Phonons in sapphire Al₂O₃ substrate for ZnO and GaN

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Abstract

By means of standard method of placing the vectors upon each ion in the basis (2-Al, 3-O) and acting by symmetry operators of sapphire space group onto the basis we obtain Lattice Mode Representation (LMR). The decomposition of the LMR onto irreducible representations (irrps) corresponding to the high symmetry point and lines results in symmetry allowed first order non-interacting modes originating from the entire first Brillouin zone. First order Raman active modes are determined by symmetrized square of Kronecker products of sapphire vector representation. The selection rules for the second and third order Raman processes follow from the symmetrized Kronecker Products (square and cubes). Frequently the irrps are complex. In such cases the time reversal symmetry (TRS) must be taken into account. We have also investigated the effect of the TRS in sapphire and ZnO which leads to an extra degeneracy.

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1. Introduction

The lattice structure of sapphire belongs to the trigonal system (space group D₃₆d–R̄3c). High quality synthetic sapphire is widely used as substrate material for solid state applications. Recent developments permit growth of heterostructures, multi-layers, and superlattices from the group-III nitrides on sapphire, and enormous progress in semiconductor research enabled fabrication of GaN-based blue emitting diodes and laser devices[1,2]. Due to the Debye frequency and mechanical isotropy, corundum is the perfect candidate for ballistic phonon experiments [3,4]. Moreover, with respect to the low absorption and incoherent cross section of both the oxygen and the aluminum ions, sapphire is a perfect candidate for inelastic scattering experiments [5–7]. Absorption by higher harmonics of the fundamental lattice vibrations (multiphonon processes) have been studied [8,9]. The present work focuses on the selection rules for multiphonon processes in sapphire, ZnO, and GaN.

2. Determination of the possible vibrational modes in Al₂O₃ with D₆d space group at k=0 of the first Brillouin zone

In order to derive the LMR [10], we have introduced twenty seven real basis vectors, three displacement and twenty four angles, shown in Fig. 1.

The angles in the Fig. 1 are defined as follows: α₁(312); α₂ (123); α₃(231); β₁(412), β₂(423), β₃(431), β₄(421), β₅(432), β₆ (413); δ₁(140), δ₂(240) and δ₃(340), for the lower pyramid. The displacements are placed at the atoms (ions) of oxygen (1) d₁, (2) d₂ and (3) d₃. Similarly we define the angles for the upper pyramid with primes. The numbers refer to the ions that make angle in a clockwise manner. The upper ions are obtained through inversion at the central aluminum atom, labeled as 4=4'. The displacements of the upper (primed displacements)
and lower pyramids (unprimed displacements) are related as follows:

\[ d_1 = -d'_1; \quad d_2 = -d'_2; \quad d_3 = -d'_3; \quad x_1(312) = x'_1(3'1'2'); \quad \ldots; \quad \delta_5(340) = \delta'_5(3'4'0'). \]

The angles of primed coordinates are equivalent to the angles of non-primed ones. Acting by symmetry operators onto the introduced basis we obtain twelve matrices, which form the LMR. It is enough to generate LMR by three generators. For the first generator we have

\[ \{ C_{+} | 0 \} = A \begin{bmatrix} d_1 \\ d_2 \\ M \\ M \\ \delta'_5 \end{bmatrix} = B \begin{bmatrix} d_1 \\ d_2 \\ M \\ M \\ \delta'_5 \end{bmatrix} \]

where

\[ A = D(\{ C_{+} | 0 \}) = \left| d_2 \ d_3 \ d_1 \ x_2 \ x_1 \ \beta_2 \ \beta_3 \ \beta_4 \ \delta_2 \ \delta_3 \ \delta_1 \ \beta_5 \ \beta_6 \ \delta_5 \ \delta_6 \ \delta_1 \right| \]

The A is a block matrix,

\[ A = \begin{bmatrix} A_1 \\ O \\ A_0 \end{bmatrix}, \text{with the sub-matrix } A_i \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix}; (i=1,\ldots,9). \]

