

Photoluminescence studies of ZnO doped with stable and radioactive impurities

A thesis submitted to

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Doctor of Philosophy

by:

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Declaration

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of Doctor of Philosophy is entirely my own work, that I have exercised reasonable care to ensure that the work is original, and does not to the best of my knowledge breach any law of copyright, and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

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Date:

for Rose
and Hilary

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List of Abbreviations

B-magnetic field

CERN-Conseil Européen pour la Recherche Nucléaire/the European Organisation for Nuclear Research

CCD-Charge-coupled device

D₀X-Neutral donor bound exciton

D₊X-Ionised donor bound exciton

DAP-donor acceptor pair

DBX-donor bound exciton

DD-Deep donor bound exciton

FWHM-full width at half maximum

FX-free exciton

g_e-electron g-value

g_h-hole g-value

g_h[⊥]-hole g-value perpendicular to the c-axis

g_h^{||}-hole g-value parallel to the c-axis

ISOLDE-isotope separator on-line

I_x-neutral and charged bound exciton complexes (where x is 1,2,3,.....)

LN₂-liquid nitrogen coolant

LO-longitudinal optical

PL-photoluminescence

PMT-photomultiplier tube

TES-two electron satellite

UV-ultraviolet

UC_x-uranium carbide

ZPL-zero phonon line

Abstract

In this work the II_b-VI compound semiconductor ZnO is doped, via ion implantation of stable and radioactive isotopes, in order to investigate the chemical nature of exciton recombinations bound to previously unidentified defects. Photoluminescence (PL) is discussed and is used extensively as the primary investigative technique.

A new defect emission feature, centred around 3.324 eV, is found to be related to Ge impurities occupying substitutional Zn sites in ZnO. This centre is investigated by temperature dependent PL, piezospectroscopy and Zeeman spectroscopy. The centre is donor-like in nature. Uniaxial stress measurements indicate that the defect centre has trigonal symmetry and applied magnetic field measurements reveal the neutral charge state of the centre and the donor-like binding mechanism.

Subsequent to this, a study is undertaken of the isoelectronic defect Hg in ZnO studying the zero phonon feature at 3.279 eV and its associated phonon replica band. Temperature dependent measurements reveal two close lying excited states with a common ground state, and a large thermal stability is reported for the defect from temperature dependent measurements. Uniaxial stress measurements reveal an excited state and a non-degenerate ground state for the defect in a centre of trigonal symmetry.

Finally, a previously studied donor binding centre related to In is observed after implantation of radioactive ¹¹⁷Ag, which decays to ¹¹⁷In, through ¹¹⁷Cd. The ¹¹⁷In then decays to ¹¹⁷Sn. This results in three lines in the near band edge spectra, two related to substitutional In and one which is tentatively proposed to be due to Sn impurities. This hypothesis is investigated further via a chemical doping technique and a positive correlation is found between Sn impurities and the appearance of the neutral bound exciton centre, I₁₀.

Chapter 1: Introduction to ZnO

1.1 Overview of ZnO

ZnO is by no means a new material to mankind, nor is the recent surge in research interest the first time that this wide-band gap semiconductor has been characterised by well-known spectroscopy techniques such as photoluminescence (PL) or absorption [1, 2]. New technological requirements, however, have drawn many researchers back to investigate ZnO again in order to see if the long-standing problem of p-type doping can be overcome at last.

With a large exciton binding energy (60 meV) and previously mentioned wide-band gap it is hoped that a room-temperature homo-junction device could be produced which could make, among other things, solid state lighting a more feasible possibility [3, 4].

The place of ZnO in the semiconductor hierarchy is seen in Figure 1.1 where the band gap of some common semiconductors is plotted against their chemical components. ZnO is a II_b-VI semiconductor and is part of a larger family of semiconducting binary compounds comprising elements from group II_b and group VI of the periodic table. This group includes metals such as Zn, Cd and Hg in binary compounds with elements from the chalcogen group (O, S, Se, Te). Overall these compounds tend to have band gaps smaller than metal-oxides and alkali-halides and larger band gaps than the elementary semiconductors, Si and Ge.

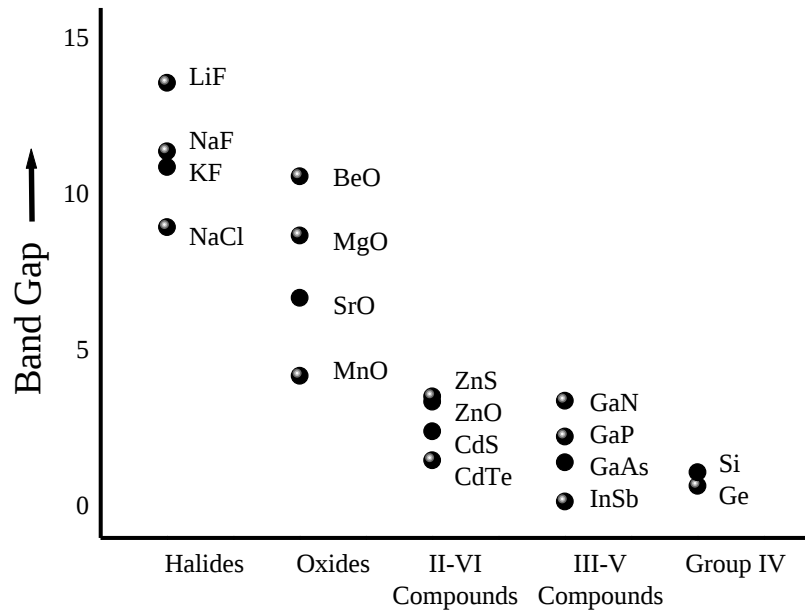


Figure 1.1: Band gap variations of compounds taken from different columns of the periodic table. Values are presented for room temperature band gaps. Values from [5] and the references therein.

The II_b-VI compounds have similar properties to III-V compounds, also seen in Figure 1.1. GaN (III-V), for example, typically crystallizes in the wurtzite structure, like ZnO (II_b-VI), while GaAs (III-V) and CdS (II_b-VI) both crystallize in the cubic zincblende configuration. Both GaN and ZnO are potentially applicable for use in UV optoelectronics; they have similar structural properties and band gaps (3.4 and 3.3 eV respectively at room temperature), however the large exciton binding energy of ZnO (60 meV compared to ~25 meV for GaN) and the capability to create high quality material for a relatively lower cost suggest that it could outrun GaN in the race for sustainable UV/blue light emitters at room temperature.

ZnO normally crystallizes in the wurtzite type structure (unlike other II_b-VI compounds) which involves a Zn cation bonding to four O anions forming a polar covalent structure. This polar covalency is even more pronounced in ZnO than in the other Zn-chalcogen compounds as

demonstrated in table 1.1. The increased electronegativity exhibited by the lower mass elements from group VI coupled with their smaller atomic radii contributes to the polar nature of ZnO and the other Zn-chalcogens. Zincblende structure ZnO and rocksalt structure ZnO exist but are rarer than the wurtzite configuration.

Table 1.1: *Electronegativity and atomic radius of the anion in the Zn-chalcogens, values taken from von Wenckstern et al. [6] and the references therein.*

	ZnO	ZnS	ZnSe	ZnTe
Electronegativity of the anion (eV)	3.44	2.58	2.55	2.1
Atomic radius of the anion (Å)	0.75	1.02	1.16	1.36

Preventing the crucial development of ZnO into optoelectronics is the barrier of reliable, reproducible and low resistivity p-type ZnO. Like some other semiconductors ZnO is asymmetric in its doping properties, that is, it can easily be doped n-type but it is difficult to dope p-type. While the p-type doping problem in ZnO has been the primary focus of many researchers recently, a fundamental understanding of the behaviour of donors in ZnO is still unresolved. Impurities that are expected to act as acceptors (such as As and Sb) are found to behave as donors [7, 8] and elements from group IV of the periodic table have unique properties in the PL emission spectrum of ZnO [9].

Apart from its potential for UV optoelectronics ZnO is a widely used compound already, as a transparent conducting oxide [10, 11], in rubber materials [12] and pharmaceutical industry [13], among other applications. Radiation hardness makes ZnO potentially applicable for use in space technology and ZnO is already used in solar cells as a transparent conductor [14] and is also used in transparent transistors [6].

ZnO is also of interest for use in nanomaterials, with ZnO nanorods, belts and thin films being produced. Well-aligned ZnO nanorods have attracted considerable attention due to their potential use in gas sensors. When used in sensors the large surface area that nanorods exhibit

increase the sensitivity of the sensor. A variety of methods exist to grow ZnO nanorods, including chemical bath deposition [15], vapor phase transport [16] or a combination of both all of which result in high quality nanorods. A recent review of ZnO research includes a more in depth comparison of current growth techniques [17]. The ease with which nanorods of ZnO are grown as well as their environmentally friendly composition make ZnO advantageous over other materials used for similar purposes. A general review of ZnO nanostructures is given by Yi *et al.* in [18]. In recent decades interest in ZnO has increased greatly as can be seen in Figure 1.2 which shows that the number of publications has increased dramatically as it became apparent that ZnO nanorods were readily producible as were single crystal ZnO substrates, although that interest appears to have peaked and may now be beginning to decrease.

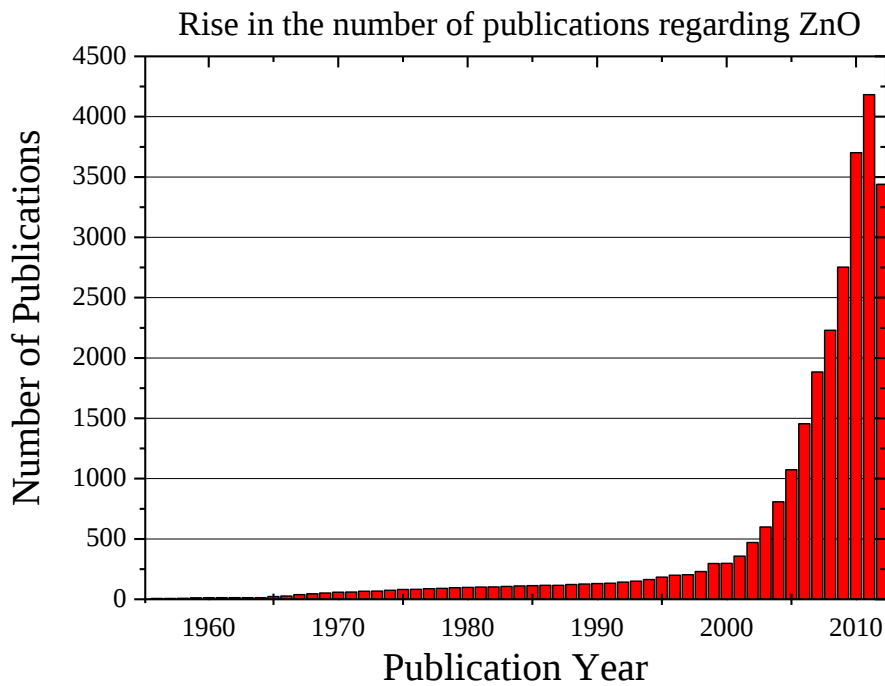


Figure 1.2: Graph demonstrating the rise in the number of publications relating to ZnO in recent decades (data taken from Web of Science [19], searching for publications with ZnO as the topic from 1960 to 2010).

1.2 Defects in ZnO

1.2.1 Intrinsic Defects in ZnO

Intrinsic defects in ZnO have been a source of controversy in the past (with some still being a source of disagreement). Zn and O interstitials, Zn_i and O_i , can occupy tetrahedrally coordinated sites (labelled $Zn_i(T)$ and $O_i(T)$ respectively) in wurtzite ZnO or octahedrally coordinated sites (labelled $Zn_i(O)$ and $O_i(O)$ respectively), although the octahedrally coordinated sites have lower formation energies than the tetrahedrally coordinated sites. The dominant native donors are the oxygen vacancy, V_O , and the zinc interstitial, Zn_i [6].

However, while V_O are thought to contribute to the frequently studied and often controversial green band emission in ZnO, studies [20, 21] show that V_O are more likely to be deep donors rather than shallow donors and hence not contributory to the intrinsic n-type conductivity observed in ZnO. Janotti and van de Walle [20] have shown that oxygen vacancies act as deep donors in n-type ZnO (~ 1.0 eV below the bottom of the conduction band) and may act as compensation centres in p-type ZnO. They conclude that V_O is not responsible for the as grown n-type conductivity exhibited in ZnO. Zn vacancies V_{Zn} are also thought to contribute to native donor properties of ZnO. Wang *et al.* [22] conclude that V_{Zn} acts as a deep acceptor in ZnO and suggest that it causes the red band emission in the PL spectrum of ZnO near 1.6 eV but that it does not participate in the green band emission as had been proposed previously.

Theoretical work [21] has suggested Zn interstitials as the dominant shallow donor in ZnO, with two native donor energies (31 meV and 61 meV) being due to Zn interstitials in their tetrahedral and octahedral positions respectively. The PL emission line I_{3a} (see table 3.1 in Chapter 3) is thought to be related to interstitial Zn defects [22].

1.2.2 Extrinsic Defects in ZnO

Extrinsic defects can be introduced by a variety of methods; some may be intentionally introduced (ion implantation, diffusion) and some may be unintentional and incorporated during the growth process. Prominent extrinsic defects in ZnO are commonly studied in an effort to understand dopant dynamics in ZnO and also to understand the origin of the intrinsic conductivity discussed above.

Prominent dopants introduced during the growth processes of single crystal ZnO produced by Cermet (Cermet Inc., USA) ZnO and Eagle-Picher ZnO are Ga, Cu, Si and Al among other elements. Work performed by McCluskey and Jokela [23] has shown the presence of several different impurities incorporated in Cermet and Eagle-Picher ZnO using secondary ion mass spectroscopy (SIMS). In Tokyo Denpa (Tokyo Denpa Ltd., Japan) hydrothermally grown ZnO single crystals concentrations of Fe, Li, K and Al are observed [24]. The Li and K impurities originate from the LiOH and KOH mineralizers used during the growth process [24, 25]. H is a well-known passivator of p-type ZnO and forms shallow donors in ZnO [26] at the bond centred site. H₂ is thought to occur interstitially in ZnO and is electrically inactive in the molecular form, forming after the H migrates through the crystal [27]. It is well established however that bond centred H is thermally unstable above 190°C, with most H in ZnO occurring as molecular H₂ [27].

1.2.2.1 Cationic substitution in ZnO

The Zn site is often the substitutional site for numerous impurities in ZnO. Many of the donor bound exciton lines exhibited in the PL spectrum are due to substitutional atoms on the cation site, such as Al, Ga, and In. Recently, work by Wahl *et al.* [7, 8] and Johnston *et al.* [9] suggests that some elements from group V of the periodic table (As and Sb) occupy the cation site rather than the anion site in ZnO as was

previously thought. These elements have similar atomic size and electronegativities to Zn which may explain why they favour the Zn site over the O substitutional site.

The familiar PL emission lines I_8 and I_9 (see table 3.1, Chapter 3) are due to substitutional Ga and In respectively, acting as recombination sites for neutral donor bound excitons. However, the I_1 and I_2 emission lines also originate from the Ga and In dopants respectively, with I_1 being due to exciton recombination at an ionised Ga donor site, Ga_{Zn}^+ and I_2 at the ionised In donor occupying a Zn site, In_{Zn}^+ . These lines are discussed in more detail in Chapter 3 of this work.

The green band in ZnO is thought to be related to substitutional Cu impurities (Cu_{Zn}). A model for how Cu behaves in ZnO was proposed by Dingle [28] and verified recently [29]. Other work by Wahl *et al.* [30] suggests that annealing samples implanted with Cu will make the Cu impurity less likely to occupy simple substitutional Zn sites as previously thought. In the same work, Wahl *et al.* show a similar effect for Ag doping of ZnO suggesting that elements from the transition metals may not form simple substitutional impurities in ZnO. Wahl *et al.* conclude that, because the lattice sites of the Ag and Cu impurities change with annealing, the Ag and Cu must be interacting with the defects nearby. This also corroborates their suggestion that Ag and Cu do not act as simple substitutional impurities in ZnO but rather form complexes with other atoms [30].

1.2.2.2 Anionic substitution in ZnO

Nitrogen has been, for a long time, thought to be the most promising dopant to produce p-type behaviour in ZnO by substituting on the anion site, replacing an oxygen atom. Much like the case of ZnS and ZnSe, it was hoped that N would form a shallow acceptor replacing the chalcogen, however this does not appear to be the case. Many groups

have tried a variety of doping methods, using various dopant sources to introduce N. Yet, despite several reports of successful p-type doping using N, the lack of reproducibility of these results by other groups, leaves the question still open [17]. N seems to form a deep acceptor rather than a shallow acceptor as in other Zn-chalcogens and although a unique method has been suggested by Yan *et al.* [31] to overcome this problem, successful, reproducible p-type ZnO using N has yet to be realised.

Phosphorus has also been used as a p-type dopant although the larger lattice distortion induced by this defect makes it possibly more likely to incorporate on the Zn site rather than the O site. The Zn-P_O bond length is predicted to be 0.25 Å larger than the Zn-O bond length (1.93 Å) and larger again when compared with the Zn-N_O bond length (1.88 Å) [24]. There are far fewer reports of ZnO achieving p-type conductivity through P doping [6]. Further down the group V column are As and Sb, both of which have been recently shown to substitute for Zn rather than O as discussed earlier [8, 7].

Apart from trying to dope ZnO p-type using substitutional impurities on the anion site, isovalent/isoelectronic impurities are also used to engineer the band gap. In the case of optoelectronic devices it is usually favourable to be able to fine tune the band gap of the material being used and a reliable bowing of the band gap of ZnO has been demonstrated for the cases of Zn_{1-x}OS_x [32], Zn_{1-x}OSe_x [33] and Zn_{1-x}OTe_x [34].

1.3 Codoping of ZnO

Codoping (or intentionally doping with multiple impurities) has been suggested as one potential method of overcoming the p-type doping problem in ZnO [31, 35]. Earlier experiments involving codoping suggest that the solubility of dopants may increase as seen in the case of

ZnO codoped with Ga and N [36] where N had a low solubility limit which was then increased by codoping with Ga. Yan *et al.* [31] however, suggest that codoping can be used to drastically reduce defect levels in wide band gap semiconductors like ZnO and diamond. Hindering the development of p-type ZnO devices is the problem of deep level acceptors, where shallow acceptors are required. The typical approach to overcoming this would be to raise the position of the deep level defect by combining other impurities and bring it closer to the crystal band edge which is considered to be the fixed component. The radical proposal by Yan *et al.* [31] effectively views the band edge as the variable and the defect position as fixed and proposing that the effective band edge position can be altered by incorporating defects or impurities that provide a local attractive potential for either electrons or holes but without having too many or too few electrons for bonding in the crystal. This is where codoping with isovalent impurities is important.

This theory has yet to be demonstrated as a route around the p-type doping problem successfully in ZnO. Although the idea certainly merits further consideration, it does not form the basis of this work specifically.

1.4 Summary and thesis layout

Presented in this work are results obtained for ZnO doped with various impurities which offer the prospect of controlling the electrical properties of ZnO. Specifically we have undertaken a study of the following impurities; Cd, In, As, Ge, Sn and Hg in order to investigate the dopant properties of some lesser understood dopant groups in ZnO particularly the isoelectronic dopants, Hg and Cd alongside some dopants from group IV of the periodic table, namely Ge and Sn. Results of these implantations are presented in subsequent chapters and preliminary analysis carried out.

This work starts by detailing the experimental equipment used in several different laboratories in Europe to study PL in ZnO. Subsequently, in the same chapter (Chapter 2) the method of doping used, ion implantation, is detailed, along with the radioactive variant of this doping method and the consequences such doping techniques can have on the implanted samples.

Chapter 3 outlines some of the principles associated with bound exciton recombination and what the features that are typically observed in ZnO samples, particularly those used for this work which were obtained from Tokyo Denpa Ltd. (Tokyo, Japan).

The results sections are separated into two broadly distinct groups of PL features. First a study on the double donor feature DD_2 , a recently observed line lower in energy than the already studied donor bound exciton lines. This line is the first of a new group of lines, preliminarily labelled the ‘Y-lines’ to be positively chemically identified and a thorough investigation of its PL properties is carried out here. This group of lines presents interesting and unique results which are discussed in detail in Chapter 4.

Subsequently the work diverges into a study of group II_b impurities in ZnO. This is the same group of the periodic table that Zn itself comes from and this group is selected in an effort to observe the rare isoelectronic traps (of which only one has been observed in a single work prior to this work [37]).

Chapter 6 of the study includes recent work on verifying the chemical origin of a prominent donor bound exciton and ionised donor bound exciton recombination feature in ZnO. The origin of one of these features (I_9) had been shown previously [38] using the radiotracer method. However, the ionised component of that line (I_2) was not observed in that work, which is found to have the same half-life dependence as I_9 here. Another feature (I_{10}) is observed which is positively identified as being related to Sn impurities occupying

substitutional Zn sites and acting as a donor bound exciton recombination centre. This line has been previously observed in works but not chemically identified until now.

Chapter 7 presents an overview of future work which is suggested to be carried out as a continuation of the findings in this work. The impurities to be investigated and the techniques used to investigate them are stated and some examples of the results they might have are provided.

All work has been carried out by the author save to the extent that work was performed as a group (for example taking it in turns to record spectra of particularly long half-life dopants implanted while at the ISOLDE facility as explained later). The only part of this work not specifically involving the author was the calculated half-life found for decaying Ga and As in Chapter 4 and for the I₂ and I₉ features in Chapter 6, which were performed by Dr. Karl Johnston of the ISOLDE Collaboration as part of the division of work within the group and where the relevant sources are cited.

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Chapter 2: Experimental techniques

2.1 Introduction

For this work only bulk single crystals of ZnO obtained from Tokyo Denpa Ltd. were used. These samples arrived undoped and were analysed as-received using PL spectroscopy. The PL spectrum (see Chapter 3 of this work) before and after annealing showed the presence of Al impurities (a common impurity in most growth techniques) along with several other unknown bound exciton complexes. The lines observed before and after annealing of these samples were not affected significantly by the doping processes used in this work nor are they the topic for this work, *i.e.* the lines studied here, relating to Hg, Ge, In and Sn are lines that were not present in as-received material.

2.2 Sample details and Preparation

Hydrothermally grown, high quality single crystals of ZnO obtained from Tokyo Denpa are well known to researchers from many institutions investigating the properties of ZnO [1, 2, 3, 4, 5, 6, 7, 8, 9]. For this work samples arrived untreated and undoped (not intentionally doped at least) in the following configurations:

- c-plane,
- a-plane,
- m-plane

A graphic illustration of each of these orientations and the sample sizes is shown below in figure 2.1. Both the c- and m-plane samples had dimensions of 10x10x0.5mm while the a-plane cut sample had dimensions of 10x4x0.5mm. The variation in thickness for these

samples was approximately 10% while the c-axis orientation was accurate to 0.5 degrees [10].

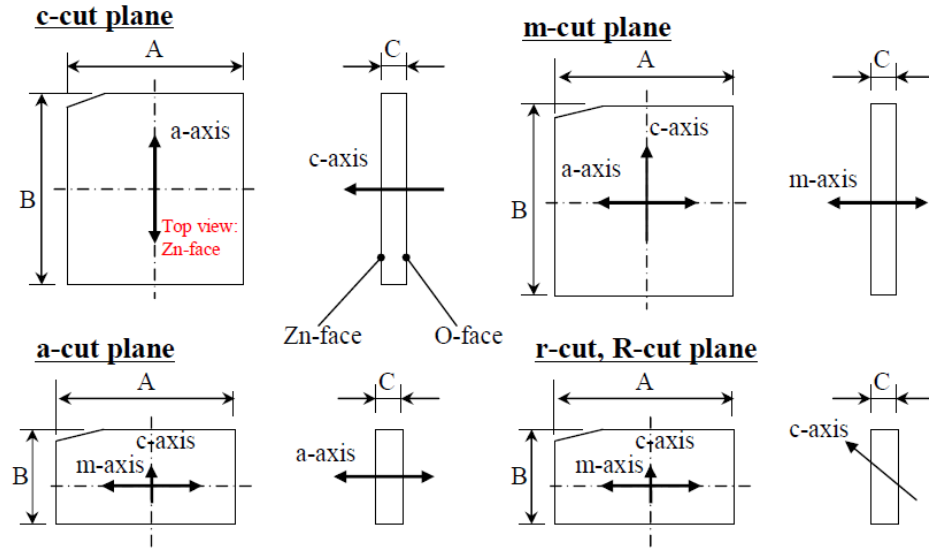


Figure 2.1: Graphic examples of sample size and axial orientation for samples used in this work. Image obtained from Tokyo Denpa Ltd. [10]

Concentrations of certain intrinsic dopants were measured by Tokyo Denpa [10] using glow discharge mass spectrometry and the measured values of dopants listed below in table 2.1.

Table 2.1: Concentrations of intrinsic dopants present in as-received ZnO from Tokyo Denpa. Values received by private communication [10].

	Li	Al	Fe	Si	Mg
Atoms per cm ³	5E15	1E15	5E14	2E17	5E15
	Cu	Cd	Mn	Ni	Cr
Atoms per cm ³	1E15	<1E16	5E15	<5E14	<1E14

Samples were mounted in cryostats and were held in place by PTFE (Polytetrafluoroethylene) tape (DCU), glue (ISOLDE) and silver paste (TU Dortmund). The glue and silver paste were removed by cleaning the samples with acetone in order to remove residue.

2.2.1 Ion Implantation

Ion implantation is a well-studied, efficient, versatile and widely used technique for introducing extrinsic defects in semiconductors. The implantation energy can be varied as can dopant concentration and distribution. Unwanted codoping of other elements is only determined by the purity of the beam and not by the (typically worse) purity of the source material used for diffusion. Unlike diffusion, ion implantation can be performed at relatively low temperatures (room temperature or lower if necessary). In the ideal implantation case a Gaussian profile is expected although this is not normally the case experimentally [11]. Heavier atoms tend to be more limited in range due to the ion losing its kinetic energy to the surrounding electrons and nuclei in the implanted material. Lighter atoms are less likely to interact with the surrounding nuclei of the target material; hence the mass determines the range of the implanted species. When the target material is isotropic and homogeneous, as in a crystal structure, the orientation of the target with respect to the ion beam can be crucial. Targets are often tilted 7° in a direction away from the normal axis of incidence of the implantation beam, in order to avoid channelling effects. In this work some of the samples implanted, as indicated in table 2.3, were tilted in this manner.

ZnO is a radiation hard compound. However, ion implantation energies tend to be higher than the threshold value required to dislodge a substitutional Zn or O atom so that intrinsic defects (vacancies, interstitials, anti-sites, dislocations) can be created. Here doping energies refers to the accelerating energy used on dopants that are being implanted and can range from 10 – 100 keV (or greater) and the binding

energy refers to the energy required to remove a constituent O or Zn atom from its native location in the ZnO crystal. Implantation in this way damages the crystal and this damage must be recovered by annealing the material, typically at high temperature (greater than 500°C). This annealing process can facilitate the diffusion of implanted atoms throughout the crystal moving them to positions in the crystal that are energetically more favourable than their location following implantation.

It should be noted that stable isotope doped samples were used after observing features in PL during work carried out at the ISOLDE facility, as explained in the next section. This was done in order to verify that observed effects were not due to unwanted dopants which can happen from time to time in radioactive isotope doped samples. For example, samples prepared at the ISOLDE facility by implantation of radioactive ^{73}As and ^{73}Ga were not used for further investigation due to the possible co-implantation of unwanted impurities, ^{73}Se for example, and also due to the complicated procedure of transporting radioactive samples to Dublin.

2.2.2 Radioactive Ion Implantation

Radioactive beams were generated using the isotope separator online technique during which nuclear fission produces by-products following the impact of a proton beam on a target (typically UC_x or ZrO and/or a plasma ion source). These isotopes are ionised and then separated using a mass separator in order to produce a beam which is accelerated and used to implant the samples. Ion beams for implantation of this type are normally accelerated to 60 keV for implanting [12, 13] although there are examples of other energies being used in other ZnO-related works, 260 keV for example [14] and 400 keV [15]. These higher energies may have damaged the crystal structure significantly more than lower energy

implantations which may have only partially been recovered during the annealing process.

Typically, radioactive studies of semiconductors involve Mössbauer spectroscopy, perturbed angular correlation (PAC) or emission channelling (EC). A good overview of radioactive ion beam implantation applied to solid state physics is given in [16]. A combination of these radioactive methods with traditional spectroscopic methods such as deep level transient spectroscopy (DLTS) [17], photoluminescence (PL) [12, 14] and diffusion studies [18] has resulted in a new way of characterising semiconductors using already well known techniques.

In this thesis, traditional PL spectroscopy is combined with radioactive ion implantation in order to identify the chemical origin of some of the unknown optical features in the PL emission spectrum of ZnO. The shortcoming of PL (*i.e.* its inability to chemically identify the origin of spectral features) is overcome by correlating the decay (or growth) of certain spectral features with the decay (or growth) of the implanted species. Since the concentrations of the implanted radioactive species change with time in a manner that can be predicted using the already known half-life of the decaying species, in turn a change in intensity of all the PL lines related to the decaying defect containing the radioactive isotope is expected to occur.

PL spectroscopy is an excellent candidate for use in conjunction with radioactive isotopes due to some practical considerations also. The small yields typically obtained in radioactive ion implantation are perfectly suited to PL which can detect weak signals in optical spectra. As a result PL is quite favourable from a safety standpoint. Sufficient yields and adequate mass separation must be achieved before the experimental procedure can begin [19]. As noted above heavy doping is not required for PL to observe significant change but high doses are still required to implant the decaying species in a reasonable time frame.

Half-life considerations must also be taken into account when performing PL in conjunction with radioactive isotopes in this manner. In the case of a short half-life of an hour or less, nearby PL facilities must be available with the ability to run fast scans of the region of the spectrum under investigation. In the case of a broad region of a spectrum that may have been significantly changed by the implanted defect, scans covering the affected region could take long times and result in crucial steps in increase/decrease in intensity of certain spectral features being missed. However, in the case of very long half-lives (weeks, months *etc.*) timing is also an issue as are experimental conditions which have to be repeated on a regular basis. This results in a decrease in reliable PL results since, for instance, if the cooling apparatus is allowed to warm up to room temperature in between scans the quantitative nature of the radioactive decay-related emission from the sample may not be reliable.

Recoil damage after the decay of a radioactive element must be taken into account when performing experiments using radioactive isotopes. Radionuclides have recoil from the decay process when they transmute into their daughter element which can in some cases be enough to force the atom from its position in the crystal lattice. This change in orientation within the structure can have noticeable effects (especially in a technique as sensitive as PL) and so must be taken into account when viewing PL spectra that are changing due to a decaying radioactive isotope.

Müller *et al.* [14] found that the recoil energy for the decay of ^{111}In to ^{111}Cd was not enough to displace an O or Zn atom from its position (although some displacements may occur). This is quite different from the case published by Johnston *et al.* [20] where the recoil energy in the decay of ^{72}Zn was much higher and secondary damage was observed after the implantation and annealing process which was due to the recoil of the daughter element during the decay. The band related to this damage is around the 1.8 eV range (discussed later). In the case of ZnO

the displacement energy is 18 eV for a Zn atom and 45 eV for O atom [21].

In work performed by Gorelkinskii and Watkins [21] electron irradiated ZnO produced two main peaks in PL which were observed at 900 nm and approximately 700 nm, following low temperature irradiation. Annealing at 100 K was enough to remove almost completely the 900 nm band but a band grows in with its peak around 680 nm, corresponding closely with the damage related band observed by Johnston *et al.* [20] in ZnO irradiated during the decay of ^{72}Ga .

While the origin of these bands is still unknown and largely unstudied their presence in the PL spectra of samples which have been implanted with radioactive isotopes and samples that have undergone ion implantation indicates their likely relationship to damage induced emission.

2.3 Experimental details for PL measurements

PL is a highly sensitive technique used to characterise semiconductors. During photoluminescence laser light of an energy greater than the band gap (E_g) of the material is used to excite electrons across the band gap and into the conduction band creating an excess of electron hole pairs. These electron hole pairs (frequently referred to as excitons) recombine within the crystal (see figure 2.2), sometimes at impurity sites as bound excitons if the semiconductor is extrinsically doped with impurities or recombine at structural defect sites or intrinsic defects (described in Chapter 1), and this recombination can result in the emission of an optically detectable photon.

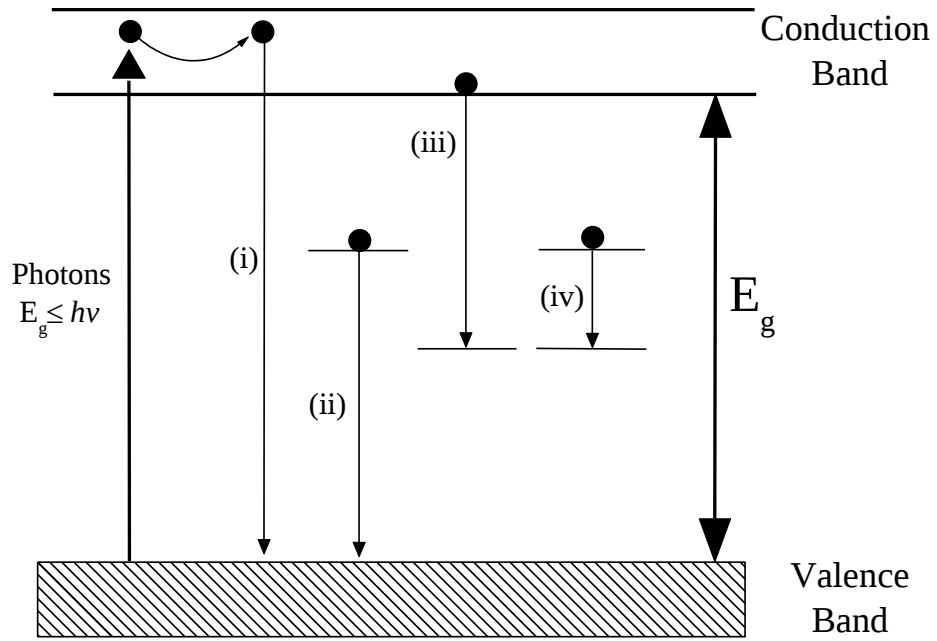


Figure 2.2: Graphical representation of electron-hole recombination in semiconductors (E_g is the value of the band gap). Here the free exciton recombination is seen (i), recombination due to bound excitons (ii), electron to acceptor transitions (iii) and donor to acceptor transitions (iv).

PL is capable of detecting defect related emissions from defect concentrations as low as 10^{10} cm^{-3} [22], very low when compared with other techniques (Hall measurements, Raman studies for example) which require much higher concentrations for detection to be possible.

An exciton can be thought of as an electron coulombically bound to a quasiparticle called a hole. A hole can be thought of as the gap left behind by a vacating electron. This lack of an electron can be treated in many respects as a positive particle with opposite charge to that of the vacating electron.

As mentioned previously, PL measurements for this work were performed in three labs; the Semiconductor Spectroscopy Laboratory in DCU, the PL Laboratory in the ISOLDE Facility at CERN and finally the PL facilities in the Technische Universität Dortmund, Germany.

In DCU two spectrometers are available for use during PL; a SPEX 1704 monochromator from Horiba, Ltd. (formerly known as Jobin-Yvon) and a smaller iHR320 Imaging Spectrometer, also from Horiba, Ltd.

In ISOLDE a SPEX 750 M series spectrometer was used when performing PL measurements, while in TU Dortmund the spectrometer was a Horiba U1000 double monochromator.

2.3.1 DCU PL laboratory arrangement

Two labs were primarily used for the PL data shown in this work; the PL lab in DCU and the PL lab in ISOLDE, CERN. Here, a general overview of the laboratory set up used in DCU is outlined. Photoluminescence is generated using the 325 nm line of a HeCd laser operating at a power less than 200 mW. The luminescence is analysed using a 1m grating spectrometer (SPEX 1704) with a photomultiplier tube (Hamamatsu model R3310-02) in photon counting mode and cooled by a Peltier system EMI FACT50 Cooler to approximately -20°C.

2.3.1.1 Grating:

A grating blazed at λ_B can normally be used adequately over the spectral range

$$\frac{2}{3}\lambda_B \leq \lambda \leq \frac{3}{2}\lambda_B \quad (2.1)$$

The resolution $\Delta\lambda$ of a diffraction grating can be obtained from:

$$\frac{\lambda}{\Delta\lambda} = Nm \quad (2.2)$$

Where N corresponds to the number of grooves in the grating, m is the order of diffraction and λ is the wavelength under observation.

The resolving power of the spectrometer is (theoretically):

$$R_T = \frac{\lambda}{\Delta\lambda} = \frac{\nu}{\Delta\nu} = 2\sin\theta \cos\phi \frac{W}{\lambda} = mN \quad (2.3)$$

where ν is the wavenumber and W is the width of the grating ruling.

This results in a resolving power of, for example, 8.3 Å/mm at 4282 Å [23]. The general layout is graphically illustrated in figure 2.3.

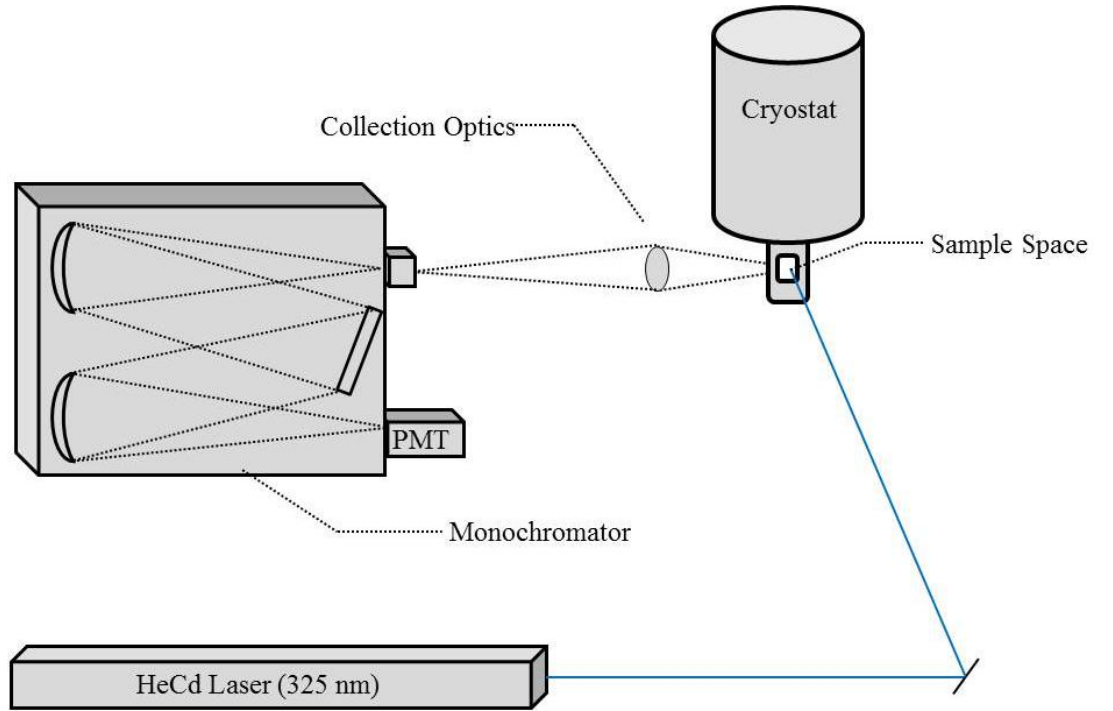


Figure 2.3: The laboratory set up for the PL lab in DCU.

The equipment and layout used in DCU are fundamentally similar to layouts used in most PL labs. A laser is used to excite the sample with a wavelength greater than the band gap of the sample and the sample is typically cooled in a cryostat to around 10K. The luminescence emitted by the sample due to recombination of excitons after excitation is focused through the entrance slits of a spectrometer which uses a diffraction grating to analyse individual wavelengths. The light from the diffraction grating is directed onto the exit slit of the spectrometer which

leads to a detector (in this case a photomultiplier tube). This photomultiplier tube (PMT) is used in photon counting mode and transmits a signal containing the data it gathers for each wavelength value to the software used by the computer for the user to interpret those data. The data are then analysed by the user and a PL spectrum obtained.

2.3.1.2 Spectral response of the SPEX1704 system

The intensity of the emission spectrum in this work is limited by two internal factors, the efficiency of the photomultiplier tube (PMT) and the efficiency of the diffraction grating. The grating used for this work (in DCU) was a 330 nm blazed ruled diffraction grating with 1200 grooves mm^{-1} (ISA Model 510-05). This grating is discussed in more detail in [24].

The PMT (Hamamatsu Model R3310-02), configured for photon counting, has a wide spectral range of 300-1040 nm [25]. It incorporates an InGaAs(Cs) photocathode and linear focused CuBeO dynodes [25]. Along with this wide spectral sensitivity the PMT is well suited to use for PL experiments because of its low dark current count (just 30 counts per second at -20°C [25]) listed as just 5 nA by the manufacturer. Figure 2.4 shows the efficiency curves for the PMT and the grating used in the DCU lab. Equations representing these curves can be found in Appendix A of [24].

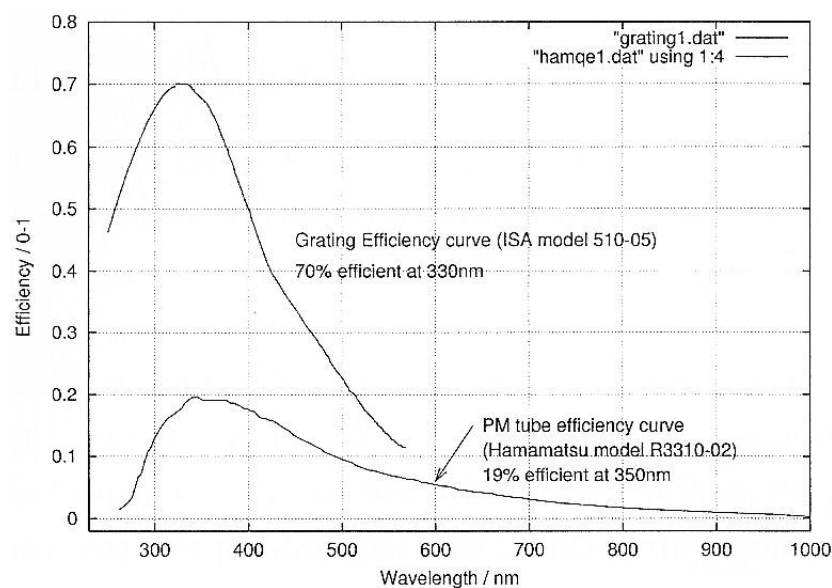


Figure 2.4: Efficiency curves for the PMT and diffraction grating used in this work taken from [23]. Equations representing these curves can be found in Appendix A of [23].

No spectra presented as part of this work were calibrated for the spectral response of the system used due to the small effect over the narrow wavelength range observed here.

2.3.1.3 iHR320 spectrometer at DCU

An iHR320 spectrometer fitted with 1200 and 2400 groove gratings were used to record spectra of samples under stress. With a resolution of 0.07 nm when using the 2400 groove/mm grating which was the grating used mostly for this work [26]. The detector is a Peltier-cooled Andor Newton EM-CCD which nominally cooled the detector to approximately -30°C.

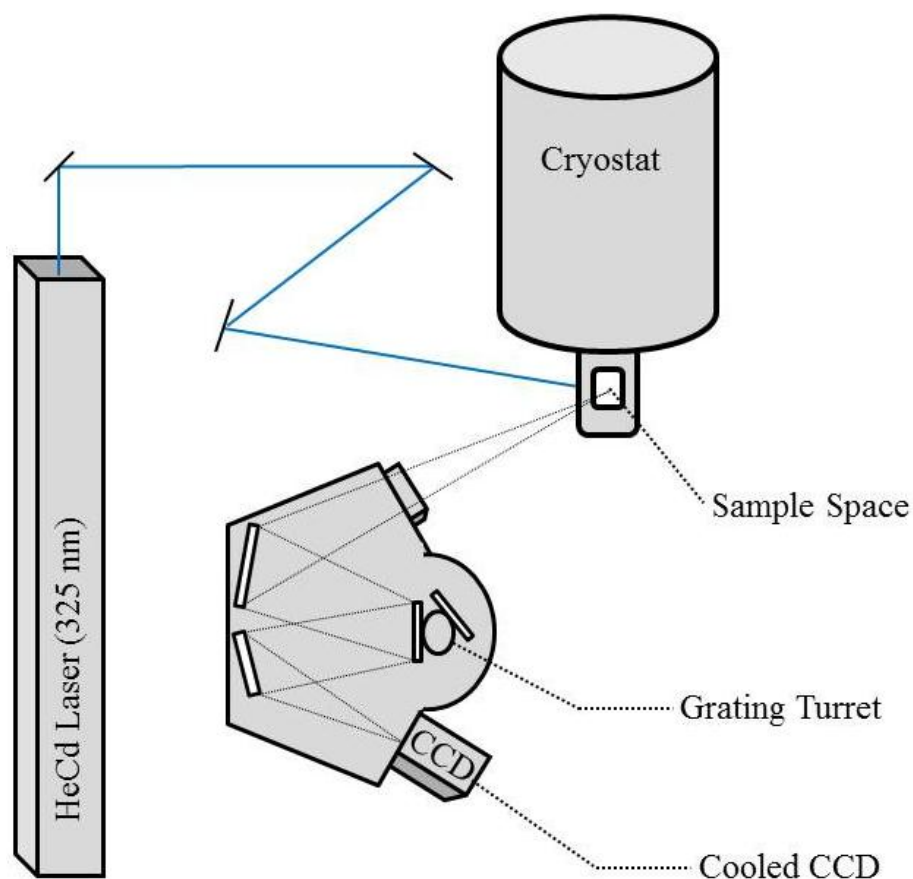


Figure 2.5: *PL configuration for use with the iHR320 spectrometer in DCU.*

2.3.2 ISOLDE Laboratory Arrangement

The PL lab used at ISOLDE is similar to the one in use at DCU but with some noteworthy differences. Luminescence is generated by the 325 nm line of a HeCd laser operation at 80 mW power. The cryostat is a Janis closed cycle cryostat and is capable of reaching temperatures of less than 4 K. The luminescence is analysed by a SPEC 0.75 m grating spectrometer equipped with a liquid nitrogen (LN₂) cooled Jobin-Yvon CCD detector.

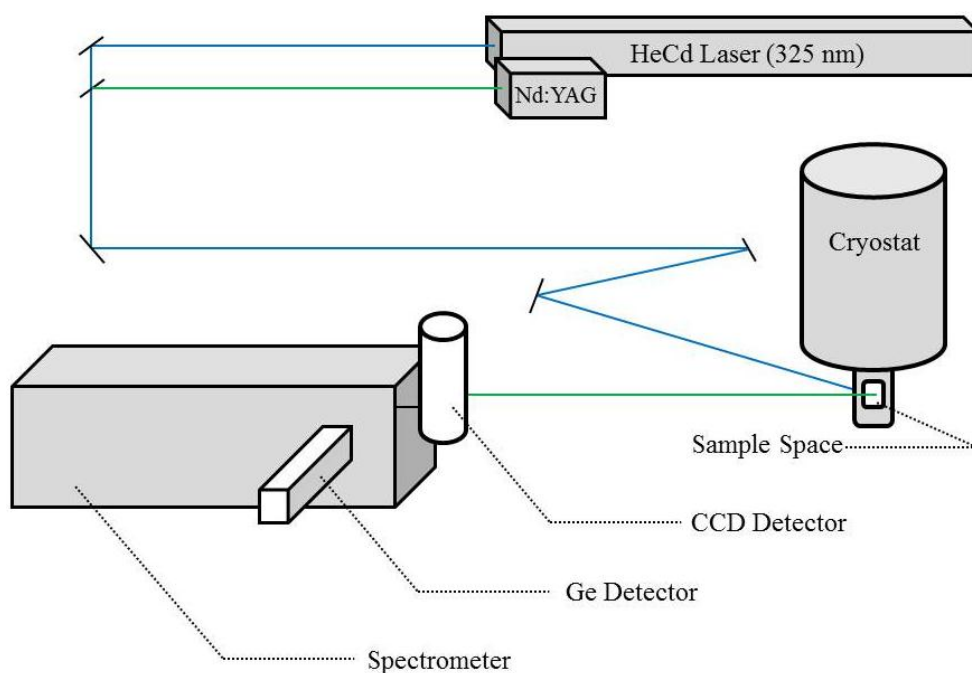


Figure 2.6: Graphical reproduction of the laboratory used in ISOLDE for PL measurements.

Figure 2.6 shows the set-up used in ISOLDE. Replacing the PMT used in DCU are two detectors; a Ge-detector, better for use at longer wavelengths and a LN₂-cooled Jobin-Yvon CCD detector for use closer to the band edge wavelength range of ZnO. The CCD detector is more suitable for work on samples that have been implanted with radioactive isotopes due to the system's ability to take the emission spectrum in much less time than a system using a PMT would take.

The diffraction grating used was 1800 grooves mm⁻¹ blazed at 400 nm. A further grating, blazed at 1.2 μm with 600 lines mm⁻¹, is available (but was not used) in ISOLDE should there be a requirement for it. Spectra recorded at the PL lab in ISOLDE were not corrected for the spectral response of the system.

