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13. ABSTRACT *(Maximum 200 words)*

A study was performed of the $Zn_xMg_{1-x}O$ alloy system bandgap bowing. The structural stability of wurtzite MgO was investigated. The high-pressure phase transition of wurtzite to rock salt was investigated for GaN.

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Final Report

Modeling of Wide Band Gap Semiconductor Alloys and Related Topics

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1. Overview

The main topic of this grant was a study of the $Zn_xMg_{1-x}O$ semiconductor alloy system. This study was motivated by the recent succes in growing bulk ZnO crystals of high electronic and optical quality and the demonstration of the possibility of lasing in ZnO quantum wells. The following topics were studied in the first year:

- Band structure of ZnO, with emphasis on the nature of the valence band ordering
- Band-gap bowing in $Zn_xMg_{1-x}O$ alloys, band structure of MgO in the wurtzite phase
- Structural stability of MgO
- Band offsets of ZnO, MgO, GaN, $LiGaO_2$.

A detailed report on these findings was presented in the first yearly report.
One important outcome of the study was the discovery of a homogeneous deformation path from wurtzite to rocksalt. This was subsequently applied to GaN in order to understand the mechanism of the high-pressure phase transition between these two phases. This work was accomplished in the second year.

2. Accomplishments

The following list provides highlights of the research.

- The band structure of ZnO was studied, in particular the ordering of the valence band maxima and the sign of the spin-orbit coupling and its dependence on the Zn 3d band positions. This work addresses a decades old controversy. Our calculations reveal that the spin-orbit coupling is indeed negative, leading to an inverted order of the valence band maxima from the usual ordering; i.e. $\Gamma_7 > \Gamma_9$. However, the interpretation of the related optical experiments is complicated by the fact that excitons are measured rather than band states. Because the exciton binding energy is comparable in magnitude to the splittings, a coupled calculation of the excitons is needed to resolve the interpretation of the optical experiments. A related question is the splitting of these levels in a magnetic field. To this end, work was started towards an ab-initio calculation of the g-tensor of the valence bands.

- The band gap bowing in $Zn_{1-x}Mg_xO$ alloys was determined and found to be rather small for zincblende structured alloys. Combined with estimates of the gap corrections in MgO and ZnO based on the known crystal structures (wurtzite for ZnO) and rocksalt for MgO and calculations of the band gap differences between wurtzite, zincblende and rocksalt for the end compounds, estimates were made for the wurtzite band gap dependence on concentration for $Zn_xMg_{1-x}O$ alloys and found to be in good agreement with experimental values in the range where these alloys have been grown, ie. up to about 30 % Mg.
- The band-offsets were determined between ZnO, MgO, AlN, GaN, InN, $LiGaO_2$, using the dielectric midgap model approach.These calculations reveal that $Zn_xMg_{1-x}O$/ZnO quantum wells have rather small offsets and that $LiGaO_2$ should be considered as an alternative barrier material to make ZnO based quantum well structures.
- The stability of MgO in the wurtzite structure was investigated. It is found to be unstable although a related phase, with an additional mirror plane, which we called h-MgO is marginally metastable. It is characterized by 5-fold bonding instead of 4-fold bonding and has flat layers instead of buckled layers.
- A homogeneous strain transformaton path was discovered between rocksalt and wurtzite. It consists in a simulatenous c/a compression and in-plane compression. Its energetics were studied for both MgO and GaN. Band structures and charge densities were calculated along the transition path and reveal that the driving mechanism for the transformation between these phases is the formation of additional bonds.
- The high-pressure phase transition from wurtzite to rocksalt was studied in detail for GaN. New insights in the mechanism of the transformation were obtained, revealing the crucial role of the internal strain coupling, and the instability of the optical vibrational modes due to their coupling to acoustic modes. It was also found that previous works significantly overestimated the transition pressure.