For the second generator we obtain

\[ \{ \sigma_1 | 00 \frac{1}{2} \} = B \begin{bmatrix} d_1 \\ d_2 \\ M \\ M \\ \delta'_5 \end{bmatrix} \]

with

\[ B = D \left( \{ \sigma_1 | 00 \frac{1}{2} \} \right) = \left| d_2 \ d_3 \ d_1 \ x_2 \ x_1 \ \beta_2 \ \beta_3 \ \beta_4 \ \delta_2 \ \delta_3 \ \delta_1 \ \beta_5 \ \beta_6 \ \delta_5 \ \delta_6 \ \delta_1 \right| \]

Finally, for the third generator we find

\[ \{ C_2 | 00 \frac{1}{2} \} = C \begin{bmatrix} d_1 \\ d_2 \\ M \\ M \\ \delta'_5 \end{bmatrix} \]

where

\[ C = D \left( \{ C_2 | 00 \frac{1}{2} \} \right) = \left| d_2 \ d_3 \ d_1 \ x_2 \ x_1 \ \beta_2 \ \beta_3 \ \beta_4 \ \delta_2 \ \delta_3 \ \delta_1 \ \beta_5 \ \beta_6 \ \delta_5 \ \delta_6 \ \delta_1 \right| \]

Proceeding in the same manner, or using multiplication tables for corundum, we obtain all the other nine matrices of LMR for sapphire. The character of the LMR together with the characters of irrops (at \( k=0 \)) of \( \text{Al}_2\text{O}_3 \) are given in the Table 1 [11].

Decomposing the LMR onto irrops listed in Table 1, we obtain the total number of first non-interacting modes and their symmetries (irrops) at \( k=0 \). From the reduction formula:

\[ a_{\mu} = \frac{1}{|\Gamma|} \sum_{\mu} \chi^{\text{LMR}}(\{ g \} | \tau) \cdot \chi^\prime_{\mu}(\{ g \} | \tau), \]

where \( \mu \) runs over irrops \( \Gamma_{1a}, \Gamma_{2a}, \Gamma_{3a}, (k=0) \) and \( F_{1a}, 2a, \Sigma_{1,2}, Y_{1,2}, L_1 (k \neq 0) \), we obtain the number of allowed modes, their symmetries, and their degeneracy’s spanned by the LMR. The characters of \( F, \Sigma, Y \) and \( L \) can be found in Ref. [11]. The obtained normal modes spanned by LMR are listed in Table 2.

### 3. Multiphonon Raman processes in sapphire

The LMR provides the number and symmetries (degeneracy) of possible first order non-interacting modes listed in Table 2. The higher phonon processes arise from mutual interaction between first order phonons. The phonon scattering processes are permitted by deformation potential together with Fröhlich interaction [13]. The deformation potential is assumed to be independent of the phonon \( k \) vector. However, in polar materials LO mode is accompanied by electric field which contributes to a long range (\( k \)-dependent) Fröhlich Hamiltonian.
From Table 2 it follows that there are eighteen \( k = 0 \) soft modes in sapphire. The frequencies of most of them have been determined by means of Raman spectroscopy (RS) Porto et al. [19] and inelastic neutron scattering (INS) [7] and also theoretically calculated within the framework of density functional perturbation theory (Heid et al. [20]). The symmetry assignment of some modes in \( \text{Al}_2\text{O}_3 \) have been also studied by Ossowski et al. [21]. They used the ML [11] tables of irps which we have applied in decomposition of the LMR for irps modes. Among the eighteen sapphire phonons there are several first order principal non-interacting Raman active modes (1-RAM). The symmetries of the 1-RAMs are obtained from the decomposition of the symmetrized squares (SQ) of the vector representation \[ |V \otimes \bar{V}|_{2} (\chi(\alpha_{2}, \beta_{2}, \gamma_{2}) \otimes \chi(\alpha_{4}, \beta_{4}, \gamma_{4}))_{2} \rightarrow \chi(\alpha_{1g}, \beta_{g}, \gamma_{g}) \]. The frequencies of the 2\( \alpha_{1g} \) and 5\( \beta_{g} \) modes have been tabulated by several authors [19]. In here we consider the multiphonon Raman processes resulting from two and three phonon scattering processes (combinations and overtones). From Table 2 it is clear that we obtain seven 1-RAMs, 2\( \alpha_{1g} \) and 5\( \beta_{g} \) (in accordance with Porto [19] and other authors). Raman selection rules are obtained from the Kronecker Products (KPs) of the seven 1-RAM, such as: \( \chi(\alpha_{1g}, \beta_{g}, \gamma_{g}) \otimes \chi(\alpha_{1g}, \beta_{g}, \gamma_{g}) \otimes E_{g}, E_{g} \otimes E_{g}, \) for two phonon processes and \( \chi(\alpha_{1g}, \beta_{g}, \gamma_{g}) \otimes \chi(\alpha_{1g}, \beta_{g}, \gamma_{g}) \otimes E_{g}, E_{g} \otimes E_{g}, E_{g}, \ldots, \) for three phonon processes with \( E_{g} \) of 418 cm\(^{-1}\) and 645 cm\(^{-1}\); \( E_{g} \) of 378, 432, 451, 578 and 751 cm\(^{-1}\). The combinations \( (\gamma_{1} \pm \gamma_{2}) \) and the overtones \( 2\gamma_{2} \) are symmetry allowed when the corresponding KP contains one of the 1-RAM. The above selection rules are also valid for modes originating from the entire first Brillouin Zone (BZ) at \( k \neq 0 \). However, in these cases the wave vector selection rules (WVSRs), (phonon momentum conservation) laws govern the respective KP’s. For example, interaction of \( \Sigma_{2} \) with \( \Sigma_{2} \); \( \Sigma_{2} \otimes \Sigma_{2} \) will result in \( \alpha_{1g} \) mode at \( k \neq 0 \) (the square of identical representation always contains identity rep) and other resulting phonons with \( k \neq 0 \) determined by WVSRs. The frequencies of \( \Sigma_{2} \) can be taken from the neutron scattering data [20].

