# Theoretical study of the relative stability of wurtzite and rocksalt phases in MgO and GaN

Sukit Limpijumnong\* and Walter R. L. Lambrecht

Department of Physics, Case Western Reserve University, Cleveland, Ohio 44106-7079

(Received 12 July 2000; revised manuscript received 28 November 2000; published 14 February 2001)

We report local density functional calculations using the full-potential linearized muffin-tin orbital method for MgO and GaN in the wurtzite and rocksalt structures and for orthorhombic structures along a homogeneous strain transition path linking wurtzite to rocksalt. MgO is found to be unstable in the wurtzite and marginally metastable in a layered hexagonal phase, labeled h-MgO, in which Mg is approximately fivefold coordinated, the stable phase being rocksalt. GaN is stable in the wurtzite at ambient pressures but exhibits a phase transition to the rocksalt. Band structures and charge densities exhibiting the bond formation as one goes from one structure to the other are presented.

DOI: 10.1103/PhysRevB.63.104103

PACS number(s): 61.50.Ks, 81.30.Hd

### I. INTRODUCTION

The relative stability of different crystallographic phases and possible high-pressure phase transformations among them have been of long-standing interest in type III-V and II-VI semiconductor compounds. Of particular interest is the interplay between tetrahedrally bonded structures, such as zinc blende (ZB) and wurtzite (WZ) on the one hand and the octahedrally bonded structure, rocksalt (RS), on the other hand. It is well known that ionicity favors high coordination and thus rocksalt. At high pressures, several of the more ionic semiconductors undergo a transition to rocksalt whereas the less ionic ones prefer a transition from zinc blende to the  $\beta$ -Sn structure.<sup>1,2</sup> On the other hand, the more ionic semiconductors have the wurtzite structure instead of the zinc blende stacking at ambient pressure and the really ionic materials (for example, NaCl, MgO) prefer rocksalt even at ambient pressure. Thus the wurtzite to rocksalt transition and the competition for stability between these two structures is of special interest.

Recently, this has become of even greater interest because of two reasons. The first is that the wurtzite to rocksalt phase transition under pressure has been observed for the III-nitrides<sup>3–9</sup> (AIN, GaN, and InN) and studied theoretically.<sup>10,11</sup> The second reason is that, recently,  $Zn_{1-x}Mg_xO$  alloys have been stabilized in the wurtzite structure.<sup>12</sup> ZnO has the wurtzite structure while MgO has the rocksalt structure. So this raises the question of rocksalt versus wurtzite structural bonding preference in this alloy system and in particular for the end compound MgO.

In the course of a preliminary study<sup>13</sup> of the stability of MgO in the wurtzite phase, we found that wurtzite is unstable towards an intermediate structure between wurtzite and rocksalt, which we call *h*-MgO and which will be described in detail below. Briefly, it corresponds to the structure obtained by a restricted relaxation of the wurtzite structure in which the hexagonal Bravais lattice of wurtzite is preserved but the internal structural parameter and c/a are relaxed. What we found is a structure with an additional mirror plane perpendicular to the sixfold axis. In simple words, instead of making bonds to only one layer, Mg prefers to bond to the layer above and below it in equal fashion and the buckled layer of wurtzite becomes flat. Thus the structure becomes approximately fivefold coordinated in-

stead of fourfold coordinated. Subsequently, we found that this structure can be transformed into rocksalt by an in-plane strain. The plane here refers to the basal plane of the wurtzite from which we started. We will show that there is a marginally small barrier between this h-MgO phase and rocksalt. However, the important point is that this suggested a direct link from wurtzite to rocksalt without any bond breaking or atom reshuffling. Instead, as we will show below, the transition involves only the formation of additional bonds. Only a combined homogeneous strain in the c/a and in-plane directions is required. It turns out that the general structure with both types of strains combined is orthorhombic. This makes sense because the orthorhombic group is a common subgroup of both the hexagonal and cubic structures. It led us to investigate the structural transformation from wurtzite to rocksalt via such intermediate orthorhombic structures and suggests in other words a simple homogeneous strain mechanism for this transformation, similar to but slightly more complicated than the well-known Bain transformation path<sup>14</sup> from fcc to bcc. We carried such a study out for GaN and reported on it in Ref. 17.

In this transformation the hexagonal wurtzite (0001) basal plane becomes the cubic rocksalt (001) plane. Because in the cubic structure this plane is equivalent to (100) and (010), the inverse transformation back to wurtzite could lead to wurtzite rotated to another direction. This type of path from one crystal structure to a rotated version of itself through an intermediate phase was considered in a general manner in the work of Boyer<sup>15</sup> and van de Waal<sup>16</sup> and is known as a magic strain. To the best of our knowledge such transitions have not been previously considered in the wurtzite system and are based on transformation of the Bravais lattice, assuming a similar transformation for the various sublattices in the case of a crystal structure with a basis. In contrast, in the transformation path examined in the present study, the sublattice displacements are a crucial aspect of the transformation. As emphasized in our previous paper, Ref. 17, the transformation consists essentially in an instability in the relative positioning of the sublattices driven by their coupling to the strain.

In this paper, we present our results on the stability investigation of MgO and provide additional details on the GaN results presented earlier. In particular, we here present electronic band structures and charge densities exhibiting the formation of the new bonds as we go from one structure to the other. These both provide insights into the bonding in these materials.

The paper is organized as follows. First we discuss the geometric aspects in Sec. II. Then we provide the necessary information on our computational method in Sec. III. Next, we present our results in Sec. IV for MgO (Sec. IV A) and for GaN (Sec. IV B). In both cases, we first present the total energy and band structure results for the end structures. For MgO, we also present the results on the energetics of the intermediate structures along the transition. We provide information about the charge densities at this point which allows us to monitor the bond formation in going from one structure to another. For GaN, we present the same information except the total energies along the transition which have been discussed elsewhere.<sup>17</sup> Instead, we focus on the charge densities and bond formation along the transition and present information on the band structure along the transition path and in particular at the transition barrier. We note that the study of both MgO and GaN provides an opportunity to compare two materials with different degrees of ionicity with respect to the present problem.