Most of the early accomplishments have been discussed in more detail in prior yearly research reports. The accomplishments of the final year are discussed below.
The main focus of the last year was a study of the high-pressure phase transition of GaN. This work grew out of our previous work on ZnO and MgO. Our interest in MgO arose from the recent interest in $Mg_xZn_{1-x}O$ alloys and ZnO quantum wells for optoelectronic applications. While ZnO has the wurtzite structure, MgO has the cubic rocksalt structure as naturally occuring crystal structure. This raises the question of the stability and properties of MgO and the alloys in the wurtzite structure. Our initial work showed that MgO is in fact unstable in the wurtzite structure. If constrained to remain hexagonal, wurtzite MgO relaxes to a structure with space group $P_{3/mmc}$, exhibiting an additional mirrorplane compared to wurtzite. It means that the basal planes become flat and that Mg is fold instead of 4-fold coordinated. Further study revealed that this structure itself is only marginally metastable and can be converted to rocksalt via a simple in-plane strain. The intermediate structures then have a side centered orthorhombic lattice. This path between wurtzite and rocksalt involving simple displacements of the atoms and triggered by a homogeneous strain on the system, then suggested a similar path could connect wurzite and rocksalt in GaN in the well-known high-pressure phase transition. Thus, we embarked on a study of this phase transition. Several interesting findings were obtained relevant to the general nature of the mechanism of the high-pressure phase transitions between tetrahedrally bonded and octahedrally bonded systems. This work led to a paper in Physical Review Letters, accepted for publication and to appear in December 2000. A second paper, providing additional details on our study and of the previous study of MgO was submitted to Phys. Rev. B. A copy of the PRL is attached as an appendix.

Other activities included finalizing publications related to a prior ONR project on wide band gap semiconductor alloys and related materials.

3. Publications and presentations

3.1 Publications

1. Identification of Raman-active phonon-modes in oriented platelts of InN and polycrystalline InN,
   J. S. Dyck, K. Kim, S. Limpijumnong, W. R. L. Lambrecht, K. Kash and J. C. Angus,
   Solid State Commun. **114**, 355-360 (2000).
2. Theoretical Studies of ZnO and Related $Mg_xZn_{1-x}O$ Alloy Band Structures,
   Walter R. L. Lambrecht, Sukit Limpijumnong, and B. Segall,
   MRS Internet J. Nitride Semicond. Res. 4S1, G6.8 (1999), also published in *GaN and Related Alloys,* edited by Stephen J. Pearton, Chihping Kuo, Alan F. Wright, Takeshi Uenoyama, Mater. Res. Soc. Symp. Proc. Vol. 537, 1999 Materials Research Society, Pittsburgh, p. G6.8.1.
3. Material Properties of GaN in the Context of Electron Devices,
   H. Morkoç, R. Cingolani, W. Lambrecht, B. Gil, H-X. Jiang, J. Lin, D. Pavlidis, K. Shenai,
   MRS Internet J. Nitride Semicond. Res. 4S1, G1.2 (1999), also published in *GaN and Related Alloys,* edited by Stephen J. Pearton, Chihping Kuo, Alan F. Wright, Takeshi Uenoyama, Mater. Res. Soc. Symp. Proc. Vol. 537, 1999 Materials Research Society, Pittsburgh, p. G1.2.1.
4. Homogeneous strain deformation path for the wurtzite to rocksalt high-pressure phase transition in GaN,
   S. Limpijumnong and W. R. L. Lambrecht, Phys. Rev. Letters (2000), accepted.
5. Theoretical study of the relative stability of wurtzite and rocksalt phases in MgO and GaN,
   S. Limpijumnong and Walter R L. Lambrecht, submitted to Phys. Rev. B

3.2 Presentations

- MRS Boston December1999, Walter R. L. Lambrecht, Sukit Limpijumnong, and B. Segall, "Theoretical Studies of ZnO and Related $Mg_xZn_{1-x}O$ Alloy Band Structures"
- International Workshop on Zinc Oxide, Dayton, OH, October 7-8, 1999, Walter R. L. Lambrecht, S. Limpijumnong and B. Segall, "Electronic band structure of ZnO and related $Mg_xZn_{1-x}O$ alloys".
- APS March Meeting 2001, Seattle, Walter R. L. Lambrecht and S. Limpijumnong, "Transformation path for the high-pressure wurtzite to rocksalt phase transition and its application to GaN"

Homogeneous Strain Deformation Path for the Wurtzite to Rocksalt High-Pressure Phase Transition in GaN

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A homogeneous orthorhombic shear strain deformation path is proposed for the wurtzite to rocksalt high-pressure transformation. Its energetics are calculated from first-principles for GaN. Previous experimental and theoretical studies of the transition pressure are discussed.

