Zeeman levels of the shallow lithium acceptor and band parameters in cadmium telluride

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T Friedrich, J Kraus, M Meininger, G Schaack and W O G Schmitt

Physikalisches Institut der Universität Würzburg Am Hubland, D-97074 Würzburg, Germany

Abstract. We have measured the energies and the Zeeman splitting of excitations of the non-ionized Li acceptor in CdTe by means of far-infrared absorption spectroscopy in order to determine the valence band parameters of the host material ($0 \leqslant B \leqslant 7\,T$, $B\|[100]$ and $B\|[110]$, $1.5\,K \leqslant T \leqslant 4.2\,K$). We have studied in detail the splitting of the G line ($1S_{3/2}(\Gamma_8) \rightarrow 2P_{3/2}(\Gamma_8)$) using polarized light; g factors for initial and final states are given. Shifts of the transition energies caused by interactions with phonons are identified and separated by a critical comparison of the excitation energies measured for Li with results published for other acceptors in CdTe. Using the recently developed theory of Schmitt and co-workers, a set of valence band parameters of the host material is obtained, which reproduces very well both the excited acceptor states at $B = 0\,T$ and the Zeeman patterns. With a value of the static dielectric constant $\varepsilon = 10.31$ taken from the literature the Baldereschi–Lipari set amounts to $\mu = 0.68$, $\delta = 0.13$, $R_0 = 30.9\,meV$. The Luttinger parameters are determined as $\gamma_1 = 4.14$, $\gamma_2 = 1.09$, $\gamma_3 = 1.62$ and $\kappa = 0.46$. We compare these numbers with results obtained by different methods and published previously in the literature.

1. Introduction

Information on the curvature, anisotropy (warping) of conduction and valence bands in bulk semiconductors and, as a consequence, on the effective masses of the charge carriers near the band extrema, can be parametrized using the $\boldsymbol{k} \cdot \boldsymbol{p}$ method (Luttinger parameters) [1]. This is a well established procedure and precise generally accepted values for the band parameters have been determined over the years for 'classic' semiconductors. For other, more exotic materials, like most of the II–VI compounds, the situation is less favourable and the numerical values of these parameters are still very much under debate.

   Here we concentrate on spectroscopic methods, and a much used experimental procedure is the determination of the energies of excited levels of a non-ionized shallow acceptor at zero external magnetic field. The envelope functions for a shallow acceptor extend far and smoothly into the unperturbed lattice, with the consequence that the acceptor energies depend on the Luttinger parameters γ_1, γ_2 and γ_3 of the host material, or equivalently on the parameters μ, δ and R_0, according to the pioneering work of Baldereschi and Lipari [2]. These authors have calculated the acceptor energies solely in terms of the valence band properties of the unperturbed host; μ expresses the strength of the heavy-hole–light-hole coupling, δ weighs the cubic contribution to the total Hamiltonian and R_0 is the effective Rydberg. For CdTe and ZnTe, Said and Kanehisa [3] have applied this theory to derive parameter sets for both materials from experimental data on the lower excited acceptor levels for $B = 0$. Their results differ considerably from the numbers determined a few years earlier by Milchberg and co-workers [4], using essentially the same experimental data but somewhat different methods of calculation.

Another approach uses data from Zeeman spectroscopic experiments either with the shallow acceptor levels [5] in the FIR or with the two-photon absorption by 2P excitons [6]. The lifting of degeneracies of acceptor states by a magnetic field gives additional information, which should allow better fits. It is well known in atomic physics that the interpretation of g-factor measurements presents a very sensitive test of the reliability of the eigenstates used for the calculations. Parameters derived from such data will deviate considerably from the previous sets for various reasons, as can be seen by comparing the sets from [3, 6] (table 3), but again relying only on Zeeman data will in general be an unsatisfyingly small basis. Accordingly, for an improved parameter set one should consider both the energy differences between acceptor states at $B = 0$ T and the Zeeman patterns of these states simultaneously.

The theoretical approach of Schmitt and co-workers [7] allows for a calculation of exactly these data. It extends the Baldereschi–Lipari method by including the effects of a finite magnetic field in the acceptor Hamiltonian in the Peierls approximation. After constructing wavefunctions of proper symmetry as linear combinations of spherical harmonics $Y_{M_L}^L$ and $J = \frac{3}{2}$ spinors, and writing the Hamiltonian in terms of spherical tensor operators, we can eliminate the angular and spinor part of the Schrödinger equation via the Wigner–Eckart theorem. Thus we reduce the problem to a large system of radial equations, which is solved numerically by a 'matrix method'. Practically exact eigenvalues (apart from chemical shifts) are obtained for the acceptor ground state and a few nearby odd-parity excited states by restricting the calculations to eigenfunctions with total angular momentum $F \leqslant \frac{13}{2}$, $F = L + J$ [7].