# **II. CRYSTAL STRUCTURES**

The wurtzite 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. In the ideal wurtzite structure, characterized by equal bond lengths, c/a is  $\sqrt{8/3}$ and u is 3/8. The parameters u and c/a, however, are not independent of each other, because for any given value of c/a specifying a uniaxial strain, u must be determined such that there is no net force on the atoms. We will see that near the ideal wurtzite structure, u increases linearly with decreasing c/a (compression) but eventually it starts varying faster and then locks into a value of 1/2. At that point, the structure acquires an additional mirror plane and we obtain the h-MgO structure. The buckled double layer in WZ, indicated by the dashed line in Fig. 1 becomes flat in h-MgO. In each layer, we then have a flat honeycomb lattice with alternating cation and anion on the corners of the hexagons. The space group changes from  $P6_3mc$  to  $P6_3/mmc$  by the introduction of this extra mirror plane. This intermediate structure is isomorphic to the layered material h-BN with the important difference, however, that here the two bond lengths perpendicular to the planes are almost equal to the three in the plane. It is interesting to compare the situation with BN. As is well known, h-BN is a layered structure similar to graphite, but with a different stacking such that B atoms sit right on top of N atoms in two successive layers. In each layer the structure consists of hexagons with alternatingly B and N atoms on the vertices. The structure is essentially threefold coordinated because the interlayer distance is too large to form a bond. Under compression of this structure along c/a, it has been found<sup>18</sup> to convert to wurtzite at some critical c/a reduction by forming a bond perpendicular to the plane. This breaks the mirror plane symmetry and the bonding becomes tetrahedral. Apparently, in MgO, under high compression of c/a,



FIG. 1. Two-step transformation of wurtzite (top) to *h*-MgO (middle) to rocksalt (bottom). The lattice parameters *a*, *b*, and *c* correspond to the side-centered orthorhombic lattice that is common to all three and the intermediate stages. The first step occurs by changing c/a, the second by changing mainly b/a with some further reduction of c/a. Here *u* specifies the internal parameter related to *c*. A second internal parameter *v* is more clearly indicated in the top view (Fig. 2).

the wurtzite structure again finds a more symmetric solution with the mirror plane reappearing and the formation of two bonds perpendicular to the plane so that the structure becomes fivefold coordinated. So the wurtzite structure with space group  $P6_3mc$  degenerates into the more symmetric  $P6_3/mmc$  either for very low or very high c/a.

The transformation from this intermediate structure to rocksalt is easiest seen in the top view (Fig. 2). As can be seen from this figure, a uniaxial compression along the  $[10\overline{1}0]$  direction, or any of its equivalent directions rotated from it by 60°, will change the rhombus shaped unit cell projection to a square. This transformation can be viewed as



FIG. 2. Top views of WZ (a) and RS (b) crystal structures: small spheres anions, large spheres cations. Empty sphere positions are indicated by dashed line circles. The parameters b and v defining the structure are indicated.

changing the side-centered orthorhombic structure with lattice parameter *b* 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* and which is indicated in Fig. 2. Again, this parameter cannot be varied independently but must be fixed by requiring the force on all atoms to be zero. Simultaneously with the changing b/a we let c/a further decrease to 1, while *u* stays at 1/2. The relation between *v* and b/a is similar to that of *u* and c/a. Once we reduce b/a close to 1, the parameter *v* locks into a symmetric position of 1/2. Finally, when both b/a and c/a are 1 we have reached the rocksalt structure.

The values of the parameters c/a, u, b/a, and v in the three structures discussed so far are indicated in Table I. Except for the value of c/a in h-MgO, which is determined by the total energy minimizations, described later in the paper, all these parameters are completely determined by geometry. Now, in addition to these four parameters, of which we can consider c/a and b/a as independent parameters and u and v as dependent parameters, we must consider the overall length scale of the structure, specified by a, or, more conveniently, the volume per pair of atoms (half a unit cell). Since we view the c/a and b/a as independent parameters, we will allow the volume to relax to the one that gives the minimum total energy.

The general problem can then be stated as mapping out the energy landscape in the parameter space of *external strains* c/a and b/a specifying the orthorhombic strain. For each of these, in principle, we have to find the minimum energy u and v to minimize the internal strain energy and the

TABLE I. Crystal structure parameters in wurtzite, *h*-MgO, and rocksalt structures.

	Ideal WZ	<i>h</i> -MgO	RS
c/a	$\sqrt{8/3} = 1.633$	1.20	1.00
и	3/8	1/2	1/2
b/a	$\sqrt{3}$	$\sqrt{3}$	1.00
v	1/3	1/3	1/2

equilibrium volume V. In this energy landscape we can then identify the number of local minima and low-energy paths and the minimum barrier to get from one local minimum to another. In practice, we explore first what the general behaviors of u versus c/a and v versus b/a are and then keep these dependences fixed as we vary the other external strain parameters.

In the case of GaN, we have provided complete maps of the total energy in this two parameter space in Ref. 17. In the case of MgO, on the other hand, we found that wurtzite is unstable. The minimum energy hexagonal structure already lies close to the c/a value of the rocksalt structure. Therefore we varied c/a simply in linear fashion with b/a as we go from the h-MgO structure to rocksalt. Thus, we take a single cut instead of exploring the whole landscape. That means the energy barrier we obtain is only an upper limit. The real barrier could be slightly lower. In any case, we should realize that the barriers we calculate are all upper limits anyway because we constrain the variations of the structure by limiting the transformation to orthorhombic strains of a single unit cell. Nevertheless, the present study provides some idea of the upper limit of the energy barriers involved and thus of the degree of metastability of the local minima.

