,7], and CdS[8-10]. In this paper, first results on a comparative study of the behavior of Li in CdS, ZnS, and CdTe will be presented.

2. Experimental Details

The PAC technique employed here measures the defect specific electric field gradient tensor (EFG) which at a particular lattice site is determined by the local electric charge distribution. Working with the radioactive probe atom ^{111}In, which decays with a half-life of 2.8 days to its daughter isotope ^{111}Cd (see Fig. 1), the EFG will generate three frequencies ω_n in the PAC time spectrum R(t) which can be described by

(1)
$$R(t) = S_0 + \sum_{n=1}^{3} S_n \cos(\omega_n t)$$
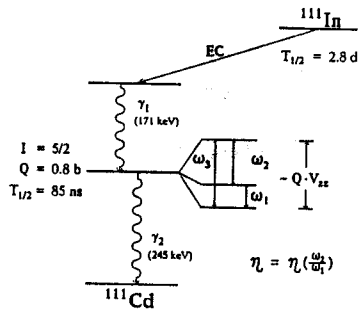
Figure 1. Nuclear decay schema of the PAC probe atom ^{111}In showing the β-decay (electron capture) and the subsequent emission of the two γ rays used for the measurement of the γγ angular correlation.

This spectrum is obtained by measuring the coincidence rate of the two γ-rays emitted by the excited ^{111}Cd nucleus as a function of the time which has passed during the detection of both γ-rays. The different components V_{ii} of the traceless tensor are obtained from the frequencies ω_n. The largest component V_{zz} is usually expressed by the coupling constant $\nu_Q = eQV_{zz}/h$ where Q is the nuclear quadrupole moment of the isomeric ^{111}Cd state ($T_{1/2} = 85$ ns) used for the detection of the EFG. As a second parameter the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ is used ($0 \leq \eta \leq 1$), which is deduced from the measured frequency ratio ω_2/ω_1 (Fig. 1). The coefficients S_o and S_n depend on the orientation of the EFG tensor with respect to the host lattice, i.e. on the orientation of the formed ^{111}In-defect complex; in addition, the coefficients depend on the fraction of ^{111}In atoms that are involved in this complex. A detailed description of PAC is found elsewhere[2].

For the PAC experiments single crystals were cut into pieces of typically 5 to 10 mm^3 size and were diffused inside of an evacuated quartz ampoule with about 10 to 20 μCi ^{111}In from a carrier free ^{111}InCl$_3$ solution. Into CdS (Eagle Picher) and ZnS (Eagle Picher) this diffusion happened under S$_2$ overpressure at 1073 K for 90 min.; into CdTe (R. Triboulet, CNRS, Meudon) the diffusion happened under Cd overpressure at 1023 K for 90 min. The PAC spectra were recorded at 295 K using a 4 detector set-up.

3. Experimental Results

For the II-VI semiconductors CdS, ZnS, and CdTe Fig. 2 shows the PAC time spectra along with their Fourier transforms that were obtained after diffusion of the respective semiconductor with Li. In all three cases, the absence of a Li specific EFG shows that ^{111}In$^+$-Li$^-$ pairs were not formed in those compounds but rather In$_M$$^+$-V$_M$$^{--}$ complexes consisting of the radioactive donor ^{111}In$_M$$^+$ and the acceptor vacancy V$_M$$^{--}$, both being situated in the

Table I. Site specific EFGs observed at the probe ^{111}In/^{111}Cd at 295 K after Li diffusion. Listed are the strength V_{zz} and the asymmetry parameter η of the EFG tensor.

CRYSTAL	$\nu_Q = eQV_{zz}/h$	$(V_{xx}-V_{yy})/V_{zz}$	COMPLEX
CdS	72.4(2) MHz	0.35(2)	In$_{Cd}$-V$_{Cd}$ [1]
	78.7(2) MHz	0.21(2)	In$_{Cd}$-V$_{Cd}$ [2]
ZnS	81.5(4) MHz	0.16(4)	In$_{Zn}$-V$_{Zn}$
CdTe	60.0(4) MHz	0.10(4)	In$_{Cd}$-V$_{Cd}$

[1] V$_{Cd}$ above or below the basal plane (Fig. 4, left)
[2] V$_{Cd}$ in the basal plane (Fig. 4, right)