PACS numbers: 61.50.Ks, 81.30.Hd

It is well known that the more ionic of the compound semiconductors undergo a high-pressure phase transition from a tetrahedrally bonded [zinc blende (ZB) or wurtzite (WZ)] to an octahedrally bonded [rocksalt (RS)] structure [1,2]. While the transition pressures of these phase transitions and their chemical trends have been studied extensively, little is so far known about the transformation *mechanism*. In this Letter, we describe a homogeneous strain transformation path from the (hexagonal) WZ to the (cubic) RS structure and analyze its energetics using first-principles total energy calculations for GaN. GaN is chosen because of the recent interest in this material and the availability of experimental data [3–5] and prior theoretical results [6–8].

The proposed homogeneous strain deformation path is similar to the well-known tetragonal Bain transformation [9] between fcc and bcc. It is more complex in the sense that the present path involves two mutually orthogonal strains lowering the symmetry of the most general intervening structures to orthorhombic (a common subgroup of both the cubic and hexagonal groups). Also, the relaxation of additional structural parameters is involved because of the occurrence of two sublattices in the crystal, and volume changes have to be taken into account along the path to describe the high-pressure transition.

We first describe the crystallographic aspects. The WZ crystal structure is characterized by three parameters, the lattice constant a, the c/a ratio, and the internal parameter u which fixes the relative position of the two hexagonal close-packed sublattices. The last parameter has to be relaxed for each c/a when we consider uniaxial strain in the c direction. We see below that, near the ideal WZ structure, u increases linearly with decreasing c/a (compression) but eventually (for $c/a \leq 1.2$) it starts to vary faster and finally locks into a value of $1/2$. At that point, the structure acquires an additional mirror plane (as shown in Fig. 1) and the space group changes from $P6_3mc$ to $P6_3/mmc$. This intermediate structure is isomorphic to the layered material h-BN with the important difference, however, that here the two nearest neighbor distances perpendicular to the planes are almost equal to the three in the plane. Because we first discovered this phase as a metastable state of MgO, we refer to it as h-MgO [10].

Next, we consider an in-plane uniaxial strain in, for example, the $[10\bar{1}0]$ direction, or any of its equivalent directions rotated from it by 60°. Such a strain, as shown in Fig. 2, can change the rhombus-shaped unit cell projection to a square. This transformation can be viewed as changing the side-centered orthorhombic structure with lattice parameters c, b, and a until b becomes equal to a. Again, there is an internal structural degree of freedom, specifying the relative positions of the two sublattices, associated with this transformation, which we call v (indicated in Fig. 2). When this parameter locks into the symmetric value of $1/2$, and b/a as well as c/a become 1, the crystal structure becomes RS. The values of the parameters c/a, u, b/a, and v in WZ and RS are indicated in Table I.

The above discussion shows that by a combination of the two independent strains c/a and b/a, specifying an orthorhombic intermediate structure, WZ can continuously be transformed into RS without any bond breaking and with very simple atomic displacements. By mapping out the energy landscape as a function of c/a and b/a (with

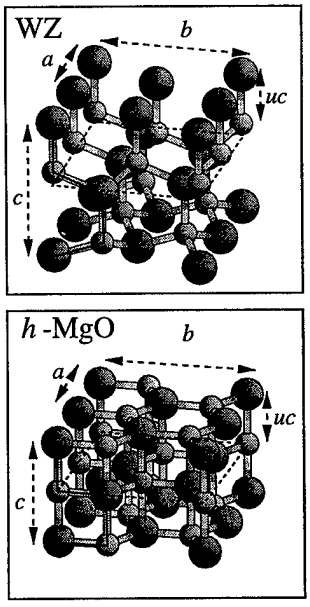

FIG. 1. Transformation of WZ to hypothetical h-MgO structure under c/a compression.

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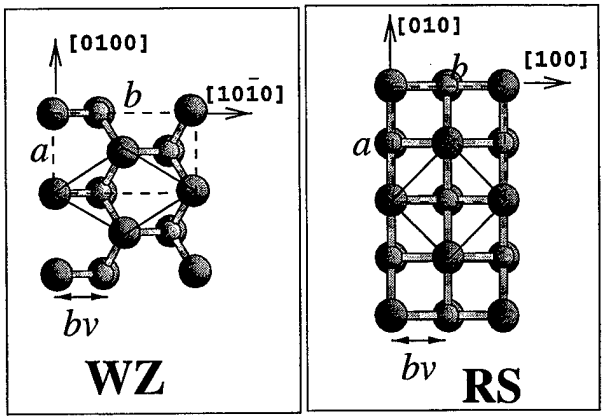

FIG. 2. Top views of WZ (left) and RS (right) crystal structures: small spheres, anions; large spheres, cations. The parameters b and v defining the structure are indicated.