2.3.3 Technische Universität Dortmund laboratory details

A schematic representation of the experimental set-up used is shown below in figure 2.7. The sample was inserted in a 7 T split-coil magnet cryostat from Oxford Instruments. The sample holder had a spherical mirror with 1.6 cm focus and 1.6 cm aperture; the lens in front of the spectrometer had an 8cm focus, so that we should have a magnification of the laser spot. As an excitation source we used the second harmonic (LBO crystal) of an optically pumped (Verdi 10 Watt laser from Coherent) Ti:Sapphire laser from Tekhnoscan (Russian company from Novosibirsk). The spectrometer is a Horiba (formerly known as Jobin-Yvon) U1000 double monochromator. For the detection a R943-02 Hamamatsu photomultiplier tube was used.

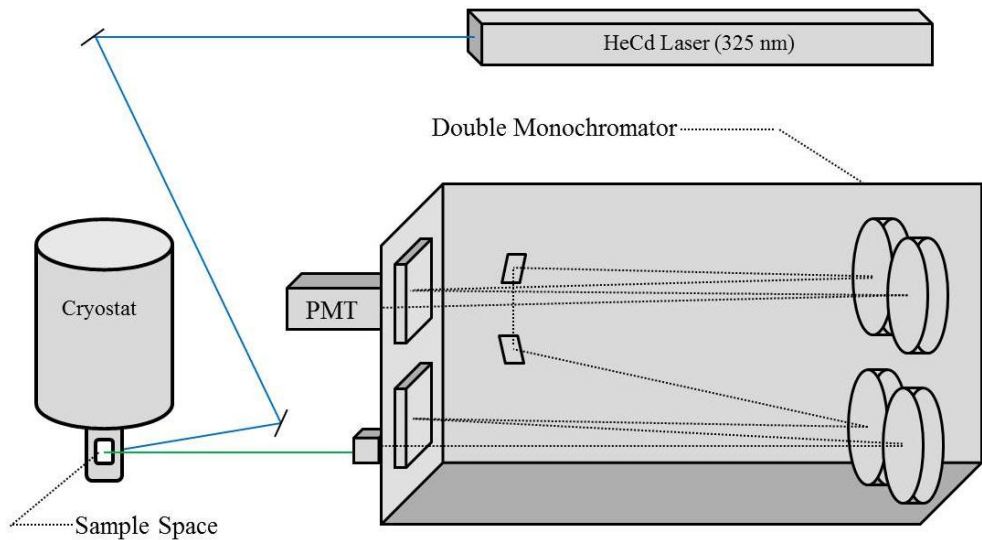


Figure 2.7: Graphical representation of the double monochromator used during PL measurements performed at TU Dortmund.

2.3.4 Piezospectroscopy apparatus in DCU

Uniaxial stress measurements (commonly called piezospectroscopy) were performed in order to investigate the symmetry of defect features

observed in this work by compressing single crystal samples along several crystal axes.

A vertically balanced sample was mounted, typically in slots designed specifically (in the Dept. of Physics mechanical workshop in DCU) for the dimensions of the samples used, between two steel pistons. These pistons were part of a sample rod modified for use in the closed-cycle cryostat (Janis Corporation, model SHI-950-5) in DCU. A piezoelectric load cell (Bofors KRA-1), produced an output voltage proportional to the force applied on the sample through the rod. A steel ball-bearing was using at the base of the load cell to transfer the force of the spring loading mechanism without transferring the twisting motion of the threaded bar to the piston. The stress apparatus used in this work is described previously in [27] and displayed in figure 2.8.

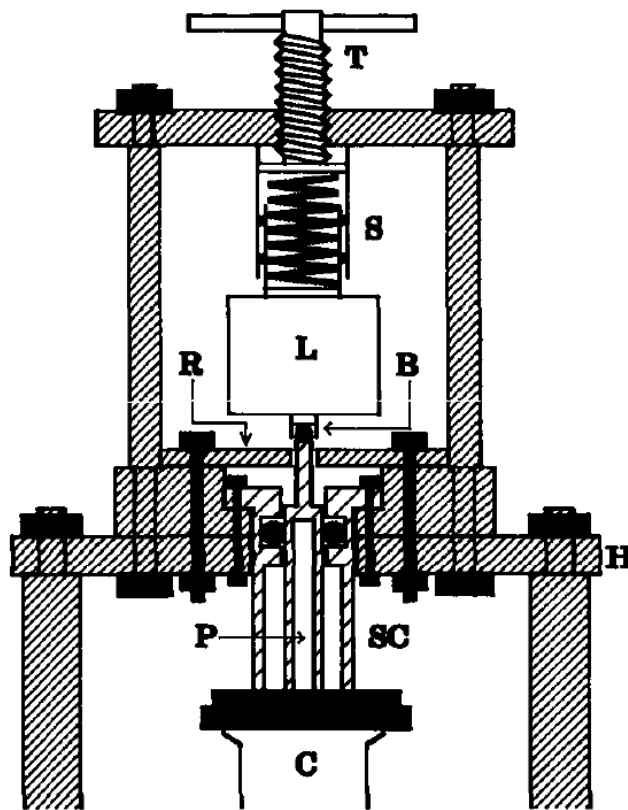


Figure 2.8: Schematic diagram of the apparatus used to generate uniaxial stress on ZnO single crystals in this work. The letters stand for: T, threaded bar; S, steel spring; L, load cell; B, retained steel bar; P, push rod; SC, stress cell; C, cryostat. From [27].

While every effort was made to maintain the consistency of the stress rig apparatus measurements, improvements to the apparatus were ongoing throughout this work. For this reason higher stress values (~ 1 GPa) were not available for all uniaxial stress experiments in which cases only data up to ~ 300 MPa are available.

2.3.5 Zeeman Spectroscopy in DCU and TU Dortmund

Two separate single coil superconducting magnets were used to perform Zeeman experiments in this work. Primarily measurements were performed in the Semiconductor Spectroscopy Laboratory in DCU with further measurements required in TU Dortmund due to a vacuum failure with the magnet in DCU. Here the apparatus is described.

In DCU Zeeman measurements were made on a single coil Oxford Instruments SMD6 superconducting magnet, up to a maximum field of 7 T, while in TU Dortmund the sample was mounted in a 7 T split-coil magnet cryostat also from Oxford Instruments.

The magnet arrangement in DCU for optical experiments is more complicated than the split-coil set-up used in TU Dortmund and so extra care had to be used in order to maximise the light signal emitted; the experimental set up is shown in figure 2.9.

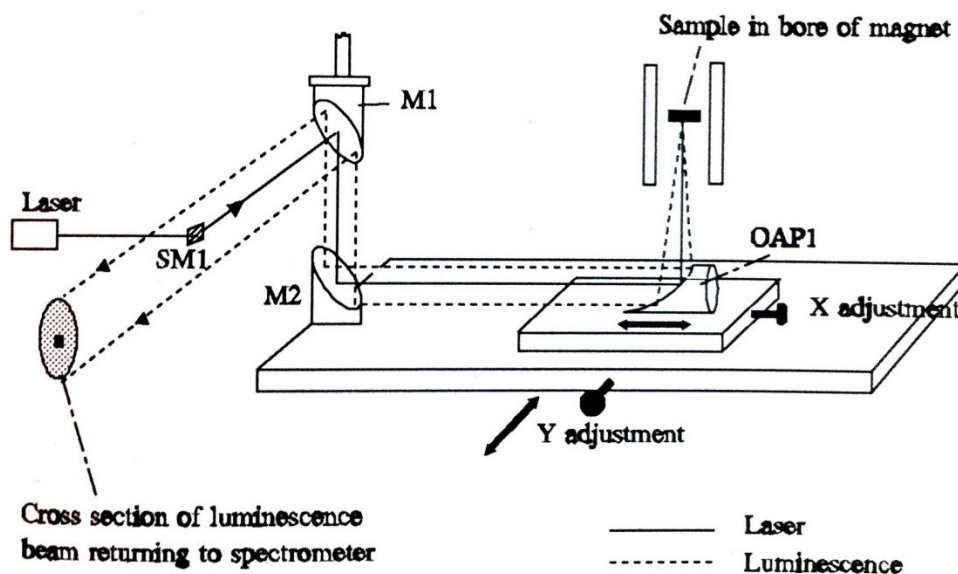


Figure 2.9: Schematic diagram of the optical path taken by the laser light incident on the sample and the resultant luminescence path back to the optical fibre of the CCD spectrometer. Taken from [28].

The laser light was directed inside the liquid-He cooled sample space of the magnet using a curved mirror (labelled OAP1 in figure 2.9) with fine adjustments possible on apparatus labelled SM1, M1 and OAP1, ensuring accurate adjustments could be performed after mounting different samples in the cryostat.

Small hand mirrors were used to verify the laser light was incident upon the sample. The luminescence generated then travelled back along the path indicated by the dashed lines in figure 2.9. The adjustable mirror (SM1) blocked little of the path used by the returning luminescence. The luminescence was focussed onto the entrance slit of the iHR320 spectrometer shown in figure 2.5.

A split-coil set-up used in TU Dortmund was significantly easier to use. The experimental set-up is shown in figure 2.7 where the superconducting magnet is incorporated in the cryostat above and below the sample space. While split-coil arrangements are limited to smaller magnetic field values than single coil set-ups although a magnetic field of 7 T (70 kG) was achieved in both DCU and TU Dortmund.

2.4 Implantations carried out as part of this work

Detailed below in table 2.2 and table 2.3 are the ion implantations (of radioactive and stable ions) performed as part of this work. Table 2.2 highlights (in orange) the elements of the periodic table of interest in this work. These elements focus on the group III donor impurities, the group IV donor impurities and the isoelectronic group IIb impurities in ZnO, as well as As which was investigated as part of the work investigating Ge.

		III _A	IV _A	V _A	VI _A	VII _A
		B	C	N	O	Cl
I _B	II _B	Al	Si	P	S	Fl
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi	Po	At

Table 2.2: Highlighted on the periodic table of elements are Zn and O (green) and the chemical dopants investigated in this material throughout this work (in orange). Group III and group VI have been extensively studied in ZnO thus far but still dopant dynamics are not fully understood.

Some implantations (namely those of stable ions that were implanted at Surrey Ion Beam Centre, England and those performed by Kroko Implantations in the United States of America) were implanted at 7° from the normal (the reasons for which are detailed earlier in §2.4 of this chapter), while implantations of radioactive isotopes in ISOLDE were implanted incident approximately normal to the sample. Radioactive samples are investigated solely in the PL lab in ISOLDE while stable ion implanted samples were analysed in DCU, ISOLDE and TU Dortmund.

Dopant Details				Sample Preparation		Implantation Process Details			
Implanted Species	Radioactive	Daughter Isotope	Half-Life	Annealing Conditions	Laboratory	Ion Fluence	Energy	Angle of Implantation	Implantation Facility
^{117}Ag	Yes	^{117}Cd	72.8 s	Annealed in vacuum for 20 minutes at 830°C	ISOLDE DCU	$5 \times 10^{12} \text{ cm}^{-2}$	60 keV	N	ISOLDE
^{73}As	Yes	^{73}Ge	80.3 days	Annealed in vacuum for 30 minutes at 800°C	ISOLDE	$5 \times 10^{12} \text{ cm}^{-2}$	60 keV	N	ISOLDE
^{74}Ge	No	-	-	Annealed in an O ₂ atmosphere for 30 minutes at 700°C and subsequently 750°C for 30 minutes	DCU	$1 \times 10^{13} \text{ cm}^{-2}$	100 keV	7°	University of Surrey Ion Beam Centre
^{74}Ge	No	-	-	Annealed in O ₂ for 30 minutes at 750°C	DCU	$1 \times 10^{13} \text{ cm}^{-2}$	100 keV	7°	Leonard Kroko, Inc.
^{74}Ge	No	-	-	Annealed in O ₂ for 30 minutes at 750°C	DCU TU Dortmund	$1 \times 10^{13} \text{ cm}^{-2}$	100 keV	7°	Leonard Kroko, Inc.
^{200}Hg	No	-	-	Annealed in air for 30 minutes at 750°C	DCU TU Dortmund	$1 \times 10^{12} \text{ cm}^{-2}$	60 keV	7°	University of Surrey Ion Beam Centre
$^{199\text{m}}\text{Hg}$	Yes	^{199}Hg	43 mins.	Annealed in air for 30 minutes at 750°C	DCU TU Dortmund	$1 \times 10^{12} \text{ cm}^{-2}$	60 keV	N	ISOLDE

Table 2.3: Details of implanted species and their radioactive daughter isotopes (if any) used for this work.

2.5 References

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Chapter 3

Luminescence processes in ZnO

Semiconductor crystals under observation during PL at low temperatures have complex spectral emissions in the near band gap region resulting from excitonic trapping and associated effects. Here, in preparation for the subsequent experimental results to be discussed as part of this work, how these spectral features can be interpreted is outlined.

3.1 Introduction

As mentioned previously, PL is a highly sensitive technique used commonly in semiconductor characterisation both at room temperature and low temperature. In the low temperature regime (5 – 20 K in this case), the thermal broadening and deactivation effects, exhibited by luminescence features at higher temperatures, are reduced and bound exciton recombinations dominate the PL emission, resulting in a rich spectrum of features. Exciton binding energy in ZnO tends to follow the trend:

$$E_{D^+X} < E_{D^0X} < E_{A^0X} \quad (3.1)$$

Where D^+X , D^0X and A^0X are the notations used for an ionised donor bound exciton, a neutral donor bound exciton and a neutral acceptor bound exciton complex, respectively. This ordering is determined by the electron and hole effective masses, which are $0.28 m_0$ and $0.58 m_0$ in ZnO, respectively [1], where m_0 is the free electron mass. The same trend is exhibited by other semiconductors such as CdS [2], although this trend is not always precise, such as for the case of CdSe and ZnSe where D^0X features have a smaller binding energy than D^+X features [3, 4].

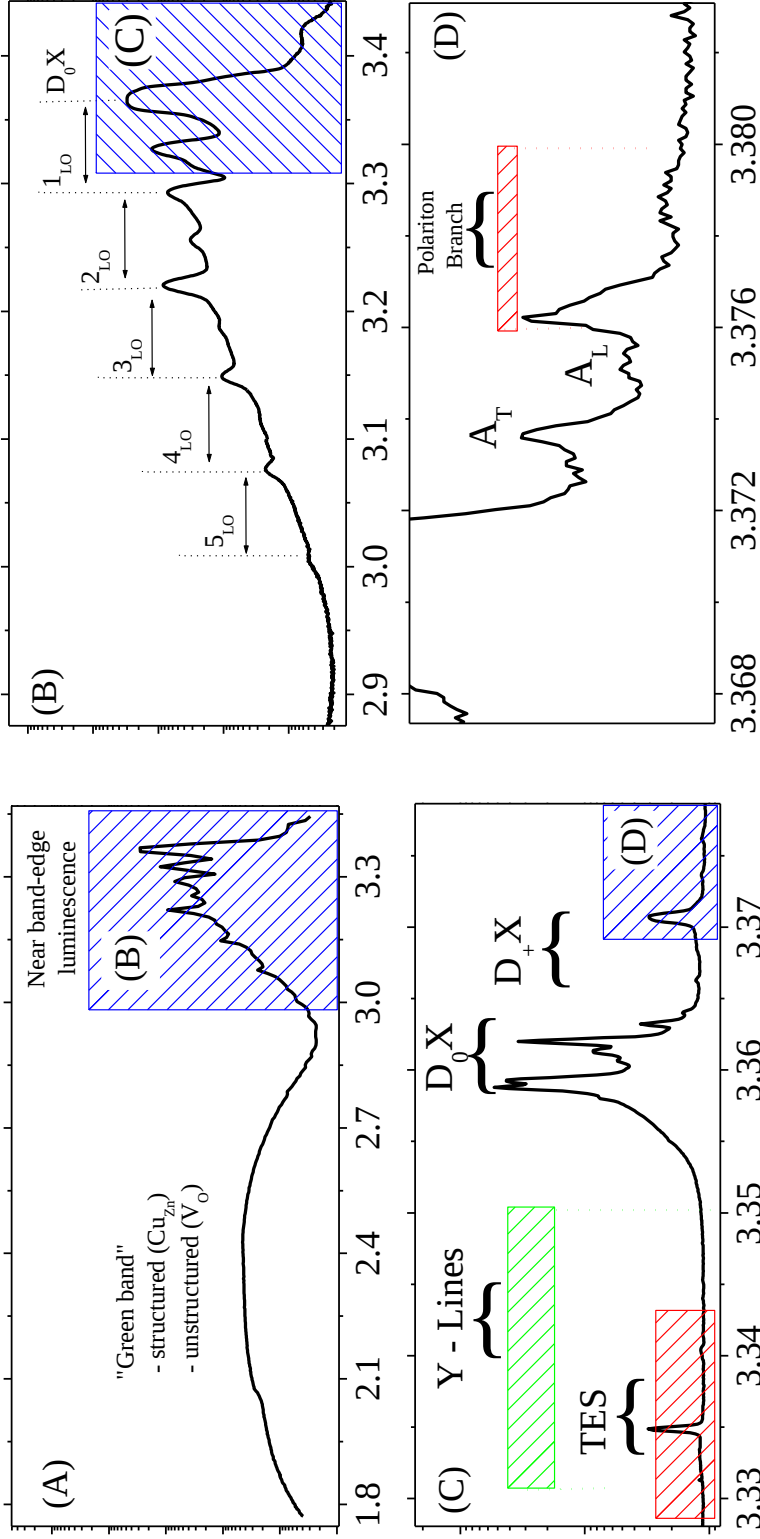
This trend, for the case of ZnO, is exhibited in the PL spectrum with the highest energy bound exciton recombinations being ionised donor bound exciton recombinations (D^+X), followed by neutral donor bound exciton recombinations (D^0X) and finally acceptor bound exciton recombinations (A^0X) although evidence for these is scarce. This decrease in emission energy corresponds to an increase in binding energy. Excitons are unlikely to bind to an ionised acceptor since a neutral acceptor and a free electron is energetically more favourable [5]. Bound exciton complexes have no translational motion freedom resulting in very sharp lines, observed in the small FWHM values of optical features for semiconductors produced with a high crystal quality. Inhomogeneous lattice strain and a high concentration of impurities in crystal structures can increase the FWHM of luminescence features in semiconductors.

3.1.1 Overview of ZnO PL characteristics at low temperatures

Some typical ZnO PL emission features are highlighted in Figure 3.1. The sample used was an undoped ZnO sample from Tokyo Denpa Ltd. (Tokyo, Japan) which was annealed at 750°C in O₂ for 30 minutes before being cooled to 10 K to record the PL spectra. As seen in Figure 3.1 (A) the PL emission can easily be divided into the near band edge luminescence already mentioned and a broad structure centred around 2.4 eV, the so-called “Green Band”.

While the Green Band does not form any part of this study its appearance is worth mentioning due to the ubiquitous nature of the Green Band in most ZnO samples regardless of the growth technique used [6, 7, 8, 9]. The origin of the green band in its unstructured form (often observed in unannealed samples [10]) is thought to be related to oxygen vacancies (V_O). The structured form of the Green Band seems to be of a fundamentally different nature, involving Cu, as shown by Dingle [7] and confirmed by Byrne *et al.* [11].

PL Intensity (Arb. Units, log scale)



Energy (eV)

Figure 3.1: Typical PL spectrum of an as-received and annealed ZnO crystal. In (A) a broad spectral scan reveals the near band edge luminescence and the commonly observed green band feature. (B) highlights the shaded region of (A) and shows the LO phonon replicas which are the dominant relaxation mode of exciton recombination. (C) highlights the near band edge luminescence in greater detail revealing the dominant D_0X region while (D) shows the free exciton recombination and polariton branch also commonly observed in ZnO. Spectra were recorded at 10 K.

The role of Cu occupying a substitutional Zn site has been clearly shown which results in a strong, sharp characteristic ZPL and an associated LO-replica band [10, 11].

The near band edge region observed in figure 3.1 (A) is highlighted in (B) where a clear LO-phonon series is observed for the donor bound exciton. The LO phonon is the dominant lattice relaxation in ZnO during PL and LO phonon replicas for most near band edge features are distinguishable. The LO phonon energy in ZnO is found typically to be between 71-73 meV [12, 13].

Figure 3.1 (C) shows the most studied region of ZnO PL spectra. The ionised and neutral donor bound exciton features are indicated as well as the Y-Line region and two-electron satellite (TES) transitions explained below.

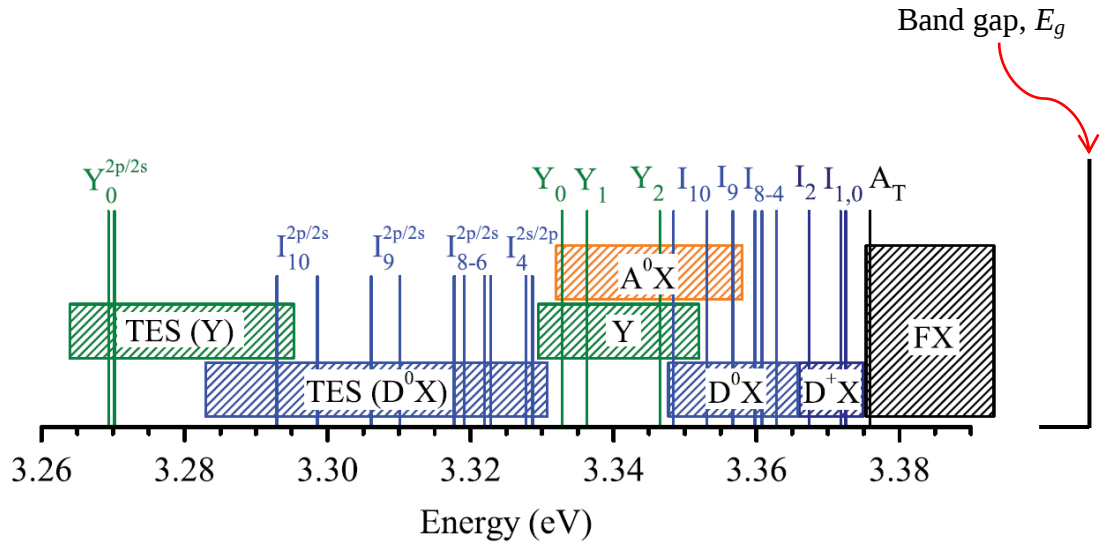


Figure 3.2: Distribution of the most frequently observed PL features in ZnO in the near band edge region, ranging from the higher energy free exciton and bound exciton features to the lower energy two electron satellites of donor bound exciton recombinations and Y-lines. The emission energies of some commonly observed lines in PL spectra are also indicated. Taken from [6]. The band gap, E_g , is also indicated at 3.436 eV.

The Y-line region is tentatively named as such based on recent work [6] suggesting that newly observed exciton recombination lines in this region, lower in energy than the D^0X or A^0X features, are in fact similar to those previously observed in ZnSe [14], which were suggested to be due to extended lattice defects, and labelled as Y-lines. Due to the prevalence of these lines in high quality crystals more work is required before unambiguous defect classification can be made. The TES features in Figure 3.1 (C) are readily distinguishable from the Y-lines because of the sharp FWHM of the Y-lines as compared to TES transitions which are much broader peaks.

Finally, Figure 3.1 (D) shows the free-exciton region of the PL spectrum where the higher (A_L) and lower (A_T) energy free excitons are observed, where A_L and A_T stand for longitudinal and transversal free A-exciton respectively. When discussing localisation energies later in this work the energy of the lower (A_T) exciton is used.

A series of photoluminescence emission lines situated between 3.373 eV and 3.350 eV of the photoluminescence spectrum of ZnO [15], labelled I_0 - I_{11} have been studied extensively, some of which are the subject of this work. The positions of several of these I_n lines are indicated graphically in Figure 3.2 above, indicating their close proximity to the band edge, E_g , along with their broad classification. Related features such as TES transitions are also indicated. However, the chemical identity of many of these lines is still unknown (see table 3.1).

TES emissions are transitions involving exciton recombination at a neutral donor site which leaves the donor in an excited state; an example is shown in Figure 3.3, the inset of which indicates graphically the mechanism for TES features. There is a difference in energy therefore equal to the difference between the first excited and ground states of the donor.

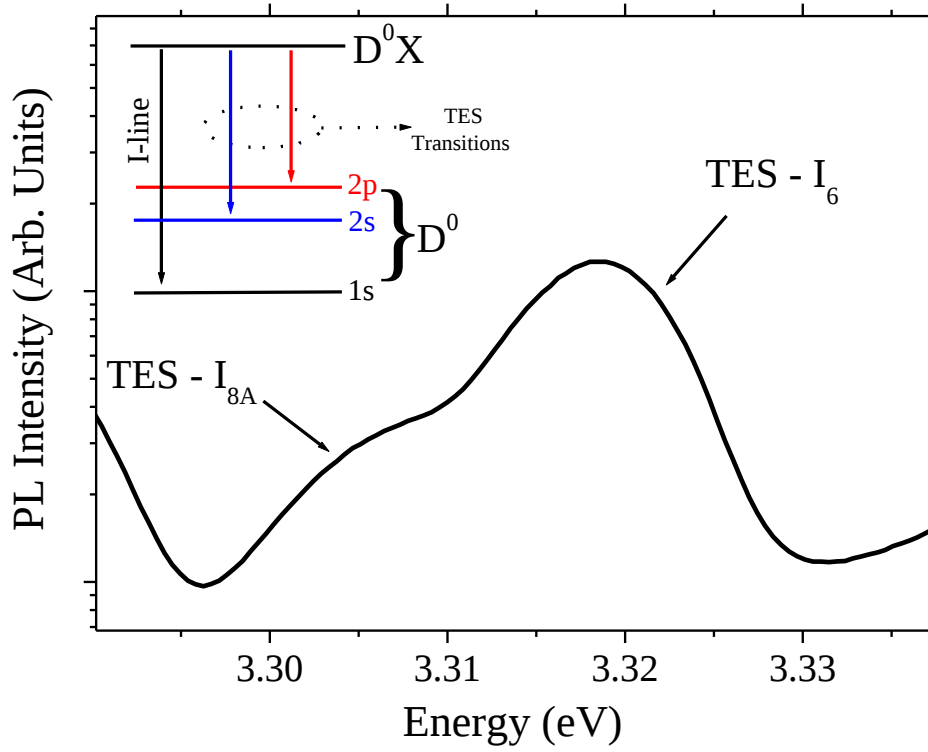


Figure 3.3: Typical PL spectrum of undoped virgin ZnO from Tokyo Denpa exhibiting TES features relating to two prominent D^0X features in ZnO. Inset is a graphical representation of the TES recombination mechanism. D^0 indicates the neutral donor core without a bound exciton.

I_0 is thought to be due to the recombination of excitons at ionised Al donor impurities (denoted Al_{Zn}^+) where the Al substitutes a Zn atom. Zeeman measurements have shown I_1 , I_2 and I_3 to be due to the recombination of excitons bound to ionised donors [16] which suggests that this region of the spectrum is where ionised donor features may be present for other impurities also.

Table 3.1: *Free and bound exciton recombinations and selected related properties. TW denotes features studied as part of this work. Wavelengths, energies and localisation energies taken from [17] for lines not studied in this work.*

Line	Wavelength (nm)	Energy (eV)	Localisation energy (meV)	Chemical identity	Reference
A_T^*	367.19	3.3770	-	-	[TW]
I_0	367.77	3.3717	3.4		[TW]
I_1^{**}	367.71	3.3718	4.1	Ga ⁺	[18]
I_{1a}	368.13	3.3679	8.0		
I_2^{**}	368.35	3.3664	8.5	In ⁺	[TW]
I_3^{**}	368.29	3.3665	9.4		
I_{3a}	368.34	3.3660	9.9		
I_4	368.34	3.3628	13.1	H	
I_5	368.86	3.3614	14.5		
I_6	368.92	3.3612	15.1	Al	[TW]
I_{6a}	368.96	3.3604	15.5		
I_7	369.01	3.3600	15.9		
I_8	369.03	3.3598	16.1	Ga	[18]
I_{8a}	369.08	3.3593	16.6		
I_9	369.37	3.3567	19.2	In	[19]
I_{10}	369.76	3.3543	22.8		[TW]
I_{11}	370.28	3.3484	27.5		

* A_T is the transversal free A-exciton state which acts as the reference line used to calculate the localisation energy value.

** I_1 , I_2 and I_3 are assigned to ionised donor bound exciton emissions [16].

The dominant neutral donor bound exciton recombinations in hydrothermally grown ZnO are the I_5 and I_6 lines [20, 21, 22]. I_5 has not yet been assigned to any particular donor. Although its presence in ZnO doped with Pb has been noted, further work is required for a convincing assignment [20, 23]. I_3/I_{3a} is also observed in some samples used in this work, however, these lines appear to overlap and no adequate separation has been achieved. I_3 is thought to be another ionised donor bound recombination [16] whereas I_{3a} may be due to recombinations at Zn interstitial sites (Zn_i) [15, 24]. I_4 is also labelled in Figure 3.2 and is thought to be related to H impurities which are incorporated during the growth process [25].

The I_6 and I_0 features are prevalent in all samples used in this work. These well understood features [15, 20, 26] have been all but unambiguously identified as being related to neutral (I_6) and ionised (I_0) Al impurities occupying Zn sites in ZnO [27, 28]. The prevalence of Al is well understood considering the presence of Al during most growth methods [29], of which the hydrothermal method is no exception, as highlighted in Chapter 2 of this work. The occurrence of the I_0 emission is likely due to ionisation of Al donors by nearby Li and Na impurities which remain in the crystal from their use as mineralizers during hydrothermal growth [21, 30]. These Al-related lines are observed in all samples used for this work and are used in many cases as a direct comparison of normal I_n line behaviour to the behaviour of newly observed features discussed in this work (comparison of shift rates under stress, thermalisation, localisation, *etc.*).

The lines I_2 and I_9 are studied in this work and chemically identified as being related to In occupying a substitutional Zn site (In_{Zn}) in the ionised (I_2) and neutral (I_9) donor states, although the I_9 feature was previously unambiguously shown to be related to In [19]. In much the same manner, the lines I_1 and I_8 were shown to be related to Ga donor impurities in ZnO [18], with the higher energy feature (I_1) due to exciton recombination at the ionised donor site and the lower energy

(I₈) feature due to the donor impurity in the neutral state. All four of these lines (I₁, I₂, I₈ and I₉) were identified using radiotracer PL [18, 19, 31]. I₁₀ is also discussed in this work and is proposed to be due to neutral Sn impurities occupying a substitutional Zn site following the decay of In to Sn as discussed in Chapter 6.

3.1.2 Room temperature PL of ZnO

The room temperature PL emission spectrum for ZnO is dominated by two features which also occur in the low temperature spectrum but with some differences. Representative spectra of virgin ZnO from Tokyo Denpa are shown in Figure 3.4 for the low temperature regime (A) and the room temperature emission (B). The main peak at room temperature, located at approximately 3.25 eV, is composed of the free exciton recombination line and its LO-phonon replicas.

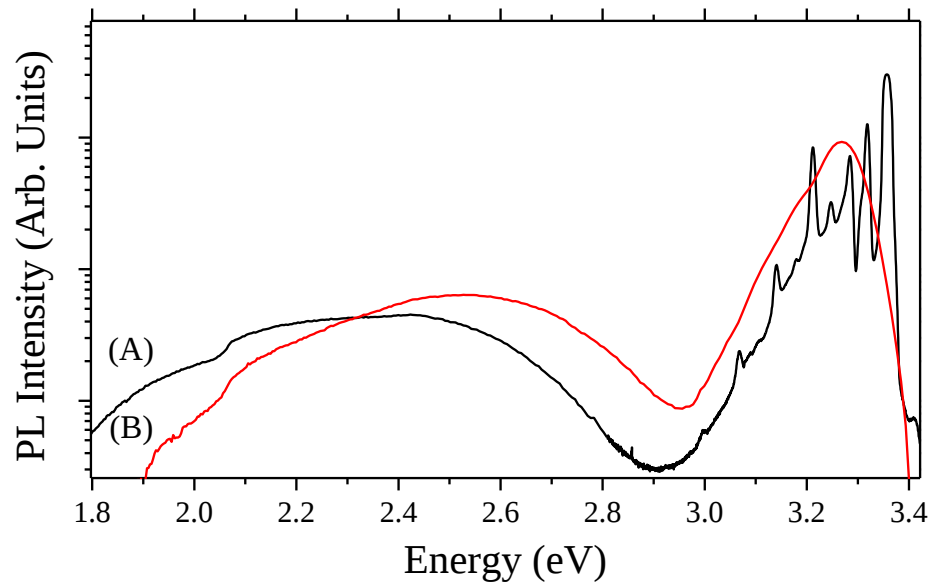


Figure 3.4: (A) low temperature (10 K) PL spectrum and (B) room temperature PL spectrum of virgin ZnO from Tokyo Denpa.

The maximum of this main peak at room temperature corresponds not to the free exciton recombination but rather the first LO-phonon replica of

the free exciton line which is not distinguishable from the rest of the peak [32]. The low-temperature spectrum has been discussed previously in §3.1.1 of this chapter and is shown only for visual comparison in figure 3.4

Emerging at 2.9 eV and extending to lower energies in Figure 3.4 (B) is the green emission band, the peak intensity of which has shifted slightly with temperature. It should be noted that a dip occurs in the spectrum just below 2.1 eV; this is a spectral artefact from within the Spex1704 spectrometer discussed in Chapter 2.

3.2 Temperature dependence

The band gap properties of semiconductors are often those of most interest for commercial applications and, as such, they have been extensively investigated for most semiconducting materials. For the purpose of this work an understanding of the processes that occur during the formation of excitons and subsequent recombination of those excitons throughout the crystal is required, including temperature effects.

The temperature dependence of semiconductor properties has been studied extensively and ZnO is no exception. The band gap of ZnO, for example, changes from 3.37 eV at 300 K to 3.44 eV at low temperatures [9, 33]. However, the temperature dependent behaviour studied in this work mostly involves the behaviour of bound exciton complexes at low temperature as discussed in the next subsection.

3.2.1 Temperature dependence of PL features

The temperature dependence of bound exciton populations at defects is of interest in this work, and is put to good use in calculating the thermal deactivation energy of certain defect centres in the near band edge

spectra, which acts as a measure of the strength of the exciton binding mechanism.

In order to arrive at an equation useful for the data analysis we start our derivation under the assumption that the probability at a temperature (T) of bound excitons forming is given by

$$p(T) = \frac{1}{1 + \left\{ g \exp \left(-\frac{\Delta E}{kT} \right) \right\}} \quad 3.2$$

where $p(T)$ is the probability of an electron-hole pair occupying a bound exciton state as a function of temperature, ΔE is the exciton binding energy relative to the free exciton energy and g is the concentration of free exciton states relative to that of the bound exciton states in the crystal [34]. Using this, we can model the intensity of emission due to exciton recombination as a function of temperature at a defect site as

$$I(T) = \frac{A}{1 + \left\{ g \exp \left(-\frac{\Delta E}{kT} \right) \right\}} \quad 3.3$$

where A is a constant of proportionality that includes factors such as capture coefficient and radiative efficiency.

In the limit of very low temperatures, the factor

$$\exp \left(-\frac{\Delta E}{kT} \right) \sim 0 \quad 3.4$$

and we have

$$I(T = 0) = I(0) = A \quad 3.5$$

Therefore, equation 3.3 becomes

$$I(T) = \frac{I(0)}{1 + \left\{ g \exp \left(-\frac{\Delta E}{kT} \right) \right\}} \quad 3.6$$

$$\frac{I(T)}{I(0)} = \frac{1}{1 + \left\{ g \exp\left(-\frac{\Delta E}{kT}\right) \right\}} \quad 3.7$$

This can be expressed as

$$\frac{I(0)}{I(T)} - 1 = g \exp\left(-\frac{\Delta E}{kT}\right) \quad 3.8$$

Taking the natural log of both sides leaves

$$\ln\left\{\frac{I(0)}{I(T)} - 1\right\} = \ln(g) - \frac{\Delta E}{kT} \quad 3.9$$

Equation 3.9 shows that a plot of $\ln\left\{\frac{I(0)}{I(T)} - 1\right\}$ versus $\frac{1}{T}$ will take the form of a linear graph with slope of $-\frac{\Delta E}{k}$, thereby allowing the bound exciton binding energy, ΔE , to be determined. For $I(0)$ we use the intensity at the lowest temperature used in the measurements (typically 4 K for this work).

In the analysis above it has been assumed that g , the ratio of free exciton states to bound exciton states, is temperature independent. However, the density of band states in a semiconductor varies as $T^{3/2}$ [34], therefore equation 3.9 must be modified to the following:

$$\ln\left\{\left(\frac{I(0)}{I(T)} - 1\right)\left(\frac{1}{T^{3/2}}\right)\right\} = \ln(g) - \frac{\Delta E}{kT} \quad 3.10$$

This equation is used to determine the binding energy ΔE for new features observed as part of this work. We return to this topic below where we analyse the temperature dependence of the components of lines that split under uniaxial stress and magnetic fields.

Apart from defects depopulating due to increasing temperature, bound exciton features can sometimes exhibit largely forbidden transitions which are only observed at liquid He temperatures or transitions from

excited states that increase in intensity with increasing temperature. The populations between these close lying states has been investigated also during this work particularly in Chapter 5 and a brief derivation of the equation used is offered here.

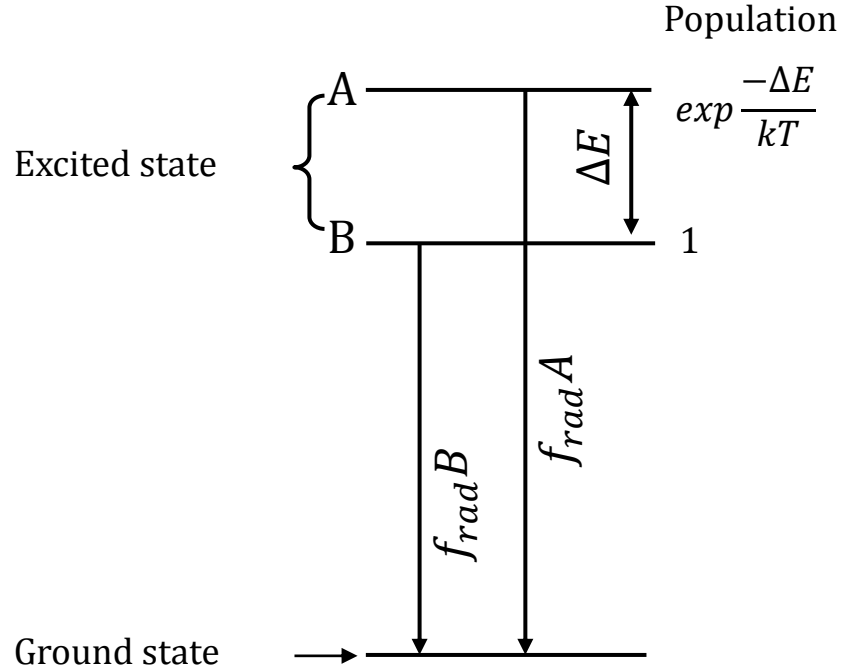


Figure 3.5: Ground state and excited state level scheme for two excited states which share a common ground state. $\exp \frac{-\Delta E}{kT}$ and 1 are the relative populations between levels in thermal equilibrium. Other notations are explained in the text.

The intensity of excitonic recombination at a defect centre is determined by

$$I \propto (f_{rad} \times pop.) \quad 3.11$$

where I is the intensity of emission in PL as before, $pop.$ is the population of excitons trapped at the defect and f_{rad} is the oscillator strength of the recombination (a dimensionless quantity used to express the strength of the transition [35]).

Therefore, taking the proportionality factor to be 1, we can write

$$I(B) = \left\{ \frac{1}{1 + \exp\left(-\frac{\Delta E}{kT}\right)} \right\} f_{rad} B \quad 3.12$$

and

$$I(A) = \left\{ \frac{\exp\left(-\frac{\Delta E}{kT}\right)}{1 + \exp\left(-\frac{\Delta E}{kT}\right)} \right\} f_{rad} A \quad 3.13$$

where $I(B)$ and $I(A)$ are the intensity of emission in PL for any two levels. These transitions are displayed in Figure 3.5. This leaves

$$\frac{I(A)}{I(B)} = \exp\left(-\frac{\Delta E}{kT}\right) \frac{f_{rad} A}{f_{rad} B} \quad 3.14$$

Taking the natural log of both sides gives

$$\ln\left\{\frac{I(A)}{I(B)}\right\} = \ln\left\{\frac{f_{rad} A}{f_{rad} B}\right\} - \frac{\Delta E}{kT} \quad 3.15$$

Plotting $\ln\left\{\frac{I(A)}{I(B)}\right\}$ against inverse temperature and choosing $\frac{1}{T}$ as the independent variable leaves us with

$$\Delta E = -mk \quad 3.16$$

where m is the slope of the graph. This allows for a direct calculation of the energy separation between energy levels of a single defect and can also show the direct relation between two close lying lines in PL as being related to a single ground state when the calculated ΔE agrees with the spectral separation of the lines.

In the discussion above, the intensity ratio of two lines is analysed as a function of temperature, from which the energy separation of the two levels involved can be extracted. The analysis can be modified in a situation where the temperature, T , remains constant but the separation

of two levels, ΔE , changes. Thus, from equation 3.15 we can choose ΔE as the independent variable, allowing $\ln \left\{ \frac{I(A)}{I(B)} \right\}$ to be plotted against ΔE , giving a slope of $-\frac{1}{kT}$. This situation arises later in the thesis where the energy separation ΔE is changed by uniaxial stress or by an applied magnetic field. In this analysis of the data, the relative intensities of two lines is examined as their energy separation is changed. This is used as a key check on the self-consistency of the interpretation of the data.

3.3 Theory of exciton states in ZnO

3.3.1 Unperturbed exciton states in ZnO

The excitons that become bound to defect sites in ZnO are formed from the lowest conduction band edge, which is s-like, and the p-like valence band maxima (VBM) located at the Γ point of the Brillouin Zone. The ordering of valence bands split by the crystal field and spin-orbit coupling in ZnO has been hotly discussed [15, 36, 37, 38] for more than 40 years and only recently appears to have been laid to rest [36, 39].

The case of the positive or negative spin-orbit coupling can be established readily from experimental results for the case of zincblende ZnO, however, the case of wurtzite ZnO (used exclusively throughout this work) is more complicated due to the dual interaction of the crystal field splitting with the spin-orbit splitting. The ordering of the valence band was deduced by first principle band structure investigations performed by Lambrecht *et al.* in [40]. An extensive history on this topic would make for interesting reading so reference is made to Chapter 4 of [9] for further discussion on this topic. A brief overview of the consensus reached on this topic follows.

Unlike most other wurtzite II_b – VI semiconductors, the valence band ordering in ZnO is: the A-band (Γ_7 configuration), the B-band (Γ_9 configuration), and the C-band (Γ_7 configuration) shown in Figure 3.6.

This unusual valence band configuration is unique to ZnO amongst the II_b – VI compounds, namely CdS, CdSe and ZnS, each of which form in the wurtzite phase but with a different valence band ordering (Γ_9 , Γ_7 , Γ_7 as compared to Γ_7 , Γ_9 , Γ_7 here) [41, 42]. The energy separation between the A and B valence bands shown in Figure 3.6 is 4.9 meV, while the much greater separation to the C valence band is a further 43.7 meV from the B valence band [15].

The free exciton in ZnO is constructed from the Γ_7 conduction band and the Γ_7 (A) valence band. The Γ_7 symmetry of both the conduction band and uppermost valence band in ZnO produces three exciton states; labelled Γ_1 , Γ_2 and Γ_5 in the C_{6v} symmetry (Schönflies notation) of the wurtzite ZnO crystal. The Γ_1 and Γ_2 states lie lower in energy than the Γ_5 state by about 1-2 meV [43, 44, 45]. These two states (Γ_1 and Γ_2) are usually taken together since no evidence of any splitting between them has been reported in ZnO. The separation between $\Gamma_{1,2}$ and Γ_5 states is a result of the different alignment of electron and hole spins for the two cases. The $\Gamma_{1,2}$ spins are aligned parallel, whereas the Γ_5 spins are aligned anti-parallel. This is shown graphically in the inset of Figure 3.6 where the crystal returns to the ground state, Γ_1 (*i.e.* a filled valence band and empty conduction band). Strong selection rules govern these processes.

Symmetry arguments show that, while the Γ_5 to Γ_1 transitions are allowed, the Γ_1 and Γ_2 to Γ_1 transitions are forbidden as it would require a spin change $\Delta s = 1$ (recalling that the Γ_1 and Γ_2 states have parallel electron and hole spins).

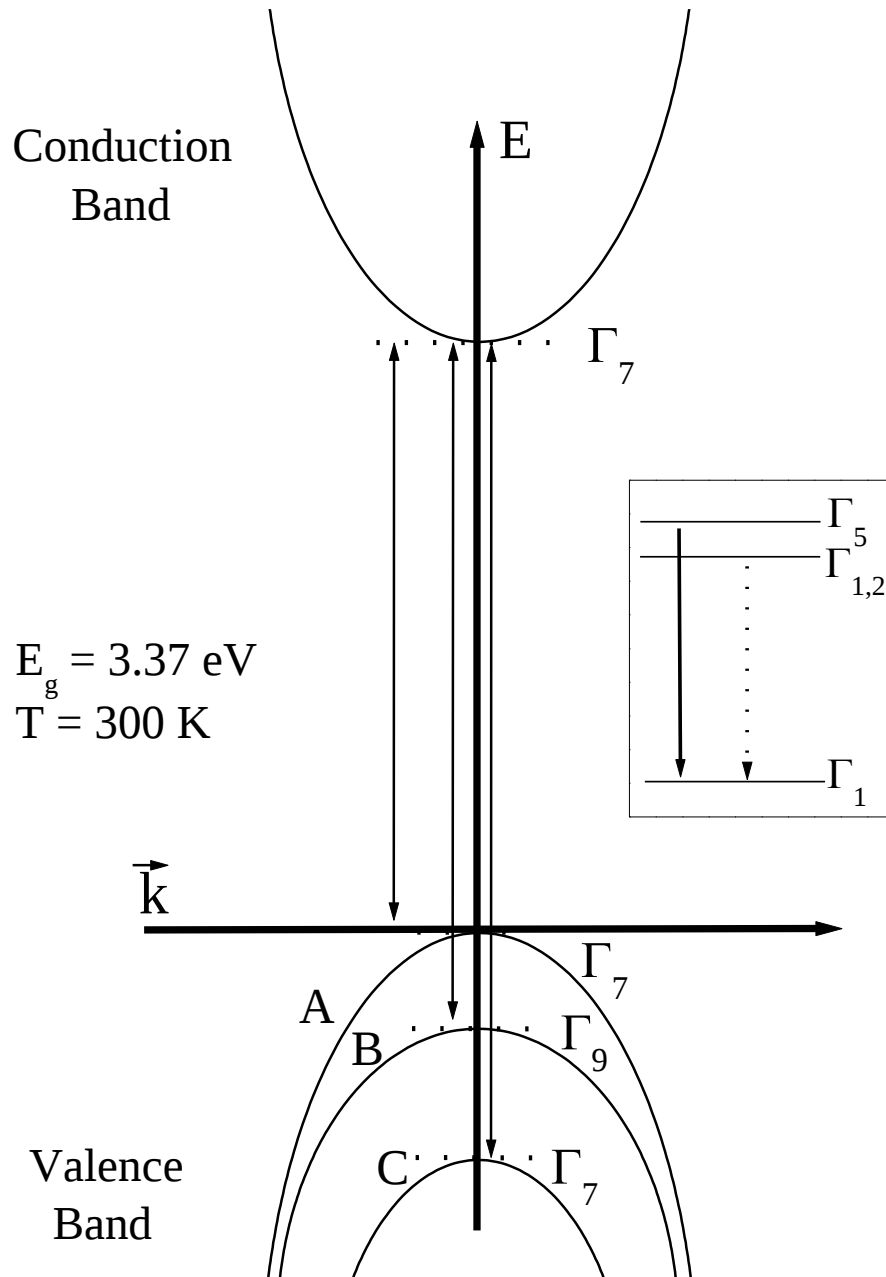


Figure 3.6: Graphical illustration of the energy gap separating the triply degenerate p -like valence band and the s -like conduction band. Excitons formed from the conduction band and the top valence band produce excitons with Γ_5 and $\Gamma_{1,2}$ symmetry (shown inset).

As a result, free exciton luminescence spectra reported in the literature are almost entirely those involving the Γ_5 initial state [6, 12, 15, 44]. Later the phrase electron-hole pair is used when discussing the Hg

centre in ZnO in order to highlight the components of the complex but electron-hole pair can be considered interchangeable with exciton in this instance.

Features studied in this work have been examined as potentially related to holes from the B- rather than the A-valence band but this prospect is ruled out given the distinct temperature, stress and magnetic field properties of the B-valence band holes discussed elsewhere [23, 43, 44].

3.3.2 Bound excitons in ZnO under uniaxial stress

For a substitutional impurity in ZnO, take Al for example (Al_{Zn}), the symmetry of the defect is C_{3v} , lower than that of the crystal (C_{6v}); a schematic diagram is shown in Figure 3.7. Here, too, stress parallel to the c-axis does not lower the symmetry of the neighbourhood of the substitutional impurity.

