Charged excitons and excitons bound to neutral impurities in wurtzite semiconductor structures

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We have established the possible symmetries for the states of charged excitons (trions) in bulk materials with the wurtzite structure and in wurtzite-based heterostructures. We considered both free trions and bound ones (or excitons bound to neutral, i.e., un-ionized impurities). From the Pauli principle for identical fermions it is shown that only one symmetry is possible for the ground state of positively charged free trions involving two holes from the same valence band. The property also holds for negatively charged free trions, except in quantum wells and some superlattices for trions whose hole lies in the *A* valence band. We established the selection rules for trion optical transitions. Only a few trions are dark. Even more, for many trions, several channels are available, in terms of symmetry, for radiative decay, which suggests fast recombination processes. A comparison is provided between exciton and trion transitions. The changes of the symmetry of the states and of the optical selection rules induced by an electric field parallel to the *c* axis have been considered. When one (several) phonon(s) is (are) involved in a process, it is always possible to connect any initial state to any final one by an optical transition.

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I. INTRODUCTION

Bulk semiconductors with wurtzite structure, e.g., II-VI ZnS and ZnO or III-V GaN, are characterized by a pronounced anisotropy of their physical properties with respect to the direction parallel and perpendicular to the *c* axis, respectively. Moreover, they present a large exciton Rydberg number. The symmetry of wurtzite-based heterostructures such as quantum wells (QW's) and superlattices (SL's) allows the existence of an electric field directed along the growth *c* axis and arising from the strain (piezoelectric effect) and from the difference in spontaneous polarizability of the well and barrier materials.

Due to the large exciton Rydberg value in the structures, charged excitons (hereafter referred to as trions) should attract a strong interest. Nevertheless, to our knowledge, the symmetry of trion states as well as the selection rules for their optical transitions have never been established. In particular, the possible channels, in terms of symmetry, for trion radiative recombination and the corresponding final-carrier-state symmetries have never been considered. The excitons bound to neutral impurities play an important role in the photoluminescence spectra of wurtzite semiconductors—for example, with the so-called I_2 line and its photon replicae in GaN. The system made of an exciton bound to a neutral impurity is similar to a trion bound to an ionized impurity and obeys the same optical selection rules. Indeed, both of them involve three carriers since, in the former case, the carrier which remains bound to the neutral impurity has to be taken into account when considering the possible symmetries of the states.

Using a group-theory method based on site-symmetry analysis,[1] we previously established[2] the genesis of Bloch states from the atomic orbitals of constituent atoms and derived the optical selection rules for electrons and excitons at the Γ point and at other symmetry points in the Brillouin zone (BZ) of the crystals with the wurtzite structure (space group C_{6v}^4). We also studied[3] the states of electrons and excitons bound to impurities and defects and their optical selection rules as well as the selection rules for transitions between Bloch and bound states. Finally, we extended our results to phonon-assisted transitions.[4] Of course, excitons are bosons and their symmetry therefore can be described by single-valued irreducible representations (irreps) only, even in the case when the spin-orbit interaction (SOI) is taken into account as it is done hereafter. On the contrary, trions are fermions and their symmetry can be described only by double-valued irreps when the SOI is taken into account. Hereafter, the labeling of point-group irreps follows Ref. 5 and the irreps of the space groups are labeled according to Ref. 6. In such a labeling of Bloch states, Γ_5 and Γ_6 irreps are exchanged in comparison with notations common for II-VI wurtzite materials.

The Kronecker products of Γ irreps for the space group C_{6v}^4 are displayed in Table I, providing the optical selection rules for direct electron transitions[2] at the Γ point of the BZ (see also Fig. 1). The vector representation in the C_{6v}^4 group is $\Gamma_1(z)+\Gamma_6(x,y)$. When the Γ_1 irrep and/or the Γ_6 one appear(s) in the Kronecker product, the transition is allowed in the *z* and/or *xy* polarization. For example, the transition between a state with the Γ_7 symmetry and a state with the Γ_9 symmetry is allowed in the *xy* polarization (Table I), whereas the transition between two Γ_7 states is allowed in any polarization.

Table I also provides the symmetries of zero-orbital-momentum excitons (hereafter referred to as *s* excitons) from the symmetries of the electron and hole they are built from. Indeed, the possible symmetries of *s* excitons built from a hole with the Γ_v^* symmetry and an electron with the Γ_c symmetry are those included in the $\Gamma_v^* \times \Gamma_c$ direct product. (The irrep associated with the hole generated by the absence of an electron with the Γ_v symmetry is Γ_v^*. Note that $\Gamma_v^* = \Gamma_v$, since all the Γ irreps of the C_{6v}^4 group are real, thus reducing their Kronecker products to simple direct products.) For GaN, there is a general agreement about the symmetries

TABLE I. Kronecker products of the irreps (single and double valued) of the space group C_{6v}^4 at the Γ point of the BZ.