### **III. CALCULATION METHOD**

We use the density functional theory<sup>19</sup> (DFT) in the local density approximation (LDA) as parametrized by Hedin and Lundqvist.<sup>20</sup> The self-consistent equations are solved using the full-potential linearized muffin-tin orbital (FP-LMTO) method,<sup>21</sup> developed by Methfessel<sup>22</sup> and van Schilfgaarde.<sup>23</sup> A triple- $\kappa$  basis set was used, with  $\kappa$  specifying the decay length of the spherical Hankel function envelope functions of the muffin-tin orbitals. The angular momentum cutoffs for each  $\kappa$ , denoted by  $l_1 l_2 l_3$ , with values  $\kappa_1^2 = -0.05$ ,  $\kappa_2^2 =$ -1, and  $\kappa_3^2 = -2.7$ , all in Ry, were as follows: dpp for Mg, O, and N, and ddp for Ga. For Mg, the semicore Mg 2pstates are treated as valence states. The augmentation of the dwaves in Ga spheres is done in terms of Ga 3d partial waves. An additional Ga 4d-like orbital is added as a "local orbital."<sup>24</sup> For GaN, this is the same procedure as adopted in our previous work,<sup>25,26</sup> which was found to give satisfactory results for elastic constants and other total energy properties. The angular momentum cutoff for the auxiliary Hankelfunction expansion in the interstitial region was  $l_{max} = 6$ . Empty spheres were used for expanding the tails of the muffin-tin orbitals in the one-center expansions but no basis set orbitals were centered on these sites. In wurtzite, one usually employs two types of empty spheres, two large ones in the empty channel (i.e., in the C positions if the atoms sit in A and B positions in the conventional AB packing description of the hcp structure) and two small ones in between the cation and anion in the *c* direction, opposite to the bond. Because we here are compressing the system to the point where the two interplanar distances become equal, we decided to eliminate the small empty spheres. The results for wurtzite were found to be in good agreement with the results using the small empty spheres. Thus we used the same set of spheres across the whole c/a range. The radii of the empty spheres were kept fixed over the whole range of c/a, for the same volume, but when varying the volume, the sphere sizes were allowed to scale with the overall length scale, as set by the cube root of the volume. The sphere radii are chosen to be as large as possible without ever overlapping. In the transformation as function of b/a, we start out with the two large empty spheres used in the wurtzite structure. The position of these empty sphere are indicated in Fig. 2. They sit in the right half of the rhombus shaped unit cell symmetric with respect to the atoms seen in the left corner as far as their horizontal position is concerned. One sits above the plane, the other below, in between the flat hexagonal layers. However, in the rocksalt structure, we wish to end up with empty spheres in the positions in the middle of the sides of the square unit cell, which means that then there are four empty spheres per unit cell. Down to a b/a ratio of 1.6, we kept two empty spheres only. Beyond it, we split the sphere in two spheres which gradually move towards the positions in rocksalt. In the regions near b/a = 1.6, we performed calculations using both sets of empty spheres and the final results were obtained by averaging between the two to ensure continuity of the results. The sphere sizes were again kept fixed as long as the volume stays fixed, but scale with volume to the 1/3power when the volume is varied. The k-point set is based on a  $4 \times 4 \times 2$  division of the reciprocal unit cell, resulting in about 20 k points in the irreducible part of the Brillouin zone.

### **IV. RESULTS**

### A. MgO

#### 1. Total energy properties and band structures of the end phases

Before we discuss the transitions we present our results in each of the crystal structures i.e., ideal WZ, *h*-BN, and RS. For *wz*-MgO, we fix all structural parameters and allow only the volume to relax. For *h*-MgO, we relaxed c/a, *u*, and volume; b/a and *v* are fixed by the crystal symmetry. For *rs*-MgO, only volume is allowed to relax, since all other crystal parameters are fixed by the crystal symmetries. Some total energy and electronic structure results for each crystal structure are shown in Table II. The electronic band structures are also calculated and presented in Figs. 3, 4, and 5 for

TABLE II. Calculated equilibrium volume V, cohesive energy  $E_c$ , bulk modulus B, LDA band gap  $E_g$ , and upper valence-band width W for wz-, h-, and rs-MgO. The values in square brackets are the parameters at the expanded volume corresponding to the common tangent construction shown in Fig. 6.

	WZ	<i>h</i> -MgO	RS
V (Å <sup>3</sup> /pair)	22.5	20.9 [24.4]	17.8 [20.0]
$E_c$ (eV/pair)	10.85	11.09 [11.05]	11.47 [11.44]
B (GPa)	137	148	178
$E_g$ (eV)	3.78 (d) <sup>a</sup>	3.50 (d) [3.18 (i)] <sup>b</sup>	5.24 (d) [3.90 (d)]
<i>W</i> (eV)	3.33	4.39 [4.04]	4.93 [4.55]

<sup>a</sup>(d)=direct gap.

<sup>b</sup>(i)=indirect gap.



*wz-*, *h-*, and *rs-*MgO, respectively. The solid lines correspond to the bands at the equilibrium volume of each phase. The dashed lines are discussed at the end of this section. (The label for the high-symmetry points follow the conventions of Bradley and Cracknell.<sup>27</sup>) Finally, we also calculated the energy vs volume curves for each structure and derived from them the bulk moduli in each structure, and the transition pressures between the different structures using the common-tangent construction. The total energies as function of volume are shown in Fig. 6.

First, we note that the equilibrium volume decreases as we go from wurtzite to h-MgO to rocksalt. Correlated with this decreasing volume we note an increase in cohesive energy; in other words, the total energy of the solid becomes lower. In the same progression, the bulk moduli increase, as is to be expected. In terms of the electronic structure, we may note that this is accompanied by an increase in valencebandwidth and a downward shift of the center of gravity of the O 2s valence band. This means that some of the occupied states obtain lower energy [with respect to the valence-band maximum (VBM)] and this is consistent with a band structure contribution lowering the total energy. This is consistent



FIG. 4. LDA band structures of h-MgO, solid lines at equilibrium volume and dashed lines at expanded volume  $V_2$  corresponding to the common tangent point shown in Fig. 6.



