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On the symmetry of phosphorous doped ZnSe

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Abstract. The site symmetry of P doped ZnSe is analysed in detail here, as the recent experiments suggest two possible symmetries T_d and C_{3V}. The reduction to C_{3V} is attributed to the presence of natural impurity, Ga. Our calculations based on molecular model and Green's functions suggest that the symmetry C_{3V} is possible with ZnSe : P when Jahn Teller distortion of about ~ 0·2 Å (towards one of Zn atom) is assumed. This has been supported by other experiments.

Keywords. ZnSe; localized vibrational modes; T_d and C_{3V} symmetries; Jahn Teller distortion; Green's function; molecular model.

1. Introduction

The wide gap semiconductor, ZnSe, is an example of potential applications in optoelectronic devices, such as blue light emitting diodes and blue diode lasers. Using the molecular beam epitaxy method, Hasse *et al* (1991) have demonstrated that ZnSe diodes lase in the bluegreen region. In spite of the fabrication of low resistivity *p*-type ZnSe using nitrogen as the dopant, doping still remains complicated. Similarly even though a lot of experimental and theoretical investigations are available in the literature for the defect modes in II–VI systems, the role of phosphorous as a *p*-type dopant in ZnSe is not fully understood. For low doping, the photoluminescence seems to be due to the recombination of excitons bounding neutral acceptors. The reported experiments (Yao and Okada 1986; Qiu *et al* 1991) could not exactly predict the nature of symmetry of the shallow acceptors introduced by the doping.

Electron spin resonance (ESR) (Watts *et al* 1971) and optically detected magnetic resonance (ODMR) (Nicholls and Davies 1979) suggest that phosphorous substitutes selenium site in ZnSe and acts as a deep acceptor at about 0·7 eV. These deep level defects under certain conditions give rise to the Dx centres (Localized vibrational modes (LVMs) for such Dx centres are already observed for GaAs : Si (Wolk *et al* 1991)).

2. Symmetry

The ESR experiments show that $[Pse]^0$ centres do not possess the T_d symmetry, as expected for any simple case. Instead, this is predicted to be C_{3V} symmetry (Watts *et al* 1971). The reduction in the symmetry is ascribed to the Jahn Teller type distortion.

Also this ESR spectra could be bleached by IR radiation with energies > 0·8 eV (Watts *et al* 1971).

Generally, phosphorous centre is expected to be non magnetic and would be of T_d symmetry in ZnSe. Then, only a Jahn Teller type distortion can lead to C_{3V} symmetry as a result of three-fold degeneracy in T_d surroundings. So, it is understood that photocreation of the neutral acceptors involves a change in the symmetry. Alternatively, another model avoids the Jahn Teller distortion where C_{3V} symmetry is possible with nearby impurity or defect, irrespective of the charge state, i.e. the non magnetic state would have C_{3V} symmetry, rather than T_d as expected.

To distinguish between these models on the nature of symmetry of P_{Se} in ZnSe, Raman spectrum for ZnSe : P,Ga is observed by Nakano *et al* (1992) in the range 180–420 cm^{-1}. There are two stronger modes at 210 and 255 cm^{-1} with weaker modes at 220 and 375 cm^{-1}. From the measurements of phonons on host ZnSe (Taylor 1967), Nakano *et al* attributed these modes, 210 and 255 cm^{-1}, to correspond to TO and LO phonon modes of ZnSe. The two weaker modes do not appear in a variety of ZnSe specimens whether for undoped or doped with elements other than phosphorous and gallium.

The polarization behaviour is also discussed by Nakano *et al* (1992), which suggests that the 375 cm^{-1} correspond to a simple substitutional centre, from T_d symmetry whereas 220 cm^{-1} corresponds to A_1 mode of either T_d or C_{3V} and could not be distinguished.

Because of this interesting behaviour of ZnSe : P, a detailed theoretical investigation is attempted here, to identify the nature of symmetry.