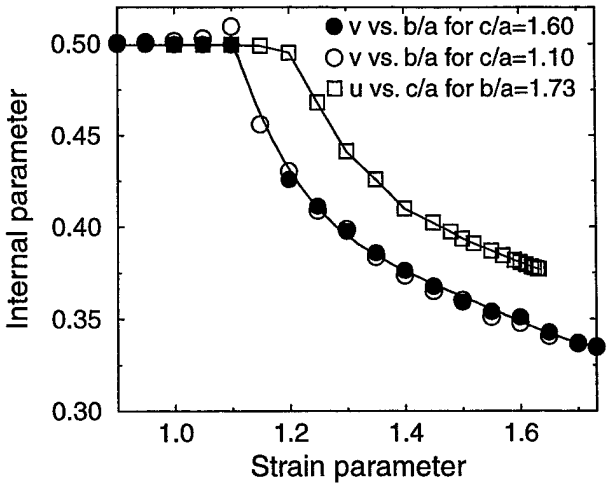

FIG. 3. Internal structural parameters as a function of strain.

relaxed internal structural parameters) and including the volume dependence of the energy at each point c/a, b/a, we can study the energetics of the phase transition.

We use the density-functional theory [11] in the local density approximation (LDA) as parametrized by Hedin and Lundqvist [12]. The self-consistent equations are solved using the full-potential linearized muffin-tin orbital method [13] with basis set and other convergence parameters described in Refs. [14–16].

Figure 3 shows how the parameters u and v behave as a function of the strains c/a and b/a, respectively. We note that in both cases an abrupt change takes place near a critical value of the uniaxial strain. At this point, the two sublattices basically lock into a symmetric position. In other words, instead of having a single (directed covalent) bond on one side, two equivalent bonds are formed on either side. Examination of the charge densities (to be published elsewhere) clearly reveals the formation of these new bonds. We find that these bonds also become less directional and more ionic in character. We found that the behavior of the curves in Fig. 3 is insensitive to volume and that they are nearly independent of each other.

Figure 4 shows the total energy minimum (as a function of volume, u, and v) as a contour plot as a function of c/a and b/a. The minimum in the upper right corner of this plot corresponds to the absolute minimum in the WZ phase. The minimum in the bottom left corner corresponds to the RS phase. This figure suggests a more-or-less straight diagonal path $[(b/a) - 1] = 1.18[(c/a) - 1]$ with a barrier to overcome at about $c/a \approx 1.2$. We note that the values of b/a and c/a where the barrier occurs are close to those where the internal parameters u and v change most rapidly and that the equilibrium volume, shown in Fig. 5, varies most steeply in this region of the parameter space.

In order to discuss the transition as a function of pressure, we next examine the change in minimum enthalpy $\Delta H = \Delta E + p\Delta V$ along the chosen path for various pressures in Fig. 6. Here, E and V are taken at the volume for which the enthalpy is minimized, or the external pressure $p = -dE/dV$, and Δ means the difference from

TABLE I. Crystal structure parameters and selected properties in WZ and RS structures, both viewed as side-centered orthorhombic. The numbers in parentheses are experimental values for which the original references can be found in Ref. [15].

	WZ	RS
c/a	1.62 (1.626)	1.00
u	0.377 (0.377)	1/2
b/a	$\sqrt{3}$	1.00
v	1/3	1/2
V (Å^3/pair)	22.1 (22.8)	17.9
Cohesive energy E_c (eV/pair)	13.6	12.9
LDA band gap E_g (eV)	2.16 (direct)	0.34 (indirect)

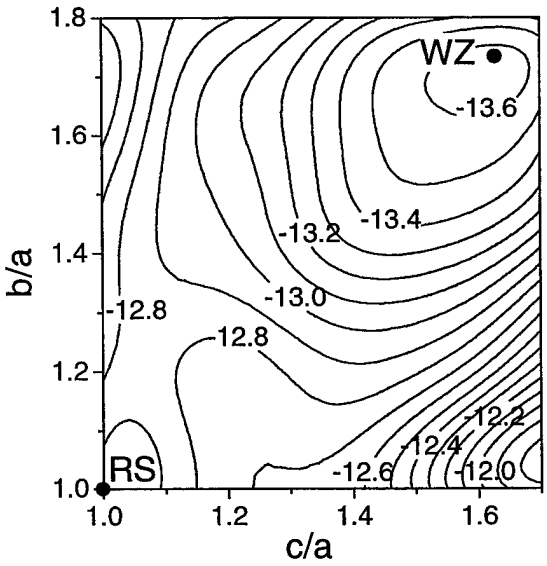

FIG. 4. Contour plot of minimum (as a function of u, v, and volume) total energy (in eV/pair) as a function of b/a and c/a in GaN.

