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Acceptor states in CdTe and comparison with ZnTe. General trends

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New experimental results are reported for the acceptors Li, Na, and P in CdTe. Their excited states are obtained from photoluminescence studies performed with a tunable dye laser. "Two-hole transition" lines from these acceptors are observed for the first time. Moreover, a new unidentified phonon with an energy of 19 meV is observed in Li- and Na-doped samples. These new results complete our understanding of the acceptor states in CdTe concerning the impurities Li, Na, Cu, Ag, and Au on Cd sites and N, P, and As on Te sites. The wealth of these data, together with similar results obtained in ZnTe, allows one to make a comparison between these two materials. It is shown that, for the cation-site (i.e., Zn or Cd) substitutional acceptors in particular, the central-cell corrections are practically independent of the nature of the semiconductor. The valence-band parameters, and thus the effective-mass acceptor states in CdTe and ZnTe, are similar. The results shown here provide a good basis for some theoretical investigations on acceptor impurites in II-VI compounds.

I. INTRODUCTION

A considerable amount of experimental data now exists for acceptor centers in II-VI compounds, particularly in ZnTe (Refs. 1–5) and CdTe.[6–10] It now seems possible to characterize some general trends in these materials about the acceptor ionization energies E_A, which are in the range $56 < E_A < 273$ meV. Up to now, eight different acceptor levels have been revealed by high-resolution techniques such as low-temperature photoluminescence (PL), PL excitation spectroscopy involving tunable dye lasers, infrared absorption, and magneto-optical analysis. Doping experiments performed on high-purity materials have shown that all these acceptors are related to substitutional impurities. The acceptor impurities of interest are the alkali metals Li and Na and the monovalent metals Cu, Ag, and Au which substitute for the cation (i.e., Zn or Cd, respectively, in ZnTe and CdTe), and also the column V elements N, P, and As which substitute for the anion (i.e., Te).

The ground state and about eight excited states of each acceptor have been precisely measured with the PL technique,[11] from the "two-hole transitions" (THT), donor-acceptor pairs (DAP), and free-to-bound (i.e., free electron-neutral acceptor) transitions. Excited states with both *S*- and *P*-like symmetry have been obtained. Additional information about the *P*-like states and the confirmation of the PL identifications have been provided by infrared absorption studies.[4,7]

In the first part of our paper we will present some recent results for the shallow acceptors Li, Na, and P in CdTe. The identification of these acceptors has been reported in previous papers.[6,8] However, only the ground-state binding energies were estimated from the peak positions of the free-to-bound transitions. Our purpose here is to get more concrete information about the binding energies as well as about the excited states of these acceptors in CdTe, and to refine and correct our earlier work on this subject, particularly for the impurities Li and Na.[6] This is done by using the DAP excitation spectroscopy technique.[12–14] We also report for the first time the results of precise measurements on the THT lines of these acceptors. In Li and Na-doped samples some new phonon lines are observed in addition to the regular TO(Γ) and LO(Γ) phonon lines.

Finally, a comparison of the ground and excited states of the acceptors in ZnTe and CdTe is made using the available data. It is shown that the energy levels in both materials are practically identical. Moreover, the valence-band parameters are very similar.

II. EXPERIMENTAL

The experiments presented in this work were performed on high-purity *p*-type CdTe crystals grown by the Bridgman technique.[15] The uncompensated acceptor concentration was about 5×10^{14} cm^{-3}. Li and Na doping was done from a nitrate solution. The details of the doping process have been given in a previous paper.[6] Doping levels between 10^{15} and 10^{17} cm^{-3} can be easily obtained by controlling the diffusion parameters. The acceptor P on a Te site in CdTe has been previously identified by PL studies made on P^+ ion implanted samples.[8] The DAP excitation spectroscopy was performed in an as-grown sample unintentionally doped with the acceptor P.

For the PL experiments, samples were freely suspended in liquid He pumped below the λ-point (1.8 K). Higher temperatures could be obtained with a hot He gas flow. The PL was excited with a tunable dye laser using "Oxazine 750" dye pumped with the red lines of a Kr^+ laser. The luminescence was passed through a *f*/5 grating monochromator, and detected by a photomultiplier with a cooled GaAs cathode. The signal was analyzed by a lock-in amplifier.

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III. EXPERIMENTAL RESULTS

A. Bound-exciton lines

The principal bound-exciton (PBE) lines[11] which dominate the PL spectra of our samples are shown in Fig. 1. They result from the recombination of excitons bound on the neutral acceptors Cu, Li, Na, and Ag. In an undoped sample [Fig. 1(a)], we observe the PBE lines of the residual acceptors Cu and Ag: A_1^{Cu} at 1.589 56 eV and A_1^{Ag} at 1.588 48 eV. These lines and the acceptors Cu and Ag have been previously studied in detail.[7,16,17] Their ionization energies are 146.0 and 107.5 meV,[7] respectively, and the exciton ground state is the $J=\frac{1}{2}$ state in the j-j coupling scheme.[17] In Fig. 1(a) a weak line near 1.5892 eV, noted as $A_1^{\mathrm{Li,Na}}$ is identified as the PBE line of the residual acceptors Li and Na. Indeed, in Li and Na doped samples, the intensity of this line increases with increasing doping level. This is shown in Figs. 1(b) and 1(c), for Li and Na doping respectively. In fact, an energy difference of about 0.07 meV is systematically observed between the PBE lines of Li and Na: A_1^{Li} at 1.589 23 eV and A_1^{Na} at 1.589 16 eV. These lines have recently been investigated by Zeeman spectroscopy and in absorption experiments.[18] It has been shown that the level ordering of the bound-exciton states for Li and Na is completely different than the level ordering of the bound excitons on the deeper acceptors Cu and Ag,[17] as well as on Au.[9] The $J=2$ level resulting from the j-j coupling of the two holes (in the neutral acceptor bound exciton) appears to be lowest in energy for the acceptors Li and Na. Moreover, this state is split by a strong cubic crystal field. Finally, the ground state of the bound exciton (i.e., the PBE lines A_1^{Li} and A_1^{Na}) has a Γ_8 symmetry resulting from further coupling of the two holes to the electron. The electron-hole exchange interaction is found to be much weaker than the cubic crystal field. A complete experimental and theoretical analysis of this effect has been made recently.[18]