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3. Localized vibrational modes due to *p* doped ZnSe

The LVMs are calculated extensively by two approaches: (i) molecular model and (ii) green's function technique.

(i) *Molecular model*: The well established technique to workout the defect modes is molecular model, where a single molecule will be considered. In brief, the dynamical matrix will be constructed from the long range and short range interactions.

On diagonalization of this matrix, one can get the normal modes and the localized vibrational mode (LVM) can be identified from the eigen displacement of the defect atom.

ZnSe possesses T_d symmetry as represented in figure 1, with selenium at the centre. When this is doped with phosphorous, it substitutes Se atom and still retains the T_d symmetry, to start with when any other deformation is not considered.

The dynamical matrix, which is 15×15 (in terms of e^2/V), is constructed as with the long and short range interactions taking only first neighbours. The short range part of the dynamical matrix is given here for continuity.

and A and B are Kellerman's constants, for the corresponding system.

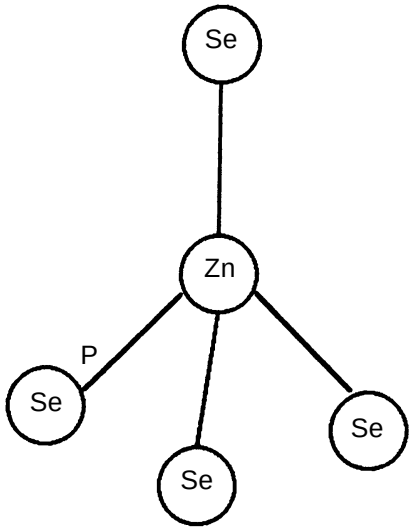

Figure 1. Molecular structure for T_d symmetry.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	A	B	B	C	D	D	E	F	– F	E	– F	F	E	– F	– F
2		A	B	D	C	D	F	E	– F	– F	E	– F	– F	E	F
3			A	D	D	C	– F	– F	E	F	– F	E	– F	F	E
4				G	H	H									
5					G	H						0			
6						G									
7							I	J	– J						
8								I	– J			0			
9									I						
10										I	– J	J			
11											I	– J		0	
12												I			
13													I	– J	– J
14														I	J
15															I

Only upper half of the matrix is given, as it is symmetric.

where

$A = (A_1 + 3A_2)/M_P$ $\quad B = (B_1 - B_2)/M_P$

$C = -A_1/\sqrt{M_{Zn}}\,M_P$ $\quad D = -B_1/\sqrt{M_{Zn}}\,M_P$

$E = -A_2/\sqrt{M_{Zn}}\,M_P$ $\quad F = -B_2/\sqrt{M_{Zn}}\,M_P$

$G = (A_1 + 3A_3)/M_{Zn}$ $\quad H = (B_1 - B_3)/M_{Zn}$

$I = (A_2 + 3A_4)/M_{Zn}$ $\quad J = (B_2 - 3B_4)/M_{Zn}$

$A_1 = (A_{ZnP} + 2B_{ZnP})/6$ $\quad B_1 = (A_{ZnP} - B_{ZnP})/6$

$A_2 = (A_{ZnP} + 2B_{ZnP})/6$ $\quad B_2 = (A_{ZnP} - B_{ZnP})/6$

$A_3 = (A_{ZnSe} + 2B_{ZnSe})/6$ $\quad B_3 = (A_{ZnSe} - B_{ZnSe})/6$

$A_4 = (A_{ZnSe} + 2B_{ZnSe})/6$ $\quad B_4 = (A_{ZnSe} - B_{ZnSe})/6$

The force constants, A_{ZnSe} and B_{ZnSe}, are worked out to construct the above dynamical matrix, from the available experimental data on elastic constants (Kusakov *et al* 1973) and phonon frequencies (Matsuo *et al* 1984) of ZnSe based on a rigid ion model, and are given in table 1 for Zn–Se bond. Such data for ZnP or ZnSe : P are not immediately available and so an approximate method is followed to work out the force constants of Zn–P. That is, A_{Zn-P} is worked from the Debye temperature (Sheleg and Kutas 1981). The same is compared with the host force constant of zinc diphosphite for which the data is available. There is a correspondence between the two (But only the previous value is considered for the present

Table 1. Constants used to evaluate LVMs for ZnSe : P in molecular model.