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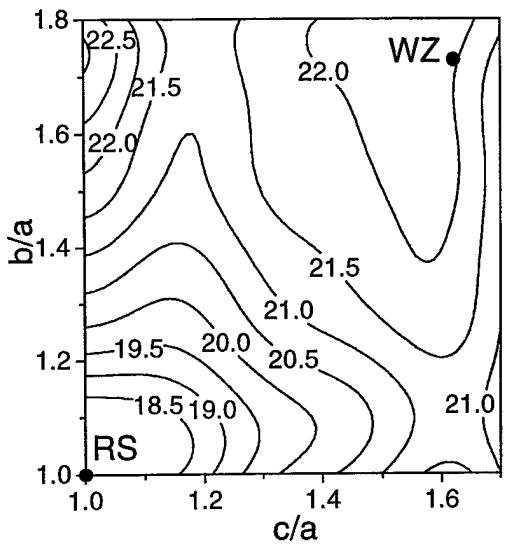

FIG. 5. Contour plot of energy minimizing volume (in Å^3) as a function of b/a and c/a in GaN.

RS. We see that the barrier between the two structures, which is about 0.7 eV/pair at zero pressure, reduces significantly with applied pressure. At 31 GPa, the RS and WZ enthalpy minima become equal, meaning that the two phases can be in equilibrium with each other. This is equivalent to the common tangent construction and defines the equilibrium transition pressure p_t. The relative volume compression of WZ from its equilibrium volume at p_t is $V_1/V_0 = 0.88$. The corresponding volume for RS at the tangent point is given by $V_2/V_0 = 0.73$.

Previous calculations [6–8] obtained a significantly higher transition pressure of 55.1, 55, and 51.8 GPa with volume compression factors $(V_1/V_0, V_2/V_0)$ of $(0.81, 0.67)$, $(0.81, 0.69)$, and $(0.82, 0.71)$, respectively. These results are sensitive to computational details. This

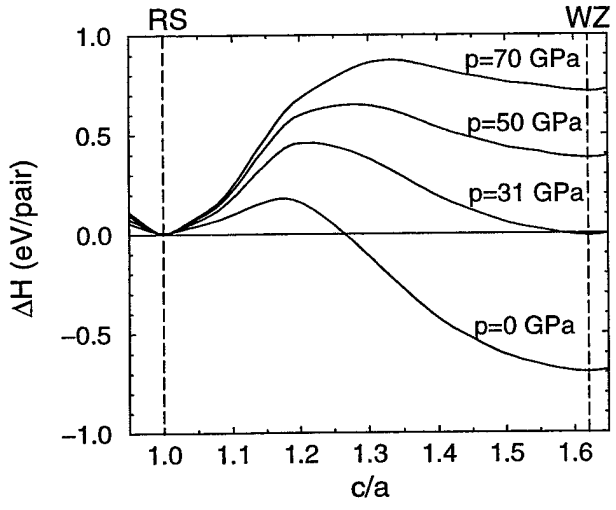

FIG. 6. Minimum enthalpy difference $\Delta H = \Delta E + p\Delta V$ with respect to RS for various pressures along the path $[(b/a) - 1] = 1.18[(c/a) - 1]$.

work uses a more complete basis set than the previous works and no shape approximations to the potential. Our approach was shown in prior work to lead to good agreement with experiment for elastic constants and vibrational frequencies [15].

The experimental results for the phase transition pressure also vary considerably: synchrotron x-ray powder diffraction gave 37 GPa [4], Mo $K\alpha$ x-ray powder diffraction gave 52.2 GPa [5], and single crystal x-ray absorption and visual inspection gave 47 GPa [3]. While the scatter among these is due to a combination of sensitivity of measurement technique and sample type, we claim that all of these values must be considered as upper limits because of slow kinetics, a phenomenon similar to undercooling. Figure 6 shows that while at 31 GPa coexistence of the two phases becomes possible from a thermodynamic point of view; the barrier for the transformation 0.45 eV/pair (2600 K) is fairly high and is reduced to 0.26 eV/pair (or 1500 K) at 50 GPa. Considering a Boltzmann factor $\exp(-H/kT)$ at room temperature, this implies an increase by a factor of 40 in transition probability from 31 GPa to 50 GPa. The experimental observation [3] that upon releasing the pressure the system stays in the RS phase down to about 30 GPa also indicates the existence of a significant barrier.

