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Zeeman spectroscopy of donor bound exciton states in ZnTe

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Résumé. — Nous avons effectué une série d'expériences d'effet Zeeman sur les raies correspondant à la recombinaison des différents états de l'exciton piégé sur le donneur neutre dans ZnTe. Elles prouvent définitivement que l'état fondamental possède la symétrie attendue de la bande de valence : Γ_8, mais mettent en évidence une anisotropie cubique beaucoup plus importante que celle mesurée dans le cas de l'exciton piégé sur l'accepteur neutre. De plus, l'important magnétisme orbital attendu pour les états de symétrie p n'est pas observé dans les états plus excités. Ce résultat est cependant compatible avec une description des états excitoniques en termes de configuration.

Abstract. — We have performed a series of Zeeman experiments on the lines corresponding to the recombination of the different states of the exciton bound to the neutral donor in ZnTe. This definitely proves that the lowest of these states has the expected Γ_8 symmetry of the valence band, while it displays a cubic anisotropy much larger than the one measured on neutral acceptor. The higher excited states do not show the large orbital magnetism expected for p-like states. This result is however consistent with a description of the exciton states in terms of configurations.

1. Introduction.

Although binding energies of exciton (X) to neutral acceptor (A^0) or donor (D^0) in direct gap cubic semiconductors can be predicted on the basis of simple models [1, 2], it appears that they are not sufficient to determine more detailed properties.

When $m_e < m_h$, the exciton bound to neutral acceptor (A^0, X) can be pictured as a negative point charge surrounded by the two hole positive charge cloud which in turn can more loosely bind the remaining electron in a pseudodonor orbital [3, 4]. The fine structure is qualitatively well understood in terms of interaction between holes and electron but no theory can yet accurately predict its magnitude or even its sign.

For the exciton bound to neutral donor (D^0, X) the situation is more complicated since the hole is only linked by the very extended negatively charged electron cloud, and hence has to be at least as delocalized as the electrons. This is not consistent with a pseudo-acceptor description which would require a smaller electron Bohr radius. One is tempted to consider that the exciton keeps its originality and orbits as a whole around the neutral donor linked to it as one hydrogen atom to the other in a hydrogen molecule. Excited states of the Bound Exciton (BE) which are seen in many cases (CdTe, InP, ZnO) are thought to be due to different orbital states of this non rigid rotator [5-7]. This model also explains why diamagnetism is weak since the exciton charge is zero (« neutral current » effect) [8].

In ZnTe, luminescence and excitation spectroscopy [9, 10] have shown that in many respects the donor behaviour is similar to other II-VI compounds like CdTe, ZnSe [5, 11]. In particular, analysis of the so-called « two electron » transition lines unambiguously shows that excited exciton states are qualitatively different from the ground exciton state for they involve opposite parity (p-like) orbital states for the hole and one electron. In order to get better insights into the fine structure of the exciton states, we report here Zeeman experiments that we have performed on the donor exciton lines in ZnTe.

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2. Experiment.

Due to the usually low doping level of donors in p-type ZnTe, it is necessary to use selective excitation in order to get reasonable light levels. This was performed by using a Coumarin 6 c.w. dye laser, the linewidth of which is less than 0.04 meV. This has the additional advantage of narrowing the donor band emission by selecting centres inside the inhomogeneous line-width [10]. But, as the position of the lines varies with the magnetic field, we generally have to adjust the excitation wavelength to recover the luminescence signal and therefore do not necessarily select the same centers. Consequently, absolute values of emission wavelength can be affected since they tend to follow the actual position of excitation ; however the splitting can be accurately measured.

Crystals of ZnTe have been grown by the Bridgman technique [12], non intentionally doped (the concentration of donors N_D is about 10^{14} cm^{-3}) and utilized as grown in order to get the smallest linewidths. Ingots are polycristalline but single crystals can easily be cleaved from them. The sample is immersed in liquid helium pumped below the λ point ($T \sim 1.8$ K) and oriented with respect to the magnetic field by rotating it in a (110) plane. Fields up to 4.5 T are obtained with a split coil superconducting magnet. Voigt or Faraday geometry can be selected. Luminescence is analysed through a high-resolution single pass 1.5 m monochromator (THR Jobin Yvon) with resolution better than 0.05 meV. One must note that the refraction of light in the tilted crystal can induce some depolarization.

