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Chapter 1

Introduction

In this chapter we briefly indicate the present status of vibrational and electronic states of sapphire (Al_2O_3), zinc oxide (ZnO) and related materials. In particular we focus on the need for appropriate theoretical and experimental methods which will lead to better understanding of the mechanical and optical properties of these compounds. The main aim of this dissertation is to study the vibrational and electronic properties of the sapphire substrate for: ZnO, GaN, BeO, 6H-SiC and others. Experimentally, some optical properties of ZnO/Al_2O_3 and GaN/Al_2O_3 have been investigated by means of low temperature photoluminescence (PL) and Raman spectroscopy (RS). Particularly, in order to distinguish the observed multiphonon processes from both materials, it is necessary to study these processes in both ZnO and Al_2O_3 separately.

Phonons are the primary excitations that influence the thermodynamic, electronic and optical properties of semiconductors and insulators. Experimentally the vibrational states can be investigated using Infrared (IR), Inelastic Neutron Scattering (INS), X-ray Scattering and RS yielding the density of states. Thermal neutron beams and X-rays can probe the entire Brillouin zone (BZ). Sapphire (α-Al_2O_3) and zinc oxide (ZnO) are the prototypes of corundum and wurtzite structures, respectively.

Wurtzite ZnO is a promising material for electronic and optoelectronic applications. Varistors, transparent conducting electrodes and surface-acoustic wave devices are conventional applications with polycrystalline material. ZnO of high quality could be used for UV light emitting diodes and laser applications [1, 2].

1.1 Vibrational Properties of Al_2O_3 and ZnO

Sapphire

Aluminium oxides, in their different modifications, are one of the dominant minerals in the earth's crust. Moreover they are widely used in physical and technical applications due to their mechanical and optical properties both in pure (α-Al_2O_3) and doped (Cr^{3+}, e.g. Ruby, Ti^{3+}, V^{3+}, Sc^{+}, Gd^{3+}, etc.) form [3, 4, 5]. The vibrational spectra of sapphire have been extensively studied since the first infrared absorption studies of Coblentz (1908) [6, 7]. Sapphire is a wide band gap indirect insulator with an energy gap $E_g \approxeq 9.3\,\text{eV}$ and high thermal conductivity. Recently the growth of high quality synthetic sapphire has turned it into a preferred substrate for materials such as ZnO, GaN, AlN, InN, CdS, MgTe, BeO, 2H-SiC, 4H-SiC, 6H-SiC, etc. Sapphire is a transparent, hard material with good chemical inertia. It supports most of the thin films in the group-III nitrides and their wurtzite $(GaN)_m(AlN)_n$ superlattices (SL) and heterostructures, e.g. AlGaN operating at high temperatures.

New developments in particle physics, in the search for Dark Matter, have turned sapphire into an excellent cryogenic phonon-scintillator due to its ability to distinguish weak interactions of massive particles and rare interaction signals from those caused by background radiations. Doped with Ti^{3+}, sapphire is used as an X-ray detector for energies in the range $15 - 60\,\text{KeV}$ [8]. Recently the density of state (DOS) of Al_2O_3 was measured by neutron spectroscopy but no appropriate group theoretical assignment of the involved phonons was provided [9]. In addition, the effect of Time Reversal Symmetry (TRS), multiphonon processes, as well as phonon selection rules have not been taken into account. At the present and in general there are no comprehensive group theoretical studies of Al_2O_3. We have therefore derived the so called Lattice Mode Representation (LMR). From the LMR we obtain the total number of first order non-interacting phonon modes and their degeneracy [10]. Moreover, we study the phonon modes with respect to TRS. In addition, we discuss the multiphonon processes in Al_2O_3. The results are compared with available experimental data.

Wurtzite ZnO

Wurtzite ZnO is a direct gap II-VI compound semiconductor. ZnO crystallizes in the hexagonal structure with two formula per unit cell. Each Zn atom is tetrahedrically surrounded by four oxygen atoms and vice versa. This tetrahedral coordination is common for several semiconductors ranging from the group IV elements over III-V compounds to II-VI compounds such as ZnO. The lattice dynamics of ZnO have been studied by several authors [11, 12, 13]. Phonon spectra have been studied by both Raman and infrared techniques. Infrared absorption data have been mostly connected with multiphonon processes, with phonons having wave vectors in the vicinity of the BZ edge [11]. The infrared reflection data yield the infrared active phonons at the zone centre. The multiphonon modes were not well resolved and therefore difficult to interpret. Futhermore, the lack of polarization data on ZnO could not unambigously determine the phonon symmetry [11]. Hewat attemped to map the phonon dispersion curve of ZnO and BeO using electron diffraction [12]. In particular Thomas et al. have measured and calculated dispersion curves with a different model for ZnO [13]. However, the authors did not discuss the effect of Time Reversal Symmetry on some phonons.

1.2 Opto-Electronic Properties of Al_2O_3 and ZnO

Sapphire. Space Group D^6_{3d} ($R\overline{3}c$)

The electronic structure of sapphire is characterized by a conduction band and two well separated valence bands. A variety of theoretical and experimental studies have been undertaken aimed at elucidating the underlying structure and electronic properties, absorption, luminescence, intrinsic and extrinsic excitations [14].

Studies have concentrated on spectral measurements in order to derive the broad features of the electronic structures from the results of several optical absorption spectroscopy such as x-ray emission, x-ray photoemission spectroscopy (XPS) and electron energy loss (EELS) spectroscopy [14]. At the present there is no theoretical work providing consistent interpretation of the spectra. It is well accepted that the valence band is grouped into two bands, but there is consensus about the widths of these bands

$(8.4 - 9.6\,\mathrm{eV})$. In particular, the low energy structures in the excitations spectra have prevented an unambiguous determination of the fundamental band [14]. We make an attempt to interpret some of the excitation spectra of complex irreducible representations (irrps); according to those the spectral energy levels of Al_2O_3 are classified.

Wurtzite ZnO. Space Group C_{6v}^4 ($P6_3mc$)

ZnO is a direct wide band gap semiconductor that crystallizes in a hexagonal structure. The energy band gap $E_g = 3.37\,\mathrm{eV}$ at room temperature and $3.5\,\mathrm{eV}$ at a very low temperature. Wide band gap semiconductors such as ZnO and GaN, etc. have received considerable attention owing to their optoelectronics properties [15]. Optical experiments near the fundamental absorption edge may be a useful tool for studying band parameters in semiconductors and insulating crystals. It has been pointed out that the shape of the absorption edge could provide information about the band symmetries in anisotropic crystal like ZnO. The line structure which can be associated with direct transition is present in the absorption or reflection edge spectrum [16]. ZnO has a strong near-band-edge excitonic absorption spectrum even at room temperature. At low temperature, luminescence of the ZnO near the band gap is dominated by several narrow lines due to the recombination of excitons bound to native impurities or structural defects [15, 17]. Recent magneto-luminescence measurement at low temperature ($T = 1.5\,\mathrm{K}$) and moderate magnetic field ($5\,\mathrm{Tesla}$) in doped ZnO shows several splittings of energy levels at the edge of the conduction band compared to the zero magnetic field. The split off energy levels are tentatively ascribed to exciton complexes bound to impurities involving TRS [18]. To the best of our knowledge there is no group theoretical model for interpretation of the splittings by taking into account the effect of TRS on electronic states in ZnO [20].

The aim of this thesis is to investigate by means of group theoretical and experimental methods the vibrational and electronic states in sapphire and ZnO throughout the entire BZ, in the absence and presence of TRS.

Chapter 2

Symmetry Aspects

In the forthcoming section we first briefly recall the necessary space group theory relevant to sapphire and wurtzite (their representations and characters). We also discuss the Frobenius-Schur criterion [21] on real and complex irreducible representations (irrps). Particularly, we discuss the Lattice Mode Representation (LMR) theory and apply it to Al_2O_3. Decomposing the reducible LMR onto irrps species throughout the entire BZ, we obtain the total number of symmetry allowed modes and their degeneracy. It is well known that the states of quasi-particles in crystals such as electrons in the conduction band, holes in the valence band, excitons, phonons, plasmons, polaritons, etc., in short "ons" are classified according to the irreducible representations of a space group . Here the wave vector runs over the entire BZ and denotes the three quantum numbers k_x, k_y, k_z [20].

2.1 Space Groups: Irreducible Representations and their Characters

It is well known that the states of quasiparticles in crystals such as electrons in the conduction band, holes in the valence band, excitons, phonons, plasmons, polaritons, etc. in shot "ons" are classified according to the irrps of a space group of a crystal. We use the irrps and their characters for the determination of optical selection rules in electronic transitions, as well as in multiphonon processes. Consequentely in the next

sections we provide the necessary group theoretical methods for TRS aspects, LMR and Optical Selection Rules (OpSRs).

The theory of 230 space group and their irrps and characters as well as Kronecker Products (KPs) together with Wave Vector Selection Rules (WVSRs) can be found in Miller and Love [22] and Cracknell, Davis, Miller and Love [23] hereafter referred to as ML and CDML tables, respectively.

2.1.1 Sapphire Al_2O_3 Structure

Sapphire can be considered as a slightly distorted arrangement of hexagonal closed packed oxygen ions with aluminium ions occupying 2/3 of the octahedral interstitial sites [24]. The space group is $D^6_{3d} - (R\bar{3}c)$, No.167 in CDML-tables [23], belonging to the trigonal system. The primitive cell is rhombohedral containing two formula units. Each unit has three oxygen and two aluminium atoms. The generators (augmenters) of small irrps and their characters for Al_2O_3 are given in CDML tables.[23]

2.1.2 Wurtzite: ZnO Structure

Wurtzite ZnO and related materials (i.e. GaN) belong to the space group $C^4_{6v} - (P6_3mc)$ with four atoms in the unit cell. The primitive cell is hexagonal [20]. The factor group for wurtzite at $\boldsymbol{k} = 0$ contains twelve symmetry operators distributed among six classes.

Using the CDML-tables [23] we group the single (SV) and double valued (DV) irrps for different $\boldsymbol{k}$ in the entire BZ.

2.2 Time Reversal Symmetry

The phonons are classified according to single valued representation (SV). The state of electrons, holes, particles with half-interger spin are classified according to the double valued representation (DV). The inclusion of spin results in spinor representations those are complex (due to the Pauli spin operators). When an irrp is complex, an extra degeneracy may occur. In such, a quantum state of "ons" are classified according to the "joint" reps $D \oplus D^*$ [22, 23]. This will affect many phenomena. For example, it will

increase the dimension of the dynamical matrices. It also will change the selection rules for optical transitions. It increases twice the degeneracy of states. It will also influence the scattering tensors and other processes taking place in crystals involving Kronecker Products of irrps. It is therefore of importance to find out which irrps of a group are complex before an analysis of experimental data is undertaken [20].

2.2.1 Criteria for Real and Complex Irreducible Representation. Point Groups

Frobenius and Schur [21] showed that it is suficient to know only the characters of an irrp to determine whether the irrp is real or complex. If the sum of characters of squares of the group elements is equal to the order of the group $|G|$, then the irrps are real: if the sum is $-|G|$ the rep is equivalent to its conjugate: and if the sum vanishes the reps D and D^* are inequivalent. For single valued and double valued (spin included) irrps of 32 crystallographic point groups we write [22]:

$$\frac{1}{|G(\boldsymbol{k})|}\sum_{\phi\subset G(k)}\chi(\{\phi^2|0\}) = \begin{cases} 1 & \text{case (a)} \\ 0 & \text{case (b)} \\ -1 & \text{case (c)}\,. \end{cases} \tag{2.1}$$

In terms of basis functions Ψ of D and Ψ^* of D^* for case (a) the Ψ and Ψ^* are linearly dependent and no extra degeneracy occurs, while for case (b) and (c), Ψ and Ψ^* are linearly independent and the states are classified according to the "joint" irrps $D \oplus D^*$ and extra degeneracy occurs.

2.2.2 Criteria for Real and Complex Irreducible Representation. Space Groups

The basis of irrps of space groups are Bloch functions $\Psi_{\boldsymbol{k}}(r) = u(\boldsymbol{r})\exp(i\boldsymbol{k}\cdot\boldsymbol{r})$, where $\boldsymbol{k}$ runs over the entire first BZ and the $\boldsymbol{\tau}$ are translations. When spin is included the TR operator is just a complex conjugation action on the function. Clearly the TR operator transforms $\boldsymbol{k}$ into $-\boldsymbol{k}$. The $\boldsymbol{k}$ is the first wave vector of the star $\{^*\boldsymbol{k}\}$. The total space

group G contains all groups of all members of the star and can be decomposed onto cosets in terms of the first wave vector of a space group $G(\boldsymbol{k})$:

$$G = G(\boldsymbol{k}) + \{\varphi_2|\boldsymbol{\tau}_2\}G(\boldsymbol{k}) + \{\varphi_3|\boldsymbol{\tau}_3\}G(\boldsymbol{k}) + \cdots + \{\varphi_\sigma|\tau\}G(\boldsymbol{k}).$$

The subscript σ is reserved for the coset representatives $\{\varphi_\sigma|\boldsymbol{\tau}_\sigma\}$. And the members of a star are obtained by symmetry operators φ of the point group $G(\boldsymbol{k}_0)$. The star of the first wave vector in the fundamental domain of a BZ is $\{^*\boldsymbol{k}\} = \{\boldsymbol{k}_1 = \varphi_1\boldsymbol{k}, \boldsymbol{k}_2 = \varphi_2\boldsymbol{k}, \boldsymbol{k}_3 = \varphi_3\boldsymbol{k}, \ldots, \boldsymbol{k}_s = \varphi_s\boldsymbol{k}\}$. Evaluation of the characters of the squared operators yields:

$$\begin{aligned}\chi(\{\varphi|\boldsymbol{\tau}_\varphi\}^2) &= \chi(\{\varphi^2|\varphi\boldsymbol{\tau}_\varphi + \boldsymbol{\tau}_\varphi\}) = \chi(\{\varphi^2|\boldsymbol{\tau}'_\varphi + \varphi\boldsymbol{\tau}_\varphi + \boldsymbol{\tau}_\varphi - \boldsymbol{\tau}'_\varphi\} \\ &= \chi(\{E|\tau_0\})\chi(\{\varphi^2|\boldsymbol{\tau}_0\})\end{aligned} \tag{2.2}$$

$$\chi(\{\varphi|\boldsymbol{\tau}_\varphi\}^2) = \exp(i\boldsymbol{k}\cdot\boldsymbol{\tau}_0)\chi(\{\varphi^2|\boldsymbol{\tau}_0\}), \tag{2.3}$$

where in the equation (2.3) the translation vector $\boldsymbol{\tau}_0 \equiv \boldsymbol{\tau}_\varphi + \phi\boldsymbol{\tau}_\varphi - \boldsymbol{\tau}'_\varphi$ has to be calculated and $\boldsymbol{\tau}'_\varphi$ is a non-primitive translation vector and is associated with the symmetry element $\phi^2 \subset G(\boldsymbol{k})$ [25, 26]. The criterion for real and complex irrps of space groups becomes:

$$\frac{|G|}{|G(\boldsymbol{k})|}\sum_{\varphi\subset G(\boldsymbol{k})}\exp(i\boldsymbol{k}\cdot\boldsymbol{\tau}_0)\chi(\{\varphi^2|\boldsymbol{\tau}'_\varphi\})\delta_{\boldsymbol{k},-\varphi\boldsymbol{k}} = \begin{cases} 1 & \text{case (a)} \\ 0 & \text{case (b)} \\ -1 & \text{case (c)}\,. \end{cases} \tag{2.4}$$

For $\boldsymbol{\tau}_0 = 0$, the criterion for real and complex representations is given by the Frobenius-Schur theorem [21]. A comprehensive discussion of TRS for space groups that takes into account the equivalence of the wave vector $\boldsymbol{k}$ (whether or not the wave vector $\boldsymbol{k}$ is taken into $-\boldsymbol{k}$ in the Brillouin zone) can be found in [10, 27, 28]. Up to now we have considered only single valued reps of space groups (spin excluded). The inclusion of spin leads to double valued reps. The criterion (equations 2.1,2.4) is also valid for spinors. In general in order to perform a calculation using equation (2.4) we must consider a system with (i) integral and (ii) half-odd-integral spin. A combination of the three cases (a), (b), and (c) with (i) and (ii) results in additional six possibilities

which can be expressed as follows:

- No extra degeneracy in case (a)(i) and (c)(ii).
- Doublet degeneracy in cases (b)(i), (b)(ii), (a)(ii) and (c)(i).

For spinor representations we also have cases (a), (b) and (c) but with different interpretation. In case (a) the spinor representation must have even dimensions and the one dimensional irrps must then belong to case (c). Case (b) is more complicated and a complete analysis is given in Ref. [28]. All other spinor irrps with real character belong to case (a). Using this theorem we have found several phonons to be TRS influenced.

The presence of TRS in crystals results in modified classification of states ("ons"), phonon dynamical matrices, energy bands, optical selection rules, and others. In the table we list the complete of matrix representations and their characters for the D_{3d}^6 and C_{6v}^4 space groups.

2.2.3 Sapphire Al_2O_3. Irreducible Representations Under Time Reversal Symmetry

For trigonal BZ the high symmetry points are Γ, T, P, F, Y, L and lines Λ, Σ. At the highest symmetry point Γ, $\boldsymbol{k} \approxeq 0$, we have the irrps $\Gamma_{1\pm,2\pm,3\pm}$ case (a), $\Gamma_{4\pm,5\pm}$ case (b) and $\Gamma_{6\pm}$ case (c), and $\boldsymbol{k} \neq 0$, the equation (2.1) must be taken into consideration for each symmetry point and line. Using equation (2.4) and CDML tables we have tested all reps of the high symmetry points and lines of sapphire. The results are:

case (a) $\Gamma_{1\pm,2\pm,3\pm}$; L_1, $F_{1\pm,2\pm}$, $Y_{1,2}$, $\Sigma_{1,2}$

case (b) $\Gamma_{4\pm,5\pm}$; $T_{1,2,3}$, $F_{3\pm}$, Y_3, $\Lambda_{1,2,4,5,6}$, $\Sigma_{3,4}$

case (c) $\Gamma_{6\pm}$; Λ_3; $T_{4,5,6}$, $F_{4\pm}$, Y_4, L_2

In case (a) no extra degeneracy arises. For cases (b) and (c) the degeneracy of the states increases twice. Consequently the states of sapphire (phonons, excitons, etc.) TRS influenced will now be classified according to irrps $\Gamma_{4\pm} \oplus \Gamma_{4\pm}^*$, $\Gamma_{5\pm} \oplus \Gamma_{5\pm}^*$, $T_1 \oplus T_1^*, \ldots$, $\Sigma_4 \oplus \Sigma_4^*, \ldots, L_2 \oplus L_2^*$. We found 17$\Lambda$, 17$T$ and 17P phonon states which are TR

influenced [29]. These modes are classified according to: $\Lambda_1(1) \oplus \Lambda_1^*(1)$, $\Lambda_2(1) \oplus \Lambda_2^*(1)$, $\Lambda_3(2) \oplus \Lambda_3^*(2)$; $T_1(1) \oplus T_1^*(1)$, $T_2(1) \oplus T_2^*(1)$, $T_3(2) \oplus T_3^*(2)$; $P_1(1) \oplus P_1^*(1)$, $P_2(1) \oplus P_2^*(1)$, $P_3(2) \oplus P_3^*(2)$. These phonons are classified by "joint rep". Comprehensive tables in Appendix Table A.17 list all Al_2O_3 irrps according to case (a), (b), or (c). The Appendix A.8.1 table lists a classification of wave vectors according to equivalence of the wave vector for Al_2O_3.

2.2.4 Wurtzite ZnO. Irreducible Representation Under Time Reversal Symmetry

Similarly for ZnO [20] we have:

case (a) Γ_j $(j = 1-6)$, $M_{1,2,3,4}$, $K_{1,2,3}$, $\Sigma_{1,2}$, $T_{1,2}$, H_3. Real reps. No extra degeneracy.

case (b) A_i $(i = 1-6)$, Δ_i $(i = 1-6)$, $H_{1,2}$, $L_{1,2,3,4}$, $U_{1,2,3,4}$, $P_{1,2,3}$ $S_{1,2}$. Complex reps.

case (c) $R_{1,2}$, $\Gamma_{7,8,9}$. Complex reps.

For other high symmetry points and lines ($\boldsymbol{k} \neq 0$) we list the result of the equivalence test among the wave vectors $\boldsymbol{k}'$s in the table in the Appendix A.8.1.

In this chapter we obtained the necessary group theoretical results needed for the analysis of optical selection rules. In the next section we outline the derivation of the Lattice Mode Representation.

2.3 Lattice Mode Representationfor Al_2O_3

In this section we derive the LMR. Our aim is to obtain the total number of the first order non-interacting modes, their symmetry and degeneracy. To this end we introduce a basis consisting of displacments and (stretch and bending) bond length angles between atoms in the unit cell. Imposing symmetry operations onto the basis, we generate the matrices of LMR. Using the multipication table Table A.1 and generator matrices we obtain the characters of the LMR. The first explicit derivation of a LMR of a full set of reducible matrices has been performed for GaN, which belongs to space group C_{6v}^4/T [20].

2.3.1 Sapphire

The primitive cell of Al_2O_3 is rhombohedral, containing two formula units. Each unit contains three oxgygen and two aluminium atoms. Taking the two unit formula in the primitive cell we obtain ten atoms with three degrees of freedom each, which yields thirty phonon modes for sapphire. In here, we define the 27-basis vector consisting of three (3) displacements and twenty four (24) angles for the reducible LMR as shown in the Figure (see Appendix B-1, page 86). Acting on the basis vector by symmetry operators we obtain the LMR. It is sufficient to generate three 27×27-matrices using the three augmenters (generators) C_3^+ (3), $\{C_{21}''/\tau\}$ (7.1) and $\{\sigma_{v1}|\tau\}$ (19.1). The angle between x-axis and y-axis is 60°. The z-axis is perpendicular to both x- and y-axes. The operator $\{\sigma_{v1}|\tau\}$ (19.1) vertical mirror, is placed along the y-axis and perpendicular to the axis of the symmetry operator $\{C_{21}''|\tau\}$ (7.1), whose axis is contained in the oxygen basal planes [29]. Proceeding in a similar manner, or using the multiplication tables for corundum, we obtain all the other nine matrices of LMR for sapphire. The characters of the LMR together with the character of irrps ($\boldsymbol{k} = 0$) of Al_2O_3 are given in the Table A.4. The first extended structure for corundum shows aluminium atoms at non equidistant sites from the oxygen planes at inequivalent sites [24]. The operator C_3^+ transform the basis vector into a vector:

$$\left[d_2\, d_3\, d_1\, \alpha_2\, \alpha_3\, \alpha_1\, \beta_2\, \beta_3\, \beta_1\, \beta_5\, \beta_6\, \beta_4\, \delta_2\, \delta_1\, \delta_3\, \alpha_2'\, \alpha_3'\, \alpha_1'\, \beta_2'\, \beta_3'\, \beta_1'\, \beta_6'\, \beta_5'\, \beta_4'\, \delta_2'\, \delta_3'\, \delta_1'\right]$$

That is

$$C_3^+ \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} = \left[d_2\, d_3\, d_1\, , \ldots ,\, \delta_2'\, \delta_3'\, \delta_1'\right] , \qquad \text{with a sub-matrix} \quad A_i = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \quad i = 1, \ldots, 9.$$

The $\widehat{A}$ is a block diagonal matrix acting upon the basis vector of sapphire to yield

$$\widehat{A} = \begin{bmatrix} A_1 & \cdots & \cdots \\ & \ddots & \\ \cdots & \cdots & A_9 \end{bmatrix}$$

$$\{C_3^+|0\} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} = \widehat{A} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} ; \quad \{C_{21}'|\tau\} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} = \widehat{B} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} ; \quad \{\sigma_{v1}|\tau\} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} \widehat{C} \begin{bmatrix} d_1 \\ d_2 \\ d_3 \\ \vdots \\ \vdots \\ \delta_1' \\ \delta_2' \\ \delta_3' \end{bmatrix} .$$

Decomposing the LMR onto irrps listed in , we obtain the total number of first non-interacting modes, their symmetries (irrps) and degeneracy in the BZ. From the reduction formula:

$$a_\mu = \frac{1}{\|g\|} \sum_\mu \chi^{LMR}(\{g|\tau\}) \chi^*(\{g|\tau\}) \tag{2.5}$$

where μ runs over irrps $\Gamma_{1\pm}$, $\Gamma_{2\pm}$, $\Gamma_{3\pm}$, $\boldsymbol{k} = 0$ and $F_{1\pm,2\pm}$, $\Sigma_{1,2}$, $Y_{1,2}$, L_1 for k $\neq 0$, we obtain the symmetry allowed normal modes spanned by LMR. The characters of F, Σ, Y and L can be found in Ref. [23].

The normal and real modes obtained by decomposition of LMR onto irrps are:

Γ : $2\Gamma_{1+} \oplus 2\Gamma_{1-} \oplus 3\Gamma_{2+} \oplus 2\Gamma_{2-} \oplus 5\Gamma_{3+} \oplus 4\Gamma_{3-}$

F : $7F_{1A+} \oplus 8F_{2A+} \oplus 6F_{1A-} \oplus 6F_{2A-}$

Σ : $13\Sigma_1 \oplus 14\Sigma_2$

Y : $13Y_1 \oplus 14Y_2$

L : $27L_1$

Due to the fact that our basis is real (displacement and angles) we obtain total number of non-interacting real modes (i.e. real irrps not TRS influenced). However, the task remains to investigate all the irrps of sapphire and find out which of those are complex. In other words, we have to investigate the phonons (irrps) in sapphire that are TRS influenced. Using the Frobenius-Schur criterion, equation (2.4), we have found $\Lambda_{1,2,3}$, $T_{1,2,3}$ and $P_{1,2,3}$ irrps to be TRS influenced. These phonon states are classified according to $\Lambda \oplus \Lambda^*$, $T \oplus T^*$ and $P \oplus P^*$rep respectively. Consequently the degeneracy doubles. In the Appendix we explicitly provide the form of the LMR matrices for sapphire and their characters ($\boldsymbol{k} = 0$) in A.5 (page 52).