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	Γ_9
Γ_1	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7	Γ_8	Γ_9
Γ_2	Γ_2	Γ_1	Γ_4	Γ_3	Γ_5	Γ_6	Γ_7	Γ_8	Γ_9
Γ_3	Γ_3	Γ_4	Γ_1	Γ_2	Γ_6	Γ_5	Γ_8	Γ_7	Γ_9
Γ_4	Γ_4	Γ_3	Γ_2	Γ_1	Γ_6	Γ_5	Γ_8	Γ_7	Γ_9
Γ_5	Γ_5	Γ_5	Γ_6	Γ_6	$\Gamma_1+\Gamma_2+\Gamma_5$	$\Gamma_3+\Gamma_4+\Gamma_6$	$\Gamma_8+\Gamma_9$	$\Gamma_7+\Gamma_9$	$\Gamma_7+\Gamma_8$
Γ_6	Γ_6	Γ_6	Γ_5	Γ_5	$\Gamma_3+\Gamma_4+\Gamma_6$	$\Gamma_1+\Gamma_2+\Gamma_5$	$\Gamma_7+\Gamma_9$	$\Gamma_8+\Gamma_9$	$\Gamma_7+\Gamma_8$
Γ_7	Γ_7	Γ_7	Γ_8	Γ_8	$\Gamma_8+\Gamma_9$	$\Gamma_7+\Gamma_9$	$\Gamma_1+\Gamma_2+\Gamma_6$	$\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_5+\Gamma_6$
Γ_8	Γ_8	Γ_8	Γ_7	Γ_7	$\Gamma_7+\Gamma_9$	$\Gamma_8+\Gamma_9$	$\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_1+\Gamma_2+\Gamma_6$	$\Gamma_5+\Gamma_6$
Γ_9	Γ_9	Γ_9	Γ_9	Γ_9	$\Gamma_7+\Gamma_8$	$\Gamma_7+\Gamma_8$	$\Gamma_5+\Gamma_6$	$\Gamma_5+\Gamma_6$	$\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4$

at the Γ point for the lowest conduction band (Γ_7 originating from Γ_1) and for the uppermost valence bands (Γ_9 and Γ_7 originating from Γ_6 and Γ_7 from Γ_1 for the *A*, *B*, and *C* transitions, respectively: see Fig. 1). The possible symmetries then are Γ_5 and Γ_6 for the *s A* excitons, and Γ_1, Γ_2, and Γ_6 for the *s B* and *C* excitons, respectively[2] (Fig. 1). The Γ_1 (Γ_6) excitons can recombine radiatively in the *z* (*xy*) polarization (Table I). The others are dark ones.[2] Even if the ordering in energy of the three upper valence bands in the other materials with the wurtzite structure is sometime different, it is widely accepted that the materials present the same set of upper-valence-band symmetries that GaN does.

To obtain the possible symmetries of excitons with orbital momentum equal to 1 (*p* excitons) one should multiply the irreps of *s* excitons by the vector representation ($\Gamma_1+\Gamma_6$). The possible symmetries of *p* excitons[2] are Γ_{1-6}.

II. SYMMETRIES OF THE FREE-TRION STATES AND OPTICAL TRANSITIONS IN BULK MATERIALS WITH WURTZITE STRUCTURE

The free-trion states can be classified according to the valence bands (holes) associated with them: A^-, B^-, C^-, AA^+, BB^+, CC^+, AB^+, AC^+, and BC^+, the first three being negatively charged, the others positively. For example, the trion A^- is made from a hole in the valence band *A* and two electrons in the conduction band; the trion AB^+ consists of two holes in valence bands *A* and *B* and an electron in the conduction band. One can read these notations otherwise, i.e., an exciton associated with a carrier. Then, A^- is a trion formed by an exciton *A* and an electron in the conduction band and the trion AB^+ is built from the exciton *A* and a hole in the valence band *B* or from the exciton *B* and a hole in the valence band *A*.

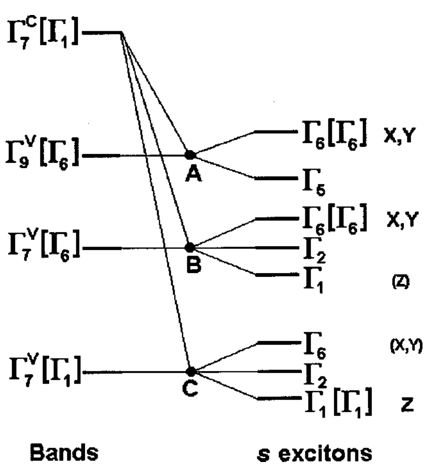

FIG. 1. Construction of *s*-exciton states from BZ center conduction- and valence-band Bloch states in GaN and $(GaN)_m(AlN)_n$ SL's with odd values of $m+n$ (space group C_{6v}^4). The labels of the irreps in brackets refer to the case when the spin-orbit interaction is not taken into account. The light polarizations in parentheses refer to the case only with taking into account the spin-orbit interaction; those in capitals are allowed in any case (Ref. 12).

The states of the trion energy band with wave vectors $\mathbf{k}$ in the vicinity of $\mathbf{k}=0$ are the most important ones from the experimental point of view. Similarly as in the case of excitons[7] or biexcitons,[8] the symmetry of trion states is determined by the direct product:

$$\Gamma_{\text{env}}\times\Gamma^{(1)}\times\Gamma^{(2)}\times\Gamma^{(3)}, \tag{1}$$

where $\Gamma^{(i)}$ ($i=1,2,3$) are the symmetries (irreps) of the states related to the extrema at $\mathbf{k}=0$ of the bands involved and Γ_{env} is the symmetry of the envelope function F_{env} of the trion state.

