International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2013): 6.14 | Impact Factor (2015): 6.391

The Investigation of Representation Symmetry of Free Atoms and their Atomic Energy Level Splittings in the ZnO Crystalline Field

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Abstract: ***Using group theoretical techniques we have investigated the representation symmetry of free dopants (Al, Ga and In) of wurtzite ZnO structure. We have also studied the symmetry of wurtzite ZnO doped with Al, Ga and In. The method allows classification of the state of dopants in the crystalline field. We show that the symmetry of free atoms is the full rotation group (FRG) and that of operators O_R (α, β, γ), where α, β and γ are the Euler angles. The FRG is reduced to the symmetry operators of the point group of ZnO (C_{6v}) when atoms are doped into the ZnO crystalline field. Our theoretical results confirm the available experimental data.***

Keywords: Representation symmetry, irreducible representations, free atoms, crystalline field, splitting

1. Introduction

Symmetry has been used in many ways to assist in and illuminate the study of atomic and molecular phenomena [1]. The symmetry of matter is a powerful framework to perceive and predict the physical world. The structure of materials is described by a combination of rotations, rotation-inversions and translational symmetries. The symmetry of an object is a set of operations, called a symmetry group, which brings the object into self-congruence. The spatial symmetry operations of translation, rotation, and rotation-inversions, give rise to 32 crystallographic point groups and 230 crystallographic space groups [2, 3].

The lattice structure of wurtzite ZnO belongs to the hexagonal system with space group C^4_{6v} [4]. Based on its thermal, electrical and opto-electrical properties, ZnO is a material with enormous device applications. One device with promising commercial potential is a UV light-emitting diode (LED) which could be combined with phosphors to produce solid state lighting [5]. Another is a transparent field effect transistors (FET), which could serve as an active element in large area displays [6]. ZnO with wurtzite structure is naturally an n-type semiconductor because of the deviation from stoichiometry due to the presence of intrinsic defects such as O vacancy and ZnO interstitials [7]. Undoped ZnO shows intrinsic n-type conductivity with very high electron densities of about 10^{21} cm^{-3} [8].

In this paper we have investigated the representation symmetry of free atoms before and after being doped into wurtzite ZnO crystal. Furthermore, we study the effect of the crystalline field on the spectral terms of an atom or ion in the crystal. The studied shallow donors in wurtzite ZnO are Al, Ga and In, The atomic ground states of these elements are: Al (n = 3, $^2P_{\frac{1}{2}}$), Ga (n = 4, $^2P_{\frac{1}{2}}$) and In (n = 5, $^2P_{\frac{1}{2}}$), see Fig. 5.2, p. 87 and Fig. 8.1, p. 115 in Ref. [9]. We have shown that the states of the dopants are doublets (s = $\frac{1}{2}$, 2s +1 = 2) and exhibit anomalous Zeeman splitting. In addition, they become shallow donors to which excitons of symmetries $\Gamma^c_7 \oplus \Gamma^v_7$ (A), $\Gamma^c_7 \oplus \Gamma^v_9$ (B) and $\Gamma^c_7 \oplus \Gamma^v_7$ (C) are bound [10].

2. Symmetry of a Free Atom

The full rotation group (FRG) of a free atom follows from the solution of the Laplace's differential equation [11].

$$\frac{\partial^2\varphi(x,y,z)}{\partial x^2}+\frac{\partial^2\varphi(x,y,z)}{\partial y^2}+\frac{\partial^2\varphi(x,y,z)}{\partial z^2}=0 \quad (1)$$

The resolution of Eq. (1) involves the introduction of polar coordinates in place of x, y and z [12]. The transformation (rotation) which takes the points in a three-dimensional (3D) space from their initial to final positions is described in terms of Euler angles α, β and γ and their attendant operators of FRG O_R (α, β, γ). These are continuous and infinite groups [11]. The basis for the operators O_R (α, β, γ) is the well-known spherical harmonics Y^l_m (θ, ϕ). The representation symmetries of free atoms are obtained from:

$$O_R(\alpha,\beta,\gamma)\,Y^l_m(\theta,\phi)=\sum_{m'} Y_m{}^l\,(\theta,\phi)\,D^l{}_{m',m}(\alpha,\beta,\gamma) \quad (2)$$