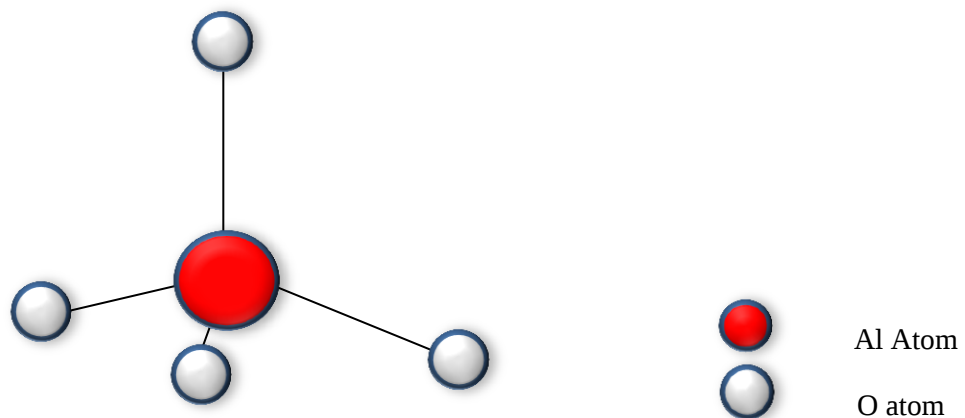


Figure 3.7: A diagram showing a simple substitutional atom, in this case Al (red), replacing a Zn atom surrounded by four O atoms (grey).

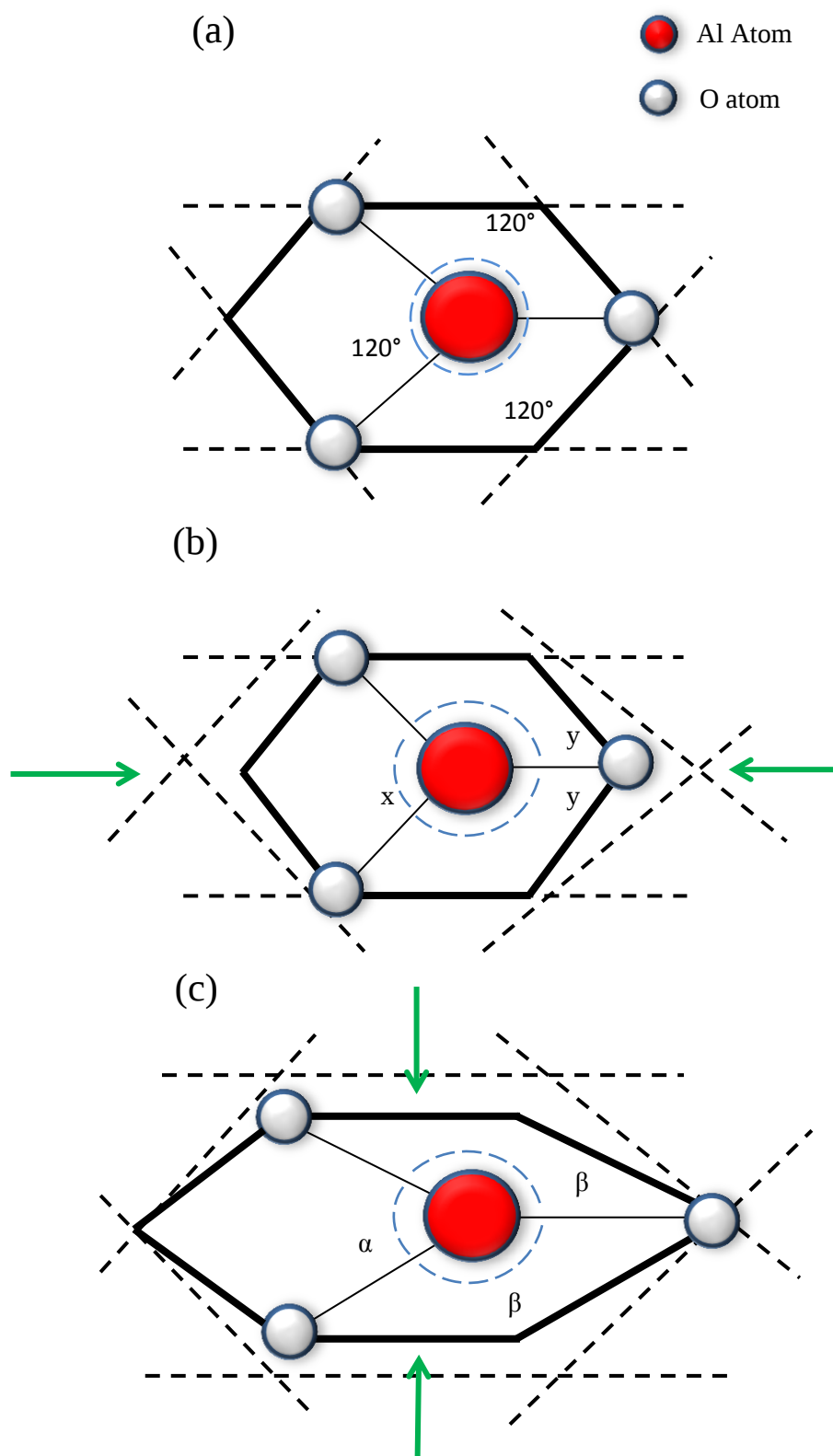


Figure 3.8: C_{3v} symmetry for a substitutional Al donor without stress (a) and for stresses along the $[10-10]$ (b) and $[1-210]$ (c) directions. Green arrows represent uniaxial applied stress directions.

For stresses perpendicular to the c-axis, the symmetry is significantly altered. Figure 3.8 shows diagrammatically what effect stress perpendicular to the c-axis has on the substitutional impurity (Al_{Zn}). Under stress along the $[10-10]$ and $[1-210]$ directions the rotations through 120° and reflection planes seen in Figure 3.8 (a) are lost and only a single reflection plane survives which reduces the symmetry from C_{3v} to C_{1h} for stress along the $[10-10]$ and $[1-210]$ directions (Figure 3.8 (b) and (c) respectively).

The work of McGlynn and Henry [45] is used here to determine the defect symmetries of bound exciton features by comparing the shift rates of those features (and their splitting components if any) under stresses along the $[0001]$, $[1-210]$ and $[10-10]$ directions of ZnO crystals. That work [45] was already shown to provide accurate defect assignments for earlier piezospectroscopy work performed in [46] where strong agreement was found between the fitted parameters and experimentally derived data for wurtzitic ZnO crystals. The notation used by McGlynn and Henry is continued in this work.

Defects in wurtzite crystals (ZnO , GaN , CdSe , *etc.*) can be classified into four distinct categories, each of which exhibits independent fitting parameters. The consistency of the fitting parameter values obtained from the shift rates of the defect emissions under stress can indicate the confidence of the defect assignment. The four categories and their shift parameters are discussed here:

- Trigonal nondegenerate defect states are perhaps the easiest to determine from stress data along any two directions since this is the only defect assignment possible for which no splitting occurs. The formula used to determine the shift rates of this class of defect is as follows:

$$R_{trig}^{nd} = \frac{\text{At1} (\alpha^2 + \beta^2 + \gamma^2) + \text{At2} (2\gamma^2 - \alpha^2 - \beta^2)}{(\alpha^2 + \beta^2 + \gamma^2)} \quad 3.17$$

where R_{trig}^{nd} is the shift rate for trigonal nondegenerate defects, $At1$ and $At2$ are shift rate parameters, to be determined from PL spectra, and α, β and γ are Cartesian direction cosines for the direction of the stress in comparison to the direction to the defect crystal axes (a further explanation of which is provided in [45]). The α, β and γ values are as follows for stress along specified crystallographic directions:

$$[0001] \rightarrow \alpha = \beta = 0, \gamma = 1 \quad 3.18$$

$$[1 - 210] \rightarrow \alpha = 0, \beta = 1, \gamma = 0 \quad 3.19$$

$$[10 - 10] \rightarrow \alpha = 1, \beta = \gamma = 0 \quad 3.20$$

Accordingly, the shift rate equations for a nondegenerate state in a defect of trigonal symmetry are as follows:

$$[0001] \text{ stress: } At1 + 2At2 \quad 3.21$$

$$[1 - 210] \text{ stress: } At1 - At2 \quad 3.22$$

$$[10 - 10] \text{ stress: } At1 - At2 \quad 3.23$$

- Trigonal degenerate (E) states do not split for stress applied along the $[0001]$ direction but split into two components along the $[10-10]$ and $[1-210]$ directions. From equation (11) in [45] the shift rates along the $[0001]$, $[10-10]$ and $[1-210]$ directions are given by:

$$[0001] \text{ stress: } A1 + 2A2 \quad 3.24$$

$$[1 - 210] \text{ stress: } \begin{matrix} A1 - A2 + B1 \\ A1 - A2 - B1 \end{matrix} \quad 3.25$$

$$[10 - 10] \text{ stress: } \begin{matrix} A1 - A2 + B1 \\ A1 - A2 - B1 \end{matrix} \quad 3.26$$

Here the parameters A_1 , A_2 and B_1 are the empirically derived fitting parameters for the defect centre.

- Monoclinic nondegenerate states also do not split for stress applied along the $[0001]$ direction of the crystal and, like the trigonal degenerate case above, split into two components along each of the $[10-10]$ and $[1-210]$ directions. The shift rates of these split components are as follows:

$$[0001] \text{ stress: } \quad Am_3 \quad 3.27$$

$$[1 - 210] \text{ stress: } \left\{ \begin{array}{l} Am_2 \\ \frac{3Am_1 + Am_2}{4} \end{array} \right. \quad 3.28$$

$$[10 - 10] \text{ stress: } \left\{ \begin{array}{l} Am_1 \\ \frac{3Am_2 + Am_1}{4} \end{array} \right. \quad 3.29$$

As can be seen, while the same number of splitting components is expected for both trigonal degenerate states and monoclinic defects in wurtzite crystals along all directions, the shift rates of these components should make a clear distinction possible.

There is also a fourth splitting possibility, namely triclinic nondegenerate states but these states have no bearing on this work so no further detail on this defect type is provided here. Suffice it to say that for any stress experiments performed as part of this work the number of split components could not be interpreted in terms of a triclinic defect, since not enough split features are observed under stress.

It should be noted that the stress shift rates found in this work are significantly less than those found for bulk ZnO previously observed [43] for ZnO by two- and three-photon excitation. Shift rates similar to those found in this work are also found recently in [6] however and those authors explain [47] the results of anomalous shift rates as being due to the massive presence of Y-line features (*cf.* §3.1 of this chapter

for an introduction to the Y-lines) which those authors attribute to extended structural defects which may result in the formation of microcrystals within the bulk sample and thus reduce the effective shift rates [48]. Another explanation proposed by the same group [47] suggests that since PL only reveals electronic information for the surface 100 nm (approximately), that at this close proximity to the surface of the crystal inhomogeneities may result in misleading shift rates. In the results supplied in [6] comparative shift rates of donor bound and Y-line features are provided and compared to those found in this work with strong agreement indicating that, while the effect is not yet fully understood, the shift rates appear reproducible during PL measurements.

3.3.2.1 Excitons in ZnO under uniaxial stress

We consider how the $\Gamma_{1,2}$ and Γ_5 exciton states of ZnO are affected by stresses parallel and perpendicular to the c-axis. For stresses parallel to the c-axis, the symmetry of the ZnO crystal is not changed, so the $\Gamma_{1,2}$ and Γ_5 labelling of the states remains the correct description. Larger stresses may affect the interactions between states, and in the limit of very large stresses (>10 GPa [52]) the crystal structure changes. However, the range of stresses used in this work is well below those extremes. In summary, it is found that the following (see Table 3.2) are the effects of stress perpendicular to the c-axis on the exciton states in ZnO.

Table 3.2: *The symmetry of exciton states in ZnO as the symmetry is reduced under perturbations from C_{6v} to C_{1h} .*

Exciton symmetry states			
C_{6v}	Γ_1	Γ_2	Γ_5
C_{3v}	Γ_1	Γ_2	Γ_3
C_{1h}	Γ_1	Γ_2	Γ_1 and Γ_2

3.3.3 Excitons in ZnO under applied magnetic fields

A common practice when investigating a new feature in luminescence (and absorption) spectra is to apply magnetic fields (anything up to 10 T is typical) to samples along certain crystallographic axes. This can help determine the charge state, ground and excited state and the nature of the exciton bound to the centre in the case of bound exciton complexes. There is a comprehensive literature on the effects of magnetic fields on exciton absorption and emission in all classes of semiconductors, with the main features summarised by Dean and Herbert [53]. Theory that was first developed and reported for CdS has formed the basis for the analysis of Zeeman data for free excitons and bound excitons of various types in ZnO [16, 54].

The analysis of Zeeman spectroscopy data can be broken down in many cases to separate studies of the electrons and the holes. This enables the main features of the Zeeman data to be explained; for the finer details, the electron-hole interactions become important. Here, we provide a general overview of the effects of magnetic fields parallel and perpendicular to the ZnO c-axis ([0001] direction) on the ground and excited states of the bound excitons of different types, in particular of D^0X and D^+X , which are of importance for this study.

The technique works by the coupling of the angular momentum of the magnetic field with the angular momenta of the unpaired particles that make up the bound exciton state. The energy shift of the unpaired particles is governed by the equation:

$$E = E_0 \pm \left\{ \frac{1}{2} \mu_B (g_h \pm g_e) \right\} \quad 3.30$$

where E_0 is the spectral energy of the feature without the influence of an external magnetic field, μ_B is the Bohr magneton, g_h is the hole g-value and g_e is the electron g-value. These last two are sometimes simply taken together and written as g_{exc} , the excitonic g-value, written as:

$$g_{exc} = |g_e \pm g_h| \quad 3.31$$

Figure 3.79 graphically illustrates the effect of an applied magnetic field perpendicular to the [0001] direction for D^0X lines. In the ground state the D^0X centre has a positive core and a single unpaired electron which couples with the applied magnetic field and splits into two distinct energy levels. This means that the Zeeman properties of the D^0X ground state are determined by those of the electron. In the excited state, which contains two electrons and a hole, the spins of the two electrons couple antiparallel with each other, leaving the hole unpaired. As a result the Zeeman properties of the D^0X centre excited state are determined by the properties of the hole.

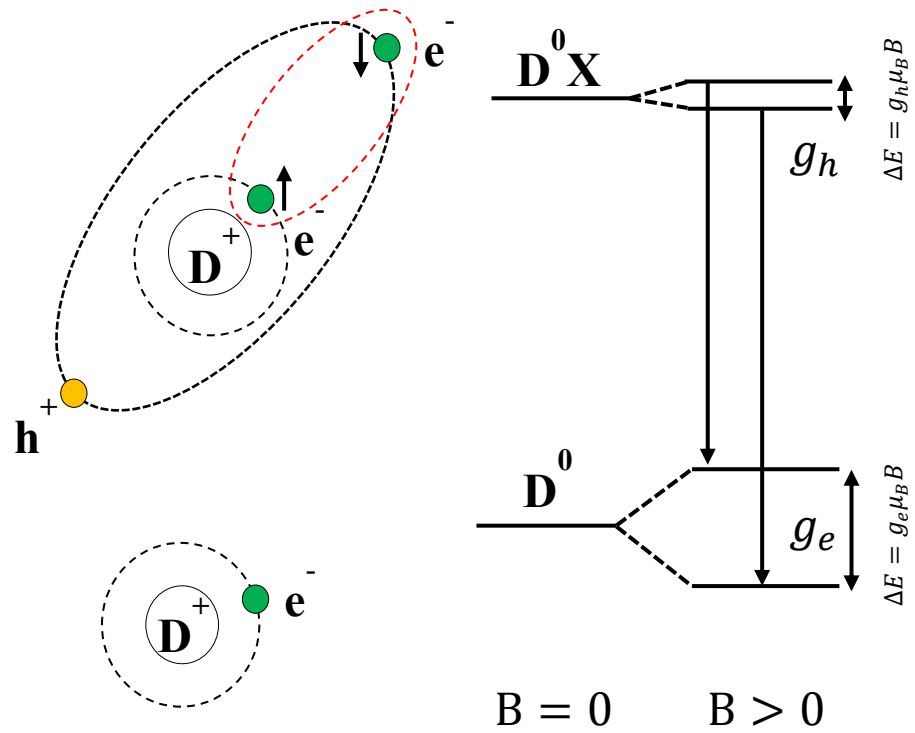


Figure 3.9: The ground state has a positive donor core, denoted as D^+ , and an unpaired electron, e^- . In the excited state there are two bound electrons and one bound hole. In this state, the splitting is given by $\Delta E = g_e \mu_B B$.

In Figure 3.9 the points above are illustrated diagrammatically for the ground and excited states of a D^0X bound exciton system. Note, somewhat counter-intuitively, the donor bound exciton Zeeman

characteristics are determined by the splitting of the hole, the ‘minor’ partner in the complex.

Now we consider the details of the values of g_e and g_h for ZnO. The electron on the donor, or D^0X complex, occupies a hydrogenic 1s state localised in the vicinity of the donor and the value of g_e is found to be isotropic (to within 0.001 of the g -value) and close to the pure spin value of 2 (1.957 [49, 25]). For the hole g -value the situation is more complex.

The hole g -value is highly anisotropic, that is, its value can vary greatly depending on the crystal orientation with respect to the applied magnetic field. Previous values reported have been approximately 0.1 for shallow bound exciton features [36] although Thomas and Hopfield note that the hole g value will be sensitive to its state of binding, since the different valence bands will be strongly mixed in bound hole states [56]. The hole g -value used in equation 3.32 can be calculated as follows:

$$g_h = \sqrt{\{|g_{h\parallel}|^2 \cos^2(\theta)\} + \{|g_{h\perp}|^2 \sin^2(\theta)\}} \quad 3.32$$

where θ is the angle between the [0001] direction and the direction of the applied magnetic field, taken from [9].

As mentioned previously in §3.3.1 of this chapter, angular dependent magneto-optical investigations have shown the upper valence band (A) to possess Γ_7 symmetry in ZnO [17]. The Γ_7 symmetry presents splitting characteristics for neutral and ionised donor and neutral acceptor bound excitons that make a distinction between these three excitonic transitions possible using PL while the sample is under an applied magnetic field.

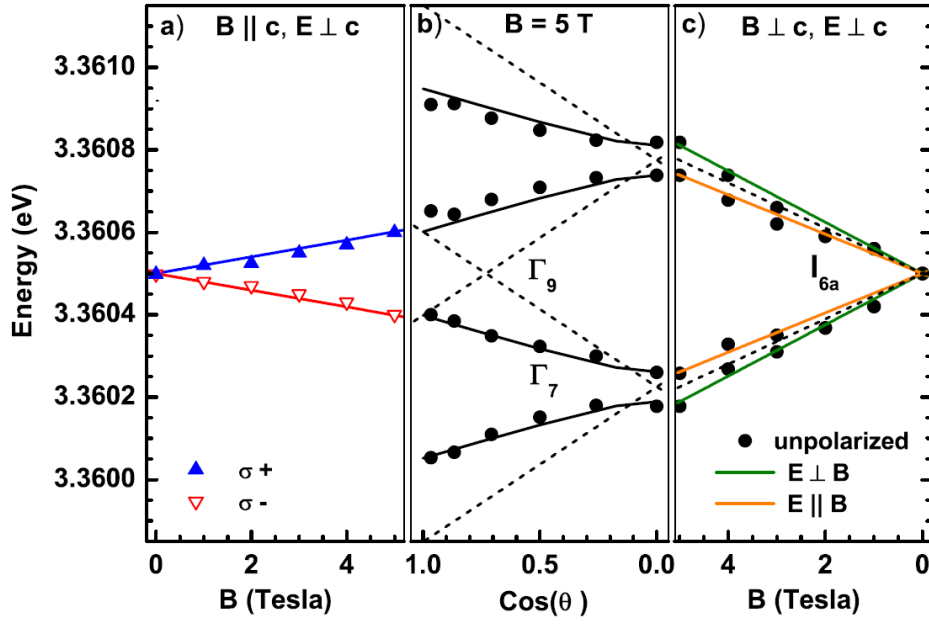


Figure 3.10: *Experimental and theoretical splitting of the I_{6A} feature in ZnO luminescence. Solid and dashed lines are explained in [50]. Taken from [50].*

Figure 3. above shows the typical magnetic field splitting of a D^0X feature in ZnO PL spectra. In (a), the parallel to c-axis configuration (when the magnetic field is along the [0001] direction), two components which are strongly polarisation dependent are observed; a higher energy ($\sigma+$) and lower energy ($\sigma-$) component. This strong polarisation is typical of spectra recorded while the magnetic field is parallel to the c-axis [6, 36, 39].

Figure 3.(c) shows the resulting line splitting for magnetic fields applied perpendicular to the c-axis, where a much larger splitting is observed. Also noteworthy for the magnetic field perpendicular to c direction is a fine splitting observed at strong magnetic fields, this fine splitting is due to the small but non-zero hole g-value which becomes more apparent at stronger magnetic fields as discussed below. Figure 3.10(b) shows angular dependence data which we return to below.

While the hole g-value is less than the electron g-value:

$$g_h < g_e \quad 3.33$$

it is still greater than zero, creating an overall splitting of the exciton recombination which can be hard to resolve without polarisation measurements. The same diagram works but in reverse for the case of A^0X features with an applied magnetic field along the [0001] direction, *i.e.* the ground state splitting is due to the hole g-value and the excited state splitting is due to the electron g-value.

Polarisation dependent measurements performed in the $B \parallel c$ configuration enable the spectral separation for the Zeeman split recombination lines at low magnetic fields since either the right ($\sigma+$) or left ($\sigma-$) circular polarised transitions can be suppressed. For the case shown in Figure 3.9, the high energy Zeeman component is $\sigma+$ polarised with the low energy component displaying pronounced $\sigma-$ polarisation in agreement with the models reported in [17] and [51].

Observed also in Figure 3. are angular dependent data; these were unfortunately not possible in this work although results for the perpendicular and parallel to c-axis orientations were possible. Full angular dependent measurements allow for a more accurate determination of the hole and electron g-values for bound exciton features.

Due to the well-known isotropism of the electron g-value in ZnO [49, 25], which is observed to change by only 0.001 with changing crystal orientation [49], the changing exciton g-value (g_{exc}) under magnetic fields parallel and perpendicular to the c-axis is attributed solely to the anisotropy of the hole g-value. This behaviour is also observed in other II-VI semiconductors such as CdS [52, 53].

The well-understood splitting behaviour of D^0X and A^0X features in ZnO can be used, in conjunction with temperature dependence, to investigate donor- or acceptor-like behaviour of spectral features. Shown in Figure 3.7 is a graphical representation of the excited and ground state splittings for donor and acceptor bound exciton centres.

Since changes due to temperature increases from low (5 K) to high (20 K) only effect the excited state in PL spectra, any change in ratio between the luminescence features while split under an applied magnetic field will come from the excited state.

For the case of D^0X with the magnetic field perpendicular to the c-axis, where the g-value is close to zero, the splitting in the excited state will be minimal and the relative intensities of the two lines will be independent of temperature [6, 36, 39]. As such, donor bound excitons typically exhibit equal relative intensities between split features in PL.

Similarly, in the case of acceptor bound exciton centres the excited state splitting is dominated by the electron g-value, while the hole state is responsible for the ground state splitting. Therefore with varying temperature a change in the relative ratios between the two split components is observed, seen because the separation is large enough.

While the case for two split components is discussed above, the Zeeman effect results in four distinct features although these are split into two groups of two features that are so closely spaced they are not resolved in this work. As an example the splitting between the D^0X line I_{6A} in Figure 3. is less than 0.1 meV at 6 T, much less than the ~ 0.3 meV resolution available for Zeeman spectroscopy reported here.

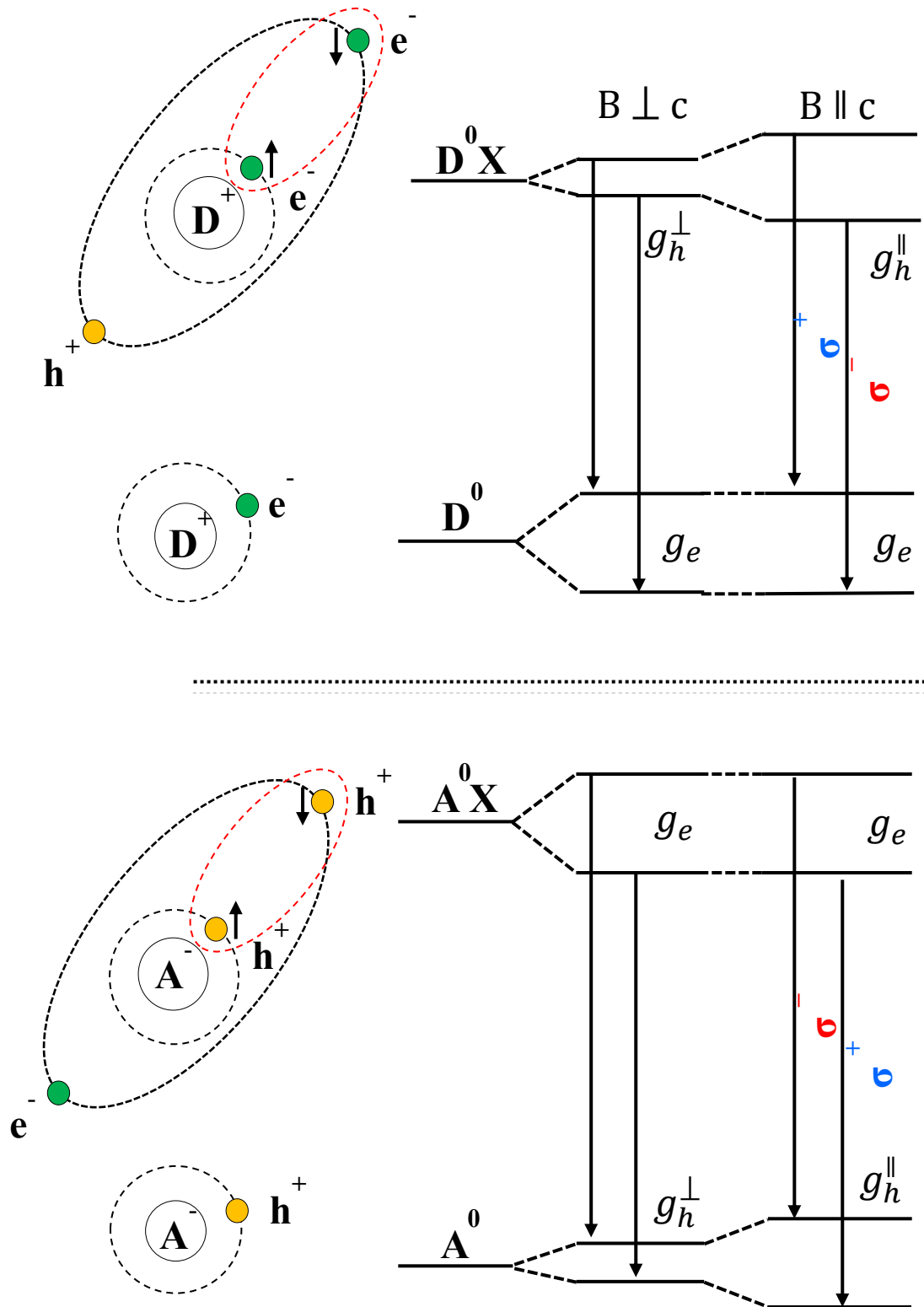


Figure 3.7: Shown here are the cases for magnetic fields applied parallel and perpendicular to the $[0001]$ direction in ZnO for the cases of donor bound excitons (above) and acceptor bound excitons (below). As can be seen the parallel to c direction produces split components which are highly polarised (σ^+ and σ^- polarised to be precise).

One possibility which has not been discussed yet is that of ionised D^+X features under applied magnetic fields, illustrated in figure 3.12. These exhibit several key differences under magnetic fields when compared with D^0X features, the most notable of which is the emergence of a lower energy forbidden line, analogous to the free exciton behaviour under magnetic fields along the perpendicular to c-axis. The excited state is responsible for the line splitting in this case which is revealed by temperature dependence studies, which we return to later in Chapter 5.

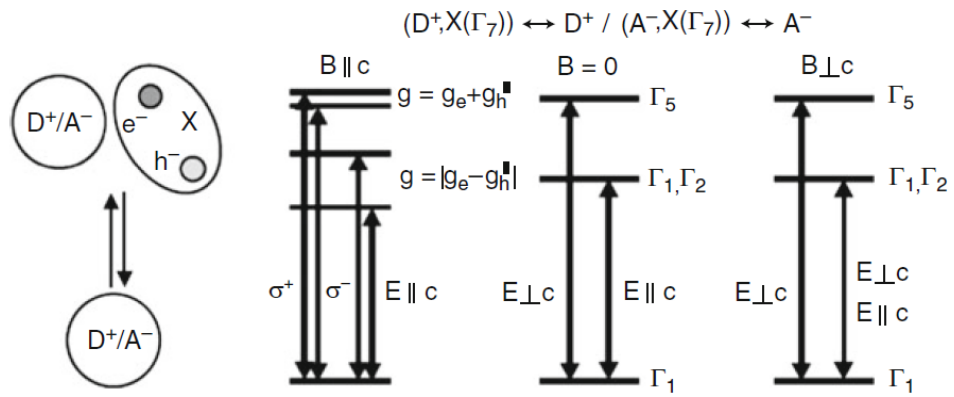


Figure 3.8: Ionised bound excitons split under magnetic fields differently from their neutral counterparts as discussed in the text. Taken from [9].

3.4 Summary

The brief theoretical grounding presented in this chapter should act to prepare the reader for the results presented subsequently in this work. All properties outlined in this chapter, the sharp FWHM of excitonic recombinations, accompanying TES transitions for D^0X lines, magnetic field measurements, temperature dependent behaviour and the behaviour of exciton recombinations under stress, will be used throughout this work in order to produce accurate assignments of the new defects discussed here.

3.5 References

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Chapter 4: Study of Ge-related luminescence in ZnO

4.1 Introduction

The search for suitable p-type impurities in ZnO has been a key feature of recent research [1, 2, 3], aimed particularly at solving the anisotropic doping nature of ZnO [4]. Impurities from group V of the periodic Table were long thought to be potential candidates in the efforts to solve this problem by forming shallow acceptor states [5], ideally by occupying the anionic O site. While this seems provisionally true for N_O [6, 7] (nitrogen occupying a substitutional site replacing a native O atom), the acceptor state formed is far above the valence band maximum, with several theoretical works yielding values greater than 150 meV [8]. Other works suggest 400 meV [9] to be the N_O acceptor level which is much too deep to be of practical use in devices. So the search moved on to other group V dopants, which have yielded theoretical results with the acceptor level residing deeper for P_O and As_O according to density functional theory calculations [5], predicting values in the region of 1 eV. However, p-type conductivity, obtained by Hall Effect measurements, was reported by Ryu *et al.* [10] for ZnO doped with As prepared by diffusion of As from a GaAs substrate. This result proved controversial at the time [5] however as the Zn may have diffused into the GaAs substrate which could have been the source of the observed p-type behaviour.

Work performed by Wahl *et al.* [11] using electron emission channelling indicated that As may not be a suitable candidate for p-type doping after all, as it preferentially occupies the cationic Zn site rather than the anionic O site. This result was contrary to expectation making it a priority for confirmation and further investigation.

Prior to the work discussed here there has been a recent effort [12, 13, 14] made to identify the remaining unidentified I_n-lines first

investigated by Reynolds *et al.* [15] along with investigating the broader behaviour of dopants in ZnO, particularly the origin and properties of the deeply bound exciton features tentatively labelled ‘Y-lines’ in earlier work [16] (the authors drawing inspiration from similar features in ZnSe for the naming of these newly observed lines). Among these recent publications there has been theoretical work aimed at investigating the role of the group IV impurities Si and Ge in ZnO [17], with both being proposed as likely n-type dopants occupying substitutional lattice cation sites. As part of this work, a new feature was observed related to Ge, the same feature that was observed in previous work involving doping with radioactive Ga (which decayed to Ge) in ZnO [18]. This chapter is concerned therefore with the identification of both Ga and Ge-related lines in the PL of ZnO.

There have been previous reports of Ge-related luminescence in ZnO also. For example, in [19] samples were grown by mixing GeO with ZnO in the source material, these samples were more like ZnO in a ternary alloy with Ge rather than ZnO single crystals doped with small amounts of Ge as performed here. In other studies of Ge in ZnO, PL lines are also attributed to colour centers in GeO rather than to isolated Ge impurities in ZnO [20, 21, 22].

This chapter begins by chemically identifying the origin of the DD₂ feature (a recently observed Y-line) by radioactive implantation of the group V dopant ⁷³As. The results corroborate the findings of previous work [12, 18] when implanting ⁷³Ga. Both ⁷³As and ⁷³Ga decay to stable ⁷³Ge producing the new feature labelled DD₂ here. The naming of the line as DD₂ is replicating the nomenclature started by Schildknecht *et al.* [23] and continued by Johnston *et al.* [12, 18]. Following this, an investigation of the general properties of the new defect is undertaken; uniaxial stress measurements are performed along two different crystal directions in order to study the defect symmetry and any orientational degeneracy exhibited by the centre. Zeeman spectroscopy is performed in order to identify the charge state of the

centre and in order to make an assignment of the feature as being neutral or ionised, and donor or acceptor. This line is, to the author's knowledge, the only chemically identified Y-line, if the lines are indeed similar in character to those reported for ZnSe [24], and therefore presents a unique perspective for investigating these new features further.

4.2 Results

4.2.1 Radiotracer measurements

The chemical nature of DD₂ was first observed in the work of Johnston *et al.* [18] by observing the effects on the PL spectrum of the decay of radioactive ⁷³Ga into stable ⁷³Ge via β^- emission. The decaying intensities of two donor bound exciton features (I₁ and I₈) were matched to the known half-life of ⁷³Ga and a new line was observed at lower energy (3.3225 eV) increasing in intensity as the ⁷³Ga transmuted into ⁷³Ge. Again the half-life dependence was calculated and the intensity of the emission was found to grow in line with the population of the ⁷³Ge daughter of the ⁷³Ga decay. Accordingly the DD₂ line was attributed to exciton recombination at a single substitutional Ge impurity occupying a Zn site (Ge_{Zn}).

The feature was labelled DD₂ in that earlier work as discussed in §4.1 of this chapter and was a curious discovery at the time due to its location in the emission spectrum, much deeper in the near band gap luminescence than donor bound exciton lines are predicted to be by effective mass theory [15]. Also mentioned earlier was the recent proposal by Wahl *et al.* that As prefers to occupy the Zn site in ZnO rather than the expected O site [11]. This finding could be tested using PL in conjunction with radioactive isotopes because of the finding above that Ge on the Zn site results in the DD₂ emission feature [12, 18]. If the DD₂ feature is observed after decay of radioactive As, one

could conclude that As must indeed occupy the substitutional Zn site giving stronger evidence to the finding of Wahl *et al.* [11]. A suitable isotope of As was found that would decay to Ge with a suitable lifetime for use with PL.

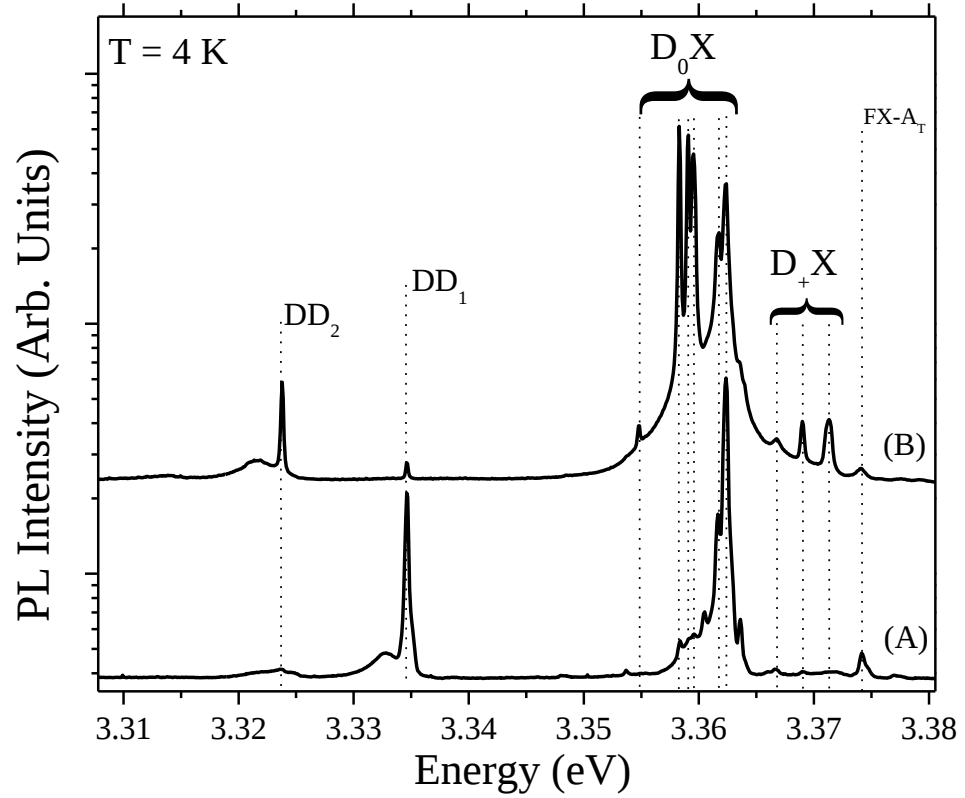


Figure 4.1: Representative spectra of Tokyo Denpa ZnO: (A) unimplanted Tokyo Denpa Ltd. ZnO and (B) ^{73}As implanted ZnO after most of the ^{73}As has decayed to ^{73}Ge .

Figure 4.1 shows emission spectra for unimplanted (A) ZnO from Tokyo Denpa and ZnO implanted with ^{73}As (B) after most of the As has decayed to Ge. While there are some changes evident in the bound exciton region (3.35 – 3.37 eV) of the spectrum these changes could not be matched to a corresponding increase or decrease of radioactive impurity populations and this region of the spectrum will not be discussed further in this section.

After implantation, the feature DD₁ (commonly observed in ZnO as discussed in Chapter 3) is not observed to change significantly in intensity over the period of five half-lives during which the spectra were recorded, so we therefore normalize all line intensities to this feature.

Figure 4.2 shows the increasing PL intensity of DD₂ with increasing time during the decay of ⁷³As (A and B) and ⁷³Ga (C and D) into stable Ge via electron capture and β⁻ emission respectively. Shown in the Figure 4.2 are representative spectra showing the increase in intensity of the DD₂ feature as the mother isotope decays to the daughter isotope. The solid line fits to the increasing intensity values represent the calculated half-life values which are found to be 78.3 ± 3.1 d and 4.9 ± 0.2 h for ⁷³As and ⁷³Ga respectively, in close agreement with tabulated half-lives of 80.3 d and 4.76 h [25].

The striking difference in quality of line shape between the ⁷³As and ⁷³Ga implanted samples is likely related to differing crystal quality between the ⁷³Ga implanted Rubicon Technology Inc. ZnO (line width ~0.9 meV) and the ⁷³As implanted Tokyo Denpa Ltd. piece (line width ~0.3 meV). Briefly, while the ZnO single crystals from both Tokyo Denpa Ltd. and Rubicon Technology Ltd. were grown hydrothermally, the Rubicon material appears to incorporate many more impurities. The band edge spectra [18] of ZnO from Rubicon Technology Ltd. contain lines relating to Ga, In, Al, and H for example, of which only two (Al and H) appear in the Tokyo Denpa Ltd. material indicating that Tokyo Denpa have a more refined growth method.

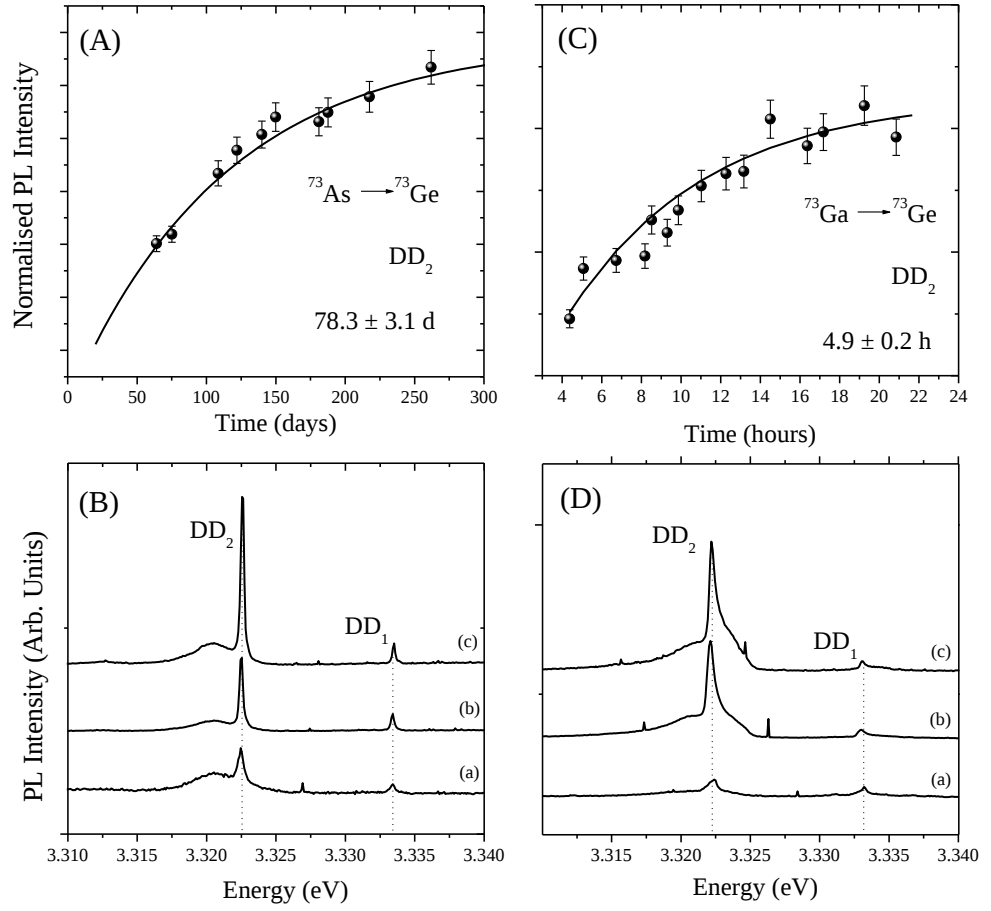


Figure 4.2: Fits to the exponential growth of the DD₂ intensity and representative spectra depicting the growth of the line DD₂ following implantation of ^{73}As (A and B) and ^{73}Ga (C and D). The three spectra, (a-c) in (B) show the increasing intensity of the DD₂ feature during the decay of ^{73}As , while (D) shows the evolution of the growth of DD₂ during the decay of ^{73}Ga , (a) being early after implantation and (c) close to the end of 5 half-lives.

4.2.2 Lattice location and recoil energy of ^{73}As and ^{73}Ga

In attributing the emission line DD₂ to substitutional Ge through the decay of radioactive ^{73}As and ^{73}Ga one must be confident of the initial location of the impurities and also confident of the lattice location of the daughter impurity after the recoil of the parent isotope after decay.

Wahl *et al.* [11] note that a substantial minority of ^{73}As atoms occupy sites other than the substitutional Zn sites after the decay of ^{73}As to ^{73}Ge . However, to this author's knowledge, there are no reports of Ga occupying a lattice location other than the simple cation substitutional impurity in ZnO (Ga_{Zn}).

The known substitutional behaviour of ^{73}As and ^{73}Ga alone is not enough to ensure that the resultant Ge dopant occupies a substitutional Zn site; the recoil energy of each decaying isotope must also be considered. ^{73}As decays to ^{73}Ge via electron capture and ^{73}Ga decays to ^{73}Ge via β^- emission with average recoil energies of approximately 1 eV and 10 eV respectively. Look *et al.* [26] suggest that the threshold for O displacement is 44 eV and for Zn displacement 34 eV. Other values reported in the literature [27] suggest that a lower dislocation value than that suggested by Look *et al.* [26] is possible, particularly for the Zn atom where values as low as 18.5 eV are reported [28]. However, even this low value for dislocating a native Zn atom is still almost twice the average recoil energy resulting from the emission of an electron during the ^{73}Ga decay. It is unlikely, therefore, that the DD₂ line is related to interstitial Ge or is luminescence induced due to damage since native Zn and O atoms in ZnO require higher energies to dislocate them from their substitutional lattice site.

The effects of radiation damage in PL emission spectra have been observed previously in semiconductors [18, 29, 30, 31, 32] and specifically in ZnO [13, 18, 29] where samples have been doped with radioactive isotopes. The recoil energies in those works were significantly higher than the values given above. In [18] the recoil energy during one decay chain was 118 eV, much larger than the estimated values for displacing a native Zn atom. This large recoil energy resulted in PL emission of a damage related band which grew in intensity over time during the radioactive decay; a similar band is observed by Agne *et al.* [29] in ZnO implanted with Hg. Since a characteristic damage related band is not observed in this work, the

resultant DD₂ feature is not assigned to damage related effects in the ZnO crystal.

Finally, since no configurations of Ga in ZnO other than the simple substitutional defect have been reported and since the majority of As atoms occupy substitutional Zn sites, the Ge-related DD₂ emission is attributed to a simple substitutional Ge atom occupying the cation (Zn) site.

4.2.3 Implantation of stable Ge

In order to further investigate the behaviour of Ge in PL emission, stable implantations were performed, the experimental details of which are presented in Chapter 2 of this work. The as-received (as-rcvd.) unimplanted PL spectrum of ZnO is shown in Figure 4.3 alongside that for a Ge-implanted and annealed sample.

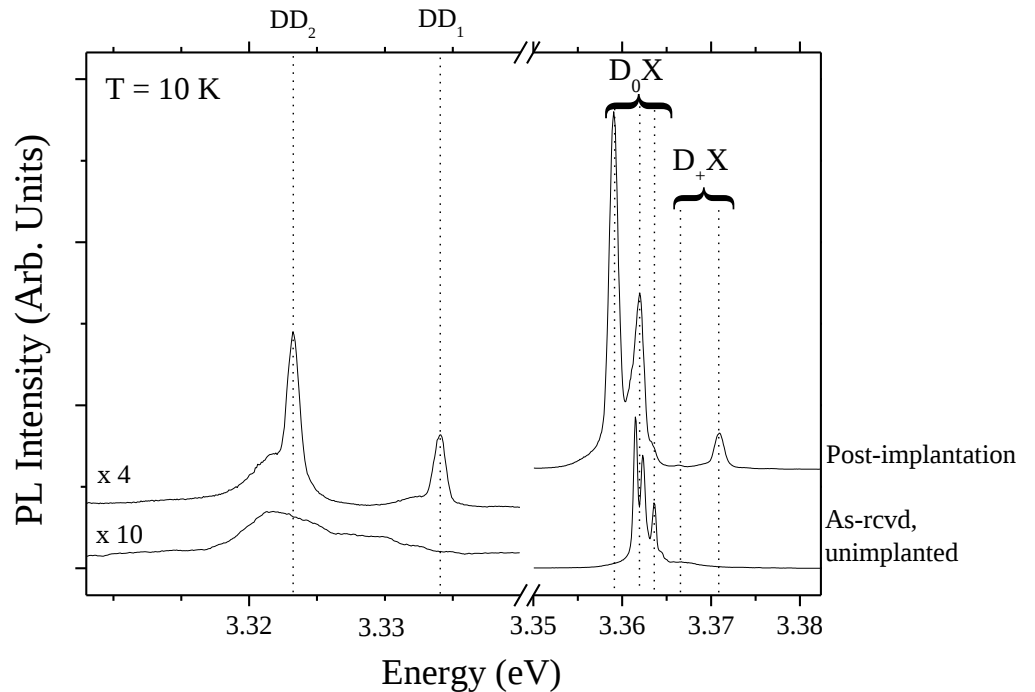


Figure 4.3: PL spectra of ZnO:Ge as-received (bottom) and after annealing (top) the sample post-implantation in an O₂ atmosphere for 30 minutes at 750°C. The energy axis has a break included to highlight the relevant lines.

Samples were annealed after implantation (some implanted at the Ion Beam Centre at the University of Surrey, England and others by Leonard Kroko, Inc. (USA) as explained in Chapter 2 of this work), using a procedure similar to that followed during the portion of the work carried out at ISOLDE. The DD_2 emission feature was observed in all Ge-implanted samples. Representative spectra for samples implanted with Ge and annealed at 700°C and 750°C are shown in Figure 4.4. The feature at 3.348 eV disappears after annealing above 700°C although it occurs in a region of the PL spectrum where many features (labelled ‘Y-lines’) have been reported so for this work it is labelled $Y_{\#}$. The band edge emission does not change significantly with annealing except that the relative intensities of donor bound exciton features change and the linewidths are somewhat broader. We note in particular that no new PL lines are observed in the D^0X region for Ge-implanted samples. No further comment is made on the D^0X features.