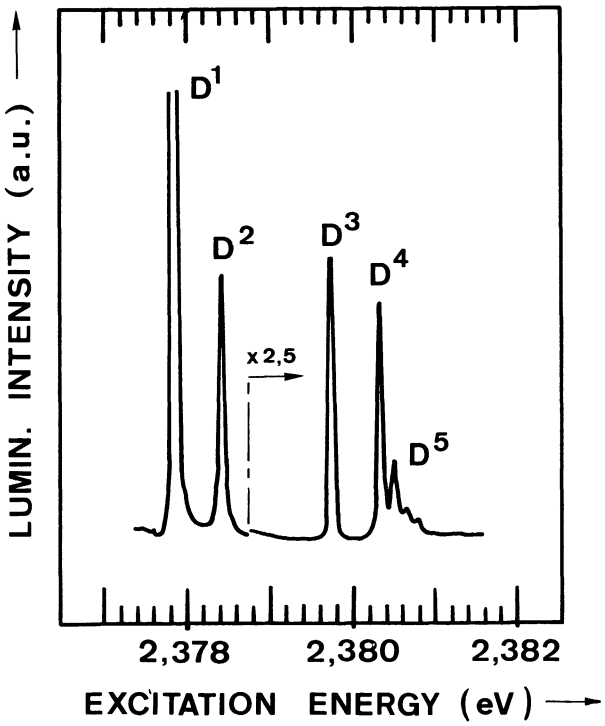

Fig. 1. — Zero field excitation spectrum of the principal donor bound exciton D^1 at $T = 1.8$ K.

3. Results.

Figure 1 shows the zero field excitation spectrum of the principal donor BE D^1 line, displaying the D^2 and D^3 lines corresponding to BE excited states which can also be seen in luminescence and D^4 and D^5 which are not usually [13]. As will be seen later (see Fig. 2), the Zeeman spectrum of D^3 is relatively simple and one line is much stronger than the others ; it is this line we selected to excite the luminescence from the [D^0, X]^{1,2} states. D^2 could also be used but strong spin memory effect during the relaxation from [D^0, X]^2 to [D^0, X]^1 makes spectrum very dependent upon which particular Zeeman component is selected, making analysis very complicated.

Zeeman spectra are presented for the three main orientations in figures 3, 4 and 5.

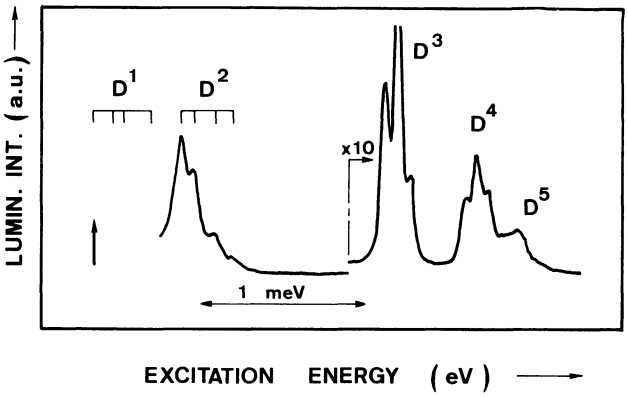

Fig. 2. — Excitation spectrum of the low energy component of the principal donor bound exciton D^1 for $\mathbf{H} /\!/ \langle 111 \rangle$ and $H = 4.33$ T at $T = 1.8$ K (see Fig. 5(a)) ; σ polarization for excitation and detection.