2.4 Connectivity Relations

From the LMR we have obtained eighteen symmetry allowed modes, not TRS affected at $\boldsymbol{k} = 0$. These are:

$$\Gamma_{vib}^{crystal} = 2\Gamma_{1+} \oplus 2\Gamma_{1-} \oplus 3\Gamma_{2+} \oplus 2\Gamma_{2-} \oplus 5\Gamma_{3+} \oplus 4\Gamma_{3-}$$

To determine all other symmetry allowed modes originating from the entire BZ we use the connectivity relations between high symmetry points and lines in BZ in the first domains in the Appendix (see Figure B-2 for reference). Splitting of states at high symmetry points and lines usually takes place by lowering of symmetry. When going from point Γ along the lower symmetry axis and points the splitting of phonons dispersion curves must occur. This effect is well known and was frequently observed experimentally in many semiconductors, mostly by Inelastic Neutron and X-ray scattering. Group theory predicts the exact kind of splitting by means of compatibility relations. In the Appendix we analyze and list the connectivity relations for modes subjected to TRS. To the best of our knowledge compatibility relations for TRS influenced phonon dispersion curves have never been taken into account.

2.5 Spinor Representation

In the we discussed the opto-electronics of sapphire and ZnO which involve the electron and hole symmetry. The inclusion of spin results in DV irrps. The spectra of ZnO on sapphire substrate exhibits several high excitonic lines near the band gap region. Frequently the laser beam reaches the sapphire substrate and therefore we may observe deep level impurities and defects of Al_2O_3. In order to distinguish the spectral lines from Al_2O_3 and optical transitions from ZnO, we focus on excitons symmetry due to TRS.

2.5.1 Spinors. Double Valued Spin Irreducible Representation

Owing to large energy gap of sapphire $E_g = 9.3\,\text{eV}$ the formation of excitons in sapphire is rather unlikely and consequently the excitonic transitions will not be discussed. An exciton (electron-hole bounded complex) symmetry results in KP of electron and hole symmetries. In ZnO we have three free main excitons: A. $\Gamma_7^{CB} \otimes \Gamma_9^{VB}$, B. $\Gamma_7^{CB} \otimes \Gamma_8^{VB}$ and C. $\Gamma_7^{CB} \otimes \Gamma_9^{VB}$. There are a number of bound excitons to neutral and ionized donors and acceptors. It is clear that due to the presence of TRS the electrons in the CB and holes in VB should be classified according to the joint irrps as follows: $\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*$, $\Gamma_7^{VB} \oplus (\Gamma_7^{VB})^*$, $\Gamma_8^{VB} \oplus (\Gamma_8^{VB})^*$, $\Gamma_9^{VB} \oplus (\Gamma_9^{VB})^*$ and therefore the corresponding exciton symmetries are: A, $(\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*) \otimes (\Gamma_7^{VB} \oplus (\Gamma_7^{VB})^*)$; B, $(\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*) \otimes (\Gamma_8^{VB} \oplus (\Gamma_8^{VB})^*)$ and C, $(\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*) \otimes (\Gamma_9^{VB} \oplus (\Gamma_9^{VB})^*)$. In the following section we analyze the effect on TRS on exciton symmetries and interpret the available experimental data.

2.5.2 Excitonic States in ZnO

In this section we briefly provide the necessary group theoretical tools to enable the discussion of excitonic excitations in ZnO and related materials. The spinor representations for ZnO are Γ_7, Γ_8 and Γ_9. Due to TRS the states of electrons in the conduction band and holes in the valence band are classified according to $\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*, \ldots, \Gamma_9^{VB} \oplus (\Gamma_9^{VB})^*$ rep. The irrp's Γ_7, Γ_8 and Γ_9 belong to case (c) and consequently an extra degeneracy is introduced. The wurzite exciton is made up of s-like state $\Gamma_1^{CB} \otimes D_{1/2} = \Gamma_7^{CB}$ in CB and three p-like hole (p_x, p_y, p_z) orbitals which transform according to the vector rep $(\Gamma_1^{VB}(z) \oplus \Gamma_5^{VB}(x,y)) \otimes D_{1/2} = \Gamma_1^{VB}(z) \otimes D_{1/2} \oplus \Gamma_5^{VB}(x,y) \otimes D_{1/2} = \Gamma_7^{VB} \oplus \Gamma_7^{VB} \oplus \Gamma_9^{VB}$

for hole states in VB. The symmetry of excitons are: $(\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*) \otimes (\Gamma_9^{VB} \oplus (\Gamma_9^{VB})^*)$ and $(\Gamma_7^{CB} \oplus (\Gamma_7^{CB})^*) \otimes (\Gamma_7^{VB} \oplus (\Gamma_7^{VB})^*)$, abbreviated as $7-9$ exciton and $7-7$ exciton respectively. Decomposition of the $7-9$ and $7-7$ excitons onto irrps gives $4\Gamma_1 \oplus 4\Gamma_2 \oplus 4\Gamma_5$ and $4\Gamma_5 \oplus 4\Gamma_6$ respectively [18].

Chapter 3

Multiphonon Processes. Selection Rules

As mentioned the number of modes and thier symmetry (degeneracy) of primary non-interacting phonons follows from the LMR, listed in, section 2.3 (subsection 2.3.1). In this section we investigate the multiphonon processes in Al_2O_3 and ZnO. Higher processes arise from the mutual interaction between first order phonons. The phonon scattering processes are permitted via deformation potential together with Fröhlich interaction [30]. The selection rules for multiphonon processes and the phonon replicas replicas measured by PL are obtained from KP's governed by WVSRs. The frequencies of phonons can be measured by means of infrared absorption, X-ray, Raman, neutron scattering, and PL.

3.1 First Order Modes in Sapphire and ZnO

Decomposing the LMR onto irrps species originating from the entire BZ we obtain the first order non-interacting modes (1OrMs), their symmetries and degeneracy.

For Sapphire at $\boldsymbol{k} \approxeq 0$ they are:

$$\Gamma \quad : \quad 2\Gamma_{1+}(A_{1g}) \oplus 2\Gamma_{1-}(A_{2u}) \oplus 3\Gamma_{2+}(A_{2g}) \oplus 2\Gamma_{2-}(A_{2u}) \oplus 5\Gamma_{3+}(E_g) \oplus 4\Gamma_{3-}(E_u).$$

and for 1OrMs at $\boldsymbol{k} \neq 0$, we have:

$$F \quad : \quad 7F_{1A+} \oplus 8F_{2A+} \oplus 6F_{1A-} \oplus 6F_{2A-}$$

Σ : $13\Sigma_1 \oplus 14\Sigma_2$

Y : $13Y_1 \oplus 14Y_2$

L : $27L_1$

From the Frobenius-Schur criterion we obtain the following TRS degenerate modes:

P : P_1, P_2, P_3

T : T_1, T_2, T_3

Λ : $\Lambda_1, \Lambda_2, \Lambda_3$

Thus it is clear that the above phonon states are classified according to:

$P_i \oplus P_i^*$, $T_i \oplus T_i^*$ and $\Lambda_i \oplus \Lambda_i^*$ with $i = 1, 2, 3$ irrps.

For wurtzite ZnO, we have:

At $\boldsymbol{k} \approxeq 0$,

$\Gamma = 2\Gamma_1 \oplus 2\Gamma_4 \oplus 2\Gamma_5 \oplus 2\Gamma_6$

In ZnO none of the phonons (SV rep) are TRS affected at $\boldsymbol{k} = 0$.

The irrps at $\boldsymbol{k} \neq 0$ are:

A : $2A_1 \oplus 2A_4 \oplus 2A_5 \oplus 2A_6$

Δ : $2\Delta_1 \oplus 2\Delta_2 \oplus 2\Delta_5 \oplus 2\Delta_6$

H : $2H_1 \oplus 2H_2 \oplus 4H_3$

P : $2P_1 \oplus 2P_2 \oplus 4P_3$

K : $2K_1 \oplus 2K_2 \oplus 4K_3$

L : $4L_1 \oplus 2L_2 \oplus 2L_3$

M : $4M_1 \oplus 2M_2 \oplus 2M_3 \oplus 4M_4$

U : $4U_1 \oplus 2U_2 \oplus 2U_3 \oplus 4U_4$

R : $8R_1 \oplus 4R_2$

$$\Sigma \ : \ 8\Sigma_1 \oplus 4\Sigma_2$$

$$Q \ : \ 6Q_1 \oplus 6Q_2$$

$$S \ : \ 6S_1 \oplus 6S_2$$

$$\Lambda \ : \ 6\Lambda_1 \oplus 6\Lambda_2$$

$$T \ : \ 6T_1 \oplus 6T_2$$

See the Table 1. in Reference, [20, 32, 33].

From the Frobenius-Schur criterion we obtain TRS degenerate modes:

A_1, A_4, A_5, A_6

$\Delta_1, \Delta_4, \Delta_5, \Delta_6$

The above modes are classified according to $A_i \oplus A_i^*$ and $\Delta_i \oplus \Delta_i^*$ rep $(i = 1, 4, 5, 6)$ with $A_1 \equiv A_4^*$, $A_5 \equiv A_6^*$, $\Delta_1 \equiv \Delta_4^*$ and $\Delta_5 \equiv \Delta_6^*$ joint irrps.

In order to study the Multiphonon Processes (MPh.Ps) we must distinguish interactions between phonons with equal and different quantum momenta ($\hbar\boldsymbol{k}$).

The Raman scattering tensor is related to the KP of the vector representation $[V]$. Since the Raman tensor is symmetric, first oder Raman Active Modes (1RAM) species are contained in the Symmetrized Square SSQ $[V]_2$, of the V, representation [20]. In other words, decomposing the $[V]_2$ onto irrps of a space group we obtain 1RAM.

3.1.1 First Order Raman Processes.

As stated, the Raman allowed modes are contained in the symmetrized part of the KP of the V rep:

$$V \otimes V = [V \otimes V]_{\text{Sym}} \oplus \{V \otimes V\}_{\text{Ant}}$$

where the indexes "Sym" and "Ant" stand for symmetrized and antisymmetrized parts, respectively.

Al_2O_3

For Al_2O_3 (sapphire) we have the vector representation:

$$V = A_{2u}(\Gamma_{2-}) \oplus E_u(\Gamma_{3-}),$$

thus the symmetrized square of vector representation (SQV) yields the following:

$$[V]_{(2)} = [\Gamma_{2-}(A_{2u}) \oplus \Gamma_{3-}(E_u)]_{(2)} = 2\Gamma_{1+}(A_{1g}) \oplus 2\Gamma_{3+}(E_g) \quad (1\text{RAM's})$$

In the LMR we find the following 1RAM $2\Gamma_{1+}(A_{1g})$ and $5\Gamma_{3+}(E_g)$:

For wurtzite ZnO, we have:

$$V = \Gamma_1(A_1) \oplus \Gamma_6(E_2)$$

And therefore

$$[V]_{(2)} = [(\Gamma_1(A_1) \oplus \Gamma_6(E_2))]_{(2)} = 2\Gamma_1(A_1) \oplus \Gamma_5(E_1) \oplus \Gamma_6(E_2) \ (1\text{RAM's})$$

Similarly for ZnO we obtain six 1RAM spanned by the decomposition onto irrps of LMR. Clearly, we deal with six Raman modes at Γ.

$$\Gamma \ : \quad 2\Gamma_1(A_1(\text{LO},\text{TO})) \oplus 2\Gamma_5(E_1(\text{LO},\text{TO})) \oplus 2\Gamma_6(E_2(\text{high},\text{low}))$$

For irrps excluding the $\Gamma-$point, $k \neq 0$.

For Sapphire:

The LMR decomposition onto real irrps yields the following real non interacting modes [29]:

$F \quad 7F_{1+} \oplus 8F_{2+} \oplus 6F_{1-} \oplus 6F_{2-}$

$\Sigma \quad 13\Sigma_1 \oplus 14\Sigma_2$

$Y \quad 13Y_1 \oplus 14Y_2$

$L \quad 27L_1$

3.2 Second Order Raman Processes

Overtones

The SQ of the real modes through the BZ, excluding the zone centre, are symmetry allowed if they contain any of the 1RAM :

$[F_{1\pm,2\pm}]_{(2)} = 2\Gamma_{1+} \oplus 2\Gamma_{3+}$ or $2F_{1\pm}$.
$[L_1]_{(2)} = \Gamma_{1+} \oplus \Gamma_{3+} \oplus F_{1+}$ or F_{2+}
$[\Sigma_{1,2}]_{(2)} = \Gamma_{3+}$ or Σ_1
$[Y_{1,2}]_{(2)} = \Gamma_{3+}$ or Σ_1

Any of the above overtones are symmetry allowed, for they contain $\Gamma_{3+}(E_g)$. Interaction of two phonons (for example F_{1+}) may lead to a creation of a phonon with $\boldsymbol{k} \approxeq 0$ measureable by RS. The allowed Γ symmetry are contained in SQ of the irrps of high symmetry.

Combinations.

The interaction of two different symmetries at the same high symmetry point may result in phonon with low or high momentum.
The KP of different irrps at $\boldsymbol{k} \neq 0$ may contain 1RAM ($k = 0$) (A_{1g} or E_g).

$F_{1\pm} \otimes F_{2\pm} = \Gamma_{2+} \oplus \Gamma_{3+}(E_g)$ or $F_{1+} \oplus F_{2+}$
$F_{1-} \otimes F_{1+} = \Gamma_{1-} \oplus \Gamma_{2-}$ or $F_{1-} \oplus F_{2-}$

The frequencies of the overtones can be estimated from experimental data[29].

Wurtzite ZnO

Overtones the SQ of 1RAM contains 1RAM:

$[\Gamma_1]_{(2)} = 2\Gamma_1(A_1)$
$[\Gamma_5]_{(2)} = 2\Gamma_1(A_1) \oplus ...$
$[\Gamma_6]_{(2)} = 2\Gamma_1(A_1) \oplus ...$

Combination modes. The KP contain 1RAM, thus are symmetry allowed[31, 38]:

$\Gamma_1 \otimes \Gamma_5 = \Gamma_5(E_1)$

$\Gamma_1 \otimes \Gamma_6 = \Gamma_6(E_2)$

$\Gamma_5 \otimes \Gamma_6 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6$

3.2.1 Third Order Raman Processes

In the third phonon Raman processes we deal with symmetrized cube of irrps. If the decomposition of symmetrized cube $[]_3$ of 1RAMs contains any of the 1RAMs, the three phonon overtone is symmetry allowed. Similarly, if the decomposition of KP of three different 1RAMs contains any of 1RAM, the combination is allowed. If an overtone enters the KP we obtain a general combination. If for example $[\Gamma_i]_2 \otimes \Gamma_i$ contains any 1RAM, where Γ_i is any of the 1RAM, the general combination is symmetry allowed.

Sapphire

At zone center of the BZ, $\boldsymbol{k} = 0$.

If the symmetrized cubes (SC) of the 1RAM contain any of the 1RAM the overtone is symmetry allowed:

$[\Gamma_{1+}]_{(3)} = 3\Gamma_{1+}(A_{1g})$

or

$[\Gamma_{3+}(E_g)]_{(2)} = 3\Gamma_{1+}(A_{1g}) \oplus 3\Gamma_{3+}(E_g)$.

Similarly if the triple KP of different 1-RAM contains any of the 1-RAM the combination is symmetry allowed:

$\Gamma_{1+} \otimes \Gamma_{1+} \otimes \Gamma_{3+} = \Gamma_{3+}$

or

$\Gamma_{1+} \otimes \Gamma_{3+} \otimes \Gamma_{3+} = \Gamma_{1+} \oplus \Gamma_{3+}$

Wurtzite Structure ZnO

Overtones

For wurtzite ZnO we obtain the following overtones:

$[\Gamma_1]_3 = \Gamma_1$

$[\Gamma_5]_3 = \Gamma_1 \oplus ....$

$[\Gamma_6]_3 = \Gamma_1 \oplus ....$

Combinations

The three phonon simple combinations are symmetry allowed for in contains 1RAM (Γ_3) and have three different symmetries in the triple KP:

$\Gamma_1 \otimes \Gamma_5 \otimes \Gamma_6 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6$

The general combination involves an overtone. There are many combinations of this type. Here we have:

$[\Gamma_1]_2 \otimes \Gamma_5 = \Gamma_5$

$[\Gamma_5]_2 \otimes \Gamma_1 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_2\}$

$[\Gamma_5]_2 \otimes \Gamma_5 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_2\}$

$[\Gamma_5]_2 \otimes \Gamma_6 = [\Gamma_1 \oplus \Gamma_5] \otimes \Gamma_6 \oplus \{\Gamma_2\} \otimes \Gamma_6$

$[\Gamma_1]_2 \otimes \Gamma_6 = \Gamma_6$

$[\Gamma_6]_2 \otimes \Gamma_1 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_2\}$

$[\Gamma_6]_2 \otimes \Gamma_5 = [\Gamma_1 \oplus \Gamma_5] \otimes \Gamma_5 \oplus \{\Gamma_2\} \otimes \Gamma_5$

$[\Gamma_6]_2 \otimes \Gamma_6 = [\Gamma_1 \oplus \Gamma_5] \otimes \Gamma_6 \oplus \{\Gamma_2\} \otimes \Gamma_6$

At $\boldsymbol{k} \neq 0$ we obtain the following:

Sapphire

There is interaction throughout the BZ, Γ-point excluded, with symmetry modes at zone centre. In the case of phonons, these will interact and are measurable at zone centre.

Overtones throughout the zone centre excluding $\boldsymbol{k} = 0$.

$[F_{1+}]_{(3)} = 3\Gamma_{1+}(A_{1g})$ or $3F_{1+}$ or $3F_{2+}$

$[F_{1-}]_{(3)} = 3\Gamma_{1-}$ or $3F_{1-}$ or $3F_{2-}$

$[F_{2+}]_{(3)} = 3\Gamma_{2+}$ or $3F_{1+}$ or $3F_{2+}$

$[F_{2-}]_{(3)} = 3\Gamma_{2-}$ or $3F_{1-}$ or $3F_{2-}$

$[Y_{1,2}]_{(3)} = T_3$ or Y_1 or Y_2

$[L_1]_{(3)} = 2L_1$

$[\Sigma_1]_{(3)} = \Gamma_{1+}(A_{1g}) \oplus 2\Sigma_3$

$[\Sigma_2]_{(3)} = 2\Gamma_{3+}(E_g) \oplus \Gamma_{2+}$

Wurtzite ZnO

Overtones $\boldsymbol{k} \neq 0$

$[K_1]_3 = [\Gamma_1 \oplus \Gamma_3]$ or K_1 or $2K_1$

$[K_2]_3 = [\Gamma_2 \oplus \Gamma_4]$ or $[K_2]$ or $2K_2$

$[K_3]_3 = [\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6]$ or $2\Gamma_5$ or $2\Gamma_6$ or
$[K_1 \oplus K_2 \oplus 2K_3]$ or $2K_1$ or $2K_2$ or $2K_3$

$[M_1]_3 = [\Gamma_1 \oplus 2\Gamma_5] \oplus \{\Gamma_2\}$ or M_1 or $M_1 \oplus M_2$ or $2M_1$ or $2M_2$

$[M_2]_3 = \Gamma_2 \oplus 2\Gamma_5$ or $\{\Gamma_1\}$ or M_2 or M_1 or M_2 or $2M_1$ or $2M_2$

$[M_3]_3 = \Gamma_3 \oplus 2\Gamma_6 \oplus \Gamma_4$ or M_3 or $M_3 \oplus M_4$ or $2M_3$ or $2M_4$

Combinations

Simple combinations.

There are many combinations of irrps spanned by LMR.

$^\star K_1 \otimes^\star K_2 \otimes \Gamma_1 = (\Gamma_1 \oplus \Gamma_3) \otimes \Gamma_1 = \Gamma_1 \oplus \Gamma_3$ or $K_1 \otimes \Gamma_1 = K_1$

$^\star K_1 \otimes^\star K_2 \otimes \Gamma_5 = (\Gamma_1 \oplus \Gamma_3) \otimes \Gamma_5 = \Gamma_5 \oplus (\Gamma_3 \otimes \Gamma_5) = \Gamma_5 \oplus \Gamma_6$ or $K_1 \otimes \Gamma_5$
$= K_3$

$^\star K_1 \otimes^\star K_2 \otimes \Gamma_6 = (\Gamma_1 \oplus \Gamma_3) \otimes \Gamma_6 = \Gamma_6 \oplus (\Gamma_3 \otimes \Gamma_6) = \Gamma_6 \oplus \Gamma_5$ or $K_1 \otimes \Gamma_6$
$= K_3$

$^\star K_1 \otimes^\star K_3 \otimes \Gamma_1 = \Gamma_5 \oplus \Gamma_6$ or $K_3 \otimes \Gamma_1 = K_3$

$^\star K_1 \otimes^\star K_3 \otimes \Gamma_5 = (\Gamma_5 \oplus \Gamma_6) \otimes \Gamma_5 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6$ or $K_3 \oplus \Gamma_5$

$$= K_1 \oplus K_2 \oplus K_3$$

$$^\star K_2 \otimes^\star K_3 \otimes \Gamma_1 = \Gamma_5 \oplus \Gamma_6 \text{ or } K_3 \otimes \Gamma_1 = K_3$$

$$^\star K_2 \otimes^\star K_3 \otimes \Gamma_5 = (\Gamma_5 \oplus \Gamma_6) \otimes \Gamma_5 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6 \text{ or } K_3 \oplus \Gamma_5$$

$$= K_1 \oplus K_2 \oplus K_3$$

$$^\star K_1 \otimes^\star K_2 \otimes^\star K_3 = (\Gamma_1 \oplus \Gamma_3) \otimes K_3 = K_3 \oplus K_3$$

.....

Sapphire

At zone centre $\Gamma-$ point we have real modes, not TRS affected.. At $\boldsymbol{k} \neq 0$ we have phonon Λ ($\Lambda_{1,2,3}$) , T ($T_{1,2,3}$) and P ($P_{1,2,3}$) single valued representation, TRS influenced.

Two Phonons. Overtones and combinations.

Without taking into consideration TRS we obtain the following overtones and combinations which are chiefly available from CDML-tables [23]:

$$[T_i]_{(2)} = 2\Gamma_{3+} \ (i = 1, 2)$$
$$[T_3]_{(2)} = 2\Gamma_{1+} \ (A_{1g})$$
$$[P_j]_{(2)} = \Gamma_{1+} (j = 1, 2) \text{ or } P_1$$
$$[P_3]_{(2)} = \Gamma_{1+} \oplus \Gamma_{3+}$$
$$[\Lambda_i]_{(2)} = \Gamma_{1+}$$
$$[\Lambda_3]_{(2)} = \Gamma_{1+} \oplus \Gamma_{3+}$$

The combination modes are as follows:

$$T_1 \otimes T_1 = \Gamma_{3+}(E_g) \oplus \Gamma_{1-} \oplus \Gamma_{2-}$$
$$T_1 \otimes T_2 = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+} \oplus \Gamma_{3-}$$
$$T_1 \otimes T_3 = \Gamma_{3+}(E_g) \oplus \Gamma_{3-}$$
$$T_2 \otimes T_3 = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+}$$
$$P_1 \otimes P_2 = \Lambda_1 \text{ or } P_1$$

$P_{1,2} \otimes P_3 = \Lambda_3$ or P_3

$\Lambda_1 \otimes \Lambda_2 = \Lambda_2$

$\Lambda_1 \otimes \Lambda_3 = \Lambda_3$

$\Lambda_2 \otimes \Lambda_3 = \Lambda_3$

Three Phonon Processes.

Overtones for three phonons are obtained by SC $[]_{(3)}$ of irrps.

$[\Lambda_i]_{(3)} = \Lambda_i$

$[T_1]_{(3)} = 3T_2 \oplus 3T_3$

$[T_2]_{(3)} = 3T_1 \oplus 3T_3$

$[T_3]_{(3)} = 3T_3$

$[P_1]_{(3)} = \Lambda_1 \oplus P_1$

$[P_2]_{(3)} = \Lambda_2 \oplus P_2$

$[P_3]_{(3)} = \Lambda_1 \oplus \Lambda_2 \oplus \Lambda_3$ or $P_1 \oplus P_2 \oplus 2P_3$

For a discussion and correct assignment of modes in dispersion curves TRS must be taken into account. TRS degeneracy provides the correct dimensionality of modes. The inclusion of the TRS effect on phonons from BZ (excluding Γ-point) yields the following results:

Two Phonon Overtones.

$[T_i \oplus T_i^*]_{(2)} = 2\Gamma_{3+}(E_g)$ ....$(i = 1, 2)$

$[T_3 \oplus T_3^*]_{(2)} = 2\Gamma_{1+}\ (A_{1g})$.....

$[P_i \oplus P_i^*]_{(2)} = \Gamma_{1+} \oplus \Gamma_{1-}$ or P_i...$(i = 1, 2)$

$[P_3 \oplus P_3^*]_{(2)} = \Gamma_{1+} \oplus \Gamma_{3+} \oplus \Gamma_{1-} \oplus$ ... or $P_1 \oplus P_2 \oplus P_3 \oplus$ ..

$[\Lambda_i \oplus \Lambda_i^*]_{(2)} = \Gamma_{1+} \oplus \Gamma_{1-}$ or Λ_1....$(i = 1, 2)$

$[\Lambda_3 \oplus \Lambda_3^*]_{(2)} = \Gamma_{1+} \oplus \Gamma_{3+} \oplus \Gamma_{1-} \oplus$ .. or $\Lambda_1 \oplus \Lambda_2 \oplus \Lambda_3 \oplus$ ...

The combination modes are as follows:

$(T_1 \oplus T_1^*) \otimes (T_1 \oplus T_1^*) = \Gamma_{3+}(E_g) \oplus \Gamma_{1-} \oplus \Gamma_{2-}$

$(T_1 \oplus T_1^*) \otimes (T_2 \oplus T_2^*) = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+} \oplus \Gamma_{3-}$

$(T_1 \oplus T_1^*) \otimes (T_3 \oplus T_3^*) = \Gamma_{3+}(E_g) \oplus \Gamma_{3-}$

$(T_2 \oplus T_2^*) \otimes (T_3 \oplus T_3^*) = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+}$

$(P_1 \oplus P_1^*) \otimes (P_1 \oplus P_1^*) = \Gamma_{3+}(E_g) \oplus \Gamma_{1-} \oplus \Gamma_{2-}...$

$(P_1 \oplus P_1^*) \otimes (P_2 \oplus P_2^*) = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+} \oplus \Gamma_{3-}...$

$(P_1 \oplus P_1^*) \otimes (P_3 \oplus P_3^*) = \Gamma_{3+}(E_g) \oplus \Gamma_{3-}....$

$(P_2 \oplus P_2^*) \otimes (P_3 \oplus P_3^*) = \Gamma_{1+}(A_{1g}) \oplus \Gamma_{2+}...$

$(\Lambda_1 \oplus \Lambda_1^*) \otimes (\Lambda_1 \oplus \Lambda_1^*) = \Lambda_1 \oplus \Lambda_1^* \oplus ....$

$(\Lambda_1 \oplus \Lambda_1^*) \otimes (\Lambda_2 \oplus \Lambda_2^*) = \Lambda_2 \oplus \Lambda_2^* \oplus ...$

$(\Lambda_1 \oplus \Lambda_1^*) \otimes (\Lambda_3 \oplus \Lambda_3^*) = \Lambda_1 \oplus \Lambda_3^* \oplus ...$

$(\Lambda_2 \oplus \Lambda_2^*) \otimes (\Lambda_3 \oplus \Lambda_3^*) = \Lambda_2 \oplus \Lambda_3^* \oplus ....$

Three Phonon Processes.