If one considers a trions as a system exciton+carrier, then the function F_{env} is the product of the envelope function $F_{\text{env}}^{\text{exc}}$ of the exciton and the envelope function $F_{\text{env}}^{e\text{-}c}$ which describes the binding between the exciton and carrier: $F_{\text{env}}=F_{\text{env}}^{\text{exc}}F_{\text{env}}^{e\text{-}c}$. Its symmetry is given by $\Gamma_{\text{env}}=\Gamma_{\text{env}}^{\text{exc}}\times\Gamma_{\text{env}}^{e\text{-}c}$. Of course, the final symmetry of a trion depends on the symmetry of the trion envelope function. For the state with the lowest trion energy, the symmetries of $F_{\text{env}}^{\text{exc}}$ and $F_{\text{env}}^{e\text{-}c}$ are expected to be Γ_1. Then the symmetry of the trion ground state is given by $\Gamma^{(1)}\times\Gamma^{(2)}\times\Gamma^{(3)}$.

The trion state of symmetry (1) has to be properly symmetrized with respect to the permutations of identical particles. Let a negatively charged trion be composed of two electrons with symmetries $\Gamma^{(1)}=\Gamma^{(2)}=\Gamma_7$ (the bottom of the lowest conduction band) and a hole with symmetry $\Gamma^{(3)}=\Gamma_9$ (the top of the uppermost valence band in GaN, for example). This is a trion A^- (or, in other words, an exciton *A* associated with an electron of symmetry Γ_7). Both electrons being in the states of the same irrep Γ_7, the space of the direct products $\Gamma_7\times\Gamma_7$ can be split into odd and even subspaces with respect to permutations of the indices of basis functions of the irreps (Ref. 9) (or, which is the same, with respect to permutations of the identical particles involved) as follows:

$$\Gamma_7\times\Gamma_7=(\Gamma_7\times\Gamma_7)^{(-)}+(\Gamma_7\times\Gamma_7)^{(+)}=\Gamma_1^{(-)}+\Gamma_2^{(+)}+\Gamma_6^{(+)}, \tag{2}$$

where the signs $\pm$ point out the permutational symmetry of the products. To obtain the whole trion function of $(-)$ permutational symmetry, the Bloch-type parts of functions have to be multiplied by the envelope functions of opposite permutational parity. Finally, the possible symmetries for the trions A^- are those included in

$$\begin{aligned}[\Gamma_{\rm env}^{+}\times\Gamma_1^{(-)}&+\Gamma_{\rm env}^{(-)}\times(\Gamma_2^{(+)}+\Gamma_6^{(+)})]\times\Gamma_9\\ &=\Gamma_{\rm env}^{(+)}\times\Gamma_9^{(-)}+\Gamma_{\rm env}^{(-)}\times(\Gamma_7^{(+)}+\Gamma_8^{(+)}+\Gamma_9^{(+)}).\end{aligned} \tag{3}$$

The permutational symmetry, although it has to be respected, cannot *a priori* exclude any of the double-valued irreps Γ_{7-9} as possible spatial symmetry of the whole trion function (see the Appendix). Which of them correspond to positive values of the trion binding energy is a question that cannot be solved by symmetry consideration. The envelope function of the state with the lowest trion energy (ground state) is expected to be of symmetry $\Gamma_1^{(+)}$. Then the only possible symmetry for this state is $\Gamma_9^{(-)}$.

By the same way, one can investigate the symmetries of trion states with other possible combinations of involved particles. But in the case when the states of identical particles are related to independent bases of irreps (equivalent or nonequivalent), their product can be made of both permutational parities. For example, the trion BC^+ (in other words, an exciton B or C associated with a hole of symmetry Γ_7) is formed by an electron of symmetry Γ_7 (the bottom of the lowest conduction band) and two holes also of symmetry Γ_7 (the tops of two different valence bands). The direct product of two independent spaces of two equivalent irreps related to different identical holes has to be doubled by their permutation. In this doubled space of the direct product, both symmetric and antisymmetric (with respect to permutation of identical holes) irreducible components can be obtained:

$$2(\Gamma_7\times\Gamma_7)=\Gamma_1^{(-)}+\Gamma_2^{(-)}+\Gamma_6^{(-)}+\Gamma_1^{(+)}+\Gamma_2^{(+)}+\Gamma_6^{(+)}. \tag{4}$$

Finally, the possible symmetries of the trions BC^+ are those included in

$$\Gamma_{\rm env}^{(+)}\times(3\Gamma_7^{(-)}+\Gamma_9^{(-)})+\Gamma_{\rm env}^{(-)}\times(3\Gamma_7^{(+)}+\Gamma_9^{(+)}). \tag{5}$$

Table II shows the symmetries of all the possible trions generated by electrons of the conduction-band bottom of symmetry Γ_7 and holes of the three uppermost valence-band tops of symmetries Γ_9, Γ_7, and Γ_7. This table shows that trions can present any of the Γ_{7-9} symmetries. Even in the case of $\Gamma_{\rm env}^{(+)}=\Gamma_1$, to which certainly corresponds the ground state of various trions, trions of any symmetry are possible, but negatively charged trions A^- (B^-,C^-) may be of symmetry Γ_9 (Γ_7) only, whereas positively charged trions with two holes from the same valence band have only the Γ_7 symmetry.