An alternative approach for the parametrization of Zeeman data is the theory of Bhattacharjee and Rodriguez [8], based solely on symmetry considerations. Here the g factors (and parameters for shifts $\sim B^2$) are fit parameters. The theory provides formulae for interconnecting the results for different point symmetries and for different directions of B in the crystal, but is not intended to calculate the acceptor energies from band parameters.

Our far-infrared spectroscopic investigations were performed on CdTe doped with lithium. Lithium is the most favourable of a number of possible dopants (Li, Na, P, As, Ag, Cu) from two points of view. First, the doping procedure is a quite simple diffusion process and the spectrum of the Li acceptor is close to an ideal acceptor with a bare Coulomb-type impurity potential. This means that the ground state of the Li acceptor is only slightly affected by the chemical nature of the dopant ('chemical shift') [3], which is usually taken into consideration by introducing an impurity-dependent screening length [9]. On the other hand some transition energies of this acceptor nearly coincide with the energy of the combination of two longitudinal optical phonons at the Γ point ($2LO(\Gamma)$) which gives rise to effects of resonant interaction (energy shifts and anomalous absorption line shapes). A critical selection of the available data is indispensable for an accurate theoretical analysis, as already mentioned by Milchberg and co-workers [4].

2. Experimental results

We performed magneto-absorption spectroscopy using a Fourier spectrometer equipped with a cryomagnet ($B \leqslant 7$ T). The oriented samples were immersed in helium at 1.5 K or 4.2 K, respectively. Details of our experimental set-up have been described in [5]. Li doping of the nominally pure CdTe samples ($10 \times 5 \times 1$ mm, slightly wedged, orientation: [100], from 'II–VI Incorporated') was performed by drying a solution of $LiNO_3$ on the sample surface and subsequently heating the sample at 450 °C for 5 h in a reducing atmosphere of 20% H_2 and 80% N_2. The transmission of the sample proved to be drastically reduced after this
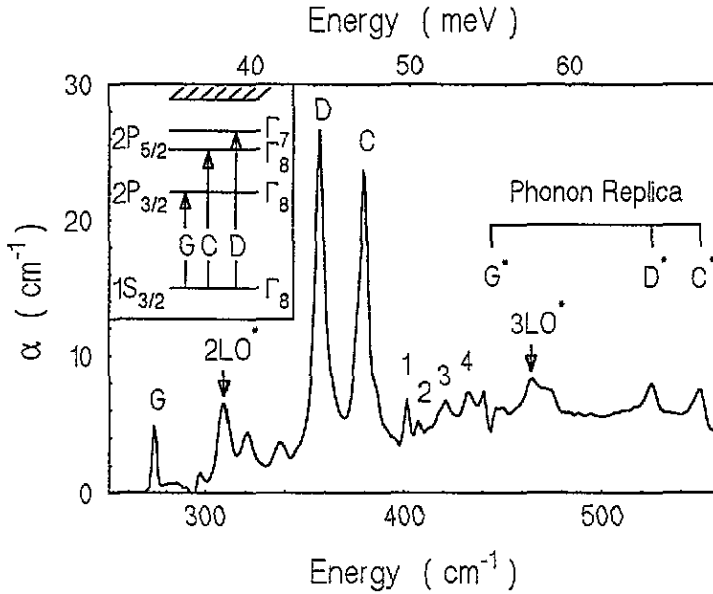
Figure 1. Extrinsic absorption of CdTe doped with Li; $T = 1.5\,\mathrm{K}$. In the inset the main lines G, C and D are assigned to transitions within the term scheme of the acceptor. The Zeeman splitting of the G line ($1S_{3/2} \to 2P_{3/2}$: $274\,\mathrm{cm}^{-1}$) has been studied in detail, the D and C lines ($1S_{3/2} \to 2P_{5/2}(\Gamma_8)$: $358\,\mathrm{cm}^{-1}$; $1S_{3/2} \to 2P_{5/2}(\Gamma_7)$: $380\,\mathrm{cm}^{-1}$) display a field-dependent shift only. The lines numbered 1–4 should be attributed to transitions $1S_{3/2} \to nP$ with $n > 2$. G*, D* and C* are the phonon replica of the G, D and C lines. The absorption bands in the range 290–340 cm^{-1} may originate from a resonant interaction of the $2\mathrm{LO}(\Gamma)$ phonon with acceptor excitations. The lines $2\mathrm{LO}^*(309.2\,\mathrm{cm}^{-1})$ and $3\mathrm{LO}^*(464.0\,\mathrm{cm}^{-1})$, also observed in photoluminescence studies [15], have already been interpreted as combinations of $\mathrm{LO}(\Gamma)$ phonons localized at the impurity site by interaction with acceptor transitions.

