

## Temperature and pressure dependence of Mg local modes in GaN

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The temperature and pressure dependence of the zone-center phonons and of the local vibrational modes of magnesium in the hexagonal modification of GaN was studied within a valence-force model. The contribution caused by thermal expansion was calculated and compared with the experiment. We find that the frequency shift of the local vibrational modes arises to a much larger extent from anharmonic decay into lower energy phonons than the shift of the GaN host modes.

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Doped III nitrides have recently been at the focus of much research because of their application in high-power optoelectronic devices.<sup>1</sup> The dopant atoms appear in the vibrational spectrum of the host modes<sup>2-4</sup> as additional structures.<sup>5</sup> The spectroscopy of these local vibrational modes (LVM) is an important tool for determining the type, the microscopic structure, and the concentration of the defects in semiconductors. The energetic position of the LVM is determined by the mass of the dopant and the strength of the bond between the dopant and its neighbor. The application of GaN as a material for high-temperature and high-power devices requires a good thermal stability. Recently, while the temperature dependence of the GaN host modes was analyzed,<sup>6,7</sup> that of the local vibrational modes in GaN has remained unreported. The temperature and pressure dependence of the local modes found in the literature is concerned with hydrogen complexes in GaAs,<sup>8,9</sup> AlAs<sup>10</sup> and GaP.<sup>11</sup>

In this letter, we calculate the temperature and pressure dependence of the host modes and the local vibrational modes of the dopant magnesium in thin films of GaN. The two significant contributions to the temperature dependence of the phonon frequency are the thermal expansion of the lattice and the decay into lower-frequency phonons. A further contribution, the temperature dependence of the strain, induced by differences in the thermal expansion coefficient of film and substrate, is small compared to the two previous contributions.<sup>7</sup> We calculated the frequency shift of the phonons in GaN due to the thermal expansion of the lattice based on the known pressure derivatives and compare these with the experimental results by means of Raman scattering. We considered the anharmonic effects in a variant of the Keating model,<sup>12</sup> which was suggested by Rücker and Methfessel.<sup>13</sup> In this model bond stretching and bond bending parameters of the ideal crystal are described as a function of the change in lattice constants. From the difference between the computed shift due to thermal expansion and the experimentally observed temperature dependence we determined the pure temperature contribution, i.e., the anharmonic decay into phonons of lower energy.

The temperature dependence of the frequencies of

phonons arises primarily from two different anharmonic contributions (see above):

$$\left(\frac{\partial\omega}{\partial T}\right)_p = \left(\frac{\partial\omega}{\partial T}\right)_v + \left(\frac{\partial\omega}{\partial V}\right)_T. \quad (1)$$

In thin film samples, there is an additional contribution from the difference of the thermal expansion coefficients of film and substrate, which we neglect here since it is small for GaN on sapphire.

The calculation of the host modes of the GaN is based on the valence force model of Keating and Kane.<sup>12,14</sup> The anisotropy of hexagonal GaN was taken into account by a set of parameters each for interactions along and perpendicular to the *c* axis. The change of the phonon spectrum due to an impurity is described by a so-called scaling factor *s*. It is a measure of the change in the interatomic forces at the impurity. In the case of local modes of magnesium was *s* = -0.15, the minus sign standing for a softening of the interatomic forces between the impurity and its nearest neighbors.<sup>15</sup>

The bond-stretching potential corresponds to a parameter  $\alpha$  and the bond bending potential to a parameter  $\beta$  in the Keating and Kane model. The potential energy (*W*) contains terms quadratic in the distortion  $\Delta$  from equilibrium geometry.

$$W = \sum_{i,j} \frac{\alpha}{a_0^2} \Delta(r_{ij}^2)^2 + \sum_{i,j,k \neq j} \frac{\beta}{a_0^2} \Delta(\mathbf{r}_{ij} \mathbf{r}_{ik})^2, \quad (2)$$

where  $a_0$  describes the lattice constant, *i* each individual atom of the calculated crystal, and *j* and *k* run over the four nearest neighbors of the atom *i* and  $\mathbf{r}_{ij}$  is a vector pointing from the *i*th to the *j*th atom. In order to describe the influence of volume changes of the crystal on phonon frequency [i.e., the second term in the Eq. (1)] higher-order terms are needed. Rücker and Methfessel<sup>13</sup> derived scaling laws for the force constants

$$\alpha = \alpha^0 \left( \frac{r_{ij}^0}{r_{ij}} \right)^n \quad (3)$$

$$\beta = \beta^0 \left( \frac{r_{ij}^0}{r_{ij}} \right)^{7/2} \left( \frac{r_{ik}^0}{r_{ik}} \right)^{7/2} \left( \frac{\Theta_0}{\Theta} \right)^{\nu}, \quad (4)$$