### 3.1. Three phonon processes: Combinations

There are many other combinations of the type \( F_{1} \otimes F_{2} \otimes F_{3} \), or \( T_{1} \otimes T_{2} \otimes T_{3} \), etc. These will be discussed elsewhere.

### 4. Experimental

The multiphonon processes have been already and frequently observed. For example in [22–24] (Fig. 3 p253) a possible overtone of \( E_{g} \) (578 cm\(^{-1}\)), internal mode of sapphire, is obtained at 1154 cm\(^{-1}\). The spectra have been taken from the sapphire side. In Ref. [23] on Fig. 8, we observe several sapphire (SA) modes combinations at 861, 917, 1155 cm\(^{-1}\). Also in Ref. [24] Fig. 6 are several overtones and combinations seen at 860, 1007 and 1395 cm\(^{-1}\). In here, we have also investigated second and third order Raman processes in GaN/Sapphire by RS. We observe second and third modes centered at 896, 926, 1046, 1210, 1540 cm\(^{-1}\). The band at 1540±12 cm\(^{-1}\) might be a combination of \( E_{g} \) (432 cm\(^{-1}\)) + \( E_{g} \) (451 cm\(^{-1}\)) + \( \alpha_{1g} \) (645 cm\(^{-1}\)). The bands present in our spectra (not shown) are in accordance with theoretically derived selection rules.

### 5. Experimental set up

The samples grown by plasma-assisted molecular beam epitaxy on (0001) sapphire were investigated by means of inelastic light scattering experiment. Raman spectra were recorded using the 514 nm Ar+ laser line for excitation and a Jobin Yvon single-pass monochromator fillet with an adge filter and a Hamamatsu C7027 thermo-electrically cooled CCD array for detection. The resolution for these spectra was about 0.5 nm at room temperature.

### 6. Discussion

In Table 3 we list some multiphonon process in corundum. Generally, optical selection rules are governed by wavevector selection rules (quasi-momentum phonon conservation law). Consider scattering process of two phonons from the point \( F \) of the BZ. The general wavevector selection rules read: \( \alpha k_{F} + \beta k_{F} = (\gamma_{1} + \gamma_{2} + \gamma_{3}) k_{F} \), where \( \alpha, \beta, \) and \( \gamma \) are symmetry operators of

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### Table 1

Characters of irreducible representations of \( D_{h}^{(3)} \) at \( k = 0 \) and the reducible Lattice Modes Representation