FIG. 5. LDA band structures of rs-MgO, solid lines at equilibrium volume and dashed lines at expanded volume  $V_1$  corresponding to the common tangent point shown in Fig. 6.

with the formation of additional bonds as will become more clear later.

The band gap of rs-MgO is significantly larger than that of wz- or h-MgO, indicating a larger splitting of bonding and antibonding states, consistent with its lower total energy. The band gap of h-MgO is slightly smaller than that of ideal wz-MgO. The smaller volume tends to increase the gap because of the usual negative sign of the band-gap deformation potential. On the other hand, the c/a compression results in an increasing absolute value of the valence-band crystal field splitting. It turns out that in ideal wurtzite MgO, the singlet  $\Gamma_1$  lies already above the doublet  $\Gamma_6$ ; i.e., the crystal field splitting  $\Delta_c = E_{\Gamma_c} - E_{\Gamma_1}$  is negative. The actual value is found to be -0.068 eV. If c/a is reduced at a fixed volume, the crystal field splitting becomes increasingly more negative and in the *h*-MgO structure it is as large as -0.95 eV. Thus, the c/a reduction counteracts the increase in gap due to the volume compression. The results show that the effect of the c/a reduction overwhelms that of the volume compression, leading to a smaller band gap.

MgO in all three of the structures investigated has a direct band gap at  $\Gamma$ . The presented LDA band gaps are listed in Table II. It is well known that the energy band gaps are not given accurately by the Kohn-Sham eigenvalues in the LDA because these do not truly represent quasiparticle excitation energies. However, the correction to the LDA gaps is only weakly dependent on the structure. If we compare our *rs*-MgO LDA gap with available experiment gap of 7.8 eV, we can estimate a correction of 2.56 eV to be applied for the other structures. Including this correction, the predicted gaps for *wz*- and *h*-MgO are 6.34 and 6.06 eV, respectively.

Figure 6 shows that the lowest-energy structure is correctly found to be rocksalt and that in order to convert to *h*-MgO we need a negative pressure of 16.2 GPa. At this pressure, the volume is expanded to  $V_1/V_0=1.12$  and the volume would then discontinuously expand to  $V_2/V_0=1.37$  in going to the *h*-MgO phase, where  $V_0$  is the volume of *rs*-MgO at zero pressure. This is of course somewhat unphysical because one cannot apply a negative pressure in the laboratory. However, one may think of alloying with ZnO as



FIG. 6. The total energy as a function of volume for rs- and wz-MgO and the common tangent construction.

leading to an expansion of the lattice constant and in this sense the result shows how big an expansion would be needed before an equilibrium between the metastable *h*-MgO and the stable rocksalt phase would occur. Of course, alloying with Zn will have other effects besides the expansion, so this consideration is only of limited practical usefulness.

We also study the band structures of both rs- and h-MgO at the expanded common tangent volumes. These are shown as dashed lines in Figs. 4 and 5. The corresponding gaps and bandwidth parameters are given in square brackets in Table II. As expected, for each structure, both band gaps and upper valence-band width are getting smaller as the crystal expands. One interesting feature is that the valence-band maximum in h-MgO shifts slightly away from the  $\Gamma$  point at the expanded volume.

#### 2. Intermediate transition structures

As mentioned in previous sections, wz-MgO is not stable. The transition from wz-MgO to rs-MgO is studied in two parts: wz-MgO to h-MgO and h-MgO to rs-MgO. The transition from ideal wz-MgO to h-MgO does not have any energy barrier and was obtained simply by minimizing the total energy with respect to the structural parameters. The total energy as a function of c/a in the range [1.2,  $\sqrt{8/3}$ ] is shown in Fig. 7 (left panel). Note that along the path from wz-MgO to *h*-MgO both b/a and v are fixed at those of wz-MgO (due to symmetries). However, u and volume are relaxed to obtain the minimum energy in the following way. The relaxed *u* as function of c/a was first determined with the volume fixed at that of ideal wz-MgO. Additional calculations show that this relation is almost independent of volume. Thus instead of relaxing u for each volume, the relation u as function of c/awas then kept fixed for the rest of the calculations. The volume which minimizes the energy at each c/a is shown in Fig. 8, while the u vs c/a relation is shown in Fig. 9.

In the vicinity of ideal WZ, u varies almost linearly with c/a. At the point when the crystal is compressed to have c/a about 1.3, u changes fairly abruptly to a value of 1/2, where it then stays fixed. This can be explained as follows. As we



PHYSICAL REVIEW B 63 104103

FIG. 7. Total energy per MgO pair in the wz-MgO  $\rightarrow h$ -MgO (left panel) and h-MgO  $\rightarrow rs$ -MgO (right panel) transitions.

discussed, the material has a tendency to form more bonds because of the ionic nature of the bonding which is insensitive to direction and therefore lower energy corresponds to higher nearest-neighbor coordination. However, at c/a near the ideal WZ structure, having u = 1/2 to form *h*-MgO would stretch the bond too far. At some point, as we reduce c/a the tendency to form two bonds instead of one wins (*u* suddenly changes to 1/2). In this step of the transformation, the total binding energy (opposite of cohesive energy) reduces monotonically from -10.85 eV/pair in *wz*-MgO to -11.09 eV/ pair in *h*-MgO (0.24 meV/pair different).

We may also note that the total energy changes most rapidly beyond  $c/a \approx 1.4$ , i.e. precisely when the u vs c/a relation starts to deviate strongly from the initial linear variation and starts to rapidly approach the symmetric value 1/2. Also, this point more or less corresponds to the inflection point of



FIG. 8. The energy minimizing volume used in the total energy calculations (Fig. 7).