Where l-integer is the orbital angular momentum quantum number, m_l = -l, …, +l is the orbital magnetic moment quantum number and $D^l_{m'm}$ (α, β, γ) is the matrix of O_R (α, β, γ) in the representation D^l based on the spherical harmonics of order l when the spin of the electron is not taken into account. Such representation is called single value representation (SVR).

$$D^l_{m'm}(\alpha,\beta,\gamma)= e^{-im'\gamma}\,d^l_{m',m}(0,\beta,0)\,e^{-im\alpha} \quad (3)$$

where the matrix elements of D^l (α, β, γ) are:

$$d^l_{m',m}(0,\beta,0)= \sum_t (-1)^t \frac{\sqrt{(l+m')!(l-m')!(l+m)!(l-m)!}}{(l+m'-t)!(l-m-t)!(t+m-m')!} \times(\cos\frac{\beta}{2})^{2l+m'-m-2t}.(\sin\frac{\beta}{2})^{2t+m-m'} \quad (4)$$

and the summation is taken over all values of t which lead to non-negative factorials. For example given l = 2, for d configuration state of atoms with m, m' = -2, -1, 0, 1, 2, we obtain the reducible representation of the FRG

$D^2_{m',m}(\alpha, \beta, \gamma)=$

$$\begin{pmatrix} A & B & C & D & E \\ F & G & H & I & J \\ K & L & M & N & O \\ P & Q & R & S & T \\ V & W & X & Y & Z \end{pmatrix} \quad (5)$$

where $A = e^{-2i\alpha}\ d^2_{22} e^{-2i\gamma}$ $B = e^{-2i\alpha}\ d^2_{21} e^{i\gamma}$,

$C = e^{-2i\alpha}\ d^2_{2O}$, $D = e^{-2i\alpha}\ d^2_{2\text{-}1} e^{-i\gamma}$,

$E = e^{-2i\alpha}\ d^2_{2\text{-}2} e^{2i\gamma}$ $F = e^{-i\alpha}\ d^2_{12} e^{-2i\gamma}$,

$G = e^{-i\alpha}\ d^2_{11} e^{-i\gamma}$ $H = e^{-i\alpha}\ d^2_{10}$,

$I = e^{-i\alpha}\ d^2_{1\text{-}1} e^{i\gamma}$ $J = e^{-i\alpha}\ d^2_{1\text{-}2} e^{2i\gamma}$

$K = d^2_{02} e^{-2i\gamma}$ $L = d^2_{01} e^{-i\gamma}$

$M = d^2_{00}$ $N = d^2_{0\text{-}1} e^{i\gamma}$

$O = d^2_{0\text{-}2} e^{2i\gamma}$ $P = e^{i\alpha}\ d^2_{\text{-}12} e^{-2i\gamma}$

$Q = e^{i\alpha}\ d^2_{\text{-}11} e^{-i\gamma}$ $R = e^{i\alpha}\ d^2_{\text{-}10}$

$S = e^{-i\alpha}\ d^2_{\text{-}1\text{-}1} e^{i\gamma}$ $T = e^{i\alpha}\ d^2_{\text{-}1\text{-}2} e^{2i\gamma}$

$V = e^{2i\alpha}\ d^2_{\text{-}22} e^{-2i\gamma}$ $W = e^{2i\alpha}\ d^2_{\text{-}21} e^{-i\gamma}$

$X = e^{2i\alpha}\ d^2_{\text{-}20}$ $Y = e^{2i\alpha}\ d^2_{\text{-}2\text{-}1} e^{i\gamma}$

$Z = e^{2i\alpha}\ d^2_{\text{-}2\text{-}2} e^{2i\gamma}$

If $\alpha = \gamma = 0$ (for rotation about one axis), the matrix becomes

$D^2_{m',m}(\beta) =$

$$\begin{pmatrix} d^2_{22} & d^2_{21} & d^2_{20} & d^2_{2-1} & d^2_{2-2} \\ d^2_{12} & d^2_{11} & d^2_{10} & d^2_{1-1} & d^2_{1-2} \\ d^2_{02} & d^2_{01} & d^2_{00} & d^2_{0-1} & d^2_{0-2} \\ d^2_{-12} & d^2_{-11} & d^2_{-10} & d^2_{-1-1} & d^2_{-1-2} \\ d^2_{-22} & d^2_{-21} & d^2_{-20} & d^2_{-2-1} & d^2_{-2-2} \end{pmatrix} \quad (6)$$