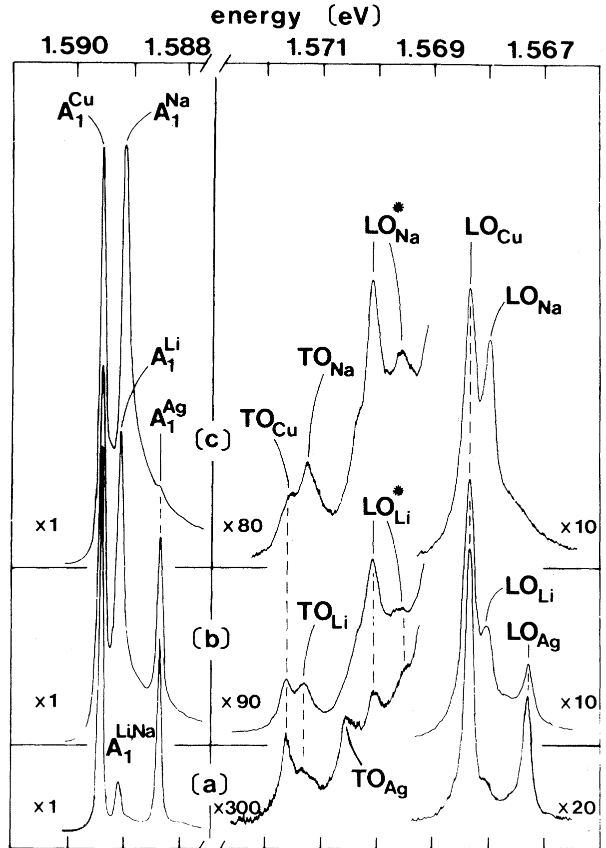

FIG. 1. PBE lines (left side) and their one-phonon replicas (right side) in CdTe. (a) As-grown $N_A-N_D=5\times10^{14}$ cm^{-3}; (b) Li-doped $N_A-N_D=7\times10^{15}$ cm^{-3}; (c) Na-doped $N_A-N_D=8\times10^{15}$ cm^{-3}. The spectra are recorded at 1.8 K with above-band-gap excitations. TO and LO are the TO(Γ) and LO(Γ) phonon replicas with the energies 17.9 and 21.2 meV. LO* is related to a new unidentified phonon of 19.0 meV related to Li or Na doping. It is probably a bound phonon.

The small difference between the two shallow acceptors Li and Na observed in the PBE lines [Figs. 1(b) and 1(c)], is shown clearly in their two-hole transition (THT) lines (Fig. 2). Indeed, the energy difference between the PBE lines is not very sensitive to the difference between the hole binding energies, while the energy difference between the THT lines of different acceptors reflects the binding energies difference. So each THT line A_n ($n=2,3,\ldots$) is shifted from the PBE line A_1 by the energy difference between the ground state $1S_{3/2}$ and the excited state $nS_{3/2}$ of the neutral acceptor.[11] The central cell corrections are much larger for the ground state than for the excited states. Therefore, the differences $1S_{3/2}$—$nS_{3/2}$ and the energies of the THT lines A_n for different acceptors vary strongly with their binding energies. This feature is commonly used in PL in order to identify precisely the acceptors.[11]

Figure 2 shows the THT lines of the acceptors Li and Na, labeled A_n^{Li} and A_n^{Na} ($n=2,3,\ldots$). A systematic shift of about 0.7 meV is observed between the Li and Na lines. This can be seen from a comparison of Fig. 2(b) (i.e., Li-doped sample) with Fig. 2(c) (i.e., Na-doped sample). The observed energy shift is not an experimental artifact since, in the as-grown sample [Fig. 2(a)], unintentionally doped with Li and Na, both Li and Na lines are observed. Moreover, the intensities of each THT series, and of the PBE lines (Fig. 1) are strongly correlated with the doping level of the diffusing species (i.e., diffusion of Li or Na). This correlation has been confirmed by the PL studies and electrical measurements performed on several Li and Na diffused samples with doping levels in the range 10^{15} cm^{-3} to a few 10^{16} cm^{-3}. A further confirmation of this difference between Li and Na will be given by the DAP excitation spectroscopy data, presented in Sec. III B.

Some interesting effects can be pointed out about the THT lines:

(i) We observe a well resolved structure in the THT lines for $n=3,4$, and 5. At least two components can be distinguished, with an energy splitting of about 0.3 meV (Fig. 2). We believe that this structure is related to the subcomponents of the neutral acceptor bound exciton in

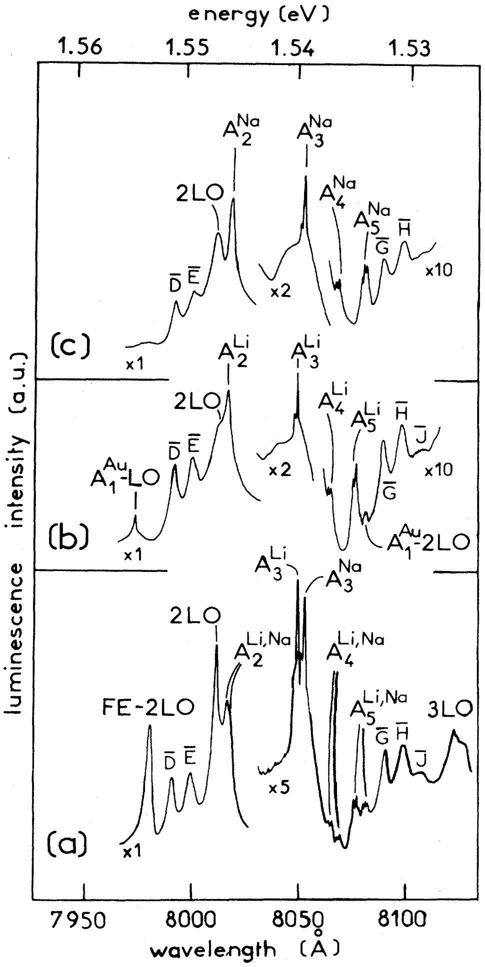

FIG. 2. THT lines of the acceptors Li and Na in CdTe, recorded at 1.8 K. (a) As-grown $N_A-N_D=5\times10^{14}$ cm^{-3}; (b) Li-doped $N_A-N_D=7\times10^{15}$ cm^{-3}; (c) Na-doped $N_A-N_D=8\times10^{15}$ cm^{-3}. In the as-grown sample both Li- and Na-THT lines are observed. The lines $\bar{D}$ to $\bar{J}$ are phonon replicas of the PBE lines (see Table I). In the Li-doped sample the PBE line of the residual acceptor Au is also observed.

the initial state (i.e., the PBE line $A_1^{\text{Li,Na}}$ and its excited states). The excited states of the PBE line A_1 cannot be seen in PL (Fig. 1), since the thermalization effects are strong at 1.8 K while they are clearly observed in absorption spectra.[18] Such a multiplet structure of the THT lines has already been observed in ZnTe doped with Li by Venghaus and Dean.[2] They have shown that this structure indeed reveals the sublevels of the bound exciton.

