Clebsch–Gordan coefficients for scattering tensors in ZnO and other wurtzite semiconductors

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Received 4 December 2009, revised 8 February 2010, accepted 10 February 2010
Published online 17 May 2010

Keywords II–VI semiconductors, Clebsch–Gordan coefficients, scattering tensor

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1 Introduction The study of scattering processes involving phonons provides important information about various physical properties of semiconductors. These processes are usually described by the different scattering tensors which are determined by appropriate experimental techniques. Applying electrical (transport) measurements, tensors like the second rank conductivity, capacitance, and resistivity tensor can be determined. The inelastic light scattering is described by a symmetric second rank tensor which can be derived with high accuracy using Raman spectroscopy. The mechanical properties of crystals depend on tensors like surface stiffness constants, determined by, e.g., Brillouin scattering, or the third rank piezoelectric tensor which involves electron–acoustic–phonon interactions. Particularly, in non-centro-symmetric crystals (zinc blende and wurtzite) the strain tensor and induced electric fields can be expressed as a third rank electromechanical tensor (see, e.g., Ref. [1]).

In this contribution we investigate scattering processes in the wide band gap semiconductor ZnO which is attracting much attention due to potential applications in, e.g., short-wavelength optoelectronic devices and surface acoustic wave modulators [2, 3]. In particular, possible inter- and intra-valley scattering processes at local extrema in the electronic band structure of ZnO are studied by Clebsch–Gordan coefficients (CGCs). These scattering processes can occur at high symmetry points due to the interaction of carriers with phonons, impurities, and dislocations. The mechanisms have been studied in a wide variety of different semiconductors. Lax and Hopfield [4] and Birman et al. [5] have investigated the selection rules for direct and indirect radiative transitions by intra- and inter-valley scattering in Si and Ge. The Raman scattering tensors in cubic Cu₂O (O₂h) were analyzed by Birman [6]. The mathematical theory of the CGCs was derived by Berenson and Birman [7] who calculated CGCs for diamond (O₁h) and rocksalt (O₅h) [8]. Birman et al. [9] have shown that the matrix elements of the Luttinger–Bir–Picus \( k \cdot p \) effective Hamiltonian can be constructed as products of the CGCs times symmetrized tensorial field quantities. They applied the method to the \( \beta \)-wolfram structure (O₂h). Kunert and Suffczynski [10, 11] developed the theory of the CGCs related to the wave vector selection rules (WVSRs) in terms of block structures. They computed the CGCs for the O₂h space group. Finally, Berenson [12] discussed the scattering tensors for crystals limited to the point groups T₄ and C₆v. However, the coefficients for ZnO have not been studied up to now. In principal, the here presented results can also be applied to...
Table 1 Clebsch–Gordan coefficient matrix for $L_1 \otimes M_1 = A_1 \oplus A_3 \oplus L_1 \oplus L_2$, $a = 1/\sqrt{2}$, $b = 1/\sqrt{3}$, $w = -1/2 + i\sqrt{3}/2$.

<table>
<thead>
<tr>
<th>WVSRS</th>
<th>$A_1$</th>
<th>$A_3$</th>
<th>$L_1$</th>
<th>$L_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_L + k_M = k_A$</td>
<td>111</td>
<td>$b$</td>
<td>$b$</td>
<td>0</td>
</tr>
<tr>
<td>$2k_L + 2k_M = k_A$</td>
<td>221</td>
<td>$b$</td>
<td>$-iw_b$</td>
<td>0</td>
</tr>
<tr>
<td>$3k_L + 3k_M = k_A$</td>
<td>331</td>
<td>$b$</td>
<td>$w^*b$</td>
<td>$wb$</td>
</tr>
<tr>
<td>$2k_L + 3k_M = k_L$</td>
<td>231</td>
<td>0</td>
<td>0</td>
<td>$ia$</td>
</tr>
<tr>
<td>$3k_L + 2k_M = k_L$</td>
<td>321</td>
<td>0</td>
<td>0</td>
<td>$-ia$</td>
</tr>
<tr>
<td>$k_L + 3k_M = 2k_L$</td>
<td>132</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$3k_L + k_M = 2k_L$</td>
<td>312</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$k_L + 2k_M = 3k_L$</td>
<td>123</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$2k_L + k_M = 3k_L$</td>
<td>213</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$U^{-1}(L_1 \otimes M_1)U = \begin{pmatrix} A_1 & 0 & 0 & 0 \\ 0 & A_3 & 0 & 0 \\ 0 & 0 & L_1 & 0 \\ 0 & 0 & 0 & L_2 \end{pmatrix}$