Cell constant a (Å)	Elastic constants in dynes [cm^2 ($\times 10^{11}$)]			Force constants (e^2/V)			
	C_{11}	C_{12}	C_{44}	A_{Zn-Se}	B_{Zn-Se}	A_{Zn-P}	B_{Zn-P}
5·6676	8·95	5·39	3·98	75·05	– 1·15	45·66	– 0·699

Table 2. Scattering symmetries of phonons.

Coordinates	Representation	
	For T_d	For C_{3V}
$z\ (y, y)\ \bar{z}$	A_1, E	A_1, E
$z\ (y, x)\ \bar{z}$	T_2	E
$z\ (x, y)\ \bar{z}$	T_2	E
$z\ (x, x)\ \bar{z}$	A_1, E, T_2	A_1, E
$z\ (x', x')\ \bar{z}$	A_1, T_2	A_1, E
$z\ (x', y')\ \bar{z}$	E, T_2	A_1, E

calculations). This is what is represented in table 1 for A_{Zn-P}.

With these parameters, the defect modes are worked for the T_d symmetry, by diagonalizing the dynamical matrix and looking at the eigen frequencies and eigen displacements. These values are given in table 3, along with the Raman measurements for LVMs. We find that there are two modes 371 cm^{-1} and 221 cm^{-1} for LVMs here (the displacement of the defect atom will fall off rapidly, exponentially, as distance goes about the defect atom for fixing an LVM). When the displacements corresponding to the 15 modes are analysed by the geometry, these modes correspond to T_2 and A_1 representation of T_d symmetry. This is explicitly shown here. When Nakano *et al* (1992) studied the defect modes the symmetry of the displacements were given for both T_d and C_{3V}, which is displayed here in table 2 for comparison with our results. The eigen displacements which we obtained from our calculations are given in table 3. Tables 2 and 3 show that 371 cm^{-1} and 221 cm^{-1} correspond to T_2 and A_1 representations of T_d symmetry. When we compare with the C_{3V} symmetry it is found that this 221 cm^{-1} belongs to this symmetry.

Since 221 cm^{-1} appears to be both in T_d and C_{3V} symmetries, it is attempted to see how this C_{3V} is possible when only P is substituted in ZnSe. The most trivial case is that there should be some other impurities present in ZnSe which brings down the symmetry, which will also be seen. When P is substituted at Se site, there is a change in force constant in Zn–P bond as there should be a distortion (Kwak *et al* 1994) like Jahn Teller type (JT).

This should be checked for C_{3V} symmetry as Nakano *et al* (1992) claim that C_{3V} and T_d could not be distinguished for 220 cm^{-1}.

Any distortion in the bond will be reflected in the force constant which is obtained as follows.

When there is a Jahn Teller (JT) type distortion it is found (Kwak *et al* 1994) that P atom moves about 0·2 Å toward one of the four neighbouring Se atoms, lowering the symmetry of the defect from T_d to C_{3V}. Since, it is reported that the relaxation is about 0·2 Å, any other computations are not carried out here to work out the relaxed coordinate of the atoms in the molecule. It is attempted to find the change in force constant, due to this relaxation, a Lennard Jones type potential is assumed for interaction between the neighbours. So in ZnSe the force constant for Zn–Se is worked out, by taking the distance between Zn and Se as 2·8338 Å in unrelaxed situation and when P moves by 0·17 Å, the new force constant can be worked out by changing the value of the distance between P(Zn) and Se as 3·0038 Å. The difference between these force constants is attributed to the contribution from JT distortion. The modified force constant A_{Zn-P} and B_{Zn-P} are given in table 4.

