

Unifying description of the wurtzite-to-rocksalt phase transition in wide-gap semiconductors: The effect of d electrons on the elastic constants

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The mechanism responsible for the wurtzite-to-rocksalt structural phase transition in zinc oxide has been studied through the *ab initio* calculations of the full phonon properties. We derive a new and general path of the transformation from the parent to the daughter phase which involves an intermediate tetragonal phase. This hypothesis has been tested through analogous calculations on other wide-gap semiconductors, and confirmed in GaN and InN, but not in AlN and SiC. As a consequence of these results, we formulate a general prediction on the effect of d -electrons on the structural and elastic properties of wurtzite semiconductors under pressure.

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Wide band-gap semiconductors zinc oxide and group-III nitrides crystallize in the $P6_3mc$ wurtzite structure at ambient conditions. Upon increasing pressure at ambient temperature, they are all known to undergo a structural phase transition to the rocksalt cubic phase. The mechanism of this transformation, recently studied by means of *ab initio* total energy calculations for GaN,¹ AlN, and InN,² and other semiconductors,³⁻⁵ has been described as a continuous deformation involving a compression of the wurtzite c/a axial ratio which, alone, would bring the system close to a hexagonal intermediate phase referred to as h -MgO.¹ However, in Ref. 2 it was shown that such an axial deformation is not observed in GaN hydrostatically compressed at least up to 200 GPa and no estimate of the pressure range where such distortion should occur in GaN is reported in Ref. 1. In general, the quest for a transformation path in a first-order phase transition does not necessarily succeed, in the sense that the daughter structure might nucleate spontaneously around a defect with no obvious deformation of the parent phase. In other words, such an analysis is rigorously justified only for second order phase transitions. However, it has been recently shown in Refs. 6–8 how the knowledge of the phonon properties is necessary in order to make correct predictions. In fact, it allows the determination of the vibrational distortions that would eventually lead, continuously, from one phase to the other at pressures higher than the transition one. This analysis corresponds to the determination of the path which would allow the least costly crossing of the transition enthalpy barrier. In that view, the study of phonon dispersion curves of semiconductors under pressure provides a key to the understanding of the phase transition mechanisms, largely unknown even in the most common cases, and the existence of possible metastable structures along the distortion can only be supported or ruled out through such analysis.

In this paper we report a first-principles study of the low- and high-pressure structural and vibrational properties of ZnO, wurtzite SiC, and of III-N compounds, namely AlN, GaN, and InN. The determination of the full phonon dispersions of wurtzite ZnO under pressure, and the favorable comparison to recent experimental data⁹ allows us to suggest a new path for the transition from the wurtzite to the rocksalt phase, which is a *a posteriori* confirmed by the analysis of

the energetics of the different structures and of the evolution of the optical phonons along the deformation. The excellent agreement between the present theoretical results and experimental data encourages the extension of our study to the nitrides, for which only scarce experimental vibrational high-pressure results have been obtained.¹⁰ We will show in the following that the wurtzite-to-rocksalt phase transition mechanism depends on the presence of d electrons on the cation. In fact, we observe that GaN and InN both show a very similar behavior to that of zinc oxide, but different from that of AlN and w -SiC. This points to a strong connection between the electronic properties of the cation, the pressure dependence of the shear elastic constants, and the mechanism of the phase transition.

As shown in Fig. 1, the transformation of a wurtzite structure into a rocksalt phase can continuously follow the “hexagonal” path, going through a compression of the c axis to $c/a \approx \sqrt{3}/2$ and a vertical displacement of a ZnO pair, bonded along the z direction, from $u=0.375$ to $u=1/2$. In this structure, each Zn(O) atom is located at the center of the equilateral triangle formed by 3 oxygen(zinc) atoms, and has two opposite bonds along the z direction, perpendicular to the triangle plane. The rocksalt structure is then obtained through the opening of the hexagonal γ angle from 60° to 90° , and the corresponding displacement of atoms which move horizontally from the center of the triangle to the center of the square resulting from the angle widening.

