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Lattice dynamics of GaN: Effects of 3*d* electrons

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We perform first-principles calculations of structural, dielectric, and lattice-dynamical properties of cubic GaN. The equilibrium structure is obtained using the plane-wave pseudopotential approach within the density-functional theory and local-density approximation. The dielectric and vibrational properties are computed within the density-functional perturbation theory. The effect of the Ga 3*d* electrons is treated by taking into account the nonlinear core corrections for the exchange and correlation energy. The importance of 3*d* electrons for the bonding strength is determined, and their influence on the dielectric and dynamical properties of GaN is analyzed and discussed. [S0163-1829(97)00231-2]

The group-III nitrides AlN, GaN, and InN are regarded as promising wide-band gap semiconductors for optoelectronic applications in the short-wavelength range as well as for high-temperature, high-power, and high-frequency electronic devices. In particular, GaN is a basic material for the realization of light-emitting diodes and lasers in the blue and UV range of the spectrum. Under ambient conditions, GaN crystallizes in the wurtzite (2*H*) structure. However, in the past few years molecular-beam epitaxy techniques have enabled the growth of GaN films of zinc-blende (3*C*) structure.[1]

In the 3*C* and 2*H* structures each atom of one kind is tetrahedrally surrounded by four atoms of the other kind; both phases have the same nearest-neighbor shell, the first difference occurs with the second neighbors. Therefore, the physical properties of both structures are quite similar, but the zinc-blende nitrides are expected to show improved electronic properties due to the reduced phonon scattering.[2] Moreover, the zinc-blende phase is hoped to be more amenable to doping than the wurtzite phase, since all of the III-V compounds which can be efficiently doped are cubic. Therefore, it is meaningful to characterize theoretically the physical properties of 3*C* GaN.

Despite the technological interest in GaN, little is known about its lattice dynamics from the theoretical point of view. Moreover, phonons are important as elementary excitations for standard characterization of the sample quality by means of first-order Raman spectroscopy.[3–7] Accurate first-principles calculations have been performed only for nonpolar zone-center phonons using either a mixed-basis[8] or the linear muffin-tin orbital (LMTO) method[9,10] within the frozen-phonon approach. A particular problem of first-principles calculations concerns the semicore Ga 3*d* electrons. The Ga 3*d* shell in GaN is not as inert as in the other Ga compounds and affects both the electronic and structural properties.[11] The breakdown of the frozen-core approximation for the Ga 3*d* states is related to the energetical resonance of Ga 3*d* and N 2*s* levels[11] and the significant overlap of Ga 3*d* with the Ga 4*s* and 4*p* charge density.[12] The computational effort for an accurate description of the strongly localized 3*d* wave functions within the plane-wave pseudopotential approach is rather extensive.[13] On the other hand, the significant overlap of the Ga 3*d* electrons with the Ga valence states can be treated within the frozen-core approximation, if the nonlinear core correction (NLCC) of Louie, Froyen, and Cohen[14] is taken into account. The NLCC both enhances the transferability of pseudopotentials and reduces considerably the computational effort. Wright and Nelson[13] showed that the structural and electronic properties of GaN can be correctly described within the plane-wave pseudopotential method and the NLCC approach. Moreover, the NLCC approach of shallow *d* electrons of group-II atoms has been already successfully applied to the description of the structural as well as of the lattice-dynamical properties of II-VI compounds.[15]

In this report we present a first-principles study of the structural properties, i.e., lattice constant a, bulk modulus B_0, and its pressure derivative B_0', of the dielectric, i.e., Born effective charge Z^{B} and dielectric constant ϵ_∞, and of the lattice-dynamical properties, i.e., the phonon frequencies, of 3*C* GaN. The ground-state properties are obtained within the local-density approximation (LDA) by minimizing the static total energy using the Vinet equation of state.[16] For the exchange-correlation potential the parametrization of Perdew and Zunger is used.[17] The Ga and N pseudopotentials are generated according to the scheme of Troullier and Martins[18] including the NLCC for the 3*d* states of Ga. The basic quantities in lattice dynamics, i.e., the harmonic interatomic force constants are computed within density-functional perturbation theory[19] generalized to the framework of NLCC.[15] The plane-wave expansion of the electronic wave functions is limited by an energy cutoff of 60 Ry to ensure the convergence of the phonon frequencies to within 3 cm^{-1}. The Brillouin zone (BZ) summations are performed using a set of 28 Chadi-Cohen special points.[20]