As usual, with these new set of parameters the dynamical matrix is constructed and solved for LVMs.

The LVMs are properly picked out from the eigen displacements in the usual way. The results are given in table 4.

Now, when this is compared with the symmetry of the eigen displacements it is seen that 220 cm^{-1} belongs to C_{3V} symmetry. This is an interesting result, as a JT type distortion naturally will affect the symmetry of the system. Kwak *et al* (1994) recently suggested by some other experiments that this JT distortion is dominant in ZnSe.

ZnSe : P,Ga: The other possibility is the natural defect. To work out the defect modes corresponding to C_{3V} symmetry, following the findings of Nakano *et al* (1992) that gallium impurity substitutes one of the Zn atom in the molecule, is considered as given in figure 2. The site symmetry is reduced to C_{3V} from T_d in this case. Here when Ga is substituted at Zn the new force constant A_{Ga-P} is worked out from the bond length and a Lennard Jones type since A_{Ga-Se} already is available (Jandl *et al* 1976). The force constant A_{Ga-P} is calculated using phonon frequency and elastic constant. The various force constants used are given in table 5.

Again the dynamical matrix for this defect pair is constructed and diagonalized for defect modes and they are given in table 6, along with the experimental values. We obtain the mode 220 cm^{-1} in this case also, but when we look at the geometry of the displacements, in relation

Table 3. LVMs calculation for ZnSe : P using molecular model in T_d symmetry.

Sl. no.	Calculated LVMs (cm^{-1})	Displacements						Experimental LVMs (cm^{-1})
		x_1	y_1	z_1	x_2	y_2	z_2	
1	371·23	0·46	0·46	0·46	– 0·31	– 0·31	– 0·31	375
2	221·58	0·028	0·028	0·028	0·21	0·21	0·21	220

Table 4. Modified force constants and LVMs for Zn–Se : P in molecular model.

Modified force constants (e^2/V)		Calculated LVMs (cm^{-1})	Displacements						Experimental LVMs (cm^{-1})
A_{Zn-P}	B_{Zn-P}		x_1	y_1	z_1	x_2	y_2	z_2	
12·300	0·819	223	0·38	0·38	0·38	– 0·39	– 0·39	– 0·39	220
		271	– 0·15	– 0·15	– 0·15	0·07	0·07	0·07	375

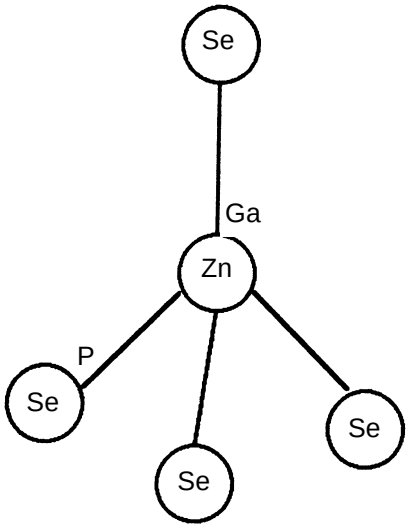

Figure 2. Molecular structure for C_{3V} symmetry.

with C_{3V} symmetry, these modes occur in the A_1 representation.

This 220 cm^{-1} occurs both in T_d and C_{3V} for A_1 representation. This indicates that there are two possibilities of ZnSe : P. It is rather difficult to identify the centre possible for this model, when other natural impurity is not considered.

The above molecular model calculations for C_{3V} symmetry (with Ga as additional additive impurity) giving 220 cm^{-1} may not be equally true for any other unidentified impurity. This is the reason why Nakano *et al* (1992) have observed Raman's spectrum for ZnSe : P,Ga.