other wide band gap semiconductors like GaN, CdS, 6H-SiC, BeO, and ZnS which crystallize in the same hexagonal $C_{6h}^4$ structure.

2 Symmetry of ZnO band structure The states of spin less quasi-particles like phonons and excitons are classified according to the single-valued irreducible representations (SV-irreps) of the crystal space group. Recently, Lambrecht et al. [13] calculated the band structure of ZnO using first principles linear muffin-tin orbital density functional theory. In their computation the spin of electrons and holes was disregarded. However, the effect of the time reversal symmetry along the high symmetry line $\Delta$ and at point $A$ was taken into account.

Figure 1 in Ref. [13] gives an overview of the ZnO band structure throughout the entire Brillouin zone (BZ). Several minima of conduction bands at high symmetry points can be distinguished, e.g., for $\Gamma, M, A, L$, and $X$. The corresponding symmetries are $\Gamma_1, M_1, A_1, L_1$, and $X_1$. The valley $A_1$ is time reversal degenerate. Therefore, its symmetry is supposed to be $A_1 \oplus (A_1') = A_1 \oplus A_3$ [14]. The maxima of the valence bands at the $\Gamma$ point and $A$ point have the symmetries $\Gamma_2$ and $A_5$, respectively.

For direct optical transitions in semiconductors, which preserve the $k$ vector, an electron can be scattered by a phonon. In such a case the scattering processes can be described by group theoretical scattering selection rules regarding only the SV-irreps [4, 5]. In most semiconductors, however, there is also an appreciable and measurable spin–orbit interaction. Consequently, the electron and hole states must be assigned by spinor representations. For ZnO, these are $\Gamma_7$ for the conduction band and $\Gamma_{2g}, \Gamma_0, \Gamma_{7g}$ for the upper valence bands. The spinor representations are also referred to as double-valued irreps (DV-irreps).

3 The wave vector selection rules: Kronecker product and Clebsch–Gordan coefficients In this section we discuss the consequences of the momentum conservation principle, when an electron in the state $k$ is scattered into another state with $k'$ due to a phonon in the $k''$ state. The momentum conservation determines the WVSRS. In ZnO as well as many other hexagonal crystals with the space group $C_{6h}^4$, there are three minima at the $L$ and $M$ points in the BZ. The first minimum at each of these points is characterized by the wave vectors $k_L(101)$ and $k_M(010)$ in the fundamental domain of the BZ [15]. The remaining two minima are derived from the $k_L$ and $k_M$ wave vectors to $2k_L(011)$, $3k_L(-111)$ and $2k_M(100)$, $3k_M(010)$, where 1, 2, and 3 are the symmetry operators according to the CDML labeling [15]. Together with $k_L(101)$ and $k_M(010)$, the wave vectors form so-called stars of the high symmetry points $L$ and $M$. Combining these six wave vectors, we obtain the WVSRS of momenta conservation which are listed in Table 1 together with the calculated coupling coefficients. The $U$ matrices for all tables are created from the elements of the Tables 1–5. For an example, see the listed $U$ matrix of Table 3.

The description of any scattering process is given by the Kronecker product (KP) of irreps which corresponds to the particles involved in such processes. For example, for

Table 2 Clebsch–Gordan coefficient matrix for $(A_1 \oplus A_1') \otimes M_1 = [L_1 \oplus L_2]$.