Overtones for three phonons are obtained by SC $[]_{(3)}$ of irrps.

$[\Lambda_i \oplus \Lambda_i^*]_{(3)} = ...(i = 1, 2)$

$[\Lambda_3 \oplus \Lambda_3^*]_{(3)} = \Lambda_1 \oplus \Lambda_2 \oplus \Lambda_3 \oplus ..$

$[T_1 \oplus T_1^*]_{(3)} = 3T_2 \oplus 3T_3....$

$[T_2 \oplus T_2^*]_{(3)} = 3T_1 \oplus 3T_3...$

$[T_3 \oplus T_3^*]_{(3)} = 3T_3...$

$[P_i \oplus P_i^*]_{(3)} = \Lambda_i \oplus ..$ or $P_i \oplus ...(i = 1, 2)$

$[P_3 \oplus P_3^*]_{(3)} = \Lambda_1 \oplus \Lambda_2 \oplus \Lambda_3 \oplus ...$ or $P_1 \oplus 2P_1 \oplus ...$

Wurtzite ZnO

Many modes are TRS infuenced at $\boldsymbol{k} \neq 0$ in ZnO. Those may interact to give modes at Γ-point. These modes may contain RAM. These will be of the type:

Overtones of TRS influenced modes:

$[A_i \oplus A_i^*]_2 = \Gamma_4 \oplus ..$

$[\Delta_i \oplus \Delta_i^*]_2 = \Delta_1 \oplus ..$

$[H_i \oplus H_i^*]_2 = \Gamma_2 \oplus \Gamma_4 \oplus ...i = 1, 2$

$[L_i \oplus L_i^*]_2 = \Gamma_4 \oplus \Gamma_6 \oplus ... i = 1, 2$

$[U_i \oplus U_i^*]_2 = \Delta_1 \oplus \Delta_5$ or $U_1 \oplus U_2 \quad i = 1, 2$

$[U_3 \oplus U_3^*]_2 = \Delta_1 \oplus ...$

$[S_i \oplus S_i^*]_2 = \Gamma_4 \oplus \Gamma_6 \oplus ...$

$[T_i \oplus T_i^*]_2 = \Gamma_1 \oplus \Gamma_5 \oplus \Gamma_3 \oplus \Gamma_6$ or Λ or Σ or T

In the appendix we provide comprehensive tables for overtones and combination modes for sapphire and ZnO, not TRS influenced. For experimental data on sapphire and ZnO the multiphonon processes of not TRS influenced phonons are given in [29, 34, 35, 36].

Chapter 4

Electronic Band Structure

The classification of electronic states in the electronic band structure is according to the same irrps used for phonons states. The electronic band structure of sapphire consists of two well separated valence bands and a conduction band. Evaristov et al. considered the band structure theoretical using the self-consistent method with symmetry adapted functions of the sapphire group. They however did not use Time Reversal Symmetry. Nevertheless, they concluded that the bottom of the conduction band has Γ-symmetry. Their simulation yielded a flat band and a larger band gap. The valence band is flat along the $\Lambda-$direction, no experimental data were obtained and therefore no conclusive evidence for an indirect band gap was established [37]. They were however able to classify the states of the band structure. In order to gain a complete knowledge of the band structure the matrix representations must be available in order to ascertain whether or not complex conjugation create new representations. From Γ point to point T (Z) along the direction Λ a splitting is observed. The high symmetry points Γ and T (Z) have the same number of symmetry elements. The splitting is not due to the lowering of symmetry alone. It is also due to the presence of Time Reversal. Evaristov et al. show that at point T (Z) that T_1 (Z_1) and T_2 (Z_2) are degenerate. However, they were not aware of TRS. When TRS is taken into account then the correct assignment follows as $T_1 \oplus T_1^*$ at high symmetry line and $\Lambda_1 \oplus \Lambda_1^*$, $\Lambda_2 \oplus \Lambda_2^*$ and $\Lambda_3 \oplus \Lambda_3^*$ along the $\Lambda-$line. A similar feature is observed in ZnO along the $\Gamma - \Delta - A$ line[39]. Here the representations flow into each other when complex conjugated, while is Al_2O_3 complex conjugation introduce new representations. In addition the phonon dispersion curve of sapphire measured by

Inelastic Neutron Scattering along the $\Lambda-$line evidences the Time Reversal and at the high symmetry point T, the state are TRS degenerate.

Chapter 5

Experimental Results

In this section we discuss the experimental available data using our derived results of LMR and multiphonon processes as well as compatibility tables.

5.1 Raman and Infrared Modes

Interpretation of Raman spectra of ZnO, sapphire (Al_2O_3), Al_2O_3 on the ZnO and vice versa requires the knowledge of the overtones and combinations modes, those originating from $\boldsymbol{k} = 0$ and $\boldsymbol{k} \neq 0$. The multiphonon processes in these compounds have been already observed by several authors[20, 31, 32, 34, 35, 38, 39]. Here we focus on the second and third order phonon transitions. The samples were grown by plasma-assisted molecular beam epitaxy on a (0001) sapphire sample using $Ar^+514\,nm$ laser line for excitation and a Jobin Yron single-pass monochromator filled with an edge filter and Hammatsu C7027 thermo-electrically cooled CCD array for detection. The resolution for these spectra was about 0.5 nm at room temperature [29]. Several spectra were recorded at room temperature. For sapphire, the frequencies of the Raman modes $2A_{1g}$ and $5E_g$ are tabulated by various authors[29, 34]. These constitute the first order Raman modes, 1RAMs.

The multiphonon processes (second and third order phonons) arise from the interaction of first order phonons via the deformation potential together with Frolich interaction. The deformation potential is assumed to be independent of the phonon $\boldsymbol{k}$ wave vector. However in polar materials the LO mode is accompanied by an electric field which con-

tributes to a long range ($\boldsymbol{k}$-dependent) Frolich Hamiltonian[30].

In the Table we give multiphonons which originate from the entire BZ with the selection rules for overtones and combinations modes of two and three phonon processes with frequencies explicitly given in Table.

5.2 Dispersion Curves

In this section we discuss the assignment of phonon modes with respect to the experimental available sapphire data obtained by means of neutron diffraction scattering. We evidence the presence of TRS along high symmetry lines and points (Λ-, P- and T-phonons) in the assignment of vibration modes throughout the BZ. Going from high symmetry point Γ to T (Z) along the $\Lambda-$line, a splitting takes place. When an irrps is complex, the time reversal must be considered. Using the Frobenius-Schur theorem, we have investigated all irrps of sapphire and found $\Lambda_{1,2,3}$, $T_{1,2,3}$ and $P_{1,2,3}$ to be complex and TRS influenced. These states are classified according to $\Lambda_i \oplus \Lambda_i^*$, $T_i \oplus T_i^*$ and $P_i \oplus P_i^*$. Therefore the degeneracy of these states doubles. The assignment of vibration modes in the sapphire sample obtained by Raman spectroscopy takes into consideration the effect of TRS on phonons [20]. The effect of TRS on the phonon dispersion curves is discussed in detail throughout the entire BZ. Compatibility tables for sapphire and wurtzite structure are also provided for reference.

Chapter 6

Conclusion

In this work the Lattice Mode Representation for sapphire was derived. This representation provides the number and symmetries (degeneracy) of possible first order non-interacting modes. An assignment of vibrational modes throughout the entire BZ was undertaken. To the best of our knowledge is the first time such an attempt has been made. The multiphonon processes selection rules for wurtzite and sapphire structures were also studied.

The effect of Time Reversal Symmetry on phonons was investigated. We have found many phonons to be TRS influenced. Experimental results of dispersion curves support this findings[3, 12]. For the first time the effect of TRS on scattering phonons processes has been taken into consideration. The physical consequences of the TRS phonon scattering processes on optical transitions are also considered. The effect must be taken into account during the interpretation of experimental data obtained by neutron, X-ray and Raman scattering.

A need of modification of existing optical selection rules (Kronecker Products) in the presence of TRS is indicated. Our results are valid for the following compounds: wurtzite: ZnO, ZnS, ZnSe, ZnTe, GaN, AlN, InN, BP, BeO, CdS, CdSe, CdTe, CuI, 2H-SiC, 4H-SiC, 6H-SiC, etc.; Trigonal: Al_2O_3, Cr_2O_3, Fe_2O_3, V_2O_3, Ti_2O_3, $AlBO_3$, $FeBO_3$, $NaNO_3$, $CaCO_3$, $ZnCO_3$, $MgCO_3$, MgTe, $MnCO_3$, $CdCO_3$, $FeCO_3$, etc.[19]

In summary a comprehensive group theoretical study on vibrational modes in sapphire in terms of the derivation of the Lattice Mode Representation and selection rules on multiphonon processes with the inclusion of Time Reversal Symmetry was undertaken.

Appendix A

Calculations and Tables

A.1 Multiplication Table for Hexagonal and Trigonal Points Groups

Symmetry elements denomination in Cracknell Davis Miller Love Tables and Kovalev setting.

Cracknell Davies Miller Love (CDML). Translated from Kovalev Multiplication Table.

Correspondence between Kovalev and CDML.

CDML	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Kovalev	1	2	3	4	5	6	9	10	11	12	7	8	13	14	15	16	17	18	21	22	23	24	19	20

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
2	3	4	5	6	49	8	9	10	59	12	7	14	15	16	17	18	61	20	21	22	71	24	19
3	4	5	6	49	50	9	10	59	60	7	8	15	16	17	18	61	62	21	22	71	72	19	20
4	5	6	49	50	51	10	59	60	55	8	9	16	17	18	61	62	63	22	71	72	67	20	21
5	6	49	50	51	52	59	60	55	56	9	10	17	18	61	62	63	64	71	72	67	68	21	22
6	49	50	51	52	53	60	55	56	57	10	59	18	61	62	63	64	65	72	67	68	69	22	71
7	12	11	58	57	56	49	6	5	4	51	50	19	24	23	22	69	68	61	18	17	16	63	62
8	7	60	11	58	57	50	49	6	5	52	51	20	19	24	23	22	69	62	61	18	17	64	63
9	8	7	12	11	58	51	50	49	6	53	52	21	20	19	24	23	70	63	62	61	18	65	64
10	9	8	7	12	11	52	51	50	49	54	53	22	21	20	19	24	23	64	63	62	61	66	65
11	58	57	56	55	60	5	4	3	2	49	6	23	70	69	68	67	72	17	16	15	14	61	18
12	11	58	57	56	55	6	5	4	3	50	49	24	23	70	69	68	67	18	17	16	15	62	61
13	14	15	16	17	18	19	20	21	22	23	24	1	2	3	4	5	6	7	8	9	10	11	12
14	15	16	17	18	61	20	21	22	71	24	19	2	3	4	5	6	49	8	9	10	59	12	7
15	16	17	18	61	62	21	22	71	72	19	20	3	4	5	6	49	50	9	10	59	60	7	8
16	17	18	61	62	63	22	71	72	67	20	21	4	5	6	49	50	51	10	59	60	55	8	9
17	18	61	62	63	64	71	72	67	68	21	22	5	6	49	50	51	52	59	60	55	56	9	10
18	61	62	63	64	65	72	67	68	69	22	71	6	49	50	51	52	53	60	55	56	57	10	59
19	24	23	70	69	68	61	18	17	16	63	62	7	12	11	58	57	56	49	6	5	4	51	50
20	19	24	23	70	69	62	61	18	17	64	63	8	7	12	11	58	57	50	49	6	5	52	51
21	20	19	24	23	70	63	62	61	18	17	64	9	8	7	12	11	58	51	50	49	6	53	52
22	21	20	19	24	23	64	63	62	61	18	65	10	9	8	7	12	11	52	51	50	49	54	53
23	70	69	68	67	72	17	16	15	14	61	18	11	58	57	56	55	60	5	4	3	2	49	6
24	23	70	69	68	19	18	17	16	15	62	61	12	11	58	57	56	55	6	5	4	3	50	49

Table A.1: Multiplication Table for Hexagonal and Trigonal Point Groups

A.2 Vector Representation for Hexagonal and Trigonal Point/Space Groups

Table A.2: Vector representation of trigonal and hexagonal groups

$E(1)$	x, y, z	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$I(13)$	$-x, -y, -z$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_6^+(2)$	$x-y, x, z$	$\begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$S_3^-(14)$	$-x+y, -x, -z$	$\begin{bmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_3^+(3)$	$-y, x-y, z$	$\begin{bmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$S_6^-(15)$	$y, -x+y, -z$	$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_2(4)$	$-x. - y, z$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$\sigma_h(16)$	$x, y, -z$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_3^-(5)$	$-x+y, -x, z$	$\begin{bmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$S_6^+(17)$	$x-y, x, -z$	$\begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_6^-(6)$	$y, -x+y, z$	$\begin{bmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$0, 0, 1$	$S_3^+(18)$	$-y, x-y, -z$	$\begin{bmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_{21}''(7)$	$x-y, -y, -z$	$\begin{bmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$1, 0, 0$	$\sigma_{v1}(19)$	$-x+y, y, z$	$\begin{bmatrix} -1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$C_{22}'(8)$	$x, x-y, z$	$\begin{bmatrix} 1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\gamma, \delta, 0$	$\sigma_{d2}(20)$	$-x, -x+y, -z$	$\begin{bmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$
$C_{23}''(9)$	$y, x, -z$	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$\delta, \gamma, 0$	$\sigma_{v3}(21)$	$-y, -x, z$	$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$C_{21}'(10)$	$-x+y, y, -z$	$\begin{bmatrix} -1 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$0, 1, 0$	$\sigma_{d1}(22)$	$x-y, -y, z$	$\begin{bmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Continued on Next Page ...

Table A.2 – Continued

$C''_{22}(11)$	$-x, -x+y, -z$	$\begin{bmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$-\delta, \gamma, 0$	$\sigma_{v2}(23)$	$x, x-y, z$	$\begin{bmatrix} 1 & 0 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$
$C'_{23}(12)$	$-y, -x, -z$	$\begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$	$-\gamma, \delta, 0$	$\sigma_{d3}(24)$	y, x, z	$\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

A.3 Table of Spinor Representations SU(2)

Spinor representations for Hexagonal and Trigonal Point and Space Groups.

Table A.3: SU(2) Matrices Representation for Hexagonal and Trigonal Point Groups

g	gI	$D_{1/2}$	$D_{1/2}$
$E(1)$	$I(13)$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$
$C_6^+(2)$	$S_3^-(14)$	$\begin{bmatrix} \frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \\ 0 & \frac{1}{2}\sqrt{3} + \frac{1}{2}i \end{bmatrix}$	$\begin{bmatrix} i\omega^* & 0 \\ 0 & -i\omega \end{bmatrix}$
$C_3^+(3)$	$S_3^-(15)$	$\begin{bmatrix} \frac{1}{2} - \frac{1}{2}i\sqrt{3} & 0 \\ 0 & \frac{1}{2}i\sqrt{3} + \frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\omega & 0 \\ 0 & -\omega^* \end{bmatrix}$
$C_2(4)$	$\sigma_h(16)$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$
$C_3^-(5)$	$S_6^+(17)$	$\begin{bmatrix} -\frac{1}{2}i\sqrt{3} + \frac{1}{2} & 0 \\ 0 & -\frac{1}{2} + \frac{1}{2}i\sqrt{3} \end{bmatrix}$	$\begin{bmatrix} \omega^* & 0 \\ 0 & \omega \end{bmatrix}$
$C_6^-(6)$	$S_3^+(18)$	$\begin{bmatrix} -\frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \\ 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \end{bmatrix}$	$\begin{bmatrix} i\omega & 0 \\ 0 & -i\omega^* \end{bmatrix}$
$C_{21}''(7)$	$\sigma_{v1}(19)$	$\begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$
$C_{22}'(8)$	$\sigma_{d2}(20)$	$\begin{bmatrix} 0 & -\frac{1}{2}i\sqrt{3} - \frac{1}{2} \\ \frac{1}{2} - \frac{1}{2}i\sqrt{3} & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega^* \\ -\omega & 0 \end{bmatrix}$
$C_{23}''(9)$	$\sigma_{v3}(21)$	$\begin{bmatrix} 0 & -\frac{1}{2}\sqrt{3} - \frac{1}{2}i \\ \frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & i\omega \\ i\omega^* & 0 \end{bmatrix}$
$C_{21}'(10)$	$\sigma_{d1}(22)$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$
$C_{22}''(11)$	$\sigma_{v2}(23)$	$\begin{bmatrix} 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} + \frac{1}{2}i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i\omega^* \\ -i\omega & 0 \end{bmatrix}$
$C_{23}'(12)$	$\sigma_{d3}(24)$	$\begin{bmatrix} 0 & \frac{1}{2}i\sqrt{3} - \frac{1}{2} \\ \frac{1}{2}i\sqrt{3} + \frac{1}{2} & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ -\omega^* & 0 \end{bmatrix}$

A.4 Character Tables for Hexagonal C_{6v}^4 and D_{3d}^6 Space groups.

A.4.1 Irreducible Representation and Factor Groups

Sapphire

The factor group of corundum structure, D_{3d}^6/T, (T pure translation lattice group), at $\boldsymbol{k} = 0$, (point Γ, centre of the BZ) has the following twelve symmetry operators divided into six classes:

$$D_{3d}^6(R\overline{3}c): \{E|000\}, \{C_3^+|00\tfrac{1}{2}\}, \{C_3^-|00\tfrac{1}{2}\}, \{C_{21}''|00\tfrac{1}{2}\}, \{C_{23}''|00\tfrac{1}{2}\}, \{C_{22}''|00\tfrac{1}{2}\}$$
$$\{I|000\}, \{S_6^-|000\}, \{S_6^+|000\}, \{\sigma_{v1}|00\tfrac{1}{2}\}, \{\sigma_{v2}|00\tfrac{1}{2}\}, \{\sigma_{v3}|00\tfrac{1}{2}\}$$

where $\boldsymbol{\tau} = (00\frac{1}{2})$ is a non-primitive translation along the principal axis. The generators ($\boldsymbol{k} = 0$) for this space group are: $\{C_3^+|0\}$, $\{C_{21}''|\tau\}$ and $\{\sigma_{v1}|\tau\}$. The sappphire irrps and their characters are listed in the Appendix. For other high symmetry points and lines ($\boldsymbol{k} \neq 0$) we have the following $G^{\boldsymbol{k}}/T$ groups and their irrps:

$$G^{\boldsymbol{k}_T}/T = \{E|000\}, \{C_3^+|00\tfrac{1}{2}\}, \{C_3^-|00\tfrac{1}{2}\}, \{C_{21}''|00\tfrac{1}{2}\}, \{C_{23}''|00\tfrac{1}{2}\}, \{C_{22}''|00\tfrac{1}{2}\},$$
$$\{I|000\}, \{S_6^-|000\}, \{S_6^+|000\}, \{\sigma_{v1}|00\tfrac{1}{2}\}, \{\sigma_{v2}|00\tfrac{1}{2}\}, \{\sigma_{v3}|00\tfrac{1}{2}\}$$

irrps: $T_{1,2,3}(2)$ (SV); $T_{4,5,6}(2)$ (DV)

$$G^{\boldsymbol{k}_\Lambda}/T = \{E|000\}, \{C_3^+|000\}, \{C_3^-|000\}, \{\sigma_{v1}|00\tfrac{1}{2}\}, \{\sigma_{v3}|00\tfrac{1}{2}\}, \{\sigma_{v2}|00\tfrac{1}{2}\}$$

irrps: $\Lambda_{1,2}(1), \Lambda_3(2)$ (SV); $\Lambda_{4,5}(1), \Lambda_6(2)$ (DV)

$$G^{\boldsymbol{k}_P}/T = \{E|000\}, \{C_3^+|000\}, \{C_3^-|000\}, \{\sigma_{v1}|00\tfrac{1}{2}\}, \{\sigma_{v3}|00\tfrac{1}{2}\}, \{\sigma_{v2}|00\tfrac{1}{2}\}$$

irrps: $P_{1,2}(1), P_3(2)$ (SV); $P_{4,5}(2)P_6(2)$ (DV)

$$G^{\boldsymbol{k}_L}/T = \{E|000\}, \{C_{21}''|00\tfrac{1}{2}\}, \{I|000\}, \{\sigma_{v1}|00\tfrac{1}{2}\}$$

irrps: $L_1(2)$ (SV); $L_2(2)$ (DV)

$$G^{\boldsymbol{k}_\Sigma}/T = \{E|000\}, \{C_3^+|000\}, \{C_{21}''|00\tfrac{1}{2}\}, \{\sigma_{v1}|00\tfrac{1}{2}\}$$

irrps: $\Sigma_{1,2}(1)$ (SV); $\Sigma_{3,4}(1)$ (DV)

$$G^{\boldsymbol{k}_{F_A}}/T = \{E|000\}, \{C_{23}''|00\tfrac{1}{2}\}, \{I|000\}, \{\sigma_{v3}|00\tfrac{1}{2}\}$$

irrps: $F_{1A\pm,2A\pm}(1)$ (SV); $F_{3A\pm,4A\pm}(1)$ (DV)

$$G^{\boldsymbol{k}_Y}/T = \{E|000\}, \{C_{21}''|00\tfrac{1}{2}\}$$

irrps: $Y_{1,2}(1)$ (SV); $Y_{3,4}(1)$ (DV)

$$G^{\boldsymbol{k}_\Sigma}/T = \{E|000\}, \{C_{22}''|00\tfrac{1}{2}\}$$

irrps: $\Sigma_{1,2}(1)$ (SV); $\Sigma_{3,4}(1)$ (DV)

The SV and DV stand for single valued and double valued representations (spinor rep) respectively.

Zinc Oxide

$$C_{6v}^4/T(P6_3mc): \{E|0\}, \{C_6^+|\tau\}, \{C_6^-|\tau\}, \{C_2|0\}, \{C_3^-|0\}, \{C_3^-|0\},$$
$$\{\sigma_{v1}|0\}, \{\sigma_{d2}|\tau\}, \{\sigma_{v3}|0\}, \{\sigma_{d1}|\tau\}, \{\sigma_{v2}|0\}, \{\sigma_{d3}|\tau\}$$

where $\boldsymbol{\tau}$ is a non-primitive translation vector $\boldsymbol{\tau} = (00\frac{1}{2})$. The generators of this space group are: $\{C_3^+|0\}$, $\{C_2|\tau\}$, $\{\sigma_{d2}|\tau\}$. In the Appendix [A2] we tabulate the ZnO irrps and their character.

Similarly for ZnO the $G^{\boldsymbol{k}}/T$ groups and their irrps, for $\boldsymbol{k} \neq 0$ are:

$$G^{\boldsymbol{k}_\Delta}/T = \{E|0\}; \{C_6^+|\tau\}, \{C_3^+|0\}, \{C_2|\tau\}, \{C_3^-\}, \{C_6^-|\tau\}, \{\sigma_{v1}|0\},$$
$$\{\sigma_{d2}|\tau\}, \{\sigma_{v3}|0\}, \{\sigma_{d1}|\tau\}, \{\sigma_{v2}|0\}, \{\sigma_{d3}|\tau\}$$

irrps: $\Delta_{1-4}(1), \Delta_{4,5}(2)$ (SV); $\Delta_{7,8,9}(2)$ (DV)

$$G^{\boldsymbol{k}_A}/T = \{E|0\}, \{C_6^+|\tau\}, \{C_3^+|0\}, \{C_2|\tau\}, \{C_3^-|0\}, \{C_6^-|\tau\},$$
$$\{\sigma_{v1}|0\}, \{\sigma_{d2}|\tau\}, \{\sigma_{v3}|0\}, \{\sigma_{d1}|\tau\}, \{\sigma_{v2}|0\}, \{\sigma_{d3}|\tau\}$$

irrps: A_{1-6} (SV); $A_{7,8,9}$ (DV)

$$G^{\boldsymbol{k}_H}/T = \{E|0\}, \{C_3^+|0\}, \{C_3^-|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{d1}|\tau\}, \{\sigma_{d3}|\tau\}$$

irrps: $H_{1,2}(1), H_3(2)$ (SV); $H_{4,5}(1)H_3(2)$ (DV)

$$G^{\boldsymbol{k}_K}/T = \{E|0\}, \{C_3^+|0\}, \{C_3^-|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{d1}|\tau\}, \{\sigma_{d3}|\tau\}$$

irrps: $K_{1,2}(1)K_3(2)$ (SV); $K_{4,5}(1)K_6(2)$ (DV)

$G^{\boldsymbol{k}_P}/T = \{E|0\}, \{C_3^+|0\}, \{C_3^-|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{d1}|\tau\}, \{\sigma_{d3}|\tau\}$

irrps: $P_{1,2}(1), P_3(2)$ (SV); $P_{4,5}(1)P_6(2)$ (DV)

$G^{\boldsymbol{k}_L}/T = \{E|0\}, \{C_2|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{v2}|0\}$

irrps: $L_{1,2,3,4}$ (SV); L_5 (DV)

$G^{\boldsymbol{k}_M}/T = \{E|0\}, \{C_2|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{v2}|0\}$

irrps: $M_{1-4}(1)$ (SV); $M_5(2)$ (DV)

$G^{\boldsymbol{k}_U}/T = \{E|0\}, \{C_2|\tau\}, \{\sigma_{d2}|\tau\}, \{\sigma_{v2}|0\}$

irrps: $U_{1-4}(1)$ (SV); $U_5(2)$ (DV)

$G^{\boldsymbol{k}_\Lambda}/T = \{E|0\}, \{\sigma_{d3}|\tau\}$

irrps: $\Lambda_{1,2}(1)$ (SV); $\Lambda_{3,4}(1)$ (DV)

$G^{\boldsymbol{k}_\Sigma}/T = \{E|0\}, \{\sigma_{v2}|0\}$

irrps: $\Sigma_{1,2}(1)$ (SV); $\Sigma_{3,4}(1)$ (DV)

$G^{\boldsymbol{k}_Q}/T = \{E|0\}, \{\sigma_{d3}|\tau\}$

irrps: $Q_{1,2}(1)$ (SV); $Q_{3,4}(1)$ (DV)

$G^{\boldsymbol{k}_R}/T = \{E|0\}, \{\sigma_{v3}|0\}$

irrps: $R_{1,2}(1)$ (SV); $R_{3,4}(1)$ (DV)

$G^{\boldsymbol{k}_S}/T = \{E|0\}, \{\sigma_{d2}|\tau\}$

irrps: $S_{1,2}(1)$ (SV); $S_{3,4}(1)$ (DV)

$G^{\boldsymbol{k}_T}/T = \{E|0\}, \{\sigma_{d2}|\tau\}$

irrps: $T_{1,2}(1)$ (SV); $T_{3,4}(1)$ (DV)

A.5 Generators for Trigonal D_{3d}^6 and Wurtzite C_{6v}^4 Space groups.