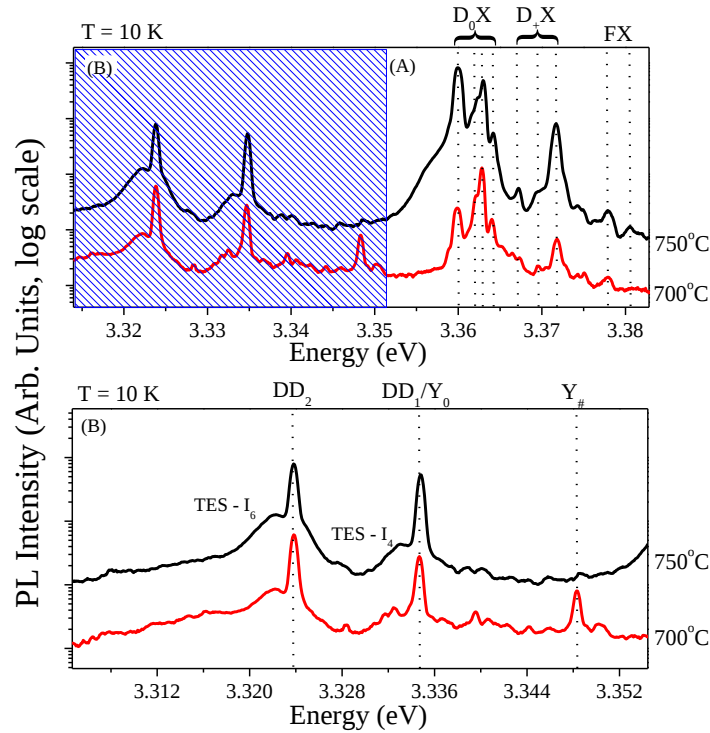


Figure 4.4: PL spectra of ZnO:Ge annealed at 700°C (red) and 750°C (black) in an O_2 atmosphere. The shaded region labelled (B) in (A) is highlighted further to show the region of interest in the PL spectrum; 3.31 to 3.35 eV.

The relative intensity of DD_2 to the band edge and DD_1 features does not change significantly with these two annealing temperatures although the overall intensity of PL emission is seen to improve after annealing at 750°C. All subsequent measurements are performed on samples annealed at 750°C and several different sample orientations (for uniaxial stress measurements specifically) are used in the course of studying the DD_2 feature. DD_2 is present in all of them with only slight variations observed in the DBX lines and Y-lines.

4.2.4 Details of DD_2 and DD_2 -related features in the PL spectrum

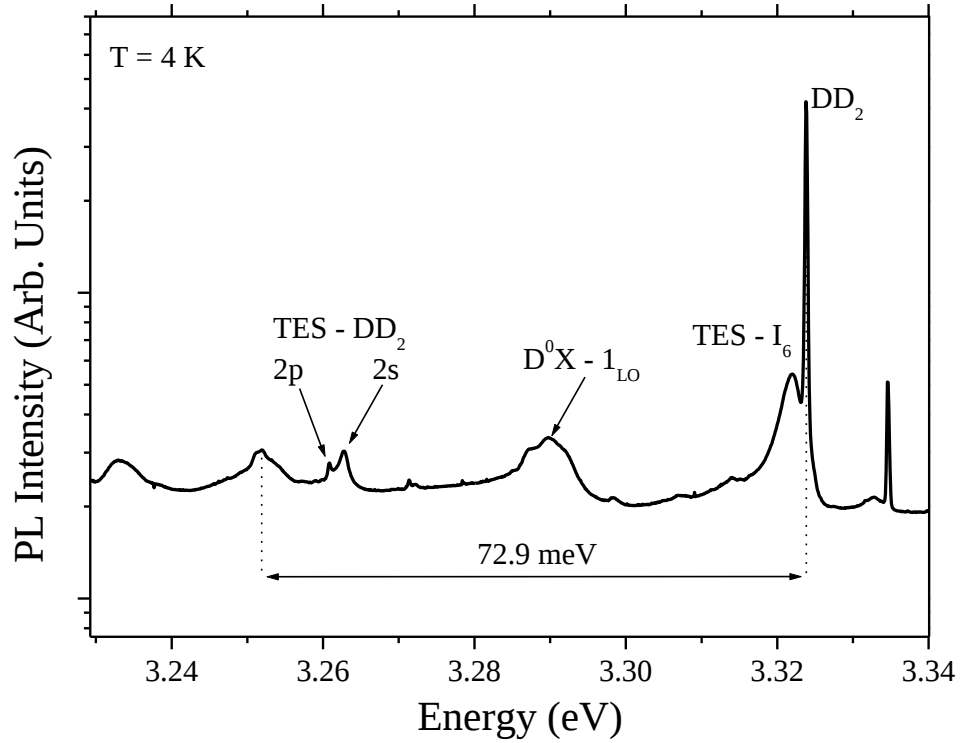


Figure 4.5: PL spectrum of Ge-doped ZnO exhibiting a strong, sharp DD_2 feature and several other lines associated with it.

Figure 4.5 shows the low temperature (4 K) PL spectrum with DD_2 and some associated features. The lowest energy peak in Figure 4.5 associated with DD_2 is at 3.251 eV and is identified as the 1_{LO} phonon

replica of DD_2 due to the spectral shift (72.9 meV) between DD_2 and this feature. In addition, the temperature dependence of this feature (shown in Figure 4.6) matches closely that of the DD_2 line so this line is positively attributed to be the 1_{LO} replica of DD_2 .

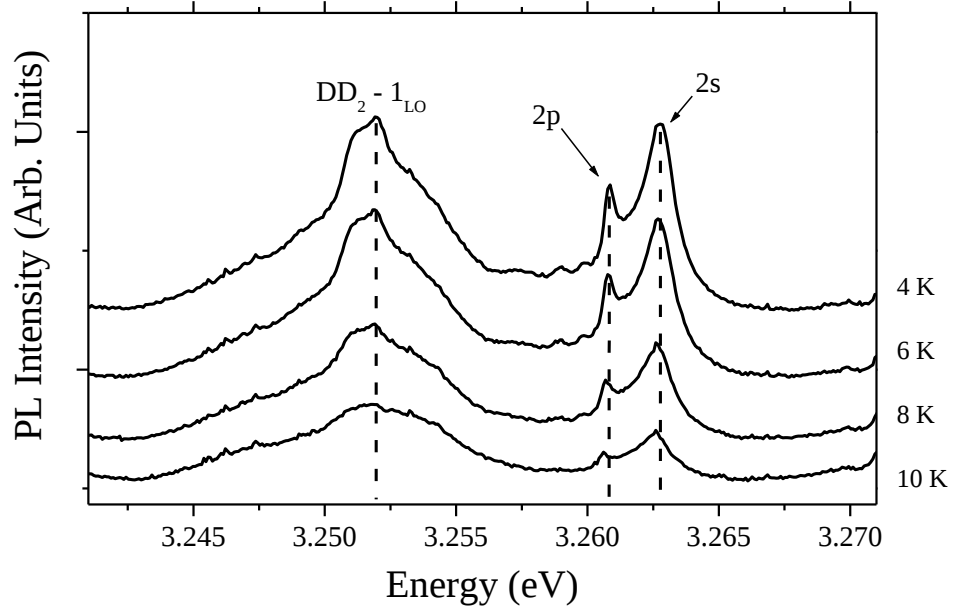


Figure 4.6: DD_2 -related emission attributed to TES and 1_{LO} transitions of the defect. Similar sharp temperature dependence is found for the DD_2 feature and the lines are not present in samples without Ge so a tentative assignment is made to a two-electron satellite and LO phonon interaction.

The temperature dependence of the PL features in the range 3.25 to 3.27 eV is shown in Figure 4.6. the features labelled 2p and 2s are possible candidates for TES transitions of the DD_2 feature. The temperature dependence of the TES transitions and 1_{LO} transition is shown in Figure 4.6 for DD_2 up to approximately 10 K, where these features become difficult to resolve. As expected they follow the temperature variation of DD_2 giving further evidence of their relationship.

Polarisation and power dependence measurements were also performed on DD_2 and D^0X lines but no notable difference were observed.

We also use this identification to calculate the ratio of the ZPL to the 1_{LO} replica. Normally the calculation of the Huang-Rhys factor [16], S , is determined using the Poisson distribution in equation 4.1 below.

$$I_n = \exp(-S) \frac{S^n}{n!} \quad 4.1$$

In this case, however, only the 1_{LO} replica is observed and so the less accurate ratio of the 1_{LO} to the ZPL is used instead. The ratios for DD_2 and donor exciton features to their respective 1_{LO} replicas are listed in the final column of Table 4.1. The table also includes other data which we refer to below.

Table 4.1: *Thermal deactivation, localisation and line energies for DD_2 and other common features in ZnO PL emission. The ratio of the ZPL intensity to the first LO replica of each feature is also listed where data were available.*

Line	Energy (eV)	Wavelength (nm)	Chemical Identity	Localisation Energy (meV)	Thermal Binding Energy (meV)	S (I_{LO}/I_{ZPL})
I_6	3.3612	368.92	Al	15.8	17.07 ± 1.3	0.216 ± 0.019
I_9	3.3571	369.37	In*	19.9	22.0 ± 1.9	-
I_{10}	3.3543	369.67	Sn	22.7	-	0.222 ± 0.020
DD_1/Y_0	3.3346	371.86	-	35.4	2.6 ± 0.3	0.0073 ± 0.001
DD_2	3.3238	373.06	Ge	53.2	2.9 ± 0.1	0.0153 ± 0.001

* Chemical identity first observed unambiguously by Müller *et al.* [13].

A value of just 0.015 is found for DD_2 , which is much smaller than the values for the neutral donor bound exciton features where the ratio tends to be greater than 0.2 [16]. This abnormally small value would seem to indicate a weak defect-lattice interaction. Typically as the localisation energy (discussed in Chapter 3 of this work) increases so

too does the Huang-Rhys factor [16] whereas for DD_2 this effect seems greatly reduced.

Shown also in the PL spectrum in Figure 4.5 are two features centred around 3.262 eV. These features, higher in energy than the LO phonon replica of DD_2 are tentatively attributed to TES transitions. A relation to DD_2 is almost certain considering the closely related thermal dependence of these features to DD_2 and their presence in PL spectra only coinciding with that of DD_2 .

Table 4.2: *TES separations for the DD_2 line and some common DBX lines and the DD_1 feature. Some abnormal energy separations are observed for DD_2 and DD_1 which appear not to follow the same trend as the DBX lines (see Figure 4.7).*

Line	Energy (eV)	Wavelength (nm)	Localisation Energy (meV)	TES - 2s (eV)	TES - 2p (eV)	ΔE (1s - 2p) (meV)	ΔE (2s - 2p) (meV)
I_6	3.3612	368.92	15.8	3.3298	3.329	38.8	0.8
I_{10}	3.3543	369.67	22.7	3.2998	3.2941	60.2	5.7
DD_1	3.3346	371.86	35.4	3.2722	3.2714	63.2	0.8
DD_2	3.3238	373.06	53.2	3.2627	3.2609	62.9	1.8

The values for these TES transitions and their calculated separations are listed in Table 4.2 and the equivalent values for the D^0X lines listed for comparison. Visual comparison of the separation values is provided in Figure 4.7.

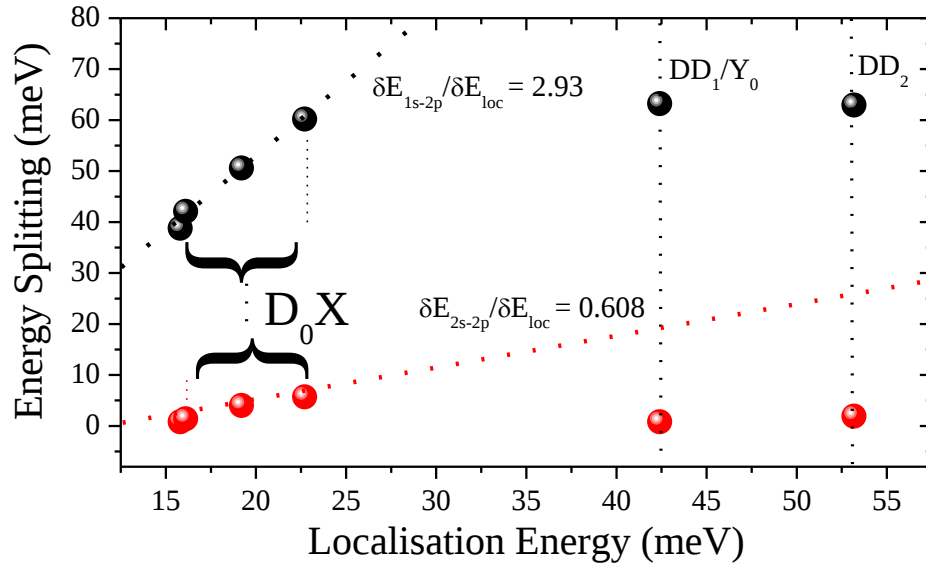


Figure 4.7: Energy separation between the first excited state and second excited states for some common donor bound exciton features and the DD_2 feature studied in this work. DD_1 is also included for comparison; DD_1 and DD_2 seem to diverge significantly from the trend found for the DBX lines and their TES separations.

D^0X features follow a linear relationship for both the TES separation with the ground state (1s–2s) and the excited state (2s–2p) splitting which increases with increasing localisation energy. DD_2 does not follow this trend but instead behaves more like the DD_1 feature (also included for comparison). Both DD_1 and DD_2 behave more like donors with a much shallower binding energy rather than the deep donors they appear to be. The assignment of features above to TES transitions involving DD_2 suggests donor-like behaviour. This assignment was made for two reasons; two-hole satellites have never been reported and Zeeman results discussed later seem to suggest donor behaviour also.

4.3 Temperature dependence measurements

Temperature dependence measurements were performed on DD₂ in order to gain more information on the nature of the exciton recombination binding mechanism. Bound exciton features in ZnO are typically investigated in the temperature range 5 – 60 K in order to calculate the thermal binding energy, ΔE , of the defect. The thermal binding energy is usually closely related to the localisation energy and for most D⁰X lines [33] it can be written

$$E_{Loc} \approx E_a \quad 4.2$$

where E_a is the thermal binding energy. Given the large localisation energy of DD₂ (53.2 meV below the lowest free exciton energy) the feature might be expected to display exceptional thermal stability. Contrary to this expectation however the DD₂ feature is no longer observable above ~ 20 K, while the I_n lines remain until around 50 K and have substantially lower localisation energies (approximately equal to or less than 20 meV). Reproducing equation 3.11 from Chapter 3 for the temperature dependence of the PL intensity gives equation 4.3 below

$$\ln \left\{ \left(\frac{I(0)}{I(T)} - 1 \right) \left(\frac{1}{T^{\frac{3}{2}}} \right) \right\} = \ln(g) - \frac{\Delta E}{kT} \quad 4.3$$

which was used to calculate a value, ΔE , by plotting the natural log of a function that includes the ratio of the lowest temperature intensity (I_0) to higher temperature intensities (I_T) against inverse temperature as seen in Figure 4.8. The $T^{\frac{3}{2}}$ factor takes account of the temperature dependence of the density of band states. A thermal binding energy of just 2.9 ± 0.1 meV is found for DD₂, sharply contrasting with its localisation value of 53.2 ± 0.1 meV but consistent with the observed thermal instability at low temperatures. The thermal binding values for D⁰X lines are included in Table 4.1 along with those for DD₁ and DD₂.

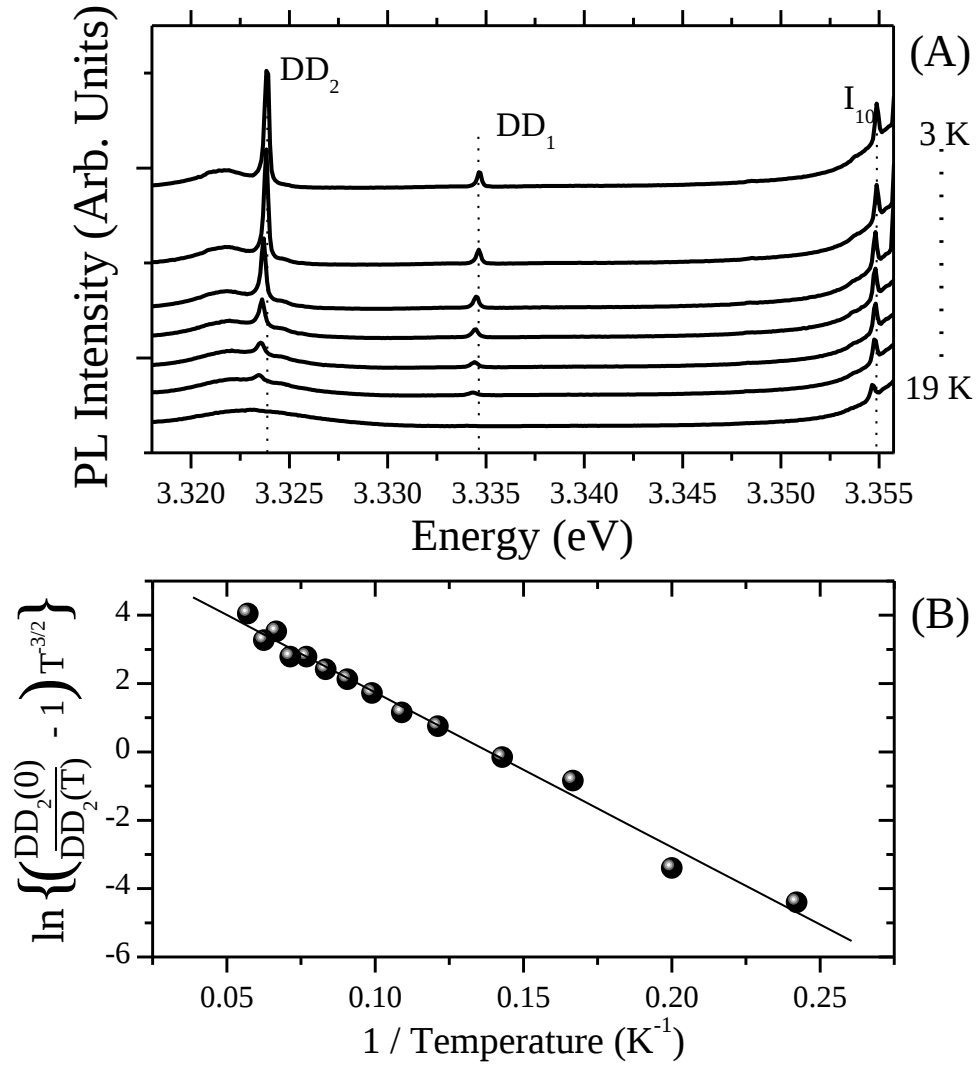


Figure 4.8: (A) PL spectra at various temperatures for ZnO:As/Ge and (B) log plot of the DD_2 line intensity compared to its low temperature value plotted against inverse temperature. See text for details of the fitting function.

Further to this calculation the temperature dependence of the localisation energy was analysed. Shown in Figure 4.9 are the temperature dependences of the DD_2 line, of the neutral donor bound exciton line I_6 , and of the free A_T – exciton. These values are used to plot localisation energy as a function of temperature as seen in Figure 4.10.

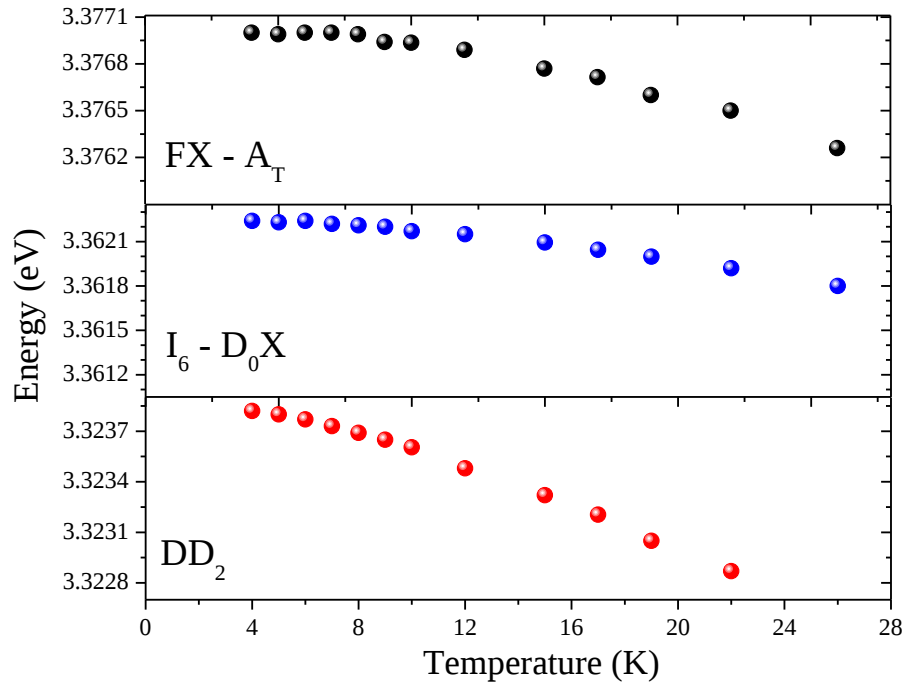


Figure 4.9: Line emission energies for the neutral donor bound exciton line I_6 , the feature studied here DD_2 and the lowest energy free exciton A_T plotted against increasing temperature (K).

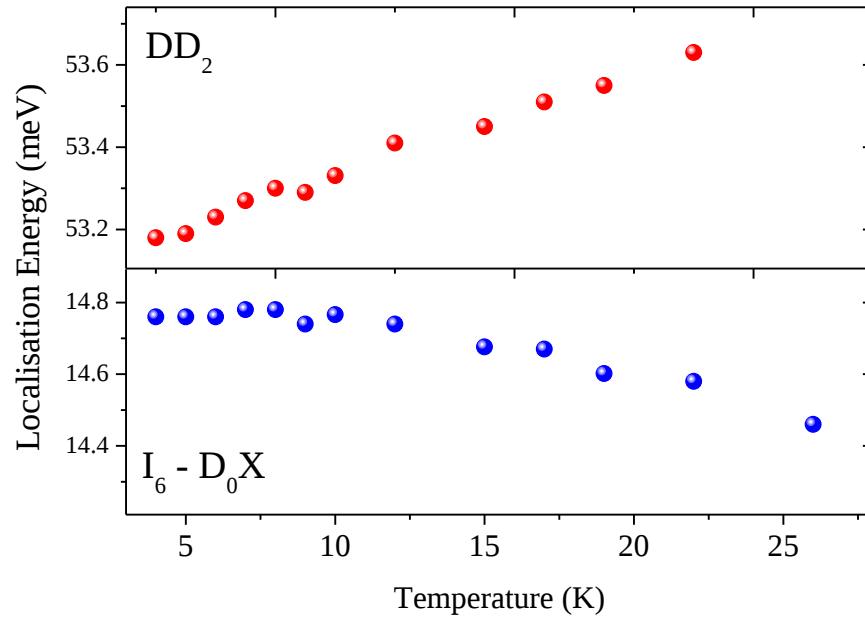


Figure 4.10: Localisation energies for the neutral donor bound exciton line I_6 and DD_2 plotted against increasing temperature. A striking difference is observed between the localisation energy changes with increasing temperature as discussed in the text.

The result shown in Figure 4.10 is a striking one as the change of localisation energy is distinctly different and opposite for the D^0X line compared to the DD_2 feature. It should be noted that the same distinct difference in changing localisation energies is observed for other neutral donor bound exciton lines compared with DD_1 . Wagner *et al.* [16] explain the decreasing localisation energy of DBX lines as being due to the increase in free carriers throughout the crystal as temperature increases which in turn causes a screening effect of the impurity potential. The curious effect of very weak binding and abnormal change in localisation of DD_2 indicates a binding mechanism different to that of the donor bound exciton recombinations.

4.4 Uniaxial stress measurements of DD_2

Piez spectroscopy of semiconductors can provide unique insight into the orientational and electronic degeneracy of excitonic recombination centres [34]. For this work uniaxial compression was applied (i) along the [0001] direction (which does not alter the lattice symmetry) and (ii) perpendicular to the same axis along the [1-210] direction (which reduces the crystal symmetry from C_{6v} to C_{2v}). Samples of different orientation were used in order to accommodate different stress directions. For pressure applied parallel to the c-axis only a shift in energy values is expected for bound exciton recombinations and any splitting should only occur for pressure applied perpendicular to the c-axis; the shift rate parallel to [0001] is still required in order to calculate the shift parameters detailed by McGlynn and Henry [35] as discussed in Chapter 3. The same DD_2 feature and D^0X lines were observed in all samples and all samples were annealed and implanted in the same manner. However, it should be noted that a variety of Y-lines appear in in samples of different orientations.

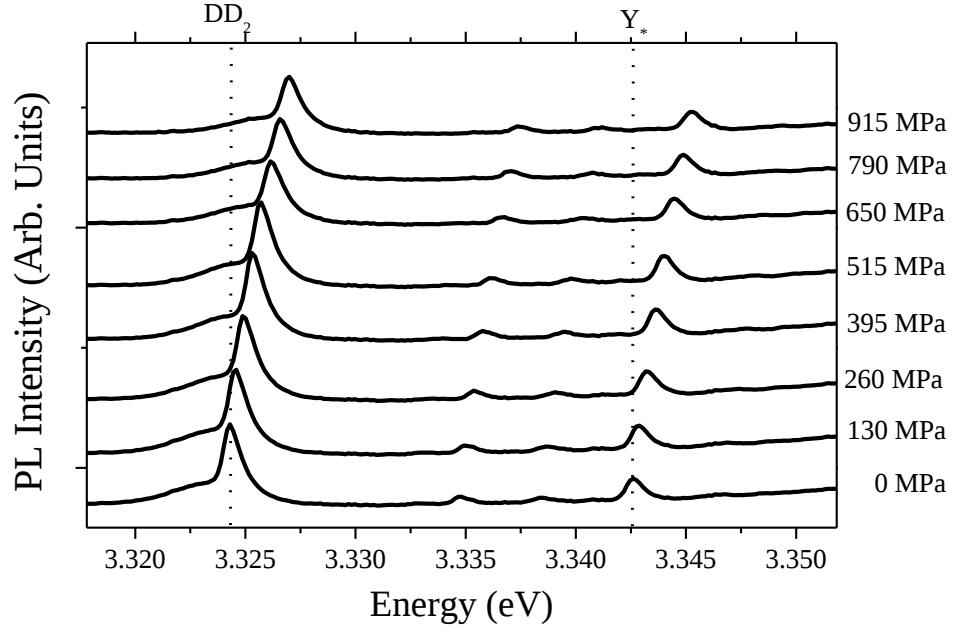


Figure 4.11: Representative spectra of the DD_2 line along with the nearby Y_* line. Y_* is not related to $Y_\#$ from Figure 4.4 (B) as explained in the text. Spectra have been vertically shifted for clarity.

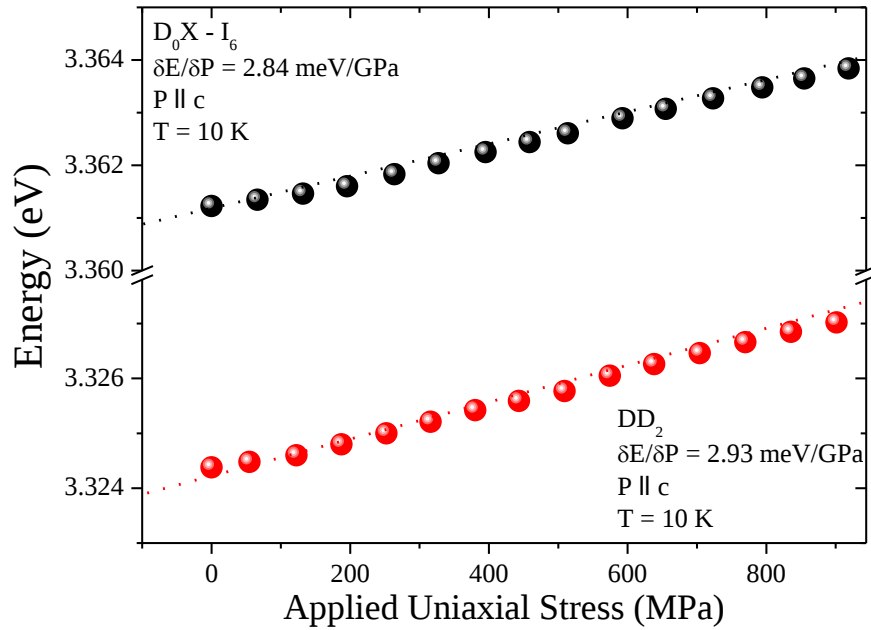


Figure 4.12: Uniaxial shift rates of the neutral donor bound feature I_6 and the line studied here, DD_2 under stress applied along the $[0001]$ direction. Solid lines correspond to linear fits to the shifting energies.

In Figure 4.11 a shift in the higher energy direction for stress applied along the c-axis is observed for DD₂ with similar results for the DBX lines (not shown); Y_{*} in Figure 4.11 should not be confused with Y_# in Figure 4.4(B); both are Y-lines that are yet unidentified or studied extensively and are beyond the scope of this work.

Figure 4.12 shows the plotted data points for the DD₂ emission energy under uniaxial stress along the [0001] direction. A direct comparison is made with a typical donor bound exciton line, I₆, which is known [14] to be related to a simple substitutional Al donor and has been well studied in ZnO (by piezospectroscopy in [16]). Values for the DD₂ shift were found by applying pressure up to 1 GPa along the c-axis and over 100 MPa perpendicular to the c-axis along the [1-210] direction (shown below in Figure 4.13).

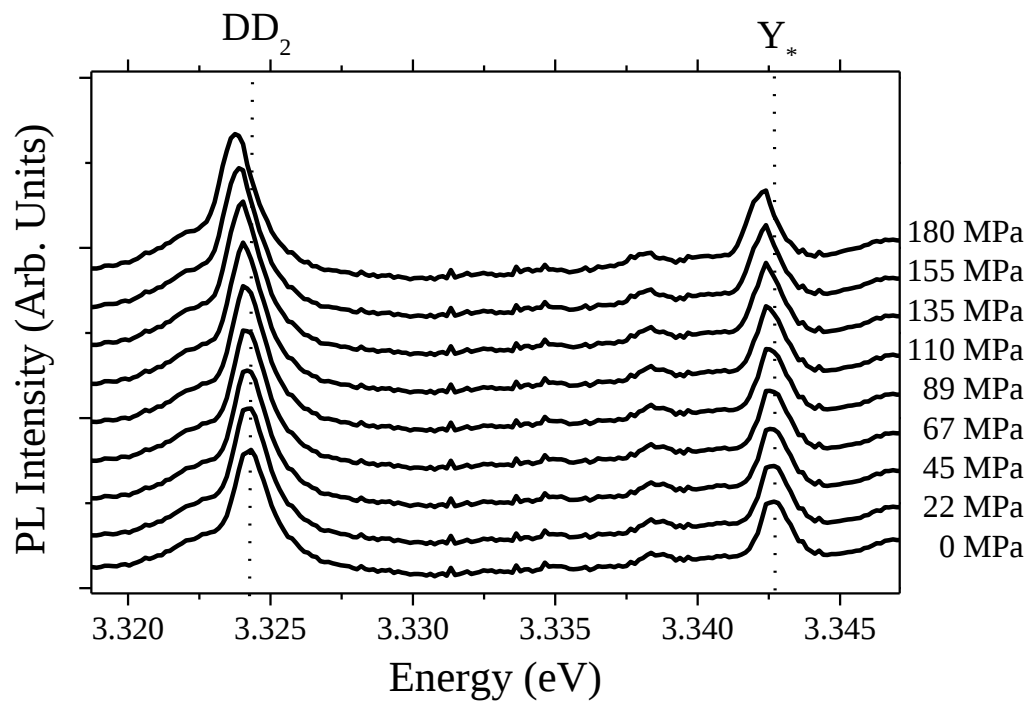


Figure 4.13: Representative spectra of DD₂ shifting under uniaxial pressure applied along the [1-210] direction. Spectra have been vertically shifted for clarity. DD₂ is not observed to split with the change in crystal symmetry.

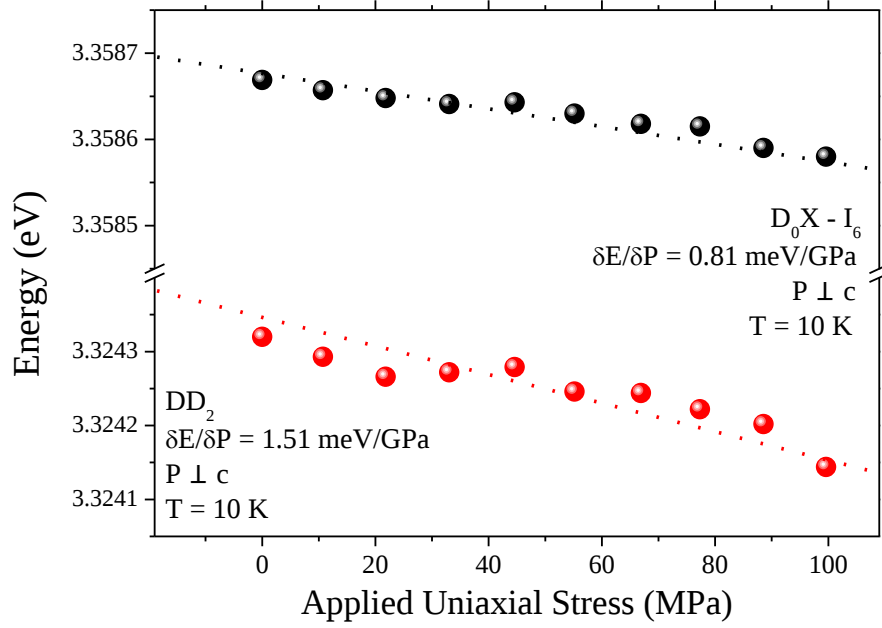


Figure 4.14: Shift rates of DD_2 and I_6 plotted for comparison for stress applied along the $[1-210]$ direction; no splitting is observed for either although a faster shift rate is noted for the DD_2 feature.

Only data for the low-stress regime were available for the $[1-210]$ direction of the crystal, which are plotted in Figure 4.14. However, a linear shift rate is found for these lower stresses (up to 200 MPa) so this shift rate can still be used for the purposes of identifying defect symmetry in the crystal.

4.5 Zeeman spectroscopy measurements

Applying magnetic fields to samples at low temperatures can affect the unpaired spin components of electrons and holes in exciton recombination [36]. For this work magnetic field values up to 7 T were applied (i) parallel to the c-axis $[0001]$ and (ii) perpendicular to the c-axis $[1-210]$, in increments of 1 T. The sample geometries for this work are illustrated in Figure 4.15.

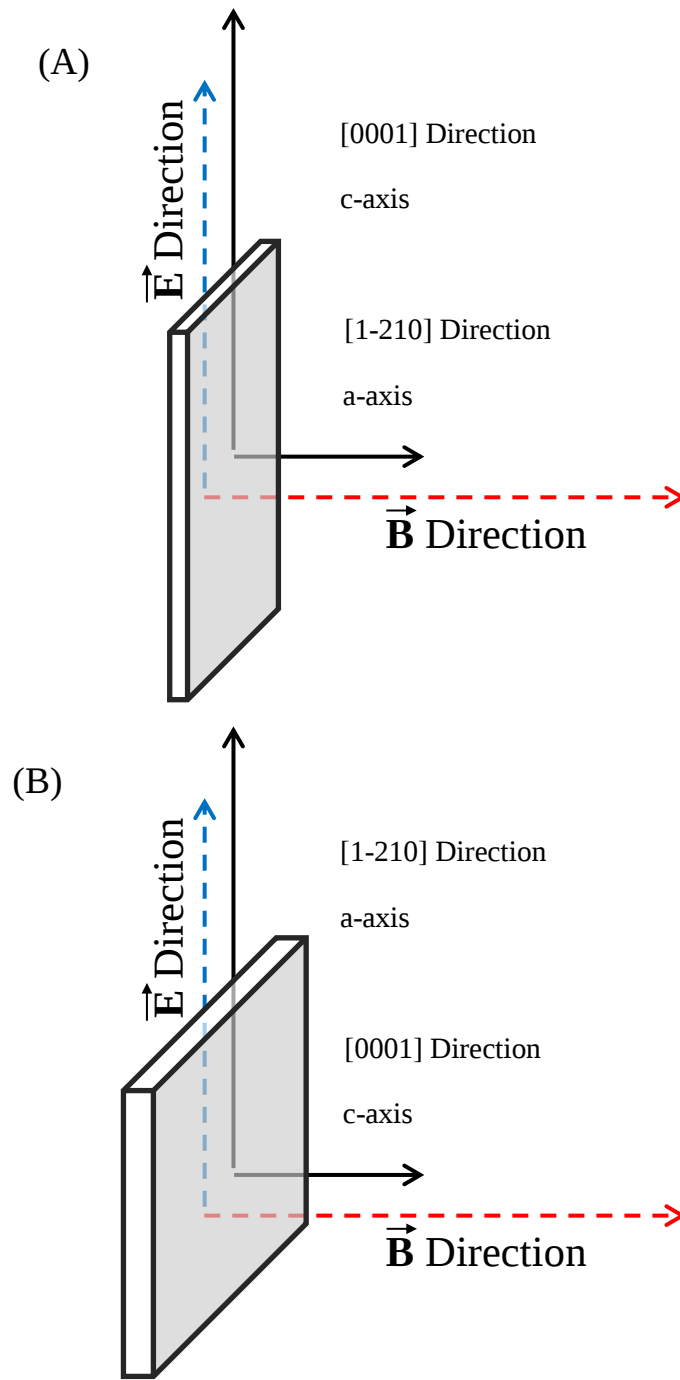


Figure 4.15: *a*-plane (A) and *c*-plane (B) samples of ZnO indicating the applied magnetic field direction with respect to the *c*-axis and *a*-axis and PL electric vector direction. Other sample orientations, detailed in Chapter 2, were also used in order to obtain different electric vector directions.

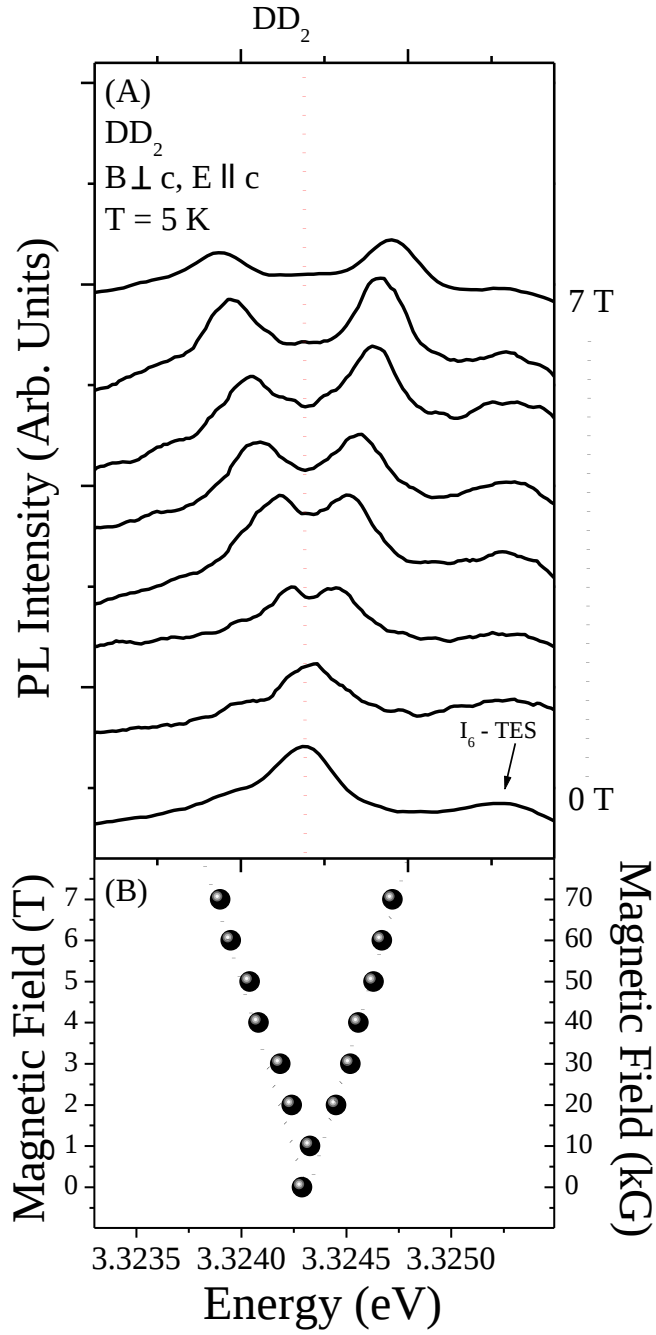


Figure 4.16: PL spectra (A) of DD_2 under applied magnetic field perpendicular to the c -axis; the direction of the electric vector of the PL with respect to the c -axis is also indicated. Plotted data points (B) of the DD_2 split components under applied magnetic field perpendicular to the c -axis plotted as a function of increasing magnetic field. Spectra in (A) have been vertically shifted for clarity.

Figure 4.16 (A) shows the PL spectra of the DD₂ line under application of magnetic fields up to 7 T in the [1-210] direction (perpendicular to the c-axis). Also in Figure 4.16 (A) is the TES related to I₆ which has already been extensively studied so no further comment on this feature is made. Figure 4.16 (A) shows a clear linear splitting of the DD₂ feature into two distinct components upon application of the magnetic field; one shifting to higher energy, the other to lower energy. Both lines are observed to maintain equal intensity (*i.e.* no thermalisation between the two lines is observed at constant temperature) and each component maintains the sharp characteristic FWHM of the zero field emission (less than 0.3 meV). The sample space is maintained at 5 K throughout in order to avoid thermal broadening of the features or shifting energy values unrelated to magnetic field effects.

The plotted line splitting of DD₂ is shown in Figure 4.16 (B) for increasing magnetic field. A linear shift of both components is observed under magnetic fields of up to 7 T.

Shown in Figure 4.17 (A) are the PL spectra for the DD₁ feature under magnetic fields along the same direction and the plotted data points of the split components for DD₁ are plotted in Figure 4.17 (B); a similar splitting pattern is observed for both features which is unsurprising considering their extensive similarities in luminescence (temperature dependence, localisation energy, stress symmetry, *etc.*). However, it should be noted that some thermalisation between split components is observed for DD₁, differing from previously published work [16].

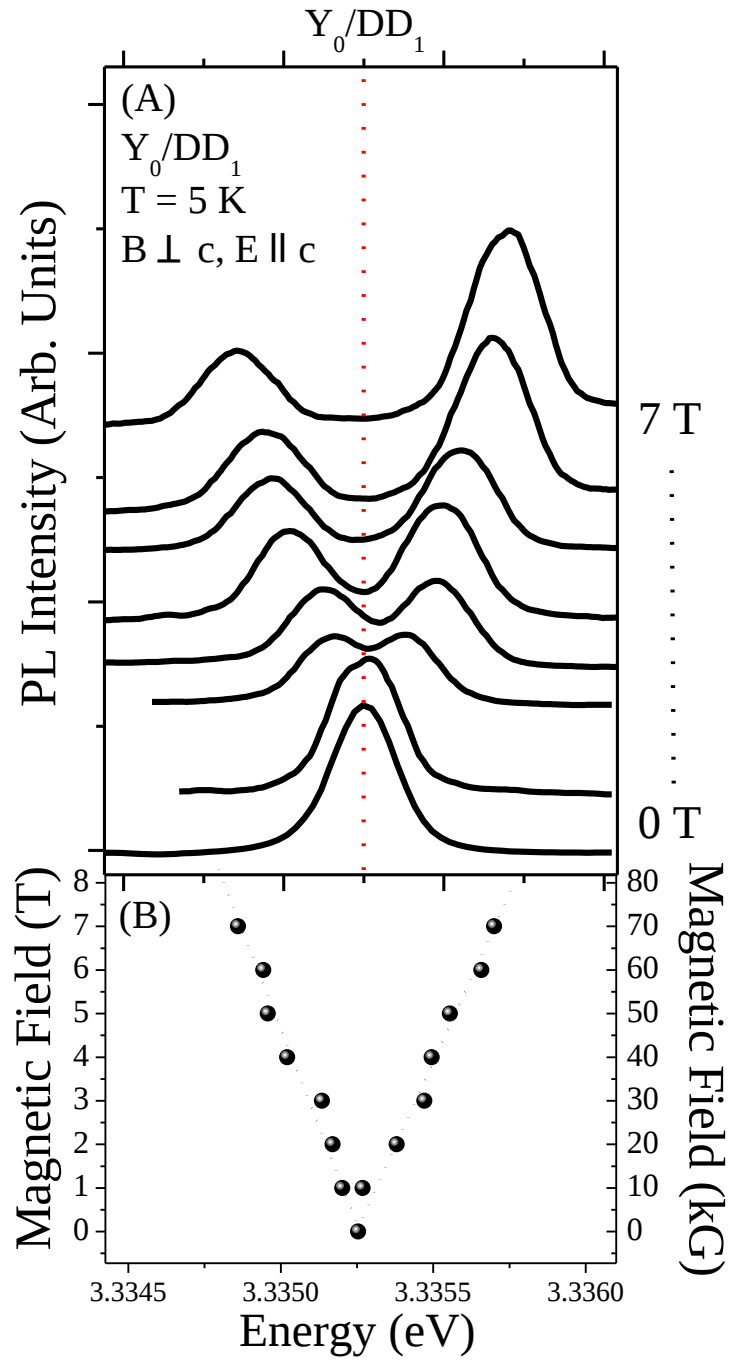


Figure 4.17: PL spectra (A) for DD_1 and plotted data points (B) of the split components under applied magnetic field perpendicular to the c -axis plotted as a function of increasing magnetic field for comparison to DD_2 in Figure 4.16. Spectra in (A) have been vertically shifted for clarity.

Upon application of a magnetic field along the [0001] direction the DD_2 feature was observed to shift linearly to higher energy values as seen in Figure 4.18 (A) and (B).

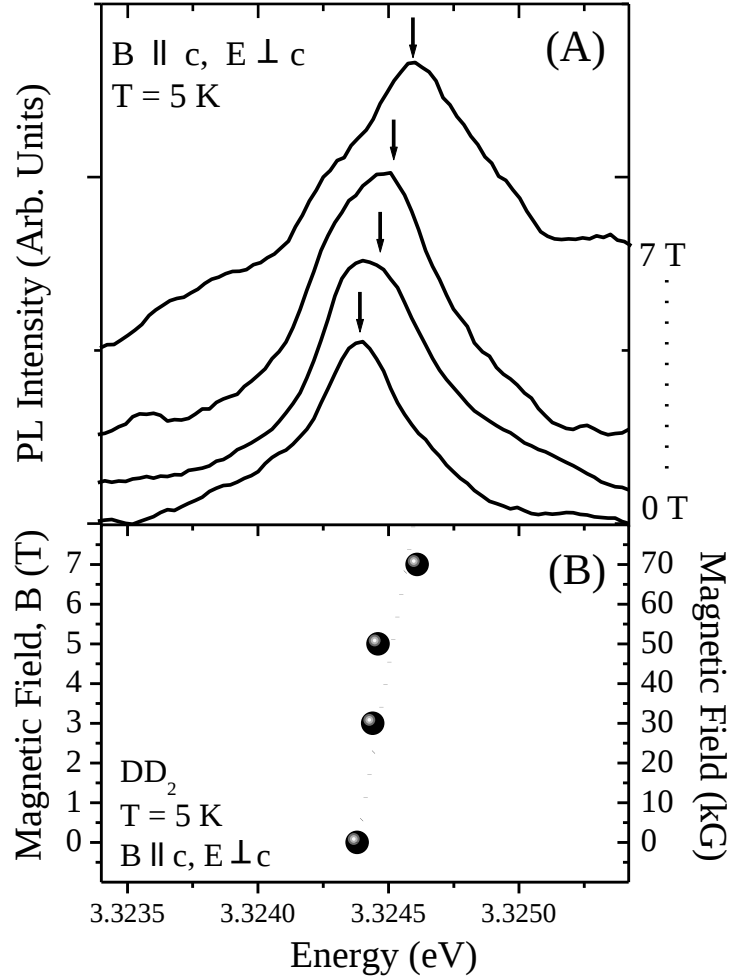


Figure 4.18: PL spectra (A) of the DD_2 line broadening under magnetic fields and plotted data points (B) of the increasing line energy of the DD_2 line emission under application of magnetic fields up to 7 T parallel to the c -axis [0001]. A split component of the line is suggested but not resolved.

A clearly resolved lower energy component, observed previously for DD_1 [16] in the same configuration, is not observed for DD_2 . However, a significant linewidth broadening is observed when compared with the zero field linewidth of 280 μ eV (0.28 meV) which increases to 520 μ eV

at maximum magnetic field ($B = 7$ T) suggesting the split component is present but not resolved. No higher resolution was available for this feature. Polarisation dependent measurements, which could unambiguously reveal any higher or lower energy components, were not possible in this work.

4.5.1 Identification of donor or acceptor nature of DD_2

As discussed in Chapter 3, the donor or acceptor nature of a neutral bound exciton feature can be identified by observing the features upon application of magnetic fields while simultaneously increasing the temperature [37, 38]. In this case only limited temperature dependence measurements were possible for DD_2 due to the already discussed thermal instability. However, the measurements made indicate a constant relative intensity for the split components as shown in Figure 4.19. The two components broaden slightly as the temperature increases but their relative intensity remains essentially the same for all four spectra.