(ii) The intensity of the THT line $A_4^{\text{Li,Na}}$ is weaker than expected in comparison with the line $A_5^{\text{Li,Na}}$, since generally a decrease of the THT line intensity with increasing n is expected. We believe that the nth THT line is due to the $1S_{3/2}-nS_{3/2}$ transition of the neutral acceptor.[11] However, the actual $S_{3/2}$ states of the acceptor are made up of hydrogenic states of orbital momentum $l=0$ (s-like) and $l=2$ (d-like).[19] Therefore, if the d-like character of the $nS_{3/2}$ state is more important than the s-like, the related nth THT line will be very weak, since the transitions $\Delta l=2$ are forbidden for the THT[11] (in the initial state the holes of the bound exciton have s-like wave functions).

The weakness of the fourth THT line $A_4^{\text{Li,Na}}$ could be due to a strong d-like character of the $4S_{3/2}$ state of the neutral acceptor. Such effects are not surprising and have already been studied in ZnTe by Herbert *et al.*[20] They have shown that the importance of the d-like character of the excited states, and thus the relative intensities of the corresponding THT lines, vary strongly with the values of the valence-band parameters R_0, μ, and δ used in the framework of the effective mass theory of Baldereschi and Lipari.[19]

(iii) The first THT line $A_2^{\text{Li,Na}}$ is unusually broadened compared to other lines of the THT series, as well as compared to those of the acceptors Cu and Ag.[7] The excitation energies, i.e., the energy differences between A_1 and A_2, are 42.9 and 43.3 meV, respectively, for Li and Na. These values are very close to the 2LO(Γ) phonon energy in CdTe (42.4 meV). In Figs. 2(b) and 2(c), the 2LO phonon replicum of the PBE line is just above the THT lines A_2. Such a broadening effect, as well as splittings of the bound hole excitation lines in Si, have been reported by Chandrasekhar *et al.*[21] They have shown that this is due to a resonant interaction of acceptor states with optical phonons, which occurs when the excitation energy of the hole between its ground and excited states is comparable to a phonon energy of the crystal. In our case, we believe that a similar resonance effect involving 2LO(Γ) phonons and the hole transition $1S$-$2S$ can explain the unusual broadening of the A_2^{Li} and A_2^{Na} lines.

In Fig. 2, besides the THT lines and the regular 2LO and 3LO phonon replicas of the PBE lines, some extra lines denoted as $\bar{D}$, $\bar{E}$, $\bar{G}$, $\bar{H}$, and $\bar{J}$ are observed. We suppose that all these lines are in fact phonon replicas of the PBE lines. Let us first examine in detail the 1-phonon sidebands of the PBE lines. In Fig. 1, high-resolution spectra show the LO(Γ) and TO(Γ) phonon replicas of the Cu, Li, Na, and Ag acceptor PBE lines. The LO and TO phonon energies are, respectively, 21.2 and 17.9 meV, in agreement with published values.[22] However, a new line between the TO(Γ) and LO(Γ) replicas increases in intensity with increasing doping level of Li and Na. It is denoted as LO* (this notation is arbitrary, since we have no evidence that this can be related to a longitudinal optical phonon), and is identified as a phonon replicum of A_1^{Li} or A_1^{Na}, involving a phonon energy of 19 meV. Actually a doublet structure is observed, with a weak component at about 0.5 meV below the LO* line.

The LO* replicum appears simultaneously with the phonon lines $\bar{D}$ to $\bar{J}$ observed in Fig. 2. They are strongly correlated with the Li or Na doping. Therefore, it is possible to identify the $\bar{D}$ to $\bar{J}$ lines as phonon replicas involving various combinations of LO(Γ) and LO* phonons, as shown in Table I. All these phonons are also observed in DAP excitation spectra, described in Sec. III B.

It can be noted that the lines $\bar{D}$ and $\bar{E}$, presently identified, respectively, as the 2LO* and LO* + LO(Γ) phonon replicas of the PBE line (see Table I), were previously attributed[6] to the THT line A_2^{Li} perturbed by a resonant interaction with optical phonons, as described in paragraph (iii). This interpretation seems to be wrong since the

TABLE I. Identification of the lines observed in DAP excitation spectra, shown in Figs. 5 and 6, for the acceptors Li, Na, and P in CdTe. The capital letters are phonon-assisted transitions, while the lower case letters are related to the excitation of the hole from its ground state $1S_{3/2}$ to an excited state which is indicated in the table. Transition energies in Li, Na, and P doped CdTe are given in the last columns. The barred letters are related to the THT or phonon replicas of the PBE lines. f and g involve the excitation of shallow donors.

Line	Identification	Li	Na	P (meV)
a	$3S_{3/2}$	49.1	49.8	58.8
$\bar{a}$	THT line-$3S_{3/2}$	49.3	49.9	58.8
b	$2P_{5/2}(\Gamma_7)$	46.8	47.5	56.6
c	$2P_{5/2}(\Gamma_8)$	44.4	45.0	53.1
d	$2S_{3/2}$	42.8	43.2	51.0
$\bar{d}$	THT line-$2S_{3/2}$	42.9	43.3	50.8
e	$2P_{3/2}$	34.1	34.9	44.9
f	donor $2S+\mathrm{LO}(\Gamma)$	31.5	31.9	
g	donor $2S+\mathrm{TO}(\Gamma)$ or LO*	29.5	29.5	
h	free electron-neutral acceptor transition			
A	TO(Γ)	17.9	17.9	
B	LO*	19.0	19.0	
C	LO(Γ)	21.2	21.2	
D	2LO*	38.0	38.1	
$\bar{D}$	2LO* replicum	38.0	38.2	
E	LO(Γ) + LO*	40.0	40.0	
$\bar{E}$	LO(Γ) + LO* replicum	40.0	40.0	
F	2LO(Γ)	42.4	42.4	42.4
$\bar{F}$	2LO(Γ) replicum	42.4	42.4	42.4
$\bar{G}$	3LO* replicum	57.1	57.1	
$\bar{H}$	LO(Γ) + 2LO* replicum	58.8	58.8	
$\bar{J}$	2LO(Γ) + LO* replicum	60.7	60.7	

present work shows that the lines A_2^{Li} and A_2^{Na} are just below the 2LO(Γ) phonon replicas of the PBE lines. Moreover, the excitation energy $1S$-$2S$ is measured unambiguously with DAP excitation spectroscopy (Sec. III B), confirming the identification of the lines A_2^{Li} and A_2^{Na}. In any case, as pointed out in paragraph (iii), the hypothesis of a resonant interaction with phonons is reasonable, but the phonon energy involved in this process

TABLE II. Acceptor states in CdTe above the valence band. Notations are from Ref. 19. Excited state energies are obtained from THT lines, DAP excitation spectroscopy, free-to-bound transitions, and infrared absorption measurements. The overall precision is about ±0.5 meV. The values in parentheses are tentative attributions. EM is the effective-mass acceptor, whose energies are calculated within the theory of Baldereschi and Lipari[19] with the following set of parameters values: $R_0=30$ meV; $\mu=0.69$, and $\delta=0.12$. The last column gives the positions of the PBE lines A_1. The acceptor impurities are on substitutional Cd sites (Li, Na, Cu, Ag, Au) or Te sites (N, P, As).