process; a number of local vibrational modes due to Li interstitials and Li complexes could be observed. In a second step the sample surfaces were etched with bromomethanole and finally annealed for 6 h in a vacuum at 500 °C together with a second, previously untreated, sample put side by side with the doped sample. It turned out that in this latter sample, which was finally used for the experiments, the absorption lines (G, D, C in figure 1) due to the Li acceptor were of reduced widths (FWHM of the G line: 1.5 cm^{-1}). Obviously, during the annealing process a very preserving diffusion process of Li across the sample surfaces into this second sample occurred, resulting in a rather homogeneous distribution of the dopants on former Cd vacancies in a favourable but unknown concentration.

The interferograms were run with up to 2^{13} sampling points, resulting in a spectral resolution $\Delta\nu = 0.15\,\mathrm{cm}^{-1}$. The absorption spectra were decomposed into a background term due to the undoped crystal and a Lorentzian frequency dependence of the absorption constant in an acceptor transition, as in [5].

In figure 2 we have plotted an example of the Zeeman splitting patterns of the G line ($1S_{3/2} \to 2P_{3/2}$) for $B\|[100]$ and polarizations $E\|B$ and $E\perp B$. The splittings and the thermalization of some transitions, which start from excited components of the ground state, are clearly visible, together with some spectral spillover (especially for $E\|B$) due to the non-ideal performance of the polarizer. Obviously the overall splitting in CdTe:Li is smaller than the same effect in isomorphous GaAs:C investigated in a previous work [5]. We have fitted the observed line positions $E(B)$ of the G line both to a relation quadratic in B:
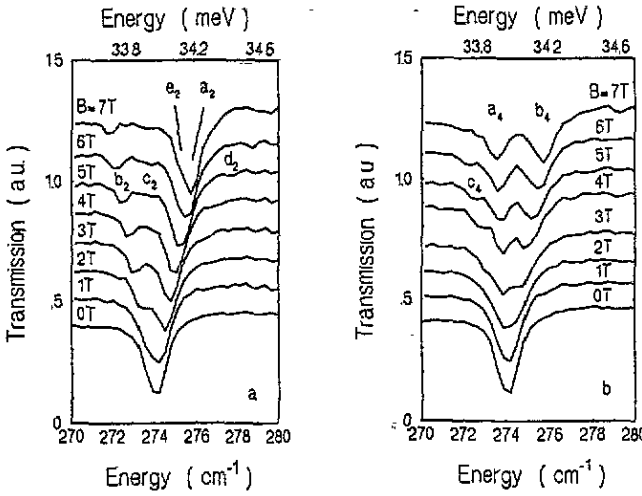
Figure 2. Zeeman splitting of the G line of the Li acceptor in CdTe. $B \parallel [100]$, $E \perp B$ (a) and $E \parallel B$ (b) as an example ($T = 1.5\,\mathrm{K}$; spectral resolution $\Delta \nu = 0.30\,\mathrm{cm}^{-1}$).

$$E(B) = E_0 + aB + bB^2 \tag{1}$$

and to one linear in B: $E(B) = E_0 + a'B$. $\tag{2}$

The parameters a, b, a' are our primary experimental results and are compiled in table 1. From these data we have determined the Zeeman splitting of both the ground ($1S_{3/2}(\Gamma_8)$) and the excited level ($2P_{3/2}(\Gamma_8)$), again using the various methods discussed in [5]. They are based on the effects of temperature on the absorption strength of the various lines, on the obvious effects of selection rules and on the necessary internal consistency of the data ('graphical method', figure 3). In table 2 we have compiled the g factors obtained in the T_d symmetry and in the approximate O_h symmetry.
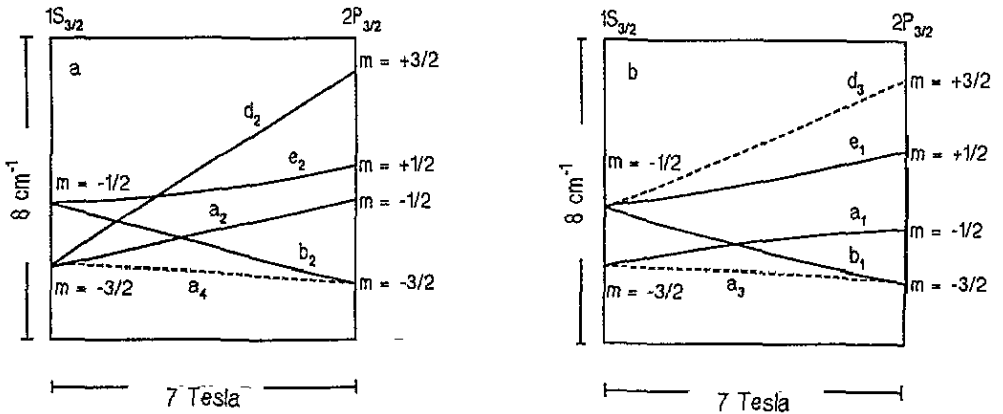