<table>
<thead>
<tr>
<th>( g )</th>
<th>( E_{g} )</th>
<th>( C_{3} )</th>
<th>( C_{3}^{*} )</th>
<th>( C_{2}(\tau) )</th>
<th>( C_{2}(\tau) )</th>
<th>( I )</th>
<th>( S_{2} )</th>
<th>( S_{2}^{*} )</th>
<th>( \sigma_{1}/\tau )</th>
<th>( \sigma_{2}/\tau )</th>
<th>( \sigma_{2}/\tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>g(CDML)</td>
<td>1</td>
<td>3</td>
<td>5</td>
<td>7.1</td>
<td>9.1</td>
<td>11.1</td>
<td>13</td>
<td>15</td>
<td>17</td>
<td>19.1</td>
<td>21.1</td>
</tr>
<tr>
<td>( f_{1} ) ( (A_{1g}) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( f_{2} ) ( (A_{2g}) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( f_{3} ) ( (E_{g}) )</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( f_{1} ) ( (A_{1u}) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( f_{2} ) ( (A_{2u}) )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
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</tr>
<tr>
<td>( f_{3} ) ( (E_{u}) )</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### Table 2

Sapphire normal modes obtained by LMR at high symmetry points and lines

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>2( \Gamma_{1} ), ( \otimes 2\Gamma_{1} ), ( \otimes 3\Gamma_{1} ), ( \otimes 2\Gamma_{2} ), ( \otimes 5\Gamma_{2} ), ( \otimes 2\Gamma_{3} ), ( \otimes 4\Gamma_{3} ) (ML Notation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F )</td>
<td>7( F_{1} ), ( \otimes 8F_{2} ), ( \otimes 6F_{1} ), ( \otimes 6F_{2} )</td>
</tr>
<tr>
<td>( \Sigma )</td>
<td>13( \Sigma_{2} ), ( \otimes 14\Sigma_{2} )</td>
</tr>
<tr>
<td>( Y )</td>
<td>13( \Sigma_{2} ), ( \otimes 14\Sigma_{2} )</td>
</tr>
<tr>
<td>( L )</td>
<td>27( L_{1} )</td>
</tr>
</tbody>
</table>

Time reversal symmetry influenced modes. 17\( A_{1}, 17\( T_{1}, 17\( T_{2} \).
7. Conclusion

- The lattice mode for corundum has been explicitly derived yielding the total number of real modes (not TRS influenced) and their symmetries (degeneracies—species) listed in Table 2.
- The effect of TRS has also been investigated (see Appendix). Several phonons; $A_{1g}$, $T_{1g}$–3 and $P_{1g}$–3 have been found to be TRS influenced. The degeneracy of these modes doubles. To our best knowledge that is the first time that the effect of TRS on vibrational modes has been indicated. The effect must be taken into account in the interpretation of experimental data obtained by neutron scattering, X-ray and RS with respect to the increase of the dimensions of corresponding dynamical matrices for phonon dispersion curves calculations.
- The selection rules for two and three phonon scattering processes have been investigated. In Table 3 we list symmetry allowed phonons resulting from two and three phonon scattering processes. Their frequencies are explicitly given.
- A comparison of the derived phonon selection rules with available data is made. A good agreement has been found.

Acknowledgement

We would like to thank Ms. L.C. Prinsloo for her experimental assistance.

Appendix A. The Time Reversal effect on Vibrational modes in Al$_2$O$_3$

When an irrp is complex, the time reversal symmetry must be taken into account. Using the Frobenius–Schur [12] theorem we have investigated all irrs of corundum. We have found $A_{1g,2g,3g}$, $T_{1g,2g,3g}$, and $P_{1g,2g,3g}$ irrs complex. Therefore, the modes $A$, $T$, and $P$ are time reversal influenced. The states are classified according to $A \otimes A^*$, $T \otimes P^*$, $P \otimes P^*$, respectively. Consequently, the degeneracy of these becomes doubled. In the case of two $A$-Phonons (influenced by TRS), the scattering processes are described by $K \otimes (A \otimes A^*) \otimes (A \otimes A^*)$. This KP has to be decomposed onto irrs (species) of the resulting in that process. Thus, we have to generate complex representations to deal with the problem. To our best knowledge this is the first-time consideration, which includes the TRS effects in the phonon scattering processes. The physical consequences of the TRS in phonon scattering processes and optical transitions will be considered elsewhere.

References