(ii) *Green's function technique*: The LVMs are worked out from Green's function technique. The detailed theory is available in Maradudin *et al* (1971) and so will not be repeated here.

To start with T_d symmetry of ZnSe : P is considered. As the perturbation matrix *dl* is (15 × 15), group theoretical simplification is done, taking the symmetry coordinates for T_d symmetry, which reduces to

$$\Gamma^{(15)} = A_1 + E + F_1 + 3F_2.$$

Similarly, we can construct the Green's functions matrix (15 × 15) for the host system from

$$g_{ab}\begin{pmatrix} 0\ l \\ k\ k' \end{pmatrix} = \frac{1}{N}\sum_{q_j} \frac{e_a(k|q_j)\, e^*(k'|q_j)}{(x^2 - x_j^2(q))} \cos\left[2\delta\ \bar{q}\cdot\bar{r}\begin{pmatrix} 0\ l \\ k\ k' \end{pmatrix}\right].$$

This is also reduced with the same symmetry coordinates. The localized modes are then calculated from

$$|I - gdl| = 0.$$

The *g* and *dl* matrices for T_2 representation is given as follows. Block diagonalized form of *g* and *dl* for isolated substitutional case when the nearest neighbours alone are included.

$$T_2 = \begin{bmatrix} \dfrac{-32Y+16B+4A_1+8P_1+4Q_1}{20} & \dfrac{4[-B-3Y+A_1+2P_1+Q_1}{10} & \dfrac{8[-R_1+4Z]}{12{\cdot}65} \\ & \dfrac{B+8Y+4A_1+4P_1+4Q_1}{5} & \dfrac{-8R_1+8Z}{6{\cdot}32} \\ & & A_1-Q_1-R_1+2S_1 \end{bmatrix},$$

T_2 for *dl* matrix

Table 5. Constants used to evaluate LVMs for the system ZnSe : P,Ga.

Force constants (e^2/V)							
A_{Zn-Se}	B_{Zn-Se}	A_{Zn-P}	B_{Zn-P}	A_{Ga-Se}	B_{Ga-Se}	A_{Ga-P}	B_{Ga-P}
75·05	– 1·15	45·66	– 0·699	– 57·02	12·23	75·96	– 0·533

Table 6. LVMs calculation for ZnSe : P,Ga using molecular model in C_{3V} symmetry.

Sl. no.	Calculated LVMs (cm^{-1})	Displacements						Experimental LVMs (cm^{-1})
		x_1	y_1	z_1	x_2	y_2	z_2	
1	446·56	0·48	0·48	0·48	– 0·31	– 0·31	– 0·31	375
2	222·45	0·036	0·036	0·036	0·17	0·17	0·17	220

Table 7. Parameters used to evaluate the Green's function for ZnSe.

Parameters ($\times 10^4$ dyn [cm])	Phonon frequency (w) $\times 10^{14}$ rads		
	Type	Experimental	Calculated
A = – 2·71	LO (Γ)	0·476	0·476
B = – 1·12	TO (Γ)	0·401	0·401
C_1 = – 0·38	LO (L)	0·471	0·468
D_1 = 0·44	TO (L)	0·414	0·397
E_1 = 0·00	LO (X)	0·414	0·411
F_1 = 0·46	TO (X)	0·424	0·414
C_2 = – 0·28			
D_2 = – 0·8			
E_2 = 0·00			
F_2 = – 1·23			

$$T_2 = \begin{bmatrix} \frac{16e\,Mw^2 - 100\Delta A}{20} & \frac{-4e\,Mw^2}{10} & \frac{40\Delta A}{12\cdot 65} \\ & \frac{e\,Mw^2}{5} & 0 \\ & & -\Delta A - \Delta B \end{bmatrix},$$

(only the upper half of the blocks are given as all the matrices are symmetric). ΔA and ΔB are change in force constants.

