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Phonons in wurtzite $(GaN)_m(AlN)_n$ superlattices: non-monotoneous dependence of the number of Raman-active modes on superlattice period

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Abstract. The symmetry of wurtzite $(GaN)_m(AlN)_n$ is established to depend on the numbers of monolayers of constituent materials in the primitive cell being C^4_{6v} (odd $m+n$) or C^1_{3v} (even $m+n$). As a result, it was shown that the number of Raman-active modes depends non-monotonically on $m+n$.

Spectacular successes in III–V nitride technology (GaN, AlN, and InN) in recent years have fostered the growth of short-period $(GaN)_m(AlN)_n$ semiconductor superlattices (SLs) [1] which can be considered as candidates for high-efficiency blue-light-emitting devices. However, the study of their phonon spectra was hindered by absence of any symmetry analysis. In the present paper, we present a complete group-theory analysis of the $(GaN)_m(AlN)_n$ SLs including the determination of their space groups, phonon symmetries, and Raman and infrared (IR) selection rules.

We use the approach that we have elaborated upon for the $(GaAs)_m(AlAs)_n$ SLs [2]. We consider the SLs as crystals with an enlarged unit cell compared with that of the parent materials (GaN and AlN). The structure of SLs, i.e., a space group G and an arrangement of atoms over the Wyckoff positions in a primitive cell, depends on the growth direction and numbers of monolayers (m, n) of constituent materials in the formula unit. For each direction of growth, these SLs constitute several crystal families specified by different space groups. Within each family, the crystals have the same space group but differ from each other by an arrangement of atoms over the Wyckoff positions. Thus, from the crystallographic point of view the SLs with different numbers of monolayers m and n are distinct crystals, even those belonging to the same family. Such a dependence of the SL crystal structure on the numbers of monolayers strongly influences its phonon states.

Bulk GaN and AlN single crystals exist in two modifications with the zinc-blende structure (space group T^2_d) and wurtzite structure (space group C^4_{6v}). The $(GaN)_m(AlN)_n$ SLs grown from zinc-blende parent GaN and AlN crystals are isostructural with the $(GaAs)_m(AlAs)_n$ ones considered in detail in [2]. Therefore, from the point of view of symmetry, the results of the analysis of $(GaAs)_m(AlAs)_n$ can be directly applied to the zinc-blende $(GaN)_m(AlN)_n$ ones. Below, we analyze the SLs formed from wurtzite parent materials (GaN and AlN) grown along the sixfold screw axis. When analyzing the SL structure, we adopt an approximation that the atoms in SLs are on the sites of a wurtzite lattice with lattice constants a and c and internal parameter u (denoting separation between anion and cation sublattices) being averages of the corresponding parameters of GaN and AlN. The approximation is reasonable since the differences in the u, a, and c parameters of GaN and AlN are less than 1.5%, 2%, and 4%, respectively. Taking this approximation into account, the coordinates of all the atoms in the lattice are well defined. As a result, we can determine both the space group and the atomic arrangement over the Wyckoff positions for a SL with arbitrary numbers of monolayers m and n.

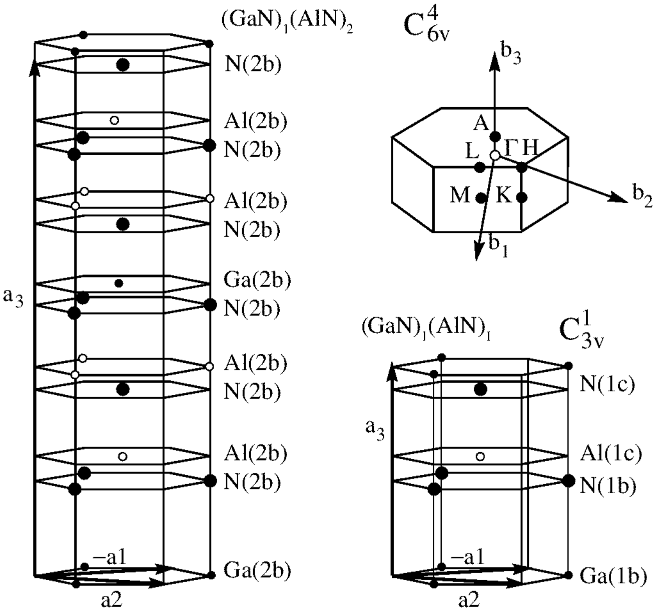

Fig. 1. The primitive unit cells of the $(GaN)_1(AlN)_1$ and $(GaN)_1(AlN)_2$ [0001] SLs and the corresponding BZ. The Wyckoff positions are given in parentheses together with the atoms.