where

$$d^2_{22} = d^2_{-2-2} = \cos^4\left(\frac{\beta}{2}\right)$$

$$d^2_{21} = -d^2_{12} = -d^2_{-2-1} = d^2_{-1-2} = \frac{1}{2}\sin[\beta(1+\cos\beta)]$$

$$d^2_{20} = d^2_{02} = d^2_{-20} = d^2_{0\text{-}2} = \sqrt{\frac{3}{8}}\sin^2(\beta)$$

$$d^2_{2-1} = d^2_{1-2} = -d^2_{-21} = -d^2_{-12} = \frac{1}{2}\sin[\beta(\cos\beta - 1)]$$

$$d^2_{2-2} = d^2_{-22} = \sin^4\left(\frac{\beta}{2}\right) \quad (7)$$

$$d^2_{11} = d^2_{-1-1} = \frac{1}{2}[2\cos(\beta) - 1][\cos(\beta) + 1]$$

$$d^2_{1-1} = d^2_{-11} = \frac{1}{2}[2\cos(\beta) + 1][1 - \cos(\beta)]$$

$$d^2_{10} = d^2_{0-1} = -d^2_{01} = -d^2_{-10} = -\sqrt{\frac{3}{2}}\sin(\beta)\cos(\beta)$$

$$d^2_{00} = \frac{1}{2}[3\cos^2(\beta) - 1]$$

If the spin s of an electron is taken into account for double value representations (DVR), the total angular momentum is j-half integer = l + s and the matrix elements of D^j are given by

$$d^j_{m',m}(0,\beta,0) = \sum_t (-1)^t \frac{\sqrt{(j+m)!(j-m)!(j+m')!(j-m')!}}{(j+m-k)!(j-m'-k)!(k+m'-m)!} \quad (8)$$

$$\times \left(\cos\frac{\beta}{2}\right)^{2j-m'+m-2k} \cdot \left(-\sin\frac{\beta}{2}\right)^{2k+m'-m}$$

where the summation is taken over all values of k which lead to non-negative factorials.

For example given $j = \frac{3}{2}$; m, m' $= \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$ we obtain

$$D^{\frac{3}{2}}(0,\beta,0) = \begin{pmatrix} d^{\frac{3}{2}}_{\frac{3}{2}\frac{3}{2}} & d^{\frac{3}{2}}_{\frac{3}{2}\frac{1}{2}} & d^{\frac{3}{2}}_{\frac{3}{2}\frac{-1}{2}} & d^{\frac{3}{2}}_{\frac{3}{2}\frac{-3}{2}} \\ d^{\frac{3}{2}}_{\frac{1}{2}\frac{3}{2}} & d^{\frac{3}{2}}_{\frac{1}{2}\frac{1}{2}} & d^{\frac{3}{2}}_{\frac{1}{2}\frac{-1}{2}} & d^{\frac{3}{2}}_{\frac{1}{2}\frac{-3}{2}} \\ d^{\frac{3}{2}}_{\frac{-1}{2}\frac{3}{2}} & d^{\frac{3}{2}}_{\frac{-1}{2}\frac{1}{2}} & d^{\frac{3}{2}}_{\frac{-1}{2}\frac{-1}{2}} & d^{\frac{3}{2}}_{\frac{-1}{2}\frac{-3}{2}} \\ d^{\frac{3}{2}}_{\frac{-3}{2}\frac{3}{2}} & d^{\frac{3}{2}}_{\frac{-3}{2}\frac{1}{2}} & d^{\frac{3}{2}}_{\frac{-3}{2}\frac{-1}{2}} & d^{\frac{3}{2}}_{\frac{-3}{2}\frac{-3}{2}} \end{pmatrix} \quad (9)$$

where

$$d^{\frac{3}{2}}_{\frac{3}{2}\frac{3}{2}} = d^{\frac{3}{2}}_{\frac{-3}{2}\frac{-3}{2}} = \cos^3\left(\frac{\beta}{2}\right)$$

$$d^{\frac{3}{2}}_{\frac{3}{2}\frac{1}{2}} =$$

$$d^{\frac{3}{2}}_{\frac{-1}{2}\frac{-3}{2}} = -d^{\frac{3}{2}}_{\frac{1}{2}\frac{3}{2}} = -d^{\frac{3}{2}}_{\frac{-3}{2}\frac{-1}{2}} = -\sqrt{3}\cos^2\left(\frac{\beta}{2}\right)\sin\left(\frac{\beta}{2}\right)$$