Figure 3. Results of the graphical method (described in detail in [5]) applied to the Zeeman splitting of the G line. The observed shifts of the Zeeman components for magnetic flux densities between 0 and 7 T (displayed in figure 5) are moved against each other along the vertical axis to find a reasonable splitting scheme of the ground state (left-hand axis) and of the excited state (right-hand axis) at $B = 7\,\mathrm{T}$ and a definite assignment of the lines to transitions between the Zeeman components of both states under consideration of the selection rules and of a sufficient thermal occupation of the ground-state components at $T = 1.5\,\mathrm{K}$. (a) $B \parallel [100]$. (b) $B \parallel [110]$. The denotations of the lines are consistent with figures 2 and 5 and table 1.

Table 1. Results of the fits for the Zeeman splitting of the G line in CdTe:Li by a parabolic (a (cm^{-1} T^{-1}), b (cm^{-1} T^{-2})) or linear (a' (cm^{-1} T^{-1})) interpolation (1, 2). Pol.: polarization of the incident light parallel or perpendicular to B. Sig.: denotation of the Zeeman components corresponding to figures 2, 3 and 5. E_0: position at $B = 0$ T as found by the parabolic interpolation, $(274.00 + 0.ii)$cm^{-1}. Err.: average deviation of an experimental point from the parabolic fit in cm^{-1}. In.: quantum number m of the initial state. Fin.: quantum number m of the final state. SO: erroneous line due to polarization spillover.

$B\parallel$	Pol.	Sig.	E_0	a	b	a'	Err.	In.	Fin.	SO
[110]	$\perp$	a_1	+01	0.2171	−0.0110	0.1460	0.03	$\frac{3}{2}$	$\frac{1}{2}$	
		b_1	−05	−0.3520	0.0107	−0.2771	0.04	$\frac{1}{2}$	$\frac{3}{2}$	
		c_1	−02	−0.1456	0.0162	−0.0134	0.05			a_3
		d_1	±00	0.4746	−0.0056	0.4352	0.03			d_3
		e_1	±00	0.1536	0.0086	0.2139	0.04	$\frac{1}{2}$	$-\frac{1}{2}$	
	$\parallel$	a_3	+04	−0.0177	−0.0052	−0.0539	0.03	$\frac{3}{2}$	$\frac{3}{2}$	
		b_3	+01	0.2716	−0.0133	0.1800	0.04			a_1
		c_3	+01	−0.2978	0.0004	−0.2952	0.03			b_1
		d_3	±00	0.4570	0.0043	0.4871	0.07	$\frac{1}{2}$	$-\frac{3}{2}$	
[100]	$\perp$	a_2	−07	0.2511	0.0008	0.2573	0.06	$\frac{3}{2}$	$\frac{1}{2}$	
		b_2	±00	−0.3177	0.0021	−0.3147	0.01	$\frac{1}{2}$	$\frac{3}{2}$	
		c_2	±00	−0.0926	0.0064	−0.0485	0.02			a_4
		d_2	±00	0.6220	0.0269	0.8079	0.08	$\frac{3}{2}$	$-\frac{3}{2}$	
		e_2	±00	0.0361	0.0155	0.1426	0.02	$\frac{1}{2}$	$-\frac{1}{2}$	
	$\parallel$	a_4	+04	−0.0462	−0.0040	−0.0744	0.03	$\frac{3}{2}$	$\frac{3}{2}$	
		b_4	+02	0.2631	−0.0053	0.2272	0.05			a_2
		c_4	±00	−0.3922	0.0143	−0.2941	0.05			b_2

For the absorption lines D and C we could not resolve a Zeeman splitting but only a shift. We abstain here from a detailed interpretation of the magnetic field dependence of these excitations, because both lines are strongly affected by a resonant interaction with the 2LO(Γ) phonon as discussed in the next section. As a consequence of this interaction with the phonon system, the D line shows a considerable asymmetry and a strong temperature-dependent variation of the lineshape, which causes a shift of the absorption maximum of this line by 3 cm^{-1} to higher energy, when the sample temperature is increased from 1.5 K to 30 K. At last the C line must be assumed to be superposed by a transition $1S_{3/2} \rightarrow 3P_{3/2}$ of small oscillator strength, which again renders the evaluation of the magnetic field dependence of this line more difficult.