We conclude that the splitting caused by the magnetic field is a ground state splitting as is observed for the case of DBX recombinations. Comparing Figure 4.19 to temperature dependent measurements on the Y-lines observed by Wagner *et al.* [16] it seems DD_2 is generally similar to those observed in that work.

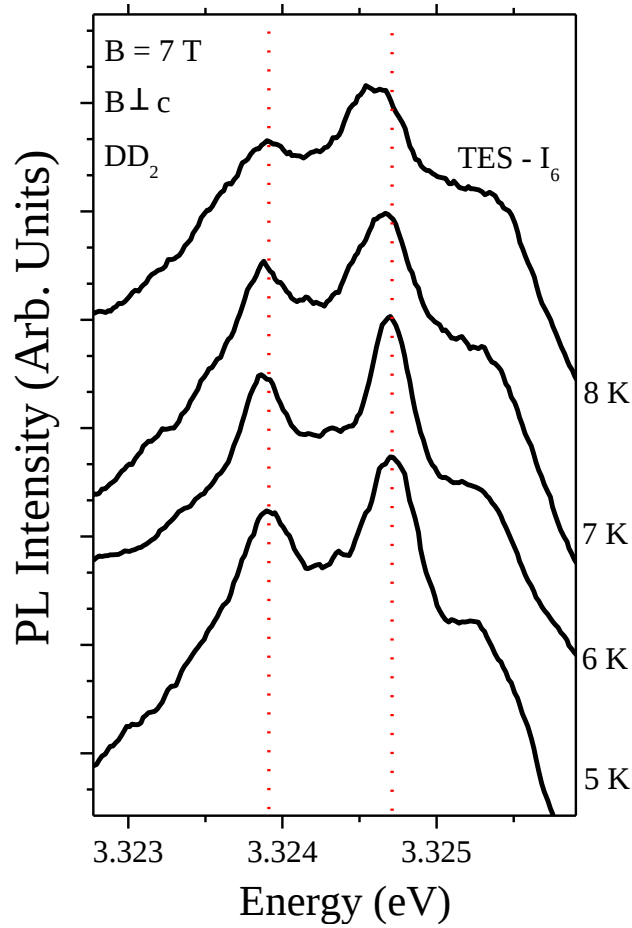


Figure 4.19: Representative spectra of the two split components of DD_2 in the Voigt configuration at maximum magnetic field ($B = 7$ T) with varying temperature. The ratio between both features remains constant with increasing temperature. Spectra have been vertically shifted for clarity.

4.6 Discussion

4.6.1 Radiotracer experiments and stable implantations

Radiotracer data presented in section 4.2 of this chapter have allowed for an unambiguous chemical assignment of the DD_2 feature to a single substitutional Ge impurity. An alternative possibility is that the Ge-related luminescence is due to a defect formed from the decay of mother Ga or As isotopes occupying a site other than an ideal substitutional Zn

site but this possibility is deemed unlikely for the reasons outlined earlier in Chapter 2 and summarised here for completeness. The recoil due to the decay of these two isotopes, ^{73}Ga and ^{73}As (via β^- emission and electron capture, respectively), has the potential to create defects in the surrounding crystal region. However, with low recoil energies for both cases (less than 10 eV) the possibility of extensive defect creation in the surrounding crystal lattice is also deemed unlikely. This implies that the Ge daughter isotopes occupy substitutional Zn sites following the decay of the mother Ga and As isotopes. Strong evidence exists for the substitution of both the Ga and As impurities as simple substitutional impurities in ZnO occupying the Zn site.

4.6.2 Temperature dependent measurements

Temperature dependent measurements indicate a weak binding mechanism observed as a small thermal binding of the exciton to the centre. This implies that the exciton as a whole quasiparticle is not bound but rather that one of the individual components (the hole or the electron) is more tightly bound to the defect than the other, with the more loosely bound particle producing the observed low thermal binding energy value.

Another noteworthy characteristic, the changing localisation energy (*cf.* Figures 4.9 and 4.10) with increasing temperature suggests a unique binding mechanism also. Typically excitons become less localised (*cf.* data for I_6 in Figure 4.10) due to an increased screening effect with increasing free carrier concentration. Wagner *et al.* [16] find similar results for the behaviour of Y_0/DD_1 and Y_1 , both of which they label as Y-lines in that work.

A weak lattice interaction is also observed by comparing the ratios of the first LO phonon replica to the zero phonon intensity where an abnormally small value is found for DD_2 when compared with the well-

known DBX lines. This property is illustrated in Figure 4.20 where this ratio is plotted as a function of localisation energy; the expected increase in LO-phonon interaction for deeper defects is not observed for both DD_1 and DD_2 .

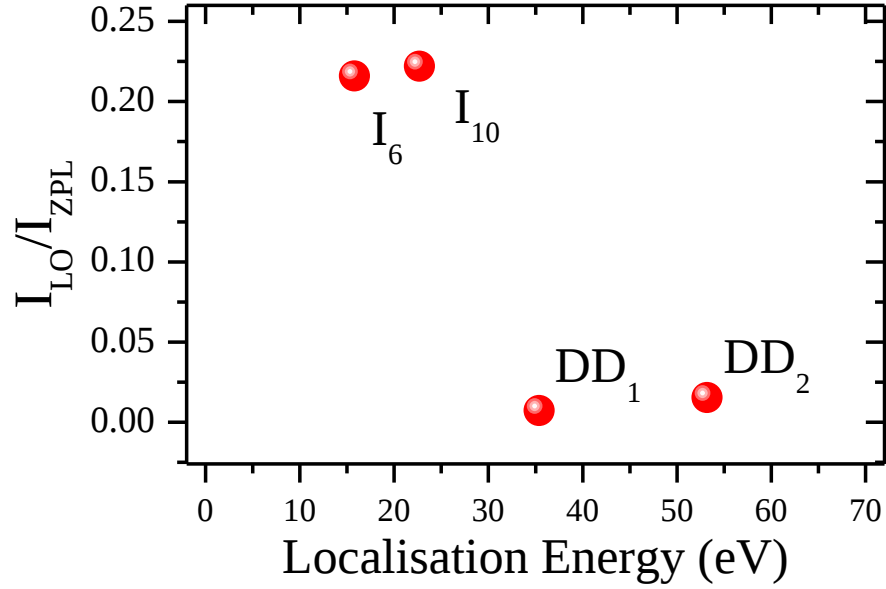


Figure 4.20: Intensity of the first LO phonon replica to the ZPL for I_6 , I_{10} , DD_1 and DD_2 plotted against localisation energy for each feature.

4.6.3 Uniaxial stress measurements

Piezospectroscopy measurements yielded vital information about the behaviour of the defect under stress applied along two different uniaxial directions. Plotted in Figure 4.21 are the energy values for DD_2 under uniaxial stress along the $[0001]$ and $[1-210]$ directions. The theoretical and experimental values for shift rates parallel and perpendicular to $[0001]$ for DD_2 and I_6 are listed in Table 4.3 along with the fitting parameters used, based on the work of McGlynn and Henry [35]. The lines in Figure 4.21 correspond to the predicted shift values. The values observed for the D^0X feature I_6 , used in Table 4.3 as a direct comparison with DD_2 , agree with those reported in the literature [16].

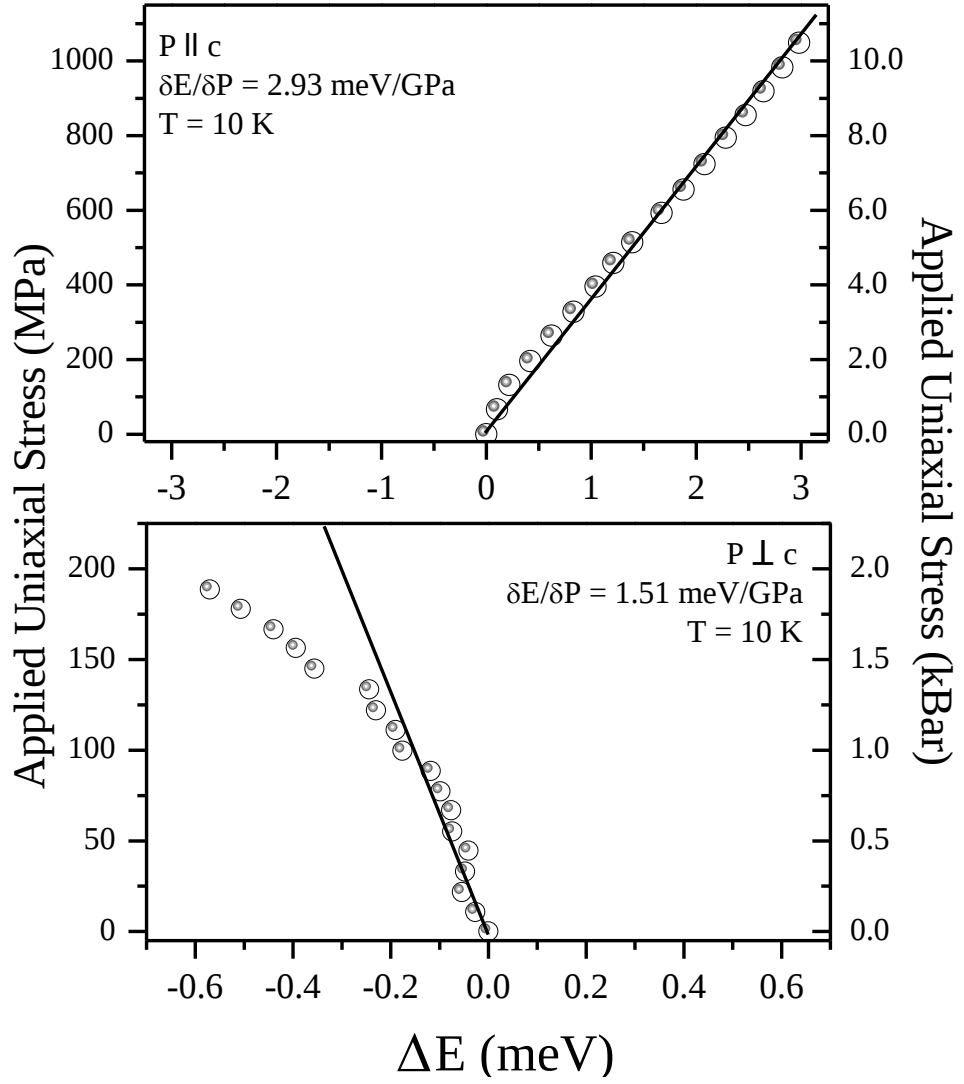


Figure 4.21: *Plotted change in energies for the DD_2 feature for uniaxial stress along the $[0001]$ and $[1-210]$ directions. The lines represent fits to the shift rates using the fitting parameters in Table 4.3. Note the different scales on the x- and y-axes of both graphs.*

Of the possibilities discussed by McGlynn and Henry [35] only one defect type applies to DD_2 , which is that of transitions between nondegenerate states of a trigonal defect, similar to the D^0X lines (none of which split with uniaxial stress). Details of the calculation can be found in Chapter 3 with the relevant equations reprinted here:

$$[0001] \text{ stress: } At_1 + 2At_2 \quad 4.4$$

$$[1 - 210] \text{ stress: } At1 - 2At2 \quad 4.5$$

The lack of splitting upon application of uniaxial stress in both [0001] and [1-210] directions makes the assignment of the feature to a trigonal defect a trivial one, as seen in Table 4.3. This supports evidence from radiotracer work suggesting Ga and As had left the resultant daughter isotope Ge occupying a substitutional site for which the local symmetry is trigonal.

Note that the shift rate in the lower panel of Figure 4.21 (for the [1-210] direction) is seen to change at higher stresses. The reason for this is unclear; when calculating the shift rate in this direction the linear, lower stress values were used.

As can be seen in Figure 4.21 and Table 4.3 a close agreement is found between theoretical and experimental shift rates providing strong support for the defect assignment.

Table 4.3: *Fitting parameters for trigonal nondegenerate defects DD_2 and I_6 ; good agreement is found for all experimental and predicted values, illustrated in Figure 4.21.*

Line	Energy (eV)	Fitted stress parameters (meV/MPa)	Shift Rates (meV/GPa)			
			[0001] $D^{im.}$		[1-210] $D^{im.}$	
			Experiment	Calculated	Experiment	Calculated
DD_2	3.3238	At1 = 0.07 At2 = 1.44	2.93	2.95	1.51	1.51
I_6	3.3612	At1 = 0.41 At2 = 1.22	2.84	2.85	0.81	0.81

The shift rate of DD_2 , particularly in the [0001] direction, highlights a further difference between the D^0X lines and the Y-lines as seen in

Figure 4.22 below. With uniaxial compression along the [0001] direction the transverse free A-exciton shifts to higher energies at a faster rate than the bound exciton features; these bound excitons therefore become more localised under stress along the c-axis.

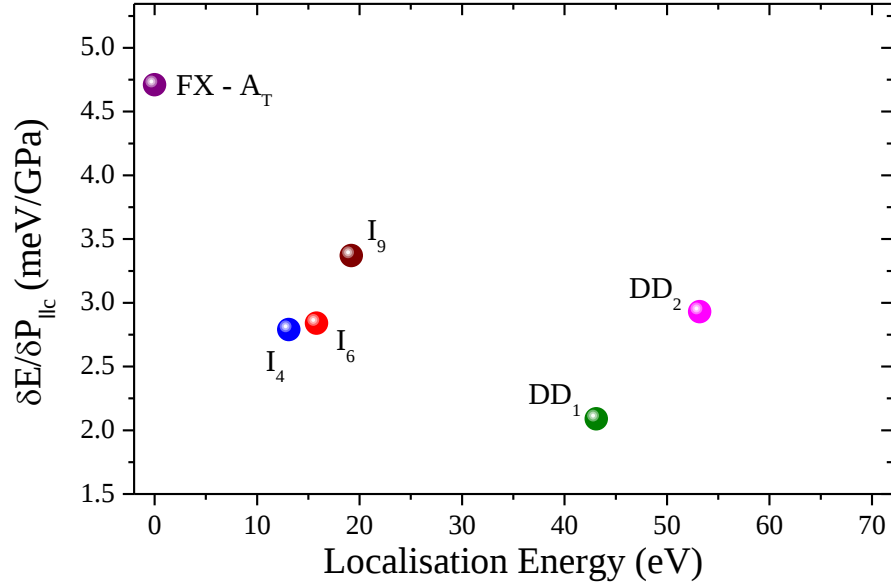


Figure 4.22: Shift rates for some commonly observed features in near band edge emission for uniaxial stress applied along the [0001] direction. Another marked departure is observed for the DD lines when compared with the neutral donor bound features.

A trend is exhibited by the D⁰X features I₄, I₆ and I₉ (and other D⁰X features not listed here) in Figure 4.22 that indicates a strong dependence of shift rate in the [0001] direction with localisation energy. A distinct trend is observed for the Y-lines DD₁ and DD₂. As indicated in Figure 4.22 similar results under uniaxial stress are found for the DD₁ feature (value taken from [16], labelled Y₀ in that work) which is also found to be a trigonal defect, shifting but not splitting under uniaxial stress in any direction.

4.6.4 Analysis of the Zeeman data

The Zeeman spectroscopy data presented in the results section previously are now analysed in the context of the theory of Zeeman spectroscopy presented in Chapter 3 with comparison drawn to the DD_1 feature particularly, given the similar behaviour observed with respect to DD_2 .

In fields applied along the $[1-210]$ crystal direction (*i.e.* perpendicular to the c -axis) the excited state fine splitting in D^0X centres due to the Γ_7 hole (from the A valence band) is minimal and is only observed at higher resolution [39]. Hence, the large observed splitting in Figure 4.16 is almost entirely due to splitting in the ground state as is the case of a D^0X , illustrated graphically in Figure 4.23

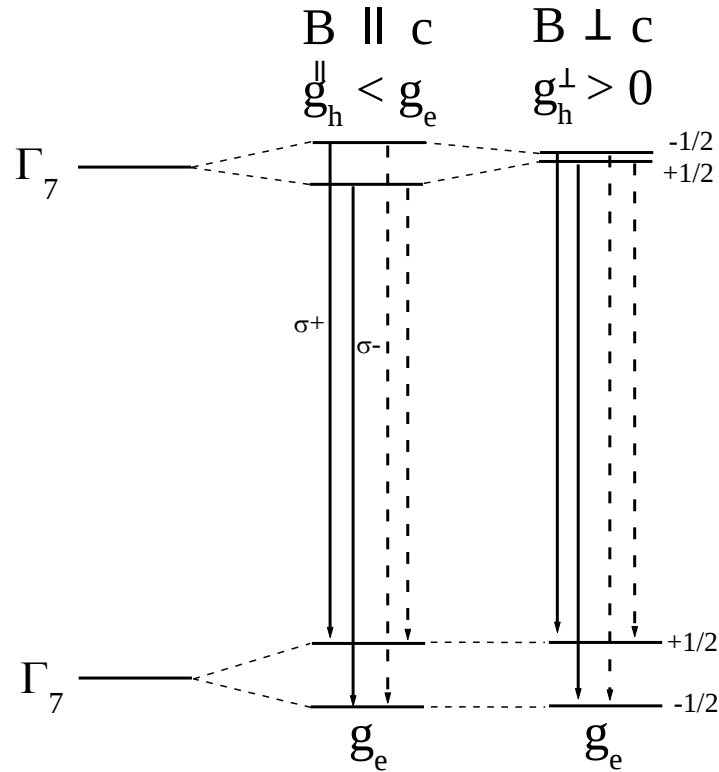


Figure 4.23: Illustration of the recombination process of an exciton bound to a neutral donor (D^0X) under magnetic fields in the $[0001]$ and $[1-210]$ directions. Dashed lines in the $[0001]$ direction are forbidden transitions. In the $[1-210]$ direction the dashed lines (fine splitting) are only observed in high resolution scans.

As explained in §4.5 of this chapter a significant broadening of the DD_2 feature was observed when the magnetic field was aligned in the $[0001]$ direction. Based on the likelihood of a second component a fitting is performed on the DD_2 feature at maximum field along the $[0001]$ direction, including an additional component at lower energy. The results of this fitting are shown in Figure 4.24.

The separation between the two fitted components of DD_2 when the magnetic field is aligned parallel to the $[0001]$ direction is approximately 250 μeV for $B = 7$ T (Figure 4.24), close to the separation of the two components of DD_1 under the same field (298 μeV).

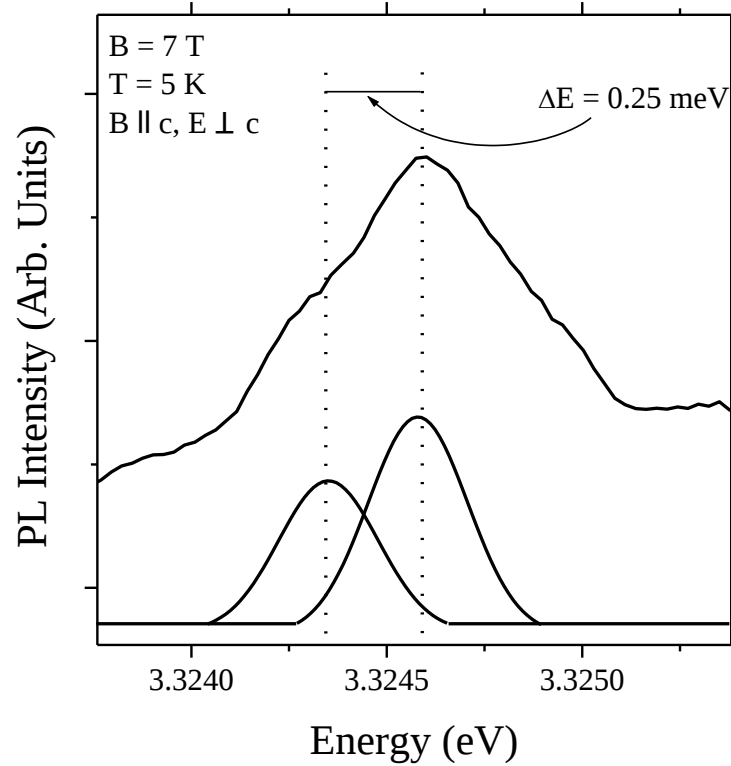


Figure 4.24: Representative spectrum of DD_2 with a magnetic field applied parallel to the c -axis. Due to the significant line broadening at higher magnetic fields (see text) the broader line shape was fitted to two peaks with FWHM values of 0.3 meV, separated by 0.25 meV.

Shown in Figure 4.25 is the same magnetic field direction as Figure 4.24, this time for the DD_1 line where a clear separation of the two components was observed. Previous work revealed right and left circular polarisation dependence for this feature also exhibited by many features in this configuration [14, 15, 16].

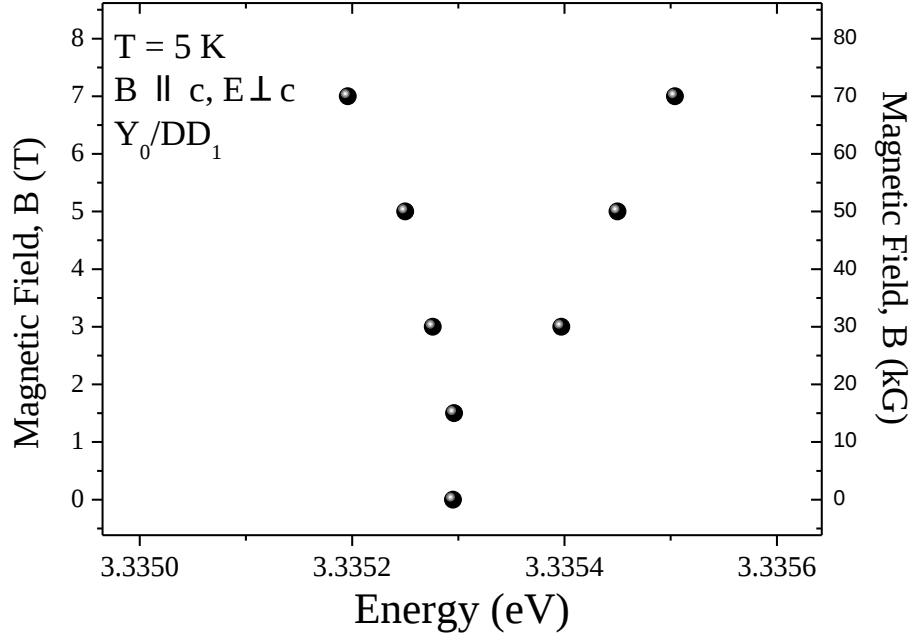


Figure 4.25: Faraday direction splitting of the DD_1 feature results in an observed line splitting and distinct polarisation of the split features.

We now calculate the excitonic g-value for DD_2 using the available data. From Chapter 3 we have

$$\Delta E = g_e \mu_B B \quad 4.7$$

Where ΔE , μ_B and B are known from experiments as 0.86 meV, $5.788 \times 10^{-5} \text{ eV T}^{-1}$ and 7 T respectively for the two split components of DD_2 for magnetic fields applied perpendicular to the c-axis (*cf.* Figure 4.17). Substituting these values into equation 4.7 results in an excitonic g-value, g_e , of 2.12 ± 0.1 for DD_2 in this configuration, close to the value calculated for DD_1 in this work (1.92 ± 0.1) and in prior work on DD_1 (labelled Y_0 in that work) by Wagner *et al.* (1.87) [16].

Angular dependent measurements were not possible for values between 0° and 90° with respect to the [0001] direction therefore more precise values for the electron and hole g-values which can be obtained from a comprehensive fit to such data are not available.

In the Faraday configuration an excitonic g-value was calculated using the energy separation from the fit peaks in Figure 4.24 which, due to the linear shift of DD₂ is effectively twice the energy shift, E, for DD₂ in Figure 4.19. A value of 0.62 was obtained, close again to that of DD₁ (0.74 in this work).

Due to the well-known isotropism of the electron g-value in ZnO, as discussed in Chapter 3, the change in exciton g-value from 2.12 to 0.62, for fields perpendicular and parallel to the c-axis respectively, is attributed entirely to the anisotropy of the hole g-value. While precise values for hole and electron g-values are not possible an estimate based on already known values for the electron g-value is possible.

Recalling from Chapter 3 that

$$g_{exc} = |g_e \pm g_h| \quad (4.8)$$

If we assume g_e , the electron g-value, to be 2.02 as found previously for DD₁ [16] then we find the following values for g-values for DD₂:

$$g_h^\perp = 0.10 \quad (4.9)$$

$$g_h^\parallel = -1.50 \quad (4.10)$$

$$g_e = 2.02 \quad (4.11)$$

agreeing with the anisotropy exhibited in the hole g-value observed in previous works [16, 36].

4.6.5 Findings from Zeeman spectroscopy measurements

Upon application of magnetic fields a linear splitting of the DD_2 feature was observed confirming the neutral nature of the defect. This linear splitting (observed also for DD_1) indicates that the excited and ground states contain one unpaired spin each typical of a neutral donor or acceptor bound state in ZnO.

In the Faraday configuration ([0001] direction) a lower energy component is not observed but its presence inferred by an increasing FWHM of the feature and similar splitting behaviour for DD_1 (where both components are resolved).

Temperature dependent measurements made with the magnetic field aligned perpendicular to the c-axis confirm a neutral donor assignment for DD_2 .

4.7 Conclusion

Presented in this chapter are results from magneto-spectroscopic measurements, piezospectroscopy, temperature dependence and radiotracer measurements. The DD_2 exciton recombination centre is found to occur at a trigonal non-degenerate donor binding centre containing a single Ge impurity, similar to donor bound exciton recombinations already studied extensively in ZnO. This work has allowed a direct confirmation of the chemical nature of one of these defect lines as a neutral substitutional Ge impurity occupying a Zn site.

Similar lines to DD_2 are observed by Dean [24] in ZnSe material grown by a variety of methods. Dean suggests a model which would result in an apparent reduction in S since the lines observed by Dean (labelled Y and Z) show abnormally low Huang-Rhys factors also [24]. Small dislocation loops are suggested, containing N number of binding sites; summing over these N sites the relaxation energy is found to be

proportional to $\frac{1}{N}$ i.e. S is proportional to $\frac{1}{N}$. An important difference, perhaps, between this work on ZnO and Dean's work on ZnSe is that the Y and Z lines in Dean's work had relatively broad full width at half-maxima; 4 meV and 6 meV for Y and Z respectively compared to the values of less than 1 meV for DD₂ in this work, comparable with donor bound exciton features. This tighter binding could result from the much larger exciton binding energy in ZnO (60 meV [40]) compared with that of ZnSe (21 meV [24]). Alternatively due to the more ionic nature of the bond in ZnO [41] the excitons could become more localised to defect sites and this reduced degree of freedom could result in less emission line broadening for Y and Z lines.

However, the precise nature of the binding mechanism, which appears to be different to that for typical donor bound exciton recombinations, and the weak lattice interaction, require further clarification.

Zeeman analysis provides confirmation of the neutral charge state at the bare defect site and evidence that the splitting upon application of magnetic fields is due to the unpaired spin of a hole in the excited state of the system when illuminated. This information allows a conclusive assignment that the DD₂ feature is a neutral donor bound exciton centre, exhibiting an abnormally small thermal binding energy which does not correspond to its localisation energy. This property, along with the shifting localisation energy during temperature dependence indicates that a distinctly different binding mechanism is used to trap excitons at the defect site. The possibility that the site only binds one component of the exciton quasiparticle cannot be ruled out.

4.7.1 A model for the DD₂ recombination centre

The aim of the research reported in this chapter is to determine as fully as possible the nature of the centre that gives rise to the DD₂ feature. We have established the following:

- (i) The recombination centre involves Ge impurities which are occupying substitutional Zn sites (Ge_{Zn}).
- (ii) The symmetry of the centre is trigonal, the same as that of a Zn atom surrounded by four O neighbours (and *vice versa*).
- (iii) The ground and excited states are both orbitally non-degenerate, consistent with electron and hole states formed from the conduction and valence band.
- (iv) The characteristics of the PL spectrum generally and of the DD_2 line under magnetic fields in particular closely resemble those of single donor bound exciton recombinations (D^0X).
- (v) The thermal binding energy of the centre in the excited state is very weak and the position of the DD_2 ZPL shifts markedly to lower energies for temperature changes from 4 – 20 K, above which temperature it is no longer detected.
- (vi) The main features of the centre closely resemble those of other PL lines which have been attributed to D^0X recombinations at, or related to, extended structural defects in ZnO [16].

Our task now is to draw conclusion regarding the composition and physical characteristics of the centre giving rise to DD_2 . We consider several possibilities:

1. Recombination at neutral Ge_{Zn} atoms

This is the simplest case to consider – that the centre consists of isolated Ge_{Zn} atoms. This would satisfy the symmetry requirement, is also consistent with the radioactivity data, and, in general terms, with D^0X recombination since Ge_{Zn} would act as a donor. However, as a group IV impurity on a group II_b Zn site, Ge would be a double donor, so the details of the exciton states would differ from those of a single donor. In particular, TES transitions for a double donor would lie at much larger separation from the principal line than for single donors. Besides that

consideration it is difficult to reconcile a large exciton localisation energy of 53 meV with a centre containing three electrons and a hole.

The possibility that the luminescence is due to the recombination of a free hole (produced under illumination) with an electron on a Ge double donor exists also. In this case, the line shape would be expected to be broad with a distribution of hole energies allowed, whereas DD_2 is notably sharp. For all of these reasons, it is unlikely that DD_2 involves a single isolated Ge_{Zn} impurity.

2. Recombination at structural defects

Given its strong similarities with the DD_1 centre, we consider the possibility that DD_2 involves D^0X recombination at some kind of structural defect as has been suggested for DD_1 in [16]. In principle, these arguments could also apply to DD_2 provided they can be reconciled with the involvement of single Ge atoms and with trigonal symmetry as observed under stress.

It is possible that crystal defects such as those proposed in the case of DD_1 (or Z_0 in [24] for example) could result in partial compensation of the Ge_{Zn} double donors, thereby creating a single donor centre. The trigonal symmetry could still apply to the core of the exciton complex even though the strain effects of a structural defect are influencing the overall electron and hole binding in the complex. This model might also account for the marked shift of DD_2 with temperature as the shift could be due to the effects of temperature on the structural defect rather than on an isolated single substitutional Ge_{Zn} impurity.

3. Compound Ge defect in ZnO

We now consider the possibility that DD_2 consists of a combination of a Ge_{Zn} substitutional impurity and another impurity or defect, *i.e.* from a compound defect in which the Ge impurity is just one of the components. Examples of such a defect would include Ge_{Zn} in combination with a nearby vacancy, or in combination with a nearby acceptor impurity such as Cu_{Zn} or Li_{Zn} . These latter cases are both deep acceptors in ZnO and they could create local potentials to attract diffusing Ge impurities into their vicinity in the crystal.

Likewise, it is possible that some implantation damage could survive the annealing process with the result that the Ge impurity finds a favourable position adjacent to such damage.

In considering these possibilities the trigonal symmetry and donor nature established from experiment must be retained. We first consider Ge-acceptor pairs, where the single acceptor (mentioned above as Cu or Li for example) partially compensates the Ge_{Zn} double donor. In order to retain trigonal symmetry, the Cu or Li site would have to lie along the c-axis in a Zn site, and the closest such site would lie one lattice constant from the location of the Ge atom. We show a schematic diagram of such a Ge-acceptor pair centre in Figure 4.26.

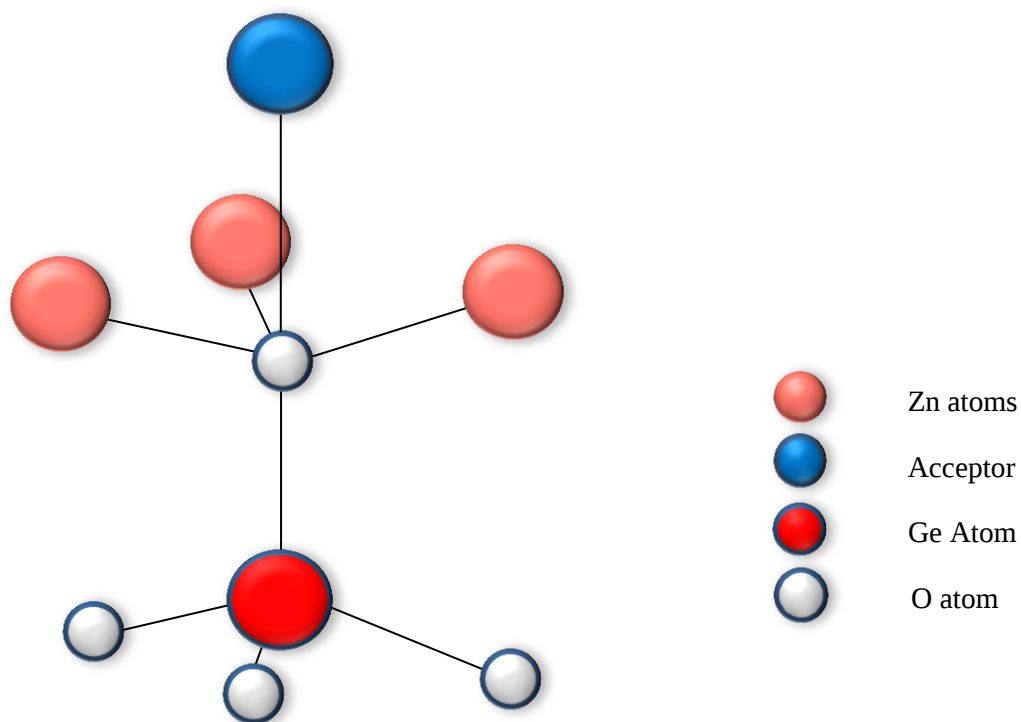


Figure 4.26: *Illustration of an acceptor nearby to the Ge impurity where the Ge replaces a Zn atom (Ge_{Zn}).*

In a similar fashion, we consider the possibility that, instead of an acceptor impurity, there could exist a Zn vacancy, V_{Zn} , along the c-axis. The electrical behaviour of V_{Zn} is that of an acceptor impurity [42, 43] so here too the required trigonal symmetry and donor character for DD_2 could be produced by a vacancy instead of an acceptor in a Zn site on the c-axis close to the Ge_{Zn} impurity. Note that the O vacancy (V_{O}) acts as a donor so it would not provide the compensation required for Ge_{Zn} [44].

The data we have available do not allow for a definite choice to be made between the alternative possibilities for DD_2 described above. The involvement of Cu or Li could, in principle, be examined by using starting ZnO material with differing amounts of these impurities for Ge implantation. However, commercially available ZnO tends to have significant levels of these already present, making the use of widely

varying Cu or Li concentrations difficult to achieve. Annealing in Zn-rich atmosphere would favour the destruction of Zn vacancies and this might provide evidence to support the involvement of Zn vacancies if the DD_2 signal was found to decrease significantly under such conditions.

For the present, we can say that the DD_2 centre is relatively simple structurally, that it involves a Ge impurity and that it acts as a single donor centre in the crystal. The involvement of a neighbouring impurity or defect situated along the c-axis in the close vicinity of the Ge_{Zn} impurity is also indicated by the available data.

4.8 References

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Chapter 5: The Hg-related isoelectronic binding centre in ZnO

5.1 Introduction

Isoelectronic dopants form an important class of impurity systems for semiconductors not least because of their ability to significantly modify the band gap properties of the host semiconductor [1, 2]. This band gap engineering is then hindered however, by low solubilities associated with isoelectronic dopants in the native crystal environment, a consequence of the large variance in the masses of substitutional isoelectronic impurities distorting the local crystal lattice [1, 2, 3, 4].

It is this difference in mass that is thought to contribute to the trapping of excitonic particles at these isoelectronic centres [5]. A changing of the atomic pseudopotential due to the isoelectronic impurity was proposed initially [6] to account for the trapping of excitons in earlier systems [3, 4, 7] but this was found to be much too small when compared to the binding energies observed for these typically deep impurities. This gives more weight to the argument that it is the local perturbation originating from the strain inducing mass change during isoelectronic doping [4, 8].

A model was proposed separating isoelectronic impurities into two distinct groups; pseudodonor and pseudoacceptor isoelectronic traps [4]. The model for the pseudodonor trap suggests that the hole quasiparticle is localised at the isoelectronic trap and the electron component of the exciton is bound coulombically to the hole. The opposite is then true for the pseudoacceptor type impurity *mutatis mutandis*.

These different binding mechanisms can be distinguished [4] in two ways. Firstly the absorption spectra for pseudodonors and pseudoacceptors are distinct from one another since only very weak absorption is observed for pseudodonors since strongly bound hole states (as in pseudodonors) overlap very little with the much broader electron wave function, resulting in a weakly observed absorption spectrum (an explanation of which is presented by Rühle

et al. in [3]). Secondly, when cooled to liquid He temperatures a forbidden transition dominates the luminescence centre (in the case of most if not all known isoelectronic exciton recombination centres thus far observed in PL). In the case of pseudodonors this forbidden ZPL is weak but with strong phonon interaction [9] whereas for the pseudoacceptor model the forbidden ZPL is observed and associated sidebands shift to lower energies correspondingly due to the cross-coupling of the allowed and forbidden states with their phonon sidebands [8, 10], a suitable explanation of this effect is offered by Hopfield *et al.* in [4].

Only one isoelectronic trap has been observed during PL in ZnO which is related to Hg [11]. Hg, also a group II_b element along with Zn and Cd, is significantly heavier than the Zn atom it is expected to replace (with an increase in the covalent radius of around 13%) resulting in a significant perturbation of the local crystal field surrounding it. The defect produces a characteristic ZPL around 3.279 eV at low temperatures in the PL emission of ZnO, including an associated phonon sideband, and was shown via radiotracer PL to be related to Hg [11]. This feature has not been observed (to this author's knowledge) in any works since and merits further study (given the rare occurrence of isoelectronic traps in ZnO) in order to gain further insight into ZnO dopant properties.

The strong localisation of the exciton (90 meV below the lowest free exciton energy) is typical of isoelectronic traps in compound semiconductors [4]; see for example Bi in GaP [9] or O in ZnTe [10] which lie approximately 100 and 400 meV below their respective free exciton energies. Other examples of isoelectronic bound excitons include N-doped GaP [8], Te-doped ZnS [12], Bi-doped InP [3], to name some well-known centres.

This chapter deals with the radioactive identification of the Hg-related features in PL emission of ZnO, confirming the result of Agne *et al.* in earlier work [11], and includes also further investigations (involving stable isotopes) into the defect centre. The chapter starts by verifying the chemical nature of the impurity centre by observing spectra of the sample after implantation of radioactive ¹⁹²Hg followed by a general discussion of the emission line's properties. This is followed by uniaxial stress measurements and Zeeman

spectroscopy measurements in order to accurately establish the defect type of the recombination centre.

An assignment of pseudoacceptor character is proposed based on the evidence provided by Zeeman, piezo- and temperature dependent spectroscopy results.

5.2 Radiotracer measurements

Radioactive ^{192}Hg was implanted into nominally undoped ZnO pieces obtained from Tokyo Denpa and subsequently annealed at 750°C to remove residual implantation damage. The PL emission of ^{192}Hg implanted ZnO is shown in Figure 5.1 (a) before the majority of the ^{192}Hg has decayed (via electron capture) into ^{192}Au and after the sample has been annealed to remove damage induced during the implantation process. As in the work of Agne *et al.* [11] a sharp ZPL emission was observed at 3.2789 eV alongside the phonon sideband also reported previously by Agne *et al.* The decay of the ZPL (referred to as the A line henceforth) and accompanying sideband was monitored over the course of five half-lives, representative spectra of which are shown in Figure 5.1 (b), and a calculated value of 3.81 ± 0.19 h was obtained for the half-life of the ZPL. This calculated half-life does not agree within the fit error with the tabulated half-life for ^{192}Hg of 4.85 h [13]. In the case of an excitonic recombination occurring at a binding site incorporating a single radioactive impurity a matched dependence on the impurity's half-life is expected [14], whereas in the case of excitonic binding at a defect involving two radiotracer impurities (of the sample isotope) the emission feature would display a decay twice as fast as that predicted from the tabulated half-life [14, 15]. In this case the calculated half-life is much closer to the tabulated half-life (4.85 h [13]) than it is to half of that value (~ 2.4 h in this case) leading to the conclusion that the defect site is indeed related to a single substitutional Hg atom involved in the recombination as proposed in [11].

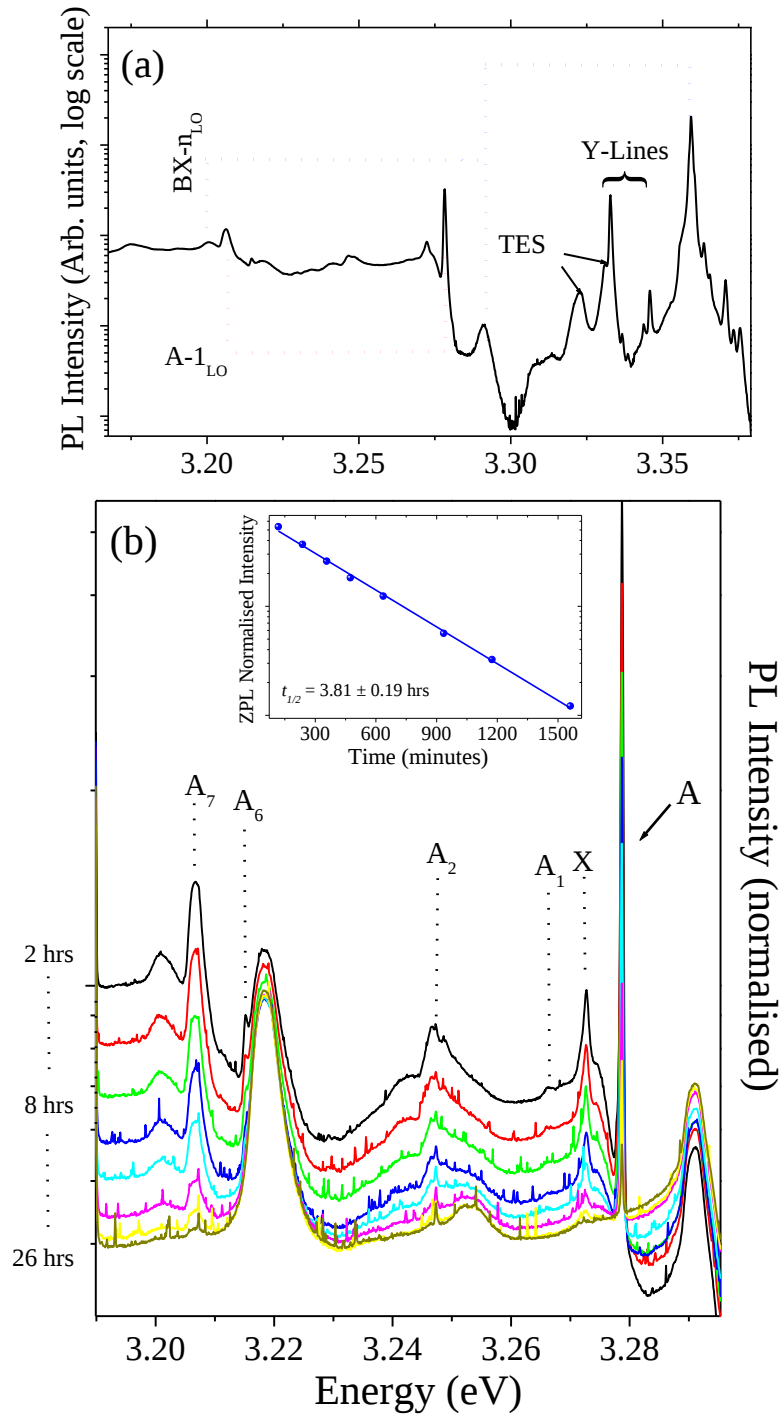


Figure 5.1: PL emission (a) from ZnO implanted with radioactive ^{192}Hg before any significant amount of the ^{192}Hg has decayed showing the bound exciton features and their LO phonon replicas and the Hg ZPL and its LO phonon replica. Representative spectra (b) of the Hg band over the period of five half-lives of ^{192}Hg . The naming nomenclature A – A₇ is from [11] with values listed in Table 5.1. Not all features observed in stable isotope implanted samples were observed in radiotracer work. The normalised Hg ZPL intensity values over the course of five half-lives are shown inset of (b) corresponding to a calculated half-life of 3.81 ± 0.19 h.

The discrepancy in half-life values is explainable by considering the production of other non-radiative defects during the decay process [16]. This effect has been observed in other works and overcome by incorporating an artificial decay function in half-life calculations to offset the discrepancy [16]. However, this method is not reliable since non-radiative effects in ZnO are not well understood compared to other materials and any value added to take decay effects into account would be circumstantial. Spectra recorded over the course of five half-lives were normalized to the strong band edge emission ($I_{6/6A}$) which was not observed to change significantly with time, the results of which are plotted in Figure 5.1 (b).

Note that not all features observed in previous work were observed here, for example the A_5 line, listed in Table 5.1, discussed later.

5.2.1 Lattice location of Hg

Of paramount importance for defect type assignment is the lattice location of the impurity under investigation. In the only other published work performed involving Hg in ZnO Agne *et al.* cite an unpublished work (which remains unpublished) by Rita *et al.* in which emission channelling measurements were used to verify the substitutional behaviour Hg exhibits, occupying the Zn site (Hg_{Zn}) [11]. What remains unknown is the concentration of the Hg atoms which occupy ideal substitutional sites compared to those that occupy interstitial sites. However, given the tendency of heavier atoms to occupy the cation (Zn) site in ZnO (even including group V impurities thought to behave as acceptors in ZnO until recently [17, 18]) and the similar outer electron configuration it is inferred that the A line studied here is due to a replaced Zn atom in the host crystal producing an isoelectronic defect which then binds an exciton.

5.3 Phonon sideband and temperature dependence

After positive identification of the chemical nature of the A-line and the associated phonon sideband, further experiments were carried out in order to investigate the defect symmetry and binding mechanism involved in trapping

excitons, as detailed in subsequent sections. All further measurements (temperature dependence, uniaxial stress measurements, etc.) were performed on samples doped with stable Hg isotopes.

PL spectra of ZnO implanted with stable Hg are shown in Figure 5.2, the A line is clearly significantly deeper than the already known DBX lines and the recently investigated Y-lines (discussed in Chapter 4), with a detailed look at the associated phonon sideband is shown in Figure 5.2 (b).

Shown in table 5.1 are the line energies (in eV) and separation values (in meV) of the Hg ZPL as observed in this work and the values listed by Agne *et al.* [11] included for comparison. It should be noted that the small discrepancy between this work and the work of Agne *et al.* for the value of the Hg features can be explained by the use of different crystals of ZnO grown by different methods (hydrothermal for this work versus chemical vapour transport for the work of Agne *et al.*) resulting in a different free exciton energy; another likely candidate for the shift is the different isotope masses used in both works although a combination of these effects is also possible [19, 20].

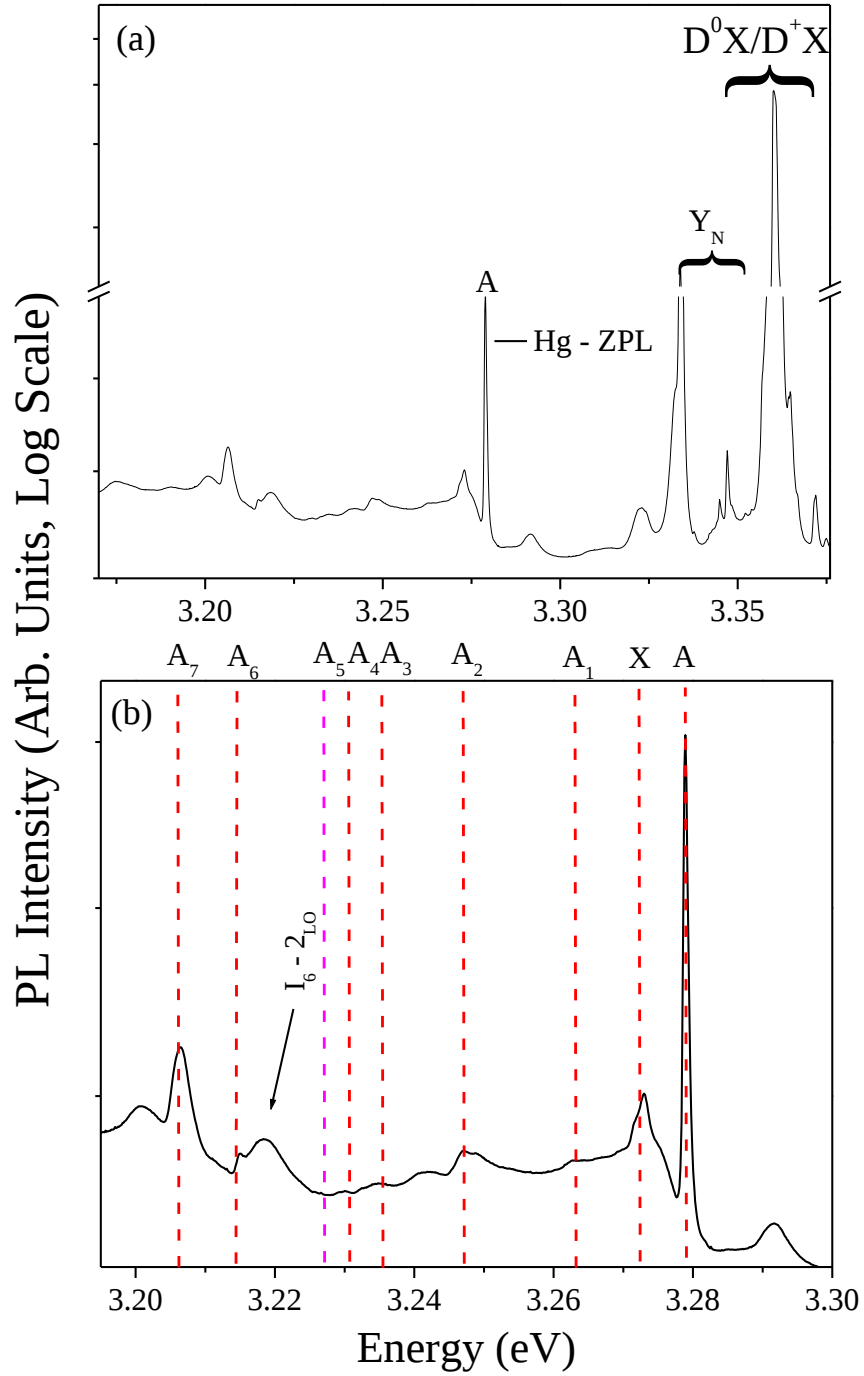


Figure 5.2: PL spectra recorded after implantation of ^{199m}Hg and annealing the sample. ^{199m}Hg is a metastable isotope of Hg and had decayed to stable ^{199}Hg by isomeric transition [13] by the time the annealing treatment was performed in order to remove implantation damage. Indicated are the donor bound exciton lines [21] and Y lines [22] (a) often observed in ZnO spectra and the region of interest (b) where the A line and its phonon replicas A_1 - A_7 are highlighted. A_5 is not observed in this work but is observed by Agne et al. [11] and is indicated for completeness.