3.1 PARAMAGNETIC EFFECT. — In the case of D^1, the spectrum can be interpreted on the basis of transitions from an excited BE quadruplet Γ_8 to the ground donor doublet Γ_6. The ground state is described by a simple Zeeman Hamiltonian

$$\mathcal{H}_g = g_e \mu_B \mathbf{H}.\mathbf{S}$$

where $S = 1/2$ and g_e is the electron gyromagnetic factor. The excited state is described by

$$\mathcal{H}_1 = \mu_B[K_1 \mathbf{H}.\mathbf{J} + L_1(H_x J_x^3 + H_y J_y^3 + H_z J_z^3)] \quad (1)$$

where $J = 3/2$ and K_1 and L_1 are the usual isotropic and anisotropic splitting factors of the hole (the subscript 1 referring to the first donor BE excited state). Comparison of figures 3, 4 and 5 shows that the anisotropy is extremely large for both D^1 and D^2 lines. Consequently, apart from the $\langle 100 \rangle$ orientation, there are always some admixtures between the $|J, m_J\rangle$ states which diagonalize $K\mathbf{H}.\mathbf{J}$ due to a large cubic term $L(H_x J_x^3 + H_y J_y^3 + H_z J_z^3)$. Thus, the selection rules are less strict.

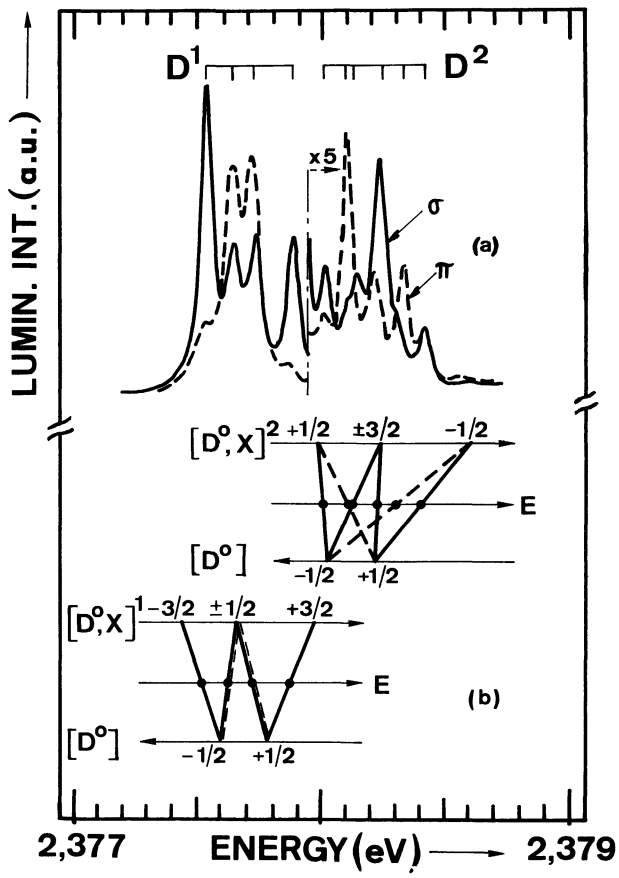

Fig. 3. — (a) Zeeman splittings of the D^1 and D^2 lines at a magnetic field of $H = 3.5$ T for $\mathbf{H} /\!/ \langle 100 \rangle$ at $T \simeq 1.8$ K for σ and π polarizations. (b) Corresponding schematic diagram showing Zeeman effects in the BE excited state $[D^0, X]^i$ and in the donor ground state $[D^0]$.

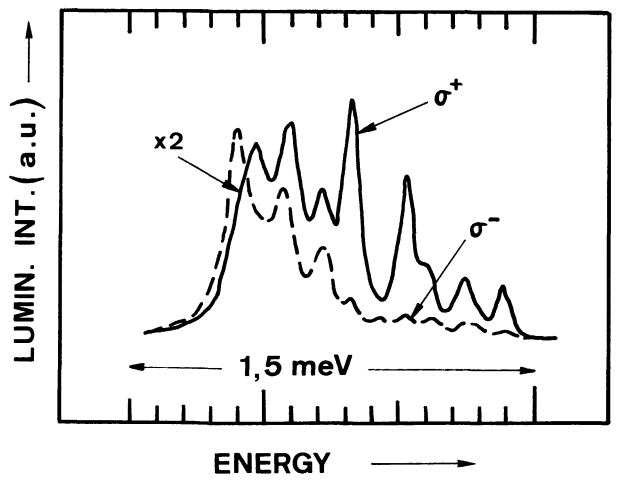

Fig. 4. — Zeeman splittings of the D^2 and D^1 lines at a magnetic field of $H = 4.5$ T for $\mathbf{H} /\!/ \langle 110 \rangle$ at $T = 1.8$ K for σ^+ and σ^- polarizations.