Table 2. g factors of the two lowest states of CdTe:Li in O_h and T_d symmetry, as determined from (1) and (2). Error: average deviation of the experimental data for the G line from the quadratic fit (1). The linear fits, using (2), are in general more reliable, as the 'graphical method' [5] indicates. For a definition of the G_i, g'_i factors see [5].

State	g factor	Linear	Quadratic
$1S_{3/2}(\Gamma_8)$: O_h, T_d	G_1	∓0.483	∓0.394
	G_2	∓0.001	∓0.001
$2P_{3/2}(\Gamma_8)$: O_h	G_1	∓0.311	±0.005
	G_2	∓0.137	∓0.259
$2P_{3/2}(\Gamma_8)$: T_d	g'_1	±2.07	±1.95
	g'_2	∓0.870	∓0.858
Error	Δ(cm^{-1})	±0.061	±0.078

The excitations in the energy range 290–340 cm^{-1} cannot be attributed to acceptor transitions, and it seems that they have to be seen in the context of the interaction between acceptors and optical phonons. This will be discussed in more detail in section 4.

Acceptor excitations of an energy above the C line (lines 1 to 4 in figure 1) lie very close to each other. An identification of the final states of these transitions is only possible by a comparison with calculated energies (table 4). This comparison can serve as a final check of the quality of our theoretical description of the acceptor problem.

3. Determination of the band parameters of CdTe

The main purpose of our work was the determination of the valence band parameters. We have used a computer program [7] to calculate the energies of shallow acceptor states and of the Zeeman splitting of the initial and final state of the G line under variation of the parameter values μ, δ, γ_1 and κ for an optimum fit. The results depend on the value chosen for the dielectric constant ε of the host material, which is unfortunately known only with very insufficient precision: values between 9.0 and 10.9 can be found in the literature [3, 6, 10–14]. In the theory of Schmitt and co-workers [7] ε scales the energy level system at $B = 0$ T by the effective Rydberg $R_0 = R_y/\varepsilon^2\gamma_1$ and the size of the Zeeman splitting by the effective field $\beta_0 = R_0/\gamma_1\mu_B$. So variations of ε can contribute to a compatibility of the theoretical description of both sets of experimental results, but not with the consequence that our calculations are really sensitive to an independent determination of ε.

Table 3. Valence band parameters of CdTe as determined in this work for three different values of the dielectric constant ε, compared with parameters compiled from the literature. γ_1, γ_2, γ_3 and κ are the Luttinger parameters [1] μ, δ and R_0 correspond to the parameter set of Baldereschi and Lipari [2]. κ_{calc}: κ values calculated according to the relation $\kappa = -\frac{1}{3}(\gamma_1 - 2\gamma_2 - 3\gamma_3 + 2) - \frac{1}{2}q$ [20] (with $q \approx 0$).

Ref.	γ_1	γ_2	γ_3	κ	κ_{calc}	μ	δ	R_0 (meV)	ε
This work	4.46	1.12	1.70	0.458	0.294	0.658	0.131	32.7	9.65 [11]
This work	4.14	1.09	1.62	0.457	0.294	0.678	0.128	30.9	10.31 [14]
This work	3.89	1.06	1.54	0.448	0.285	0.694	0.124	29.5	10.9 [10]
[3]	5.3	1.62	2.1		0.75	0.72	0.09	29.7	9.3
[6]	4.11	1.08	1.95	0.35	0.63	0.78	0.21	32.8	10.0
[4, 15]						0.69	0.12	30.0	
[16]	5.3	1.7	2.0		0.70	0.71	0.06		
[17]	5.98	2.18	2.48		1.28	0.8	0.05	24.2	
[18]	5.29	1.89	2.46	1.27	1.29	0.84	0.11		
[19]				0.31					