Table 5.1: Line energies of the A line for this work and the work of Agne et al. and its associated phonon replica band. Also indicated are the assignments made by Agne et al. based on Raman measurements [11].

Line	This work		Agne et al. [11]		Assignment
	Energy (eV)	ΔE (meV)	Energy (eV)	ΔE (meV)	
A	3.2789 (c-plane)	-	3.2765	-	ZPL
	3.27886 (a-plane)				
X	3.2732	5.7	3.27025	6.25	?
A ₁	3.2669	12.0	3.2642	12.3	E ₂ ^{low}
A ₂	3.2475	31.4	3.2441	32.4	B ₁ ^{low}
A ₃	3.2329	46.0	3.2298	46.7	A ₁ (TO)
A ₄	3.2300	48.9	3.2274	49.1	E ₁ (TO)
A ₅	*	*	3.2215	55.0	E ₂ ^{high}
A ₆	3.2154	63.5	3.2124	64.1	B ₁ ^{high}
A ₇	3.207	72.9	3.2036	72.9	E ₁ (LO)

* Not observed in this work, observed in work by Agne et al.

Agne et al. identify the lines A₁-A₇ as phonon replicas of the ZPL involving acoustic and optical phonons. This increased lattice interaction compared to DBX centres is not only consistent with isoelectronic centres in other semiconductors (such as the N isoelectronic trap in GaP [4]) but is also consistent with the increases exciton localisation at the defect which exhibits a localisation energy of 90 meV, much greater than the DBX lines (usually less than 20 meV [21]). This increased lattice interaction is observed in PL spectra as a larger ratio of the LO replica intensity to the A line intensity as listed in

Table 5.2. Included in Table 5.2 are values of the I_{LO}/I_{ZPL} ratio for the donor bound exciton recombinations with noticeably different values.

Table 5.2: *Line energies, localisation and intensity ratio of the zero phonon line and first LO replica for two well-known DBX lines and the A line. A much larger value is found for I_{LO}/I_{ZPL} for the Hg A line agreeing with its larger localisation from the free exciton energy.*

Line	Energy (eV)	Wavelength (nm)	Chemical Identity	Localisation Energy (meV)	I_{LO} / I_{ZPL}
I_6	3.3612	368.92	Al	15.8	0.22 ± 0.02
I_9	3.3571	369.37	In	19.9	0.22 ± 0.02
Hg – ZPL	3.2789	378.18	Hg	98.1	0.64 ± 0.06

Temperature dependence of the Hg-centre

The temperature dependence of the A line was also measured. The representative spectra for the lower temperature regime behaviour of the Hg-ZPL can be seen in Figure 5.3. While not enough data points were available for an accurate determination of the thermal binding energy a strong thermal stability is clear, corresponding to the deeply bound state of the exciton. This agrees with the strong binding character observed for such traps in previous works [1, 4, 9].

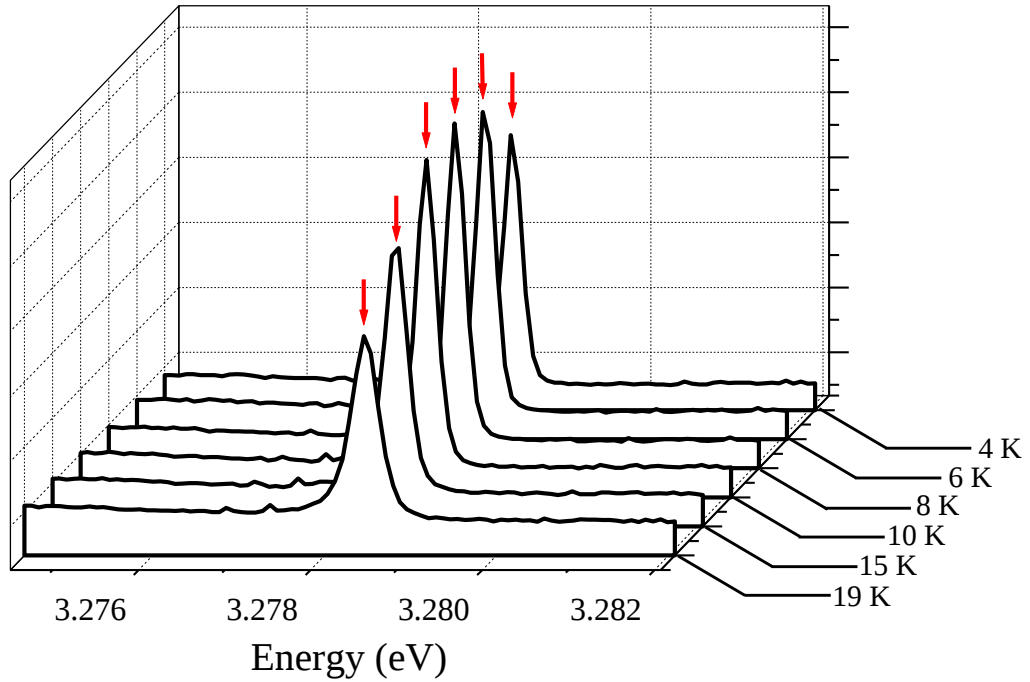


Figure 5.3: *Temperature dependence measurements at low temperatures resulted in a slight increase in luminescence intensity likely related to shallower binding centres becoming depopulated.*

A comparison of the change in localisation energy (the separation from the free exciton to the zero phonon emission) was possible with the available data and is shown in Figure 5.4. Figure 5.4 reveals similar behaviour to that exhibited by the DBX lines [22] indicating similar binding mechanisms (quite unlike the case found for DD₂ discussed in Chapter 4) giving added weight to the theory that the entire excitonic particle is strongly localised at the defect. The similarity to DBX lines and difference to DD₂ from Chapter 4 is highlighted for the A-line in Figure 5.5, which displays temperature dependence PL spectra from 4 – 40 K.

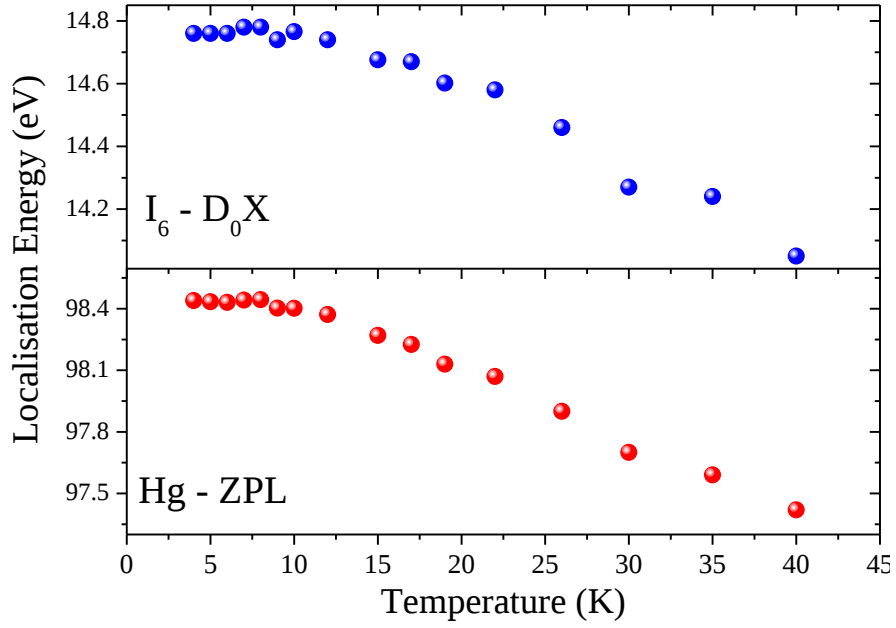


Figure 5.4: Change in localisation energy plotted as a function of temperature for the well-known DBX line I_6 and the Hg A line. A similar shift is observed for both indicating a similar binding mechanism.

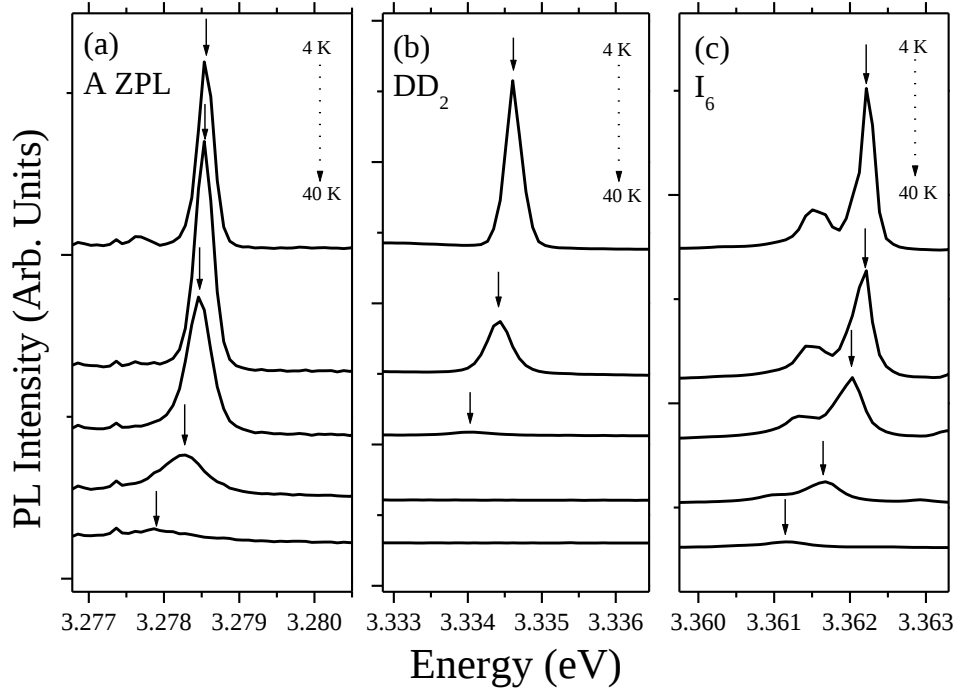


Figure 5.5: Comparison of the A-line (a), the DD_2 line from Ge (b), and the neutral DBX line I_6 with increasing temperature demonstrating the strong thermal binding energy exhibited by the Hg centre.

The assignment to the A line as being due to exciton recombination is concluded not only from its sharp FWHM (~ 0.3 meV), characteristic of exciton recombination [21], but also from power dependence measurements which show a linear $I_A = I_L^{1.13}$ dependence as shown by Agne *et al.* [11], where I_A is the observed A line intensity and I_L is the exciting power of the light source used to generate PL. A linear relationship is expected in the case of exciton recombination [23]. Similar measurements were performed for this work (not shown) and a linear relationship was also obtained.

The forbidden transition in the Hg-centre

Isoelectronic dopants resulting in a ZPL often feature low energy components of the ZPL at liquid He temperatures [4, 9, 11]. In this work a further spectral feature observed was that of a forbidden transition, labelled B, 0.90 meV below the A line transition (0.86 meV in the work by Agne *et al.* [11]) which only appears at temperatures below 5 K as shown in Figure 5.6.

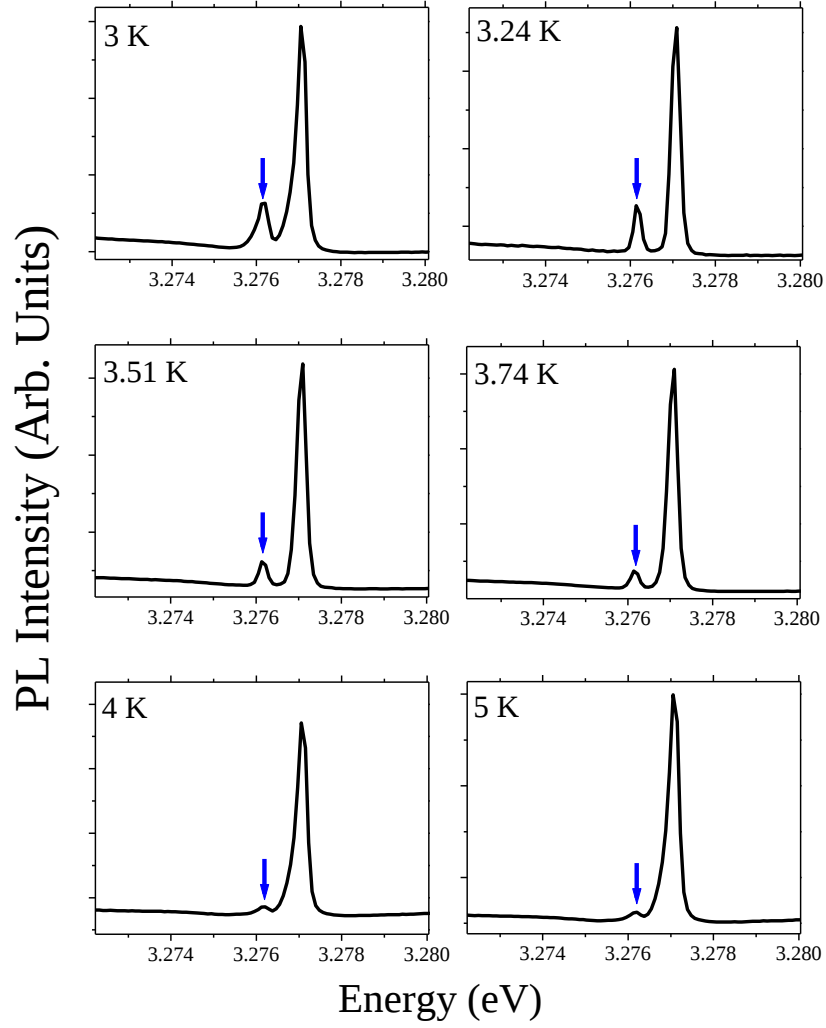


Figure 5.6: *Low temperature spectra of the allowed A-line and forbidden B-line transition of the Hg ZPL. Below 3 K (not shown here) the B-line transition dominates and the A line becomes difficult to observe.*

The A and B lines are clearly separated in this work below 5 K allowing for a more accurate determination of the line energies. A graphical representation of how the allowed and forbidden levels populate is shown in Figure 5.7. The temperature dependence of the A and B lines was also measured and the natural log of the ratio of I_A to I_B plotted against the inverse temperature is shown in Figure 5.8, where I_A and I_B are the intensities of the A and B transitions, respectively.

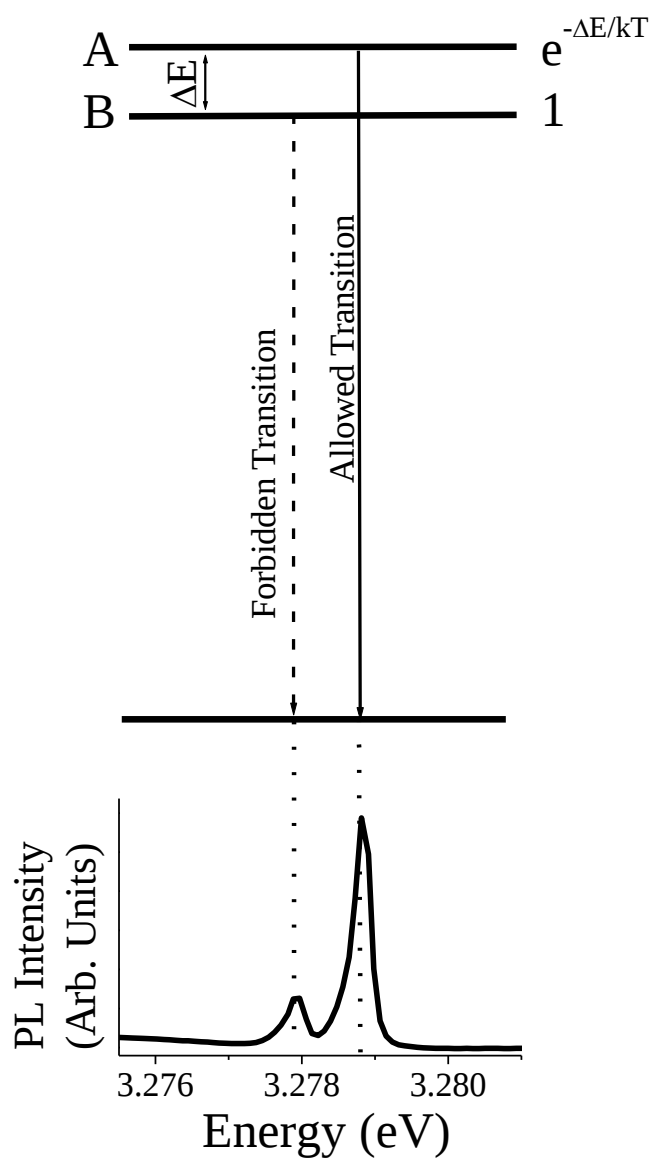


Figure 5.7: Graphical representation of the allowed A-line and forbidden B-line transition of the Hg ZPL. The allowed transition is observed from 3 – 60 K while the forbidden B transition is only observed below 5 K. The energy separation ΔE between A and B can be obtained from temperature dependence measurements if a common ground state is shared by both lines, which should be comparable to the spectral energy separation.

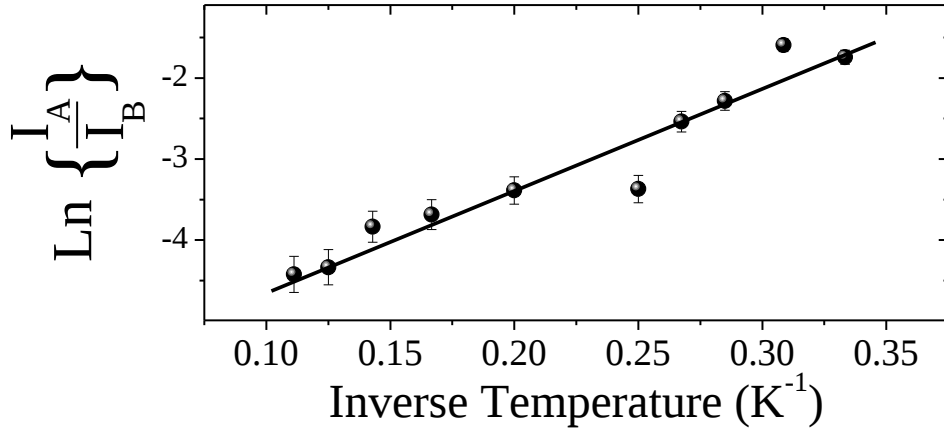


Figure 5.8: Natural log of the intensity of the A and B transitions plotted as a function of inverse temperature yielding a value of 1.06 ± 0.10 meV in good agreement with the observed spectral separation (0.90 meV).

A value of 1.06 ± 0.10 meV is calculated for the thermalisation energy between the A and B transitions (*cf.* Figure 5.8), ΔE_{AB} , corresponding well with the observed spectral peak separation of 0.90 meV. This good agreement confirms that the lines have a common ground state.

Thermalisation between the A and B lines is also evident in the shape and position of the LO replica of the lines. In Figure 5.9 (a) the two Hg-related ZPL features can be seen; A at a temperature of 10 K and B at 2 K dominating the ZPL emission. In Figure 5.9 (b) the corresponding LO emission of each ZPL can be seen 72.9 meV lower in energy from their respective zero-phonon emissions. Note also the corresponding change in energy of the ‘X’ feature for spectra recorded at 2 and 10 K.

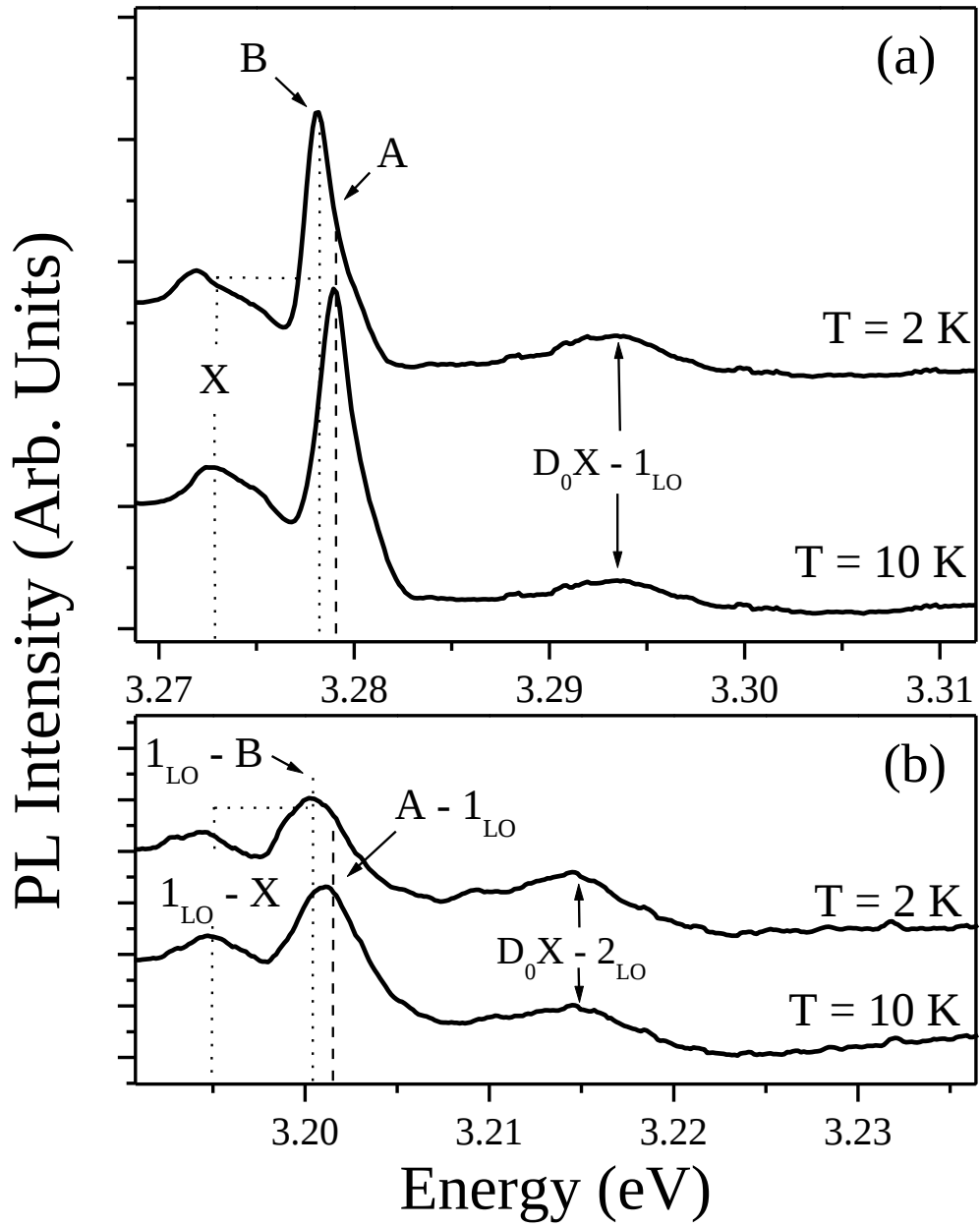


Figure 5.9: Zero phonon features and phonon sidebands of the Hg A and B features. In (a) it can be clearly seen that the A ZPL disappears almost entirely around 2 K where the forbidden B transition dominates, the X feature also shifts in energy by around 0.9 meV indicating a close relation to the B-line. In (b) the first LO phonon replica of each line in (a) is observed with the 1_{LO} replica shifting to lower energies showing the phonon sideband shifts with the B ZPL. Spectra have been vertically shifted for clarity.

5.4 Uniaxial Stress Measurements

Stress along the [0001] direction

In order to investigate the defect centre further, piezospectroscopic measurements were performed applying uniaxial stress parallel [0001] and perpendicular, [1-210] and [10-10], to the c-axis. In spectra of samples under uniaxial stress parallel to the c-axis, shown in Figure 5.10, a linear shift (+3.95 meV/GPa) is observed without any observed splitting as reported for most bound exciton features observed in near band gap luminescence for stress along the [0001] direction [22, 24, 25]. However, as seen in Figure 5.11, a significant decrease in luminescence intensity is observed, uncharacteristic of native donor bound exciton features which were observed to maintain their line shape and intensity under stress up to 1 GPa. No significant line broadening or change in shift rate was observed for the A line for stress parallel to the c-axis as shown in Figure 5.10. However, the PL intensity is found to decrease significantly as the stress is increase as shown in Figure 5.11.

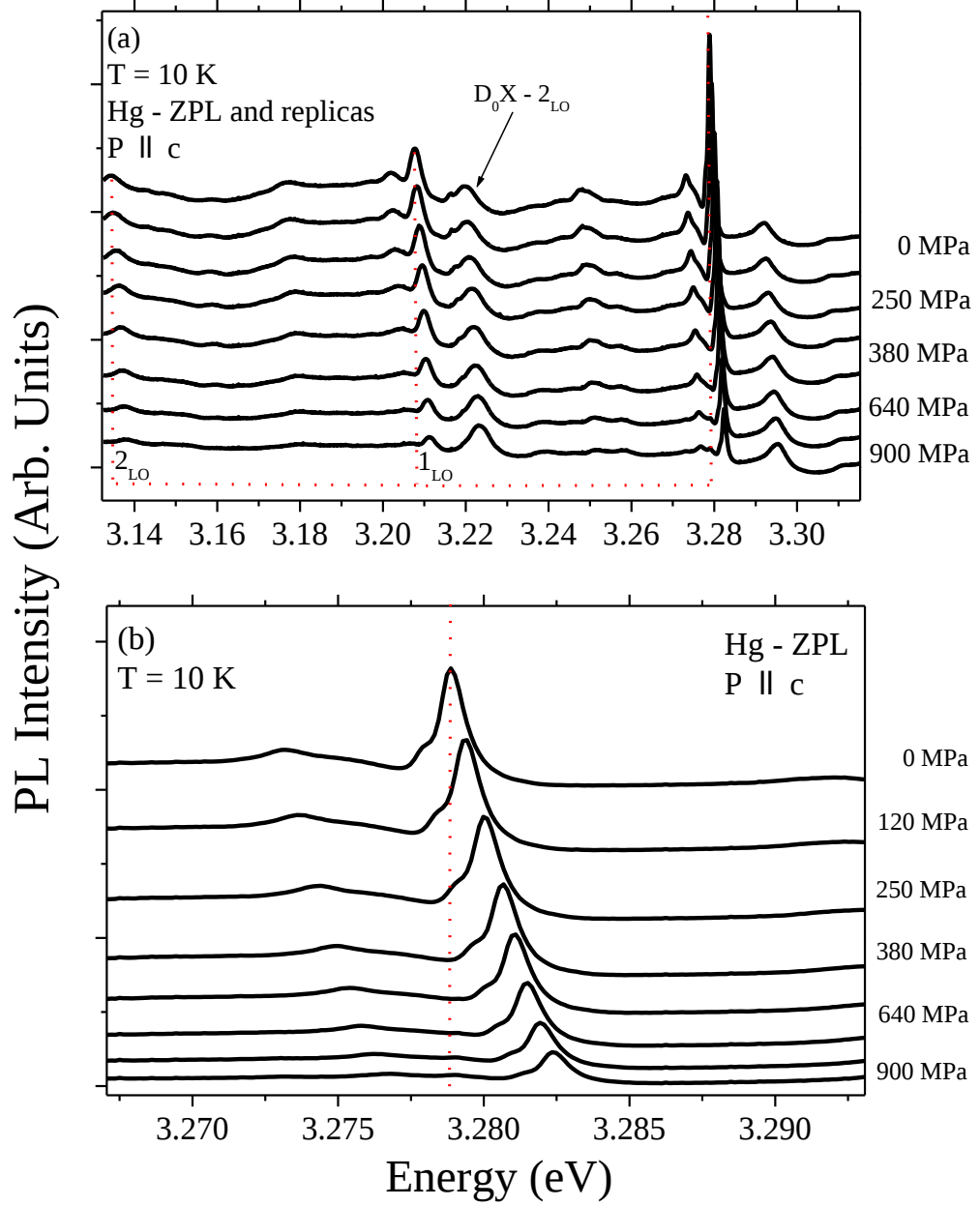


Figure 5.10: Representative spectra of the A line and its phonon side-band (a) and the A line magnified (b) under uniaxial stress along the [0001] direction. Spectra have been vertically shifted for clarity with dashed lines (red) indicating the zero stress positions of the spectral features. The shoulder in (b) at zero stress is the forbidden B transition discussed in the text.

The change in PL intensity under stress in the sidebands is essentially the same as that for the ZPL. The B line transition observed as a shoulder in Figure 5.10 (b) is not observed to increase or split under uniaxial stress, *i.e.* the A and B lines behave identically under stress along the [0001] direction.

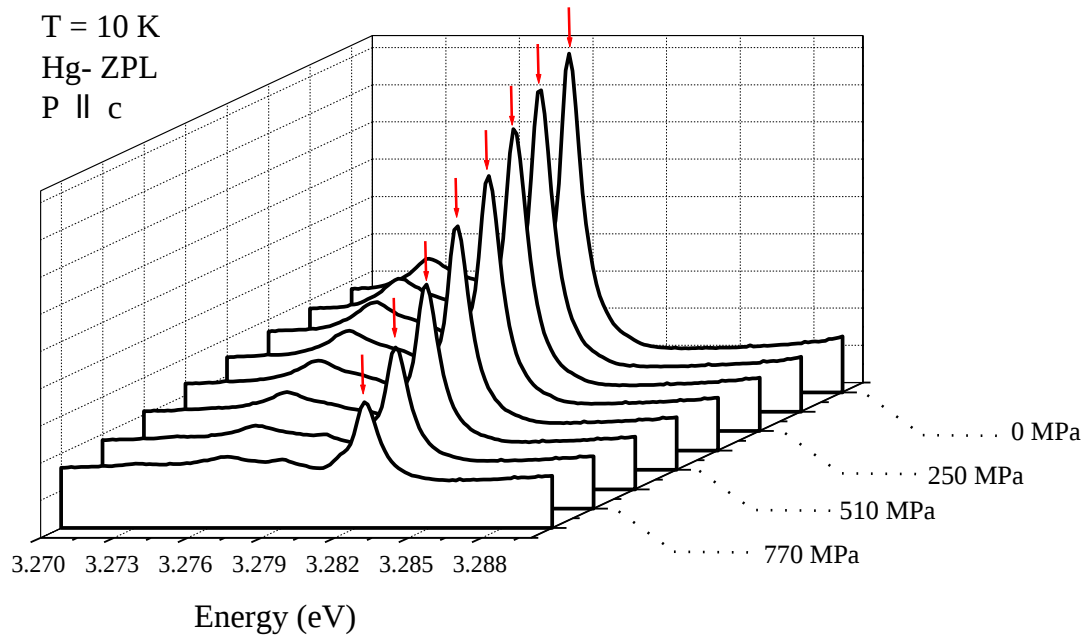


Figure 5.11: Representative spectra of the A line and its phonon side-band under uniaxial stress along the $[0001]$ direction.

The decrease of the A line transition seen in Figure 5.10 and 5.11 contrasts with the behaviour of the D^0X LO replicas which maintain their intensities up to 900 MPa (Figure 5.10 (a)).

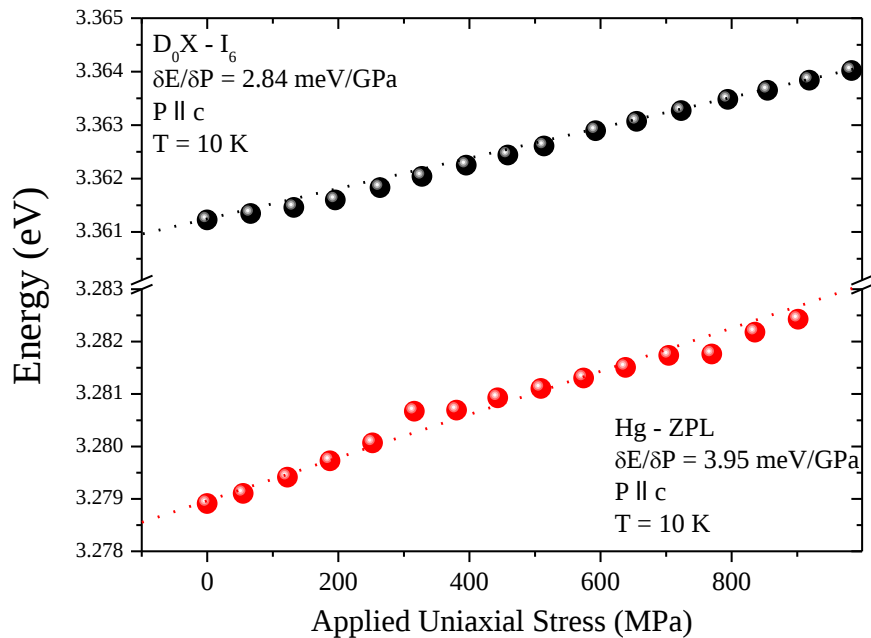


Figure 5.12: Zero phonon line energies plotted as a function of applied uniaxial stress along the $[0001]$ direction. The dashed lines indicate fits according to the stress parameters provided by McGlynn and Henry [25].

For comparative purposes the linear shift rates of both the D^0X feature I_6 (related to Al [21]) and the Hg – ZPL for uniaxial stress applied along the [0001] direction are plotted in Figure 5.12. Data for both features were obtained from the same sample and the shift rate for I_6 verified with previous work on the same defect [22]. The full data set for stress along the [0001] direction is shown in Figure 5.14 (a). It should be noted that whether the Hg line is assigned to a trigonal E or monoclinic nondegenerate state the shift rate fitting for stress applied parallel to the c-axis remains the same.

Uniaxial stress along the [1-210] direction

Stress applied perpendicular to the c direction, along [1-210], revealed an obvious orientational or electronic degeneracy in the defect transition. The A line was observed to split into two distinct components under stress values of approximately 100 MPa as seen in Figure 5.13. One component of the A line moves in the high energy direction while all other spectral features in the near band edge emission and the other A line component move towards lower energies. The full data set of stress along the [1-210] direction is shown in Figure 5.14 (b). It is clear from the data that the higher energy component of A undergoes a reversal with the line departing from its initial positive linear shift rate under stress. This is attributed to anti-crossing effects [26] as the defect interacts with an unobserved higher energy state as indicated in Figure 5.14 (b). While this feature (the source of the anti-crossing behaviour) was not observed directly during PL measurements, including temperature dependent measurements, further PLE studies might be able to reveal this transition [27].

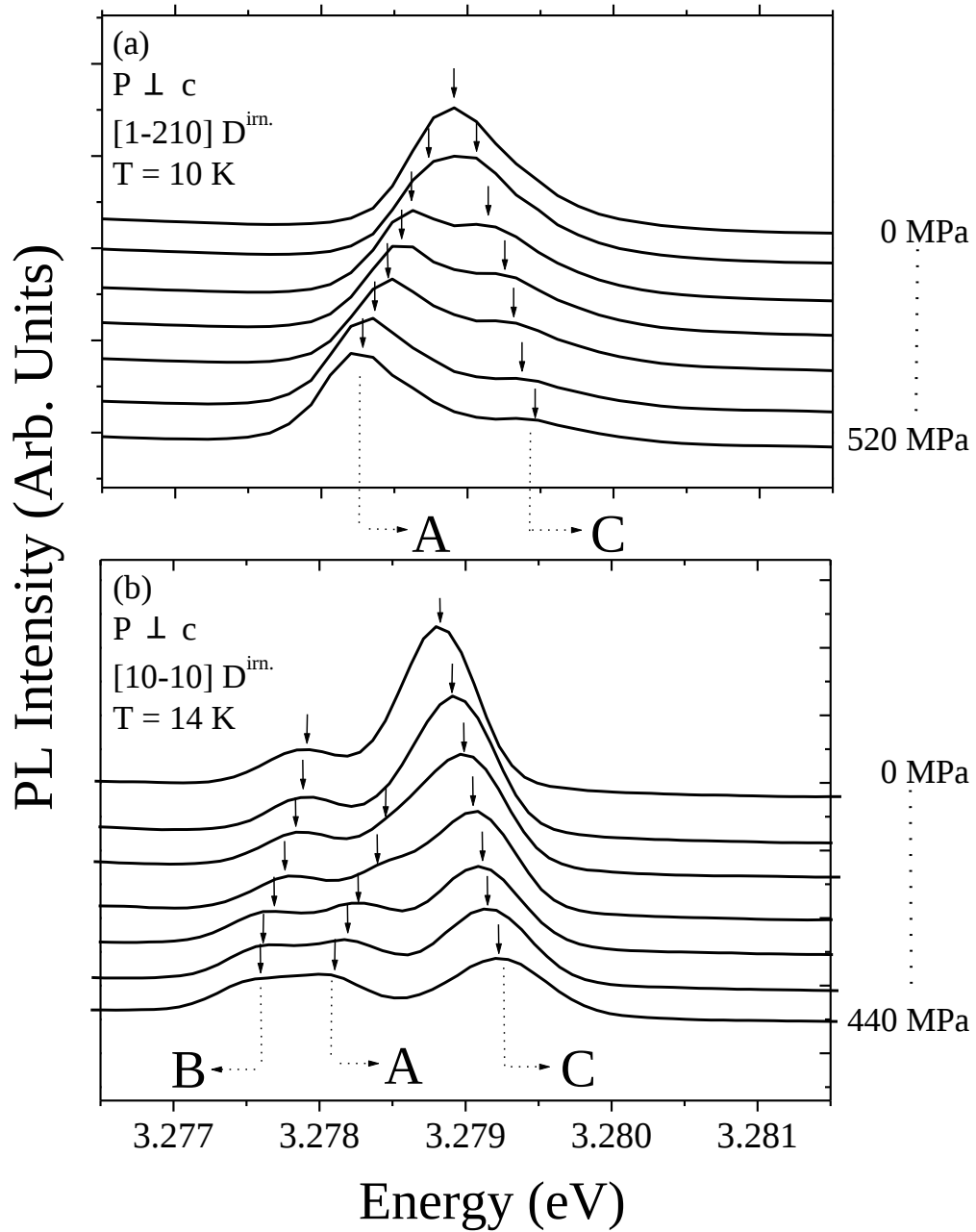


Figure 5.13: Representative spectra (a) for the A-line under uniaxial stress perpendicular to the c -axis along the $[1-210]$ direction. A higher energy feature appears under stress greater than 100 MPa indicating a possible degeneracy in the defect centre. Line intensity remains relatively constant even under pressures greater than 1 GPa. Representative spectra (b) of the A- and B-lines, and the splitting of A into a higher energy component labelled C and lower energy line which remains called A under stress along the $[10-10]$ direction. Spectra are vertically stacked for clarity.

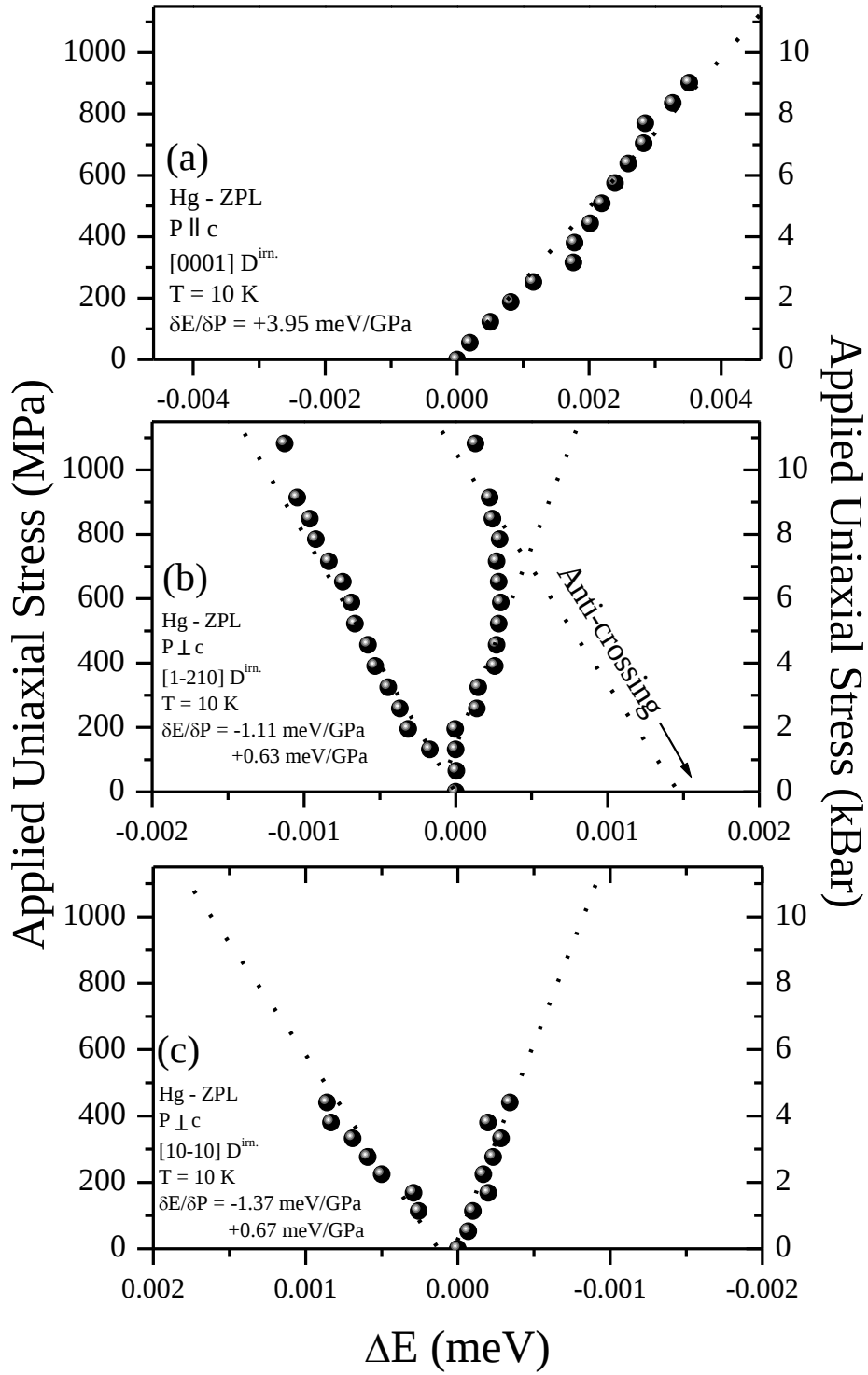


Figure 5.14: Energy shifts from the A ZPL at zero stress for uniaxial stress applied along the [0001] direction (a), along the [1-210] direction (b) and along the [10-10] direction (c). Anti-crossing resulting from the interaction with an unobserved higher energy level is seen in (b) at stresses greater than 500 MPa.

Uniaxial stress along the [10-10] direction

Stress applied perpendicular to the c direction, along [10-10], resulted in a similar splitting pattern with the A line splitting into two components, one moving to higher energies and one moving to lower energies, as seen in Figure 5.13 (b). Interestingly the relative intensities of the split components was reversed with the more intense feature moving to higher energies with applied stress, the opposite was found for stress along the [1-210] direction. The B line is observed at zero stress in this case possibly due to the use of an upgraded higher resolution spectrometer compared with the CCD spectrometer used for previous stress measurements. While the shift rate of the B line was recorded (-0.91 meV/GPa) no splitting was observed for this feature. In the absence of good data for the B line, the stress analysis will focus on the A line alone. Note that from this point on the higher energy split component is referred to as the C line.

5.5 Zeeman spectroscopy measurements

The Hg-doped ZnO samples were placed in strong ($B = 7$ T) magnetic fields at low temperatures (5 K) in different orientations in order to investigate the bound exciton recombination. The temperature was maintained at 5 K throughout to ensure that any variations in the line shape or position were magnetic field related only, except of course when temperature dependent measurements were carried out as discussed later.

With the magnetic field applied parallel to the [0001] direction and with the electric vector of the emitted light either parallel or perpendicular to the direction of the magnetic field, no splitting was observed. A line broadening becomes apparent however as seen in Figure 5.15 when the direction of the magnetic field is perpendicular to the electric vector of the light where the FWHM of the line is increased by approximately 14%. The FWHM of the line increase likely indicates a splitting that is not resolved in this work.

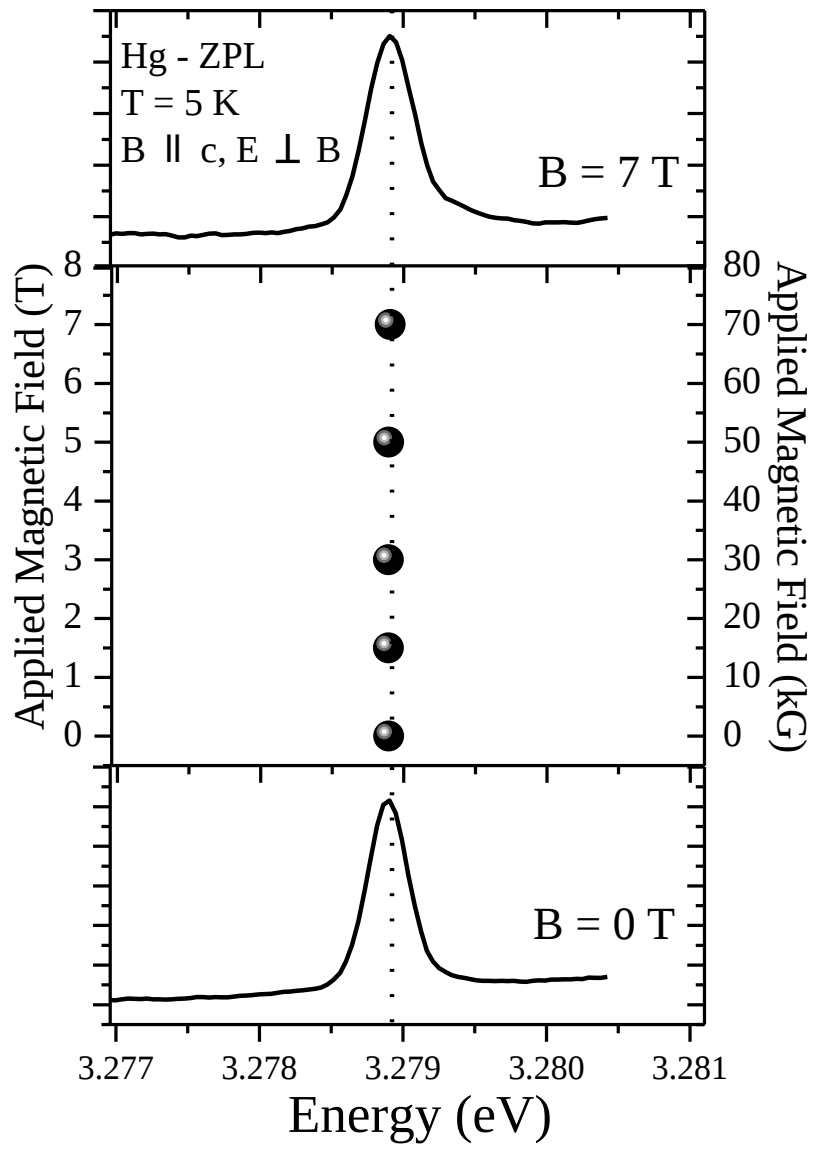


Figure 5.15: PL spectra recorded for the luminescence electric vector direction perpendicular to the direction of the magnetic field. No shift or splitting is apparent up to field values of 7 T.