TABLE II. Permutational and spatial symmetries of free trion functions in bulk materials with the wurtzite structure and SL's with odd value of $m+n$ (space group C_{6v}^4).

$\Gamma_{\rm env}$	$(+)$	$(-)$
$\Gamma_{c,v}$	$(-)$	$(+)$
A^-	Γ_9	Γ_7, Γ_8, Γ_9
B^-, C^-	Γ_7	Γ_7, Γ_9
AA^+	Γ_7	Γ_7, Γ_8
BB^+, CC^+	Γ_7	Γ_7, Γ_9
AB^+, AC^+	Γ_7, Γ_8, Γ_9	Γ_7, Γ_8, Γ_9
BC^+	Γ_7, Γ_9	Γ_7, Γ_9

Table I allows us to study the optical transitions of trions to a carrier and a photon by setting one state to be that of the trion and the other that of the carrier. When a negatively (positively) charged trion can decay radiatively, the final state is that of an electron (hole). Negatively charged Γ_7 (Γ_9) trions decay with emission of a photon of any (xy) polarization and a Γ_7 final electron, whereas negatively charged Γ_8 trions are dark. Positively charged Γ_7 trions decay with emission of a photon of any or xy polarization and a Γ_7 or Γ_9 final hole ($\Gamma_7$trion$^+\rightarrow xyz+\Gamma_7$ hole or $xy+\Gamma_9$ hole). One has also the transitions $\Gamma_8$trion$^+\rightarrow xy+\Gamma_9$ hole and $\Gamma_9$trion$^+\rightarrow xy+\Gamma_7$ hole or $z+\Gamma_9$ hole. Note that the same selection rules are valid for the inverse transition carrier+photon$\rightarrow$trion.

In each transition, wave vector and energy conservation laws have to be taken into account. The wave vector $\mathbf{k}_t$ of the trion is also that ($\mathbf{k}_c$) of the final carrier since the photon wave vector is negligible. E_t (E_c) and m_t (m_c) being the internal energy and effective mass, respectively, of the trion (carrier) and $\hbar\omega$ the photon energy, one has

$$E_t+\hbar^2\mathbf{k}_t^2/2m_t=\hbar\omega+E_c+\hbar^2\mathbf{k}_c^2/2m_c, \quad \mathbf{k}_t\approx\mathbf{k}_c. \tag{6}$$

Here m_c being generally smaller than m_t, the photon energy is at most equal to E_t-E_c. One can therefore expect broad emission bands since trions with nonzero momentum can radiatively recombine, the momentum being then transferred to the carrier. In addition, from the point of view of symmetry, two channels for radiative recombination are available for any positively charged trion except the Γ_8 one, which has only one channel. The two corresponding emitted photons are expected to have energies slightly different one from the other due to the different final-carrier states. This also should contribute to broaden the peaks when the two transitions cannot be separated in the spectra due to insufficient resolution of the measurement. For the same reasons, fast recombination processes are expected to occur in time-resolved experiments Such properties have been reported for free trions in GaAs/AlGaAs QW's.[10]

TABLE III. Kronecker products of the irreps (single and double valued) of the point group C_{3v} and of the space group C_{3v}^1 (at the Γ point of the BZ, with the replacement of a_1, a_2, e, $\overline{e}_1^{(1)}$, $\overline{e}_1^{(2)}$, and $\overline{e}_2$ irreps of the C_{3v} group by the Γ_1, Γ_2, Γ_3, Γ_4, Γ_5, and Γ_6 irreps of the C_{3v}^1 group).

	a_1	a_1	e	$\overline{e}_1^{(1)}$	$\overline{e}_1^{(2)}$	$\overline{e}_2$
a_1	a_1	a_2	e	$\overline{e}_1^{(1)}$	$\overline{e}_1^{(2)}$	$\overline{e}_2$
a_2	a_2	a_1	e	$\overline{e}_1^{(2)}$	$\overline{e}_1^{(1)}$	$\overline{e}_2$
e	e	e	a_1+a_2+e	$\overline{e}_2$	$\overline{e}_2$	$\overline{e}_1^{(1)}+\overline{e}_1^{(2)}+\overline{e}_2$
$\overline{e}_1^{(1)}$	$\overline{e}_1^{(1)}$	$\overline{e}_1^{(2)}$	$\overline{e}_2$	a_1	a_2	e
$\overline{e}_1^{(2)}$	$\overline{e}_1^{(2)}$	$\overline{e}_1^{(1)}$	$\overline{e}_2$	a_2	a_1	e
$\overline{e}_2$	$\overline{e}_2$	$\overline{e}_2$	$\overline{e}_1^{(1)}+\overline{e}_1^{(2)}+\overline{e}_2$	e	e	a_1+a_2+e

III. TRIONS BOUND TO IONIZED IMPURITIES IN BULK MATERIALS WITH WURTZITE STRUCTURE (OR EXCITONS BOUND TO NEUTRAL IMPURITIES)