In the case of D^1 line, polarization and resolution of Zeeman components allow a fit to be obtained separately for $\langle 100 \rangle$ and $\langle 111 \rangle$ orientations and

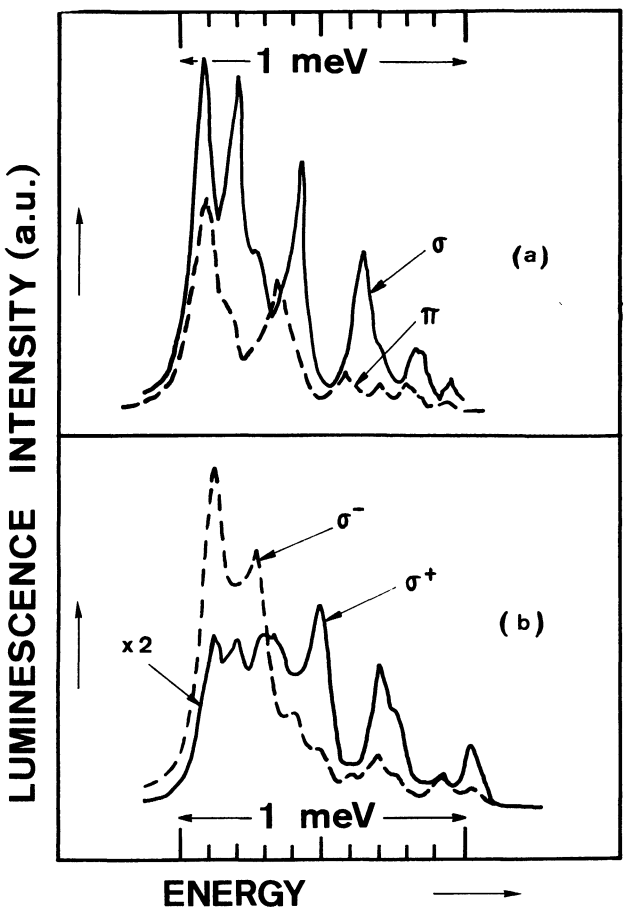

Fig. 5. — Zeeman splittings of the D^1 and D^2 lines for $\mathbf{H} /\!/ \langle 111 \rangle$ at $T = 1.8$ K. (a) : $H = 4.33$ T; σ, π polarizations. (b) : $H = 4.5$ T; σ^+, σ^- polarizations.

the resulting parameters are satisfactorily compared. The best fit is again compared to experimental $\langle 110 \rangle$ results and data shown in table I clearly describe precisely the Γ_8 excited state. It is to be noted that an experiment has been performed in Faraday geometry (see Fig. 5) to check the actual signs of g's.

As is usual for short lived exciton states, the excited state populations do not reach thermal equilibrium although they are not too far from it (at 1.8 K He bath temperature, the effective temperature is about 4 K).

In the case of D^2 line, $\langle 100 \rangle$ data are reasonably well fitted by two sets of parameters which would correspond to two different labelling of detected transitions. However, in contrast with D^1, neither set is capable of explaining the other orientation results even when extremely large diamagnetic splitting is arbitrarily introduced. Table II shows the lack of agreement between models and experiment. We have to note that the splitting of the lines is close to be proportionnal to the magnetic field even up to the region where D^1 and D^2 components are overlapping. So, the complexity of the D^2 spectrum cannot be explained by a Zeeman coupling with the $[D^0, X]^1$ states. The data presented in table II still show clearly

Table I. — *Resulting parameters deduced from polarization and resolution of Zeeman components of* D^1 *for the three main orientations of the magnetic field H* ($g_{1/2}^{\sim}$, $g_{3/2}^{\sim}$ *are defined in the appendix*; g_e *is the electron g value in the* Γ_6 *neutral donor ground state*; *K and L are the usual isotropic and anisotropic splitting factor of the hole as precised in the text*; (a) *and* (b) *indicate two independent fits from which resulting values of K and L are deduced*; *these values and the formulae given in the appendix lead to the « calculated » values of* $g_{1/2}^{\sim}$ *and* $g_{3/2}^{\sim}$ *in the case of* $\mathbf{H} /\!/ \langle 110 \rangle$).