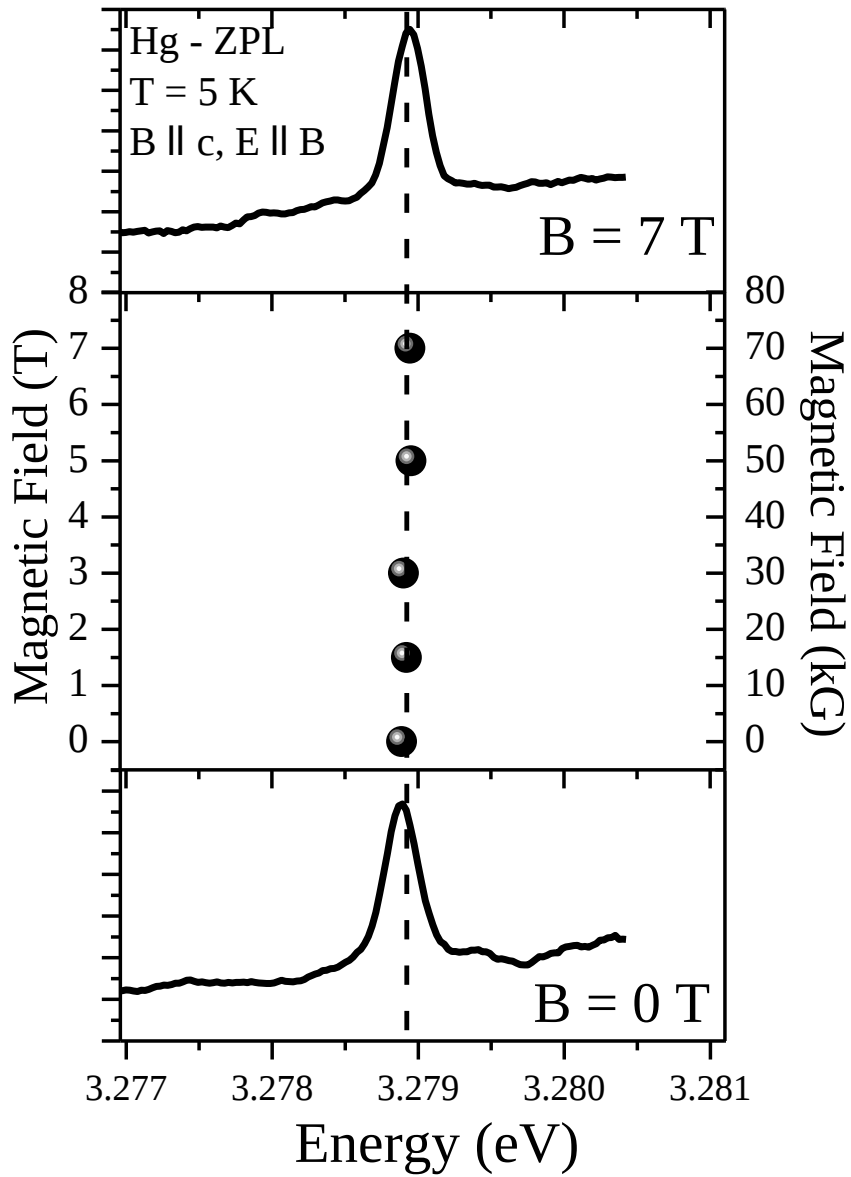


Figure 5.16: PL spectra recorded where the luminescence is emitted with the electric vector of the emission parallel to the magnetic field direction for field values of 0 and 7 T. No shift or splitting is apparent; however, the FWHM of the line increases by 5%.

An increase of only 5% is observed when the magnetic field and electric vector directions of propagation are parallel. It is possible that a small splitting occurs that is not resolved here.

Data points and representative spectra for field values from 0 to 7 T are shown in Figures 5.15 (for the electric vector perpendicular to the magnetic field) and 5.16 (for parallel to the magnetic field). A marginal shift is observed in Figure

5.16 from 0 to 7 T of around 0.05 meV; without polarisation data however such a small shift cannot be commented on further.

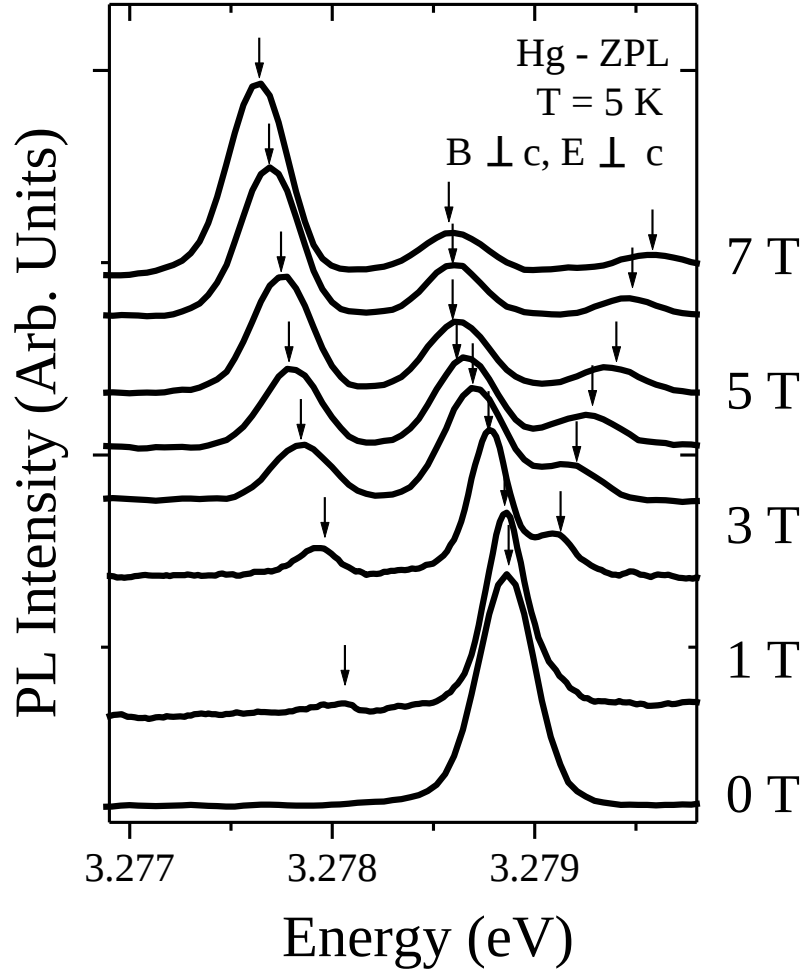


Figure 5.17: The Hg ZPL under a magnetic field in the $[1-210]$ direction. A strong thermalisation is observed of the lower energy B line which emerges at 3.278 eV. A higher energy feature A^* appears at stronger magnetic field values. Spectra have been vertically shifted for clarity.

Magnetic fields were also applied, in increments of 1 T, up to 7 T with the magnetic field direction perpendicular to the c-axis. Again, data were recorded with the electric vector of the emitted light parallel (Figures 5.17, 5.19, 5.20 and 5.21) and perpendicular (Figure 5.18) to the magnetic field direction. Figure 5.19 shows the plotted data points from 0 to 7 T. The B line, discussed earlier, located 0.90 meV to the low energy side of A, is observed to increase in intensity with increasing magnetic field. Additionally a new feature, A^* , is

observed to split from the A line on the high energy side of A. Similar results were obtained for the electric vector of the light perpendicular to the magnetic field as seen in Figure 5.18. A small energy shift from data set to the other is noted (0.1 meV). It is possible that this shift was a result of using different spectrometers during measurements (one spectrometer in TU Dortmund and one in the SSL in Dublin) as explained in Chapter 2.

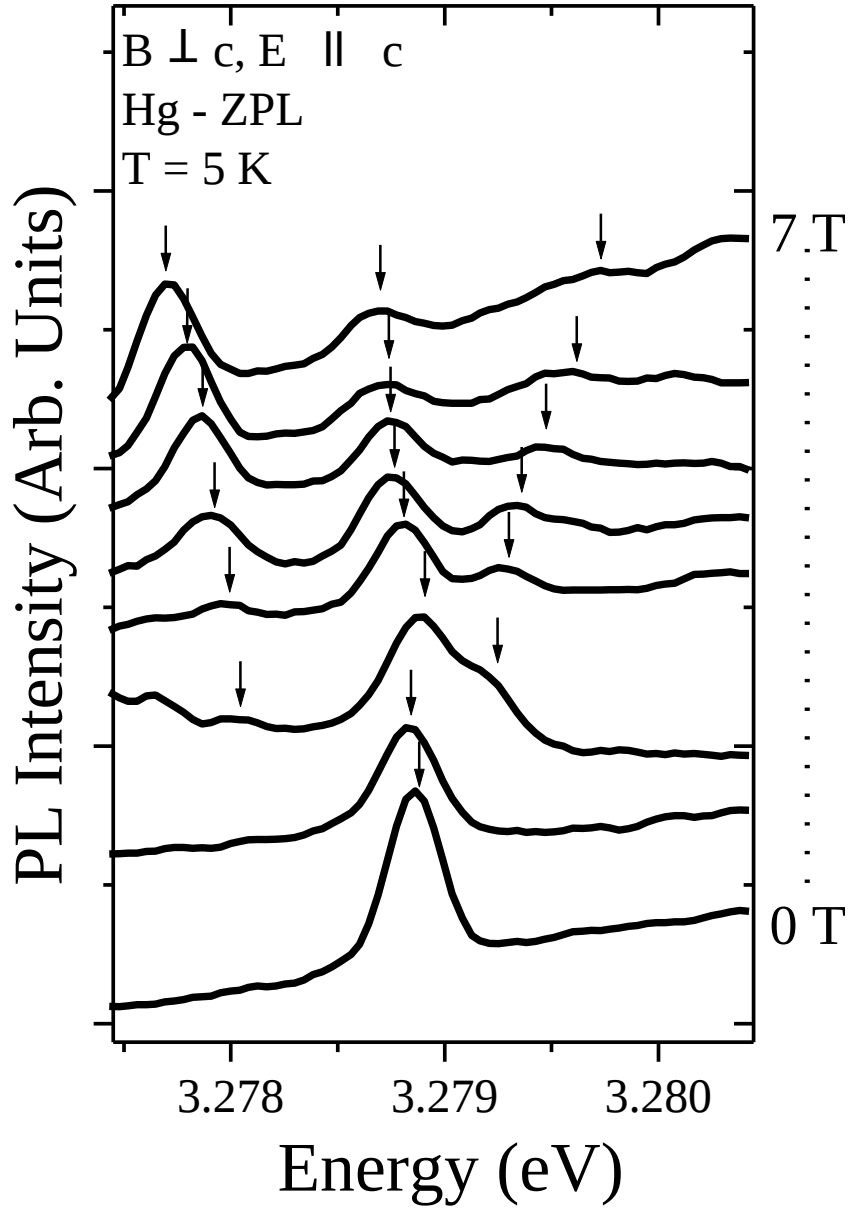


Figure 5.18: Plotted energy shifts of the three components upon application of magnetic field strengths up to 7 T for fields applied perpendicular to the $[0001]$ direction. The electric vector of the light is polarised parallel to the direction of the magnetic field in this case.

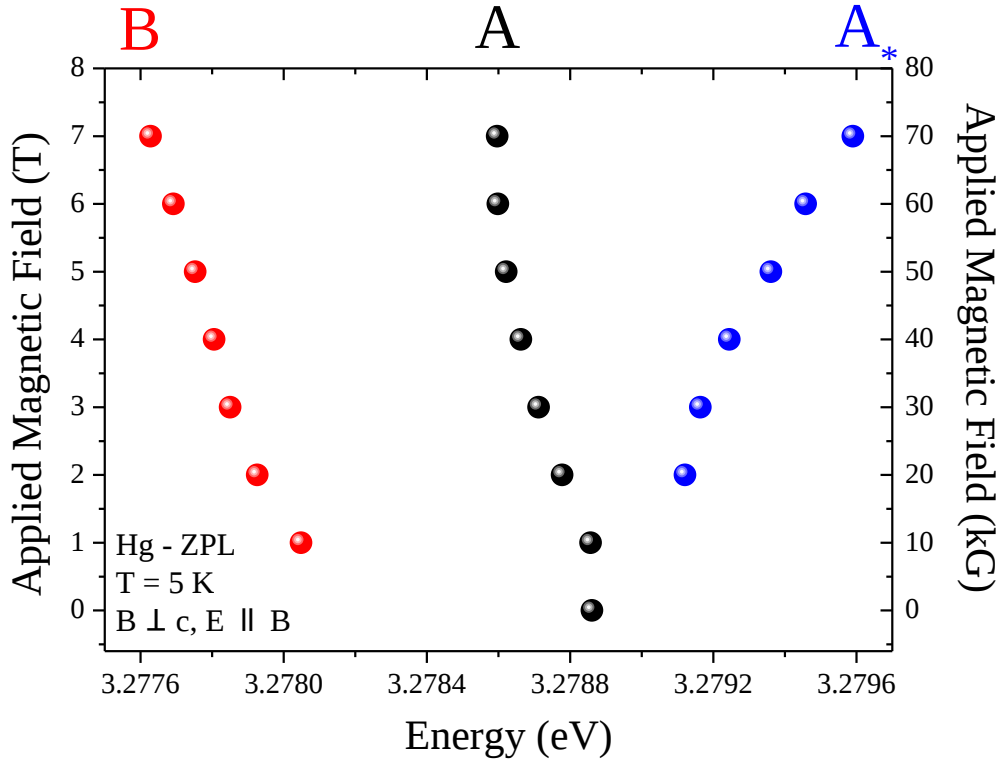


Figure 5.19: *Plotted energy shifts of the three components upon application of magnetic field strengths up to 7 T for fields applied perpendicular to the [0001] direction. The electric vector of the light is polarised parallel to the direction of the magnetic field in this case.*

The temperature dependence measurements performed during Zeeman spectroscopy are shown in Figures 5.20 and 5.21. Recall, from Chapter 3, that the excited state splitting while the magnetic field is perpendicular to the c-axis depends on the electron g-value for A^0X features, whereas for a D^0X feature in the same direction the excited state splitting is related to the hole g-value. Recall also that for D^+X lines and the free exciton in ZnO both the hole and electron g-values determine the excited state splitting. Temperature dependence measurements can help distinguish the nature of the excited state splitting, by providing data of the thermalisation between components. The temperature dependence of the A- and B-line components for magnetic fields perpendicular to the c-direction are shown in Figure 5.20.

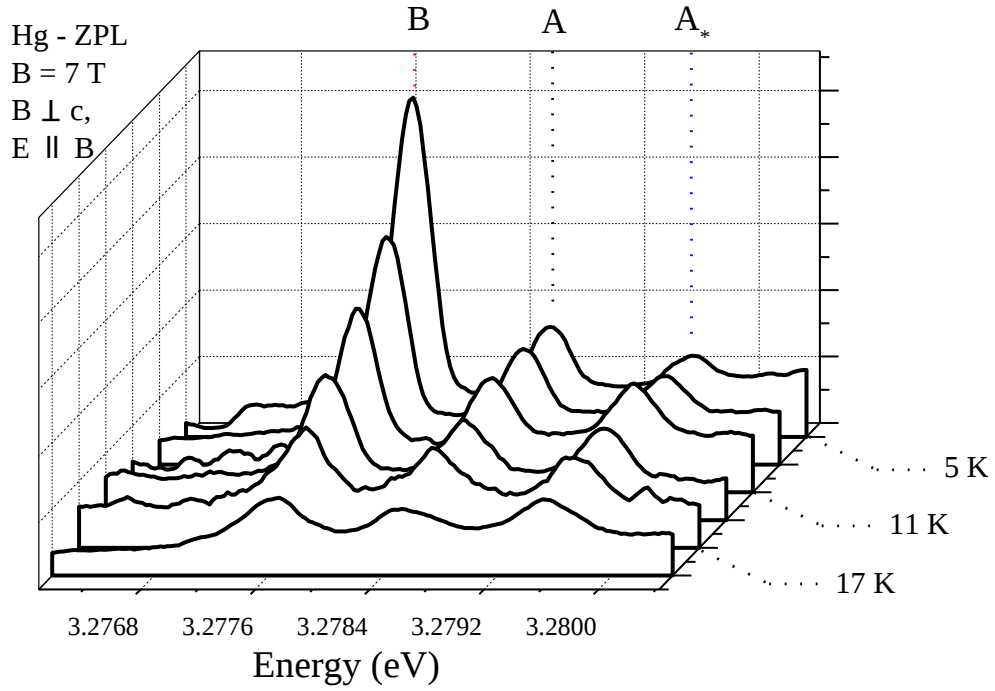


Figure 5.20: *Temperature dependence studies of the Hg – ZPL split components in the perpendicular to c -axis configuration, at constant magnetic field ($B = 7 \text{ T}$). The strong thermalisation of the B line in Figure 5.19 is now seen to reverse with increasing temperature.*

The peak intensities from Figure 5.20 were used to calculate the thermalisation between the components and plotted in Figure 5.21. The change of intensity between the A and A_* lines is plotted in Figure 5.21, where the spectra are vertically stacked for clarity (a) and the natural log of the ratio between A and A_* is plotted against inverse temperature (b). The details of this calculation were outlined in §3.2.1 of Chapter 3. The calculated energy separation between A and A_* is found to be $\sim 0.7 \text{ meV}$, close to their spectral separation of 1.0 meV indicating that A and A_* thermalise with increasing temperature. This information acts as strong evidence for the observed splitting occurring in the excited state [22, 28].

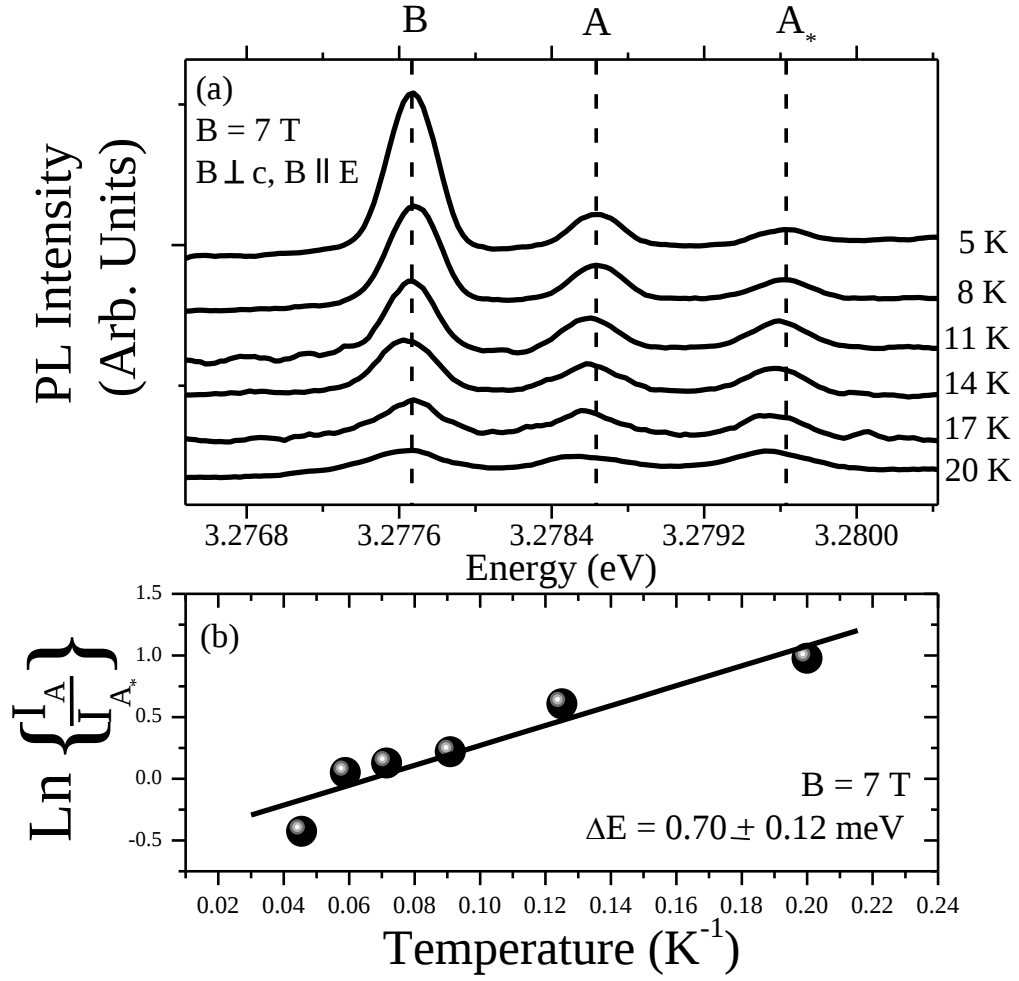


Figure 5.21: The ratio of the intensities of A and A_* , the newly emerged feature, appear to shift linearly (a) allowing for a calculation of their energy separation shown in (b), found here to be 0.70 ± 0.12 meV smaller than the spectroscopic separation of 1.0 meV. Spectra in (a) have been vertically shifted for clarity.

5.6 Discussion

5.6.1 Uniaxial stress data analysis

A key consideration in stress data analysis is to determine if observed splittings occur in either the initial or final state (or both). Examining the temperature dependence provides a means of addressing this since excited state splittings will show thermalisation effects while ground state splittings will not. In this case an adjustment of temperature was not possible with the uniaxial stress cell included in the cryostat but the intensity ratios of split components were

examined as a function of spectral separation. If the ratios change then the splitting is in the excited state. In the same vein, this behaviour can distinguish between the lifting of electronic and orientational degeneracy.

The stress splitting pattern observed for the A line is as follows:

[0001] direction – no splitting observed

[1-210] direction – two components

[10-10] direction – two components

Trigonal nondegenerate states do not split for stress along any direction [25] (parallel or perpendicular to the c-axis) so the split feature in the [1-210] and [10-10] directions rules out this assignment. Triclinic nondegenerate states do not split for stress parallel to the c-axis although a splitting into three components due to orientational degeneracy is predicted in the perpendicular to c-axis direction; since only two features are observed here this likelihood is also ruled out.

We recall from Chapter 3 that the observed splitting behaviour is expected for two cases:

- (i) E to A transitions for a trigonal defect
- (ii) A to A for a monoclinic defect.

Both of these are predicted to shift but not split with pressure applied along the c-axis and split into two components under stress along either of the [1-210] or [10-10] directions [25].

We now consider these two cases separately to determine which provides the better explanation for the data obtained for the A-line. The splitting components for both the [10-10] and [1-210] directions allowed for the calculation of the stress parameters for the cases of both monoclinic and trigonal E cases, the results of which are displayed in Table 5.3.

Table 5.3: Observed and predicted shift rates for the A line feature and its splitting component. Parameters are fitted for two defect types; trigonal E and monoclinic nondegenerate states using the parameters published in [25]. The trigonal E to A state more closely matches the observed shifts.

Defect Assignment	Line	Energy (eV)	Fitted stress parameters (meV/MPa)	Shift Rates (meV/GPa)					
				$[0001] D^{irn.}$	$[0001] D^{irn.}$	$[1-210] D^{irn.}$	$[1-210] D^{irn.}$	$[10-10] D^{irn.}$	$[10-10] D^{irn.}$
				Experiment	Calculated	Experiment	Calculated	Experiment	Calculated
Trigonal E	Hg – ZPL	3.3279	A1 = 1.17	+3.95	+3.95	-1.11	-1.24	-1.37	-1.24
			A2 = 1.39 B1 = -0.83			+0.63	+0.68	+0.67	+0.68
Monoclinic	Hg – ZPL	3.3279	Am1 = -1.69	+3.95	+3.95	-1.11	-1.11	-1.37	-1.69
			Am2 = 0.63 Am3 = 3.95			+0.63	+0.63	+0.67	+0.05

When comparing the calculated and experimental values for the cases of (i) trigonal E to A states and (ii) monoclinic A to A states, a closer match is found for the former as seen in table 5.3. The fitting parameters listed in Table 5.3 (A1, A2, *etc.*) are explained in Chapter 3 although a more complete description can be found in [25].

Figure 5.22 shows the experimental and calculated shift rates for; (a) the A line under stress along the [0001] direction; (b) the A line and its split component under stress along the [1-210] direction and (c) the A line and its split component under stress along the [10-10]. Dashed lines indicate calculated shifts for a trigonal E to A state transition showing the experimental and calculated shift rates are well-matched. The red dashed line in Figure 5.22 (c) indicates the calculated fitting for a monoclinic defect.

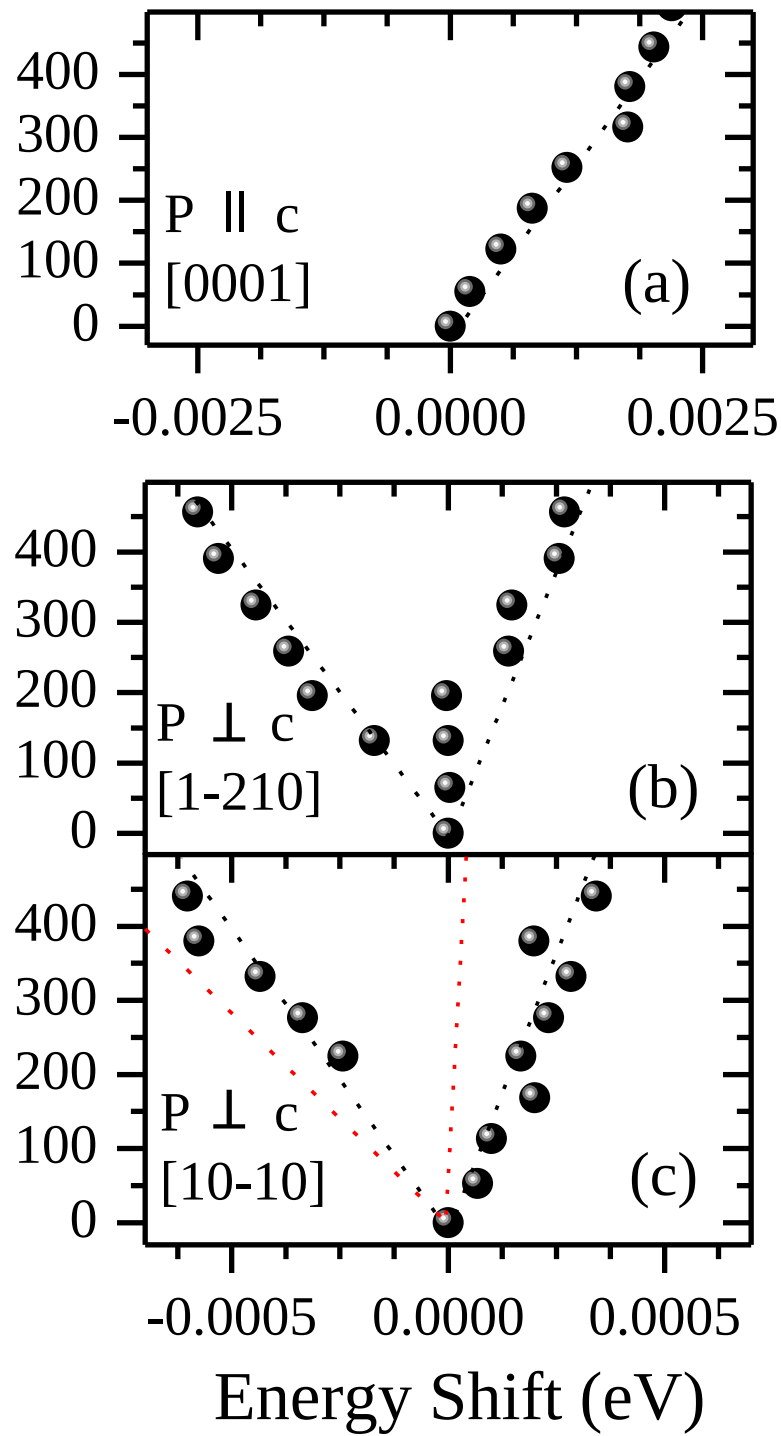


Figure 5.22: Shifting emission line energies of the A line under uniaxial stress along the $[0001]$ (a), $[1-210]$ (b) and $[10-10]$ (c) directions plotted as a function of energy shift ΔE versus applied stress. Dashed lines represent fittings according to fitting parameters calculated for a trigonal E defect. The red dotted lines in (c) correspond with the expected shift rates if the defect was monoclinic in nature. Values from Table 5.3.

Further verification of the trigonal E to A defect assignment is provided by examining the thermalisation (if any) between the two split components. This is found by plotting the natural log of the intensity ratio of both split components against their energy separation under increasing stress and using the slope to deduce the effective sample temperatures, the theory of which was explained in Chapter 3. Deducing the temperatures to be within a factor of about two of the nominal temperature would provide the necessary confirmation.

As seen in Figure 5.23, temperatures of approximately 6 K and 5 K are found for the [10-10] and [1-210] directions, with nominal experimental temperatures of 14 and 10 K, respectively.

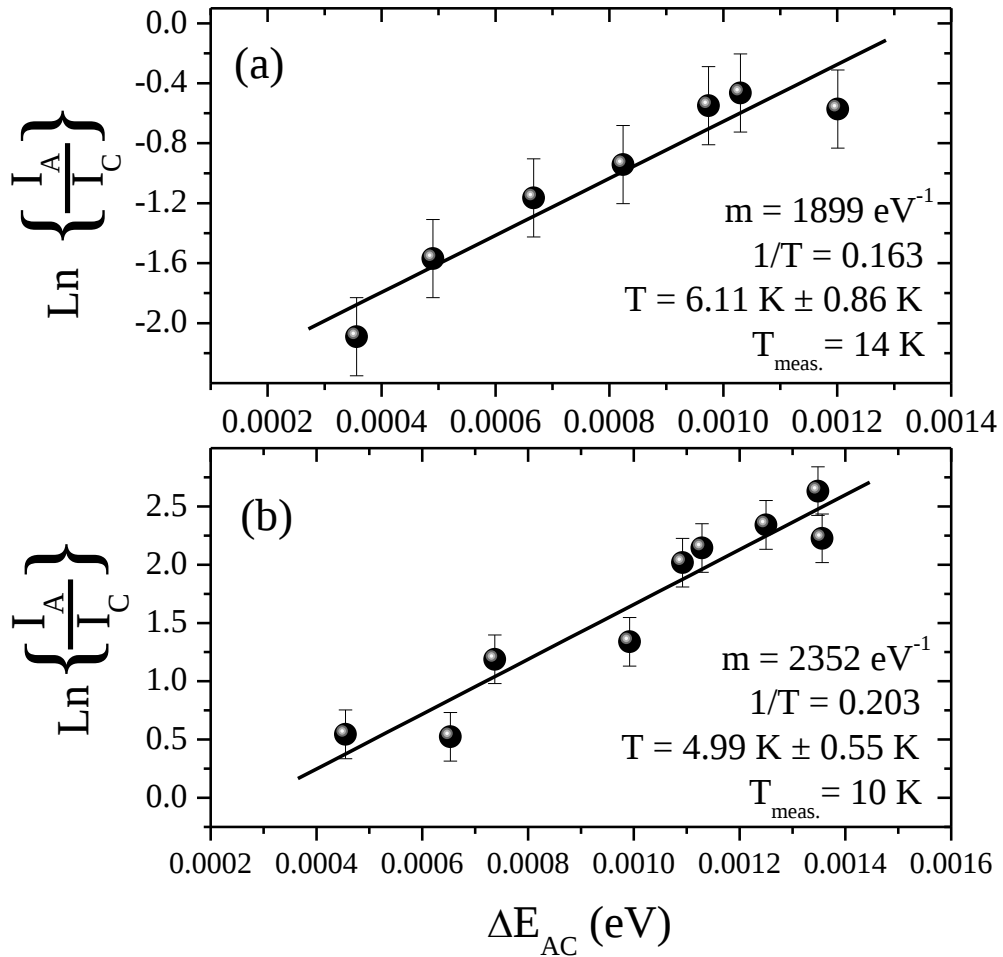


Figure 5.23: Experimental plots of the natural log of the split components under stress of the Hg A line where I_A and I_C correspond to the intensities of the lines A and C. (a) is for uniaxial stress applied along the [10-10] direction while (b) is for stress applied along the [1-210] direction.

These values are sufficiently close to the nominal temperatures at which the experiments were carried out to confidently conclude that the observed splittings are electronic in origin rather than orientational.

These results also rule out a monoclinic assignment of the defect and a trigonal E to A state is the favoured explanation. Additionally, since only two split components are observed, the E state splitting is concluded to lie solely in the excited state of the centre, not the ground state therefore confirming that the A-line corresponds to an E to A transition.

The main finding in Table 3.2 in Chapter 3 is that none of the exciton states split under c-axis stress (where the symmetry is C_{3v}) but the Γ_5 exciton state splits into two levels for stresses perpendicular to the c-axis. This is in agreement with the main finding in the stress data where the A-line is found to shift but not split for stress parallel to the c-axis and to split into two components for stresses perpendicular to the c-axis.

5.6.2 Zeeman data analysis

The analysis that follows is based on the PL emission observed here as being due to the Hg centre occupying a substitutional Zn site and a single electron and hole pair becoming localised at the Hg site. We do not consider the binding mechanism whereby the electron-hole pair becomes bound in the vicinity of the Hg atom, instead we focus on examining the excitons involved and their behaviour during Zeeman spectroscopy measurements.

Recall from the theory of free exciton states from Chapter 3 that the Γ_7 valence and conduction band symmetries produce excitons of $\Gamma_{1,2}$ and Γ_5 symmetry. The basic description of free excitons in ZnO presented in Chapter 3 also applies to the states of electron-hole pairs bound at defect or impurity sites where no other free particle is present. A common example of such an impurity in ZnO is the ionised donor (D^+X) which is a donor impurity that has lost its electron. The resulting positively charged donor atom is found to provide a binding centre for an electron-hole pair (exciton); several examples of D^+X lines are known [8, 21, 29]. The D^+X energy levels are also described as

having $\Gamma_{1,2}$ and Γ_5 exciton symmetry in exact analogy to the case of free excitons, and the same selection rules govern these recombination centres.

In addition to D^+X centres it is possible for isovalent impurities (which are electrically neutral) to act as binding centres for excitons as explained earlier [1, 2, 3, 4, 7, 8]. However, the only example of this type in ZnO is for Hg. Here, we develop the theory of exciton states under stress and magnetic fields after which we apply this theory to the new data presented in this work for ZnO implanted with Hg.

We will not consider other details of free excitons such as polariton effects and the occurrence of transverse and longitudinal free exciton features in the luminescence as they do not feature in the analysis that follows.

The main findings of the data are presented in Figure 5.24 below.

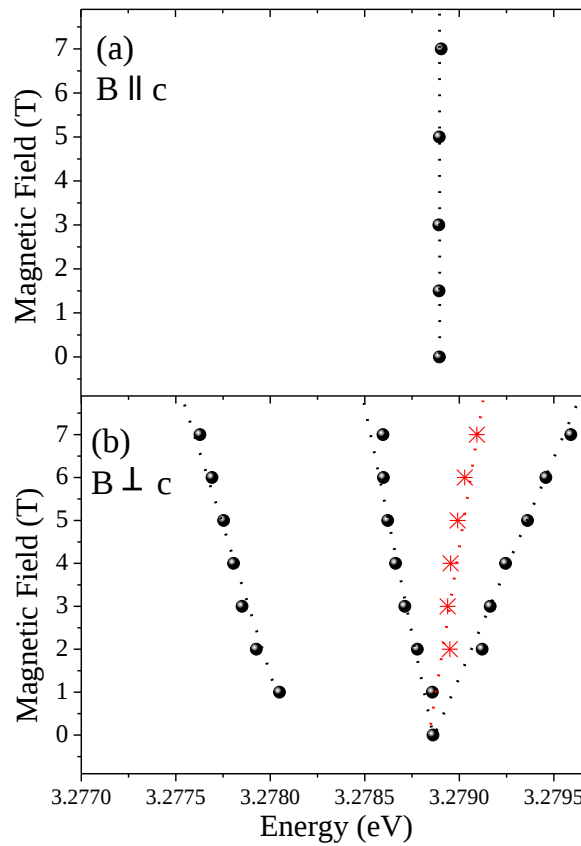


Figure 5.24: Data are plotted for the A-line behaviour under an applied magnetic field in the parallel to c direction (a) and the perpendicular to c direction (b). The data points are indicated by filled circles. The star symbols (red) show the “centre of gravity” of the A line components under the magnetic field.

We see from Figure 5.24 that the A-line (3.2788 eV) remains unsplit for magnetic fields parallel to the c-axis, though there is a slight broadening, so we can conclude that the effective g value for this direction of the magnetic field is approximately zero. For the magnetic field perpendicular to the c-axis, we note that the A-line splits asymmetrically, with the centre of gravity (mid-point between the two components) shifting towards higher energy. The B line (around 3.278 eV) behaviour is more complex with its intensity increasing significantly as the field increases.

We return to this matter below, but first we analyse the A-line data in terms of the Thomas and Hopfield model as subsequently developed by others for excitons in ZnO [8, 22, 29].

5.6.2.1 The A-line Zeeman data

In the C_{6v} symmetry of the crystal, the Γ_5 exciton state consists of an electron and hole with anti-parallel spins. The local C_{3v} symmetry of the Hg impurity centre (analagous to the Al substitutional defect detailed in Chapter 3) does not lift the degeneracy of the Γ_5 exciton state so we base the analysis on the normal Γ_5 exciton state of the C_{6v} symmetry group. This approach has been shown to be successful for a variety of impurity bound excitons [21, 22, 29].

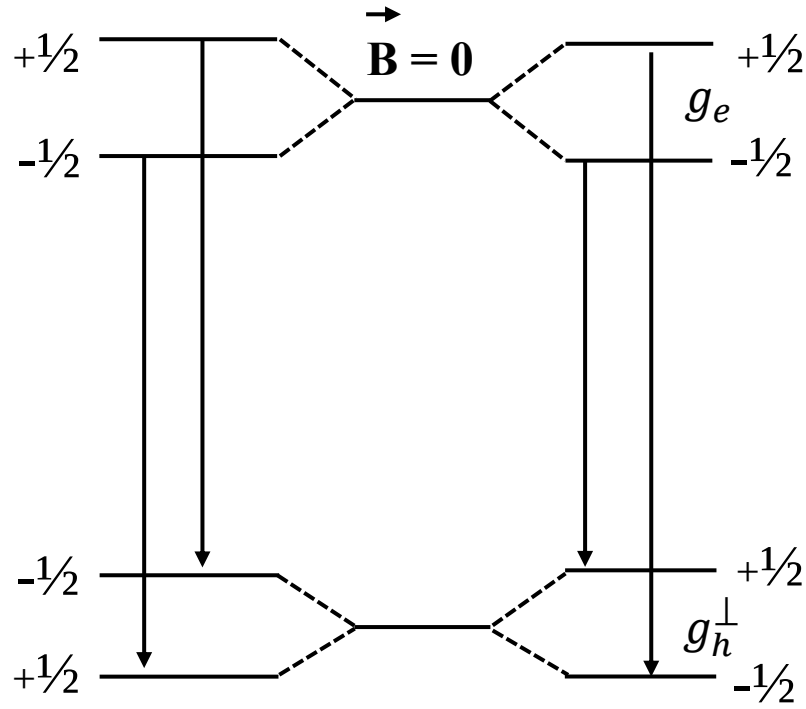


Figure 5.25: Candidates for the splitting behaviour exhibited by the A-line components. The hole g-value determines the lower spin components while the electron g-value determines the upper components.

Figure 5.25 above shows two possibilities for the Γ_5 state under a magnetic field, B . The electron and hole have antiparallel spins. For the left hand side, the ordering of the $+1/2$ and $-1/2$ states is different for the electron and hole. In this situation, assuming the g-values g_e and g_h are equal in magnitude, the spectral line will not split. However, if the ordering of the $+1/2$ and $-1/2$ levels under the magnetic field is the same (as for the right hand side of Figure 5.25) then the spectral line will split into two components for non-zero magnetic fields.

In the case of the A-line for Hg-implanted ZnO, and for the magnetic field aligned parallel to the c-axis, the experimental result obtained is that the line does not split, so we conclude that the electron and hole behave as shown on the left hand side of Figure 5.25, *i.e.* the effective g-value, g_{eff} is approximately zero indicating that g_h and g_e are approximately equal and opposite. The small broadening that is observed for the A-line as the magnetic field values increase

could be accounted for if the magnitudes of the hole and electron g-values were slightly different.

Next we consider the case for the magnetic field perpendicular to the c-axis, either along the m- or a-axes ([10-10] and [1-210] respectively). Here, the line is found to split into two components, and in addition the centre of gravity shifts towards higher energies.

The higher energy component shift rate of the A-line in Figure 5.25 is 0.104 meV T^{-1} while the lower energy component shift rate is $-0.041 \text{ meV T}^{-1}$. This means that the centre of gravity shifts upwards, to higher energy values, at a rate of $+0.031 \text{ meV T}^{-1}$. If we remove this centre of gravity shift from the two components of the A-line we find that each line shifts at a rate of 0.072 meV T^{-1} . We now use this result to make deductions regarding g-values and return later to the causes of the centre of gravity shift. From the equation:

$$\Delta E = g_{eff} \mu_B B \quad 5.1$$

we get the shift rate of each line as

$$\frac{\Delta E}{B} = \frac{1}{2} g_{eff} \mu_B \quad 5.2$$

Using the value for the A-line after accounting for the centre of gravity shift of the components (0.072 meV T^{-1}) gives

$$g_{eff} = 2.49 \quad 5.3$$

for the A-line in a magnetic field perpendicular to the c-axis.

Summarising the findings for the A-line we have

$$g_h^{\parallel} \cong g_e \quad 5.4$$

$$|g_e + g_h^{\perp}| = 2.49 \quad 5.5$$

5.6.2.2 B-line Zeeman data

The B-line results from spin-forbidden transitions and is therefore not normally observed unless the temperature is below 5 K, for which the initial state is largely populated. Under magnetic fields parallel to the c-axis and at a temperature of 5 K, the B-line was not observed for any magnetic field

strengths used. However, for magnetic fields applied perpendicular to the c-axis a dramatic effect was observed. The B-line is observed weakly at low field values ($B = 1$ T), after which it grows rapidly in intensity as shown in the results section earlier.

The plotted data for the B-line are shown in Figure 5.26 for magnetic fields applied perpendicular to the c-axis. In the diagram an equal but opposite centre of gravity shift to that observed for the A-line is included, indicated by the red circles and dashed red line.

The rationale for doing this is linked to the reason for the marked dependence of the B-line intensity on the applied magnetic field, which we now examine.

As noted above, the initial state of the B-line consists of an electron and hole with aligned spins (total spin, $s = 1$). Transitions to the ground state (spin, $s = 0$) are spin-forbidden. The B-line initial state is designated $\Gamma_{1,2}$ where the labels are those of the C_{6v} symmetry group of the crystal explained earlier here and in Chapter 3. A magnetic field applied perpendicular to the c-axis has Γ_5 symmetry [30] which results in a mixing of the $\Gamma_{1,2}$ and Γ_5 exciton states. Consequently, transitions from the $\Gamma_{1,2}$ states (*i.e.* the B-line here) acquire some oscillator strength from the A-line (Γ_5) and the B-line intensity grows as the magnetic field is increased. This interaction, between the $\Gamma_{1,2}$ and Γ_5 states also accounts for the centre of gravity shifts that have been described above.

There are several examples of this phenomenon in the ZnO literature related to the case of D^+X lines [8, 29] and also to the case of free excitons [31]. In all of these cases, the bound exciton contains a single electron-hole pair with two levels separated by 1-2 meV where the levels correspond to either parallel or anti-parallel spins. The case of Hg-implanted ZnO examined here is another example of such a bound electron-hole pair.

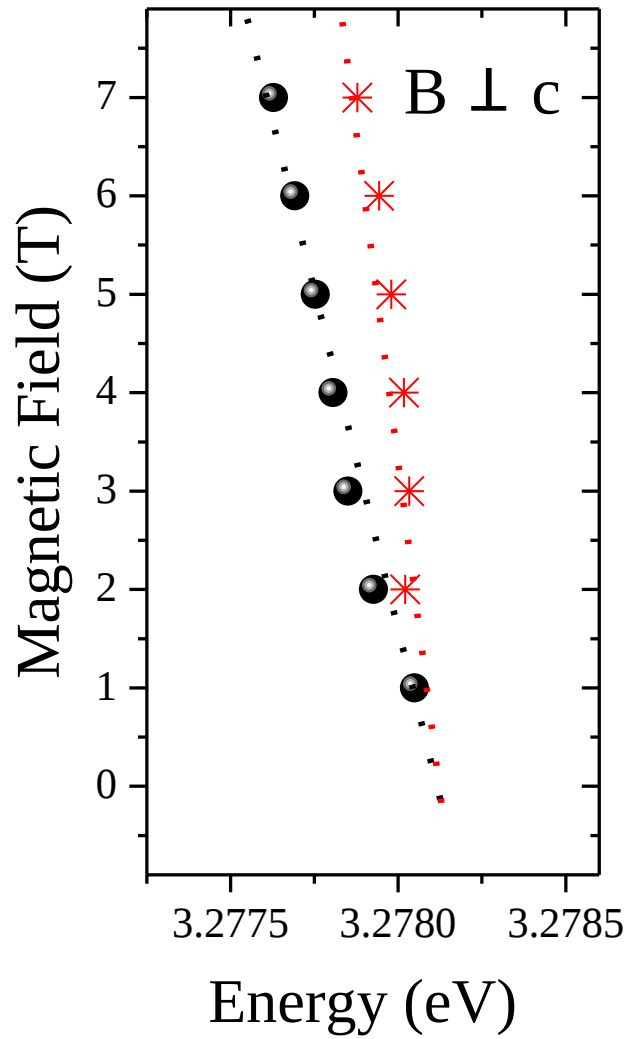


Figure 5.26: *Plotted energy shift for the B-line under magnetic fields perpendicular to the c-axis. The red stars represent the opposite centre of gravity shift to that observed for the A-line.*

Returning to the data, a g-value for the B-line can now be extracted. We start with the case for magnetic fields perpendicular to the c-axis. There is an implicit assumption in Figure 5.26 that the B-line, like the A-line, splits into two components under the magnetic field. Definitive proof of this has not been obtained as the line is initially very weak and thermalisation will favour just one line (the observed one) as the magnetic field strength increases. This assumption is reasonable in the context of the full set of data for the two lines, as explained below.

From the data in Figure 5.26 the measured B-line shift rate is $-0.074 \text{ meV T}^{-1}$. If we subtract the centre of gravity shift of 0.031 meV T^{-1} from this we obtain a shift rate of $-0.043 \text{ meV T}^{-1}$. Comparison to the shift rate of the A-line (0.072 meV T^{-1}) the B-line shift is considerably smaller in magnitude. This turns out to be a useful pointer in the analysis, as we now demonstrate. The schematic energy level diagram below illustrates the situation for the A- and B-lines.

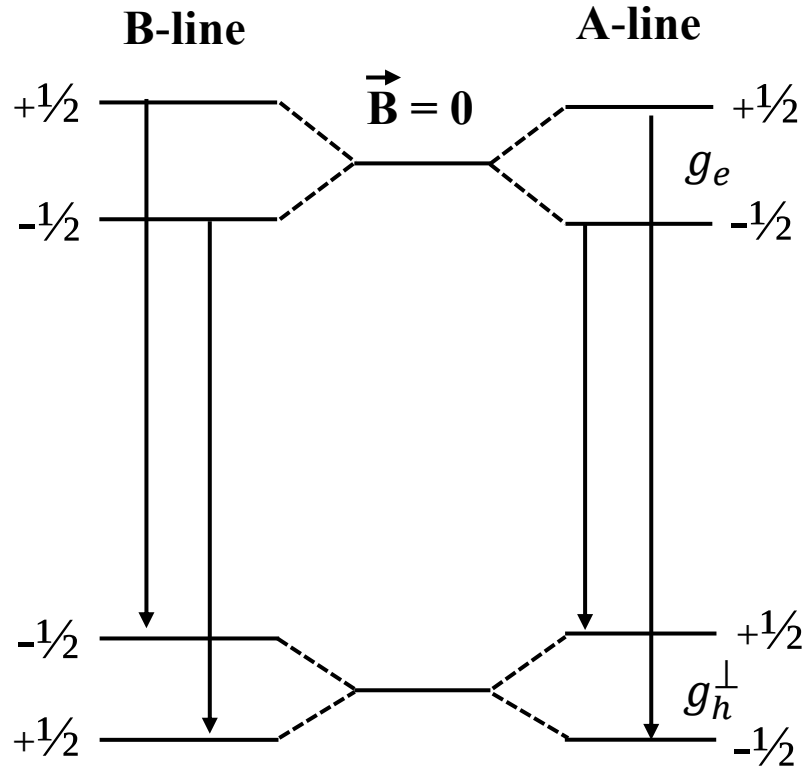


Figure 5.27: Schematic energy level diagram for the A and B transitions under magnetic fields for magnetic fields applied perpendicular to the c-axis.

Here, we see that the B-line will undergo a smaller splitting than the A-line, as the former involved parallel spins for the electron and hole. It can be easily seen that if the ordering of the spins in the hole were reversed, then the B-line component shift rate (and splitting) would be larger than that of A, contrary to experiment.

We conclude therefore that the sign of the hole g-value when the magnetic field is aligned perpendicular to the c-axis is as indicated in Figure 5.27, *i.e.* the

hole g-value is positive. Using the shift rate of $-0.043 \text{ meV T}^{-1}$ gives an effective g-value of 1.48.

5.6.2.3 Calculation of g-values

We are now in a position to extract the electron and hole g-values for the Hg centre in ZnO, albeit with some assumptions having to be made. From the magnetic field aligned perpendicular to the c-axis data we have the values in Table 5.4.