FIG. 9. Relaxed u as function of c/a at fixed volume (i.e., wz-MgO's relaxed volume).

the volume vs c/a. So it is clearly in the range 1.4 > c/a > 1.3 that the transition from a fourfold-coordinated to a fivefold-coordinated structure starts happening. It is the formation of a new bond that lowers the energy. This then rapidly drives the volume to decrease faster, which further lowers the energy.

The transition from *h*-MgO to *rs*-MgO is more complicated to study since it involves the variation of all five structural parameters. To simplify matters, we first note that the relaxed *u* is 1/2 for all c/a less than 1.3. We still have to deal with four parameters. While minimizing the total energy with respect to three parameters (volume, c/a, and v) for each b/a is too time consuming, we choose to minimize only the volume and v while c/a is taken to vary linearly with b/a from that of *h*-MgO to that of *rs*-MgO.

The behavior of v vs b/a calculated in this manner is shown in Fig. 10. It shows clearly a similar behavior as that of u as function of c/a. First, it varies linearly with a small slope; then it suddenly jumps to the symmetric value. We verified that this behavior of v as function of b/a is actually independent of c/a. In other words, if we keep c/a fixed at any value between 1.6 and 1.0 during the b/a variation, the relaxed values of v vs b/a fall almost on the same curve.

We see that the *h*-MgO structure is only marginally metastable. There is, essentially, just a large almost constant energy plateau as the structure is sheared along the *b* direction. The activation energy between the *h*-MgO and the energy barrier is only 0.02 eV/pair. The barrier is located at  $b/a \approx 1.5$ . We note that the value of the energy barrier is quite sensitive to the relaxation of the internal parameter *v*. If, instead of the relaxed *v*, a *v* varying linearly between 1/3 and 1/2 is used, the barrier height is overestimated to be 0.1 eV/pair above the *h*-MgO structure. After the transformation passes the barrier the binding energy drops sharply and has a minimum at -11.47 eV/pair in the *rs*-MgO phase (0.38 meV/pair lower than the *h*-MgO phase).

Again, this is clearly correlated with the behavior of v as function of b/a. As v starts changing rapidly from 1/3 to 1/2,



FIG. 10. Relaxed v as function of b/a with simultaneous variation of c/a linearly from 1.2 (as in *h*-MgO) to 1.0 (*rs*-MgO). Here u and volume are relaxed at each point.

the energy starts rapidly decreasing. This is because the bonding in the planes changes from threefold to fourfold. Or taking into account the two bonds perpendicular to the plane, the overall coordination changes from fivefold to sixfold. Figure 8 shows that this is again accompanied by a more rapid decrease in equilibrium volume.

# 3. Charge densities

The valence charge densities (including the semicore Mg 2p electrons) are shown as (logarithmically spaced) contour plots superposed on a gray scale intensity image in the  $(11\overline{2}0)$  plane cutting through atoms (using the hexagonal notation), for the wz- and h-MgO are shown in Figs. 11(a) and 11(b), respectively. One may notice that even in the ideal wurtzite structure [Fig. 11(a)], the bonding is very ionic, leading to almost spherical charge densities around each atom. Very little, however noticeable, covalent bonding is apparent. As we go to h-MgO [Fig. 11(b)], a new bond between the Mg at the bottom-left corner and O at the topleft corner is clearly formed. But most of all the charge density is distributed more uniformly around the atoms. The formation of the sixth bond results from compressing h-MgO in the direction perpendicular to c crystal axis. Hence it is easier to see in a plot of the charge density in the basal plane. Figure 11(c) shows the valence charge densities plot in the (0001) plane through atoms of *h*-MgO and Fig. 11(d) shows the same cut of rs-MgO. We can see that an addition bond between Mg at the top-left corner and O at the bottom-left corner is clearly formed as we go from h-MgO to rs-MgO.

#### 4. Summary of MgO results

It is clear that the transition from the ideal wz-MgO to rs-MgO is driven by the formation of new bonds. In the first step, for compression along c/a the energy decreases monotonically, indicating that fourfold bonding is unstable for MgO. In the second step, compressing b/a, there is a small



FIG. 11. Charge density plot of MgO: (a) ideal wurtzite structure in the  $(11\overline{2}0)$  plane through the atoms, (b) and (c) *h*-MgO structure in the  $(11\overline{2}0)$  plane and (0001) plane through the atoms, and (d) rocksalt structure in the (001) plane through the atoms. Note the formation of additional bonds on the left of (b) compared to (a) and on the left of (d) compared to (c). Since the calculations include Mg 2*p*, we see higher electron density at the Mg core than at the O core.

activation energy, indicating a marginal metastability of the fivefold-coordinated h-MgO followed by a rapid formation of the final sixth bond ending up in the preferred rocksalt structure. Along the way, the equilibrium volume keeps decreasing, and more rapidly so, in the region where the new bonds start forming. The band structures indicate an overall increase in gap between bonding and antibonding states with compression, in agreement with increasing ionicity. It is somewhat counteracted by the valence-band splitting under uniaxial c/a compression in the first step. The formation of the new bonds is indicated by the increasing valence band width and the downward shift of the O 2s band. Overall, there is a tendency towards a more symmetric distribution of the bonds around each atom. This, is of course, not surprising and indicates the dominance of ionic over covalent bonding effects.

# B. GaN

#### 1. Total energy properties and band structures of the end phases

First, we present our results for wz- and rs-GaN separately. The relaxed crystal parameters, total energy and electronic structure results are shown in Table III. Similar to MgO and other binary compounds, GaN has a smaller volume per atom in the RS than in the WZ structure. The relaxed wz-GaN crystal parameters are quite close to those of the ideal WZ structure. The wurtzite structure is found to be 0.7 eV/pair lower in total binding energy than the rocksalt structure. The energy volume curves are shown in Fig. 12, and indicate a transition pressure of 31 GPa, at a volume

### SUKIT LIMPIJUMNONG AND WALTER R. L. LAMBRECHT

TABLE III. Calculated equilibrium volume V, c/a, u and cohesive energy  $E_c$ , LDA band gap  $E_g$ , and upper valence-band width W, for wz- and rs-GaN. The values in square brackets are the parameters at the volume corresponding to the common tangent construction shown in Fig. 12.