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TABLE I. Summary of the calculated (with  $B=200$  GPa) “a” and the observed Grüneisen parameters  $\gamma$  in hexagonal GaN. Experimental values for Grüneisen parameters were taken from “b.”

| Modes                      | $\gamma$<br>experiment | $\gamma$<br>calculated |
|----------------------------|------------------------|------------------------|
| $E_2$ (low)                | -0.4                   | 0.09                   |
| $E_1$ (TO)                 | 1.41                   | 1.28                   |
| $A_1$ (TO)                 | 1.47                   | 1.31                   |
| $E_2$ (high)               | 1.50                   | 1.37                   |
| $E_1$ (LO)                 |                        | 0.84                   |
| $A_1$ (LO)                 | 1.37                   | 1.19                   |
| $262\text{ cm}^{-1}$ (LVM) |                        | 0.47                   |
| $656\text{ cm}^{-1}$ (LVM) |                        | 0.44                   |

<sup>a</sup>Reference 21.

<sup>b</sup>Reference 17.

where the superscript 0 refers to the unstrained bond lengths and  $\Theta_0$  to the angle enclosed between unstrained bonds.  $\Theta/\Theta_0$  is the change in angle due to the strain. The remaining parameters describing the long-range interaction between the next-nearest neighbors continue unchanged, i.e., for these parameters we used those of the undoped hexagonal GaN. In our calculations the effective charge  $Z^*$  also remained unchanged.

As input for the calculation we used the parameters of pure GaN from a calculation of the full phonon dispersion curves<sup>3,15</sup> and the lattice constants as a function of temperature.<sup>16</sup> In determining the contribution of the anharmonic decay to the temperature dependence of the localized vibrational modes we proceeded as follows. First we determined the effects of thermal expansion, i.e., we found  $n$  and  $\nu$ , the exponents in the  $r_{ij}$  dependence of the anharmonic valence-force parameter  $\alpha$  and  $\beta$ . The difference to the experimentally observed frequency shifts then constitutes the first term in Eq. (1). On the basis of the values  $n=4$  and  $\nu=0.93$ , which Rucker and Methfessel used in Si and Ge, we fitted our model to the experimental Grüneisen parameters determined from the shift of the  $\Gamma$  phonon frequencies under pressure.<sup>17,18</sup> For  $n=6.3$  and  $\nu=0.9$  we found good agreement with the experimental Grüneisen parameters  $\gamma = B/\omega(\partial\omega/\partial P)$ , where  $B$  is the bulk modulus, and  $\omega$  is the phonon frequency (Table I). The model also reproduces qualitatively the unusually small  $\gamma$  of the  $E_2$  (low) mode. An extension to a volume dependence of the next-nearest neighbor forces also reproduces the negative sign, which is, however, not the focus of this letter. A full description of the anomalies in  $\gamma$  may be found in Ref. 19.

In the upper inset of Fig. 1 we show the Raman results for the  $E_2$  (high) mode together with our calculations of the thermal-expansion effects between 3 and 550 K. The  $E_2$  (high) phonon frequency experiences a softening of about  $6\text{ cm}^{-1}$  with increasing temperature. The shift of this host mode as calculated from the thermal expansion is about  $2.6\text{ cm}^{-1}$  the larger contribution thus coming from the first term in Eq. (1). While Liu *et al.*<sup>6</sup> reported a similar shift of the  $E_2$  (high) phonon frequency Link *et al.*<sup>7</sup> observed a shift of only  $\sim 4\text{ cm}^{-1}$  in the same temperature range. They thus arrive at the conclusion that thermal expansion contributes most to the shift in Eq. (1) which is an unusual finding for solids.

