

LOCAL VIBRATIONAL MODES AT TRANSITION-METAL IMPURITIES IN HEXAGONAL AlN AND GaN CRYSTALS

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Abstract. We present a detailed experimental and theoretical study of local vibrational modes (LVMs) at transition-metal (TM) impurities in wurtzite-type crystals. The energies of the LVMs of Fe^{3+} and Ti^{2+} in hexagonal GaN and Fe^{3+} in hexagonal AlN are calculated with a modified valence-force model of Keating and Kane, which was generalized for hexagonal symmetries including long-range Coulomb forces. The valence-force parameters of the perfect crystals are calculated by fitting the phonon dispersion curves to experimental Raman data of GaN and to ab-initio calculations of AlN. The valence-force parameters in the vicinity of the defect are determined using the scaling-factor approximation. The dynamical matrix is set up for a cluster of 295 vibrating atoms, which is embedded in the non-vibrating crystal, taking the TM as the central atom. The eigenvalues of the dynamical matrix give the vibration frequencies. The LVMs were selected due to their large vibration amplitudes of the atoms close to the defect as obtained from the eigenvectors of the dynamical matrix. The calculated energies of the LVMs are in good agreement with the results obtained by our photoluminescence and photoluminescence excitation measurements. We present the calculated impurity and the ligand induced isotope shifts of the LVMs. The energy differences with respect to different impurity isotopes were found to be smaller than 1 meV per nucleon and therefore could not be observed because of the experimental linewidth of 1.5 meV for the corresponding photoluminescence zero-phononlines. We also demonstrate the delocalization of LVMs with energy in the phononbands due to hybridization with crystal phonons.

Introduction

In the last few years the interest in the wide bandgap semiconductors, especially in the nitrides, has been strongly increased. With the nitride based semiconductors InN, GaN and AlN the band-gap can be varied between 1.9 eV (bandgap of InN) and 6.3 eV (bandgap of AlN). The aim of this paper is to give a comprehensive study on LVMs at various transition metal (TM) centers in these compounds. We here focus on the wurtzite-type crystals of AlN doped with Fe [5, 2], and GaN doped with Fe [3] or Ti [4], respectively.

The Energy of the local vibrational modes of the Fe^{3+} defect in GaN is determined experimentally by photoluminescence (PL). In the 1.2988 eV luminescence band LVMs at 37.3 meV, 39.2 meV, 85.5 meV and 88.9 meV are observed. The 1.2988 eV luminescence is attributed to the Fe^{3+} (${}^4\text{T}_1\text{-}{}^6\text{A}_1$)-transition [1, 3].

Figure 1 shows a low-temperature photoluminescence-excitation spectrum of the Fe zero-phonon line for a Fe doped GaN crystal at 1.8 K [3]. There are several phonon satellites with a distance of 75 meV, coupled to the (Fe^{3+} ,e,h) transition [3].

A luminescence line at 1.1934 eV was detected with low-temperature photoluminescence measurements of a Ti and Cr doped GaN crystal at 1.8 K, which is attributed to the Ti^{2+} [4] center or to the Cr^{4+} center [2]. We attribute it to the (${}^1\text{E-}{}^3\text{A}_2$)-transition of Ti^{2+} and not to Cr^{4+} [10]. A LVM at 87 meV has been observed in the photoluminescence spektrum of hexagonal AlN crystals [5] doped with Fe.

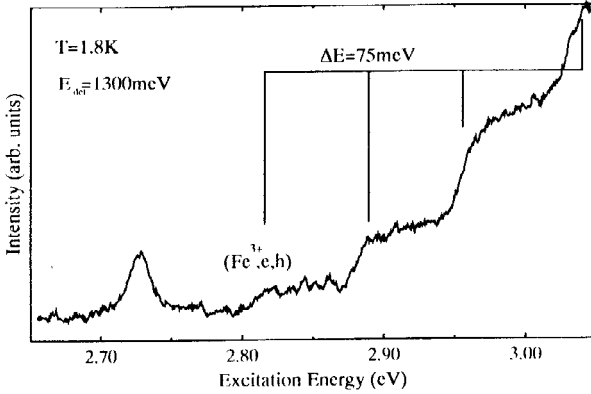


Figure 1: Low temperature photoluminescence excitation spectrum of a Fe doped GaN crystal at 1.8 K.

Theoretical Model

Our theoretical model is based on the harmonic approximation and the modified valence-force model of Keating and Kane, which was originally developed for crystals of cubic symmetry. The model for bond stretching and bond bending forces of Keating was extended by Kane to include up to third nearest neighbour interactions and long-range Coulomb forces. This model was generalized by us for hexagonal symmetry. In cubic crystals there are eight independent parameters. Because of the anisotropy in the direction of the *c*-axis there are fourteen independent parameters in crystals under hexagonal symmetry. To obtain the phonon-dispersion curves and the valence-force parameters of the perfect crystal, the long-range coulomb forces are calculated using the Ewald method.