For continuity, to work out the Green's functions for ZnSe, the phonons and eigen displacements should be worked out. This is done in a rigid ion model, taking the central and non central forces into account (Plummelle and Vandevyver 1976). The parameters are refined in a least squares technique and are given in table 7 (With these phonons, the mean square amplitudes of Zn and Se are worked out, for comparison with the Green's functions).

The Green's functions are then worked out with the above phonons. To check the correctness of the Green's functions, the mean square amplitude of ZnSe is calculated and compared with the result from the previous experiment and they are 4·148 $Å^2$ and 4·57 $Å^2$, respectively. The agreement is good. So these green's functions will be used hereafter for defect modes calculation.

To start with, both A_1 and T_2 representations are considered, for ZnSe : P, having T_d symmetry. The force constants are again from table 1 already given. The defect modes thus calculated are 214 cm^{-1} and 370 cm^{-1}. Experimental values are 220 cm^{-1} and 375 cm^{-1} respectively, for these two representations.

We could see that there are two localized modes 375 cm^{-1} and 220 cm^{-1} in these two representations, supporting the information arrived in the molecular model.

But we should see whether this 220 cm^{-1} is appearing in C_{3V} representation.

As suggested by Nakano *et al* (1992), first ZnSe : P,Ga is tried in this technique. The same force constants as in table 4 are used for the evaluation of defect modes. But here, no group theoretical simplification is carried out as this is involved with C_{3V}. So the full (15 × 15) matrix is used along with the full *dl* matrix to evaluate $|I–gdl|$.

The defect modes are identified from where $|I–gdl|$ goes to zero. When ZnSe : P,Ga is assumed (for C_{3V} symmetry), the LVM is 229 cm^{-1} and when ZnSe : P with JT distortion is assumed, it is 224 cm^{-1} and experimental LVMs are 220 and 375 cm^{-1}.

The localized mode 220 cm^{-1} is again reproduced in this configuration with the allowed degeneracy, whereas 375 cm^{-1} is seen only in T_d symmetry.

These two investigations reveal that both modes could be identified in T_d symmetry and 220 cm^{-1} alone in C_{3V} even though in C_{3V} symmetry, an additive impurity Ga is assumed to occupy one of the Zn site deliberately.

4. Discussion

It is understood from experiments that neutral $[Pse]^0$ centres in ZnSe : P should have T_d symmetry whereas

when JT distortion is encountered then $[Pse]^-$ may have C_{3V} symmetry, as a result of the three-fold degeneracy in T_d surroundings (Watts *et al* 1971) leading to a deep centre. The bond length between P atom and one of the four nearest neighbours Zn atom is increased by 0·05 Å. Nakano *et al* (1992) from this Raman measurements on ZnSe : P,Ga have shown that there is an LVM 220 cm^{-1} appearing in this configuration, which has C_{3V} symmetry. Even though from our calculations both by molecular model and Green's functions for C_{3V} symmetry for ZnSe : P,Ga this mode is observed, this is not the aim.

Kwak *et al* (1994) while studying the LVMs from first principles in ZnSe : P observed that one of the Zn atom will move towards P thereby reducing the symmetry to C_{3V}. Taking this, the LVMs are worked out in the modified configuration of ZnSe : P atom and parameters. It is interesting to see that this 220 cm^{-1} appears here with the required degeneracy.

So, this present investigation predicts that ZnSe : P can have C_{3V} symmetry (to explain the LVM 220 cm^{-1}) provided JT distortion is taken into account. Since P is amphoteric impurity in ZnSe, the other possibility of P substituting Zn site is also considered for the present calculations. It is found out again that the 220 cm^{-1} is appearing in the A_1 representation of C_{3V} symmetry arising due to JT distortion.

In conclusion, it is to be mentioned that ZnSe : P can have C_{3V} where JT distortion is assumed with about ~ 0·2 Å of relaxation of one of the atom towards P.

Further work is going on to see whether an interstitial defect will also have C_{3V} symmetry, by working out the LVMs.

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