sublattice of the metallic group II element Cd or Zn. The identical complexes, as recognized by the identical EFGs, are formed - only less pronounced - during diffusion of these II-VI compounds with the radioactive ^{111}In probe atoms.
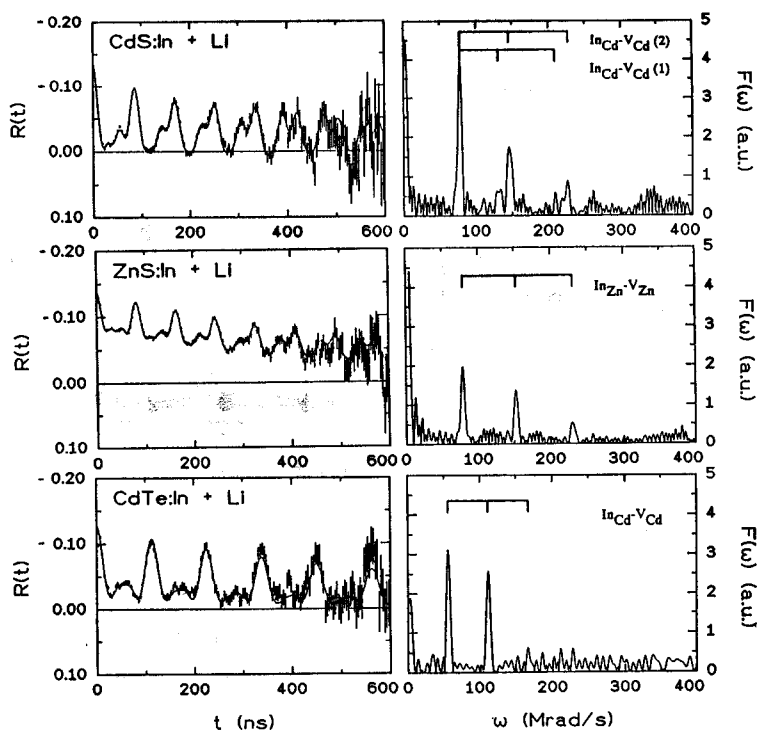
Figure 2. PAC time spectra and their associated Fourier transforms measured after Li diffusion. The corresponding values of the different EFGs are listed in Table I.

<u>CdS</u> : The ^{111}In doped crystals were diffused with Li at 793 K (30 min.). A least-squares fit to the measured PAC time spectrum (Fig. 2, top) yields that two different EFGs what is also visible by the two frequencies triplets in the associated Fourier transform. Their coupling constants ν_Q along with the respective asymmetry parameters η are listed in Table I. Both EFGs are already known to be caused by the trapping of Cd vacancies[9,10].

<u>ZnS</u>: The ^{111}In doped crystals were diffused with Li at 793 K (30 min.). The least-squares fit to the PAC spectrum (Fig. 2, middle) yields a single EFG that is characterized by $\nu_Q = 81.5$ MHz and $\eta = 0.16$. The identical EFG is also found directly after the diffusion of ^{111}In into the ZnS crystal; only the fraction of the ^{111}In-defect complexes was again increased by the presence of Li.

The influence of the Li-diffusion temperature on the fraction of the formed In-defect complexes shows Fig. 3 (left panel); here, the diffusion time was always 30 min.. In order to separate the effects caused by the presence of Li from possible modification of the crystal solely caused by the respective diffusion temperature, a second ZnS crystals was identically

treated, however, withoutLi. The first data point results from the doping of the crystals with ^{111}In at 1073 K. It is evident that there is no influence of Li on the In-defect fraction below 580 K. Above this temperature,however, Li seems to diffuse into ZnS thereby stabilizing and enhancing the In-defect fraction considerably as compared to the ZnS crystal that was heated to the same temperatures without Li.
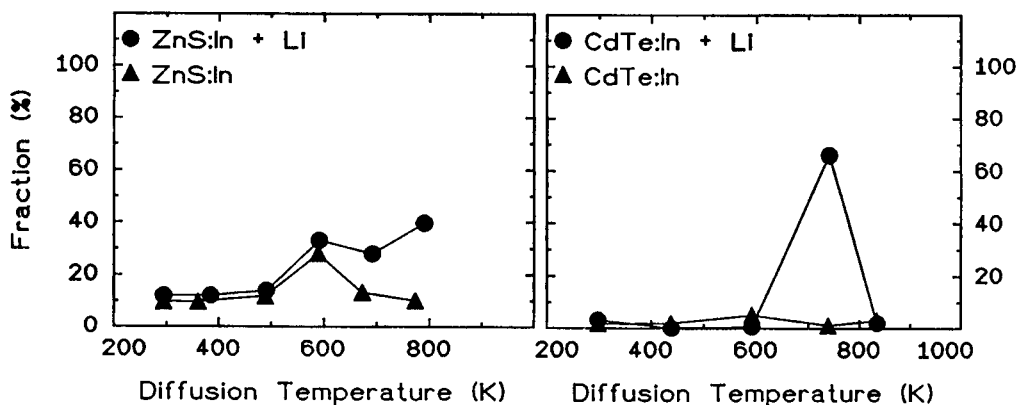

Figure 3. Influence of the diffusion temperature of Li on the fraction of $In_M{}^+$-$V_M{}^{--}$ pairs observed at 295 K.

CdTe: After diffusion of an ^{111}In doped crystal with Li at 720 K (30 min.) the PAC spectrum shown in Fig. 2 (bottom) again reveals no Li specific EFG. For the observed EFG that is characterized by ν_Q = 60.0 MHz and η = 0.10 is well-known from previous PAC experiments and has been identified as the $In_{Cd}{}^+$-$V_{Cd}{}^{--}$ pair[6,7].