However, a different distortion, that will be referred to as “tetragonal” in the following, is shown in the right part of Fig. 1. In this case the wurtzite hexagonal angle, as suggested above from the behavior of the elastic constants, at first opens up¹¹ and the atoms move horizontally to the center of the square, while c/a and u remain still rather close to the wurtzite typical values; each Zn(O) is located at the body center of square pyramid formed by 5 oxygen(zinc) atoms. The NaCl phase then occurs through a decreasing of the c/a ratio which concomitantly brings the Zn(O) atoms from the body center to the base center of the pyramid, i.e., $u=1/2$. We underline here that the study of the transition mechanisms and of these intermediate phases is not carried out per se, and those phases should *not* be observed under hydrostatic conditions in any of these compounds. However, their structures allow a simple and interesting description of the

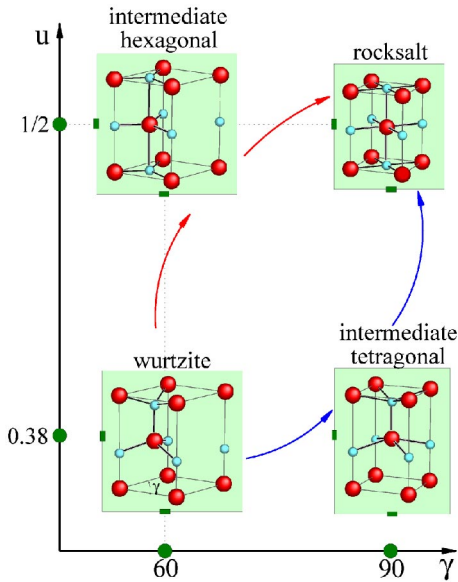


FIG. 1. (Color online) The four structures in the ab angle- u internal coordinate plane. The optimal c/a ratio is about 1.61 and 1.74 for the wurtzite and tetragonal structures (bottom), where $u \approx 0.38$, and 1.29 and $\sqrt{2}$ for the hexagonal and rocksalt structures (top), where $u=1/2$.

high-pressure wurtzite fundamental properties, enlightened by the phase transition.

We adopt the density-functional theory (DFT) framework and the local density approximation (LDA). Our calculations are performed within the plane-wave/pseudopotential scheme, using the PWSCF code.¹² *Ab initio* phonon dispersion curves are determined through the density-functional perturbation theory (DFPT),¹³ implemented in the same code. Typically in semiconductors the cation is satisfactorily described by including the s electrons in the valence band, and freezing the d electrons in the core. Their effects are usually well taken into account by adopting the nonlinear core-corrections (NLCC).¹⁴ However, this approximation may give unphysical results in wide-gap compounds: for example, in zinc oxide the rocksalt phase is predicted as the most stable one even at ambient pressure. The explicit treatment of d electrons and their inclusion in the valence band is thus a costly but necessary improvement to the reliability of the results. Pseudopotentials for Zn and O are thus chosen according to the Troullier-Martins approach.¹⁵ A cutoff of 75 Ry and special sets of \mathbf{k} points following the Monkhorst-Pack scheme with $8 \times 8 \times 4$ grids in the wurtzite phase showed convergence of frequencies better than 1 cm^{-1} .

We obtain for wurtzite (rocksalt) ZnO an equilibrium volume of 23.76 \AA^3 (19.49 \AA^3), and a bulk modulus pressure dependence of $155 + 4.29 * P$ GPa ($198 + 4.65 * P$ GPa) in excellent agreement with the experimental data (see Ref. 16, and references therein). The common tangent construction predicts the wurtzite-to-rocksalt phase transition to take place at 7.6 GPa, which compares favorably to the experimental estimate of an equilibrium transition pressure of 6.0 GPa.¹⁷ In principle, the phase transformation could occur any path in the γ - c/a deformation plane between the “hexagonal” and the “tetragonal” limits (see Fig. 1). These struc-

tures both have a fivefold coordination, consistent with the increase of coordination from 4 to 6 along the wurtzite-to-rocksalt transition. However, transition paths through the tetragonal region of the distortion plane have a more favorable enthalpy landscape. In fact, the transition from the wurtzite to the hexagonal phase would only occur at about 20.0 GPa. At that pressure, however, this latter phase, more stable than the NaCl structure at ambient pressure, would be thermodynamically unstable, since a hexagonal-to-rocksalt phase transition would take place at about 4.0 GPa. Interestingly, the transition from the wurtzite to the tetragonal phase would occur at 9.8 GPa, just above the theoretical and the experimental transition pressures to the rocksalt structure. The tetragonal phase would also be unstable with respect to the NaCl one, the transition pressure between the two being 0.8 GPa. These results show that the tetragonal phase has a lower enthalpy than the hexagonal phase along the wurtzite-to-rocksalt transformation path. This can be explained by considering that even though both the tetragonal and the hexagonal intermediate structures have a fivefold coordination, their volumes (per ZnO formula) in terms of the zinc-oxygen bond distance d_{ZnO} are about $2.3d_{\text{ZnO}}^3$ and $2.75d_{\text{ZnO}}^3$, respectively. In other words, at the same bond distance volume is more efficiently occupied in the tetragonal structure.