	WZ	RS
V (Å <sup>3</sup> /pair)	22.1 [19.6]	17.9 [16.2]
c/a	1.62 [1.62]	1.00 [1.00]
и	0.377 [0.377]	1/2 [1/2]
В	196	243
$E_c$ (eV)	13.67 [13.45]	12.95 [12.79]
$ \frac{E_g \text{ (eV)}}{W \text{ (eV)}} $	2.16 (d) [3.07 (d)] <sup>a</sup> 7.28 [8.22]	0.34 (i) [1.42 (i)] <sup>b</sup> 8.33 [9.16]

a(d) = direct gap.

<sup>b</sup>(i)=indirect gap.

compression of  $V_1/V_0 = 0.88$ , and accompanied by a volume reduction to  $V_2/V_0 = 0.73$  in rocksalt, where  $V_0$ ,  $V_1$ , and  $V_2$ are the volume of wz-GaN at zero pressure, the volume of wz-GaN at 31 GPa, and the volume of rs-GaN at 31 GPa, respectively. These results of course agree with those of Ref. 17 where we obtained them directly from the enthalpies instead of the common tangent construction in the energy versus volume curves.

The band structures and total energy properties of wz-GaN have recently received a lot of attention. Our present results are similar to those published earlier, an overview of which can be found in recent reference works on III-nitrides.<sup>28</sup> Figures 13 and 14 show the electronic band structures along high-symmetry points in the first Brillouin zone (BZ) of wz- and rs-GaN, respectively, both at their minimum energy volume and at the common tangent points. The latter are relevant to the study of the phase transition. Our calculated wz-GaN LDA band gap is 2.16 eV and direct at  $\Gamma$ , which is in good agreement with other LDA calculations.<sup>29,28</sup> The experimental value of the gap of



FIG. 12. The total energy as a function of volume for rs- and wz-GaN and the common tangent construction.



FIG. 13. LDA band structures of wz-GaN: solid line, wurtzite phase equilibrium volume ( $V_0$ ); dashed line, compressed volume ( $V_1$ ) corresponding to the common tangent point shown in Fig. 12.

wz-GaN was determined by Monemar<sup>30</sup> to be  $3.503^{+0.005}_{-0.002}$  eV at 1.6 K including exciton binding energy corrections to the exciton gap. This value was recently confirmed by work of Eckey *et al.*,<sup>31</sup> who find an A exciton gap of 3.4800 eV, a binding energy of the A exciton of 27 meV, and hence a gap of 3.507 eV. Both of these measurements were on thick GaN epilayers which were shown to be very nearly strain free. Thus LDA underestimates the bandgap by 1.35 eV. Our LDA band gap of rocksalt GaN is 0.34 eV. Assuming that the correction to the band gap due to the quasiparticle selfenergy effects is approximately independent of the structure, we obtain an estimated gap of 1.69 eV for rs-GaN. Note that this is probably a slight overestimate because if the gap decreases, the self-energy correction also decreases because the gap correction is inversely proportional to the dielectric constant which in turn is inversely proportional to the gap. In rs-GaN the VBM is located away from  $\Gamma$  (approximately 40% away from  $\Gamma$  toward K), while the conduction-band minimum (CBM) is at X. This is in agreement with the earlier work by Christensen and Gorczycka<sup>10</sup> as far as the loca-



FIG. 14. LDA band structures of rs-GaN: solid line, rocksalt phase equilibrium volume; dashed line, compressed volume ( $V_2$ ) corresponding to the common tangent point shown in Fig. 12.

tion of the band extrema is concerned and close as far as the value of the LDA gap, which they obtained to be 0.6 eV.

We also examined the band structures of both wz- and rs-GaN at the transition pressure (compressed volume). These band structures are presented as dashed lines in Figs. 13 and 14. The band structures of both crystal structures deform in similar way with volume compression: the band gaps become larger and the upper valence band width increases. The changes in band gaps and band widths are summarized in Table III.

# 2. Band structure at transition barrier

In contrast to MgO, GaN is stable in the wurtzite structure. Thus, *a priori*, there is no reason why we should first decrease c/a and then b/a in transforming from WZ to RS. Instead we need to explore the complete parameter space. This was done in our earlier paper.<sup>17</sup> One outcome of this study was that the minimum energy path from wurtzite to rocksalt lies along a more or less straight path in the c/a-b/aparameter plane. Thus, we consider a transformation path in which b/a is vayring linearly with c/a between their end values of wurtzite and rocksalt.

To further understand the nature of the transition, we examined the band structure of GaN along this transformation path. Although along the minimum total energy path for the transformation, c/a, b/a, and volume all change together, it is of interest to discuss the separate effects of these parameters. Volume compression increases the gap as is well known because the hydrostatic deformation potential is negative as in most semiconductors. The uniaxial c/a reduction on the other hand tends to decrease the gap because of the increasing splitting of the valence band. Under a large c/acompression the  $\Gamma_1$  singlet and  $\Gamma_6$  doublet states are interchanged from their ordering at equilibrium  $(\Gamma_6 > \Gamma_1)$  and the slope of the  $\Gamma_1$  energy as function of c/a is twice that of the  $\Gamma_6$ .<sup>26</sup> For the large distortions considered here these effects are comparable in magnitude and of order 1 eV but of opposite sign.