	Binding energies (meV)								
Acceptor	$1S_{3/2}$	$2P_{3/2}$	$2S_{3/2}$	$2P_{5/2}(\Gamma_8)$	$2P_{5/2}(\Gamma_7)$	$3S_{3/2}$	$4S_{3/2}$	$5S_{3/2}$	$6S_{3/2}$	A_1 (eV)
EM[a]	56.8	23.8	15.8	15.3	11.7	8.6				
Li[b,c]	58.0	23.9	15.1	13.6	11.2	8.7	5.7	3.4		1.589 23
Na[b,c]	58.7	23.8	15.4	13.7	11.2	8.8	5.8	3.4		1.589 16
Cu[d]	146.0		21.6	15.1	11.4	10.0	6.1	4.3	3.1	1.589 56
Ag[d]	107.5		19.6	15.0	11.3	9.6	5.9	4.0	3.0	1.588 48
Au[e]	263		28	(16)		(12)	(9)			1.576 06
N[f]	56.0									(1.589 2)
P[c,f]	68.2	23.3	17.4	15.1	11.6	9.4	5.7	3.7	3.1	1.588 97
As[f]	92.0		18.8			9.7	5.9	3.8		1.589 70

[a] Reference 32.

[b] Reference 6.

[c] This work.

[d] Reference 7.

[e] Reference 9.

[f] Reference 8.

would be that of 2LO rather than 2TO as suggested previously.[6]

In spite of the fact that the LO* phonon is definitely identified experimentally, its origin is not well understood. Such a phonon has already been observed in II-VI alloys.[2,10,23–25] In As-doped ZnTe, Nakashima *et al.*[23] interpreted it as a gap local mode. In P-doped ZnTe, Venghaus *et al.*[24] identified it with an X-optical phonon of the ZnTe lattice. However, optical studies performed by Venghaus and Dean[2] in As- and P-doped ZnTe have shown that the phonon energy is, in fact, impurity dependent. After a detailed discussion, Venghaus and Dean[2] suggested that it was a type of bound phonon. In Li-doped CdTe, Neu *et al.*[10] also observed the LO* phonon, and identified it with a TO(X) phonon. In a further study performed in Li- and Na-doped CdTe, Neu[25] suggested that this could be an impurity-dependent bound phonon rather than TO(X), since he observed a difference of 0.4 meV between the LO*-phonon energies observed in Li- and Na-doped CdTe.

We have studied several acceptor impurities in CdTe, but the LO* phonon, particularly the lines $\bar{D}$ to $\bar{J}$ (see Fig. 2) resulting from its combinations with LO(Γ) phonons, have only been observed in samples containing Li or Na. Even for the shallow P acceptor (see below), only TO(Γ) and LO(Γ) phonons are observed. Indeed, according to the bound phonon theory of Dean, Manchon, and Hopfield[26] the energy difference of 10 meV between P, Li and Na acceptors can make a great difference in the strength of the interaction which gives rise to the bound phonon effects possibly responsible for the replicum LO*. It can also be noted that the intensities of the two phonon [2LO* and LO*+LO(Γ)] replicas $\bar{D}$ and $\bar{E}$ (see Fig. 2) are stronger than the intensity of the LO* replicum (see Fig. 1). The unusual strength of the multiphonon replicas of Li and Na is probably due to the close energy match with the $1S_{3/2}$—$2S_{3/2}$ transition for these two acceptors, which does not exist for P or any of the other acceptors (see below and Table II in Sec. IV). The phonon lines D and E are also observed in selectively excited DAP spectra (see Sec. III B), and they disappear when their positions are at lower energies than the DAP band maximum energy, while the 2LO(Γ) Raman line F is always observed (see Fig. 5 in Sec. III B). This confirms that some resonance effects exist for the lines D and E. It is difficult to give a definite interpretation for the origin of the LO* phonon. However, it can be seen that the LO* phonon and related lines appear only with Li and Na acceptors. Therefore, it might be possible that the LO*-phonon replicas involve bound phonons rather than lattice phonons. A further attempt to identify it with a local impurity mode can be quickly excluded, since the local mode energies of Li and Na in CdTe are much greater than 19 meV, and a significant difference must be found between the Li and Na.[27]

In an unintentionally doped sample, a new acceptor has been observed. It has been identified as P on a Te site. Indeed, the new PL lines (i.e., the PBE and THT lines, DAP and free-to-bound transitions) are those of the acceptor P on a Te site, recently investigated in P$^+$ ion-implanted samples.[8]

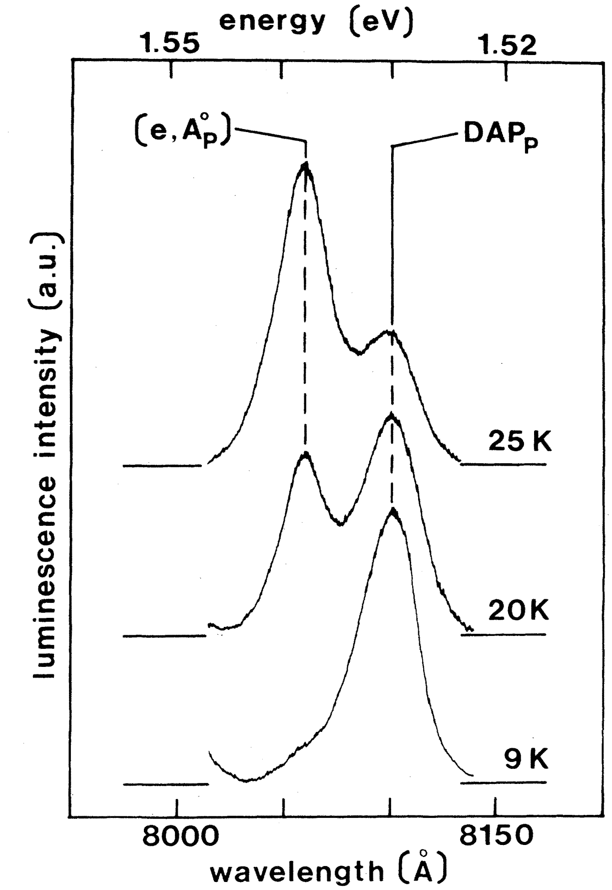

FIG. 3. DAP band and the free-electron neutral acceptor transition (e,A_P^0) related to the acceptor P in CdTe. The PL spectra are recorded with a low excitation power, i.e., 0.1 mW unfocused, so that the DAP band maximum is shifted to low energies. On heating the sample, the free-to-bound transition increases, and its peak energy gives the ionization energy of the acceptor P, 68.2 meV. The indicated temperature is the free electron equilibrium temperature deduced from the shape of (e,A_P^0). It is close to the lattice temperature since the PL is excited with photons having an energy of 1.61 eV, which is close to the band gap (1.606 eV).