We then focus on the vibrational properties of zinc oxide, only partially known to this date. No *ab initio* or experimental determination of its complete phonon dispersion curves, either at ambient or high pressure, can be found in the literature, except for the experimental study of the four lowest branches along the Γ - M reciprocal space direction, and the four lowest branches along the Γ - A direction.¹⁸ In the following we will refer to z as the $[0001]$ direction in the wurtzite structure, whose reciprocal space counterpart corresponds to Γ - A . We chose 4 different pressures to calculate the vibrational properties of ZnO in the wurtzite phase, i.e., $P=0, 5.6, 11.9,$ and 19.0 GPa, the last two calculations being performed by constraining the system in the wurtzite structure, beyond the thermodynamic transition pressure. The resulting transverse acoustic branches of the phonon dispersion curves at ambient pressure and at $P=19$ GPa are reported in Fig. 2.

We observe that, as pressure increases, all transverse acoustic branches, namely ΓA , ΓM , and ΓK , have a negative variation, as well as the optical E_2^{low} phonon at Γ , which are degenerate with the TA branch at the A point. In other words, the lowest high-symmetry phonons and their entire branches soften due to the effect of pressure. This trend continues beyond the transition pressure, but only at $P=19$ GPa we do observe an unstable mode. At that pressure, the three TA branches have a negative slope at Γ . According to elasticity theory, the slopes at the Brillouin zone (BZ) center of the TA branch along the ΓA direction and of the one propagating in the plane perpendicular to ΓA and polarized along the vertical z axis are related to the elastic constant c_{44} ; analogously, the slope at Γ of the branch perpendicular to ΓA and polarized along z is related to c_{66} . These results thus show that the c_{44} and c_{66} elastic constants soften under pressure, in excellent agreement with the experimental observation,¹⁹ and reach negative values at $P=19$ GPa. This result is very interesting because the cell deformation associated with these constants corresponds to a variation of the hexagonal angle.

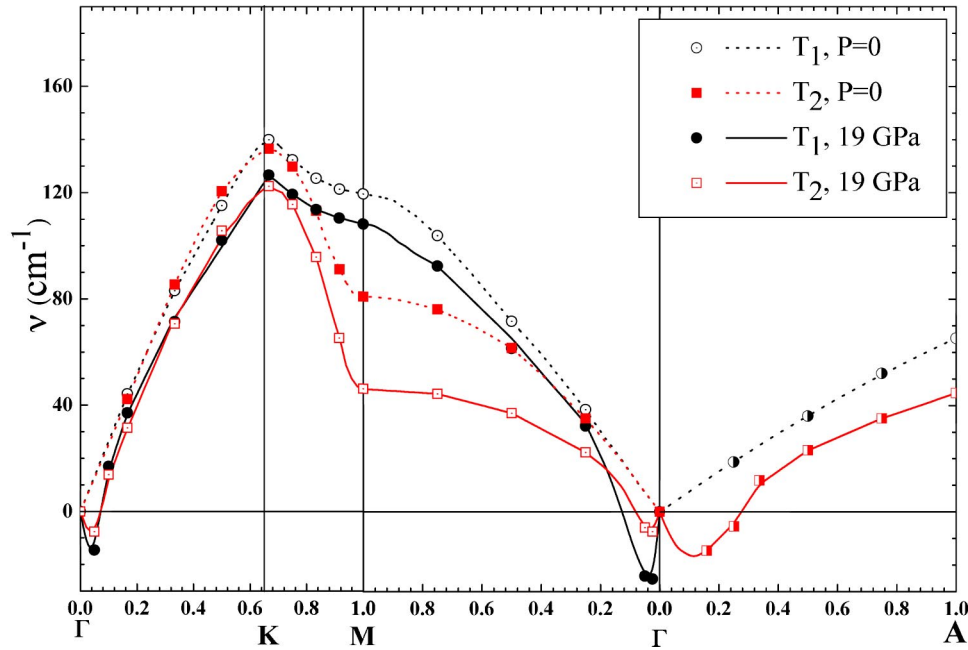


FIG. 2. (Color online) Transverse acoustic branches of zinc oxide at ambient pressure and at $P=19$ GPa.