			$g_{1/2}^{\sim}$	$g_{3/2}^{\sim}$	g_e	K	L
	$H /\!/ \langle 100 \rangle$	(a)	−0.03	0.46	−0.41 ± 0.01	−0.09 ± 0.01	0.24 ± 0.01
	$H /\!/ \langle 111 \rangle$	(b)	0.66	0.38	−0.40	−0.06 ± 0.01	0.22 ± 0.01
	$H /\!/ \langle 110 \rangle$	exp	0.61 ± 0.11	0.44 ± 0.02	−0.35 ± 0.08		
		calc	0.56 ± 0.08	0.41 ± 0.07		↰	↰
	Resulting values				−0.41 ± 0.01	−0.07 ± 0.03	0.23 ± 0.02

Table II. — *Resulting parameters deduced from polarization and resolution of Zeeman components of* D^2 *for the three main orientations of the magnetic field H*; *the parameters* $g_{1/2}^{\sim}$, $g_{3/2}^{\sim}$, g_e, *K and L are defined in table I.* (i) *and* (j) *indicate the two possible fits for the same orientation of the magnetic field* $\mathbf{H} /\!/ \langle 100 \rangle$; *for each of these fits, the values of K and L are deduced and lead to the « calculated » values of* $g_{1/2}^{\sim}$ *and* $g_{3/2}^{\sim}$ *for the two other orientations of the magnetic field H.*

			$g_{1/2}^{\sim}$	$g_{3/2}^{\sim}$	g_e	K	L
	$H /\!/ \langle 100 \rangle$	(i)	−1.59	0.28	−0.42	−1.75	0.65
		(j)	−1.59	0	−0.42	−1.79	0.79
	$H /\!/ \langle 111 \rangle$	(i′)	0.37	0.59		↵	↵
		(j′)	0.79	0.46		↵	↵
		exp	0.63 ± 0.07	0.48 ± 0.02			
	$H /\!/ \langle 110 \rangle$	(i″)	0.61	−0.20		↵	↵
		(j″)	0.40	−0.13		↵	↵
		exp	0.54 ± 0.09	−0.12 ± 0.03			

the order of magnitude of the Zeeman effect which is comparable to D^1 data. However, we cannot describe quantitatively the results by assuming the $[D^0, X]^2$ state is a Γ_8 quartet. The remaining possibility, namely that D^2 results from accidental degeneracy between two or several multiplets, cannot be accurately checked given the present accuracy of experimental results.

The D^3 and D^4 lines are much simpler since they always split into three components (see Fig. 2) with no detectable anisotropy. The $[D^0, X]^{3,4}$ excited state is well represented by a Γ_6 representation which has to be isotropic in cubic symmetry; the corresponding effective spin Hamiltonian is

$$\mathcal{H}_{3,4} = g_{3,4}\, \mu_B\, \mathbf{H}.\mathbf{S}$$

with g value close to g_e but of opposite sign :

$$g_3 \sim g_4 \sim 0.41 .$$

3.2 DIAMAGNETIC EFFECT. — Apart from the paramagnetic effect discussed above, there is a contribution from diamagnetic effect which is twofold. The main one is a centre of gravity diamagnetic shift [3] and results from the difference between excited and ground state shifts. For D^1 it is slightly anisotropic ranging from $(1.0 \pm 0.2) \times 10^{-2}$ meV.T^{-2} for $\mathbf{H} /\!/ \langle 100 \rangle$ to $(0.8 \pm 0.2) \times 10^{-2}$ meV.T^{-2} for $\mathbf{H} /\!/ \langle 111 \rangle$. For D^2 it is only when $\mathbf{H} /\!/ \langle 100 \rangle$ that a reliable value $(0.7 \pm 0.2) \times 10^{-2}$ meV.T^{-2} can be derived. The diamagnetic splitting [14] between

the gravity centres of the $m_J = \pm 1/2$ and $m_J = \pm 3/2$ Zeeman components is much smaller but significant for D^1 since it has to be introduced in order to fit the paramagnetic data. Its value is typically 0.1×10^{-2} meV.T^{-2}.