The b/a distortion on the other hand lowers the bands at other **k** points leading to an indirect gap. The band structure at the barrier point in the transition is shown in Fig. 15. The (unstable) structure here is side-centered orthorhombic. The Brillouin zone for this structure is related to that of wurtzite by a compression along one of the directions and an extension along the other in the basal plane, resulting in a distorted hexagonal prism. The top view of this Brillouin zone is shown in Fig. 16. This means that there are now two inequivalent wurtzite M-like points (middle of the sides of the hexagon). These are labeled N for the short side and Mfor the long side. The corners of the hexagon become K(joining two long sides) and P (joining a long and a short side).  $\Gamma$  is at the center as usual. The points on the Brillouin zone surface in the  $k_z = \pi/c$  plane are labeled in parentheses. The minimum of the conduction band is seen to occur at the N point and the indirect gap almost vanishes (0.1 eV). Further compression to rocksalt increases the gap although it stays indirect and the conduction band minimum location evolves into the X point of the fcc BZ. The band structure at the transition point is drastically different from the wurtzite



FIG. 15. LDA band structures of GaN at c/a=1.1 and b/a= 1.2. The Brillouin zone labels are shown in Fig. 16 and their relation to those in wurtzite is discussed in the text.

band structure. Note, for example, that the valence bands has several nearly equal maxima and that the valence band states are much more equally spaced over the width of the valence band at  $\Gamma$ . Also, the two topmost valence bands are pushed back together again. Although there appears to be a doublet, this near degeneracy is not exact. The symmetry is so low that the degeneracies are all completely lifted even at  $\Gamma$ .

So as the crystal passes through the unstable barrier region, the band gap appears to nearly close, possibly turning GaN into a semimetal or, at least, indirect narrow gap semiconductor with band gap in the infrared instead of the visible. Whether this is really the case or not is difficult to ascertain because of the uncertainties of LDA on the gap. On the other hand, as mentioned in Ref. 17 a closing of the gap is consistent with the observation that the samples became opaque to visible light at the onset of the phase transition.<sup>3</sup> While this could also be due to disorder effects, our results provide a simple explanation for this behavior. While the system passes through the unstable barrier region, the band gap falls below the visible cutoff. Further investigation of the



FIG. 16. Top view of the Brillouin zone for the side-centered orthorhombic transition structure of GaN at c/a=1.1 and b/a = 1.2. The labels *N*, *P*, *M*, *K*, and  $\Gamma$  are for the projection in the  $k_z=0$  plane. The corresponding points on the Brillouin zone surface  $(k_z = \pi/c)$  are labeled in parentheses.



FIG. 17. Charge density plot GaN: (a) wurtzite structure in the  $(11\overline{2}0)$  plane through the atoms, (b) and (c) at an intermediate step of the transformation from wurtzite to rocksalt, with c/a = 1.10 and b/a = 1.20 in the (100) plane and the (001) plane through the atoms, and (d) rocksalt structure in the (001) plane through the atoms. Note the formation of an additional bond in the *z* direction and the flattening of the Ga-N basal plane double layers as we go from (a) to (b) and also the formation of additional bond as we go from (c) to (d). Since the calculations include Ga 3*d*, we see higher electron density around Ga than around N.

band structure during the transition could help confirm our proposed transition path.

# 3. Charge densities

Finally, we display in Fig. 17 the charge density of GaN at some selected points along the suggested transformation path. The charge densities around the atoms are now seen to be more distorted from the spherical shape than in the MgO case. This is indicative of the more covalent bonding. As for MgO, we see progressively the formation of additional bonds as in the case of MgO. Firstly, we look at the charge density plot of wz-GaN in the (11 $\overline{2}0$ ) plane and compare it with the plot of the equivalent cut of an intermediate structure during the transformation, c/a = 1.1 and b/a = 1.2 representing the barrier, shown in Fig. 17(b). One can clearly see that a new bond is formed between Ga in the bottom-left corner and N in the top-left corner. As the transformation goes further from the intermediate structure to the final structure, rocksalt, an additional in-plane bond is formed. As for MgO, this is most clearly seen in top view. Figures 17(c) and 17(d) show the charge density plot in the basal plane, which is equivalent to the (0001) plane in hexagonal notation, of the intermediate structure. Again, we can see the sixth bond (between the Ga at the top-left corner and N at the bottom-left corner) forming as the transformation goes from the intermediate structure to rocksalt. As these new bonds form, the overall charge densities become more spherical, indicating a more and more ionic type of bonding as we further compress.

# V. CONCLUSION

In this paper, we investigated the relative stability of rocksalt and wurtzite in MgO and GaN, examples for which either one or the other is the stable phase at ambient pressure, and the transitions from one structure to the other.

The main conclusions for the more ionic compound MgO are that the wurtzite structure itself is unstable but a structure closely related to it, which we labeled h-MgO is marginally metastable. This structure differs from wurtzite only in the existence of an additional mirror plane or, in other words, in the fact that the basal plane layers are flat or that the wurtzite internal parameter u = 1/2. It means that for this ionic compound a fivefold coordination is preferred over a fourfold bonding. By examining the evolution of the minimum energy volume and *u* as function of c/a we put the sudden formation of an additional bond in evidence. The charge densities and band structures as function of the c/a variation were presented and provide additional evidence of the formation of the bond. Next, it was shown that an additional uniaxial compression in the basal plane along a  $[\bar{1}100]$  direction transforms the structure to the stable rocksalt structure with formation of one more bond. Again, the formation of this bond happens suddenly when a critical compression is reached and the internal coordinate, describing the relative position of the two sublattices suddenly changes to its value where the system acquires an additional symmetry. The formation of the bonds was shown by means of the charge densities and the changes in the band structure were discussed in terms of known deformation potentials. At the moment these new bonds form, the system also undergoes a faster reduction in volume because of the bond contraction.