The resulting values of the equilibrium structural parameters and of the dielectric quantities are reported in Table I. To characterize the accompanying lattice-dynamical proper

TABLE I. Ground-state, dielectric, and dynamical properties of 3*C* GaN. The experimental data for B_0, B_0', and ϵ_∞ have been taken from those of the 2*H* GaN.

	a (Å)	B_0 (Mbar)	B_0'	Z^B	ϵ_∞	ϵ_0	ω_{LO} (cm^{-1})	ω_{TO} (cm^{-1})
Calc.[a]	4.44	2.07	3.94	2.65	5.41	9.70	750	560
Calc.[b]	4.29	2.34	4.09	2.60	4.90	8.98	803	593
Calc.[c]							687	481
Calc.[d]	4.46	2.01	3.90					603
Expt.	4.49 (Ref. 22)	2.37 (Ref. 27)	4.3 (Ref. 27)		5.29 (Ref. 4)		741 (Ref. 4)	555 (Ref. 4)
		1.88 (Ref. 23)	3.2 (Ref. 23)		5.35 (Ref. 25)		740 (Ref. 5)	555 (Ref. 5)
							743 (Ref. 6)	552 (Ref. 6)

[a] Present calculation including NLCC for the Ga 3*d* electrons.

[b] Present calculation with Ga 3*d* electrons treated as completely frozen in the core.

[c] As in case *b* but using the experimental lattice constant.

[d] Full-potential LMTO, Kim *et al.* (Ref. 9).

ties the zone-center optical phonon frequencies are also given. The calculated values within the NLCC approach are compared with experimental data and with results obtained by completely neglecting the Ga 3*d* electron effects.

The data listed in Table I show that the inclusion of NLCC considerably improves the theoretical results in comparison with the experimental data. The strong overestimation of the covalent GaN bonding is widely canceled. In particular, the underestimation of the lattice constant of about 5% is reduced to 1%. Simultaneously the value of the bulk modulus is remarkably reduced by about 13%. The observed small discrepancy between the lattice parameter obtained from LDA calculation and from experiment is typical and remains, even if temperature effects are taken into account.[21] The experimental values[22,23] of the bulk modulus available for the wurtzite GaN scatter to a larger extent than the theoretical ones using different approaches.[13] Thus, a distinct statement about the accuracy of the NLCC approach for this quantity is not possible. We note that the above described influence of the Ga 3*d* electrons is in good agreement with the full-potential LMTO findings of Fiorentini *et al.*.[11,24]

The Ga 3*d* electrons influence the Born effective charge Z^B only slightly reducing its value by about 2%. On the other hand, the value of the dielectric constant ϵ_∞ depends on the volume and on the contribution of the Ga 3*d* charge density to the exchange-correlation potential. According to the Penn formula with $\epsilon_\infty - 1 \sim V^{1/3}$, one might expect that the value of ϵ_∞ only increases by about 3% when the NLCC for the Ga 3*d* electrons is used. However, we observe an increase of ϵ_∞ by about 10%. Obviously, the NLCC approximation improves considerably the exchange-correlation potential of the valence electrons and modifies, therefore, the electronic screening. These contributions are neglected when the *d* electrons are treated as completely frozen in the core. The calculated value of $\epsilon_\infty = 5.41$ slightly overestimates the measured dielectric constants of 2*H* GaN of 5.29 (Ref. 4) or 5.35.[25] This overscreening is a well-known drawback of the LDA.[19] The predicted static dielectric constant $\epsilon_0 = 9.70$ differs by a factor of 1.8 from ϵ_∞. Thus, the lattice polarizability of GaN is significantly larger than that of, e.g., BN, SiC, or GaAs.