The necessary and relevant standard matrices for generation of the matrix representations for Space Groups are given below. The standard matrices together with the multiplication table generate the matrix representation of the space group.

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad 2 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \qquad 3 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$$

$$4 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \qquad 5 = \begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix} \qquad 8 = \begin{bmatrix} -\omega^* & 0 \\ 0 & -\omega \end{bmatrix}$$

Sapphire

$\Gamma-$Point Al_2O_3

$\{g/\tau\}$	dim	3	7	19.1
Γ_{1+}	1	E	E	E
Γ_{2+}	1	E	$-E$	$-E$
Γ_{3+}	2	5	2	2
Γ_{1-}	1	E	E	$-E$
Γ_{2-}	1	E	$-E$	E
Γ_{3-}	2	5	2	-2
Γ_{4+}	1	$-E$	iE	iE
Γ_{5+}	1	$-E$	$-iE$	$-iE$
Γ_{6+}	2	8	$-i3$	$-i3$
Γ_{4-}	1	$-E$	iE	$-iE$
Γ_{5-}	1	$-E$	$-iE$	iE
Γ_{6-}	2	8	$-i3$	$i3$

Λ line Al_2O_3

$\{g/\tau\}$	dim	3	19.1
Λ_1	1	E	iE
Λ_2	1	E	$-iE$
Λ_3	2	5	$T2$
Λ_4	1	$-E$	$T, -iE$
Λ_5	1	$-E$	T, iE
Λ_6	2	8	$T, -i3$

Σ line Al_2O_3

$\{g/\tau\}$	dim	$57.1(y, x, 1/2+z)$
Σ_1	1	E
Σ_2	1	$-E$
Σ_3	1	iE
Σ_4	1	$-iE$

F_A Point A-setting Al_2O_3

$\{g/\tau\}$	dim	57.1	69.1
$F_{A_{1+}}$	1	E	E
$F_{A_{2+}}$	1	$-E$	$-E$
$F_{A_{1-}}$	1	E	$-E$
$F_{A_{2-}}$	1	$-E$	E
$F_{A_{3+}}$	1	iE	iE
$F_{A_{4+}}$	1	$-iE$	$-iE$
$F_{A_{3-}}$	1	iE	$-iE$
$F_{A_{4-}}$	1	$-iE$	iE

F_B B-setting Al_2O_3

$\{g/\tau\}$	dim	11.1	23.1
$F_{B_{1+}}$	1	E	E
$F_{A_{2+}}$	1	$-E$	$-E$
$F_{B_{1-}}$	1	E	$-E$
$F_{B_{2-}}$	1	$-E$	E
$F_{B_{3+}}$	1	iE	iE
$F_{B_{4+}}$	1	$-iE$	$-iE$
$F_{B_{3-}}$	1	iE	$-iE$
$F_{B_{4-}}$	1	$-iE$	iE

L-line Al_2O_3

$\{g/\tau\}$	dim	7.1	19.1
L_1	2	4	$-i3$
L_2	2	$i4$	2

T Point Al_2O_3

$\{g/\tau\}$	dim	3	7.1	19.1
T_1	2	5	2	$i3$
T_2	2	5	2	$-i3$
T_3	2	E	4	$-i3$
T_4	2	8	$-i3$	2
T_5	2	8	$-i3$	-2
T_6	2	$-E$	$i4$	2

P point Al_2O_3

$\{g/\tau\}$	dim	3	19.1
P_1	1	E	T, E
P_2	1	E	$T, -E$
P_3	2	5	$-3T$
P_4	1	$-E$	$-ET$
P_5	1	$-E$	iET
P_6	2	8	$-i2T$

Y-point Al_2O_3

$\{g/\tau\}$	dim	7.1
Y_1	1	E
Y_2	1	$-E$
Y_3	1	iE
Y_4	1	$-iE$

C-point Al_2O_3

$\{g/\tau\}$	dim	19.1
C_1	1	T, E
C_2	1	$T, -E$
C_3	1	$T, -iE$
C_4	1	T, iE

E-point Al_2O_3

$\{g/\tau\}$	dim	21.1
E_1	1	T, E
E_2	1	$T, -E$
E_3	1	$T, -iE$
E_4	1	T, iE

Zinc Oxide

$\Gamma-$Point ZnO

$\{g/\tau\}$	dim	3	4.1	22.1
Γ_1	1	E	E	E
Γ_2	1	E	E	$-E$
Γ_3	1	E	$-E$	E
Γ_4	1	E	$-E$	$-E$
$\Gamma_5(+)$	2	5	E	2
$\Gamma_6(+)$	2	5	$-E$	2
$\Gamma_7(-)$	2	8	$(+i)\,4$	$(-i)\,3$
$\Gamma_8(-)$	2	8	$(-i)\,4$	$(-i)\,3$
$\Gamma_9(-)$	2	$-E$	$(+i)\,4$	$(-i)\,3$

$\Delta-$Line ZnO

$\{g/\tau\}$	dim	3	4.1	22.1
Δ_1	1	E	T, E	T, E
Δ_2	1	E	T, E	$T, -E$
Δ_3	1	E	$T, -E$	T, E
Δ_4	1	E	$T - E$	$T, -E$
$\Delta_5(+)$	2	5	T, E	$T, 2$
$\Delta_6(+)$	2	5	$T, -E$	$T, 2$
$\Delta_7(-)$	2	5	$T, -E$	$T, 2$
$\Delta_8(-)$	2	8	$T, (+i)\,4$	$T\,(-i)\,3$
$\Delta_9(-)$	2	$-E$	$T, (-i)\,4$	$T, (-i)\,3$

Λ−Line ZnO

$\{g/\tau\}$	1	24.1
Λ_1	1	E
Λ_2	1	$-E$
$\Lambda_3(-)$	1	$(-i)\,E$
$\Lambda_4(-)$	1	$(+i)\,E$

Σ−Line ZnO

$\{g/\tau\}$	dim	23
Σ_1	1	E
Σ_2	1	$-E$
$\Sigma_3(-)$	1	$(-i)\,E$
$\Sigma_4(-)$	1	$(+i)\,E$

A-Point ZnO

$\{g/\tau\}$	dim	3	4.1	22.1
A_1	1	E	iE	iE
A_2	1	E	$-iE$	$-iE$
A_3	1	E	$-iE$	$-iE$
A_4	1	E	$-iE$	$-iE$
$A_5(+)$	2	5	$(+i)\,E$	2
$A_6(+)$	2	5	$(-i)\,E$	2
$A_7(-)$	2	8	4	2
$A_8(-)$	2	8	-4	2
$A_9(-)$	2	$-E$	$+4$	2

H-Point ZnO

$\{g/\tau\}$	dim	3	22.1
H_1	1	E	iE
H_2	1	E	$-iE$
$H_3(+)$	2	5	$(-i)\,3$
H_4	1	$-E$	E
H_5	1	$-E$	$-E$
$H_6(-)$	2	8	2

K-Point

$\{g/\tau\}$	dim	3	22.1
K_1	1	E	E
K_2	1	E	$-E$
$K_3(+)$	2	5	2
K_4	1	$-E$	iE
K_5	1	$-E$	$-E$
$K_6(-)$	2	8	$(-i)\,3$

L-Point ZnO

$\{g/\tau\}$	dim	4.1	20.1
L_1	1	iE	iE
L_2	1	iE	$-iE$
L_3	1	$-iE$	iE
L_4	1	$-iE$	$-iE$
L_5	2	4	2

M-Point ZnO

$\{g/\tau\}$	dim	4.1	20.1
M_1	1	E	E
M_2	1	E	$-E$
M_3	1	$-E$	E
M_4	1	$-E$	$-E$
M_5	2	$(+i)\,4$	$(-i)\,3$

U-Point ZnO

$\{g/\tau\}$	dim	4.1	20.1
U_1	1	T, E	T, E
U_2	1	T, E	$T, -E$
U_3	1	$T, -E$	T, E
U_4	1	$T, -E$	$T, -E$
U_5	2	$T, (-i)\,4$	$(-i)\,3$

R-line ZnO

$\{g/\tau\}$	dim	23
R_1	1	E
R_2	1	$-E$
R_3	1	$-iE$
R_4	1	iE

S-line ZnO

$\{g/\tau\}$	dim	20.1
S_1	1	iE
S_2	1	$-iE$
S_3	1	E
S_4	1	$-E$

P-point ZnO

$\{g/\tau\}$	1	3	22.1
P_1	1	E	TE
P_2	1	E	$T, -E$
P_3	2	5	$T2$
P_4	1	$-E$	T, iE
$P_5(-)$	1	$-E$	$T, (+i)\, E$
$P_6(-)$	2	8	$T, (-i)\, 3$

$$\omega = \exp(i\frac{2\pi}{3}) = \frac{1}{2}i\sqrt{3} - \frac{1}{2}$$

A.6 Matrix Representations for D_{3d}^6 and C_{6v}^4 Space Groups

Character Tables and Matrix elements for SV and DV irreducible representations D_{3d}^6 (Space Group No. 167)

Table A.4: Character of the Lattice Mode Representation and character of the Single Valued Representation for Sapphire at Γ point

$\{g/\tau\}$	E	C_3^+	C_3^-	C_{21}''/τ	C_{23}''/τ	C_{22}''/τ	I	S_6^-	S_6^+	σ_{v1}/τ	σ_{v3}/τ	σ_{v2}/τ
$\{g/\tau\}$	1	3	5	7.1	9.1	11.1	13	15	17	19.1	21.1	23.1
$\Gamma_{1+}(A_{1g})$	1	1	1	1	1	1	1	1	1	1	1	1
$\Gamma_{2+}(A_{2g})$	1	1	1	−1	−1	−1	1	1	1	−1	−1	−1
$\Gamma_{3+}(E_g)$	2	−1	−1	0	0	0	2	−1	−1	0	0	0
$\Gamma_{1-}(A_{1u})$	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
$\Gamma_{2-}(A_{2u})$	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1
$\Gamma_{3-}(E_u)$	2	−1	−1	0	0	0	−2	1	1	0	0	0
$\chi^{\mathrm{LMR}}\{g/\tau\}$	27	0	0	−1	−1	−1	3	0	0	−1	−1	−1

g	E 1	C_3^+ 3	C_3^- 5	C_{21}''/τ 7.1	C_{23}''/τ 9.1	C_{22}''/τ 11.1	I 13	S_6^- 15	S_6^+ 17	σ_{v1}/τ 19.1	σ_{v3}/τ 21.1	σ_{v2}/τ 23.1
Γ_{1+}	1	1	1	1	1	1	1	1	1	1	1	1
Γ_{2+}	1	1	1	−1	−1	−1	1	1	1	−1	−1	−1
Γ_{3+}	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$
Γ_{1-}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
Γ_{2-}	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1
Γ_{3-}	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}-\omega&0\\0&-\omega^*\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega^*\\-\omega&0\end{bmatrix}$
Γ_{4+}	1	−1	1	i	$-i$	i	1	−1	1	i	$-i$	i
Γ_{5+}	1	−1	1	$-i$	i	$-i$	1	−1	1	$-i$	i	$-i$
Γ_{6+}	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\-\omega&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\-\omega&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega\\\omega^*&0\end{bmatrix}$
Γ_{4-}	1	−1	1	i	$-i$	i	−1	1	−1	$-i$	i	$-i$
Γ_{5-}	1	−1	1	$-i$	i	$-i$	−1	1	−1	i	$-i$	i
Γ_{6-}	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}-\omega&0\\0&-\omega^*\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega^*\\\omega&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
χ^{LMR}	27	0	0	−1	−1	−1	3	0	0	−1	−1	−1

Table A.5: Matrix Representations for Sapphire at $\boldsymbol{k} = \mathbf{0}$ Γ Point

$\{g/\tau\}$	E	C_3^+	C_3^-	C_{21}''/τ	C_{23}''/τ	C_{22}''/τ	I	S_6^-	S_6^+	σ_{v1}/τ	σ_{v3}/τ	σ_{v2}/τ
$\{g/\tau\}$	1	3	5	7.1	9.1	11.1	13	15	17	19.1	21.1	23.1
T_1	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$\begin{bmatrix}-i&0\\0&i\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
T_2	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
T_3	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
T_4	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}-\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
T_5	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\-\omega&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$
T_6	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}i&0\\0&-i\end{bmatrix}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$

Table A.6: Matrix of Irreducible Representations at $\boldsymbol{k \neq 0}$ T Point

Table A.7: Table of Characters of Irreducible Representation at Point T

g	1	3	5	7.1	9.1	11.1	13	15	17	19.1	21.1	23.1
T_1	2	-1	-1	0	0	0	0	$-B,T$	B,T	0	0	0
T_2	2	-1	-1	0	0	0	0	B,T	$-B,T$	0	0	0
T_3	2	2	2	0	0	0	0	0	0	0	0	0
T_4	2	1	-1	0	0	0	0	B,T	B,T	0	0	0
T_5	2	1	-1	0	0	0	0	$-B,T$	$-B,T$	0	0	0
T_6	2	2	2	0	0	0	0	0	0	0	0	0
g^2	1	5	3	1	1	1	1	5	3	$1t_0$	$1t_0$	$1t_0$
$T_{1,2}$	2	-1	-1	2	2	2	2	-1	-1	2ω	2ω	2ω
$T_{3,6}$	2	2	2	2	2	2	2	2	2	2ω	2ω	2ω
$T_{4,5}$	2	-1	1	2	2	2	2	-1	1	2ω	2ω	2ω

$$B = \sqrt{3}\omega = \exp(2\pi i \boldsymbol{k}_T \cdot \boldsymbol{t}_0)$$

$$T = \exp(2\pi i(1/6, 1/6, 1/6) \cdot (1/2, 1/2, -1/2) = \exp(i\pi/6)$$

T_{1-6} irrps belong to case (c).

$$\omega' = \exp(i\pi\alpha(1/3, 1/3, 1/3) \cdot (1, 1, 1)) = \exp(i\alpha\pi)$$

$$T = \exp(2\pi i(\alpha, \alpha, \alpha) \cdot (1/6, 1/6, 1/6)) = \exp(i\pi\alpha)$$

All irrps are complex Λ_{1-6} . There is no symmetry element in G^{k_Λ} that takes $+k_\Lambda$ to $-k_\Lambda$. This is the degeneracy type (d)

L Point Al_2O_3

$\{g\|\tau\}$	E	C_{21}''/τ	I	σ_{v1}/τ
$\{g\|\tau\}$	1	7.1	13	19.1
L_1	$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & -1\\ -1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\ 1 & 0\end{bmatrix}$
L_2	$\begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix}$	$\begin{bmatrix}i & 0\\ 0 & -i\end{bmatrix}$	$\begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}$

Table A.8: Table of Matrix Irreducible Representation at Point P

	E	C_3^+	C_3^-	σ_{v1}/τ	σ_{v3}/τ	σ_{v2}/τ
$\{g/\tau\}$	1	3	5	19.1	21.1	23.1
P_1	1	1	1	1	1	1
P_2	1	1	1	-1	-1	-1
P_3	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$
P_4	1	-1	1	i	$-i$	i
P_5	1	-1	1	$-i$	i	$-i$
P_6	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$\begin{bmatrix}0&-\omega\\\omega^*&0\end{bmatrix}$

Table A.9: Table of Matrix Irreducible Representation at Point Λ

$\{g/\tau\}$	E	C_3^+	C_3^-	σ_{v1}/τ	σ_{v3}/τ	σ_{v2}/τ
$\{g/\tau\}$	1	3	5	19.1	21.1	23.1
Λ_1	1	1	1	$1, T$	$1, T$	$1, T$
Λ_2	1	1	1	$-1, T$	$-1, T$	$-1, T$
Λ_3	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$
Λ_4	1	-1	1	$-1, iT$	$1, iT$	$-1, iT$
Λ_5	1	-1	1	$1, iT$	$-1, iT$	$1, iT$
Λ_6	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}-\omega^*&0\\0&-\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}0&\omega^*\\-\omega&0\end{bmatrix}$	$\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$

F Point Al_2O_3 (A setting)

$\{g\|\tau\}$	E	C_{23}''/τ	I	σ_{v3}/τ
$\{g/\tau\}$	1	9.1	13	21.1
$F_{A_{1+}}$	1	1	1	1
$F_{A_{2+}}$	1	-1	1	-1
$F_{A_{1-}}$	1	1	-1	-1
$F_{A_{2-}}$	1	-1	-1	1
$F_{A_{3+}}$	1	$-i$	1	$-i$
$F_{A_{4+}}$	1	i	1	i
$F_{A_{3-}}$	1	$-i$	1	i
$F_{A_{4-}}$	1	i	-1	$-i$

F Point Al_2O_3 (B-setting)

$\{g\|\tau\}$	E	C_{22}''/τ	I	σ_{v2}/τ
$\{g/\tau\}$	1	11.1	13	23.1
$F_{B_{1+}}$	1	1	1	1
$F_{B_{2+}}$	1	-1	1	-1
$F_{B_{1-}}$	1	1	-1	-1
$F_{B_{2-}}$	1	-1	-1	1
$F_{B_{3+}}$	1	$-i$	1	$-i$
$F_{B_{4+}}$	1	i	1	i
$F_{B_{3-}}$	1	$-i$	1	i
$F_{B_{4-}}$	1	i	-1	$-i$

Table A.10: Table for Reality Test of Λ Line

g	1	3	5	19.1	21.1	23.1
Λ_1	1	1	1	$1, T$	$1, T$	$1, T$
Λ_2	1	1	1	$-1, T$	$-1, T$	$-1, T$
Λ_3	2	-1	-1	0	0	0
Λ_4	1	-1	1	$-i, T$	i, T	$-i, T$
Λ_5	1	-1	1	i, T	$-i, T$	i, T
Λ_6	2	1	-1	0	0	0
g^2	1	5	3	$1t_0$	$1t_0$	$1t_0$
$\Lambda_{1,2}$	1	1	1	$1\omega'$	$1\omega'$	$1\omega'$
Λ_3	2	-1	-1	$1\omega'$	$1\omega'$	$1\omega'$
$\Lambda_{4,5}$	1	-1	1	$1\omega'$	$1\omega'$	$1\omega'$
Λ_6	2	-1	1	$1\omega'$	$1\omega'$	$1\omega'$

Σ-line Al_2O_3

$\{g\|\tau\}$	E	C''_{23}/τ
$\{g/\tau\}$	1	9.1
Σ_1	1	1
Σ_2	1	-1
Σ_3	1	$-i$
Σ_4	1	i

Y Point Al_2O_3

$\{g\|\tau\}$	E	C'_{21}/τ
$\{g/\tau\}$	1	7.1
Y_1	1	1
Y_2	1	-1
Y_3	1	i
Y_4	1	$-i$

B Point Al_2O_3

$\{g\|\tau\}$	E	C''_{23}/τ
$\{g\|\tau\}$	1	9.1
B_1	1	1
B_2	1	-1
B_3	1	i
B_4	1	$-i$

Q Point Al_2O_3

$\{g\|\tau\}$	E	C''_{22}/τ
$\{g\|\tau\}$	1	11.1
Q_1	1	1
Q_2	1	-1
Q_3	1	i
Q_4	1	$-i$

C line Al_2O_3

$\{g\|\tau\}$	E	σ_{v1}/τ
$\{g/\tau\}$	1	19.1
C_1	1	$1,\ T$
C_2	1	$-1,\ T$
C_3	1	$-1, iT$
C_4	1	$1, iT$

D Line Al_2O_3

$\{g\|\tau\}$	E	σ_{v2}/τ
$\{g/\tau\}$	1	23.1
D_1	1	$1,\ T$
D_2	1	$-1,\ T$
D_3	1	$-1, iT$
D_4	1	$1, iT$

E line Al_2O_3

$\{g\|\tau\}$	E	σ_{v3}/τ
$\{g\|\tau\}$	1	21.1
E_1	1	$1,\ T$
E_2	1	$-1,\ T$
E_3	1	$-1, iT$
E_4	1	$1, iT$

Character Tables and Matrix elements for SV and DV irreducible representations C_{6v}^4

ZnO	E	C_6^+/τ	C_3^-	C_2/τ	C_3^+	C_6^-/τ	σ_{v1}	σ_{d2}/τ	σ_{v3}	σ_{d1}/τ	σ_{v2}	σ_{d3}/τ
$\{g/\tau\}$	1	2.1	3	4.1	5	6.1	19	20.1	21	22.1	23	24.1
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
Γ_3	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1
Γ_4	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1
Γ_5	2	1	−1	2	−1	−1	0	0	0	0	0	0
Γ_6	2	−1	−1	−2	−1	1	0	0	0	0	0	0
Γ_7	2	i	1	0	−1	0	0	0	0	0	0	0
Γ_8	2	$-i$	1	0	−1	0	0	0	0	0	0	0
Γ_9	2	0	−2	0	2	0	0	0	0	0	0	0

Table A.11: Character Table of ZnO at Γ point

ZnO $\{g/\tau\}$	E 1	C_6^+/τ 2.1	C_3^- 3	C_2/τ 4.1	C_3^+ 5	C_6^-/τ 6.1	σ_{v1} 19	σ_{d2}/τ 20.1	σ_{v3} 21	σ_{d1}/τ 22.1	σ_{v2} 23	σ_{d3}/τ 24.1
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
Γ_3	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1
Γ_4	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1
Γ_5	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -\omega^* & 0 \\ 0 & -\omega \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \omega^* & 0 \\ 0 & \omega \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ \omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ \omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -\omega^* \\ -\omega & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ \omega^* & 0 \end{bmatrix}$
Γ_6	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \omega^* & 0 \\ 0 & \omega \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} \omega^* & 0 \\ 0 & \omega \end{bmatrix}$	$\begin{bmatrix} -\omega & 0 \\ 0 & -\omega^* \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega^* \\ \omega & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -\omega \\ -\omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega^* \\ \omega & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ \omega^* & 0 \end{bmatrix}$
Γ_7	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -i\omega & 0 \\ 0 & -i\omega^* \end{bmatrix}$	$\begin{bmatrix} -\omega^* & 0 \\ 0 & -\omega \end{bmatrix}$	$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix}$	$\begin{bmatrix} -i\omega^* & 0 \\ 0 & i\omega \end{bmatrix}$	$\begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ -\omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i\omega^* \\ -i\omega & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & i\omega \\ -i\omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & i\omega \\ -i\omega^* & 0 \end{bmatrix}$
Γ_8	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} i\omega & 0 \\ 0 & i\omega^* \end{bmatrix}$	$\begin{bmatrix} -\omega^* & 0 \\ 0 & -\omega \end{bmatrix}$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$	$\begin{bmatrix} \omega & 0 \\ 0 & \omega^* \end{bmatrix}$	$\begin{bmatrix} i\omega^* & 0 \\ 0 & -i\omega \end{bmatrix}$	$\begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega \\ -\omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & i\omega^* \\ i\omega & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i\omega \\ i\omega^* & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & \omega^* \\ -\omega & 0 \end{bmatrix}$
Γ_9	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$	$\begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & i \\ i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$

Table A.12: Table of Zinc Oxide Matrix Representations at k = 0 Γ Point

$\{g/\tau\}$	E	C_6^+/τ	C_3^-	C_2/τ	C_3^+	C_6^-/τ	σ_{v1}	σ_{d2}/τ	σ_{v3}	σ_{d1}/τ	σ_{v2}	σ_{d3}/τ
$\{g/\tau\}$	1	2.1	3	4.1	5	6.1	19	20.1	21	22.1	23	24.1
Δ_1	1	$1, T$	1	$1, T$	1	$1, T$	1	$1, T$	1	$1, T$	1	$1, T$
Δ_2	1	$1, T$	1	$1, T$	1	$1, T$	-1	$-1, T$	-1	$-1, T$	-1	$-1, T$
Δ_3	1	$-1, T$	1	$-1, T$	1	$-1, T$	-1	$1, T$	-1	$1, T$	-1	$1, T$
Δ_4	1	$-1, T$	1	$-1, T$	1	$-1, T$	1	$-1, T$	1	$-1, T$	1	$-1, T$
Δ_5	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$T\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$T\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T^2\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$T^2\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$	$T\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$
Δ_6	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$T\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$T\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T^2\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega^*\\\omega&0\end{bmatrix}$	$T^2\begin{bmatrix}0&-\omega\\-\omega^*&0\end{bmatrix}$	$T\begin{bmatrix}0&1\\1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&-\omega^*\\\omega&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega\\\omega^*&0\end{bmatrix}$
Δ_7	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$T\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$T\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T^2\begin{bmatrix}0&-i\\-i&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$T^2\begin{bmatrix}0&i\omega^*\\i\omega&0\end{bmatrix}$	$T\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&i\omega\\i\omega^*&0\end{bmatrix}$	$T\begin{bmatrix}0&-\omega^*\\\omega&0\end{bmatrix}$
Δ_8	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$T\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$T\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T^2\begin{bmatrix}0&i\\i&0\end{bmatrix}$	$T\begin{bmatrix}0&\omega\\-\omega^*&0\end{bmatrix}$	$T^2\begin{bmatrix}0&-i\omega^*\\-i\omega&0\end{bmatrix}$	$T\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&-i\omega\\-i\omega^*&0\end{bmatrix}$	$T\begin{bmatrix}0&-\omega^*\\\omega&0\end{bmatrix}$
Δ_9	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$T\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}\omega^*&0\\0&\omega\end{bmatrix}$	$T\begin{bmatrix}\omega&0\\0&\omega^*\end{bmatrix}$	$T^2\begin{bmatrix}0&-i\\-i&0\end{bmatrix}$	$T\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&i\\i&0\end{bmatrix}$	$T\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$T^2\begin{bmatrix}0&i\\i&0\end{bmatrix}$	$T\begin{bmatrix}0&-1\\1&0\end{bmatrix}$