The symmetry of any atomic site in the crystal is C_{3v}. All the states are classified according to the irreps of this point group. The bound-carrier states can have symmetry of any double-valued irrep $\overline{e}_1^{(1)}$, $\overline{e}_1^{(2)}$, and $\overline{e}_2$ (the SOI being taken into account). The bound excitons can have the symmetry of any single-valued irrep, i.e., a_1, a_2, and e. The three single-valued irreps and the double-valued irrep $\overline{e}_2$ are real, whereas $\overline{e}_1^{(1)}$ and $\overline{e}_1^{(2)}$ are complex conjugate ones.[5] The possible symmetries for the states of a bound trion are included in the direct product of the irreps of the envelope function and of the three carriers. The product has to be symmetrized according to the Pauli principle. The general considerations in the Appendix are also valuable for this case, and the Pauli principle does not impose *a priori* restrictions on the possible symmetries of trion states. When the two carriers with the same nature (electron or hole) are in the same state, the space of the direct product of their states is split as follows into odd and even subspaces with respect to the permutations of the two identical particles:

$$\overline{e}_1^{(1)}\times\overline{e}_1^{(1)}=\overline{e}_1^{(2)}\times\overline{e}_1^{(2)}=a_2^{(+)},$$

$$\overline{e}_2\times\overline{e}_2=a_1^{(-)}+a_2^{(+)}+e^{(+)}. \tag{7}$$

Equation (7) shows that, when the trion envelope function is symmetric under the permutation of the identical particles, the symmetry of each of the latters is necessarily $\overline{e}_2$ since the whole trion function has to be of $(-)$ permutational symmetry with respect to them. The spatial symmetry of the pair of identical particles is then a_1. When the states of the identical particles are related to independent irreps (equivalent, such as, for example, two $\overline{e}_1^{(1)}$ states with different energies, or nonequivalent, such as, for example, one $\overline{e}_1^{(1)}$ and one $\overline{e}_2$ state), their product can be made of both permutational parity.

The Kronecker products of C_{3v} group irreps are displayed in Table III providing the selection rules for optical transitions [the vector representation for the C_{3v} group is $a_1(z)+e(x,y)$]. It can be seen that a trion with $\overline{e}_1^{(1)}$ or $\overline{e}_1^{(2)}$ symmetry has one channel to radiatively recombine by emitting a *xy*-polarized photon and one channel by emitting a *z*-polarized photon. A trion with $\overline{e}_2$ symmetry has two channels to recombine by emitting an *xy*-polarized photon and one channel by emitting a photon with any polarization. The photon energy depends on the nature of the final-carrier state. That can induce a broadening of the peak related to the $\overline{e}_2$ trion recombination in the *xy* polarization as well as a fast decay associated to several lifetimes in time-resolved experiments for any trion.

It is also possible to imagine that the final carrier is transferred into a Γ Bloch state corresponding to the C_{6v}^4 space group (Γ_7 conduction state, Γ_7 or Γ_9 valence state). The subduction procedure[1] provides the following correspondences: $\Gamma_9\rightarrow\overline{e}_1^{(1)}+\overline{e}_1^{(2)}$ and Γ_7, $\Gamma_8\rightarrow\overline{e}_2$. Therefore a Γ_9 final-carrier state can replace, in a process, a $\overline{e}_1^{(1)}$ or $\overline{e}_1^{(2)}$ bound one and a Γ_7 state a $\overline{e}_2$ one. The inverse processes are available for the recombination of free trions with the final carrier being in a bound state. Of course, the energy of a bound carrier is lower than that of a free one at the Γ point. Bloch states at the other BZ symmetry points could be involved in the same manner,[2] the momentum conservation law being then satisfied by emitting or absorbing one or several phonons.

IV. SYMMETRIES OF TRION STATES AND OPTICAL TRANSITIONS IN WURTZITE-BASED HETEROSTRUCTURES

We previously established that the space group of the $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SL's is C_{6v}^4 for odd values of $m+n$ and C_{3v}^1 for even ones.[11] The space symmetry of the $(\mathrm{GaN})_m/\mathrm{AlN}$ QW's (including single interfaces) is described by the $P3m1$ (DG69) layer group whatever is the m value.[12] The space group C_{3v}^1 is a semidirect product of its layer subgroup $P3m1$ and its invariant subgroup T of lattice translations along the z axis ($C_{3v}^1=P3m1\wedge T$). Therefore, the layer group is isomorphic to the factor group C_{3v}^1/T of space group C_{3v}^1 with respect to T ($P3m1\leftrightarrow C_{3v}^1/T$).[12] In all the heterostructures, any atom of the lattice occupies a site with the C_{3v} symmetry.[12]

It can therefore be concluded that the results we established above in terms of symmetry (the permutational symmetry included) for the Γ point of bulk materials with the wurtzite structure are still valid at the Γ point of SL's with odd values of $m+n$.