Despite our intention to derive the band parameters of CdTe mainly from the Zeeman splitting of acceptor states, we cannot relinquish the consideration of some absolute energies of sufficient reliability. The parameters given in table 3 were determined for three different values of ε taken from the literature by minimizing the square of the deviation between the experimental and theoretical results of a selected set of data, where we have scaled down the deviations of the excited-state energies at $B = 0$ T by a factor of 0.1 because of their larger absolute values compared to energy shifts caused by the Zeeman splitting. We restricted our analysis to P states in order to avoid the necessity to take the central-cell effect into consideration. Furthermore, we had to regard possible modifications of some transition energies by interaction with phonons. Milchberg and co-workers [4] have

already pointed out a systematic variation of the observed energy difference [15] between the $2P_{5/2}$ states (distance between the D and C lines) with the ground-state binding energy of the acceptor and they find a good agreement with their calculated energy difference when the excitations of $2P_{5/2}$ states occur far from the $2LO(\Gamma)$ line. This effect of a resonant interaction of acceptor transitions with the $2LO(\Gamma)$ phonon becomes more obvious in a plot of the excited-state energy against transition energy from the $1S_{3/2}$ ground state (figure 4). Significant variations of the measured P-state binding energies are observed when their excitation energies nearly coincide with the $2LO(\Gamma)$ line. From this plot we draw the conclusion that the C and D lines of P and of the deeper acceptors are unaffected by interaction with the two-phonon process as a consequence of the resonance behaviour, and the same conclusion should be valid for the G line of the Li acceptor. The energy difference between the D and C lines (the splitting of the $2P_{5/2}$-state) is caused by the cubic term of the acceptor Hamiltonian, and should imply essential information for a precise determination of the parameter δ, as already mentioned in [4].
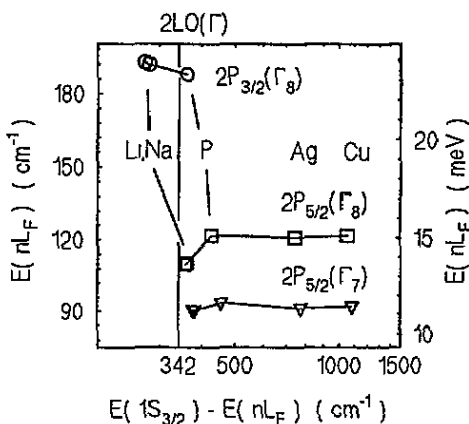

Figure 4. Binding energies of excited P states of acceptors Li, Na, P, Ag and Cu against the energy difference from the ground state $1S_{3/2}$ as measured by photoluminescence [15]. The plot confirms the interpretation that the variation of the observed binding energy of a state nL_F with the transition energy $E(1S_{3/2} \rightarrow nL_F)$ is affected by resonant interaction with the $2LO(\Gamma)$ phonon (vertical line).

Table 4. Comparison between the binding energies of acceptor states in CdTe calculated with the second parameter set displayed in table 3 (E_{calc}) and the experimental values used in our fit (E_{exp}). The binding energies measured for the Li acceptor (E_{Li}) from photoluminescence data [15] or from our FIR absorption spectra (figure 1, determined with a ground-state energy of $467\,cm^{-1}$) deviate from the calculated energies mainly as a consequence of resonant interaction with the $2LO(\Gamma)$ phonon ($2S_{3/2}$, $2P_{5/2}$) or caused by the central-cell effect ($1S_{3/2}$).

State	$E_{calc}(cm^{-1})$	$E_{exp}(cm^{-1})$	$E_{Li}(cm^{-1})$
$1S_{3/2}$	460		467 [15,21]
$2P_{3/2}$	191	193	193 (G line)
$2S_{3/2}$	136		121 [15]
$2P_{5/2}(\Gamma_8)$	124	122	109 (D line)
$2P_{5/2}(\Gamma_7)$	93.5	93.5	87 (C line)
$3P_{3/2}$	87.5		
$3S_{3/2}$	70		70 [15]
$3P_{5/2}(\Gamma_8)$	63		65 (line 1)
$3P_{5/2}(\Gamma_7)$	49.5		

The excited-state energies (E_{exp}) compiled in table 4 and the Zeeman splitting of the G line are the basis of our fit and are well described by our theory. Precise values of the valence band parameters can only be given with a well known dielectric constant ε. The