Table A.13: Matrix Representation of Δ Point

$\{g/\tau\}$	E	C_6^+/τ	C_3^-	C_2/τ	C_3^+	C_6^-/τ	σ_{v1}	σ_{d2}/τ	σ_{v3}	σ_{d1}/τ	σ_{v2}	σ_{d3}/τ
$\{g/\tau\}$	1	2.1	3	4.1	5	6.1	19	20.1	21	22.1	23	24.1
A_1	1	i	1	i	1	i	1	i	1	i	1	i
A_2	1	i	1	i	1	i	-1	$-i$	-1	$-i$	-1	$-i$
A_3	1	$-i$	1	$-i$	1	$-i$	1	i	-1	i	-1	i
A_4	1	$-i$	1	$-i$	1	$-i$	-1	$-i$	1	$-i$	1	$-i$
A_5	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}i\omega^* & 0\\0 & i\omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}i & 0\\0 & i\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & -\omega\end{bmatrix}$	$\begin{bmatrix}i\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}0 & i\\i & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega*\\\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & i\omega\\-i\omega^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & i\omega*\\-i\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\omega\\\omega* & 0\end{bmatrix}$
A_6	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}0 & -i\\-i & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega^*\\\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\omega^*\\-i\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -i\omega*\\i\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\omega\\\omega* & 0\end{bmatrix}$
A_7	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}0 & -i\\-i & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega\\-\omega^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\omega^*\\\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -\omega\\\omega^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega^*\\\omega & 0\end{bmatrix}$
A_8	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}0 & i\\i & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega\\-\omega^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega^*\\-\omega & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega\\-\omega^* & 0\end{bmatrix}$	$\begin{bmatrix}0 & \omega^*\\\omega & 0\end{bmatrix}$
A_9	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}\omega^* & 0\\0 & \omega\end{bmatrix}$	$\begin{bmatrix}\omega & 0\\0 & \omega^*\end{bmatrix}$	$\begin{bmatrix}0 & -i\\-i & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

Table A.14: Table of Matrix Representation of A point ZnO

g	1	2.1	3	4.1	5	6.1	19	20.1	21	22.1	23	24.1
A_1	1	i	1	i	1	i	1	i	1	i	1	i
A_2	1	i	1	i	1	i	-1	$-i$	-1	$-i$	-1	$-i$
A_3	1	$-i$	1	$-i$	1	-1	-1	i	-1	i	-1	i
A_4	1	$-i$	1	$-i$	-1	$-i$	1	$-i$	1	$-i$	1	$-i$
A_5	2	$-i$	-1	$2,T$	-1	-1	0	0	0	0	0	0
A_6	2	i	-1	$2,T$	-1	0	0	0	0	0	0	0
A_7	2	$-B,T$	1	0	-1	B,T	0	0	0	0	0	0
A_8	2	B,T	1	0	-1	$-B,T$	0	0	0	0	0	0
A_9	2	0	-2	0	2	0	0	0	0	0	0	0
g^2	1	$3t_0$	5	$1t_0$	3	$5t_0$	1	$1t_0$	1	$1t_0$	1	$1t_0$
$A_{1,2,3,4}$	1	$1(-1)$	1	$1(-1)$	1	$1(-1)$	1	$1(-1)$	1	$1(-1)$	1	$1(-1)$
$A_{5,6}$	2	$2(-1)$	-1	$2(-1)$	2	$-1(-1)$	2	$2(-1)$	2	$2(-1)$	2	$2(-1)$
$A_{7,8}$	2	$2(-1)$	-1	$2(-1)$	2	$-1(-1)$	2	$2(-1)$	2	$2(-1)$	2	$2(-1)$
A_9	2	$2(-1)$	2	$2(-1)$	-2	$2(-1)$	2	$2(-1)$	2	$2(-1)$	2	$2(-1)$

Table A.15: Reality Test A point ZnO

For A_{1-6} irrps (SV) belong to

Character Table for ZnO $\Delta-$line

All irreducible representations are complex Δ_{1-9}. There is no symmetry element that takes $+k_\Delta$ to $-k_\Delta$. This type of degeneracy is case (x) ,(d)

H-Point ZnO

$\{g/\tau\}$	1	3	5	20.1	22.1	24.1
H_1	1	1	1	i	i	i
H_2	1	1	1	$-i$	$-i$	$-i$
H_3	2	-1	-1	0	0	0
H_4	1	-1	1	-1	1	-1
H_5	1	-1	1	1	-1	1
H_6	2	1	-1	0	0	0

K-Point ZnO

$\{g/\tau\}$	1	3	5	20.1	22.1	24.1
K_1	1	1	1	1	1	1
K_2	1	1	1	-1	-1	-1
K_3	2	-1	-1	0	0	0
K_4	1	-1	1	$-i$	i	$-i$
K_5	1	-1	1	i	$-i$	i
K_6	2	1	-1	0	0	0

M-Point ZnO

$\{g/\tau\}$	1	4.1	20.1	23
M_1	1	1	1	1
M_2	1	1	-1	-1
M_3	1	-1	1	-1
M_4	1	-1	-1	1
M_5	2	0	0	0

U-point ZnO

$\{g/\tau\}$	1	4.1	20.1	23
U_1	1	$1,T$	$1,T$	1
U_2	1	$1,T$	$-1,T$	-1
U_3	1	$-1,T$	$1,T$	-1
U_4	1	$-1,T$	$-1,T$	1
U_5	2	0	0	0

$\{g/\tau\}$	1	2.1	3	4.1	5	6.1	19	20.1	21	22.1	23	24.1
Δ_1	1	$1,T$	1	$1,T$	1	$1,T$	1	$1,T$	1	$1,T$	1	$1,T$
Δ_2	1	$1,T$	1	$1,T$	1	$1,T$	-1	$-1,T$	-1	$-1,T$	-1	$-1,T$
Δ_3	1	$-1,T$	1	$-1,T$	1	$-1,T$	-1	$1,T$	-1	$1,T$	-1	$1,T$
Δ_4	1	$-1,T$	1	$-1,T$	1	$-1,T$	1	$-1,T$	1	$-1,T$	1	$-1,T$
Δ_5	1	$-1,T$	-1	$2,T$	-1	$-1,T$	0	0	0	0	0	0
Δ_6	2	$1,T$	-1	$2,T$	-1	$1,T$	0	0	0	0	0	0
Δ_7	2	$-B,T$	1	0	-1	B,T	0	0	0	0	0	0
Δ_8	2	B,T	1	0	-1	$-B,T$	0	0	0	0	0	0
Δ_9	2	0	2	0	2	0	0	0	0	0	0	0
g^2	1	$3t_0$	5	$1t_0$	3	$5t_0$	1	$1t_0$	1	$1t_0$	1	$1t_0$
$\Delta_{1,2,3,4}$	1	$1(-1)$	1	$2(-1)$	1	$1(-1)$	1	$1(-1)$	1	$1(-1)$	2	$1(-1)$
$\Delta_{5,6}$	2	$1(-1)$	-1	$2(-1)$	-1	$-1(-1)$	2	$2(-1)$	2	$2(-1)$	2	$2(-1)$
$\Delta_{7,8}$	2	$1(-1)$	1	$2(-1)$	-1	$-1(-1)$	2	$2(-1)$	2	$2(-1)$	2	$2(-1)$
Δ_9	2	$-2(-1)$	2	$2(-1)$	2	$2(-2)$	2	$2(-1)$	2	$-2(-1)$	2	$2(-1)$

Table A.16: Reality test for Δ point in ZnO

L-point ZnO

$\{g/\tau\}$	1	4.1	20.1	23
L_1	1	i	i	1
L_2	1	i	$-i$	-1
L_3	1	$-i$	i	-1
L_4	1	$-i$	$-i$	1
L_5	2	0	0	0

Λ-Line ZnO

$\{g/\tau\}$	1	24.1
Λ_1	1	1
Λ_2	1	1
Λ_3	1	-1
Λ_4	1	-1

Σ-Line ZnO

$\{g/\tau\}$	1	23
Σ_1	1	1
Σ_2	1	-1
Σ_3	1	i
Σ_4	1	$-i$

Q-Line ZnO

$\{g/\tau\}$	1	24.1
Q_1	1	i
Q_2	1	$-i$
Q_3	1	-1
Q_4	1	1

R-Line ZnO

$\{g/\tau\}$	1	23
R_1	1	1
R_2	1	-1
R_3	1	$-i$
R_4	1	i

S-Line ZnO

$\{g/\tau\}$	1	20.1
S_1	1	i
S_2	1	$-i$
S_3	1	1
S_4	1	-1

T-Line ZnO

$\{g/\tau\}$	1	20.1
T_1	1	1
T_2	1	-1
T_3	1	i
T_4	1	$-i$

C-Line ZnO

$\{g/\tau\}$	1	24.1
C_1	1	$1,T$
C_2	1	$-1,T$
C_3	1	$-i,T$
C_4	1	i,T

D-Line ZnO

$\{g/\tau\}$	1	23
D_1	1	1
D_2	1	-1
D_3	1	i
D_4	1	$-i$

Table A.17: Symmetry Type of Irreducible Representation for Sapphire

High Symmetry points and lines	Real and (SV) Representation	Complex Representation (SV and DV)	
Γ	$\Gamma_{1\pm,2\pm,3\pm}\,(SV)$		$\Gamma_{4\pm,5\pm,6\pm}\,(DV)$
Λ		$\Lambda_{1,2,3}\,(SV)$	$\Lambda_{4,5,6}\,(DV)$
T		$T_{1,2,3}\,(SV)$	$T_{4,5,6}\,(DV)$
F	$F_{1\pm,2\pm}\,(SV)$		$F_{3\pm,4\pm}\,(DV)$
L	$L_1\,(SV)$		$L_2\,(DV)$
P		$P_{1,2,3}\,(SV)$	$P_{4,5,6}\,(DV)$
Σ	$\Sigma_{1,2}\,(SV)$		$\Sigma_{3,4}\,(DV)$
Y	$Y_{1,2}\,(SV)$		$Y_{3,4}\,(DV)$

A.7 Classification of Irreducible Representations. Reality Test

Single Valued Representation Time Reversal subjected

ZnO : A_{1-6} Δ_{1-6} P_{1-3}

Al_2O_3 : Λ_{1-3} P_{1-3} T_{1-3}

Single Valued Representation Time Reversal affected

ZnO : $\Gamma_{6,7,8}$ $\Delta_{7,8,9}$ $A_{7,8,9}$ $\Lambda_{3,4}$ $P_{4,5,6}$ $K_{4,5,6}$ $H_{4,5}$ $R_{3,4}$
$S_{3,4}$ L_5 M_5 U_5

Al_2O_3 : $\Gamma_{4\pm,5\pm,6\pm}$ $P_{4,5,6}$ $\Lambda_{4,5,6}$ $T_{4,5,6}$ $\Sigma_{4,5}$ $F_{A3\pm,4\pm}$ $Y_{3,4}$ L_2

Table A.18: Symmetry Type of Irreducible Representation for Zinc Oxide

Symmetry	Real Representation	Complex Representation (SV and DV)	
Γ	$\Gamma_{1-6}\,(SV)$		$\Gamma_{7,8,9}\,(DV)$
A		$A_{1-6}\,(SV)$	$A_{7,8,9}\,(DV)$
Δ		$\Delta_{1-6}\,(SV)$	$\Delta_{7,8,9}\,(DV)$
K	$K_{1,2,3}\,(SV)$		$K_{4,5,6}\,(DV)$
H	$H_{1,2,3}$		$H_{4,5,6}\,(DV)$
P	$P_{1,2,3}\,(SV)$		$P_{4,5,6}\,(DV)$
M	$M_{1-4}\,(SV)$		$M_5\,(DV)$
U	$U_{1-4}\,(SV)$		$U_5\,(DV)$
L	$L_{1-4}\,(SV)$		$L_5\,(DV)$
Λ	$\Lambda_{1,2}(SV)$		$\Lambda_{3,4}\,(DV)$
Σ	$\Sigma_{1,2}\,(SV)$		$\Sigma_{3,4}\,(DV)$
Q	$Q_{1,2}\,(SV)$		$Q_5\,(DV)$
R	$R_{1,2}\,(SV)$		$R_{3,4}\,(DV)$
S	$S_{1,2}\,(SV)$		$S_{3,4}\,(DV)$
T	$T_{1,2}\,(SV)$		$T_{3,4}\,(DV)$
C	$C_{1,2}$		
D	$D_{1,2}$		

A.8 Wave Vector Selection Rules

The interaction of particles or quasiparticles, for example phonons described by the KP. The wave vector selection rules (WVSR) governs also the multiphonon selection rules in a crystal. The Kronecker products of irrps obey the WVSR. For a Λ- phonon interaction, for example, this means the Kronecker product $\Lambda \otimes \Lambda = \Lambda$ is to be interpreted as follows:

$$\hbar g_i \boldsymbol{k}_\Lambda + \hbar g_j \boldsymbol{k}_\Lambda = \hbar \boldsymbol{k}_\Lambda$$

where $\hbar g_i \boldsymbol{k}_\Lambda$ and $\hbar g_j \boldsymbol{k}_\Lambda$ are arms of $\boldsymbol{k}_\Lambda$ in the star $\{{}^*\boldsymbol{k}_\Lambda\}$ and $\boldsymbol{k}_\Lambda$ is the first wave vector according to which the irrps of the $G^{\boldsymbol{k}_\Lambda}$ transform. The equation represents the conservation of momemtum of a quasiparticle, in this case the phonon. In the following tables we list the WVSR for interaction of particles (quasiparticles) in general and for Symmetrized Wave Vector Selection Rules (SWVSR) which are relevant for Raman scattering processes. The inclusion of TRS does not change the optical selection rules. The inclusion of TRS only increases the number of state with the same symmetry.

A.8.1 Symmetrized Wave Vector Selection Rules

The necessary theory for the decomposition of symmetrized kronecker products (SKP) has been outlined by several authors and in the CDML tables. The SKP and the selections rules are used in connection with the Raman allowed modes and multiphonon processes. There are useful for the interpertation of the phonon dispersion curves and electronic band structure of crystals. In here we list all the two particle (quasi-particle) interaction without taking into account the Time Reversal Symmetry.

Symmetrized squares (SKP) and Wave Vector Selection Rules for Sapphire $\mathbf{Al_2O_3}$

$\Gamma \otimes \Gamma = \Gamma$

$$\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Gamma + (1)\boldsymbol{k}_\Gamma = \boldsymbol{k}_\Gamma \\
&\Gamma_{3+} \otimes \Gamma_{3+} = \Gamma_{3-} \otimes \Gamma_{3-} = [\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2+}\} \\
&\Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{2+} \otimes \Gamma_{2+} = \Gamma_{1-} \otimes \Gamma_{1-} = \Gamma_{2-} \otimes \Gamma_{2-} = [\Gamma_{1+}] \oplus \{\} \\
&\Gamma_{3+} \otimes \Gamma_{3+} = \Gamma_{3-} \otimes \Gamma_{3-} = [\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2+}\} \\
&\Gamma_{4+} \otimes \Gamma_{4+} = \Gamma_{5+} \otimes \Gamma_{5+} = \Gamma_{4-} \otimes \Gamma_{4-} = \Gamma_{5-} \otimes \Gamma_{5-} = [\Gamma_{2+}] \oplus \{\} \\
&\Gamma_{6+} \otimes \Gamma_{6+} = \Gamma_{6-} \otimes \Gamma_{6-} = [\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1+}\}
\end{aligned}$$

$P \otimes P = \Gamma \oplus P$

$$\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_P + (7)\boldsymbol{k}_P = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (7)\boldsymbol{k}_P + (7)\boldsymbol{k}_P = \boldsymbol{k}_P \\
&P_1 \otimes P_1 = P_2 \otimes P_2 = 1:[\Gamma_{1+}] \oplus \{\Gamma_{2-}\} \qquad 2:[P_1] \oplus \{\} \\
&P_3 \otimes P_3 = [\Gamma_{1+} \oplus \Gamma_{3+} \oplus \Gamma_{1-}] \oplus \{\Gamma_{2+} \oplus \Gamma_{2-} \oplus \Gamma_{3-}\} \\
&\qquad\qquad 2:[P_1 \oplus P_3] \oplus \{P_2\} \\
&P_4 \otimes P_4 = P_5 \otimes P_5 = [\Gamma_{2+}] \oplus \{\Gamma_{1-}\} \qquad 2:[P_2] \oplus \{\} \\
&P_6 \otimes P_6 = [\Gamma_{2+} \oplus \Gamma_{3+} \oplus \Gamma_{2-}] \oplus \{\Gamma_{1+} \oplus \Gamma_{1-} \oplus \Gamma_{3-}\} \\
&\qquad\qquad 2:[P_2 \oplus P_3] \oplus \{P_1\}
\end{aligned}$$

$T \otimes T = \Gamma$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_T + (1)\boldsymbol{k}_T = \boldsymbol{k}_\Gamma$$

$$T_{1+} \otimes T_{1+} = T_{2+} \otimes T_{2+} = T_{1-} \otimes T_{1-} = T_{2-} \otimes T_{2-} = [\Gamma_{1+}] \oplus \{\}$$

$$T_{3+} \otimes T_{3+} = T_{3-} \otimes T_{3-} = [\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2+}\}$$

$$T_{4+} \otimes T_{4+} = T_{4-} \otimes T_{4-} = T_{5+} \otimes T_{5+} = T_{5-} \otimes T_{5-} = [\Gamma_{2+}] \oplus \{\}$$

$$T_{6+} \otimes T_{6+} = T_{6-} \otimes T_{6-} = [\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1+}\}$$

$\Lambda \otimes \Lambda = \Gamma \oplus \Lambda$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Lambda + (7)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Gamma$$

$$\texttt{Channel}\,2: \quad (1)\boldsymbol{k}_\Lambda + (1)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Lambda$$

$$\Lambda_1 \otimes \Lambda_1 = \Lambda_2 \otimes \Lambda_2 = 1 : [\Gamma_{1+}] \oplus \{\Gamma_{2-}\} \qquad 2 : [\Lambda_1] \oplus \{\Lambda_1\}$$

$$\Lambda_3 \otimes \Lambda_3 = 1 : [\Gamma_{1+} \oplus \Gamma_{3+} \oplus \Gamma_{1-}] \oplus \{\Gamma_{2+} \oplus \Gamma_{2-} \oplus \Gamma_{3-}\}$$

$$2 : [\Lambda_1 \oplus \Lambda_2] \oplus \{\Lambda_2\}$$

$$\Lambda_4 \otimes \Lambda_4 = \Lambda_5 \otimes \Lambda_5 = 1 : [\Gamma_{2+}] \oplus \{\Gamma_{1-}\} \qquad 2 : [\Lambda_2] \oplus \{\}$$

$$\Lambda_6 \otimes \Lambda_6 = 1 : [\Gamma_{2+} \oplus \Gamma_{3+} \oplus \Gamma_{2-}] \oplus \{\Gamma_{1+} \oplus \Gamma_{1-} \oplus \Gamma_{3-}\}$$

$$2 : [\Lambda_2 \oplus \Lambda_3] \oplus \{\Lambda_1\}$$

$F \otimes F = \Gamma \oplus F$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_F + (7)\boldsymbol{k}_F = \boldsymbol{k}_\Gamma$$

$$\texttt{Channel}\,2: \quad (3)\boldsymbol{k}_F + (5)\boldsymbol{k}_F = \boldsymbol{k}_F$$

$$F_{1+} \otimes F_{1+} = F_{2+} \otimes F_{2+} = F_{1-} \otimes F_{1-} = F_{2-} \otimes F_{2-} = [\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\}$$

$$2 : [F_{1+}] \oplus \{F_{2+}\}$$

$$F_{3+} \otimes F_{3+} = F_{4+} \otimes F_{4+} = F_{3-} \otimes F_{3-} = F_{4-} \otimes F_{4-} = [\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\}$$

$$2 : [F_{2+}] \oplus \{F_{1+}\}$$

$\Sigma \otimes \Sigma = \Gamma \oplus \Sigma \oplus \Sigma \oplus D$

$$\begin{aligned}
&\texttt{Channel}\,1: && (\ 1)\boldsymbol{k}_\Sigma + (13)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (\ 1)\boldsymbol{k}_\Sigma + (\ 1)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,3: && (15)\boldsymbol{k}_\Sigma + (17)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: && (\ 1)\boldsymbol{k}_\Sigma + (15)\boldsymbol{k}_\Sigma = \boldsymbol{k}_D \\
&\Sigma_1 \otimes \Sigma_1 = \Sigma_2 \otimes \Sigma_2 = && 1:[\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1-} \oplus \Gamma_{3+}\} \qquad 2:[\Sigma_1] \oplus \{\} \\
& && 3:[\Sigma_1] \oplus \{\Sigma_2\} \qquad 4:[D_1] \oplus \{D_2\} \\
&\Sigma_3 \otimes \Sigma_3 = \Sigma_4 \otimes \Sigma_4 = && 1:[\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2-} \oplus \Gamma_{3-}\} \qquad 2:[\Sigma_2] \oplus \{\Sigma_1\} \\
& && 3:[\Sigma_1] \oplus \{\Sigma_1\} \qquad 4:[D_2] \oplus \{D_1\}
\end{aligned}$$

$L \otimes L = \Gamma \oplus F_A$

$$\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_L + (\,1)\boldsymbol{k}_L = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_L + (\,3)\boldsymbol{k}_L = \boldsymbol{k}_{F_A} \\
&L_{1+} \oplus L_{1+} = L_{2+} \oplus L_{2+} = L_{1-} \oplus L_{1-} = L_{2-} \oplus L_{2-} = && [\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\} \\
& && 2:[F_{A1+}] \oplus \{F_{A2+}\} \\
&L_{3+} \oplus L_{3+} = L_{3-} \oplus L_{3-} = L_{4+} \oplus L_{4+} = L_{4-} \oplus L_{4-} = && [\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\} \\
& && 2:[F_{A2+}] \oplus \{F_{A1+}\}
\end{aligned}$$

$Y \otimes Y = \Gamma \oplus \Sigma \oplus \Sigma \oplus E$

$$\begin{aligned}
&\texttt{Channel}\,1: && (\ 1)\boldsymbol{k}_Y + (13)\boldsymbol{k}_Y = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (17)\boldsymbol{k}_Y + (17)\boldsymbol{k}_Y = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,3: && (13)\boldsymbol{k}_Y + (15)\boldsymbol{k}_Y = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: && (\ 1)\boldsymbol{k}_Y + (15)\boldsymbol{k}_Y = \boldsymbol{k}_E \\
&Y_1 \otimes Y_1 = Y_2 \otimes Y_2 = && 1:[\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1-} \oplus \Gamma_{3-}\} \qquad 2:[\Sigma_1] \oplus \{\} \\
& && 3:[\Sigma_1] \oplus \{\Sigma_2\} \qquad 4:[E_1] \oplus \{E_2\} \\
&Y_3 \otimes Y_3 = Y_4 \otimes Y_4 = && 1:[\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2-} \oplus \Gamma_{3-}\} \qquad 2:[\Sigma_2] \oplus \{\} \\
& && 3:[\Sigma_2] \oplus \{\Sigma_1\} \qquad 4:[E_2] \oplus \{E_1\}
\end{aligned}$$

$C \otimes C = \Gamma \oplus \Sigma \oplus C \oplus D$

$$\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_C + (7)\boldsymbol{k}_C = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_C + (9)\boldsymbol{k}_C = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,3: && (1)\boldsymbol{k}_C + (1)\boldsymbol{k}_C = \boldsymbol{k}_C \\
&\texttt{Channel}\,4: && (5)\boldsymbol{k}_C + (1)\boldsymbol{k}_C = \boldsymbol{k}_D \\
&C_1 \otimes C_1 = C_2 \otimes C_2 = && 1:[\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_1] \oplus \{\Sigma_2\} \\
& && 3:[C_1] \oplus \{\} \quad 4:[D_1] \oplus \{D_2\} \\
&C_3 \otimes C_3 = C_4 \otimes C_4 = && 1:[\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_2] \oplus \{\Sigma_1\} \\
& && 3:[C_2] \oplus \{\} \quad 4:[D_2] \oplus \{D_1\}
\end{aligned}$$

$D \otimes D = \Gamma \oplus \Sigma \oplus C \oplus D$

$$\begin{aligned}
&\texttt{Channel}\,1: && (\ 1)\boldsymbol{k}_D + (11)\boldsymbol{k}_D = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (17)\boldsymbol{k}_D + (23)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,3: && (\ 1)\boldsymbol{k}_\Sigma + (\ 3)\boldsymbol{k}_\Sigma = \boldsymbol{k}_C \\
&\texttt{Channel}\,4: && (\ 1)\boldsymbol{k}_\Sigma + (\ 1)\boldsymbol{k}_\Sigma = \boldsymbol{k}_D \\
&D_1 \otimes D_1 = D_2 \otimes D_2 = && 1:[\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_1] \oplus \{\Sigma_2\} \\
& && 3:[C_1] \oplus \{C_2\} \quad 4:[D_1] \oplus \{\} \\
&D_3 \otimes D_3 = D_4 \otimes D_4 = && 1:[\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_1] \oplus \{\Sigma_2\} \\
& && 3:[C_2] \oplus \{C_1\} \quad 4:[D_2] \oplus \{\}
\end{aligned}$$

$E \otimes E = \Gamma \oplus \Sigma \oplus C \oplus E$

$$\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_E + (\ 9)\boldsymbol{k}_E = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (5)\boldsymbol{k}_E + (11)\boldsymbol{k}_E = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,3: && (3)\boldsymbol{k}_E + (\ 3)\boldsymbol{k}_E = \boldsymbol{k}_C \\
&\texttt{Channel}\,4: && (3)\boldsymbol{k}_E + (\ 5)\boldsymbol{k}_E = \boldsymbol{k}_E \\
&E_1 \otimes E_1 = E_2 \otimes E_2 = && 1:[\Gamma_{1+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{2-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_1] \oplus \{\Sigma_2\} \\
& && 3:[C_1] \oplus \{\} \quad 4:[E_1] \oplus \{E_2\} \\
&E_3 \otimes E_3 = E_4 \otimes E_4 = && 1:[\Gamma_{2+} \oplus \Gamma_{3+}] \oplus \{\Gamma_{1-} \oplus \Gamma_{3-}\} \quad 2:[\Sigma_2] \oplus \{\Sigma_1\} \\
& && 3:[C_2] \oplus \{\} \quad 4:[E_2] \oplus \{E_1\}
\end{aligned}$$