Our analysis is valid for a SL made of two binary materials with a wurtzite structure and an identical cation or anion. If the difference in the lattice parameters between both materials cannot be neglected, our analysis remains valid at least for pseudomorphic SLs.

We have determined that the wurtzite $(GaN)_m(AlN)_n$ SL' grown along the [0001] direction form two families with space groups C^4_{6v} and C^4_{3v} (hexagonal Bravais lattice) correspoding to odd and even values of $m + n$, respectively. The crystal structures of typical representatives of these two different families are presented in Fig. 1 together with the corresponding Brillouin zone (BZ). For odd values of $m + n$, the nonsymmorphic space group C^4_{6v} of the SL is that of the bulk, the sixfold screw axis being conserved, whereas for even values of $m + n$ the improper translation $(00\frac{1}{2})$ is lost with the sixfold screw axis being replaced by the threefold rotation one. The symmetry of the latter family is described by the symmorphic C^1_{3v} space group. The atomic arrangements over the Wyckoff positions for both SL families are shown in columns 1–4 of Tables 1 and 2. The numbers preceding the chemical element symbols denote the number of such atoms at the Wyckoff positions listed in column 5 together with their coordinates and site symmetry groups.

Next we obtained the phonon symmetry in the $(GaN)_m(AlN)_n$ SLs using the method of induced band representations of space groups [3]. The results are presented in Tables 1 and 2. The symmetries of phonon modes at the symmetry points of the BZ are given by indices of small irreducible representations (irreps) (columns 7–9) induced by those irrreps β (column 6) of site symmetry groups according to which the local atomic displacements (x, y, z) are transformed. (The labelling of small irreps follows [4]).

The sets of normal modes at the symmetry points of the BZ are obtained by summing up contributions of all the atoms in the primitive cell. As a result, for the SLs with C^4_{6v} we

Table 1. Phonon symmetry in $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SLs with the space group $\mathrm{C}_{3\mathrm{v}}^1$.

Atomic arrangement						Γ	K	M
$m = 1$	$m = 2$	$m = 2s + 1$	$m = 2s$	$\mathbf{q}$	β	(000)	$\left(\frac{1}{3}\frac{1}{3}0\right)$	$\left(\frac{1}{2}00\right)$
$n = 1$	$n = 2$	$n = 2t + 1$	$n = 2t$			$\mathrm{C}_{3\mathrm{v}}$	C_3	C_s
	1Ga	$\frac{m+1}{2}$Ga	$\frac{m}{2}$Ga	$1b$	$a_1(z)$	1	2	1
1Ga	1Al	$\frac{n-1}{2}$Al	$\frac{n}{2}$Al	$\left(\frac{1}{3}\frac{2}{3}z\right)$	$e(x, y)$	3	1,3	1,2
1N	2N	$\frac{m+n}{2}$N	$\frac{m+n}{2}$N	$\mathrm{C}_{3\mathrm{v}}$				
	1Ga	$\frac{m-1}{2}$Ga	$\frac{m}{2}$Ga	$1c$	$a_1(z)$	1	3	1
1Al	1Al	$\frac{n+1}{2}$Al	$\frac{n}{2}$Al	$\left(\frac{2}{3}\frac{1}{3}z\right)$	$e(x, y)$	3	1,2	1,2
1N	2N	$\frac{m+n}{2}$N	$\frac{m+n}{2}$N	$\mathrm{C}_{3\mathrm{v}}$				

Table 2. Phonon symmetry in $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SLs with the space group $\mathrm{C}_{6\mathrm{v}}^4$.

Atomic arrangement						Γ	K	M
$m = 1$	$m = 1$	$m = 2$	$m = 2s + 1$	$\mathbf{q}$	β	(000)	$\left(\frac{1}{3}\frac{1}{3}0\right)$	$\left(\frac{1}{2}00\right)$
$n = 2$	$n = 4$	$n = 3$	$n = 2t$			$\mathrm{C}_{6\mathrm{v}}$	$\mathrm{C}_{3\mathrm{v}}$	$\mathrm{C}_{2\mathrm{v}}$
2Ga	2Ga	4Ga	$2m$Ga	$2b$	$a_1(z)$	1,4	3	1,4
4Al	8Al	6Al	$2n$Al	$\left(\frac{1}{3}\frac{2}{3}z\right)$	$e(x, y)$	5,6	1,2,3	1,2,3,4
6N	10N	10N	$2(m + n)$N	$\mathrm{C}_{3\mathrm{v}}$				

have

$$\begin{aligned}
\Gamma &\to \Gamma = \Gamma_{\mathrm{opt}} + \Gamma_{\mathrm{ac}} = 2(m+n)(\Gamma_1 + \Gamma_4 + \Gamma_5 + \Gamma_6), \quad \Gamma_{\mathrm{ac}} = \Gamma_1 + \Gamma_6,\\
K &\to 2(m+n)(K_1 + K_2 + 2K_3),\\
M &\to 2(m+n)(2M_1 + M_2 + M_3 + 2M_4).
\end{aligned} \tag{1}$$