The NLCC approximation of Ga 3*d* electrons gives rise also to a substantial change of the transverse-optical (TO-) phonon frequency at the zone center from the value of 593 cm^{-1} to 560 cm^{-1}. The obtained TO-phonon frequency is only slightly higher (by about 1%) than the Raman scattering data.[4–6] In order to estimate the pure volume effects on the phonon spectra, we also calculated the zone-center phonon frequencies using the experimental lattice constant and treating the Ga 3*d* electrons as completely frozen in the core. As shown in Table I, the obtained values of the LO- and TO-phonon modes are too small. Therefore, the excellent agreement between the NLCC and experimental results cannot be explained by a mere expansion of the volume of the unit cell but rather by a combination of the volume effects and contributions of Ga 3*d* charge density to the exchange-correlation energy of the valence electrons. This agreement indicates that the main contribution of the Ga 3*d* electrons to the structural and lattice-dynamical properties of GaN is correctly described by the NLCC approach. Thus, for the properties under consideration it is not necessary to treat the Ga 3*d* electrons completely as valence electrons.

It is worth mentioning that the Ga 3*d* electrons contributions reduces the value of the LO-TO splitting considerably from 210 cm^{-1} to 190 cm^{-1}, towards the experimental first-order Raman data of 186 cm^{-1},[4] 185 cm^{-1},[5] or 191 cm^{-1}.[6] As already shown for the value of the TO-phonon frequency this remarkable decrease (by about 10%) of the LO-TO splitting is based on both volume and polarization effects of Ga 3*d* electrons (see also Table I).

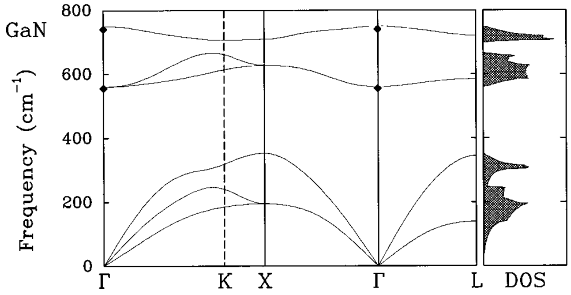

FIG. 1. Calculated phonon dispersion curves and the phonon density of states for 3*C* GaN. Experimental first-order scattering data from Ref. 4 are denoted by diamonds.

TABLE II. Zone-boundary frequencies of GaN. The values in parenthesis are obtained with Ga $3d$ electrons treated as completely frozen in the core.

q point	TA	LA	TO	LO
X	195	353	628	709
	(219)	(373)	(665)	(765)
L	139	345	585	720
	(157)	(368)	(618)	(776)

The phonon dispersion curves of $3C$ GaN along high-symmetry lines of the BZ are displayed in Fig. 1 together with the corresponding one-phonon density of states (DOS). Since only few first-order Raman experiments have been performed for this semiconductor the direct comparison with the experiment is only possible for the zone center (see also Table I). In view of the agreement between the theoretical and experimental zone-center phonon frequencies the present parameter-free calculations can be considered as reliable predictions for the full phonon band structure of $3C$ GaN. Due to the relatively large mass difference between gallium and nitrogen atoms, the optical branches of $3C$ GaN are rather flat. Thus, as shown for the DOS, a gap not only separates the acoustic- and optical-phonon branches (from 353.2 to 560.7 cm^{-1}), but also the LO- and the TO-phonon modes (from 666.7 to 698.9 cm^{-1}). In order to characterize the effect of the d electrons on the complete phonon spectra, the zone-boundary phonon modes at the X and L point have been also determined treating the Ga $3d$lectrons as completely frozen in the core. As shown in Table II the general trend is the same as for the zone-center phonon frequencies. The neglect of the $3d$ electron effects leads to an overestimation not only of the phonon frequencies but also of the splitting between the LO and TO modes.