Symmetrized Squares (SKP) and Wave Vector Selection Rules for ZnO

$\Gamma \otimes \Gamma = \Gamma$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Gamma + (1)\boldsymbol{k}_\Gamma = \boldsymbol{k}_\Gamma$$

$$\Gamma_1 \otimes \Gamma_1 = \Gamma_2 \otimes \Gamma_2 = \Gamma_3 \otimes \Gamma_3 = \Gamma_4 \otimes \Gamma_4 = [\Gamma_1] \oplus \{\}$$

$$\Gamma_5 \otimes \Gamma_5 = \Gamma_6 \otimes \Gamma_6 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_2\}$$

$$\Gamma_7 \otimes \Gamma_7 = \Gamma_8 \otimes \Gamma_8 = [\Gamma_2 \oplus \Gamma_6] \oplus \{\Gamma_1\}$$

$$\Gamma_9 \otimes \Gamma_9 = [\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4] \oplus \{\Gamma_1\}$$

$\Delta \otimes \Delta = \Delta$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Delta + (1)\boldsymbol{k}_\Delta = \boldsymbol{k}_\Delta$$

$$\Delta_1 \otimes \Delta_1 = \Delta_2 \otimes \Delta_2 = \Delta_3 \otimes \Delta_3 = \Delta_4 \otimes \Delta_4 = [\Gamma_1] \oplus \{\}$$

$$\Delta_5 \otimes \Delta_5 = \Delta_6 \otimes \Delta_6 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_2\}$$

$$\Delta_7 \otimes \Delta_7 = \Delta_8 \otimes \Delta_8 = [\Gamma_2 \oplus \Gamma_6] \oplus \{\Gamma_1\}$$

$$\Delta_9 \otimes \Delta_9 = [\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4] \oplus \{\Gamma_1\}$$

$\Lambda \otimes \Lambda = \Gamma \oplus \Lambda \oplus \Lambda \oplus \Sigma$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Lambda + (4)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Gamma$$

$$\texttt{Channel}\,2: \quad (1)\boldsymbol{k}_\Lambda + (1)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Lambda$$

$$\texttt{Channel}\,3: \quad (6)\boldsymbol{k}_\Lambda + (2)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Lambda$$

$$\texttt{Channel}\,4: \quad (6)\boldsymbol{k}_\Lambda + (1)\boldsymbol{k}_\Lambda = \boldsymbol{k}_\Sigma$$

$$\Lambda_1 \otimes \Lambda_1 = \Lambda_2 \otimes \Lambda_2 = 1 : [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_3 \oplus \Gamma_6\} \qquad 2 : [\Lambda_1] \oplus \{\}$$

$$3 : [\Lambda_1] \oplus \{\Lambda_2\} \qquad 4 : [\Sigma_1] \oplus \{\Sigma_2\}$$

$$\Lambda_3 \otimes \Lambda_3 = \Lambda_4 \otimes \Lambda_4 = 1 : [\Gamma_3 \oplus \Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_5\} \qquad 2 : [\Lambda_2] \oplus \{\}$$

$$3 : [\Lambda_2] \oplus \{\Lambda_1\} \qquad 4 : [\Sigma_2] \oplus \{\Sigma_1\}$$

$\Sigma \otimes \Sigma = \Gamma \oplus \Lambda \oplus \Sigma \oplus \Sigma$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_\Sigma + (4)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Gamma$$

$$\texttt{Channel}\,2: \quad (1)\boldsymbol{k}_\Sigma + (2)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Lambda$$

$$\texttt{Channel}\,3: \quad (1)\boldsymbol{k}_\Sigma + (1)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Sigma$$

$$\texttt{Channel}\,4: \quad (6)\boldsymbol{k}_\Sigma + (2)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Sigma$$

$$\Sigma_1 \otimes \Sigma_1 = \Sigma_2 \otimes \Sigma_2 = 1 : [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_4 \oplus \Gamma_6\} \qquad 2 : [\Lambda_1] \oplus \{\Lambda_2\}$$

$$3 : [\Sigma_1] \oplus \{\} \qquad 4 : [\Sigma_1] \oplus \{\Sigma_2\}$$

$A \otimes A = \Gamma$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_A + (1)\boldsymbol{k}_A = \boldsymbol{k}_\Gamma$$

$$A_1 \otimes A_1 = A_2 \otimes A_2 = A_3 \otimes A_3 = A_4 \otimes A_4 = [\Gamma_4] \oplus \{\}$$

$$A_5 \otimes A_5 = A_6 \otimes A_6 = [\Gamma_4 \oplus \Gamma_6] \oplus \{\Gamma_3\}$$

$$A_7 \otimes A_7 = A_8 \otimes A_8 = [\Gamma_3 \oplus \Gamma_5] \oplus \{\Gamma_4\}$$

$$A_9 \otimes A_9 = [\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3] \oplus \{\Gamma_4\}$$

$H \otimes H = \Gamma \oplus K$

$$\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_H + (2)\boldsymbol{k}_H = \boldsymbol{k}_\Gamma$$

$$\texttt{Channel}\,2: \quad (2)\boldsymbol{k}_H + (2)\boldsymbol{k}_H = \boldsymbol{k}_K$$

$$H_1 \otimes H_1 = H_2 \otimes H_2 = [\Gamma_4] \oplus \{\Gamma_2\} \qquad 2 : [K_2] \oplus \{\}$$

$$H_3 \otimes H_3 = [\Gamma_4] \oplus \{\Gamma_2\} \qquad 2 : [K_2 \oplus K_3] \oplus \{K_1\}$$

$$H_4 \otimes H_4 = H_5 \otimes H_5 = [\Gamma_2] \oplus \{\Gamma_4\} \qquad 2 : [K_1] \oplus \{\}$$

$$H_6 \otimes H_6 = [\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_5] \oplus \{\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_6\}$$

$$2 : [K_1 \oplus K_3] \oplus \{K_2\}$$

$K \otimes K = \Gamma \oplus K$

$$\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_K + (1)\boldsymbol{k}_K = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (2)\boldsymbol{k}_K + (2)\boldsymbol{k}_K = \boldsymbol{k}_K \\
&K_1 \otimes K_1 = K_2 \otimes K_2 = [\Gamma_1] \oplus \{\Gamma_3\} \qquad 2 : [K_1] \oplus \{\} \\
&K_3 \otimes K_3 \qquad\qquad = [\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_5] \oplus \{\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_6\} \\
&\qquad\qquad\qquad\quad 2 : [K_1 \oplus K_3] \oplus \{K_2\} \\
&K_4 \otimes K_4 = K_5 \otimes K_5 = [\Gamma_3] \oplus \{\Gamma_1\} \qquad 2 : [K_2] \oplus \{\} \\
&K_6 \otimes K_6 \qquad\qquad = [\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_5\} \\
&\qquad\qquad\qquad\quad 2 : [K_2 \oplus K_3] \oplus \{K_1\}
\end{aligned}$$

$L \otimes L = \Gamma \oplus M$

$$\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_L + (1)\boldsymbol{k}_L = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (2)\boldsymbol{k}_L + (3)\boldsymbol{k}_L = \boldsymbol{k}_M \\
&L_1 \otimes L_1 = L_2 \otimes L_2 \quad = L_3 \otimes L_3 \\
&\qquad\qquad\qquad\quad = L_4 \otimes L_4 = [\Gamma_4 \oplus \Gamma_6] \oplus \{\} \qquad 2 : [M_4] \oplus \{M_3\} \\
&L_5 \otimes L_5 \qquad\qquad = [\Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus 2\Gamma_5 \oplus \Gamma_6] \oplus \{\Gamma_4 \oplus \Gamma_6\} \\
&\qquad\qquad\qquad\quad 2 : [M_1 \oplus M_2 \oplus 2M_3] \oplus \{M_1 \oplus M_2 \oplus 2M_4\}
\end{aligned}$$

$M \otimes M = \Gamma \oplus M$

$$\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_M + (1)\boldsymbol{k}_M = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (2)\boldsymbol{k}_M + (3)\boldsymbol{k}_M = \boldsymbol{k}_M \\
&M_1 \otimes M_1 = M_2 \otimes M_2 \quad = M_3 \otimes M_3 \\
&\qquad\qquad\qquad\quad = M_4 \otimes M_4 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\} \qquad 2 : [M_1] \oplus \{M_2\} \\
&M_5 \otimes M_5 \qquad\qquad = [\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus 2\Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_5\} \\
&\qquad\qquad\qquad\quad 2 : [2M_2 \oplus M_3 \oplus M_4] \oplus \{2M_1 \oplus M_3 \oplus M_4\}
\end{aligned}$$

$P \otimes P = \Delta \oplus P$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_P + (2)\boldsymbol{k}_P = \boldsymbol{k}_\Delta \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_P + (2)\boldsymbol{k}_P = \boldsymbol{k}_P \\
&P_1 \otimes P_1 = P_2 \otimes P_2 && = [\Delta_1] \oplus \{\Delta_3\} \qquad 2 : [P_1] \oplus \{\} \\
&P_3 \otimes P_3 && = [\Delta_1 \oplus \Delta_4 \oplus \Delta_5] \oplus \{\Delta_2 \oplus \Delta_3 \oplus \Delta_6\} \\
& && \quad 2 : [P_1 \oplus P_3] \oplus \{P_2\} \\
&P_4 \otimes P_4 = P_5 \otimes P_5 && = [\Delta_3] \oplus \{\Delta_1\} \qquad 2 : [P_2] \oplus \{\} \\
&P_6 \otimes P_6 && = [\Delta_2 \oplus \Delta_3 \oplus \Delta_6] \oplus \{\Delta_1 \oplus \Delta_4 \oplus \Delta_5\} \\
& && \quad 2 : [P_2 \oplus P_3] \oplus \{P_1\}
\end{aligned}
$$

$Q \otimes Q = \Gamma \oplus \Lambda \oplus \Lambda \oplus \Sigma$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_Q + (4)\boldsymbol{k}_Q = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_Q + (1)\boldsymbol{k}_Q = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: && (6)\boldsymbol{k}_\Sigma + (2)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,4: && (6)\boldsymbol{k}_Q + (1)\boldsymbol{k}_Q = \boldsymbol{k}_\Sigma \\
&Q_1 \otimes Q_1 = Q_2 \otimes Q_2 && = [\Gamma_4 \oplus \Gamma_6] \oplus \{\Gamma_2 \oplus \Gamma_5\} \qquad 2 : [\Lambda_2] \oplus \{\} \\
& && \quad 3 : [\Lambda_2] \oplus \{\Lambda_1\} \qquad 4 : [\Sigma_1] \oplus \{\Sigma_2\} \\
&Q_3 \otimes Q_3 = Q_4 \otimes Q_4 && = [\Gamma_2 \oplus \Gamma_5] \oplus \{\Gamma_4 \oplus \Gamma_5\} \qquad 2 : [\Lambda_1] \oplus \{\} \\
& && \quad 3 : [\Lambda_1] \oplus \{\Lambda_2\} \qquad 4 : [\Sigma_2] \oplus \{\Sigma_1\}
\end{aligned}
$$

$R \otimes R = \Gamma \oplus \Lambda \oplus \Sigma \oplus \Sigma$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_R + (4)\boldsymbol{k}_R = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_R + (2)\boldsymbol{k}_R = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: && (1)\boldsymbol{k}_R + (1)\boldsymbol{k}_R = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: && (6)\boldsymbol{k}_R + (2)\boldsymbol{k}_R = \boldsymbol{k}_\Sigma \\
&R_1 \otimes R_1 = R_2 \otimes R_2 && = [\Gamma_4 \oplus \Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_5\} \qquad 2 : [\Lambda_2] \oplus \{\Lambda_1\} \\
& && \quad 3 : [\Lambda_1] \oplus \{\} \qquad 4 : [\Sigma_1] \oplus \{\Sigma_2\} \\
&R_3 \otimes R_3 = Q_4 \otimes Q_4 && = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_4 \oplus \Gamma_6\} \qquad 2 : [\Lambda_1] \oplus \{\Lambda_2\} \\
& && \quad 3 : [\Lambda_2] \oplus \{\} \qquad 4 : [\Sigma_2] \oplus \{\Sigma_1\}
\end{aligned}
$$

$S \otimes S = \Gamma \oplus \Lambda \oplus \Sigma \oplus T$

$$
\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_S + (4)\boldsymbol{k}_S = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (6)\boldsymbol{k}_S + (6)\boldsymbol{k}_S = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: \quad (2)\boldsymbol{k}_S + (3)\boldsymbol{k}_S = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: \quad (6)\boldsymbol{k}_S + (2)\boldsymbol{k}_S = \boldsymbol{k}_T \\
&S_1 \otimes S_1 = S_2 \otimes S_2 \quad = [\Gamma_4 \oplus \Gamma_6] \oplus \{\Gamma_2 \oplus \Gamma_5\} \qquad 2 : [\Lambda_2] \oplus \{\} \\
&\qquad\qquad\qquad\qquad\quad\; 3 : [\Sigma_1] \oplus \{\Sigma_2\} \qquad 4 : [T_2] \oplus \{T_1\} \\
&S_3 \otimes S_3 = S_4 \otimes S_4 \quad = [\Gamma_2 \oplus \Gamma_5] \oplus \{\Gamma_4 \oplus \Gamma_5\} \qquad 2 : [\Lambda_1] \oplus \{\} \\
&\qquad\qquad\qquad\qquad\quad\; 3 : [\Sigma_2] \oplus \{\Sigma_1\} \qquad 4 : [T_1] \oplus \{T_2\}
\end{aligned}
$$

$T \otimes T = \Gamma \oplus \Lambda \oplus \Sigma \oplus T$

$$
\begin{aligned}
&\texttt{Channel}\,1: \quad (1)\boldsymbol{k}_T + (4)\boldsymbol{k}_T = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: \quad (6)\boldsymbol{k}_T + (6)\boldsymbol{k}_T = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: \quad (2)\boldsymbol{k}_T + (3)\boldsymbol{k}_T = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: \quad (6)\boldsymbol{k}_T + (2)\boldsymbol{k}_T = \boldsymbol{k}_T \\
&T_1 \otimes T_1 = T_2 \otimes T_2 \quad = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_3 \oplus \Gamma_6\} \qquad 2 : [\Lambda_1] \oplus \{\} \\
&\qquad\qquad\qquad\qquad\quad\; 3 : [\Sigma_1] \oplus \{\Sigma_2\} \qquad 4 : [T_1] \oplus \{T_2\} \\
&T_3 \otimes T_3 = T_4 \otimes T_4 \quad = [\Gamma_3 \oplus \Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_5\} \qquad 2 : [\Lambda_2] \oplus \{\} \\
&\qquad\qquad\qquad\qquad\quad\; 3 : [\Sigma_2] \oplus \{\Sigma_1\} \qquad 4 : [T_2] \oplus \{T_1\}
\end{aligned}
$$

$S \otimes S = \Gamma \oplus \Lambda \oplus \Sigma \oplus T$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_S + (4)\boldsymbol{k}_S = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (6)\boldsymbol{k}_S + (6)\boldsymbol{k}_S = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: && (2)\boldsymbol{k}_S + (3)\boldsymbol{k}_S = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: && (6)\boldsymbol{k}_S + (2)\boldsymbol{k}_S = \boldsymbol{k}_T \\
&S_1 \otimes S_1 = S_2 \otimes S_2 = [\Gamma_4 \oplus \Gamma_6] \oplus \{\Gamma_2 \oplus \Gamma_5\} && 2 : [\Lambda_2] \oplus \{\} \\
&\qquad\qquad 3 : [\Sigma_1] \oplus \{\Sigma_2\} && 4 : [T_2] \oplus \{T_1\} \\
&S_3 \otimes S_3 = S_4 \otimes S_4 = [\Gamma_2 \oplus \Gamma_5] \oplus \{\Gamma_4 \oplus \Gamma_5\} && 2 : [\Lambda_1] \oplus \{\} \\
&\qquad\qquad 3 : [\Sigma_2] \oplus \{\Sigma_1\} && 4 : [T_1] \oplus \{T_2\}
\end{aligned}
$$

$T \otimes T = \Gamma \oplus \Lambda \oplus \Sigma \oplus T$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_T + (4)\boldsymbol{k}_T = \boldsymbol{k}_\Gamma \\
&\texttt{Channel}\,2: && (6)\boldsymbol{k}_T + (6)\boldsymbol{k}_T = \boldsymbol{k}_\Lambda \\
&\texttt{Channel}\,3: && (2)\boldsymbol{k}_T + (3)\boldsymbol{k}_T = \boldsymbol{k}_\Sigma \\
&\texttt{Channel}\,4: && (6)\boldsymbol{k}_T + (2)\boldsymbol{k}_T = \boldsymbol{k}_T \\
&T_1 \otimes T_1 = T_2 \otimes T_2 = [\Gamma_1 \oplus \Gamma_5] \oplus \{\Gamma_3 \oplus \Gamma_6\} && 2 : [\Lambda_1] \oplus \{\} \\
&\qquad\qquad 3 : [\Sigma_1] \oplus \{\Sigma_2\} && 4 : [T_1] \oplus \{T_2\} \\
&T_3 \otimes T_3 = T_4 \otimes T_4 = [\Gamma_3 \oplus \Gamma_6] \oplus \{\Gamma_1 \oplus \Gamma_5\} && 2 : [\Lambda_2] \oplus \{\} \\
&\qquad\qquad 3 : [\Sigma_2] \oplus \{\Sigma_1\} && 4 : [T_2] \oplus \{T_1\}
\end{aligned}
$$

$U \otimes U = \Delta \oplus U$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_U + (4)\boldsymbol{k}_U = \boldsymbol{k}_\Delta \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_U + (2)\boldsymbol{k}_U = \boldsymbol{k}_U \\
&U_1 \otimes U_1 = U_2 \otimes U_2 = U_3 \otimes U_3 = U_4 \otimes U_4 && \\
&\qquad\qquad = [\Delta_1 \oplus \Delta_5] \oplus \{\} && 2 : [U_1] \oplus \{U_2\} \\
&U_5 \otimes U_5 && = [\Delta_2 \oplus \Delta_3 \oplus \Delta_4 \oplus \Delta_5 \oplus 2\Delta_6] \oplus \{\Delta_1 \oplus \Delta_5\} \\
&\qquad\qquad && 2 : [2U_2 \oplus U_3 \oplus U_4] \oplus \{2U_1 \oplus U_3 \oplus U_4\}
\end{aligned}
$$

$C \otimes C = \Delta \oplus C \oplus C \oplus D$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (\ 1)\boldsymbol{k}_\Sigma + (4)\boldsymbol{k}_\Sigma = \boldsymbol{k}_\Delta \\
&\texttt{Channel}\,2: && (\ 1)\boldsymbol{k}_\Sigma + (2)\boldsymbol{k}_\Sigma = \boldsymbol{k}_C \\
&\texttt{Channel}\,3: && (\ 1)\boldsymbol{k}_\Sigma + (1)\boldsymbol{k}_\Sigma = \boldsymbol{k}_C \\
&\texttt{Channel}\,4: && (16)\boldsymbol{k}_\Sigma + (2)\boldsymbol{k}_\Sigma = \boldsymbol{k}_D \\
&C_1 \otimes C_1 = C_2 \otimes C_2 = [\Delta_1 \oplus \Delta_5] \oplus \{\Delta_3 \oplus \Delta_6\} && 2 : [C_1] \oplus \{\} \\
&\qquad\qquad\qquad\qquad 3 : [C_1] \oplus \{C_2\} && 4 : [D_1] \oplus \{D_2\} \\
&C_3 \otimes C_3 = C_4 \otimes C_4 = [\Delta_3 \oplus \Delta_6] \oplus \{\Delta_1 \oplus \Delta_5\} && 2 : [C_2] \oplus \{\} \\
&\qquad\qquad\qquad\qquad 3 : [C_2] \oplus \{C_1\} && 4 : [D_2] \oplus \{D_1\}
\end{aligned}
$$

$D \otimes D = \Delta \oplus C \oplus D \oplus D$

$$
\begin{aligned}
&\texttt{Channel}\,1: && (1)\boldsymbol{k}_D + (4)\boldsymbol{k}_D = \boldsymbol{k}_\Delta \\
&\texttt{Channel}\,2: && (1)\boldsymbol{k}_D + (2)\boldsymbol{k}_D = \boldsymbol{k}_C \\
&\texttt{Channel}\,3: && (1)\boldsymbol{k}_D + (1)\boldsymbol{k}_D = \boldsymbol{k}_D \\
&\texttt{Channel}\,4: && (6)\boldsymbol{k}_D + (2)\boldsymbol{k}_D = \boldsymbol{k}_D \\
&D_1 \otimes D_1 = D_2 \otimes D_2 = [\Delta_1 \oplus \Delta_5] \oplus \{\Delta_4 \oplus \Delta_6\} && 2 : [C_1] \oplus \{C_2\} \\
&\qquad\qquad\qquad\qquad 3 : [D_1] \oplus \{\} && 4 : [D_1] \oplus \{D_2\} \\
&D_3 \otimes D_3 = D_4 \otimes D_4 = [\Delta_4 \oplus \Delta_6] \oplus \{\Delta_1 \oplus \Delta_5\} && 2 : [C_2] \oplus \{C_1\} \\
&\qquad\qquad\qquad\qquad 3 : [D_2] \oplus \{\} && 4 : [D_2] \oplus \{D_1\}
\end{aligned}
$$

A.9 Characters for Lattice Mode Representation

The matrices for LMR were derived in Ref. [29].

Characters of irreducible representations of D_{3d}^6 space group and the reducible lattice mode representation (LMR).

$\{g/\tau\}$	E	C_3^+	C_3^-	C_{21}''/τ	C_{23}''/τ	C_{22}''/τ	I	S_6^-	S_6^+	σ_{v1}/τ	σ_{v3}/τ	σ_{v2}/τ
$\{g/\tau\}$	1	3	5	7.1	9.1	11.1	13	15	17	19.1	21.1	23.1
$\Gamma_{1+}(A_{1g})$	1	1	1	1	1	1	1	1	1	1	1	1
$\Gamma_{2+}(A_{2g})$	1	1	1	−1	−1	−1	1	1	1	−1	−1	−1
$\Gamma_{3+}(E_g)$	2	−1	−1	0	0	0	2	−1	−1	0	0	0
$\Gamma_{1-}(A_{1u})$	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1
$\Gamma_{2-}(A_{2u})$	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1
$\Gamma_{3-}(E_u)$	2	−1	−1	0	0	0	−2	1	1	0	0	0
$\chi^{\mathrm{LMR}}\{g/\tau\}$	27	0	0	−1	−1	−1	3	0	0	−1	−1	−1

Normal Modes obtained by Lattice Mode Representation at high symmetry points and lines of D_{3d}^6 space group (Notation according to Ref. [23])

$\Gamma : 2\Gamma_{1+} \oplus 2\Gamma_{1-} \oplus 3\Gamma_{2+} \oplus 2\Gamma_{2-} \oplus 5\Gamma_{3+} \oplus 4\Gamma_{3-}$

$F : 7F_{1+} \oplus 8F_{2+} \oplus 6F_{1-} \oplus 6F_{2-}$

$\Sigma : 13\Sigma_1 \oplus 14\Sigma_2$

$Y : 13Y_1 \oplus 14Y_2$

$L : 27L_1$

Matrices for Wurtzite were derived in Ref. [20].

Normal Modes obtained by Lattice Mode representation at high symmetry points and lines of C_{6v}^4 space group (Notation according to Ref. [23]).

A.10 Table for Connectiviy Relations

Connectivity for Sapphire

$$\Gamma \to F : \Gamma_{1+} \to F_{1+},\ \Gamma_{2+} \to F_{2+},\ \Gamma_{3+} \to F_{1+} \oplus F_{2+},\ \Gamma_{1-} \to F_{2-},$$
$$\Gamma_{3-} \to F_{1-} \oplus F_{2-}$$

$$\Gamma \to \Lambda : \Gamma_{1+} \to \Lambda_1,\ \Gamma_{2+} \to \Lambda_2,\ \Gamma_{3+} \to \Lambda_3,\ \Gamma_{1-} \to \Lambda_2,\ \Gamma_{3-} \to \Lambda_3$$

$$\Gamma \to \Sigma : \Gamma_{1+} \to \Sigma_1,\ \Gamma_{2+} \to \Sigma_2,\ \Gamma_{3+} \to \Sigma_1 \oplus \Sigma_2,\ \Gamma_{1-} \to \Sigma_1,\ \Gamma_{2-} \to \Sigma_2,$$
$$\Gamma_{3-} \to \Sigma_1 \oplus \Sigma_2$$

$$T \to Y : T_1 \to Y_1 \oplus Y_2,\ T_2 \to Y_1 \oplus Y_2,\ T_3 \to Y_1 \oplus Y_2$$

$$T \to L : T_1 \to L_1,\ T_2 \to L_1,\ T_3 \to L_1$$

$$T \to P : T \to P \oplus P$$

$$L \to Y : L_1 \oplus L_2 \to 2Y_1 \oplus 2Y_2$$

$$F \to \Sigma : F_{1+} \to \Sigma_1,\ F_{2+} \to \Sigma_2,\ F_{1-} \to \Sigma_1,\ F_{2-} \to \Sigma_2$$

Connectivity for Wurtzite are given in Ref. [20].

A.11 Kronecker Products

The Kronecker products are computer calculated and available in CDML–tables [23]. Here we extract the relevant KP for SV and DV representations at Γ point.