4. Discussion.

4.1 HOLE MAGNETIC ANISOTROPY. — The most remarkable feature of donor BE states is certainly the extreme anisotropy of the magnetic splitting. On the contrary, the hole magnetic behaviour as seen on the ground state of neutral acceptors is almost isotropic [12, 15-19] ($K = -0.6 \pm 0.01$, $L = -0.1 \pm 0.1$). This is also very different for the hole belonging to the free exciton where a much smaller value is reported [20] $\left(K = -0.2 \pm 0.2,\ L = 0.04\ {}^{+\,0.04}_{-\,0.02}\right)$. In the donor case, the large extension of the hole wavefunction makes it somewhat similar to free hole Landau levels [6] which could be calculated from the Luttinger spin Hamiltonian. It appears very clearly that the magnetic moment of the hole depends very strongly on the envelope wavefunction. This is to be expected from the form of the Luttinger spin Hamiltonian where it is obvious that terms like $\gamma_2(J_x^2 k_x^2 + J_y^2 k_y^2 + J_z^2 k_z^2)$ directly couple the momentum $\mathbf{k}$ and the « spin » $\mathbf{J}$. The observed cubic anisotropy certainly implies a large difference in γ_2 and γ_3 coefficients which is consistent with theoretical [21] as well as some [20] if not all [22] experimental results.

4.2 ELECTRON g VALUE. — The sign of the electron g_e factor is consistent with most previous experiments apart from donor acceptor pair selective excitation [19] or O.D.M.R. [23] which remain a mystery. In this context we note that the present experiment actually deals with the same entity, the neutral donor ground state, as for the donor acceptor pairs. Other negative electron g values were in fact measured in different states like the acceptor BE [12, 15, 24]. It looks like the remaining discrepancy can only be accounted for, if the thermal equilibrium among spin levels is not reached before donor acceptor recombination.

4.3 LACK OF ORBITAL MAGNETIC MOMENT IN THE EXCITED STATES. — Previous studies of two electron lines associated with the recombination of $[D^0, X]^{1,2,3}$ levels have shown that whereas $[D^0, X]^1$ has electrons and hole in s-like even symmetry orbitals, $[D^0, X]^{2,3}$ must involve excitation of one electron and the hole in p-like odd symmetry orbitals [9, 10]. An attractive model suggested by different authors [5, 25] describes the exciton loosely bound around the donor which retains the s-like internal symmetry of the free exciton. It corresponds to the usual hydrogen molecule model which has proven to be quite good in calculating the binding energy of donor BE in CdS for instance [1, 26]. The excited states are then sought among non rigid rotator states of this « molecule ». Quantitative agreement can even be reached in case of InP [6]. The fact that electron and hole orbit together around the donor cancelling each other's charge (the « neutral current » effect [8, 14]) explains nicely that a weak diamagnetism is observed in GaP [8, 27]. Moreover it might also explain why the $[D^0, X]^{2,3}$ states observed in this experiment do not show the large orbital magnetism associated with p-like orbital of the small effective mass electron [10].

However we think there is a serious drawback in such a description of excited states. One describes the total envelope wavefunction of the BE as a direct product of donor electron $\psi_D(r_e)$ wavefunction by the exciton wavefunction $\chi(R_X).\phi(R_e - R_h)$ where ϕ represents the internal motion of the electron R_e with respect to the hole R_h and χ the motion of the centre of gravity R_X of the exciton :

$$\Psi = \psi_D(r_e).\chi(R_X).\phi(R_e - R_h).$$

At this stage the indiscernability of the two electrons at r_e and R_e must be taken into account by antisymmetrizing the total wavefunction [25]. Indeed it was shown that the exchange interaction between the two electrons is the dominant contribution to the binding energy of the exciton.