For SL's with even values of $m+n$ and QW's, the results

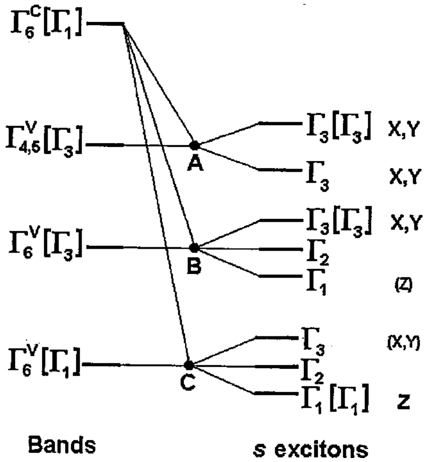

FIG. 2. Construction of *s*-exciton states from BZ center conduction- and valence-band Bloch states in $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SL's with even values of $m+n$ (space group C_{3v}^1) and in $(\mathrm{GaN})_m/\mathrm{AlN}$ QW's (layer group DG69). The notation is the same as in Fig. 1.

in terms of symmetry for the Γ point are those deduced from the C_{6v}^4 space group by subduction of its irreps onto its subgroups C_{3v}^1 and DG69 with the following correspondence of irreps: $\Gamma_1\rightarrow\Gamma_1$, $\Gamma_2\rightarrow\Gamma_2$, $\Gamma_3\rightarrow\Gamma_2$, $\Gamma_4\rightarrow\Gamma_1$, $\Gamma_5\rightarrow\Gamma_3$, $\Gamma_6\rightarrow\Gamma_3$, $\Gamma_7\rightarrow\Gamma_6$, $\Gamma_8\rightarrow\Gamma_6$, and $\Gamma_9\rightarrow\Gamma_4+\Gamma_5$. In Fig. 2 are given the generally accepted notation (*A*, *B*, and *C*) for the transitions between the conduction and valence bands which are used here to classify the excitons and trions in these structures. The notation arises by the subduction procedure from the *A*, *B*, and *C* transitions in bulk materials with the wurtzite structure. The subduction procedure transforms Table I into Table III (optical selection rules) where one has only to replace the a_1, a_2, e, $\overline{e}_1^{(1)}$, $\overline{e}_1^{(2)}$, and $\overline{e_2}$ irreps by the Γ_1, Γ_2, Γ_3, Γ_4, Γ_5, and Γ_6 ones since the site symmetry of any atom is C_{3v}. Permutational and spatial symmetries of different parts of states of trion in SL's with even values of $m+n$ and QW's are given in Table IV (which also can be obtained by subduction from Table II). The ground state of any free positively charged trion with two holes from the same valence band is of symmetry Γ_6. This is also the case for negatively charged free B^- and C^- trions, whereas A^- trions can have the Γ_4 or Γ_5 symmetry. The Γ_4 and Γ_5 irreps are complex conjugate and correspond to the same energy level when no magnetic field is applied to the structure. It can be readily seen (Table III, Fig. 2) that negatively charged Γ_4 or Γ_5 (Γ_6) trions decay with emission of a photon with the *xy* (any) polarization and a Γ_6 final electron. Positively charged Γ_4 (Γ_5) trions decay with a photon with the *z* polarization and a Γ_4 (Γ_5) hole or a photon with the *xy* polarization and a Γ_6 hole. Positively charged Γ_6 trions decay with emission of a photon with the *xy* polarization and a Γ_4 or Γ_5 hole or with emission of a photon with any polarization and a Γ_6 hole.

TABLE IV. Permutational and spatial symmetries of free-trion functions in $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SL's with even values of $m+n$ (space group C_{3v}^1) and in $(\mathrm{GaN})_m/\mathrm{AlN}$ QW's (layer group DG69).

Γ_{env}	$(+)$	$(-)$
$\Gamma_{c,v}$	$(-)$	$(+)$
A^-	Γ_4, Γ_5	Γ_4, Γ_5, Γ_6
B^-, C^-	Γ_6	Γ_4, Γ_5, Γ_6
AA^+	Γ_6	Γ_6
BB^+, CC^+	Γ_6	Γ_4, Γ_5, Γ_6
AB^+, AC^+	Γ_4, Γ_5, Γ_6	Γ_4, Γ_5, Γ_6
BC^+	Γ_4, Γ_5, Γ_6	Γ_4, Γ_5, Γ_6

Bound excitons and trions obey the same selection rules as in bulk materials since the site symmetry is C_{3v} in any case. In heterostructures, it is worth noticing that energy values for trapping of single carriers and excitons depend on the location of the impurity, in particular on its distances to interfaces. This can induce some dispersions of transition energies, but without change in symmetry, and hence in the selection rules, since any site of the lattice presents the C_{3v} symmetry.

Finally, in the heterostructures, an electric field directed along the growth axis lifts the translational symmetry of SL's along the growth axis and lowers their space symmetry to the $P3m1$ (DG69) one, the symmetry of any atomic site remaining described by the C_{3v} group. The electric field therefore induces no change in symmetry for the QW's. It simply lowers the symmetry of any SL to that of QW's.[12]

V. PHONON-ASSISTED TRANSITIONS IN BULK MATERIALS AND HETEROSTRUCTURES

We previously showed that, in bulk materials with the wurtzite structure[4] and in wurtzite-based heterostructures,[12] any couple of extended and/or bound states can be connected by a phonon-assisted transition. The phonons we took into account are those at high-symmetry points in the BZ, i.e., phonons with a high density of states, ensuring that the transition probabilities are reasonably high. The result holds whatever are the number of phonons involved in the process and the polarization of the emitted photon (parallel or perpendicular to the *c* axis). Of course, the energy of the photon depends on the nature of the phonon(s) (and eventually on its own polarization), if several processes are available. All these properties are still valid for trion transitions as well as for transitions of excitons bound to neutral impurities.

