1. Introduction

Wurtzite (\(C_{4v}^{6}\) -space group) wide band semiconductors: ZnO, GaN, 6H-SiC, etc., have received considerable attention owing to their opto-electronic properties. Phonons are the primary excitations that influence the thermodynamics and the transport properties of materials. In order to understand materials phenomena we study phonons thoroughly.

Sapphire \(\text{Al}_2\text{O}_3\) is a very common material on the Earth’s crust that crystallizes in the trigonal space group \(D_{3d}^{6}\). The excellent mechanical and optical properties of sapphire in its pure and doped form makes it a material of choice for various physical and technological applications. It is frequently used as substrate for growing thin films of semiconductor such as GaN, ZnO, ZnS, etc.

Ge, Si and Diamond with the space group \(O_{h}^{7}\) are well known compounds with a large variety of technological applications.

The effect of time reversal symmetry on vibrational modes, electronic states and optical properties of these compounds is still not well understood. It is our aim to comprehensively investigate the impact of TRS on the properties of these materials. TRS has also has an impact on scattering processes of semiconductors. We shall briefly indicate some consequences of TRS on optical transistions.
2. Space and Time Reversal Symmetry. Phonons and Electronic States of Quasiparticles in Wurtzite, Trigonal and Cubic Crystals.

States of quasiparticles such as phonons, electrons in conduction band (CB), holes in the valence band (VB), excitons, plasmons, polaritons, magnons, etc., in the absence of the TRS are classified according to the irreducible representations (irrps) $D^k_j$ of the space group $G^k$. The wave vector $k$ runs over the entire first Brillouin zone (BZ) and determines the high symmetry points and lines. In wurtzite BZ they are $\Gamma, A, M, K, L, H, R, Q, S, \Delta, \Sigma, \Lambda, U$ and $P$; in trigonal crystals: $\Gamma, T, P, F, Y, L, \Lambda$ and $\Sigma$ and in cubic crystal structures $\Gamma, W, X, Z(V), Q, S, A, \Lambda, \Delta$ and $\Sigma$. All these high symmetry points and lines have own set of irrps. The irrps of the 230 space groups and their characters are well established and available in CDML tables [1]. In the tables the generators of single and double valued irrps are given. The states of phonon-spinless quasiparticles are classified according to the single valued (SV) irrps, while states of electrons, holes, and therefore excitons according to double valued (DV) irrps. Frobenius and Schur (F-Sch.) showed that when an irrp is complex an extra degeneracy may occur. They derived the so-called reality test for irrps which is of the form:

$$ R = \frac{i}{\hbar} \sum_{g \in G^k} \chi_k(g^2) \delta_{k,-gk} = +1(a), \quad -1(c), \quad 0(b) \quad (1) $$

where all the quantities have their usual meaning [2, 3]. In the case (a) the irrps are real and there is no extra degeneracy, while in (b) and (c) cases an extra degeneracy occurs. In these cases the states of quasiparticles will be classified according to the direct sum of $D^k_j$ and $(D^k_j)*$. This classification of the states reflects both space and time reversal symmetry. Consequently, the degeneracy (the dimension of $D^k_j$) doubles.

In this paper we shall investigate irrps of a space group using F-Sch. criterion (equation (1)) to determine whether or not the TRS is present in a crystal. Using the equation (1) we have investigated all SV and DV irrps of wurtzite, trigonal and cubic crystals.

2.1. Single Valued irrps. Phonons

As mentioned above SV irrps are used for the classification of spinless quasiparticles. The following irrps belong to (b) or (c) cases of equation (1). All others not listed belong to case (a).

| Case   | Wurtzite | Trigonal | Cubic |
|--------|----------|----------|-------|
| Wurtzite | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | None. All irrps are real (case (a)). There is no TRS degeneracy. |
| Trigonal | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | |
| Cubic  | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | |
|        | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | |
|        | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | |

The resulting classification of the vibrational states in these crystals subjected to TRS is:

| Wurtzite | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ |
| Trigonal | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ |
| Cubic  | $A_{1-6}, \Delta_{1-6}, P_{1,2,3}, L_{1-4}, H_{1,2,3}$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ | $\Lambda_i, P_i, T_i \ (i = 1, 2, 3)$ |

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

The displacement representation [4, 5, 6] 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 $\Gamma$, $A$ and line $\Delta$ are:

- $\Gamma$ : $2\Gamma_1 \oplus 2\Gamma_4 \oplus 2\Gamma_5 \oplus 2\Gamma_6$
- $A$ : $2A_1 \oplus 2A_4 \oplus 2A_5 \oplus 2A_6$
- $\Delta$ : $2\Delta_1 \oplus 2\Delta_4 \oplus 2\Delta_5 \oplus 2\Delta_6$

Using compatibility relations, the resulting modes assignment along the $\Gamma - \Delta - A$ axis is:
Point $\Gamma$: $\Gamma_1 \oplus \Gamma_5, \Gamma_6, \Gamma_4, \Gamma_5, \Gamma_6, \Gamma_4$ and $\Gamma_1$

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

Line $\Delta$: the dispersion curves connect the points $\Gamma$ and $A$ when going from the bottom to the top on the $A$ axis side: $\Delta_5, \Delta_5^*, \Delta_1, \Delta_1^*, \Delta_5, \Delta_5^*, \Delta_1$ and $\Delta_1^*$.