A very interesting feature has been found for the TO-phonon branch. The maximum of this branch is not located at the zone center as it is the case of BN, SiC, or GaAs, but at the X point, the boundary of the BZ. The wave-vector dispersion of the TO mode resembles that of highly ionic crystals like NaCl, MgO, and ZnS. In Fig. 2 we present the calculated values of the ratio $\omega_{\mathrm{TO}}(X)/\omega_{\mathrm{TO}}(\Gamma)$ for the III-V nitrides BN, AlN, and GaN as a function of the square root of the mass ratio of the constituent atoms. The ratios $\omega_{\mathrm{TO}}(X)/\omega_{\mathrm{TO}}(\Gamma)$ lie very close to the straight line indicating that the mass approximation is satisfactory fulfilled by the considered phonon frequencies although the mass approximation cannot be applied to the full phonon spectra of these semiconductors.[26] This peculiarity can be explained in terms of the covalent and ionic contribution to the bonding of these materials. Whereas, the bonding of BN is strongly covalent, the ionic and covalent contributions to the bonding of AlN are nearly of the same order. In the case of GaN the ionic contribution slightly dominates over the covalent one. This finding is supported by the trend of the Born effective charge of these materials: $Z^{\mathrm{B}}(\mathrm{BN})=1.93$, $Z^{\mathrm{B}}(\mathrm{AlN})=2.56$, and $Z^{\mathrm{B}}(\mathrm{GaN})=2.65$. Another support arises from the behavior of the TA branches in Fig. 1. In contrast to other III-V compounds, the TA branches of GaN do not show a pronounced flattening away from the zone cente as indicated by the ratio $\omega^2_{\mathrm{TO}}(X)/\omega^2_{\mathrm{TA}}(X)\approx 3$. This behavior is a consequence of the increased strength of the central forces versus the noncentral ones and, hence, of the ionic bonding.

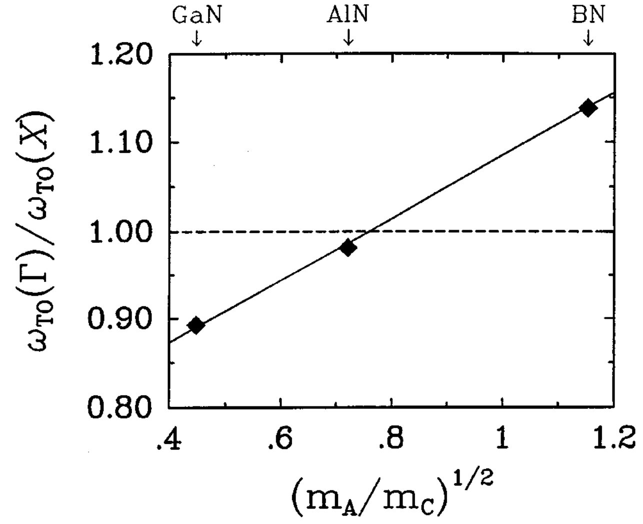

FIG. 2. Ratio of the transverse-optical-phonon frequencies at the X and Γ point of the BZ of BN, AlN, and GaN versus the square root of the ratio of the corresponding cation and anion atomic masses. The diamonds denote the *ab initio* results. The solid line is only a guide to the eye.

In conclusion, we have presented a detailed analysis of structural, lattice dynamical, and dielectric properties of $3C$ GaN as obtained using the DFT and NLCC approach for the shallow Ga $3d$ electrons. The lattice constant, the high-frequency dielectric constant, and the zone-center phonon frequencies agree at a level of a few percent with the corresponding experimental data. This agreement gives us onfidence in the reliability of the approximation used, in particular for the phonon frequencies outside the Γ point where neutron scattering data do not exist and for the predicted static dielectric constant. We have found a significant improvement in the description of various ground-state properties by the inclusion of the $3d$ electron effects using the NLCC approach. In particular, the bond strength is weakened and the interatomic distance between the nearest neighbors is increased. Moreover, the Ga $3d$ electrons affect the phonon frequencies and the static and high-frequency dielectric constants. The considerably decrease of the LO- and TO-phonon frequencies as well as of the LO(Γ)-TO(Γ) splitting cannot be explained by a simple increase of the lattice constant but is rather due to both the volume and the polarization contributions of the shallow Ga $3d$ electrons.

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