method used in [14] seems to us to be the most direct and accurate method of determining ε ($\varepsilon = 10.31$ for $T \rightarrow 0$ K). The highest compatibility in the description of the excited-state energies at $B = 0$ T and the Zeeman pattern of the G line is also achieved for $\varepsilon > 10$. The results displayed in table 4 (E_{calc}) and in figure 5 are calculated using the second parameter set given in table 3 ($\varepsilon = 10.31$ [14]). The comparison of the calculated (E_{calc}) and measured $1S_{3/2}$ ground-state energy (E_{Li}, from [15, 21]) confirms the assumption of a small central-cell effect for the Li acceptor in agreement with [3]. The larger deviation between the calculated (E_{calc}) and measured (E_{Li}) energy of the $2S_{3/2}$ state must again be seen mainly as an effect of resonant interaction with $2\text{LO}(\Gamma)$. Line 1 in figure 1 can be identified as a transition to the $3P_{5/2}(\Gamma_8)$ state, and is well reproduced by our theory. In table 3 the parameters obtained are compared with values in the literature. Our parameters μ, δ and R_0 are in good agreement with the results of Milchberg and co-workers [4]—derived from the evaluation of acceptor excitations at $B = 0$ T only—but our set should be of increased reliability because of the larger amount of evaluated experimental data. The evaluation of magnetic data only [6] or the omission of a critical selection of unperturbed acceptor-level energies at $B = 0$ T [3] results in band parameters which differ significantly from ours. Our parameter $\kappa = 0.46$ is slightly larger than the values given in [6, 19]. Within realistic errors of the parameters γ_i the relation [20]

$$\kappa = -\tfrac{1}{3}(\gamma_1 - 2\gamma_2 - 3\gamma_3 + 2) - \tfrac{1}{2}q \tag{3}$$

(with $q \approx 0$) is fulfilled for all of our parameter sets given in table 3.

4. Bound phonons

In the following we try to interpret some absorption lines, mainly in the energy range 290–340 cm^{-1} (between the G and D lines), which cannot be attributed to acceptor excitations. We tend to assume that these lines are again a consequence of the interaction between acceptor excitations and optical phonons. All these lines show a very small, but observable, magnetic-field dependence which demonstrates that the origin of these excitations is not of purely vibrational type.

The coupling of the LO phonon to donor [22] or acceptor excitations [23] was interpreted as the origin of a LO phonon bound state. The energy difference of this localized vibrational lattice mode from the LO(Γ) line corresponds to a binding energy and was found to depend on the energy difference from the lowest-lying electronic transition of the impurity. A significant increase of this binding energy mediated by resonant interaction of the $2\text{LO}(\Gamma)$ phonon with acceptor excitations was suggested by Venghaus and Dean [24] as a result of their photoluminescence measurements on several acceptors in ZnTe. The same situation of an approximate coincidence of acceptor excitations with the energy of $2\text{LO}(\Gamma)$ is given in the case of CdTe doped with shallow acceptors, as already mentioned in the last section. Molva and co-workers [15] observed in their photoluminescence studies on Li- and Na-doped CdTe an excitation of an energy 153 cm^{-1} called 'LO*' and the combinations 2LO* and 3LO*, which are absent from the spectra of CdTe doped with deeper acceptors, and they prefer the interpretation that LO* is a bound phonon of the type described above. We identify two absorption lines in our far-infrared spectra at 309 cm^{-1} and 464 cm^{-1} (figure 1) with 2LO* and 3LO* in spite of their slightly larger peak energies compared to the values given in [15]. The weaker lines in the energy range 290–340 cm^{-1} (at 297 cm^{-1}, 321 cm^{-1} and 337 cm^{-1}) lie close to combinations TO(Γ)+LO* (299 cm^{-1}), LO(Γ)+LO* (325.5 cm^{-1}) and $2\text{LO}(\Gamma)$ (342 cm^{-1}). Better agreement with measured line positions is obtained with