<table>
<thead>
<tr>
<th>WVSRS</th>
<th>$ab'$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_A + k_M = k_L$</td>
<td>111</td>
<td>11</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\pm i$</td>
<td>0</td>
</tr>
<tr>
<td>$2k_A = k_L$</td>
<td>122</td>
<td>12</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$\pm i$</td>
<td>0</td>
</tr>
<tr>
<td>$k_A + 3k_M = 3k_L$</td>
<td>133</td>
<td>13</td>
<td>0</td>
<td>0</td>
<td>$\pm i$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$U^{-1}((A_1 \oplus A_1') \otimes M_1)U = \begin{pmatrix} L_1 & 0 \\ 0 & L_2 \end{pmatrix}$
the scattering of an electron from the $L$ valley into the $M$
valley, the KP $L \otimes M$ must be decomposed into irrps of
phonons. For this purpose, we use the comprehensive tables
for KPs of the 230 space groups by Cracknell et al. [15]
(CDML). The CGCs are the elements of a unitary matrix that
reduces the direct KP of two reducible or irrps onto a sum of
blocks of irreps contained in the product $D^{(k)}_L \otimes D^{(k')}_M$ with

\[ U^{-1}D^{(k)}_L \otimes D^{(k')}_M U = \sum_{\rho'} c_{\ell\ell'} D^{(k')}_{\rho'}, \]

where all quantities have their usual meaning [7]. The KP
reflects different kinds of interactions like electron–hole,
electron–phonon, phonon–phonon, etc. which are normally
treated as perturbation of an unperturbed Hamiltonian. In
other words, the CGCs matrix diagonalizes the perturbation
terms. Selected CGCs for ZnO are listed in Tables 1–5. For
detailed calculations of CGCs in other space groups, please
refer to the Berenson–Birman–Kunert method [7, 10, 11].

**4 Scattering processes in ZnO** Despite the fact that
ZnO is a direct band gap semiconductor, inter- and intra-
valley scattering processes are possible. Carriers in
carriers are scattered by their interaction with many
different defects, like stacking faults, dislocations, surfaces,
interfaces, and impurities. Very common impurities with
high concentrations in ZnO are, e.g., the group III donors Al,
Ga, and In in the neutral $(l_0, l_8, l_9)$ and ionized charge state
$(l_0, l_1, l_2)$ [16, 17]. Raman scattering in resonance with
excitonic states results in a strong increase of the Raman
cross-section due to the exciton–phonon interaction in ZnO
[18]. In terms of electrical transport, the Boltzmann kinetic
equation includes the effects on the distribution function $f(k)$
due to the applied field, diffusion of carriers, and scattering
by phonons and impurities [19, 20]. The scattering processes
are determined by appropriate matrix elements of the
relevant Hamiltonian. These matrix elements, in turn, depend
on the symmetry and obey certain selection rules. From the band structure of ZnO [13], we can easily derive the
symmetries of the valence bands and conduction bands at
the high symmetry points $L$, $M$, and $A$. Here, we determine
the CGCs for the intra- and inter-valley scattering processes
involving the emission of phonons in ZnO. These CGCs are
listed in Tables 1–4. For an excitation energy $E > 3.8$ eV, the
creation of excitons at the high symmetry point $A$ is possible.
The symmetries for these excitons are listed in Table 5.

**5 Tables of coefficient matrices** Following the
general introduction about scattering processes in ZnO, we
now provide detailed tables of CGCs for various scattering
processes. For scattering processes between different valleys
of the conduction band, the following KPs are required:
$L \otimes M, L \otimes \Gamma, L \otimes A, M \otimes \Gamma, M \otimes A,$ and $\Gamma \otimes A$. In Table 1,
we list the CGCs for electron scattering between the $L_1$ and
$M_1$ valleys resulting in large phonon momenta of $A_1, A_5, L_1,$
and $L_2$ symmetries ($L_1 \otimes M_1 = A_1 \oplus A_5 \oplus L_1 \oplus L_2$).