As for ZnS, the influence of the Li diffusion temperature on the formation of the $In_{Cd}{}^+$-$V_{Cd}{}^{--}$ pairs was investigated (Fig. 3, right panel). Whereas temperatures up to 820 K are not able to produce any $In_{Cd}{}^+$-$V_{Cd}{}^{--}$ pairs in CdTe the presence of Li gives rise to a very pronounced increase in the pair fraction at 720 K. The strong decrease of the formed complexes above this temperature can be explained by a too small binding energy of the pairs.

## 4. Discussion

For CdS, ZnS and CdTe the PAC results show:

i) Because no donor-acceptor pairing of the type $In_M{}^+$-$Li_M{}^-$ is observable Li doping does not lead to a measurable population of the Li_M acceptor states at the respective diffusion temperatures.

ii) Li doping enhances the concentration of acceptor vacancies $V_M{}^{--}$ what becomes visible through the enhanced formation of $In_M{}^+$-$V_M{}^{--}$ pairs. A detailed identification of this complex has been performed for CdS[9,10] as well as in CdTe[6,7]. The similar EFGs observed for the In-defect complexes in the three II-VI compounds (see Table I) as well as the similar formation conditions represent a strong hint that also the complex in ZnS is caused by a trapped $V_M{}^{--}$ defect and, therefore, corresponds to an $In_{Zn}{}^+$-$V_{Zn}{}^{--}$ pair.

From these results it is concluded that the incorporation of Li is governed by the reaction

(2) $Li_M^- \rightleftarrows Li_i^+ + V_M^{--}$
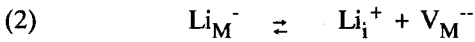
which, at least at the time of Li diffusion, is strongly shifted to the right hand site resulting in the formation of interstitial Li_i^+ and a vacancy V_M^{--}; this complex still acts as a single acceptor and , therefore, can produce *p*-conductivity in a II-VI crystal. Since both elements, In and Li, form donor states it is easily understandable that no In-Li pairing occurs, and since the introduction of Li is accompanied by the formation of a vacancy an enhancement of In_M^+-V_M^{--} pairs has to occur, as well.

For Li in ZnSe also Sasaki and Oguchi based on density-functional calculations arrived at the conclusion that the acceptor Li_{Zn} is unstable against disintegration into a vacancy V_{Zn} and interstitial Li_i[11]. On the other hand, the formation of Li_i donors in CdS contradicts photoluminescence experiments by Henry et al. which claim the formation of Li_{Cd} states in the CdS lattice[12,13]. It should be noted that the behavior of Li observed by PAC is common to all, here investigated II-VI compounds in spite of their different band gap energies and bonding characters, and, second, that the states of both the donor In and the acceptor Li are affected by the same intrinsic defect, the metallic vacancy V_M.
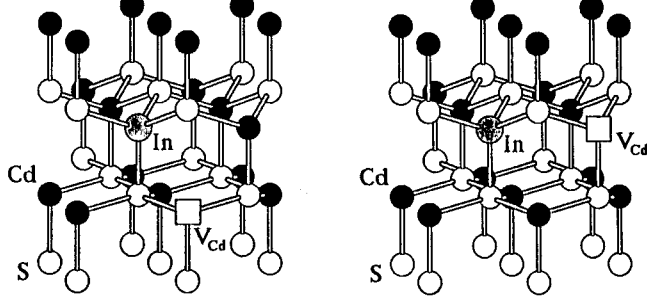
Figure 4. Atomistic model of CdS showing the two different In_{Cd}^+-V_{Cd}^{--} complexes associated with the two different EFGs (see Table I).

The fact that for CdS two different EFGs are observed (see Table I) which both belong to the In_{Cd}^+-V_{Cd}^{--} pair is easily explainable on the basis of the hexagonal lattice structure of CdS: The distances between In_{Cd} and V_{Cd} are slightly different if the trapped vacancy resides above/below or inside of the basal plane of the hexagonal lattice (see Fig. 4). This effect is strongly reduced for the ZnS lattice because its c/a ratio of 1.6368 is closer to the ideal ratio of c/a = 1.6330, at which both distances become equal, than the ratio c/a = 1.6238 of CdS; in the cubic lattice of CdTe the respective distances are obviously identical. Consequently, for ZnS and CdTe only a single EFG characterizes the In_M^+-V_M^{--} pairs.

The data in Fig. 3 clearly illustrate that a minimum temperature is required for the observation of the Li induced increase in the fraction of In_{Cd}^+-V_{Cd}^{--} pairs. This temperature is about 580 K and 720 K for ZnS and CdTe, respectively, and might be indicative for the onset of the diffusivity of Li atoms in these compounds on a μm scale. Further studies,

however, are necessary in order to understand this correlation more quantitatively, as well as the influence of the higher diffusion temperatures on the observed pair fractions.

Information on complexes formed between a group III donor and a metallic vacancy can also be obtained from electron spin resonance b(ESR) experiments. Up to now, this information is only available for ZnS where the formation of D_{Zn}-V_{Zn} pairs (D = Al, Ga, In), so-called A-centers, has been reported[14], whereas for CdS and CdTe similar information is not available. Like the EFG tensor in the PAC experiment also the corresponding g tensor, characterizing these pairs in the ESR experiment, is not axially symmetric.

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