Figure 3 shows the DAP band of this acceptor. On heating the sample, we can observe the emergence of the free electron-neutral acceptor transition band, labeled (e,A_P^0). The ionization energy of the acceptor is obtained from the peak position of this band:[28]

$$E_A=(68.2\pm0.5)\ \text{meV}\ . \tag{1}$$

This is exactly the ionization energy of the acceptor P in CdTe, which was reported previously.[8]

Figure 4 shows the PBE line A_1^{P} at 1.588 97 eV and the THT lines A_n^{P} with $n=2$–6, which are recorded with a resonant excitation on the PBE line A_1^{P}, so that their intensities are strongly enhanced. However, the DAP transitions partially mask the excited states with $n\geq3$. Furthermore, two extra lines labeled b and c are probably due to selectively excited DAP via the acceptor excited states $2P_{5/2}(\Gamma_7)$ and $2P_{5/2}(\Gamma_8)$, respectively.[19] Since the incident laser light is not totally absorbed by the bound

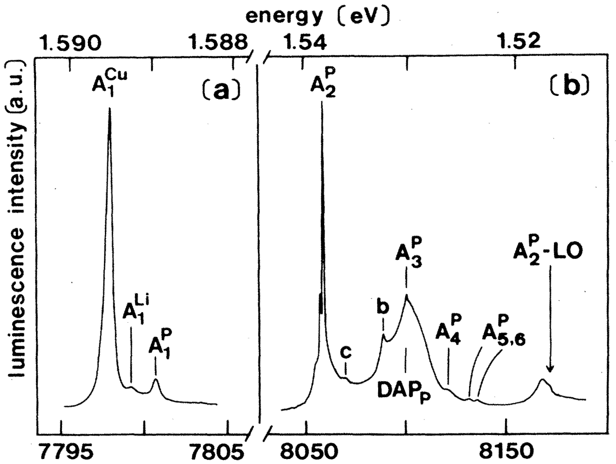

FIG. 4. Pl spectra recorded at 1.8 K in an unintentionally P-doped CdTe sample. (a) The PBE lines of Cu, Li, and P; (b) THT lines series of the acceptor P, recorded with a resonant excitation on the PBE line A_1^P at 1.588 97 eV. The excited states for $n \geq 3$ are masked by the residual DAP band. *b* and *c* probably involve selectively excited donor-acceptor pairs (see Table I).

excitons, a fraction of the light is able to excite selectively donor-acceptor pairs via their excited states. The lines *b* and *c* will be analyzed in detail in Sec. III B.

The strongest THT line A_2^P is at 1.5381 eV, and the measured energy difference $1S$—$2S$ of the acceptor P is 50.8 meV. Excitation spectra of A_2^P (i.e., recording the intensity of A_2^P when scanning the dye laser energy) allowed us to establish the relationship between A_1^P and A_2^P since the intensity of the latter was strongly enhanced when the dye laser energy was on A_1^P. Similar experiments have been reported previously for other acceptors THT and PBE lines in CdTe[7] and in ZnTe.[2] Finally, all these characteristic luminescence lines are identical to those of the acceptor P in CdTe,[8] suggesting its identification with this impurity.

Using the THT series of the acceptors Li, Na, and P, it is straightforward to calculate their binding energies with the well-known empirical formula[1,5,7]

$$E_n = E_1 - E_A + E_0 n^{-x}, \quad n \geq 2 \tag{2}$$

with E_1 and E_n the luminescence energies of the lines A_1, and A_n,E_A the acceptor binding energy (i.e., the ground state $1S_{3/2}$ energy) above the valence band. E_0 and x are fitting parameters. An x-value in the range 1.7—1.8 has given good results for several acceptors in CdTe,[7,8] ZnTe,[1,5] as well as in other materials.[29,30] The binding energies are (in meV)

$$E_A(\text{Li}) = 58.0, \quad E_A(\text{Na}) = 58.7, \quad E_A(\text{P}) = 68.2 \; . \tag{3}$$

The precision of this estimate is about ±0.3 meV. However, it is interesting to compare these values with those obtained directly from the free-to-bound transitions. Fortunately, the same values within the experimental error have been found: 68.2 meV for P from Eq. (1) and Ref. 8; 57.8 meV for Li and 58.8 meV for Na from Ref. 6.

Using E_A and the THT energies we can estimate the energies of S-like excited states of the acceptors. The results will be presented in Sec. IV.

B. Selective excitation of DAP

Selective excitation of donor-acceptor pairs is a powerful technique which allows one to obtain both the S- and P-like symmetric states of acceptors and donors. It has been extensively studied in several materials.[12-14] The principle of this experiment is very simple and has been presented in detail in previous works.[12-14] Experimentally, when the PL is excited with below-the-band-gap photons (energy E_1), sharp peaks appear (energy E_2) superimposed on the broad DAP band. The difference, $E_1 - E_2$, is that between the ground state $1S$ and an excited state of S- or P-like symmetry of the acceptor or the donor. Donor or acceptor related lines can be easily distinguished since their energies are very different [e.g., in CdTe $E_D = 14$ meV and $E_A(\text{Li}) = 58$ meV]. The characteristic feature of these lines is that they follow the dye laser energy, i.e., $E_1 - E_2$ remains nearly constant, and they disappear for selectively excited pair distances $R > 300$ Å. The process is efficient for R in the range 100—300 Å.

Figure 5 shows the results obtained from Li-, Na-, and P-doped CdTe samples. As explained above, several lines appear at the high-energy side of the DAP bands, and disappear progressively when they reach the DAP band maximum. The lines related to the internal excitations of the acceptors are labeled by small letters, while capital letters are related to phonon lines. The barred letters are used in order to distinguish the THT lines and the phonon replicas of the PBE lines A_1^{Li}, A_1^{Na}, or A_1^P (see Sec. III A) from the lines related to the selectively excited DAP. The measured energy differences are strictly identical, but the recombination process involved in both cases are rather different. The replicas of the PBE lines (i.e., THT or phonon lines) are observed when the dye laser energy is above the PBE line energy or close to it. Even if the dye laser energy is asymptotically equal to 1 meV below the PBE line, these replicas are observed. This suggests an anti-Stokes excitation process of the bound exciton. Such effects have been clearly observed in the spectra recorded in the zero-phonon and one-phonon regions of the PBE lines.