In the lower image of Fig. 1 we show calculated fre-

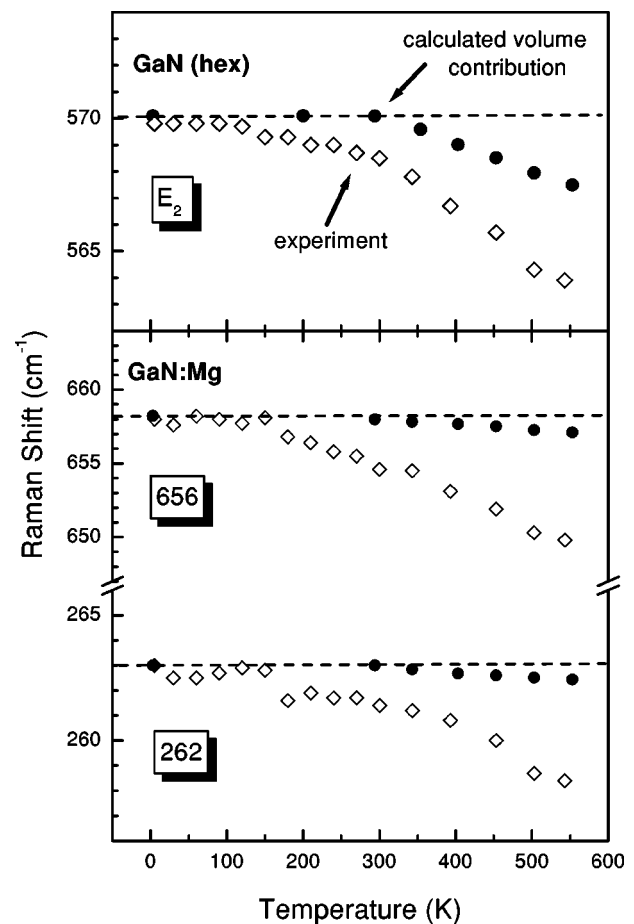


FIG. 1. Frequency of the  $E_2$  (high) mode (upper) and local vibrational modes of the magnesium impurity (lower) in hexagonal GaN vs temperature; open diamonds represent the experimental temperature dependence (data taken from Ref. 20), filled circles the calculated volume contribution. The broken lines represent the phonon energies at low temperature.

quencies of the two strongest local vibrational modes of the Mg impurity at  $262$  and  $656\text{ cm}^{-1}$  as a function of temperature.<sup>20</sup> The thermal-expansion contributions for the  $262$  and  $656\text{ cm}^{-1}$  LVMs are  $0.6$  and  $1.3\text{ cm}^{-1}$ , respectively, which corresponds to calculated Grüneisen parameters of  $0.47$  and  $0.44$ , i.e., they have a much smaller pressure dependence than the host modes (Table I). The small pressure dependence is also typical for local vibrational modes of hydrogen complexes in GaAs and in AlSb.<sup>8,9</sup>

The similar frequency shift (about  $6\text{ cm}^{-1}$ ) of the  $E_2$  mode and the LVM at  $656\text{ cm}^{-1}$  in the temperature range between 3 and 500 K can be explained by the comparable amplitudes  $A_q$  of these vibrations. McCluskey *et al.*<sup>11</sup> showed that the shift of a local vibrational mode is proportional to the lattice thermal energy. This is given by:  $Nf/2 \sum A_q^2$ , where  $N$  is the number of the atoms and  $f$  the nearest neighbor force constant. The frequencies of the two Mg local vibrational modes considered here lie in a range of high density of phonon states of the host modes, i.e., the LVMs hybridize with the host phonons losing their strong localization around the Mg impurity. Therefore the amplitudes of the LVM differ little from those of the host phonons with the result that the temperature shifts are similar. Figure 1 shows that the difference between the experiment and the computed volume contributions for the local vibrational modes is much larger than for the host modes.

In conclusion, we presented the temperature dependence of the  $E_2$  host mode and local vibrational modes of a Mg impurity in hexagonal GaN. We described the thermal-expansion contribution for the investigated modes by a variant of the valence-force model of Keating and Kane, which considers the anharmonic change of the Keating parameters with volume. From the shift of the phonon frequencies we calculated the LVM Grüneisen parameters, which we found to be much smaller than for the host modes. The temperature dependence of the local vibrational modes of Mg although similar in magnitude to that of the host modes in GaN, is to a much larger extent determined by the anharmonic decay into lower-energy phonons than that of the host modes.

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