Table 5.4: *Shift rates and effective g-values for the A and B lines observed in this work.*

	Shift rate (meV T^{-1})	Effective g-value, g_{eff}
A-line	0.072	2.49
B-line	0.043	1.48

Thus, we have

$$|g_e + g_h^\perp| = 2.49 \quad 5.6$$

$$|g_e - g_h^\perp| = 1.48 \quad 5.7$$

From these we find

$$g_e = 1.98 \quad 5.8$$

$$g_h^\perp = 0.50 \quad 5.9$$

$$g_h^\parallel \cong 2 \quad 5.10$$

This g_e value of 1.98 is very close to the known electron g-value in ZnO (1.96 [32, 33]) but returns a large hole g-value of 0.50 for magnetic fields aligned perpendicular to the c-axis. This hole g-value is larger than those reported to date, for which the value is typically close to zero as explained in Chapter 3. In practice, a zero hole g-value corresponds to there being no effect on hole states for magnetic fields perpendicular to the c-axis. This would apply to pure ZnO

valence band states but could not be expected to apply to holes bound strongly at an impurity centre. Indeed this point was clearly made in the first studies of bound excitons in II-VI compounds [8]. The results presented here suggest that the hole component of the Hg centre isoelectronic bound exciton is strongly localised at the impurity. The hole g-value for magnetic fields aligned parallel to the c-axis is included for completeness.

5.6.3 Radiotracer and stable implantation of ZnO with Hg

Radiotracer implantation of ^{192}Hg and ^{197}Hg into ZnO pieces resulted in the unambiguous finding that a zero phonon emission and associated sideband are related to substitutional Hg impurities in ZnO. Emission channelling measurements from an earlier unpublished work referenced in [11] verified the substitutional location of the Hg impurities.

A stronger lattice interaction was observed as an increase in the $I_{\text{LO}}/I_{\text{ZPL}}$ ratio as seen in table 5.2. This increased interaction follows the trend exhibited by all simple substitutional exciton recombinations in ZnO, see for example the D^0X recombinations listed also in table 5.2, where an increase in localisation of the bound exciton corresponds with an increased lattice interaction.

A comparison of the change in intensity and localisation energy with increasing temperature with the D^0X feature I_6 is seen in Figures 5.4 and 5.5, where similar behaviour with changing temperature is observed for I_6 and the A-line. This indicates that the whole exciton is bound at the defect site, unlike the case for DD_2 in chapter 4 where distinctly different localisation behaviour was observed during temperature dependence.

Temperature dependent measurements allowed for study of the forbidden transition and a shared ground state for the A and B lines demonstrated using the equations described in Chapter 3. A strong thermalisation of the features is observed in the 2 – 5 K temperature range which allowed for observation of the B line only (at $T = 2$ K). The B line was observed as a sharp ZPL of similar intensity to the A line at $T = 10$ K. The associated phonon sideband was also observed the shift to lower energies by approximately 0.9 meV. This observation of a sharp no phonon line and its associated sideband allows the

feature to be attributed to a pseudo-acceptor feature under the guidelines published by Hopfield *et al.* in [4] given the distinct characteristics displayed in PL and absorption spectroscopy that allow pseudo-acceptor and pseudo-donor features to be identified.

5.7 Conclusion

When ZnO is implanted with Hg a characteristic ZPL feature (3.279 eV) and associated sideband are observed. A strong exciton binding is exhibited by the feature, characterised by the large localisation (90 meV) energy and strong thermal binding behaviour.

Zeeman spectroscopy and piezospectroscopy provided results strikingly different from the dominant donor bound exciton features in ZnO. One aspect of the dopant centre investigated here is the source of the excited state degeneracy encountered for uniaxial stress applied along the [1-210] and [10-10] directions of the crystal. This is found to be due to the Γ_5 exciton state splitting into Γ_1 and Γ_2 states when bound to the defect (which now assumes C_{1h} symmetry) under uniaxial stress. This readily explains the splitting of the A-line observed here and is confirmed by the thermalisation behaviour exhibited by both components during stress indicating the shared ground state of both. A higher energy state causes an anti-crossing effect for one of the stress directions in this work. This higher energy state could be revealed by PLE measurements.

Upon application of a magnetic field in the direction parallel to c-axis the A line ZPL feature was observed to broaden but no splitting was observed. This is explained by a large hole g-value for the magnetic field aligned parallel to the c-axis close to the electron g-value [33]. When applied perpendicular to the c-axis the A-line was observed to split into two components and a mixing of states between A and the forbidden transition B resulted in a pronounced B-line being observed with increasing magnetic field strengths, meaning three lines were observed in total; the A and A^* feature and the forbidden B-line, although a fourth component (related to B) is suggested but not observed directly. Temperature dependent studies on the A and A^* transitions result in a clear

thermalisation between both features indicating that the splitting of the A-line is in the excited state.

Further measurements are required in order to verify the polarisation of the A-line when under an applied magnetic field along the [0001] direction, while angular dependent measurements would reveal the precise symmetry of the exciton state exhibited by the bound exciton at the defect.

To summarise, for Hg-implanted ZnO PL studies provided a clear example of an isoelectronic bound exciton centre. Temperature dependence, piezospectroscopy and Zeeman spectroscopy measurements are all explainable as a localised electron-hole pair trapped in the vicinity of the defect centre. The centre appears to bind the hole tightly, as exhibited by the large hole g-value returned by Zeeman measurements. This suggests the centre is pseudodonor in nature although this remains to be confirmed.

5.8 References

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Chapter 6 Observation of neutral and ionised donor bound exciton features related to In and Sn

6.1 Introduction

After investigating the group IV impurity Ge and group II_b impurity Hg in ZnO in Chapters 4 and 5 of this work, an experiment investigating two similar but equally under-studied dopants was conceived: the group IV impurity Sn and the other group II_b element Cd.

As noted in chapter 1, isoelectronic doping is a method for band gap engineering and has already been demonstrated for the case of Cd [1] and Mg [2] ternary alloys with ZnO. Cd is a group II_b transition metal, along with Zn and Hg, and makes a good candidate for isoelectronic doping of ZnO. However, a low solubility limit has been reported [1] so only minor modifications can be made to the band gap of ZnO while maintaining its wurtzite structure (since CdO crystallizes in the cubic structure). If it is to be used as a band gap modifier in ZnO a better understanding of its interaction (and the interaction of other isovalent impurities) with the ZnO crystal is required. The effects of Cd doping on the PL spectrum of ZnO, with smaller doses than those used for band gap engineering, has been given less attention than doping for the purposes of band gap engineering. It is this low concentration regime (much like the Ge and Hg studied previously in this thesis) that is studied here.

For the case of Cd a PL study, similar to that for Hg, is performed to investigate if a Cd related band (*i.e.* a ZPL and its LO-phonon replicas) is observed. Cd is heavier than Zn but not as heavy as Hg and has an electronegativity only slightly greater than that of Zn (the electronegativity of Cd and Zn is 1.69 and 1.65 respectively on the Pauling scale). Since Cd and Hg have the same covalent radius (0.148 nm) if the band produced from Hg acting as an isoelectronic trap is due

solely to the deformation of the lattice due to its size, then a similar band should be observed in the Cd doped case.

The group IV impurity Sn, much like Ge and Si, could potentially form a double donor defect if occupying a substitutional Zn site [3]. Since substitutional Ge resulted in the production of the deep Y-line defect labelled DD₂ in Chapter 4 of this work, the production of a unique Y-line related to Sn could shed some light on the chemical identity of the other Y-line features.

A suitable radioactive decay chain linking Cd to Sn was available at the ISOLDE Facility whereby laser ionised ¹¹⁷Ag was implanted into pieces of ZnO obtained from Tokyo Denpa Ltd. The use of radioactive dopants in conjunction with PL is discussed in further detail in Chapter 2. ¹¹⁷Ag transmutes (with a relatively short half-life of just under 73 s) into ¹¹⁷Cd thus presenting an opportunity to study Cd-related features in the PL spectrum and monitor their decay as the Cd dopant decays into ¹¹⁷In, with a half-life of 2.49 h. The ¹¹⁷In half-life (43.2 m) allows us to observe the decay of In-related features also. In is a known substitutional donor (In_{Zn}) as previously shown by Müller *et al.* [4], however, for a long period I₉ was thought to be related to Na impurities [5, 6] and was proposed to be an acceptor bound exciton recombination. This was later shown to be incorrect by first showing that the feature is in fact donor in nature [7] and secondly by its positive chemical identification reported by Müller *et al.* [4].

Expected ionised In⁺ donor related features in the PL spectrum were not observed in [4]. An exciton feature, labelled I₂, was identified in previous work by Strassburg *et al.* [7] in ZnO samples doped with N. Furthermore, ¹¹⁷In decays into ¹¹⁷Sn, allowing for an opportunity to study Sn as a substitutional impurity in ZnO.

Experimental details can be found in Chapter 2. Stable ion implantation was performed at Surrey, UK at the Surrey Ion Beam Facility and radioactive ion implantation was performed at ISOLDE, CERN. PL of

stable isotope implanted samples was performed at DCU and the radioactive isotope implanted samples analysed in ISOLDE, CERN (*cf.* Chapter 2 for more details).

6.2 Lattice location of $^{117}\text{Ag}/^{117}\text{Cd}/^{117}\text{In}/^{117}\text{Sn}$ in ZnO

While most of the ^{117}Ag has already decayed into ^{117}Cd by the time the annealing process is completed, some important aspects of its properties within the ZnO lattice should be noted. Kang *et al.* [8] find ZnO thin films exhibit p-type properties when doped with Ag. As a group I_b element Ag could potentially function as an acceptor if substituted on the Zn (cation) site. Kang *et al.* observe a peak in the PL emission spectrum which is attributed to an A⁰X recombination [9]. Wahl *et al.* find some interesting properties of Ag dopants in ZnO [10] and report that only 30% of Ag atoms occupy almost ideal substitutional sites; this percentage decreases with annealing treatments.

Cd is expected to form a simple substitutional impurity in ZnO. As stated earlier it is also from group II_b of the periodic table along with Hg and Zn. Given its similar covalent radius (0.131 nm and 0.148 nm for Zn and Cd respectively) and similar electronegativities (*cf.* Section 3.1) a simple substitution for Zn is expected (and indeed observed as we show below) in this work.

While the lattice locations of Ag, Cd and In have been studied previously, very little work has been performed regarding the lattice location of Sn in ZnO. However, given the tendency for heavier atoms (or of similar atomic mass) to occupy Zn sites [10, 11, 12, 13, 14, 15] in ZnO, it can be inferred that Sn would most likely occupy a substitutional Zn site (Sn_{Zn}). Of course in this work the Sn does not have a choice and is essentially forced onto a Zn site after the decay of ^{117}In .

6.3 Observation of the In-related I_9 and I_2 features

The PL emission of undoped ZnO from Tokyo Denpa Ltd. is shown in Figure 6.1 in order to highlight the line energies of three spectral features not observed in ZnO from Tokyo Denpa. Shown in detail in Figure 6.1 is the band edge emission.

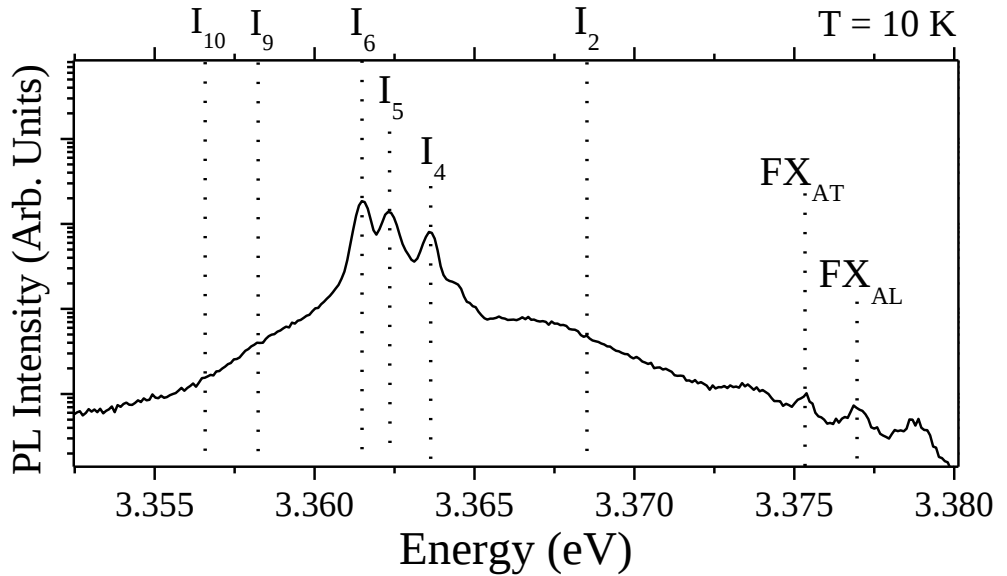


Figure 6.1: PL spectrum of as-received, c-plane grown ZnO, recorded at low temperatures. No annealing or intentional doping has been performed on the sample. I_{10} , I_9 , and I_2 are not observed in this sample or any other sample when studied in the as-received state. Similarly after annealing treatments I_{10} , I_9 , and I_2 are also not observed in Tokyo Denpa Ltd. ZnO pieces.

The longitudinal and transversal free A-exciton states are shown along with the frequently studied I_n lines (*cf.* Chapter 3 for a more detailed discussion of these features and nearby PL features). Labelled with dotted lines are the energies where I_{10} , I_9 and I_2 , are observed in other works [4, 16, 17]. No trace of these lines is observed in Tokyo Denpa ZnO before or after annealing treatments. Hydrothermally grown ZnO from Tokyo Denpa tends to exhibit the I_4 , I_5 and I_6 lines predominantly

[17]; no change in the presence of these features in PL is observed during the radioactive decay experiment.

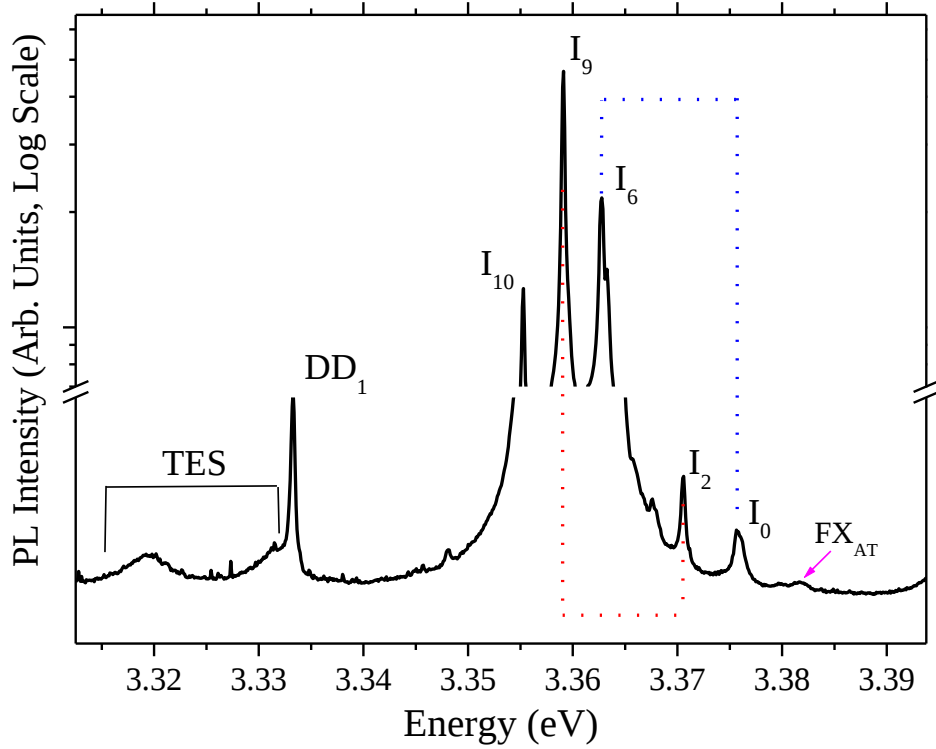


Figure 6.2: PL spectrum of ZnO doped with ^{117}Cd , which decayed to ^{117}In revealing not only the well known I_9 feature but also provided unambiguous data on the rarely observed I_2 feature, also related to In. A break is included in the vertical axis since I_{10} , I_9 and I_6 are much greater in intensity than other features at low temperature.

Figure 6.2 displays the PL spectrum of the ^{117}Cd doped ZnO. After implantation with ^{117}Cd , the first PL spectra were recorded approximately halfway through the first half-life of ^{117}Cd (due to the time taken to cool the sample down below 10 K) so the majority of the ^{117}Cd population had still not transmuted into ^{117}In . No spectral features in the near band edge emission were observed to decrease significantly with time as the radioactive ^{117}Cd decayed. Other regions of the PL spectrum were recorded also, including regions as deep as 300 meV below the band gap but still no features were observed that could be attributed to ^{117}Cd .

Seen also in Figure 6.2 are the Al-related PL features I_6 and I_0 (discussed in more detail in Chapter 3), which are not observed to change significantly with time. Also indicated in Figure 6.2 are the resultant I_9 and I_2 features which were observed to decrease in intensity as the In transmuted into Sn.

Figure 6.3 shows representative spectra of the I_9 feature and surrounding PL features at three times during the ^{117}In decay. Recorded spectra were normalised to the DD_1 feature, discussed previously throughout this work, which is not observed to change significantly with time throughout all measurements; all spectra are normalised to this feature. The I_9 feature is observed to decrease with time while the I_{10} and $I_{6/6A}$ features nearby maintain their intensity.

As mentioned in the introduction section of this chapter, this finding was no surprise since earlier experiments performed by Müller *et al.* [4] had shown In to be the chemical origin of the I_9 feature.

However, what was not observed in that work [4] was the D^+X line also suspected to be related to substitutional In impurities, labelled I_2 in previous works [16] and shown to be D^+X in nature previously [18]. That line appears in this work at an energy of 3.3662 eV and also decreases in intensity as the ^{117}In population transmutes into ^{117}Sn . Representative spectra of PL measurements are shown in Figure 6.4 showing the intensity of the I_2 feature decrease over time. These spectra were also normalised to the DD_1 feature (not shown in Figure 6.4).

Data points for the intensities of both features are plotted in Figure 6.5. The calculated value of the half-life from the plots in Figure 6.5 is 43 ± 3 minutes for both features, in close agreement with the tabulated value [19] of 43.2 minutes. It should be noted that this calculation was performed by Dr. Karl Johnston of the ISOLDE Collaboration at CERN, Geneva.

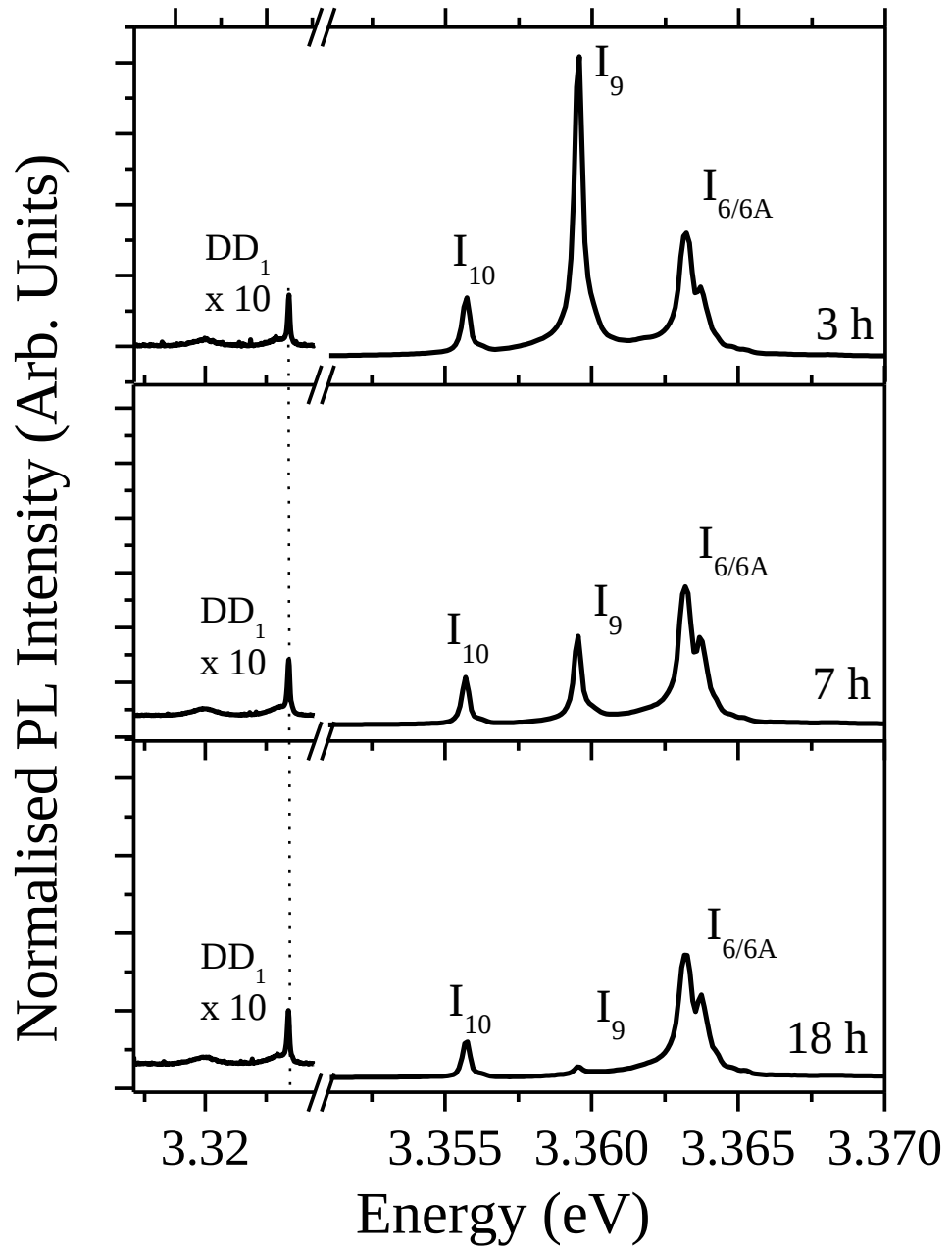


Figure 6.3: Representative spectra demonstrating the decreasing PL intensity of the In-related feature I_9 . The uppermost spectrum was recorded approximately 2 hours after the annealing treatment. The middle panel was recorded after approximately 7 hours where I_9 can be observed to decrease in intensity significantly and in the final (bottom) panel most of the In has now transmuted into Sn. Spectra were normalized to the DD_1 feature indicated with a dashed line.

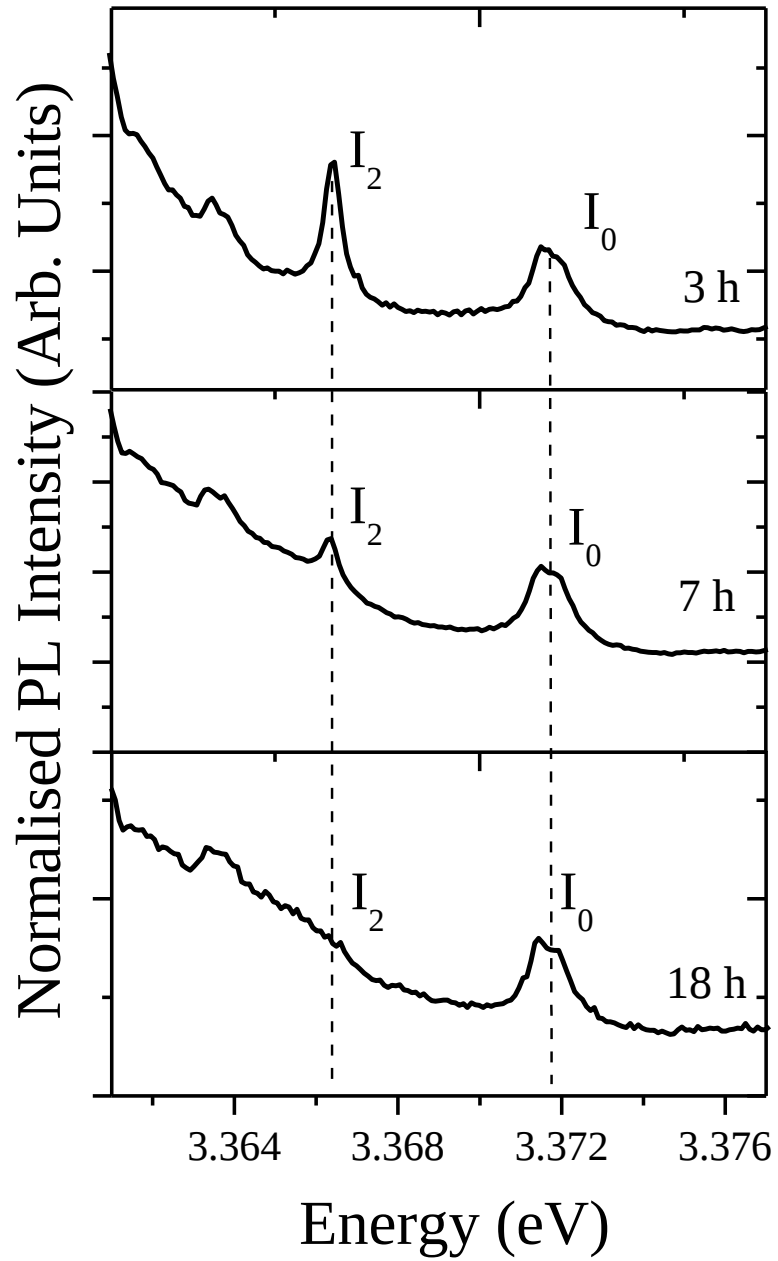


Figure 6.4: Representative spectra demonstrating the decreasing PL intensity of the In-related feature I_2 . The uppermost spectra were recorded approximately 2 hours after the annealing treatment. The middle panel was recorded after approximately 7 hours where I_2 can be observed to decrease in intensity significantly and in the final (bottom) panel most of the In has now transmuted into Sn and the I_2 PL line is not observable. Spectra were normalized to the DD_1 feature (not shown).

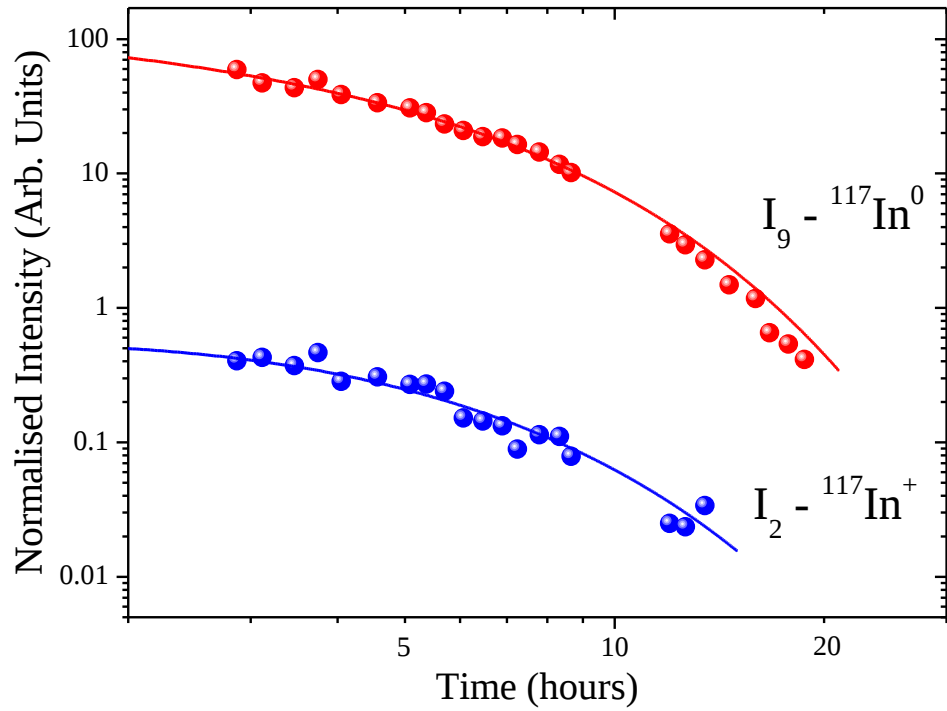


Figure 6.5: Normalised line intensities for the I_9 and I_2 features. Solid lines represent exponential line fittings. Spectra were normalized to the DD_1 feature indicated with a dashed line in Figure 6.3 above. Analysis of these data points was carried out by Dr. Karl Johnston of the ISOLDE Collaboration at CERN, Geneva.

A line appeared after the sample was implanted with ^{117}Cd , labelled I_{10} , which is not observed in ZnO samples from Tokyo Denpa Ltd. [16, 17]. The possibility of stable ^{117}Sn contaminating the implantation beam cannot be ruled out, particularly if the sample was side-by-side during the implantation process with another sample which may have been implanted with large doses of stable ^{117}Sn . Therefore another experiment was devised in order to investigate the possibility of the I_{10} line being related to Sn.

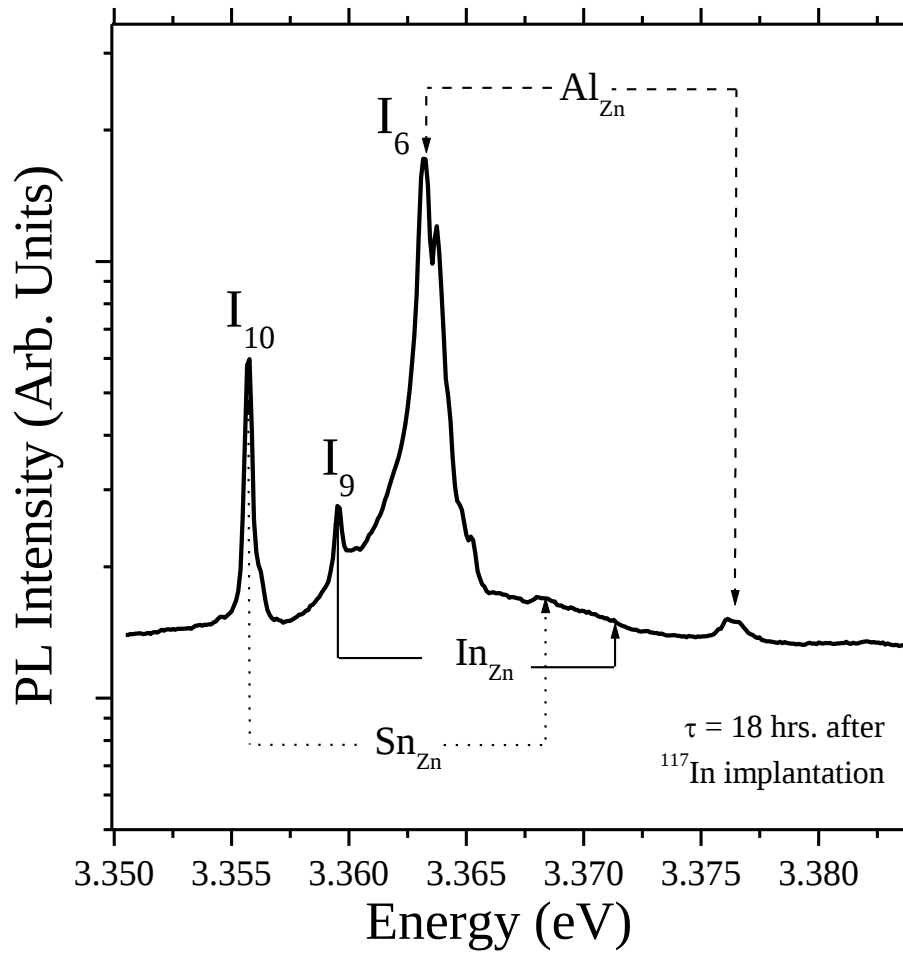


Figure 6.6: PL spectrum of ZnO doped with ^{117}Cd . The I_{10} feature is indicated with a dashed line, labelled Sn_{Zn} to indicate its possible relation to Sn impurities; the higher energy region indicated represents the region where ionised bound exciton recombination occurs although no distinct feature is observed at this energy in this work perhaps due to the low levels of dopant implanted.

Indicated in Figure 6.6 is the PL spectrum for the sample near the end of the decay of In to Sn. The I_9 line is still visible whereas I_2 is not. The I_{10} line is almost as intense as the strongest I line, I_6 . To investigate the possible association of I_{10} with Sn, after the work at ISOLDE the same sample was delivered to DCU to be studied further. The sample was annealed in O_2 for 30 minutes at 750°C in order to restore any lost crystal quality after the radioactive decay of the dopants. The PL spectra recorded are shown in Figure 6.7 where the unimplanted top-half of the

sample exhibits the typical PL emission from ZnO obtained from Tokyo Denpa, Ltd. (A). The bottom half (B) of Figure 6.7 shows the I_{10} feature and its accompanying LO-phonon replicas.

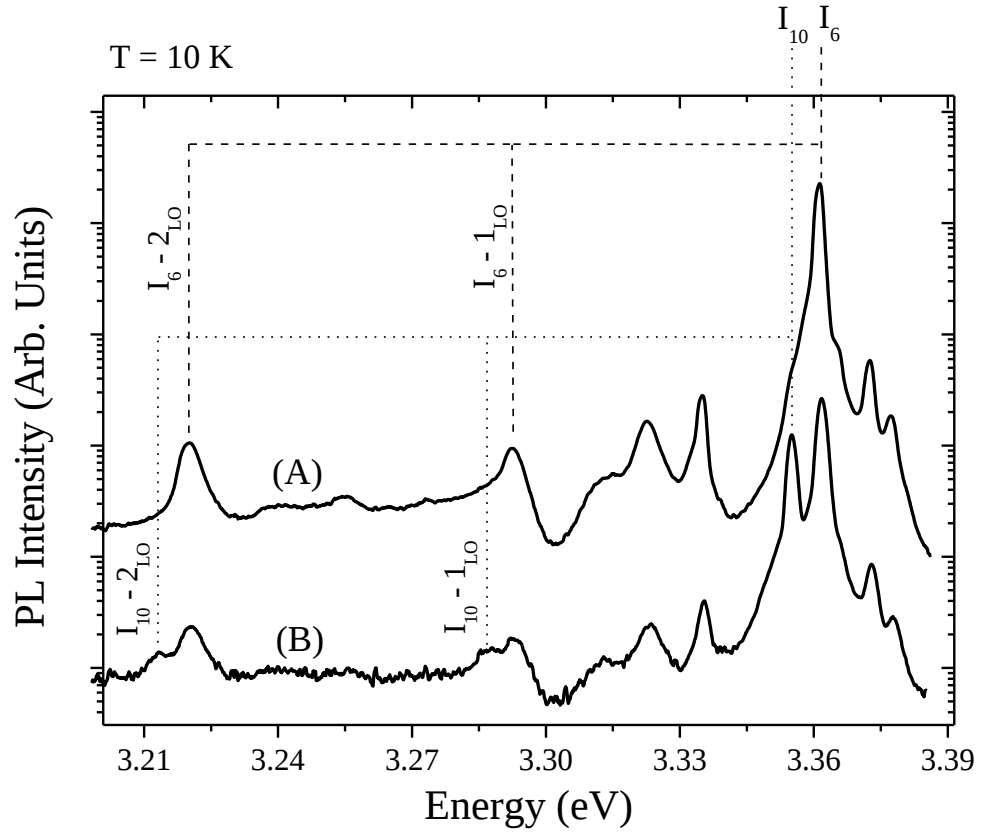


Figure 6.7: PL spectra of ZnO after the transmutation of most radioactive species of mass 117 (Ag, Cd, In) into stable ^{117}Sn . This sample was returned to Dublin and annealed in an O_2 atmosphere for 30 minutes in order to remove the possible damage induced during radioactive decay. (A) represents the region of the sample (the top half of the O-face) left relatively unimplanted given the quality of spectrum and lack of new features. (B) is the likely the region of highest implantation dose and the I_{10} feature remains prominent here; also indicated are the 1_{LO} and 2_{LO} lattice relaxations associated with I_{10} . Spectra have been vertically shifted for clarity.

6.4 Chemical diffusion of Sn into ZnO

After the observation of the I_{10} feature during the decay of radioactive Cd and In, an experiment was devised which involved doping single crystals of ZnO via a chemical diffusion technique. The concentration of Sn in as-received samples was measured by glow discharge mass spectrometry by Tokyo Denpa Ltd. and reported to be less than the detection limit of the measuring technique [20], hence explaining why the I_{10} feature is rarely observed in ZnO obtained from Tokyo Denpa.

A doping technique other than ion implantation was proposed by a colleague in Dublin City University, Dr. Daragh Byrne. He suggested a method that would allow Sn to replace Zn atoms on the Zn face of a single crystal substrate after which the sample could be annealed and the Sn impurities allowed to diffuse into the crystal. This method was used successfully for controlled doping of ZnO with enriched isotopes of Cu [21].

Since the doping method is outside the normal routine of ion implantation of stable and radioactive impurities the experimental details are included here.

Single crystal ZnO was soaked in an aqueous tin (II) chloride solution (10mg / ml) for 120 s before being removed and rinsed with deionised water. This was followed by drying under a nitrogen gas flow. The sample was then annealed at 700°C for 3 hours in order to facilitate the diffusion of Sn into the sample, before being cooled to room temperature, after which PL measurements were performed.

The PL spectrum of the sample doped in this way is shown in Figure 6.8. The I_{10} peak is distinguishable from the I_6 band edge emission (shown inset of Figure 6.8). The appearance of the I_{10} line only in samples doped with Sn impurities and not in samples without Sn present serves as strong evidence that the I_{10} line is related to Sn, corroborating our finding that the line is associated with Sn impurities produced via implantation and decay.

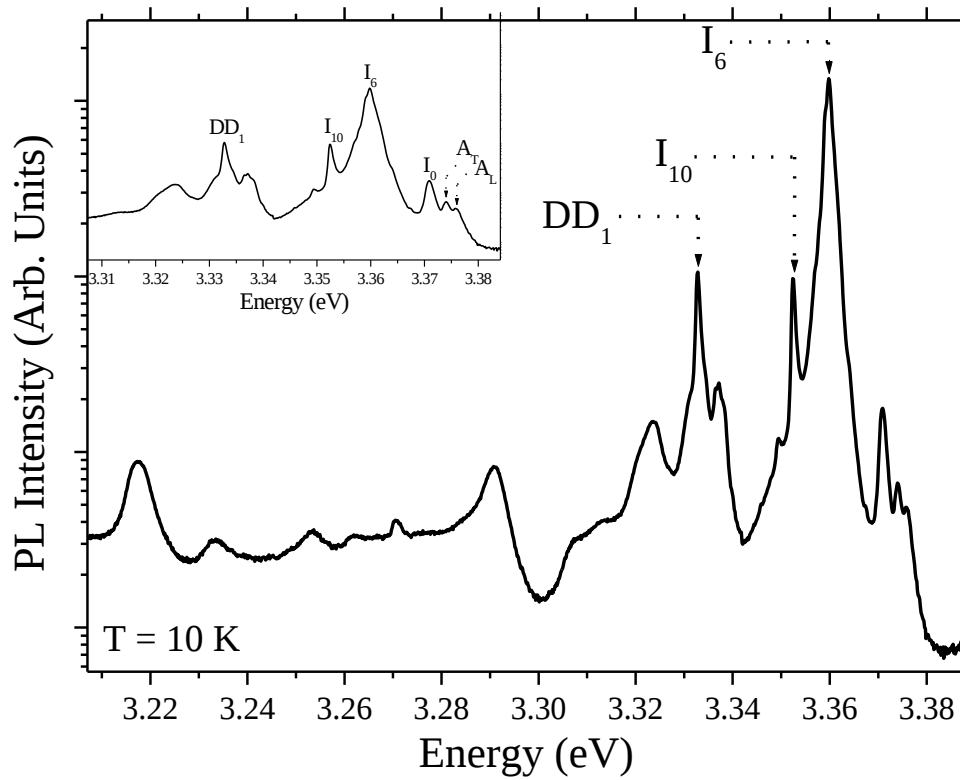


Figure 6.8: PL spectrum of ZnO doped via chemical diffusion of Sn. For details see text. Once again the I_{10} feature appears in the region where neutral donor bound exciton features are expected (highlighted inset). DD_1 is a deep donor bound exciton feature and I_6 is a shallow donor bound exciton feature, both have been indicated to illustrate the similarity in spectral position between the Sn-feature, I_{10} , and well-known D^0X lines (I_6 in this case). I_0 has also been indicated to show the spectral location of ionised donor bound exciton lines.

6.5 Conclusions

The I_9 feature is due to exciton recombination at substitutional neutral indium impurities occupying a Zn site (In_{Zn}). The I_2 recombination occurs in a region of the PL spectrum where, theoretically, the ionized version of donor bound exciton recombinations should be present as explained in Chapter 3 [18]. The I_2 feature, along with the neutral donor bound exciton feature I_9 , are both seen to decay at a rate consistent with

the ^{117}In half-life and so are unambiguously attributed to bound exciton recombinations at neutral In donors (I_9) and ionized In donors (I_2).

Much the same as I_6 and I_0 for Al, and I_8 and I_1 for Ga, I_9 and I_2 are D^0X and D^+X are the lines for ZnO doped with In [4, 16].

The work involving implantation of radioactive isotopes in this chapter has unambiguously identified a prominent donor bound exciton recombination feature (In_{Zn}) in ZnO and its ionized counterpart (In_{Zn}^+). No notable PL features due to substitutional cadmium are observed in this sample. A subsequent experiment which involved doping ZnO by diffusion of Sn resulted in the I_{10} line which was observed here perhaps due to Sn contamination in the beamline or by accidental co-implantation. A positive chemical identification of this line was observed in two separate samples doped with Sn, an impurity which is typically below the detection limit of the method used by the producer to characterise the material.

6.6 References

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Chapter 7 Conclusions and future work

7.1 Conclusions

The Ge-related DD_2 line described in Chapter 4 exhibited some unusual properties when compared to other DBX lines in ZnO. Temperature dependence studies in particular revealed a weak thermal binding property and curious localisation behaviour. The data we have available do not allow for a definite choice to be made between the alternative possibilities for the DD_2 line. As discussed, the involvement of Cu or Li could, in principle, be examined by using starting ZnO material with differing amounts of these impurities for Ge implantation. However, commercially available ZnO tends to have significant levels of these already present, making the use of widely varying Cu or Li concentrations difficult to achieve. For now, we can say that the DD_2 centre is relatively simple structurally, that it involves a Ge impurity and that it acts as a single donor centre in the crystal. The involvement of a neighbouring impurity or defect situated along the c-axis in the close vicinity of the Ge_{Zn} impurity is also indicated by the available data.

When ZnO is implanted with Hg a characteristic ZPL feature (3.279 eV) and associated sideband are observed. A strong exciton binding is exhibited by the feature, characterised by the large localisation (90 meV) energy and strong thermal binding behaviour. Zeeman spectroscopy and piezospectroscopy provided results strikingly different from the dominant D^0X features in ZnO. One aspect of the dopant centre investigated here is the source of the excited state degeneracy encountered for uniaxial stress applied along the $[1-210]$ and $[10-10]$ directions of the crystal. This is found to be due to the Γ_5 exciton state splitting into Γ_1 and Γ_2 states when bound to the defect (which assumes C_{1h} symmetry) under uniaxial stress. This readily explains the splitting of the A-line observed here and is confirmed by the thermalisation behaviour exhibited by both components during stress indicating the

shared ground state of both. Upon application of a magnetic field in the direction parallel to c-axis the A line ZPL feature was observed to broaden but no splitting observed. This is explained by a large hole g-value close to the electron g-value. When applied perpendicular to the c-axis the A-line was observed to split into two components and a mixing of states between A and the forbidden transition B resulted in a pronounced B-line observed with increasing magnetic field strengths, meaning three lines were observed in total; the A and A* feature and the forbidden B-line, although a fourth component (related to B) is suggested but not observed directly. Temperature dependent studies on the A and A* transitions result in a clear thermalisation between both features indicating that the splitting of the A-line is in the excited state. In Chapter 6 the I₉ feature is found to be due to exciton recombination at substitutional neutral indium impurities occupying a Zn site (In_{Zn}). The I₂ recombination occurs in a region of the PL spectrum where, theoretically, the ionized version of donor bound exciton recombinations are present. The I₂ feature, along with the neutral donor bound exciton feature I₉, are both seen to decay at a rate consistent with the ¹¹⁷In half-life and so are unambiguously attributed to bound exciton recombinations at neutral In donors (I₉) and ionized In donors (I₂). Much the same as I₆ and I₀ for Al, and I₈ and I₁ for Ga, I₉ and I₂ are D⁰X and D⁺X are the lines for ZnO doped with In. A subsequent experiment which involved doping ZnO by diffusion of Sn resulted in the I₁₀ line which was observed here perhaps due to Sn contamination in the beamline or by accidental co-implantation. A positive chemical identification of this line was observed in two separate samples doped with Sn, an impurity which is typically below the detection limit of the method used by the producer to characterise the material. The precise nature of the I₁₀ defect is not yet known and merits further work.

To date we have investigated the PL behaviour of Ge impurities in ZnO and the PL emission related to isoelectronic Hg traps in ZnO. Both of these impurity systems are relatively new and not yet fully understood, highlighting the need for additional work to gain further insight. To this

end, some further experiments are suggested for the future based on this researcher's findings thus far; these suggestions are presented below.

7.2 Future Work

7.2.1 Zeeman experiments

Zeeman splitting experiments have been put to good use previously in ZnO [4, 5] and have identified the region of the ZnO PL spectrum that is due to ionised donor bound exciton recombination [6]. In this work they have aided in the identification of the charge state of the defects in question.

While angular dependent measurements were not possible, a prediction of the behaviour of DD_2 is possible based on the behaviour of other similar features (DBX lines, DD_1 , etc.). Four components are predicted in this model under application of magnetic fields between 0° and 90° with respect to the c-axis. The lowest and highest energy components (not observed in Faraday configuration) result from transitions that are forbidden under spin considerations. Further measurements are required to verify this behaviour however, although given the similarity so far displayed between DD_2 and DD_1 and the likelihood that DD_2 is due to the recombination of an A-band (Γ_7) exciton a similar splitting should occur for DD_2 .

What was not possible in this work however is listed below in bullet point form to highlight the gaps not yet filled by previous Zeeman investigation:

- Ge: for the case of Ge-doped ZnO angular dependence measurements would allow for unambiguous assignment of the valence band from which the bound exciton originates. Also angular dependence would allow for a more accurate calculation

for the hole g-value and electron g-value than that presented in Chapter 4 of this work.

- Hg: the Hg-related exciton trap presented some interesting splitting components under the influence of a magnetic field. While a clear splitting was not resolved in Chapter 5 of this work for the application of a magnetic field parallel to the [0001] direction, several components were observed in the perpendicular to c direction ([1-210] for example). Angular dependence would clearly indicate the behaviour of the splitting components with changing crystal orientation, necessary to accurately identify the splitting state of the feature and calculate the hole and electron g-values of the defect.
- Hg: another possibility for the Hg-related defect would be to lower the temperature to less than 2 K so that only the B line (forbidden) transition is observed which would allow for the observation of the splitting of the B component (if any).
- Ge and Hg: polarisation measurements were not possible during this work but would be an interesting prospect for future work for both the DD₂ and Hg ZPL features observed here. Polarisation measurements in the Faraday and Voigt configuration can indicate the preferred emission of the PL observed during application of a magnetic field.

7.2.2 Photoluminescence Excitation Studies

A tuneable laser source could be used to perform PLE (photoluminescence excitation) measurements, giving an insight into the nature of the new defects found so far as part of this work. Similar work was performed on ZnO by McCabe [7] to great effect, the results of which were able to aid in the assignment of the origin of the observed luminescence features. In this case PLE could be used to:

- Ge: identify the excited states (if any) of the DD₂ feature, similar work was performed on DD₁ resulting in the identification of some nearby excited states of the emission [8].
- Hg: PLE could allow for a positive identification of the level which is the source of the anti-crossing observed under stress in the [1-210] direction in Chapter 5 of this work.

7.2.3 Dual-excitation studies

Previous work by other groups has shown that excitons formed from the conduction band and heavy hole (B) valence band have distinct properties under temperature dependence [9]. Dual excitation could be achieved for example using a HeCd laser operating at 325 nm wavelength as in this work in conjunction with the same laser's 442 nm line, or perhaps a frequency doubled Nd:YAG laser operating at 532 nm. Infrared illumination was used by Thomas and Hopfield [10] to diminish the PL emission of some lines in the ionised donor bound exciton region of ZnO while others seemed to increase in intensity. This effect merits further investigation now that the presence of these ionised donor bound excitons can be more controlled and the chemical species can be specified.

7.2.4 Absorption measurements and time-resolved PL

Absorption measurements specifically for the Hg-defect would allow for additional confirmation of the assignment of the centre as being pseudodonor in nature since pseudodonor traps are distinct from pseudoacceptor traps in absorption spectroscopy. In the case of isoelectronic acceptor a strong absorption property is expected unlike the case for isoelectronic donor whereby a very different spectrum is expected in absorption (*i.e.* not a “mirrored” spectrum), further details

of this property are reported in [11]. Time resolved measurements would allow for a direct further comparison with other known isoelectronic centres in semiconductors [12] which are observed to exhibit much longer decay lifetimes when compared to donor and acceptor bound exciton features in those semiconductors [13].

7.3 References

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