Al_2O_3 (space group No. 167 A) D_{3d}^6

$$\Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{2+} \otimes \Gamma_{2+} = \Gamma_{1-} \otimes \Gamma_{1-} = \Gamma_{2-} \otimes \Gamma_{2-} = \Gamma_{4+} \otimes \Gamma_{5+} = \Gamma_{4-} \otimes \Gamma_{5-} = \Gamma_{1+}$$

$$\Gamma_{1+} \otimes \Gamma_{2+} = \Gamma_{1-} \otimes \Gamma_{2-} = \Gamma_{4+} \otimes \Gamma_{4+} = \Gamma_{5+} \otimes \Gamma_{5+} = \Gamma_{4-} \otimes \Gamma_{4-} = \Gamma_{5-} \otimes \Gamma_{5-} = \Gamma_{2+}$$

$$\Gamma_{1+} \otimes \Gamma_{3+} = \Gamma_{2+} \otimes \Gamma_{3+} = \Gamma_{1-} \otimes \Gamma_{3-} = \Gamma_{2-} \otimes \Gamma_{3-} = \Gamma_{4+} \otimes \Gamma_{6+} = \Gamma_{5+} \otimes \Gamma_{6+}$$
$$= \Gamma_{4-} \otimes \Gamma_{6-} = \Gamma_{5-} \otimes \Gamma_{6-} = \Gamma_{3+}$$

$$\Gamma_{1+} \otimes \Gamma_{1-} = \Gamma_{2+} \otimes \Gamma_{2-} = \Gamma_{4+} \otimes \Gamma_{5-} = \Gamma_{5+} \otimes \Gamma_{4-} = \Gamma_{1-}$$

$$\Gamma_{1+} \otimes \Gamma_{2-} = \Gamma_{2-} \otimes \Gamma_{1-} = \Gamma_{1-} \otimes \Gamma_{2+} = \Gamma_{1-} \otimes \Gamma_{2-} = \Gamma_{4+} \otimes \Gamma_{4-} = \Gamma_{5+} \otimes \Gamma_{5-} = \Gamma_{2-}$$

$$\Gamma_{1+} \otimes \Gamma_{3-} = \Gamma_{2+} \otimes \Gamma_{3-} = \Gamma_{3+} \otimes \Gamma_{1-} = \Gamma_{3+} \otimes \Gamma_{2-} = \Gamma_{1-} \otimes \Gamma_{3+} = \Gamma_{4+} \otimes \Gamma_{6-}$$
$$= \Gamma_{5+} \otimes \Gamma_{6-} = \Gamma_{6+} \otimes \Gamma_{4-} = \Gamma_{6+} \otimes \Gamma_{5-} = \Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{3-}$$

$$\Gamma_{1+} \otimes \Gamma_{4+} = \Gamma_{2+} \otimes \Gamma_{5+} = \Gamma_{1-} \otimes \Gamma_{4-} = \Gamma_{2-} \otimes \Gamma_{5-} = \Gamma_{4+} \otimes \Gamma_{1+} = \Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{4+}$$

$$\Gamma_{1+} \otimes \Gamma_{5+} = \Gamma_{2+} \otimes \Gamma_{4+} = \Gamma_{1-} \otimes \Gamma_{5-} = \Gamma_{2-} \otimes \Gamma_{4-} = \Gamma_{5+}$$

$$\Gamma_{1+} \otimes \Gamma_{6+} = \Gamma_{2+} \otimes \Gamma_{6+} = \Gamma_{3+} \otimes \Gamma_{4+} = \Gamma_{3+} \otimes \Gamma_{5+} = \Gamma_{1-} \otimes \Gamma_{6-} = \Gamma_{2-} \otimes \Gamma_{6-}$$
$$= \Gamma_{3-} \otimes \Gamma_{4-} = \Gamma_{3-} \otimes \Gamma_{5-} = \Gamma_{6+}$$

$$\Gamma_{1+} \otimes \Gamma_{4-} = \Gamma_{2+} \otimes \Gamma_{5-} = \Gamma_{1-} \otimes \Gamma_{4+} = \Gamma_{2-} \otimes \Gamma_{5+} = \Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{4-}$$

$$\Gamma_{1+} \otimes \Gamma_{5-} = \Gamma_{2+} \otimes \Gamma_{4-} = \Gamma_{1-} \otimes \Gamma_{5+} = \Gamma_{2-} \otimes \Gamma_{4+} = \Gamma_{1+} \otimes \Gamma_{1+} = \Gamma_{5-}$$

$$\Gamma_{1+} \otimes \Gamma_{6-} = \Gamma_{2+} \otimes \Gamma_{6-} = \Gamma_{3+} \otimes \Gamma_{4-} = \Gamma_{3+} \otimes \Gamma_{5-} = \Gamma_{1-} \otimes \Gamma_{6+} = \Gamma_{2-} \otimes \Gamma_{6+}$$
$$= \Gamma_{3-} \otimes \Gamma_{4+} = \Gamma_{3-} \otimes \Gamma_{5+} = \Gamma_{6-}$$

$$\Gamma_{3+} \otimes \Gamma_{3+} = \Gamma_{3-} \otimes \Gamma_{3-} = \Gamma_{6+} \otimes \Gamma_{6+} = \Gamma_{6-} \otimes \Gamma_{6-} = \Gamma_{1+} \oplus \Gamma_{2+} \oplus \Gamma_{3+}$$

$$\Gamma_{3+} \otimes \Gamma_{6+} = \Gamma_{3-} \otimes \Gamma_{6-} = \Gamma_{4+} \oplus \Gamma_{5+} \oplus \Gamma_{6+}$$

$$\Gamma_{3+} \otimes \Gamma_{6-} = \Gamma_{3-} \otimes \Gamma_{6+} = \Gamma_{4-} \oplus \Gamma_{5-} \oplus \Gamma_{6+}$$

ZnO (space group No.186) C_{6v}^4

$$\Gamma_1 \otimes \Gamma_1 = \Gamma_2 \otimes \Gamma_2 = \Gamma_3 \otimes \Gamma_3 = \Gamma_4 \otimes \Gamma_4 = \Gamma_1$$

$$\Gamma_1 \otimes \Gamma_2 = \Gamma_3 \otimes \Gamma_4 = \Gamma_2$$

$$\Gamma_1 \otimes \Gamma_3 = \Gamma_2 \otimes \Gamma_4 = \Gamma_3$$

$$\Gamma_1 \otimes \Gamma_4 = \Gamma_2 \otimes \Gamma_3 = \Gamma_4$$

$$\Gamma_1 \otimes \Gamma_5 = \Gamma_2 \otimes \Gamma_5 = \Gamma_3 \otimes \Gamma_6 = \Gamma_4 \otimes \Gamma_6 = \Gamma_5$$

$$\Gamma_1 \otimes \Gamma_6 = \Gamma_2 \otimes \Gamma_6 = \Gamma_3 \otimes \Gamma_5 = \Gamma_4 \otimes \Gamma_5 = \Gamma_6$$

$$\Gamma_1 \otimes \Gamma_7 = \Gamma_2 \otimes \Gamma_7 = \Gamma_3 \otimes \Gamma_8 = \Gamma_4 \otimes \Gamma_8 = \Gamma_7$$

$$\Gamma_1 \otimes \Gamma_8 = \Gamma_2 \otimes \Gamma_8 = \Gamma_3 \otimes \Gamma_7 = \Gamma_4 \otimes \Gamma_7 = \Gamma_8$$

$$\Gamma_1 \otimes \Gamma_9 = \Gamma_2 \otimes \Gamma_9 = \Gamma_3 \otimes \Gamma_9 = \Gamma_4 \otimes \Gamma_9 = \Gamma_9$$

$$\Gamma_5 \otimes \Gamma_5 = \Gamma_6 \otimes \Gamma_6 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5$$

$$\Gamma_5 \otimes \Gamma_6 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_6$$

$$\Gamma_7 \otimes \Gamma_5 = \Gamma_6 \otimes \Gamma_8 = \Gamma_8 \oplus \Gamma_9$$

$$\Gamma_5 \otimes \Gamma_9 = \Gamma_6 \otimes \Gamma_9 = \Gamma_7 \oplus \Gamma_8$$

$$\Gamma_7 \otimes \Gamma_7 = \Gamma_8 \otimes \Gamma_8 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_6$$

$$\Gamma_7 \otimes \Gamma_8 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$$

$$\Gamma_8 \otimes \Gamma_9 = \Gamma_9 \otimes \Gamma_7 = \Gamma_5 \oplus \Gamma_6$$

$$\Gamma_9 \otimes \Gamma_9 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$$

$$\begin{aligned}
\Gamma_7 \otimes \Gamma_5 \otimes \Gamma_9 &= (\Gamma_8 \oplus \Gamma_9) \otimes \Gamma_9 = (\Gamma_8 \otimes \Gamma_9) \oplus (\Gamma_9 \otimes \Gamma_9) \\
&= \Gamma_5 \oplus \Gamma_6 \oplus \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \\
&= \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5 \oplus \Gamma_6 \\
&= \Gamma_7 \otimes (\Gamma_5 \otimes \Gamma_9) = \Gamma_7 \otimes (\Gamma_7 \oplus \Gamma_8) = (\Gamma_7 \otimes \Gamma_7) \oplus (\Gamma_7 \otimes \Gamma_8) \\
&= \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_6 \oplus \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5
\end{aligned}$$

$$\begin{aligned}
\Gamma_7 \otimes \Gamma_5 \otimes \Gamma_7 &= (\Gamma_8 \oplus \Gamma_9) \otimes \Gamma_7 = (\Gamma_8 \otimes \Gamma_7) \oplus (\Gamma_9 \otimes \Gamma_7) \\
&= (\Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5) \oplus (\Gamma_5 \oplus \Gamma_6) \\
&= \Gamma_3 \oplus \Gamma_4 \oplus 2\Gamma_5 \oplus \Gamma_6
\end{aligned}$$

A.12 Spinors Calculations for Hexagonal and Trigonal Groups

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \sigma_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Spin matrices

$E(1)$, $I(13)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = 0$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

$C_6^+(2)$, $S_3^-(14)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = \frac{\pi}{3}$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2) = \begin{pmatrix} \frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \\ 0 & \frac{1}{2}\sqrt{3} + \frac{1}{2}i \end{pmatrix}$$

$C_3^+(3)$, $S_3^+(15)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = \frac{2\pi}{3}$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2) = \begin{pmatrix} \frac{1}{2} - \frac{1}{2}i\sqrt{3} & 0 \\ 0 & \frac{1}{2}i\sqrt{3} + \frac{1}{2} \end{pmatrix}$$

$C_2(4)$, $\sigma_h(16)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2) = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix}$$

$C_3^-(5)$, $S_6^+(17)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = \frac{4\pi}{3}$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} -\frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \\ 0 & \frac{1}{2}i\sqrt{3} - \frac{1}{2} \end{pmatrix}$$

$C_6^-(6)$, $S_3^+(18)$

$\lambda = 0$
$\mu = 0$
$\nu = 1$
$\theta = \frac{5\pi}{3}$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} -\frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \\ 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \end{pmatrix}$$

$C_{21}''(7)$, $\sigma_{v1}(19)$

$\lambda = 1$
$\mu = 0$
$\nu = 0$
$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix}$$

$C_2'(8)$, $\sigma_{d2}(20)$

$\lambda = \frac{\sqrt{3}}{2}$
$\mu = \frac{1}{2}$
$\nu = 0$
$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & -\frac{1}{2}i\sqrt{3} - \frac{1}{2} \\ \frac{1}{2} - \frac{1}{2}i\sqrt{3} & 0 \end{pmatrix}$$

$C_{23}''(9)$, $\sigma_{v3}(21)$

$\lambda = \frac{1}{2}$
$\mu = \frac{\sqrt{3}}{2}$
$\nu = 0$
$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & -\frac{1}{2}\sqrt{3} - \frac{1}{2}i \\ \frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \end{pmatrix}$$

$C_{21}'(10)$, $\sigma_{d1}(22)$

$\lambda = 0$
$\mu = 1$
$\nu = 0$
$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$$

$C''_{22}(11)$, $\sigma_{v2}(23)$

$\lambda = -\frac{1}{2}$

$\mu = \frac{\sqrt{3}}{2}$

$\nu = 0$

$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} + \frac{1}{2}i & 0 \end{pmatrix}$$

$C'_{23}(12)$, $\sigma_{d3}(24)$

$\lambda = -\frac{\sqrt{3}}{2}$

$\mu = \frac{1}{2}$

$\nu = 0$

$\theta = \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2}i\sqrt{3} - \frac{1}{2} \\ \frac{1}{2}i\sqrt{3} + \frac{1}{2} & 0 \end{pmatrix}$$

Spinors with $\theta + 2\pi$

$\overline{E}(\overline{1} = 49)$, $\overline{I}(\overline{13} = 61)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

$\overline{C_6^+}(\overline{2} = 50)$, $\overline{S_3^-}(\overline{14} = 62)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = \pi/3 + 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} \frac{1}{2}i - \frac{1}{2}\sqrt{3} & 0 \\ 0 & -\frac{1}{2}\sqrt{3} - \frac{1}{2}i \end{pmatrix}$$

$\overline{C_3^+}(\overline{3} = 51)$, $\overline{S_3^+}(\overline{15} = 63)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = 2\pi/3 + 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} \frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \\ 0 & -\frac{1}{2}i\sqrt{3} - \frac{1}{2} \end{pmatrix}$$

$\overline{C_2}(\overline{4} = 52)$, $\overline{\sigma_h}(\overline{16} = 64)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = 3\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2} - \frac{1}{2}i\sqrt{3} \\ -\frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \end{pmatrix}$$

$\overline{C_3^-}(\overline{5}=53)$, $\overline{S}_6^+(\overline{17}=65)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = 4\pi/3 + 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} \frac{1}{2}i\sqrt{3} + \frac{1}{2} & 0 \\ 0 & \frac{1}{2} - \frac{1}{2}i\sqrt{3} \end{pmatrix}$$

$\overline{C_6^-}(\overline{6}=54)$, $\overline{S}_3^+(\overline{18}=66)$

$\lambda = 0$

$\mu = 0$

$\nu = 1$

$\theta = 5\pi/2 + 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2} - \frac{1}{2}i\sqrt{3} \\ -\frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \end{pmatrix}$$

$\overline{C_{21}''}(\overline{7}=55)$, $\overline{\sigma}_{v1}(\overline{19}=67)$

$\lambda = 1$

$\mu = 0$

$\nu = 0$

$\theta = \pi + 2\pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix}$$

$\overline{C_2'}(\overline{8}=56)$, $\overline{\sigma}_{d2}(\overline{20}=68)$

$\lambda = \sqrt{3}/2$

$\mu = 1/2$

$\nu = 0$

$\theta = 2\pi + \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2}i\sqrt{3} + \frac{1}{2} \\ \frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \end{pmatrix}$$

$\overline{C}_{23}''(\overline{9}=57)$, $\overline{\sigma}_{v3}(\overline{21}=69)$

$\lambda = 1/2$

$\mu = \sqrt{3}/2$

$\nu = 0$

$\theta = 2\pi + \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & \frac{1}{2}\sqrt{3} + \frac{1}{2}i \\ \frac{1}{2}i - \frac{1}{2}\sqrt{3} & 0 \end{pmatrix}$$

$\overline{C}_{21}'(\overline{10}=58)$, $\overline{\sigma}_{d1}(\overline{22}=70)$

$\lambda = 0$

$\mu = 1$

$\nu = 0$

$\theta = 2\pi + \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\,(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z)\sin(\theta/2)$$
$$= \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

$\overline{C}''_{22}(\overline{11}=59)$, $\overline{\sigma}_{v2}(\overline{23}=71)$

$\lambda = -1/2$

$\mu = \sqrt{3}/2$

$\nu = 0$

$\theta = 2\pi + \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2) = \begin{pmatrix} 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \\ \frac{1}{2}\sqrt{3} + \frac{1}{2}i & 0 \end{pmatrix}$$

$\overline{C}'_{23}(\overline{12}=60)$, $\overline{\sigma}_{d3}(\overline{24}=72)$

$\lambda = -\sqrt{3}/2$

$\mu = 1/2$

$\nu = 0$

$\theta = 2\pi + \pi$

$$D_{1/2} = \sigma_1 \cos(\theta/2) - i\left(\lambda\sigma_x + \mu\sigma_y + \nu\sigma_z\right)\sin(\theta/2) = \begin{pmatrix} 0 & \frac{1}{2} - \frac{1}{2}i\sqrt{3} \\ -\frac{1}{2}i\sqrt{3} - \frac{1}{2} & 0 \end{pmatrix}$$

$$-\omega^* = \exp(i\pi/3) = \frac{1}{2}i\sqrt{3} + \frac{1}{2} \qquad \omega = \exp(i2\pi/3) = \frac{1}{2}i\sqrt{3} - \frac{1}{2}$$

$$\exp(i\pi) = -1 \qquad \omega^2 = \omega^* = \exp(i4\pi/3) = -\frac{1}{2}i\sqrt{3} - \frac{1}{2}$$

$$-i\omega^* = i\exp(i\pi/3) = \frac{1}{2}i - \frac{1}{2}\sqrt{3} \qquad i\omega = i\exp(i2\pi/3) = -\frac{1}{2}\sqrt{3} - \frac{1}{2}i$$

$$i\exp(i\pi) = -i \qquad i\omega^* = i\exp(i4\pi/3) = \frac{1}{2}\sqrt{3} - \frac{1}{2}i$$

Example of multiplication of two symmetry operators matrices (Spinors)

$$21 \times 6 = 70(\overline{22}) = \begin{pmatrix} 0 & -\frac{1}{2}\sqrt{3} - \frac{1}{2}i \\ \frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \end{pmatrix}\begin{pmatrix} -\frac{1}{2}\sqrt{3} - \frac{1}{2}i & 0 \\ 0 & \frac{1}{2}i - \frac{1}{2}\sqrt{3} \end{pmatrix}$$

$$= \begin{pmatrix} 0 & \left(\frac{1}{2}\sqrt{3} - \frac{1}{2}i\right)\left(\frac{1}{2}\sqrt{3} + \frac{1}{2}i\right) \\ -\left(\frac{1}{2}\sqrt{3} - \frac{1}{2}i\right)\left(\frac{1}{2}\sqrt{3} + \frac{1}{2}i\right) & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1.0 \\ -1.0 & 0 \end{pmatrix}$$

The multiplication of Vector Representations (Jones Symbols) yields, e.g., $21 \times 6 = 22$, while the multiplication of spinor representations yields $D_{1/2}(\overline{10} \text{ or } \overline{22}) = -D_{1/2}(10 \text{ or } 22)$

$$\begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ -1 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 1 & -1 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The correct choice for the result in multiplication table is $\overline{22}$. The multiplication

table in this work is in accordance with CDML multiplication tables and translation from Kovalev tables to CDML-tables as well.

Appendix B

Figures and Diagrams

In this section we present all the figures and diagrams related to the theoretical explanations given in the text.

B.1 Lattice Mode Representation

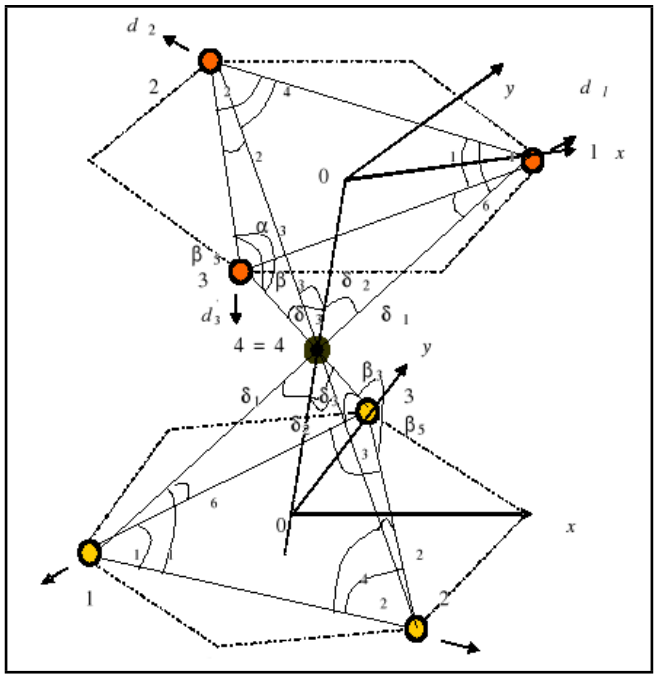

Figure B-1: Arrangement of Atoms in Sapphire

The angles in the Fig. B-1 are defined as follows for the lower pyramid:

$\alpha_1(312)$, $\alpha_2(123)$, $\alpha_3(231)$, $\beta_1(412)$, $\beta_2(432)$, $\beta_3(431)$

$\beta_4(421)$, $\beta_5(432)$, $\beta_6(413)$, $\delta_1(140)$, $\delta_2(240)$, $\delta_3(340)$.

The displacements are placed at the atoms(ions) of oxygen (1)d_1, (2)d_2 and (3)d_3

B.2 Brillouin Zone for Sapphire and Wurtzite

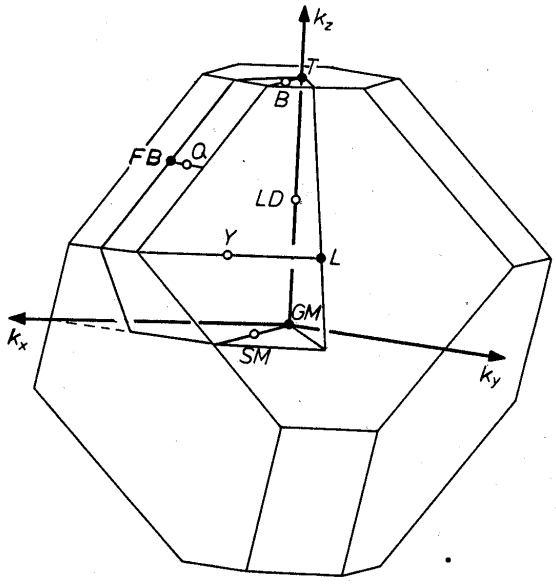

Figure B-2: Brillouin zone for sapphire structure

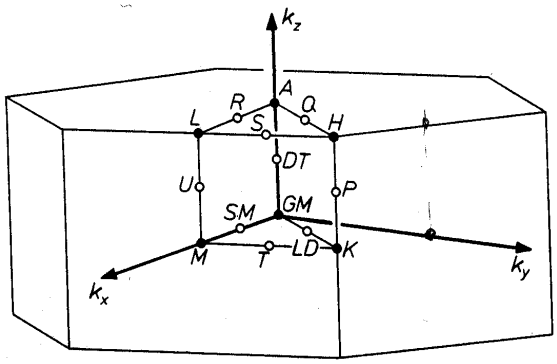

Figure B-3: Brillouin Zone for GaN and ZnO structure

B.3 Dispersion Curves for Sapphire and Wurtzite

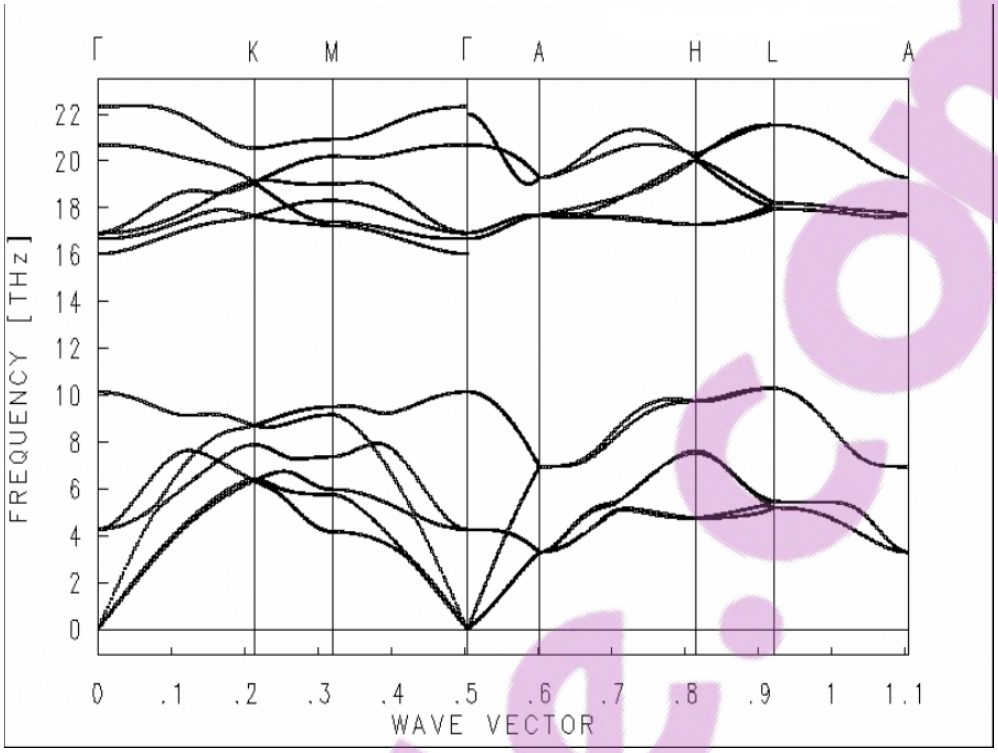

Figure B-4: Phonon dispersion curve for GaN

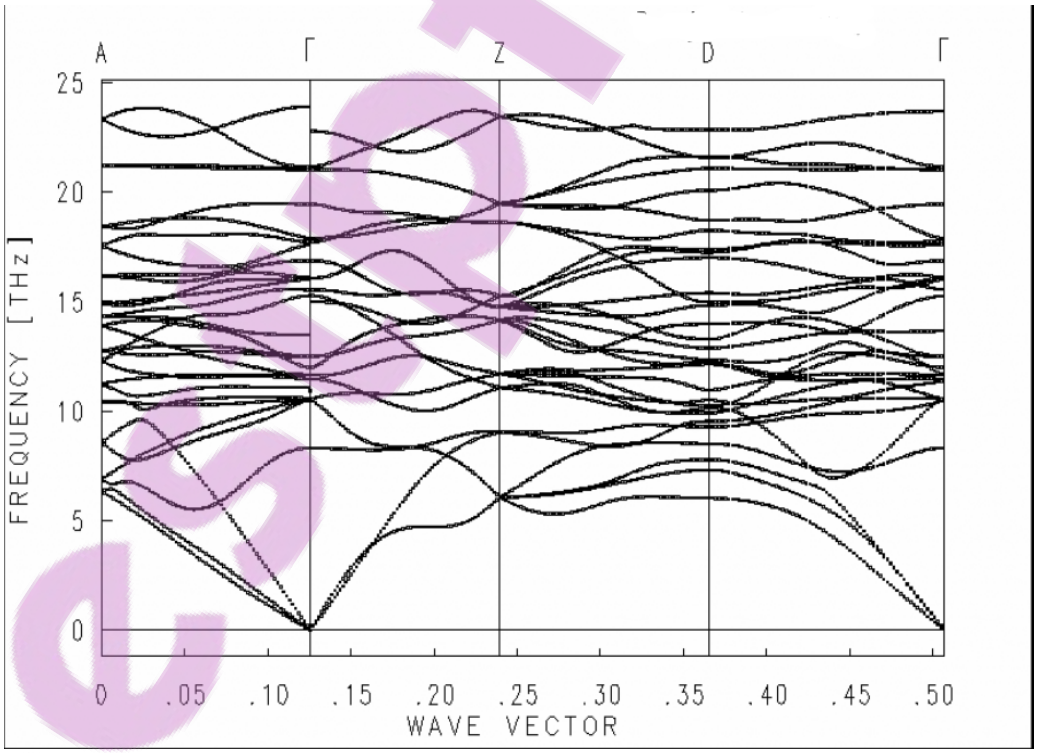

Figure B-5: Phonon dispersion curve of sapphire

B.4 Raman Spectra

The Raman Spectra of Sapphire and GaN were measured at room temperature.