For GaN, the situation is different in the sense that the wurtzite phase is stable at ambient pressures. Upon a combined compression of c/a and b/a, with b/a the above inplane compression along  $[\bar{1}100]$ , the systems undergoes a phase transition to rocksalt, which was previously described.<sup>17</sup> Here we presented the charge densities along this transformation path, again evidencing the formation of additional bonds and we discussed the band structures at the wurtzite and rocksalt phases and at the transition barrier point. In contrast to MgO where the band gap stays direct all along the transformation, it becomes indirect in the GaN case. In particular at the transition barrier point, the band gap almost vanishes. This could be a signature of the transition. Further experimental investigation of this could lead to a confirmation of our proposed model for the wurtzite to rocksalt transition. The band structure details presented here could be useful for this purpose. We also presented results on lattice constants, bulk moduli, transition pressures and the accompanying volume distortions for the two phases.

# ACKNOWLEDGMENT

This work was supported by the Office of Naval Research under Grant No. N00014-98-1-0160.

- \*Present address: Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304.
- <sup>1</sup>J. R. Chelikowsky and J. K. Burdett, Phys. Rev. Lett. 56, 961 (1986).
- <sup>2</sup>N. E. Christensen, S. Satpathy, and Z. Pawlowska, Phys. Rev. B **36**, 1032 (1987).
- <sup>3</sup>P. Perlin, C. Jauberthie-Carillon, J. P. Itie, A. S. Miguel, I. Grzegory, and A. Polian, Phys. Rev. B 45, 83 (1992).
- <sup>4</sup>H. Xia, Q. Xia, and A. L. Ruoff, Phys. Rev. B 47, 12 925 (1993).
- <sup>5</sup>M. Ueno, M. Yoshida, A. Onodera, O. Shimomura, and K. Takemura, Phys. Rev. B 49, 14 (1994).
- <sup>6</sup>M. Ueno, A. Onodera, O. Shimomura, and K. Takemura, Phys. Rev. B **45**, 10123 (1992).
- <sup>7</sup>P. Perlin, C. Jauberthie-Carillon, J. P. Itie, A. San Miguel, I. Grzegory, and A. Polian, High Press. Res. **71**, 96 (1991).
- <sup>8</sup>P. Perlin, I. Gorczyca, S. Porowski, T. Suski, N. E. Christensen, and A. Polian, Jpn. J. Appl. Phys., Suppl. **32**, 334 (1993).
- <sup>9</sup>S. Uehara, T. Masamoto, A. Onodera, M. Ueno, O. Shimomura, and K. Takemura, J. Phys. Chem. Solids 58, 2093 (1997).
- <sup>10</sup>N. E. Christensen and I. Gorczyca, Phys. Rev. B 50, 4397 (1994).
- <sup>11</sup>A. Muñoz and K. Kunc, Phys. Rev. B 44, 10 372 (1991).
- <sup>12</sup> A. Ohtomo, M. Kawasaki, T. Koida, K. Masubichi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **72**, 2466 (1998).
- <sup>13</sup>W. R. L. Lambrecht, S. Limpijumnong, and B. Segall, MRS Internet J. Nitride Semicond. Res. **4S1**, G6.8 (1999).
- <sup>14</sup>E. C. Bain, Trans. Am. Inst. Min., Metall. Pet. Eng. **70**, 25 (1924).
- <sup>15</sup>L. L. Boyer, Acta Crystallogr., Sect. A: Found. Crystallogr. 45, FC29 (1989).
- <sup>16</sup>B. W. van de Waal, Acta Crystallogr., Sect. A: Found. Crystallogr. 46, FC17 (1990).

- <sup>17</sup>S. Limpijumnong and W. R. L. Lambrecht, Phys. Rev. Lett. 86, 91 (2001).
- <sup>18</sup>R. M. Wentzcovitch, S. Fahy, M. L. Cohen, and S. G. Louie, Phys. Rev. B **38**, 6191 (1988).
- <sup>19</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
- <sup>20</sup>L. Hedin and B. I. Lundqvist, J. Phys. C 4, 2064 (1971).
- <sup>21</sup>O. K. Andersen, O. Jepsen, and M. Šob, in *Electronic Band Structure and its Applications*, edited by M. Yussouff (Springer, Heidelberg, 1987), p. 1.
- <sup>22</sup>M. Methfessel, Phys. Rev. B 38, 1537 (1988).
- <sup>23</sup>M. van Schilfgaarde (private communication).
- <sup>24</sup>D. Singh, Phys. Rev. B **43**, 6388 (1991).
- <sup>25</sup>K. Kim, W. R. L. Lambrecht, and B. Segall, Phys. Rev. B 53, 16 310 (1996); 56, 7018 (1997).
- <sup>26</sup>K. Kim, W. R. L. Lambrecht, B. Segall, and M. van Schilfgaarde, Phys. Rev. B 56, 7363 (1997).
- <sup>27</sup>C. J. Bradley and A. P. Cracknell, *The Mathematical Theory of Symmetry in Solids* (Clarendon, Oxford, 1972).
- <sup>28</sup>W. R. L. Lambrecht, in *Gallium Nitride (GaN)*, edited by J. I. Pankove and T. D. Moustakas, *Semiconductors and Semimetals*, Vol. 50 (Academic Press, New York, 1997), Chap. 12, pp. 369– 407.
- <sup>29</sup>A. F. Wright and J. S. Nelson, Phys. Rev. B 50, 2159 (1994).
- <sup>30</sup>B. Monemar, Phys. Rev. B **10**, 676 (1974).
- <sup>31</sup> L. Eckey, L. Podlowski, A. Göldner, A. Hoffmann, I. Broser, B. K. Meyer, D. Volm, T. Steibl, K. Hiramatsu, T. Detchprom, H. Amano, and I. Akasaki, in *Silicon Carbide and Related Materials 1995*, edited by S. Nakashima, H. Matsunami, S. Yoshida, and H. Harima, Institute of Physics Conference Series No. 142 (Institute of Physics, Bristol, 1996), p. 943.