$$d^{\frac{3}{2}}_{\frac{3}{2}\frac{-1}{2}} = d^{\frac{3}{2}}_{\frac{-1}{2}\frac{3}{2}} = d^{\frac{3}{2}}_{\frac{1}{2}\frac{-3}{2}} = d^{\frac{3}{2}}_{\frac{-3}{2}\frac{1}{2}} = \sqrt{3}\cos(\frac{\beta}{2})\sin(\frac{\beta}{2})$$

$$d^{\frac{3}{2}}_{\frac{3}{2}\frac{-3}{2}} = d^{\frac{3}{2}}_{\frac{-3}{2}\frac{3}{2}} = -\sin^3(\frac{\beta}{2}) \quad (10)$$

$$d^{\frac{3}{2}}_{\frac{1}{2}\frac{1}{2}} = d^{\frac{3}{2}}_{\frac{-1}{2}\frac{-1}{2}} = \cos(\frac{\beta}{2})[3\cos^2(\frac{\beta}{2}-2)]$$

$$d^{\frac{3}{2}}_{\frac{1}{2}\frac{-1}{2}} = -d^{\frac{3}{2}}_{\frac{-1}{2}\frac{3}{2}} = \sin(\frac{\beta}{2})[3\sin^2(\frac{\beta}{2}-2)]$$

Since the character of a rotation depends only on the angle of rotation and not on the direction of the rotation axis, we can find the characters of D^l and D^j using

$$\chi^l(\beta) = \frac{\sin[(l+\frac{1}{2})\beta]}{\sin(\frac{\beta}{2})} \quad (11)$$

for SVR and

$$\chi^j(\beta) = \frac{\sin[(j+\frac{1}{2})\beta]}{\sin(\frac{\beta}{2})} \quad (12)$$

for DVR. Where the angle β is an arbitrary angle of rotation about any direction of the rotation axis. We have considered the symmetry of free atoms and the classification of their states according to reducible D^l and D^j of the FRG.

3. Splitting of atomic energy levels of Al, Ga and In, in the crystalline field of ZnO point group

In order to highlight that the ZnO is naturally doped by Al, Ga and In, we have shown and tabulated six excitonic transition lines $I_{6a,}$ $I_{8,}$ I_9 and I_0, I_1, I_2, where $I_{6a,}$ I_8 and I_9 are neutral exciton complexes bound to Al, Ga and In impurity of ZnO, respectively [10]. These lines are accompanied by higher energetic lines I_2, I_1, and $I_{0.}$ The neutral bound excitonic line I_{6a} was correlated to I_1, I_8 was correlated to I_1 and I_9 was correlated to I_2 (see Fig.1 in Ref. [10]).

When an atom is doped into a crystal, its electron will be perturbed by the crystalline field, i.e., since an electric field is produced at the position of the atom by all other atoms in the crystal, according to many authors [13, 14]. The electric field has the symmetry of one of the crystal point groups. In this case, the energy levels of unperturbed system will be classified according to the representations of the FRG. The level belonging to l-representation will be (2l + 1)-fold degeneracy for SVR and (2j + 1)-fold degeneracy for DVR [15]. For wurtzite ZnO, the crystal point group is C_{6v} [16]. The characters for SVR and DVR are calculated and tabulated in tables 1 and 3 respectively for C_{6v}. Using the Eqs, (11) and (12) we obtain the characters of the rotation groups of the free atoms in D^l and D^j representations (see tables 2 and 4).

Table 1: SVR character table for C_{6v} using CDML labelling [4]

C_{6v}	E	C_6 (3)	C_6^2 (2)	C_6 (2)	σ_v (3)	$\sigma_{v'}$ (3)
Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	-1	-1
Γ_3	1	-1	1	-1	1	-1
Γ_4	1	-1	1	-1	-1	1
Γ_5	2	2	-1	-1	0	0
Γ_6	2	-2	-1	1	0	0

4. Discussions

For the orbital angular momentum l, the spectral terms of an atom are classified according to SVR ($D^l_{m',m}$ (α, β, γ)) of the FRG of the atom; while for the total angular momentum j, the states are classified according to DVR ($D^j_{m',m}$ (α, β, γ)). The D^l and D^j representations are reduced into irreducible representations of C_{6v} by means of the reduction formulas:

$$a_\mu = \frac{1}{g}\sum_\mu g_i \chi_i^l(\beta)\chi_i^{(\mu)}(\beta) \quad (13)$$

$$a_\sigma = \frac{1}{g}\sum_\sigma g_i \chi_i^j(\beta)\chi_i^{(\sigma)}(\beta) \quad (14)$$