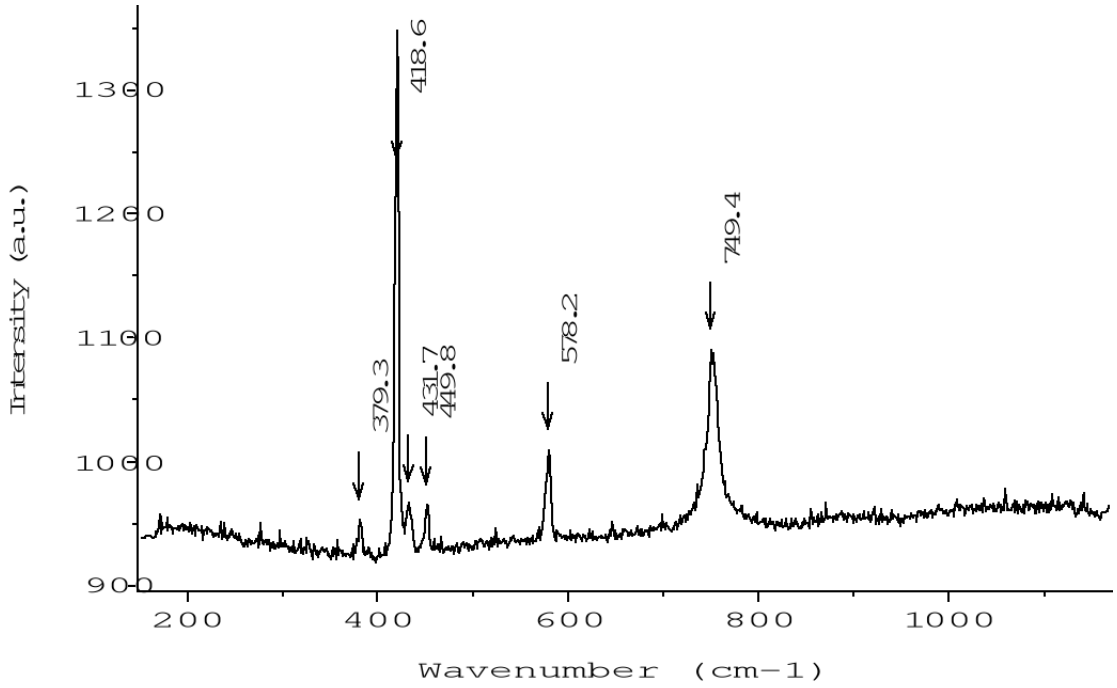

Figure B-6: Sapphire spectrum at room temperature

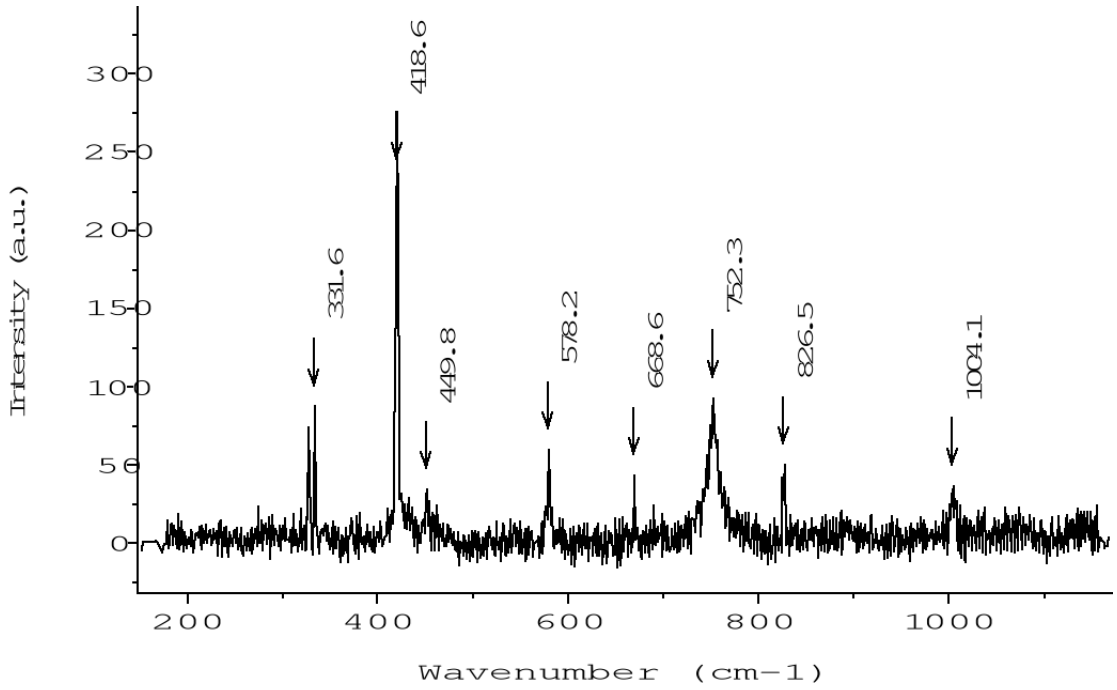

Figure B-7: Sapphire spectrum at room temperature showing second order modes

Raman Spectra of GaN side supported on Sapphire

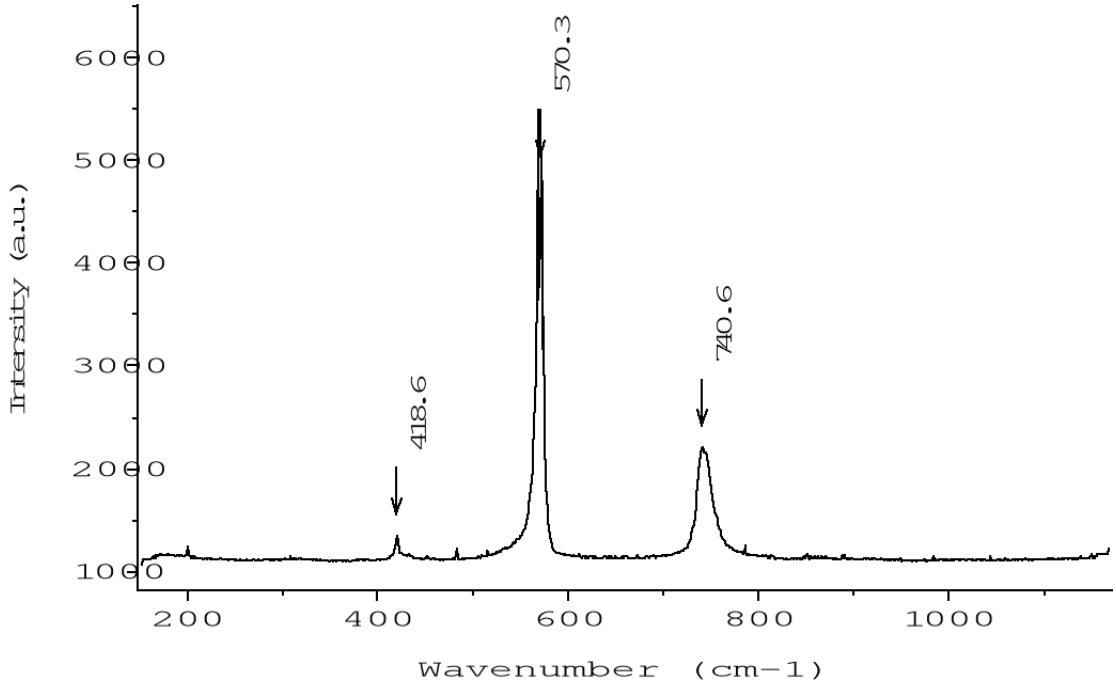

Figure B-8: Raman spectrum of GaN on sapphire substrate

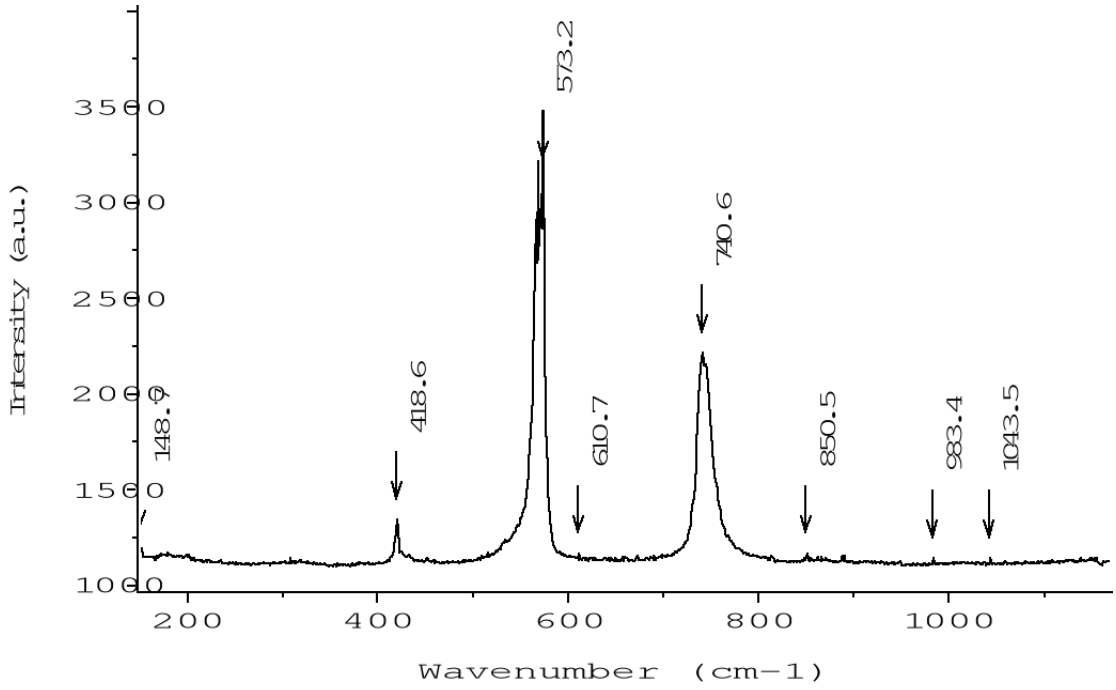

Figure B-9: GaN Raman spectrum at room temperature with sapphire modes visible

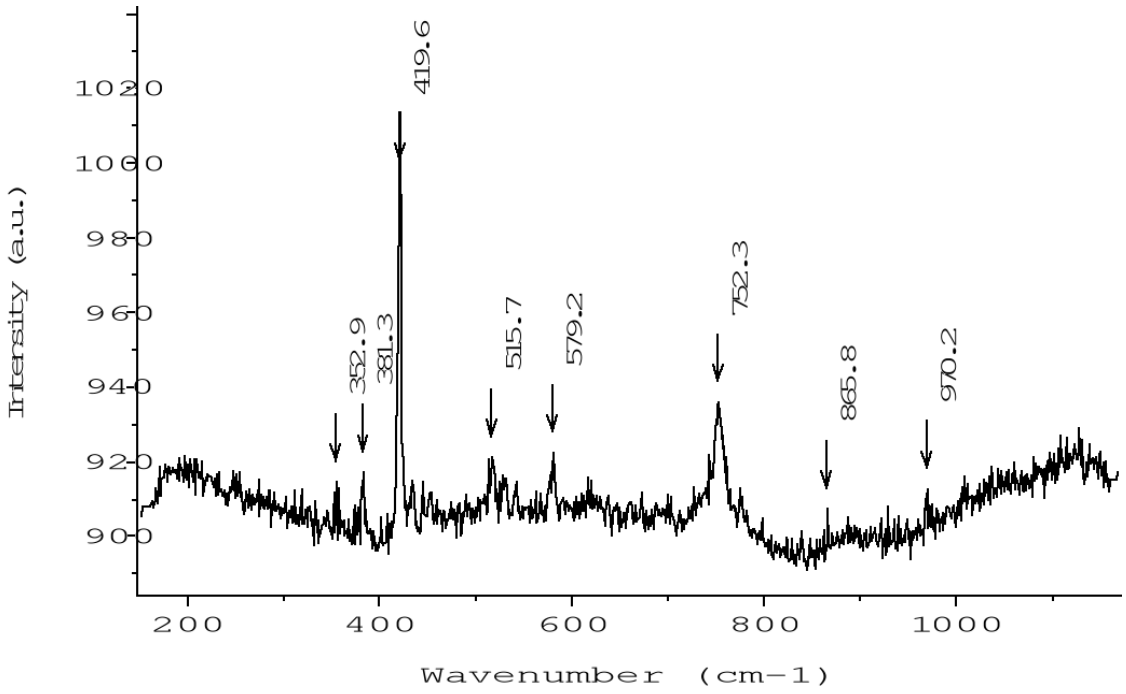

Figure B-10: Raman Spectra of sapphire showing overtones

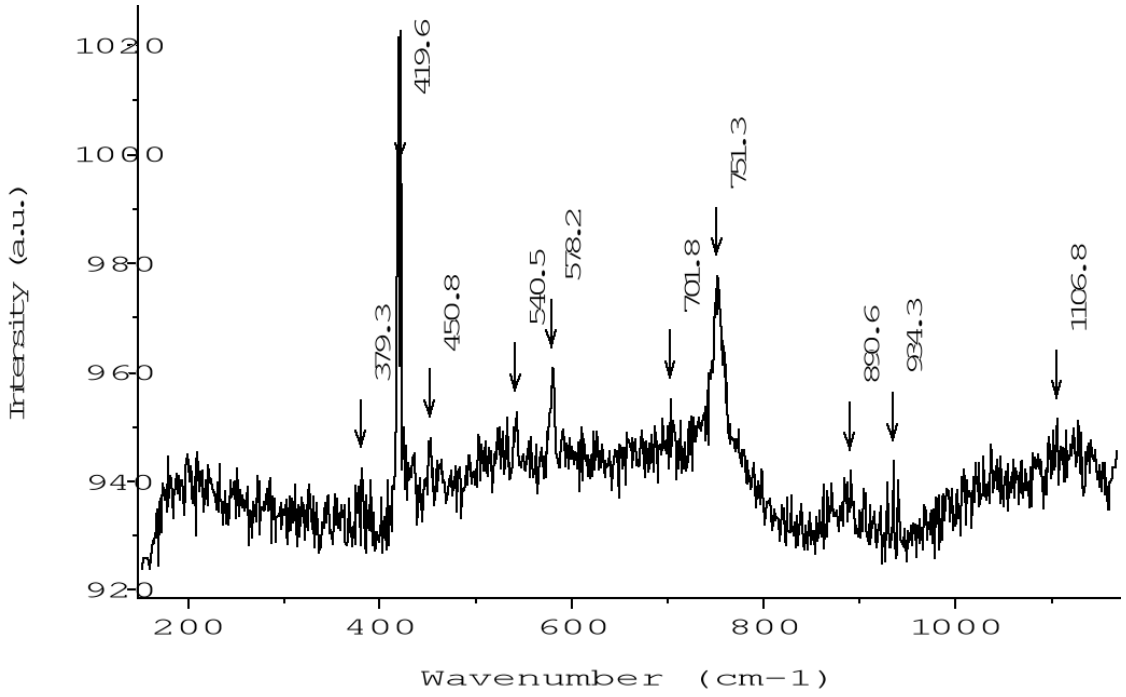

Figure B-11: Overtones and combination modes of Raman Sapphire

B.5 Electronic Band Gap of Sapphire and ZnO

B.5.1 Discussion of line $\Gamma - \Delta - A$ for Wurtzite.

The displacement representation [20, 27, 32] provides the number of normal modes and their symmetries in the entire BZ. In the wurtzite structure the normal modes spanned by displacement representation at critical points Γ, A and line Δ are:

$$\begin{aligned}
\Gamma &: \quad 2\Gamma_1 \oplus 2\Gamma_4 \oplus 2\Gamma_5 \oplus 2\Gamma_6 \\
A &: \quad 2A_1 \oplus 2A_4 \oplus 2A_5 \oplus 2A_6 \\
\Delta &: \quad 2\Delta_1 \oplus 2\Delta_4 \oplus 2\Delta_5 \oplus 2\Delta_6
\end{aligned}$$

Using compatibility relations, the resulting modes assignment along the $\Gamma - \Delta - A$ axis is:

Point Γ : $\Gamma_1 \oplus \Gamma_5$, Γ_6, Γ_4, Γ_5, Γ_6, Γ_4 and Γ_1

Point A : $A_5 \oplus A_5^\star$, $A_1 \oplus A_1^\star$, $A_5 \oplus A_5^\star$ and $A_1 \oplus A_1^\star$

Line Δ : the dispersion curves connect the points Γ and A when going from the bottom to the top on the A axis side: Δ_5, $\Delta_5^\star$, Δ_1, $\Delta_1^\star$, Δ_5, $\Delta_5^\star$, Δ_1 and $\Delta_1^\star$.

Using CDML tables we have derived all Γ, Δ and A irrps. We have found the following relations. $A_1^\star = A_4$, $A_5^\star = A_6$, $\Delta_1^\star = \Delta_4$, $\Delta_5^\star = \Delta_6$. Figure 1 displays assignment of the schematic dispersion curves of the $\Gamma - \Delta - A$ region of the BZ subjected to TRS for wurtzite compounds in terms of joint irrps. For simplicity we used straight lines for connectivity.

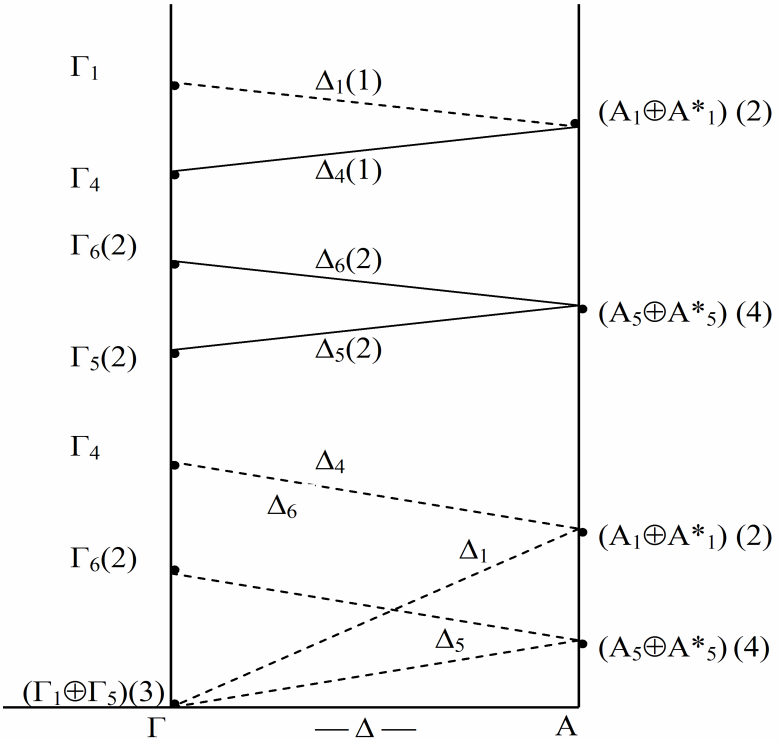

Figure B-12: Dispersion curve scheme for ZnO under Time Reversal

B.5.2 Discussion of the $\Gamma - \Lambda - Z$ Line in Sapphire

Heidi et al.[4] have used the ab initio lattice dynamics in sapphire to obtain the lattice modes. They obtain the frequencies and degeneracies for infra red and Raman modes. The dispersion curves for $\Lambda-$phonons and $\Sigma-$phonons are calculated and compared with their experimental data from neutron scattering. However, they did not assign the modes in the dispersion curves. In this work we proved that the modes at $T\,(Z)$ are TRS subjected. With help of connectivity relations and total number of modes from the LMR we are able to assign the modes correctly. A similar feature already observed with ZnO structure.

Along the $\Lambda-$line, the one dimensional representation $\Lambda_{1,2}$ (DV-phonons), when TRS is considered gives the correct degeneracy: $\Lambda_1 \oplus \Lambda_1^*(2) + \Lambda_2 \oplus \Lambda_2^*(2) \rightarrow T_3 \oplus T_3^*(4)$. There are 10 one-dimensional $\Lambda-$rep (DV-phonons). At $\Gamma-$ point we assign the modes to measured values through Inelastic Neutron Scattering and Raman scattering.

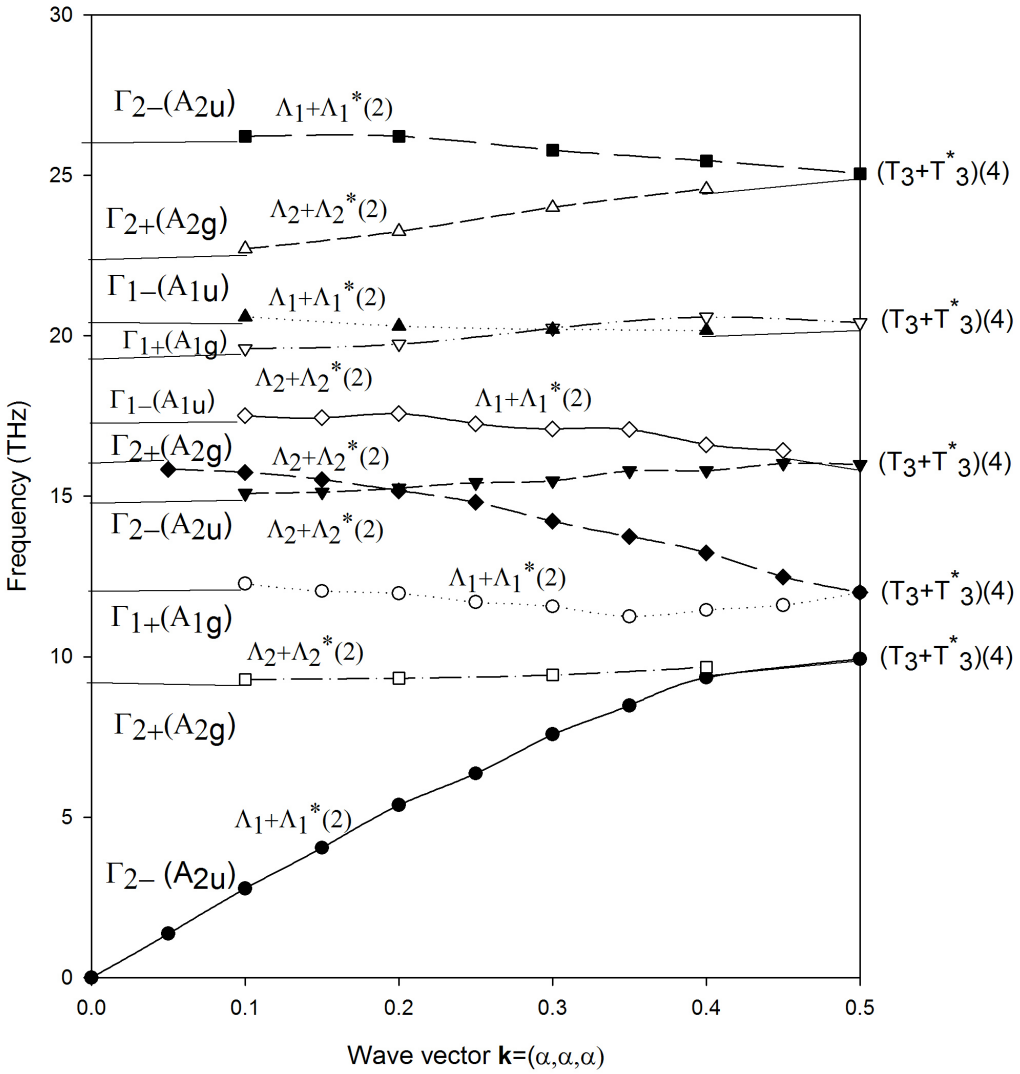

Figure B-13: Phonon dispersion curve of sapphire under Time Reversal Symmetry

Here we have plotted the one dimensional representation along the $\Lambda-$ line (Λ_1 and Λ_2). In round brackets the degeneracy of the representation is given. There are 10 two-dimensional representations (20 phonon modes) without taking TRS in consideration. When TRS is taken into account the sum of degneracy along the Λ line $2\times(\Lambda_3(2)\oplus\Lambda_3^*(2))$ $\longmapsto$ $2\times\Lambda_3(4)$, matches the pretricted degeneracy at high symmetry point $T(8)$. The number of phonons obtained by LMR and their degeneracy agrees with the measured phonons by Inelastic Neutron scattering to 30 phonons.

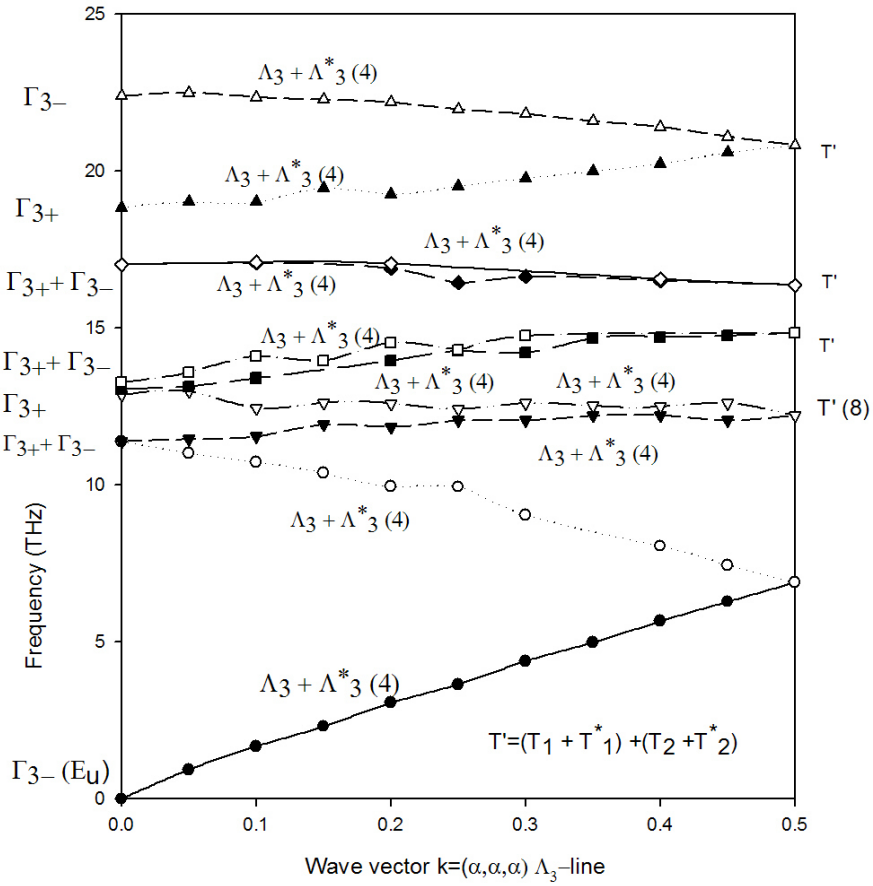

Figure B-14: Phonon dispersion curves of α-Al_2O_3 in Γ-Λ-T

Appendix C

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