The non rigid rotator states are obtained by changing $\chi(R_X)$ from a s-like $\chi_s^1(R_X)$ in the case of $[D^0, X]^1$ to a p-like $\chi_p^2(R_X)$ or $\chi_p^3(R_X)$ for $[D^0, X]^2$ or $[D^0, X]^3$ respectively. The two other constituent wavefunctions $\psi_D(r_e)$ and $\phi(R_e - R_h)$ which are the same in ground and excited states are even under inversion. Then, the overall parity is even for the total envelope wavefunction of $[D^0, X]^1$ but odd for $[D^0, X]^{2,3}$. This would imply that dipolar transitions are forbidden in the last two cases (the actual parity is determined by the periodic part of the Bloch wavefunction $u_k(r)$ which being different for electrons and holes takes care of the change in parity during a dipolar transition). This is contrary to the observation that D^2 and D^3 have at most oscillator strengths 3 to 4 times smaller than D^1 as seen on absorption [16] or excitation spectra (Fig. 1). On the opposite, the model which was used in reference [9], describes the total envelope wavefunction as a sum of direct products of one particle wavefunctions :

$$\Psi = \sum \psi(r_e).\phi(R_e).\chi(R_h).$$

Each term represents a « configuration » [28]. The actual wavefunction is obtained after appropriate antisymmetrization. It is through different configuration admixtures that correlation between electrons and hole is taken into account. The main terms of Ψ in the case of $[D^0, X]^1$ and $[D^0, X]^{2,3}$ are respectively :

$$[D^0, X]^1 : \Psi^1 \simeq \psi_{1s}(r_e).\phi_{1s}(R_e).\chi_s(R_h)$$

$$[D^0, X]^{2,3} : \Psi^{2,3} \simeq \psi_{1s}(r_e).\phi_{2p}(R_e).\chi_p(R_h).$$

In that case, the overall parities of $[D^0, X]^{1,2,3}$ states are all the same and no dipolar transition to the ground state is forbidden. The transition from $[D^0, X]^{2,3}$ to the $[D^0]_n$ excited state [13] (two electron transition) involves the recombination between the $\psi_{1s}(r_e)$ and $\chi_p(R_h)$ states and leaves the system in the 2p state. It is forbidden in the dipole approximation but since it involves the main configuration it is only slightly less intense than the principal line [9]. For $[D^0, X]^1$ the coupling of the two electron orbital momenta ($L = 0$) and spins ($S = 1/2$) gives a total momentum $J = 0$ because of Pauli exclusion principle. $[D^0, X]^1$ has the symmetry of the hole which, being in a $L = 0$ state, displays the Γ_8 symmetry of the valence band. We can try to follow a similar qualitative description of the coupling in the case of $[D^0, X]^{2,3,\cdots}$ excited exciton states. There, the problem is much more complex since one has to couple 3 spins and 3 orbital momenta, only one of which is zero. As in the case of delocalized orbitals of shallow centres in semiconductors, we will neglect spin-orbit interactions. We now present a possible scheme of coupling which would explain the ordering of levels, keeping in mind that without a knowledge of the actual magnitude of interactions, it cannot be relied on quantitatively.

The excited configuration requires the coupling of 3 spins and 2 orbital momenta $L = 1$. The experimental evidence is that there is no orbital momentum left so that the hole and electron $L = 1$ states couple to form $L_1 + L_2 = 0$. This is the opposite situation from Hund's rule for electronic configurations which states that among the largest S value, the ground state has the largest L. But, this can be due to the fact that the electrostatic interaction repels electrons while it attracts electron and hole. The exchange coupling of the spins usually tends to align hole or electron spins together, that is the ground state is expected to be $J = 1$ when coupling two s and p electrons together, while it is also $J = 2$ for an electron 1/2 and a hole 3/2. It is far from obvious in the donor case to know in which order these couplings should be introduced, but it seems reasonable in any case that the largest J should be the lowest. Then, the $J = 5/2$ should come first and would be split into a Γ_8 and a Γ_7 states by the cubic crystal field. In view of the extremely large magnetic cubic anisotropy we observe, it is not too surprising that the cubic splitting is so large between D^2 and D^3.