For l-integer and j-half integer, respectively. The g and g_i stand for the order of the point group and the number of the symmetry operators in a class, respectively. The χ^l and χ^j stand for the characters of the FRG O_R (α, β, γ); and $\chi\,\mu$ and $\chi\,\sigma$ are characters of a point group of the crystalline field. $\mu \equiv \Gamma_1, \Gamma_2 \ldots \Gamma_6$ and $\sigma \equiv \Gamma_7, \Gamma_8, \Gamma_9$.

The characters $\chi^l(\beta)$ and $\chi^j(\beta)$ are listed in the tables 2 and 4, respectively, with the characters of Γ_i (i = 1, 2, 3,..., 6) and Γ_k (k = 7, 8, 9) tabulated in tables 1 and 3, respectively.

Using the reduction formulas in Eqs. (13) and (14), we determined the Zeeman splittings of the spectral terms of the free atoms and for greater understanding we have shown that if the free atoms are doped into ZnO crystal, then levels split into new terms belonging to the irreducible representations of the crystal point group C_{6v} (see tables 2 and 4 last columns).

Table 2: Characters of classes of C_{6v} in the (2l+1)-dimensional representation D^l and the resolution of D^l into irreducible representation of C_{6v} using CDML labelling [4].

l	E	C_6^3	C_6^2 (2)	C_6 (2)	σ_v (3)	σ_v (3)	Splittings
0	1	1	1	1	1	1	$D^0 = \Gamma_1$
1	3	-1	0	-1	-1	-1	$D^1 = \Gamma_2+\Gamma_5$
2	5	1	-1	1	1	1	$D^2 = \Gamma_1+\Gamma_5+\Gamma_6$
3	7	-1	1	-1	-1	-1	$D^3 = \Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5+\Gamma_6$
4	9	1	0	-2	1	1	$D^4 = \Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5+2\Gamma_6$
5	11	-1	-1	-1	-1	-1	$D^5 = \Gamma_2+\Gamma_3+\Gamma_4+2\Gamma_5+2\Gamma_6$
6	13	1	1	1	1	1	$D^6 = 2\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+2\Gamma_5+2\Gamma_6$

Table 3: DVR character table for the double point group C_{6v} using CDML labelling [4]

			C_6^3	C_6^4	C_6	C_6^2	C_6^5	σ_v (3)	$\sigma_{v'}$ (3)
C_{6v}	E	R	C_6^3 R	C_6^2 R	C_6^5 R	C_6^4 R	C_6 R	σ_v R(3)	$\sigma_{v'}$' R(3)
Γ_7	2	-2	0	1	$\sqrt{3}$	-1	$-\sqrt{3}$	0	0
Γ_8	2	-2	0	1	$-\sqrt{3}$	-1	$\sqrt{3}$	0	0
Γ_9	2	-2	0	-2	0	2	0	0	0

Consider for example l = 2 and $\mu \equiv \Gamma_1, \Gamma_5$ and Γ_6 .

For $\mu \equiv \Gamma_1$:

$$\frac{1}{12}[(5\times1)+(1\times1)+2(-1\times1)+2(1\times1)+3(1\times1)+3(1\times1)]=1$$

For $\mu \equiv \Gamma_5$:

$$\frac{1}{12}[(5\times2)+(1\times2)+2(-1\times-1)+2(1\times-1)+3(1\times0)+3(1\times0)]=1$$

For $\mu \equiv \Gamma_6$:

$$\frac{1}{12}[(5\times2)+(1\times-2)+2(-1\times-1)+2(1\times1)+3(1\times0)+3(1\times1)]=1$$

We conclude that $D^2 = \Gamma_1 + \Gamma_5 + \Gamma_6$. The d-state of free atoms splits into Γ_1, Γ_5 and Γ_6 belonging to SVR of C_{6v} (see the last column, fourth row of Table 2).