VI. CONCLUSION

The free excitons present some limitations for optical recombination. Indeed, in crystals with the C_{6v}^4 space group (the bulk materials and SL's with odd values of $m+n$) (Fig. 1, Table I), only the Γ_1 and Γ_6 excitons can radiatively recombine, whereas the Γ_{2-5} ones are dark. In structures with the C_{3v}^1 space group (the SL's with even values of $m+n$ and any QW) (Fig. 2, Table III), the Γ_1 and Γ_3 excitons can radiatively recombine, whereas the Γ_2 ones are dark. Last, the excitons bound to ionized impurities obey the same selection rules[3] as the free excitons at the Γ point in structures with the C_{3v}^1 space group (one has only to replace the Γ_1, Γ_2, and Γ_3 irreps by the a_1, a_2, and e ones, respectively).

If one considers the set of trions corresponding to a free or bound exciton with a given symmetry, the total number of channels for their radiative recombination in any structure (bulk, SL, or QW) is much larger that it is for the exciton itself. As a matter of fact, a carrier with any of the three double-valued symmetries in the relevant group (the C_{6v}^4, C_{3v}^1, or C_{3v} one) can be associated with the exciton to build a trion. Moreover, among the free trions, only the negatively charged Γ_8 ones (structures with the C_{6v}^4 space group) are dark. The positively charged free trions have at least two possible channels, in symmetry terms, to radiatively recombine, except the Γ_8 ones, which have only one. Last, at least two channels are available for the radiative recombination of any bound trion. Obviously, the energy of the emitted photon depends on the final-carrier state. Let us also remark that the number of possible channels for trion recombination is even increased if the final-carrier state is a free (bound) one when dealing with a bound (free) trion.

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APPENDIX

Let $|q\rangle \equiv |\mathbf{k},\gamma,m,\mu\rangle$ be a full group-theoretical notation of a one-electron orbital where m numbers the basis vectors of the allowed double valued irrep γ of the wave vector group $G_{\mathbf{k}} \subset$ space group G, and μ discriminates between independent bases of equivalent irreps of $G_{\mathbf{k}}$. This function (with other irrep basis vectors) transforms according to the double-valued irrep ($\mathbf{k}$, γ) of the group $G_{\mathbf{k}}$ and double-valued irrep ($*\mathbf{k},\gamma$) of the space group G where $*\mathbf{k}$ means the star of the wave vector $\mathbf{k}$.

In the two (or three) bands approximation, any excited state of trion type is described by a linear combination of the Slater determinants $\Psi(q_1,q_2,q_3)$, which correspond to two electrons in the states $|q_1\rangle$ and $|q_2\rangle$ of the conduction band and one hole in the state $|q_3\rangle$ of the valence band for a negatively charged trion (one electron in the state $|q_1\rangle$ of the conduction band and two holes in the states $|q_2\rangle$ and $|q_3\rangle$ of the valence bands for a positively charged trion). These determinants have necessary properties with respect to permutations of identical particles (Pauli principle). On the other hand, a determinant $\Psi(q_{c1},q_{c2},q_{v3})$—for example, for negatively charged trions—transforms with its partners according to a double-valued irrep contained in the direct product[7] $(*\mathbf{k}_{c1},\gamma_{c1})\times(*\mathbf{k}_{c2},\gamma_{c2})\times(*\mathbf{k}_{v3},\gamma_{v3})^*$ where $(*\mathbf{k}_{v3},\gamma_{v3})^*$ means irrep complex conjugated to the irrep $(*\mathbf{k}_{v3},\gamma_{v3})$.

The space Ω of the determinants $\Psi(q_1,q_2,q_3)$ is closed with respect to all the operations of the space group G: i.e., it is a space of some reducible rep β of G. The space Ω contains the subspaces of all the double-valued irreps of G. This affirmation is evident for the states with $\mathbf{k}_{c1}$, $\mathbf{k}_{c2}$, $\mathbf{k}_{v3}$, and $\mathbf{k}=\mathbf{k}_{c1}+\mathbf{k}_{c2}-\mathbf{k}_{v3}$ of general position in the BZ as these states have only translation symmetry. Let us prove that, in the space Ω, there are the states of all the possible symmetries (of all the double-valued irreps) with $\mathbf{k}$ on the symmetry elements in the BZ.