Next, we wish to clarify the status of our model in relation to the actual transition mechanism in real samples. There is clear experimental evidence that the crystal does not transform as a single homogeneous domain by the fact that, after the reversal of the strain, the Raman lines broadened significantly, indicating that some degree of polycrystallinity resulted from the cycling process [3]. Yet, no amorphization was observed. The large volume compression by more than 20% from WZ to RS at the transition pressure would lead to enormous strain between transformed regions and untransformed surrounding material, which has to be released by some mechanism. These secondary effects determining the microstructure of the sample accompanying the actual crystallographic transformation are beyond the scope of this paper.

An important prediction of our model is the relative crystallographic orientation of the WZ and RS phases: $(0001)_{WZ} \parallel (001)_{RS}$, with $[10\bar{1}0]_{WZ} \parallel [100]_{RS}$ and $[0100]_{WZ} \parallel [010]_{RS}$, contrary to the naive expectation $(0001)_{WZ} \parallel (111)_{RS}$ based on closed-packing considerations of the sublattices. Unfortunately, no experimental information is presently available on this question. Even if secondary strain relaxation phenomena will affect the nature of the interface between transformed and untransformed parts of the sample, one may expect the relative orientation of the crystallographic domains to be maintained. Our model also suggests that a combination of uniaxial and hydrostatic stress would facilitate the transition.

It was suggested in the past that zone boundary transverse acoustic phonon softening plays an important role in

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the ZB-RS transitions. In fact, the values of the negative mode Grüneisen parameters of these modes were found to be correlated approximately linearly with the transition pressures in a series of materials [17]. In WZ, the E_2^{low} mode at Γ is essentially a folded zinc blende TA phonon mode at L and also has a negative mode Grüneisen parameter [3,18]. Nevertheless, the phase transitions clearly take place at pressures far below the pressure required for this mode to pass through zero and become a true "soft mode." Furthermore, the displacement pattern of the E_2^{low} mode does not lead to RS at all. So, a true soft-mode explanation is not applicable. On the other hand, our model indeed predicts the crystal to become softer against shear type acoustic deformations under pressure, as is evidenced by the decreasing curvature of the enthalpy versus uniaxial distortion in Fig. 6. The crucial point is the corresponding reaction of the sublattice coupling. The atomic motions involved in the u and v relaxations, which drive the transition by the new bond formations, are in fact closely related to the optic A_1 and E_2^{high} vibrational modes at Γ. Similarly, the ZB-RS transition corresponds to a shift of the equilibrium sublattice displacement (u, u, u) from $u = 1/4$ to $u = 1/2$ and is thus related to the optical vibration mode. Thus, the softening of the lattice against shear distortions under pressure indirectly leads to changes in the optic modes because of the internal strain coupling of shear to optic modes. The latter become unstable beyond a critical shear and hence lead to the phase transition.

An interesting observation by Perlin *et al.* [3] is that at the onset of the phase transition the crystal turned black and the Raman signal was lost. While there are many possible disorder related explanations for this behavior, it is interesting to note that our calculations predict an almost closing of the gap (0.1 eV) as the structure passes through the (unstable) barrier region between the two structures. While pure volume reduction would tend to increase the gap, the c/a compression tends to decrease the gap and the b/a compression makes it indirect. Beyond the barrier configuration towards RS the gap increases again due to the continuing volume compression but stays indirect.

In summary, we have identified a simple homogeneous orthorhombic shear strain path, along which WZ can continuously be transformed into RS, and have investigated the energetics along this path for GaN. We found a lower critical transition pressure from the common tangent construction than that obtained in previous calculations and by experiments. The discrepancy with experiment is attributed to slow kinetics in view of the calculated magnitude of the barrier found along the proposed transition path. Our calculations predict an almost vanishing band gap at the transition barrier, which is consistent with, although not proven by, experimental observations of the loss of transparency of the crystal at the start of the transition. We expect our model to apply to other WZ-RS transitions. Our model of a homogeneous transformation may be viewed as the long wavelength limit of acoustic phonon modes corresponding to an orthorhombic shear strain superposed on the uniform volume compression. The softening of the structure with respect to shear under pressure in turn leads to an instability of the optic modes. The related sublattice relative displacements leading to the structural transition are driven by the formation of additional bonds.

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