Table 4: Characters of C_{6v} in the (2j+1)-dimensional representation and the resolution of D^j into irreducible representations of C_{6v} using CDML labelling [4], where $K_{i;\, i=}$ 1, 2, 3,…, 9 stands for symmetry operators of the double point group C_{6v}.

j	K_1	K_2	K_3	K_4	Splittings
$\frac{1}{2}$	**2**	**-2**	**1**	**0**	$D^{\frac{1}{2}} = \Gamma_7$
$\frac{3}{2}$	**4**	**-4**	**0**	**-1**	$D^{\frac{3}{2}} = \Gamma_7 + \Gamma_9$
$\frac{5}{2}$	**6**	**-6**	**0**	**0**	$D^{\frac{5}{2}} = \Gamma_7 + \Gamma_8 + \Gamma_9$
$\frac{7}{2}$	**8**	**-8**	**0**	**1**	$D^{\frac{7}{2}} = \Gamma_7 + 2\Gamma_8 + \Gamma_9$
$\frac{9}{2}$	**10**	**-10**	**0**	**-1**	$D^{\frac{9}{2}} = \Gamma_7 + 2\Gamma_8 + 2\Gamma_9$
$\frac{11}{2}$	**12**	**-12**	**0**	**0**	$D^{\frac{11}{2}} = 2\Gamma_7 + 2\Gamma_8 + 2\Gamma_9$

Continued. Characters of C_{6v} in the (2j+1)-dimensional representation and the resolution of D^j into irreducible representations of C_{6v} using CDML labelling [4], where $K_{i;\, i=}$ 1, 2, 3… ,9 stands for symmetry operators of the double point group C_{6v}.

j	K_5	K_6	K_7	K_8	K_9	Splittings
$\frac{1}{2}$	$\sqrt{3}$	**-1**	$-\sqrt{3}$	**0**	**0**	$D^{\frac{1}{2}} = \Gamma_7$
$\frac{3}{2}$	$\sqrt{3}$	**1**	$-\sqrt{3}$	**0**	**0**	$D^{\frac{3}{2}} = \Gamma_7 + \Gamma_9$
$\frac{5}{2}$	**0**	**0**	**0**	**0**	**0**	$D^{\frac{5}{2}} = \Gamma_7 + \Gamma_8 + \Gamma_9$
$\frac{7}{2}$	$-\sqrt{3}$	**1**	$\sqrt{3}$	**0**	**0**	$D^{\frac{7}{2}} = \Gamma_7 + 2\Gamma_8 + \Gamma_9$
$\frac{9}{2}$	$-\sqrt{3}$	**1**	$\sqrt{3}$	**0**	**0**	$D^{\frac{9}{2}} = \Gamma_7 + 2\Gamma_8 + 2\Gamma_9$
$\frac{11}{2}$	**0**	**0**	**0**	**0**	**0**	$D^{\frac{11}{2}} = 2\Gamma_7 + 2\Gamma_8 + 2\Gamma_9$

Consider j = $\frac{3}{2}$ and $\sigma \equiv \Gamma_7$ and Γ_9

For $\sigma \equiv \Gamma_7$

$$\frac{1}{24}[(4\times2)+(-4\times-2)+2(0\times0)+2(-1\times1)+2(\sqrt{3}\times\sqrt{3})+2(1\times-1)+2(-\sqrt{3}\times-\sqrt{3})+6(0\times0)+6(0\times0)]=1$$

For $\sigma \equiv \Gamma_9$

$$\frac{1}{24}[(4\times2)+(-4\times-2)+2(0\times0)+2(-1\times-2)+2(\sqrt{3}\times0)+2(1\times2)+2(-\sqrt{3}\times0)+6(0\times0)+6(0\times0)]=1$$

The j = $\frac{3}{2}$ level splits into Γ_7 and Γ_9 symmetries of C_{6v}.

$D\frac{3}{2} = \Gamma_7 + \Gamma_9$ (see the last column, third row of Table 4).

More results regarding the splitting of atomic levels when atoms are doped into ZnO crystal are tabulated in Table 2 and 4.

5. Conclusion

ZnO is naturally n-type semiconductor. The shallow donors Al, Ga and In have been studied. The symmetry of the free atoms is FRG. When these atoms are substitutionally placed to Zn sites of the ZnO crystal point group C_{6v} . Using the characters of C_{6v} and of D^l and D^j in l and j representations, respectively, by means of the reduction formulas in Eqs. (13) and (14), we find the number of times that each irreducible representation of C_{6v} is contained in the l and j representations. Thus we determine how the degenerate level splits in the crystalline field.

6. Acknowledgements

It is a pleasure to acknowledge the very fruitful discussions with Dr Fred J. Nambala for his contributions and support in the preparation of the manuscript.

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