The strongest line, labeled *d*, results from the $1S_{3/2}$—$2S_{3/2}$ transition of the acceptor hole. This process has the greatest probability. In P-doped samples [Fig. 5(c)], this line is unambiguously identified. The internal excitation energy $1S_{3/2}$—$2S_{3/2}$ deduced from this figure is the same as that obtained from the THT lines in Fig. 4, 51 meV (see Table I). The same observation can also be made for Li- and Na-doped samples [Figs. 5(a) and 5(b)]. Furthermore, in these samples, we can distinguish easily the 2LO-phonon line (line F) from the $1S_{3/2}$—$2S_{3/2}$ transition (line d), whose energies are comparable (see Table I). The phonon line F is about one order-of-magnitude weaker than the line d, as shown in Fig. 5(b) (Na-doped sample). In Li-doped samples the F and d lines overlap. However, in both Li- and Na-doped samples, for excitation energies lower than 1.581 eV, the d line disappears,

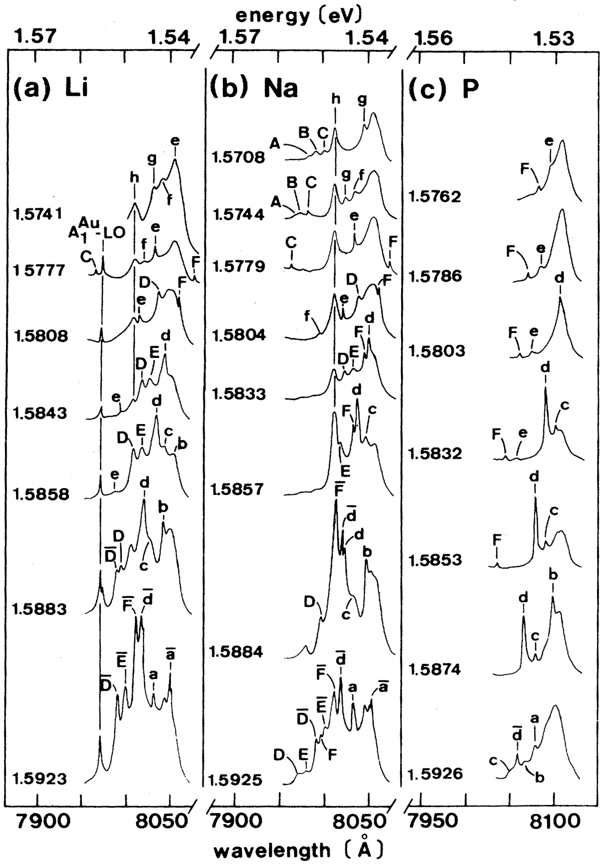

FIG. 5. Selective excitation of DAP in CdTe, recorded at 1.8 K, for the acceptors Li (a), Na (b), P (c). The excitation energy (in eV) is indicated at the left side of each spectrum. The identification of the observed peaks is shown in Table I. The capital letters are phonon related, while the lower case letters indicate peaks involving internal excitations of the acceptors. The barred letters are the THT or phonon replicas of the PBE lines.

because the selectively excited pair distance R exceeds 300 Å. The two-phonon line F can still be observed, since it probably involves a Raman process with 2LO(Γ) phonon energy. Its intensity is very weak. Therefore, the d line observed in Li-doped samples is also due to a $1S_{3/2}$—$2S_{3/2}$ transition. This result confirms the identification of the THT lines A_2^{Li} and A_2^{Na} in Fig. 2 (see Sec. III A).

Transitions to other excited states, such as $3S_{3/2}$, $2P_{5/2}(\Gamma_8)$, $2P_{5/2}(\Gamma_7)$, and $2P_{3/2}$, are also observed in Li-, Na-, and P-doped samples. The transition energy $1S_{3/2}$—$3S_{3/2}$ (line a) is identical to its value determined from THT lines (see Table I). $2P_{5/2}$ states have been observed in infrared absorption spectra of Li-doped CdTe crystals, reported by Svob *et al.*[31] Recently, these transitions have also been observed by Milchberg *et al.*[32] in both Li- and Na-doped samples. The results of the infrared absorption measurements are in perfect agreement with our experimental values for the $2P_{5/2}$ states. The identification of the line e as the $1S_{3/2}$—$2P_{3/2}$ transition, as well as the identification of the $2P_{5/2}$ states of the acceptor P, are made on the basis of theoretical estimates of the acceptor states with the effective-mass theory of Baldereschi and Lipari.[19] The P-like excited states of the acceptors are not disturbed by central cell corrections. This will be discussed in detail in Sec. IV, taking into account all the acceptor impurities in CdTe.

As explained above besides the F line related to 2LO(Γ) phonons, other phonon lines labeled A, B, C, D, and E are also observed. The lines A and C are due respectively to the emission of TO(Γ) and LO(Γ) phonons, while B, D, and E involve a phonon of 19 meV, denoted as LO* (see Table I). They were already observed as the phonon replicas of the PBE lines (see Figs. 1 and 2). Discussion about the possible origin of the LO* phonon was made in Sec. III A.

Figures 5(a) and 5(b) also show phonon-assisted $1S$-$2S$ transitions of shallow donors (lines f and g). In p-type

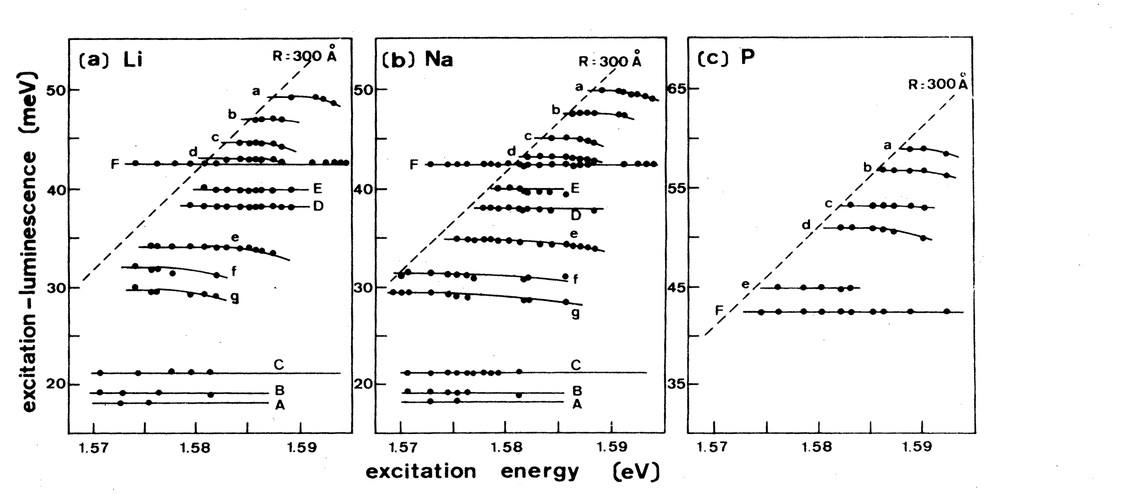

FIG. 6. The plot of the energy differences between the excitation energy and the energies of the peaks observed in Fig. 5 vs the excitation energy. The limit $R = 300$ Å is indicated with dashed lines. The labels are defined in Table I.