Note that, in the space Ω, there are the states with all the $\mathbf{k}$ in the BZ. At first consider the direct product $|q_2\rangle|q_3\rangle^* = |\mathbf{k}_{c2},\gamma_{c2}\rangle|\mathbf{k}_{v3},\gamma_{v3}\rangle^*$ with $\mathbf{k}_{c2}=\mathbf{k}_{v3}=\mathbf{k}$ in the general position which transforms according to single-valued identity Γ_1 $[\mathbf{k}+(-\mathbf{k})=0]$ irrep of little group $G_{\mathbf{k}}$ (or the identity irrep of little co-group $F_{\mathbf{k}}=C_1$), as there is only one small irrep $\gamma_{c2}=\gamma_{v3}=1$ of the little group $G_{\mathbf{k}}\subset G_{\mathbf{k}c1}$ consisting of translations only. The number of points in the star $*\mathbf{k}$ with respect to the little co-group $F_{\mathbf{k}c1}$ is equal to its order. The set of $|q_2\rangle|q_3\rangle^* = |\mathbf{k}_{c2},\gamma_{c2}\rangle|\mathbf{k}_{v3},\gamma_{v3}\rangle^*$ corresponding to all the points of $*\mathbf{k}$ forms the space ω invariant under all the operations of $G_{\mathbf{k}c1}$ and transforms according to Γ' $[\mathbf{k}+(-\mathbf{k})=0]$ rep of $G_{\mathbf{k}c1}$. In the general case, all single- and double-valued irreps of the little group $G_{\mathbf{k}'}$ (small and others) are in one-to-one correspondence to the projective single- and double-valued irreps of the little co-group $F_{\mathbf{k}'}$ with appropriate factor systems.[13] In these projective irreps of $F_{\mathbf{k}'}$ the matrices (and characters) of elements $R\in F_{\mathbf{k}'}$ are the same as of those irreps of $G_{\mathbf{k}'}$ which map the corresponding elements $(R|\mathbf{v}_R)\in G_{\mathbf{k}'}$. Projective reps of point groups have many properties of ordinary reps. In particular, the space ω is the space of the single-valued rep γ' of $F_{\mathbf{k}'}$ induced by the identity γ irrep of $F_{\mathbf{k}}\subset F_{\mathbf{k}c1}$ $[\gamma' = \gamma_1(F_{\mathbf{k}})\uparrow F_{\mathbf{k}c1}]$. The rep γ' is a regular rep of $F_{\mathbf{k}c1}$ and contains every single-valued irrep of $F_{\mathbf{k}'}$ as many times as its dimension. The characters $\chi^{(\gamma')}(R)$ of all the elements $R \in F_{\mathbf{k}c1}$ in the γ' rep are zero except $\chi^{(\gamma')}(E)=n_{\mathbf{k}c1}$ (the order of $F_{\mathbf{k}c1}$). Let α be any m_β-dimensional double-valued irrep of $F_{\mathbf{k}c1}$ with appropriate factor system. The direct product $\gamma'\times\alpha$ is also a double-valued rep of $F_{\mathbf{k}c1}$ with the same factor system and with the characters $\chi^{(\gamma'\times\alpha)}(R)=\chi^{(\gamma')}(R)\chi^{(\alpha)}(R)$.

The m_j-dimensional double-valued irrep α_j is contained in the direct product $\gamma'\times\alpha$, $\mathbf{r}_j^{(\alpha)}=m_j$, $m_\alpha\neq 0$ times, and, therefore, all double-valued irreps α_j are contained in the direct product $\gamma'\times\alpha$. Due to the one-to-one correspondence between small irreps of little groups and projective irreps of co-groups with appropriate factor systems, this proves that the reducible rep β of G in the space Ω of the determinants $\Psi(q_1,q_2,q_3)$ contains all the double-valued irreps of G.

The space Ω can be decomposed in subspaces which correspond to these irreps of the space group by usual group-theoretical methods. In other words, one can form the linear combinations of the determinants related to the double-valued irreps of the space group:

$$\Phi(\mathbf{k},\gamma,m,\mu')\equiv\Phi(q') = \sum_{q_1q_2q_3} C(q';q_1,q_2,q_3)\Psi(q_1,q_2,q_3), \tag{A1}$$

the coefficients $C(q';q_1,q_2,q_3)$ being found by symmetry considerations. In the two- (three-) band approximation, the states of a trion energy band are the linear combinations of

$\Phi(q')$ of the same symmetry with the coefficients found by solution of the Schrödinger equation for the system under consideration. It is obvious that the wave functions of trions states have the necessary properties with respect to permutations of identical Fermi particles (electrons and holes). It can be concluded from the above that the Pauli principle imposes no restrictions on the possible symmetries (double-valued irreps) of trion states.

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[1] R. A. Evarestov and V. P. Smirnov, in *Site Symmetry in Crystal: Theory and Applications*, 2nd ed., Vol. 108 of Springer Series in Solid Sciences, edited by M. Cardona (Springer, Heidelberg, 1997).

[2] P. Tronc, Yu. E. Kitaev, G. Wang, M. F. Limonov, A. G. Panfilov, and G. Neu, Phys. Status Solidi B **216**, 599 (1999).

[3] P. Tronc, Yu. E. Kitaev, G. Wang, and M. F. Limonov, Phys. Status Solidi B **210**, 471 (1998).

[4] P. Tronc, Yu. E. Kitaev, G. Wang, M. F. Limonov, and G. Neu, Physica B **302–303**, 291 (2001).

[5] C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).

[6] S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Boulder, Co, 1967).

[7] M. Balkanski and J. des Cloizeaux, J. Phys. Radium **22**, 41 (1961).

[8] F. Bassani, J. J. Forney, and A. Quattropani, Phys. Status Solidi B **65**, 591 (1974).

[9] J. P. Elliot and P. J. Dawber, *Symmetry in Physics* (Clarendon, London, 1979).

[10] D. Sanvitto, R. A. Hogg, A. J. Shields, D. M. Whittaker, M. Y. Simmons, D. A. Ritchie, and M. Pepper, Phys. Rev. B **62**, R13 294 (2000).

[11] Yu. E. Kitaev, M. F. Limonov, P. Tronc, and G. N. Yushin, Phys. Rev. B **57**, 14 209 (1998).

[12] Yu. E. Kitaev and P. Tronc, Phys. Rev. B **64**, 205312 (2001).

[13] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, New York, 1974).