In the initial stages of the phase transformation each path involves different phonons and elastic constants: the hexagonal distortion is mainly characterized by a compression of the c axis and the consequent vertical displacement of ZnO pairs, related to the B_1 optical phonon. The tetragonal distortion involves instead the c_{66} elastic constant and the E_2 optical phonon. In order to confirm our hypothesis, we studied the vibrational properties along this deformation. As these endpoint phases can be considered as the same monoclinic structure with a γ angle equal to 60° and 90° respectively, we carried out *ab initio* phonon calculations for 6 intermediate stages of the deformation by varying γ . At each stage calculations were performed at the Γ point, and at different c/a ratios, in order to understand the role of both contributions to the phase transition. We report in Fig. 3 the behavior of the E_2^{low} phonon as function of the angular deformation at differ-

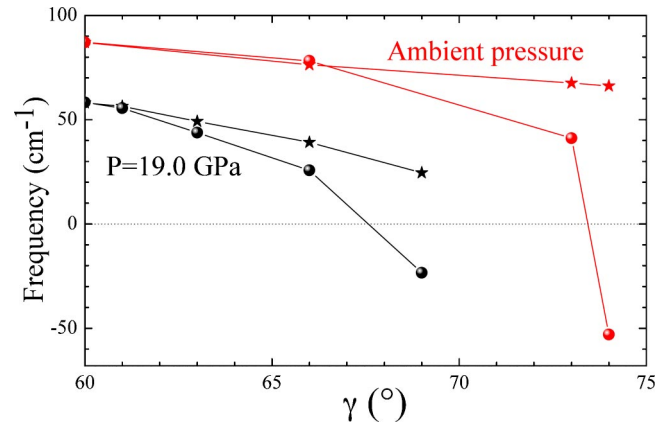


FIG. 3. (Color online) Frequency of the E_2^{low} optical phonons as function of the “tetragonal” distortion, i.e., the variation of the hexagonal angle, at two different pressures. The phonon splitting is due to the loss of the hexagonal symmetry. Phonon softening occurs at rather small angle distortions at high-pressure, and even at ambient pressure such deformation would make the wurtzite phase unstable.

ent pressures. We observe that this phonon actually softens, even under ambient condition, because of this distortion, and that the effect is enhanced at high pressure. On the other hand, the effect of a lower c/a ratio seems to go in the opposite direction, showing once more that the hexagonal path is rather unlikely. These results allow us to affirm that the wurtzite-rocksalt transition in ZnO is characterized, at first, by an angle opening towards a tetragonal phase, coupled with a horizontal displacement of atoms, and then, before the tetragonal structure actually occurs, by a lowering of the c/a ratio to the rocksalt value $\sqrt{2}$ and a corresponding vertical repositioning of atoms.

The wurtzite-rocksalt phase transition is observed in many other technologically relevant wide-gap semiconductors, most notably the group III-nitrides. We carried out analogous calculations for AlN, GaN, InN, and for w -SiC, in order to understand whether the transformation mechanism we propose for ZnO is intrinsic to this phase transition, or if it depends on the specific compound. In Table I the transition pressures from the wurtzite phase are reported. We observe that the tetragonal phase is never stable or metastable in AlN or SiC: thus our proposed wurtzite-to-rocksalt transformation path is unlikely for these compounds. Gallium and indium nitrides, on the contrary, behave similarly to zinc oxide: for

TABLE I. Transition pressures for zinc oxide and the three nitrides from the wurtzite structure to each one of the three other phases. The tetragonal phase is unstable (i.e., it has no local minimum) in AlN and SiC.

		Hexagonal	Tetragonal	Rocksalt
ZnO	$P_{w \rightarrow}$ (GPa)	20.0	9.8	7.6
AlN	$P_{w \rightarrow}$ (GPa)	24.7		8.3
GaN	$P_{w \rightarrow}$ (GPa)	182.5	50.8	33.5
InN	$P_{w \rightarrow}$ (GPa)	39.7	17.7	11.7
SiC	$P_{w \rightarrow}$ (GPa)	197.9		63.5