samples two shallow donors are systematically observed. The $1S$-$2S$ energies, measured from the "two-electron transitions"[11] with resonant excitations on the PBE lines, are 10.3 and 10.7 meV, respectively. In CdTe, at least five PBE lines are observed, each of them corresponding to an excited state of the neutral donor-bound exciton,[33] as in ZnTe.[34] With resonant excitations on these lines, two distinct series of two-electron transitions are observed, suggesting the presence of two different donors, with the binding energies 13.7 and 14.3 meV, respectively. Moreover, the relative intensities of the two series vary from sample to sample, while within a given series the intensity ratios are rather constant. The resolution of Fig. 5 is not enough to distinguish the two donors within the lines f and g. The line h is due to the recombination of a conduction band electron with an acceptor hole.

Figure 6 shows the plot of the transition energies, deduced from Fig. 5, versus the dye laser energy. The dashed lines indicate the limit $R = 300$ Å, where the lines related to the DAP recombination process disappear. At high excitation energies, when the selective excitation is made on close pairs with $R \leq 100$ Å, the measured transition energy is smaller than its actual value. This effect is due to polarization interactions which occur in the initial state of the neutral donor-acceptor pair, before the recombination, between the bound hole and the bound electron.[35] Such effects can lower the transition energy by about 1 meV. For moderate pair distances (i.e., R greater than the Bohr radius), this interaction can be approximated with a Van der Waals type of interaction, varying as R^{-6}.

Therefore, the actual transition energies are measured at the limit $R \rightarrow \infty$ (i.e., at low excitation energy). All the values obtained from Fig. 6 near the dashed lines (the limit $R = 300$ Å) are shown in Table I.

Similar experiments in Li-doped CdTe have been reported by Neu *et al.*[10] They have measured the DAP excitation spectra, that is, they have recorded the PL intensity of a selected donor-acceptor pair in the DAP band, while scanning the dye laser energy. Our values of the Li-acceptor transitions are in very good agreement with their results.

IV. DISCUSSION

The experimental results presented above can be used to obtain the ordering of the energy levels of the shallow acceptors Li, Na, and P in CdTe. These data complete our knowledge of the acceptor impurities in this material, since investigations about some other acceptors such as Cu, Ag, Au, N, and As were previously reported.[6–9,16] All these results, together with the published values, are summarized in Table II. Some remarks can be made about the energies reported in this table. It can be noted that the identification of the acceptors and their electronic structure has been performed with the correlation of doping experiments with electrical measurements and the analysis of the samples by high-resolution techniques such as PL, infrared absorption, and magneto-optical studies.

From the PL we obtain the following information:

(i) The bound exciton lines A_n lead to a precise identification of each acceptor; also, the energy levels corresponding to $nS_{3/2}$ states up to $n=6$ can be obtained from the THT series.

(ii) Both S- and P-like symmetric states of the acceptors are observed with the selective excitation of DAP transitions, or with the excitation spectra of DAP, which are similar experiments.

(iii) The ground state (i.e., $1S_{3/2}$ level) energy of the acceptor is measured directly with the free electron-neutral acceptor transition.

In addition to the PL results, P-like symmetric states are obtained from infrared absorption measurements. Therefore, the energy values shown in Table II are measured at least two times by two different techniques for most of the acceptors in CdTe.

Generally, such experiments involve the internal excitations of the bound hole, i.e., the measured energies are that of the $1S$-nS,nP transitions. The binding energies can only be obtained from the free-to-bound transition (for the ground state) or from the THT series, since the empirical formula (2) fits this series very well in several materials.

The transition energies, obtained from the DAP excitation spectroscopy or from infrared absorption measurement, are usually fitted to the effective-mass theory of Baldereschi and Lipari,[19] in order to get the binding energies. However, this fitting process requires knowledge of the modified valence-band parameters R_0, μ, and δ used in the framework of the effective-mass theory. In most cases these parameters are not well known so that they are simply considered as fitting parameters. Unfortunately, such a fitting process can give erroneous binding energies. Indeed it can be easily shown[32] that two completely different sets of valence-band parameter values can lead to identical transition energies within the experimental error, while, obviously, the binding energies are drastically different.

In Li-doped CdTe, the excitation energies of the hole have already been reported by Neu *et al.*,[10] who used DAP excitation spectroscopy, and by Svob *et al.*,[31] who have reported infrared absorption measurements. Our values of the $1S$-nS,nP transition energies shown in Table I, are in very good agreement with their results for the acceptor Li in CdTe. However, the binding energies reported in Refs. 10 and 31 are systematically (about) 3 meV greater than the actual values shown in Table II. We believe that this systematic shift, which does not disturb the transition energies, is inherent in the fitting process used in Refs. 10 and 31, as explained above. This last comparison demonstrates the necessity of the direct measurement of the ground-state binding energy (i.e., $1S_{3/2}$ level), with the THT series and/or with the free-to-bound transition.

With the actual values of the binding energies shown in Table II, it is possible to obtain a more accurate fit with the effective mass theory[19] and for the valence-band parameters R_0, μ, and δ. The fit is performed only for the excited states, which are not disturbed by the central cell corrections, as can be seen in Table II. This is particularly true for the P-like symmetric states, except for the $2P_{5/2}(\Gamma_8)$ level of the acceptors Li and Na (see Table II). This disagreement is not well understood; however, the transition energy $1S$-$2P$ is close to the $2LO(\Gamma)$ phonon energy, suggesting some resonant interaction. Detailed discussion about that problem and about the infrared absorption spectra of Li-, Na-doped, and undoped CdTe, as well as the details of fitting the valence-band parameters, are presented in Ref. 32 and will be reported in a later paper. The results are

$$R_0=30\pm3\ (\text{meV})\ ,$$
$$\mu=0.69\pm0.03\ , \tag{4}$$
$$\delta=0.12\pm0.1\ .$$

These values are in satisfactory agreement with that deduced from the actual valence-band parameters γ_1, γ_2, and γ_3 as measured with cyclotron resonance experiments.[36] However, such a comparison is difficult, since in both experiments polaron effects cannot be taken into account in a simple way due to the complexity of the valence-band structure. Therefore, it is more reasonable to assume that the parameters R_0, μ, and δ [Eq. (4)] are only useful fitting parameters, rather than the actual valence-band parameters.