whereas for the SLs with $\mathrm{C}_{3\mathrm{v}}^1$ symmetry the sets of normal modes are

$$\begin{aligned}
\Gamma &\to \Gamma = \Gamma_{\mathrm{opt}} + \Gamma_{\mathrm{ac}} = 2(m+n)(\Gamma_1 + \Gamma_3), \quad \Gamma_{\mathrm{ac}} = \Gamma_1 + \Gamma_3,\\
K &\to 2(m+n)(K_1 + K_2 + K_3)\\
M &\to 2(m+n)(2M_1 + M_2).
\end{aligned} \tag{2}$$

Below, for the BZ-center phonons we give the correspondence between the two commonly used sets of irrep notations together with IR-active components and non-zero terms of the Raman tensor shown in parentheses:

$$\begin{aligned}
\mathrm{C}_{6\mathrm{v}}^4 : \Gamma_1 &= A_1(z; xx, yy, zz), \ \Gamma_4 = B_1(\text{silent}), \ \Gamma_5 = E_2(xx, yy, xy),\\
\Gamma_6 &= E_1(x, y; yz, xz);\\
\mathrm{C}_{3\mathrm{v}}^1 : \Gamma_1 &= A(z; xx, yy, zz), \ \Gamma_3 = E(x, y; xx, yy, xy, yz, xz).
\end{aligned} \tag{3}$$

From Eqs. (1)–(3) it is seen that in the $\mathrm{C}_{6\mathrm{v}}^4$ SLs there exist the E_1 modes that are Raman active in the xz and yz polarizations and nonactive in xx and yy polarizations, whereas

Table 3. Numbers of Raman and IR active modes in wurtzite $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SLs.

$m+n$	bulk	2	3	4	5	6	$m+n$ (odd) (C_{6v}^4)	$m+n$ (even) (C_{3v}^1)
Raman	4	6	16	14	28	22	$[6(m+n)-2]$	$[4(m+n)-2]$
IR	2	6	10	14	18	22	$[4(m+n)-2]$	$[4(m+n)-2]$

on the C_{3v}^1 SLs all modes are Raman active in the xx and yy polarizations. Therefore, in analyzing Raman spectra it is easy to distinguish SLs with C_{3v}^1 and C_{6v}^4. Thus Raman scattering can serve as a test of SL quality since it is sensitive to a change of the SL period within a monolayer. Analyzing Eqs. (1)–(3) it is interesting to notice that, when increasing the number of monolayers $(m+n)$ in the formula unit, the number of Raman-active modes increases nonmonotonically. The results are summarized in Table 3.

It is seen that the numbers of Raman-active modes are governed by different equations: $[6(m+n)-2]$ and $[4(m+n)-2]$ for the SLs with C_{6v}^4 symmetry and C_{3v}^1 symmetry, respectively. As a result, when adding one monolayer to a SL with an odd $m+n$ value, the number of Raman-active modes decreases. At the same time, the number of IR-active modes is given by the same equation $[4(m+n)-2]$ for both SL families, i.e. it depends monotonically on the $m+n$ value.

Thus, the $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SLs should be considered as crystals specified by their own space group rather than a simple superposition of bulk parent materials. We have obtained that the SLs belong to two crystal families specified by space groups C_{3v}^1 and C_{6v}^4, depending on whether $m+n$ is even or odd. The dependence of the SL point symmetry on the numbers of monolayers leads to drastic changes in the symmetry of phonon states and selection rules. As a consequence, from polarized Raman spectra one can easily distinguish the SL belonging to different families. Finally, a spectacular property of the $(\mathrm{GaN})_m(\mathrm{AlN})_n$ SLs is a nonmonotoneous dependence of the number of Raman-active modes on $m+n$, whereas the number of IR-active modes increases monotonically.

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References

[1] M. Asif Khan, J. N. Kuznia, D. T. Olson, T. George, and W. T. Pike, *Appl.Phys.Lett.* **63**, 3470 (1993).

[2] Yu. E. Kitaev, A. G. Panfilov, P. Tronc, and R. A. Evarestov, *J.Phys.: Condens.Matter* **9**, 257 (1997); *ibid.* **9**, 277 (1997).

[3] R. A. Evarestov and V. P. Smirnov, *Site Symmetry in Crystals: Theory and Applications* Vol. 108 of Springer Series in Solid State Sciences, ed. M. Cardona (Springer, Heidelberg, 1993; second edition 1997).

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