4.4 DIAMAGNETIC EFFECT. — The diamagnetic effect on the D line is the difference between the actual diamagnetic effect on excited and ground states. Assuming that the contributions of the three particles add, one sees that the measured value corresponds to the exciton contribution. If the electron has an orbit equivalent to the donor ground state, one expects for it a diamagnetic effect determined by an effective mass $m^* = 0.1\ m_e$ and a Bohr radius $a \sim 40$ Å equal to 0.6×10^{-2} meV.T^{-2}. The measured value 10^{-2} meV.T^{-2} does not correspond to the « neutral current » quenching observed in GaP donor [8, 14]. Instead, the hole contribution rather adds as a relatively independent particle. Still it is surprising that this value does not increase for the excited state $[D^0, X]^2$ in view of the much larger radii expected for 2p orbitals. This indicates that there must be a strong correlation between hole and electron motion.

5. Conclusion.

The magnetic field effects on the donor BE have been described. They are quite similar to the results obtained in the case of InP [6]. This confirms the apparent « universality » of the behavior of the neutral donor BE complex in direct gap cubic semiconductors.

The main result is the very large cubic anisotropy of the two lowest $[D^0, X]^{1,2}$ states. We have proposed a model which accounts for the lack of orbital magnetism in the excited states while retaining the p-like character of the orbital of one hole and electron of the complex.

Acknowledgments.

We wish to thank J. L. Pautrat and N. Magnea who kindly supplied the high quality ZnTe samples used in this work.

Appendix.

The diagonalization of the Zeeman Hamiltonian [1] for a Γ_8 state ($J = 3/2$) in cubic symmetry leads for the three main orientations of the magnetic field **H** to Zeeman eigenstates $|\tilde{m}_J\rangle$ with exact energies $g_{\tilde{m}_J}.\tilde{m}_J\,\mu_B H$ given by [29] :

	$\lvert \tilde{3/2} \rangle$	$g_{3/2}^{\sim}$	$\lvert \tilde{1/2} \rangle$	$g_{1/2}^{\sim}$
$\mathbf{H} /\!/ \langle 100 \rangle$	$\lvert 3/2 \rangle$	$\frac{2}{3}P$	$\lvert 1/2 \rangle$	$2Q$
$\mathbf{H} /\!/ \langle 110 \rangle$	$\alpha \lvert 3/2 \rangle + \beta \lvert -1/2 \rangle$	$\frac{1}{6}[P + Q + \sqrt{7(P^2+Q^2) - 2PQ}]$	$\alpha' \lvert 1/2 \rangle + \beta' \lvert -3/2 \rangle$	$\frac{1}{2}[-P - Q + \sqrt{7(P^2+Q^2) - 2PQ}]$
$\mathbf{H} /\!/ \langle 111 \rangle$	$\gamma \lvert 3/2 \rangle + \delta \lvert -3/2 \rangle$	$\frac{1}{3}\sqrt{3(P^2+Q^2) + 2PQ}$	$\lvert 1/2 \rangle$	$P - Q$ (×)

where P and Q are two parameters whose relationship with K and L defined in equation (1) is :

$$K = -\frac{1}{12}P + \frac{9}{4}Q$$

$$L = \frac{1}{3}P - Q\,.$$

In addition, let us note that even if the anisotropic part of the Zeeman Hamiltonian (1) is small in comparison with the isotropic part, these exact energies lead to formulae slightly different from those published in reference [6].

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[13] In a previous paper [9], the D_n^i notation was used to specify a line originating from the ith donor BE excited state $[D^0, X]^i$ and terminating in the nth shell of the neutral donor $[D^0]_n$. We refer here to the same notation but, we will not mention the subscript « n » since all lines correspond to the $n = 1$ ground state of the neutral donor.

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