Table 2 displays the CGCs for linear combinations of
wave functions of phonons with large momenta $hk_{L_1}$ and
$hk_{L_2}$ which originate from the scattering of electrons
occupying the conduction band minima of $A_1$ and $M_1$
symmetry ($(A_1 \oplus A_5^+ \oplus M_1 = [L_1 \oplus L_2]$).

Tables 3 and 4 consist of CGCs for scattering processes
of electrons occupying three different sub-valleys with
momenta $hk_{M_1}, 2hk_{M_2}$, and $3hk_{M_3}$ which belong to one
minimum of the CB valley $M_1$. The scattering processes
resulting in low momentum ($hk_F \approx 0$) of $\Gamma_1$ and $\Gamma_5$ phonons
are shown in Table 3 ($M_1 \otimes M_1 = [\Gamma_1 \oplus \Gamma_5]$). The CGCs

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**Table 3** Clebsch–Gordan coefficient matrix $M_1 \otimes M_1 = [\Gamma_1 \oplus \Gamma_5]$, $b = 1/\sqrt{3}, w = -1/2 + i\sqrt{3}/2$.

<table>
<thead>
<tr>
<th>WVRs</th>
<th>$\sigma' \sigma''$</th>
<th>$aa'$</th>
<th>$a''$</th>
<th>$M_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_M + 2k_M = 3k_M$</td>
<td>111</td>
<td>11</td>
<td>c</td>
<td>0</td>
</tr>
<tr>
<td>$k_M + 3k_M = 2k_M$</td>
<td>123</td>
<td>12</td>
<td>0</td>
<td>w</td>
</tr>
<tr>
<td>$2k_M + k_M = 3k_M$</td>
<td>231</td>
<td>13</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$2k_M + 3k_M = k_M$</td>
<td>222</td>
<td>21</td>
<td>-c</td>
<td>0</td>
</tr>
<tr>
<td>$3k_M + k_M = 2k_M$</td>
<td>333</td>
<td>22</td>
<td>0</td>
<td>w'</td>
</tr>
<tr>
<td>$3k_M + 2k_M = k_M$</td>
<td>312</td>
<td>23</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$U^{-1}(M_1 \otimes M_1) U = [M_4]$
for $M_4$ phonons with large momentum are listed in Table 4 ($M_1 \otimes M_1 = [M_4]$).

In Table 5, we display an example of the symmetries and CGCs of possible excitons at the A point for $(A_7)^{CB} \otimes (A_9)^{VB}$. The conceivable excitons of A symmetries have low momentum and the same symmetries as the $\Gamma'$ excitons. It should be noted that the valence band symmetry at the A point in Table 5 describes a hole state from the B valence band as has been proven in a recent magneto-optical study of the valence band ordering in ZnO by Wagner et al. [21].

6 Discussion  The CGCs provided in this work have several important applications. Principally, they are defined as coefficients between basis functions of the irrops contained in the KP and the basis functions of the product of two irrops

$$\psi^{k\sigma\alpha l\gamma}_a = \sum_{\sigma a} \sum_{\sigma' a'} \left( \begin{array}{c|c|c|c} k & l' & l'' & \gamma' \\ \sigma & a & \sigma' & a' \end{array} \right) \Phi_a^{k\sigma l} \Phi_a^{k\sigma' l'},$$

where

$$U_{\sigma a \sigma' a'}^{l l'} = \left( \begin{array}{c|c|c|c} k & l' & l'' & \gamma' \\ \sigma & a & \sigma' & a' \end{array} \right) \left( \begin{array}{c|c|c|c} k & l' & l'' & \gamma' \\ \sigma & a & \sigma' & a' \end{array} \right)$$

are the matrix elements of the CGCs. The symbols $a, a'$, and $a''$ indicate the matrix elements of the KP $l \otimes l'$ and the representation contained in the KP ($l''$). These symbols $a, a'$, and $a''$ enumerate also the basis wave functions of the irrops $l, l'$, and $l''$, respectively (see Eq. (4)). The $k, k'$ and $k''$ stand for wave vectors (momenta $hk$) of quasi particles involved in scattering processes such as electrons and phonons. The $U$ matrix (CGC matrix) has two important physical meanings.