Using CDML tables we have derived all $\Gamma$, $\Delta$ and $A$ irrps. We have found the following relations. $A_1^* = A_4$, $A_5^* = A_6$, $\Delta_1^* = \Delta_4$, $\Delta_5^* = \Delta_6$. 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.

![Image of schematic dispersion curves](image)

Fig.1 Phonon assignment along the $\Gamma - \Delta - A$ axis.

### 2.3. Experimental Evidence

The very first experimental proof of the existence of TRS have been provided by Hewat and Thoma [7, 8] and reference herein. by inelastic neutron scattering. They observed experimental data on a $\Delta$-line phonon dispersion curve TR degenerate. More recently Ruf [9] et. al. studied the phonon dispersion curves in GaN by inelastic X-ray scattering in Fig.2 in [9]. Their data gave evidence of the existence of TRS. With the help of our Figure 1 it is easy to understand experimental evidence of TRS obtained by Hewat, Thoma, Ruf and others [7, 8, 9]. A number of lattice dynamics calculations by means of density functional theory and ab initio theory have been reported [10, 11, 12], providing further evidence of TRS degeneracy. Sapphire has similar features on high the symmetry $\Lambda$-line which have been proven theoretically and experimentally by Heid, Schrober and Ossowski [12, 13, 14, 15].

### 2.4. Double Valued irrps. Electrons, holes and excitons

Inclusion of spin results in DV irrps (spinors) for electron and hole states. These states transform according to DV irrps. We have briefly discussed the selection rules for the excitons symmetries in the presence of TRS with respect to phonon scattering processes, previously discussed by Birman and Ganguly [16] without consideration of the effect of TRS on the exciton symmetry. For the Hamiltonian of the exciton-phonon interaction one needs the exact symmetry for the exciton and phonon. The exciton symmetry results from the product of electrons and holes symmetries. For
ZnO the A-exciton has the symmetry $\Gamma_{CB}^7 \otimes \Gamma_{VB}^9 = \Gamma_5 \oplus \Gamma_6$. The splitting onto two single states $\Gamma_5$ and $\Gamma_6$ is due to exchange interaction. The irrops $\Gamma_{CB}^7$ and $\Gamma_{VB}^9$ are DV irrops (spinors) and belong to case (c) in equation (1). Therefore, the TRS must be taken into account. The resulting A-exciton symmetry due to TRS is $[\Gamma_{CB}^7 \oplus \Gamma_{CB}^7] \otimes [\Gamma_{VB}^9 \oplus \Gamma_{VB}^9] = 4\Gamma_5 \oplus 4\Gamma_6$, and in this case the exchange interaction splits the exciton state into four $\Gamma_5$ and $\Gamma_6$ states. Clearly, the inclusion of TRS results in three more states of $\Gamma_5$ and $\Gamma_6$ symmetries, with different energy levels, compared to the selection rules without TRS. In other words, the TRS does not introduce states of new symmetries, but introduces more states of the same symmetries. Consequently, TRS does not change the existing optical selection rules tabulated in many books [1], but it may affect the enhanced Raman scattering processes in crystals. These involve a creation and destruction of intermediate states of crystals. The interaction of excitons with phonons is determined by Kronecker product of exciton and phonon symmetry $D_{j}^{\text{Exciton}} \otimes D_{j}^{\text{Phonon}}$. These KP's have to be evaluated by the standard group theoretical decomposition of the reducible rep onto irrops.

3. Conclusion
We have investigated the effect of TRS on vibrational modes in wurtzite, trigonal and cubic structures. For these structures the single valued representations of time reversal degenerate states are given. The symmetry of excitons in wurtzite time reversal subjected is discussed. Inclusion of TRS may result in an increase of time reversal degenerate phonon states of the exciton-phonon interaction for enhanced Raman scattering processes. 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: wurzite: ZnO, ZnS, ZnSe, ZnTe, GaN, AlN, InN, BP, BeO, CdS, CdSe, CdTe, CuI, 2H-SiC, 3H-SiC, 4H-SiC, 6H-SiC, etc.; Trigonal: Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, V$_2$O$_3$, Ti$_2$O$_3$, AlBO$_3$, FeBO$_3$, NaNO$_3$, CaCO$_3$, ZnCO$_3$, MgCO$_3$ MgTe, MnCO$_3$, CdCO$_3$, FeCO$_3$, etc.; Cubic: Ge, Si, Diamond, etc.

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