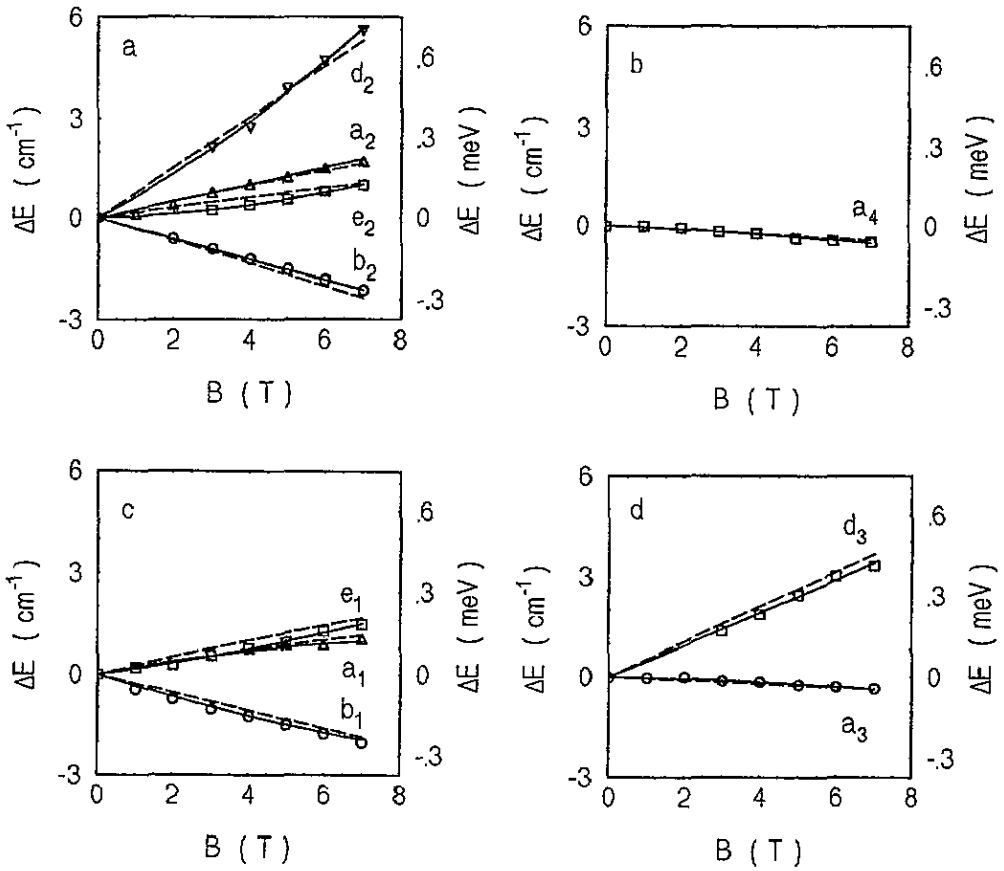**Figure 5.** Comparison of the measured and calculated Zeeman splitting of the G line of the Li acceptor in CdTe for $B\|[100]$ (with polarizations $E\perp B$ (*a*) and $E\|B$ (*b*)) and $B\|[110]$ ($E\perp B$ (*c*) and $E\|B$ (*d*)). The theoretical Zeeman splitting (broken lines) is calculated using the second parameter set displayed in table 3. The full lines are fits to the experimental points corresponding to equation (1).

the assumption of a further excitation LO** of an energy of about $166\,\text{cm}^{-1}$, which allows one to construct the combinations LO**+LO* ($320.5\,\text{cm}^{-1}$) and LO**+LO(Γ) ($337\,\text{cm}^{-1}$). Finally, an absorption line at $474\,\text{cm}^{-1}$, close to 3LO*, could be interpreted as LO**+2LO* ($475\,\text{cm}^{-1}$). A conclusive interpretation of LO* and LO** cannot be given at the moment, but it appears to be reasonable to assume that combinations of two types of bound phonon of different symmetry are observed [22]. Because of the resonance behaviour of the interaction the strength of the binding energy depends on the number of acceptor transitions of proper symmetry with an energy close to the 2LO(Γ) line as well as on their energy difference from this line. The binding energies should have their counterparts in shifts of acceptor transitions of corresponding symmetry to higher energy. With these presumptions the more strongly bound phonon mode LO* must be interpreted as being of P type, because several excitations of acceptor states of P symmetry ($2P_{5/2}(\Gamma_8)$, $2P_{5/2}(\Gamma_7)$, $3P_{3/2}$) are able to contribute resonantly to the binding energy ($16\,\text{cm}^{-1}$). LO** should be of S symmetry and its smaller binding energy ($5\,\text{cm}^{-1}$) is almost completely determined by the resonant coupling of 2LO(Γ) to the transition $1S_{3/2} \rightarrow 2S_{3/2}$.

5. Conclusions

As the main result of our work we state the following conclusions. Valence band parameters of semiconductors should be determined from experimental data that probe energy levels both at zero and at finite magnetic field. Both types of data should be considered in a well balanced way. The acceptor energies at $B = 0\,\mathrm{T}$ may be influenced in a rather uncontrollable manner by a central-cell correction, affecting essentially the ground state, as well as by interaction with the phonon system. In spite of the necessity of introducing a further parameter κ, the simultaneous evaluation of the Zeeman splitting can be assumed to increase the reliability of the determined band parameters.

Our conclusion is not new, but is supported by experiences in other fields in solid state physics, where energy levels in solids have to be parametrized. The determination of crystal-field parameters in compounds containing 3d or 4f electrons is a well known example: in the case of many crystal-field parameters (low symmetry), only a crystal-field analysis involving g-factor data is reliable [25].

Acknowledgments

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