The theoretical energies are reported in Table II. The good agreement obtained with the effective mass theory[19] confirms the identification of the experimental lines. Naturally this agreement is obtained for the excited states which are not disturbed by chemical shift effects.

Similar investigations on acceptors in ZnTe have been performed for the acceptor impurities Li, Na, Cu, Ag, Au, P, and As.[1–5,37] Figure 7 shows a comparison of the ground state and some excited state energies in ZnTe and CdTe for several acceptors and also for the effective-mass acceptor. For simplicity all the excited states are not shown in this figure. Striking similarities between the energy levels in both materials are observed over a wide range of binding energies ($E_A=56$ to 270 meV). Moreover, the valence-band parameters are nearly similar leading to comparable effective-mass acceptor states energies,[20,37] as shown in Fig. 7. The central cell corrections are practically independent of the nature of the semiconductor.

Intuitively, our feeling is that, for the cation site (i.e., Zn or Cd sites) substitutional impurities, the observation of rather identical central-cell corrections in CdTe and ZnTe can be associated with the fact that the elementary cluster is the same (i.e., the four nearest-neighbor Te atoms), which leads to comparable local electronic densities around the impurity core. This is a consequence of the strong ionic part of the bond. The Phillips ionicities of ZnTe and CdTe are 0.609 and 0.717, respectively.[38] The electronic densities around the Te atoms are more significant than those around the Cd or Zn atoms. Furthermore, the valence bands of ZnTe and CdTe are constructed with p-like orbitals of Te atoms. Therefore, it is not surprising to find nearly the same valence-band parameters and thus the same effective-mass acceptor energies. So, on the basis of the results shown in Fig. 7, it seems that the divergences from the effective-mass acceptor states are mostly due to the impurity core.

Let us examine the trends in the Te-site acceptor states. Within the simple hypothesis presented above for cation site acceptors, some differences may exist for the Te-site acceptors since the elementary cluster is not the same in ZnTe and in CdTe. Indeed, the binding energies of cation-site acceptors are slightly greater in ZnTe than in CdTe, while just the opposite situation is observed for Te-site acceptors (see Fig. 7). These small differences between ZnTe and CdTe may be attributed to the fact that CdTe is more ionic than ZnTe, i.e., the electronic densities around the Te atoms are more important in CdTe than in ZnTe, leading to stronger perturbations on Te-site acceptor states but smaller perturbations on cation-site acceptor states in CdTe compared with ZnTe. However, there is little data on Te-site acceptors, therefore we cannot assert whether the observed differences are significant or not.

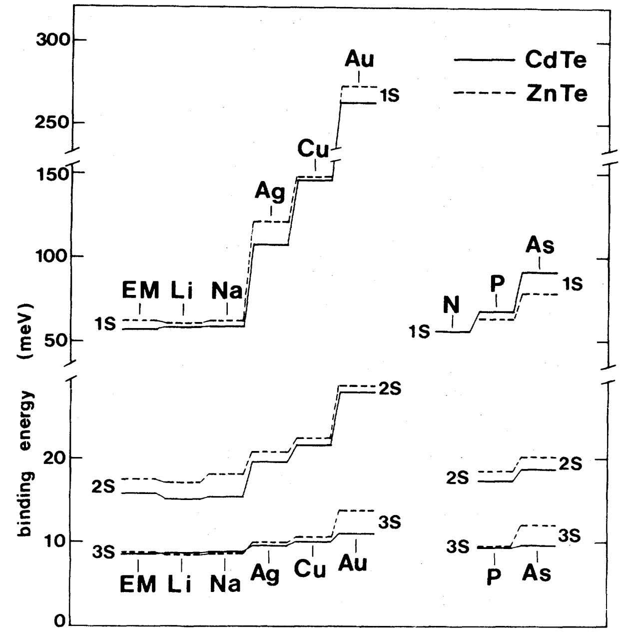

FIG. 7. Comparison of the binding energies of the states $1S_{3/2}$, $2S_{3/2}$, and $3S_{3/2}$ in CdTe and ZnTe for several acceptor impurities and for the theoretical effective-mass acceptor states (labeled EM). For CdTe the values are taken from the Table II. For ZnTe the values are from Refs. 1–5, 20, and 37.

More detailed discussions on the general trends of the acceptor states in II-VI compounds can be found in the literature.[29,39] As can be seen in Table I of the paper of Dean *et al.*,[29] the general trends for the cation-site acceptors in other II-VI materials support our observations. However data for other II-VI materials are not as extensive as for ZnTe and CdTe. In particular, there is a lack of data for the anion site acceptors such as N, P, and As making any comparison impossible. It seems that P is a deep acceptor in the sulfides and selenides,[39] while As is observed only in ZnSe, ZnTe (see Table I of Ref. 29), and CdTe. The acceptor N has been identified in ZnSe (Ref. 40) and CdTe.[8]

We believe that the wealth of the data accumulated on acceptor impurities in Te compounds now provides a good basis for theoretical investigations on acceptor impurities in II-VI compounds.

V. SUMMARY

We have presented new experimental data for the acceptors Li, Na, and P in CdTe. The excited states of these acceptors, which were previously identified,[6,8] have been obtained from PL measurements performed with a tunable dye laser. Two-hole transitions of these acceptors are reported for the first time. Both *S*- and *P*-like symmetric states of the acceptors are obtained with THT series, DAP transitions and free-to-bound transitions, illustrating the usefulness of the PL technique for studying the electronic structure of the acceptors. The same technique has already been applied to most of the acceptor impurities in CdTe.[6–9,16] It is now possible to give the overall scheme of the acceptor states in CdTe for the impurities Li, Na, Cu, Ag, Au, N, P, and As. The results are summarized in Table II. The energy values given in that table have been improved upon by using several different measurements involving high-resolution techniques, such as PL, as shown in this work, and infrared absorption.[4,7,31,32] A very good agreement with the effective mass theory of Baldereschi and Lipari[19] has been obtained for all the acceptors.

Some particular electron-phonon interactions have been examined in Li- and Na-doped samples. A new phonon replicum of 19 meV has been observed, probably involving some bound phonons.

Finally, a comparison has been made between the acceptor states in CdTe and ZnTe, as shown in Fig. 7. In ZnTe several acceptor impurities have been identified with the same experimental techniques used in CdTe.[1–5,14,20,37] We have tried to explain the strong similarities between ZnTe and CdTe with a simple hypothesis involving the ionicity of these materials. Particularly for the cation-site substitutional acceptors, our feeling is that the acceptor states are comparable since the elementary clusters, i.e., four neighboring Te atoms, are the same. More generally, it seems that the divergences from the effective-mass acceptor states are mostly due to the impurity core. We think that on the basis of these experimental observations a theoretical investigation could be performed to provide a general understanding of acceptor impurity states in II-VI compounds.

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