On the one hand, it yields suitable linear combinations of the appropriate symmetry allowed basis functions of irrops ($l''$) contained in the KP in terms of product wave functions of $l \otimes l'$ (see Eqs. (2) and (3)). On the other hand, the $U$ matrix diagonalizes any KP of two irrops ($l \otimes l'$) and brings the irrop $l''$ to the matrix diagonal block form (see Eq. (1) and the equations below the Tables 1–5).

For example, using our coefficients listed in Table 3, the appropriate symmetries of the $\Gamma_5$ wave functions contained in $M_1 \otimes M_1$ can be determined to:

$$\psi_{11}^{\Gamma_5} = \frac{1}{\sqrt{3}} \left\{ \psi_{11}^{kM_1} + w \psi_{22}^{2kM_1} + w^* \psi_{33}^{3kM_1} \right\},$$

$$\psi_{22}^{\Gamma_5} = \frac{1}{\sqrt{3}} \sqrt{w^*} \left\{ \psi_{11}^{kM_1} + w^* \psi_{22}^{2kM_1} + w \psi_{33}^{3kM_1} \right\},$$

Next, the CGCs can also be used in the determination of the scattering tensors $P$. When expanded in powers of $kQ$, we have [20]:

$$P_{\alpha\beta} = P_{\alpha\beta}^0 + \sum_{\mu \nu} P_{\alpha\beta}^{\mu\nu} k_i \cdot Q(\mu \nu) + \cdots$$

and in terms of CGCs they are

$$P_{\alpha\beta}^{\mu\nu} = \sum_{\mu \nu} c(\mu \nu) U_{\alpha\mu \gamma}^{l l'} M_{l l'}^{\alpha \beta}(\mu \nu),$$

where $P$ is the first order scattering tensor, and $U$ is the matrix of the CGCs. The quantities in the above equations have their usual meanings [20]. The CGCs can also be used in the description of morphic effects [12], higher infrared order moment expansion, diagonalization of phonon dynamical matrices, as well as in the description of Gunn effect (inter-valley electron–phonon interaction) (see Ref. [1] and references therein). The coefficients can essentially be utilized in the construction of the effective Luttinger–Bir–Picus Hamiltonian matrix elements [9]:

$$H(K) = \sum_k a_k \delta_{k, g} \sum_i X_i^k K_i^{k+k'} \sum_j X_j^{k'} K_j^{k+k'},$$

where $a$ is the constant and $K_i$ is Hermitian. The $X_i$ span the $l$-dimensional linear vector space consisting of independent matrices. Birman et al. [9] have shown that the matrices are exactly the CGCs and therefore each element of an effective Hamiltonian matrix is a sum of symmetry adapted components of invariants times a CGC with the reduced matrix given by means of the Wigner–Eckart theorem:

$$H_{\alpha\beta}(K) = \sum_k a_k \sum_i (U^{-1})_{\alpha i}^{k+k'} K_i^{k+k'}.$$  

Using the CGCs and invariants, Birman et al. [9] constructed the effective Hamiltonian matrix for Diamond ($\Omega_{15}$) with the $k \cdot p$ expansion method to the second order degree in $k$ of the twofold degenerate $\Gamma_{12}$ state. With the here provided CGCs, a similar approach can be applied to construct the effective Hamiltonians for ZnO.

7 Conclusion In summary, we have studied the scattering tensors in ZnO by means of CGCs. Starting from existing band structure calculations, the CGCs were derived from selection rules for inter- and intra-valley scattering processes. For scattering processes in the same valley, both cases of low and large momentum of the quasi-particles were considered. In addition, the symmetries and CGCs of excitons at the high symmetry point A were determined.

Acknowledgements The work is supported by the RSA-Poland exchange program.

References