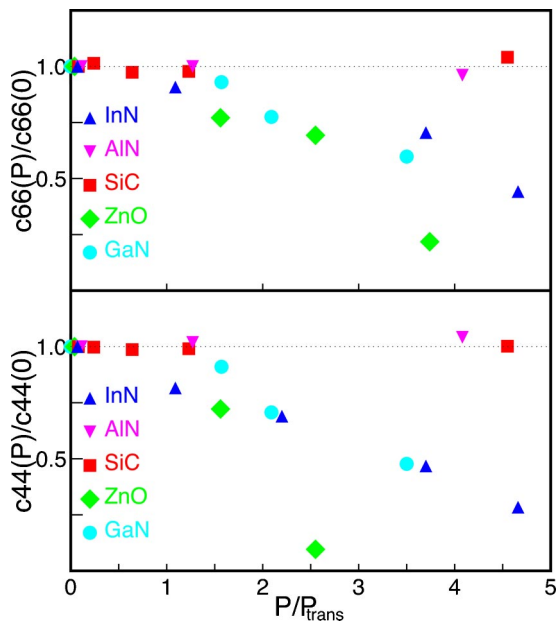


FIG. 4. (Color online) Evolution of c_{44} and c_{66} elastic constants under pressure with respect to their ambient pressure values, and as a function of the respective wurtzite-to-rocksalt transition pressure P_r .

both the transition from the wurtzite to the tetragonal phase would occur at much lower pressures than the one to the hexagonal phase.

These results seem to be more general and interesting: the study of the c_{44} and c_{66} elastic constants under pressure (see Fig. 4) show that they would not soften in AlN and SiC up to 5 times their respective wurtzite-to-rocksalt transition pressure, while they would in GaN and InN. In other words, in gallium nitride and indium nitride, similarly to zinc oxide, the shear instability associated to the tetragonal transition path eventually occurs, even if at pressures higher than the wurtzite-rocksalt transition pressure. This suggests that the tetragonal deformation mechanism is energetically *and* dynamically favorable with respect to the hexagonal path. On the contrary, both the energetics and the stiffness of the shear elastic constants seem to rule out the tetragonal transformation path in AlN and *w*-SiC. The similar behavior of ZnO, GaN, InN, as well as of CdS,⁵ could be interpreted in terms of a *d* electron-induced softening of the c_{44} and c_{66} elastic constants. Interestingly, the very fact that the hexagonal intermediate phase has been described and labeled in Ref. 1 after MgO, which of course does not contain *d* electrons, points in the same direction.

This result should be thus interpreted through the electronic properties of these systems. However, the study of

their band structure and charge density at low and high pressure does not reveal any significant effect due to the presence of *d* electrons. Analogously, the analysis of ionicity and steric effects does not seem to yield an answer, since these properties in GaN look more similar to those of AlN rather than those of InN. A qualitative interpretation of the relation between *d* electrons and the softening of the c_{44} and c_{66} elastic constants can instead be obtained through the Keating model, which relates these elastic constants, in tetrahedrally-coordinated semiconductors, to bond-bending and, thus, to second-neighbor interactions. In other words, the softening of the TA modes in *d*-electrons-containing systems may be due to the increased screening of the Coulomb forces between cations at increasing pressure. To clarify this issue, we have carried out a detailed analysis of the different contributions to the total energy, at ambient and high pressure, in both the wurtzite phase and in a structure slightly distorted along the tetragonal deformation. We considered ZnO, GaN, AlN, and a *d*-electron-free GaN. We observe, for all of them at high pressure, an increase of the one-electron energy, almost completely counterbalanced by a decrease of the Ewald term, of the exchange-correlation energy, and of the electron-electron repulsive (Hartree) contribution. The relative gain in energy due to this last term is however about twice as important in ZnO and GaN than it is in AlN and in the NLCC, *d*-electron-free GaN.

In conclusion, we show in this work that the commonly observed transition from the fourfold coordinated wurtzite to the sixfold coordinated rocksalt phase occurs through a quasitetragonal deformation which links, in a crystallographic simple way, the two endpoint structures. This hypothesis is confirmed in ZnO, GaN, and InN (but not in AlN and *w*-SiC) by the study of the energetics, and strongly supported by the experimental and *ab initio* determination of the shear constants and phonons under pressure. On the other hand, the recently suggested hexagonal deformation path seems possible only in wurtzite semiconductors containing light (*d* electron-free) cations, such as AlN and *w*-SiC, and can be inferred for other compounds such as BN. The study of the transformation paths leads to important, general predictions on the dynamical and elastic pressure properties of the whole family of wurtzite wide-gap semiconductors, such as the softening of TA modes and of the c_{44} and c_{66} elastic constants in ZnO, GaN, and InN, or the independence of the wurtzite internal parameter u on pressure.²⁰ These predictions, experimentally verified for ZnO, are to be demonstrated by experiments for GaN and InN.¹⁰

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