For the calculation of the LVMs we used this model to set up the dynamical matrix of a cluster of 295 vibrating atoms, which is embedded in the non-vibrating perfect crystal and taking the TM as the central atom. The valence-force parameters in the vicinity of the defect are determined using the scaling-factor approximation which is defined by $p_d = p + ps$, where p is any of the valence-force parameters of the perfect crystal and p_d the corresponding parameter at the defect site, and s is the scaling factor which was varied between -0.2 and 1.0 . A negative s indicates a local softening of the interatomic forces near the defect and a positive s means that the defect site is stronger bound than the atoms of the perfect crystal. The vibration frequencies were obtained from a numerical diagonalization of the dynamical matrix. The LVMs were selected from their large vibration amplitudes of the atoms in the vicinity of the defect as obtained from the corresponding components of the eigenvector of the dynamical matrix.

Based on the harmonic approximation the mass dependence of the energy of a LVM mode is associated with the sum of the squares of the three corresponding components of the eigenvector of the dynamical matrix A^2 and we have

$$\frac{\partial \hbar\omega}{\partial M} = -\frac{\hbar\omega}{2M} A^2. \quad (1)$$

This equation allows the determination of the shift of the energy of a LVM with respect to different impurity or ligand isotopes from the corresponding eigenvector of the dynamical matrix. In general three different isotope effects are possible in hexagonal crystals.

case a: The isotope shift depends on a different impurity mass.

case b: The ligand in the direction of the *c*-axis is replaced by a different isotope.

case c: One of the three other ligands is replaced by a different isotope. This causes a split of the otherwise twofold degenerated LVMs of *E*-symmetry.

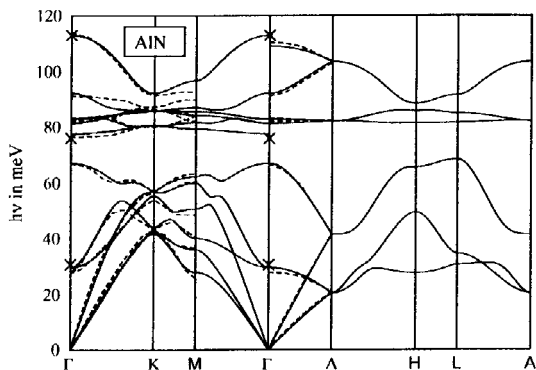


Figure 2: Calculated phonon-dispersion curves of AlN. The ab-initio calculated phonon-dispersion curves of Karch et al. are drawn with dashed lines. Some experimental values are shown with crosses [11].

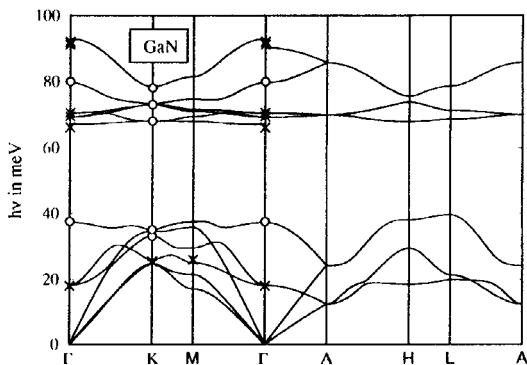


Figure 3: Calculated phonon-dispersion curves of GaN. The experimental energy values [8] are drawn with crosses and the additional used points due to the comparison with AlN are drawn with circles.

Results

The valence-force parameters of Keating and Kane for the perfect hexagonal AlN crystal were obtained from fitting to theoretical phonon-dispersion curves of Karch et al. [9]. Figure 2 shows the phonon-dispersion curves of AlN. Near the Γ -Point the fit is very good, but in the region of the boundary of the Brillouin zone the fit shows deviations up to 5 meV at the optical branches. This is in the energy region between 80 meV and 95 meV. The acoustic phonon branches are well adapted.

The valence-force parameters for the perfect hexagonal GaN crystal were calculated from fitting to experimental data [8]. Because of the nonexistence of neutron scattering data there are only a few values from Raman measurements [8] available, which are insufficient to obtain a unique determination of the parameters. To resolve this problem we suppose on the one hand a similarity between the Phonon-dispersion curves of GaN and AlN and on the other hand we assume that they are well adapted if the calculation of the local vibrational modes coincides with the experiments. The phonon-dispersion curves of GaN are shown in Fig. 3.

Figure 4 and Figure 5 show the dependence of the energy of the LVMS on the scaling factor for the Fe^{3+} defect in AlN and GaN. We selected the LVMS by the condition that the sum of the squared components of the eigenvector corresponding to the atoms in the first three shells around the defect is larger than 0.2. An agreement with the experimental values is achieved for a scaling factor of $s = 0.23$. This means the force constants in the vicinity of the defect are 23 % stronger than the force constants of the perfect crystal.

Ti behaves different in comparison to the Fe defect. There is an experimentally determined LVM with an energy close to the bottom of the optical phonon band. That gives reason to the assumption that the appropriate scaling factor is negative. We selected the LVMS by the condition that the sum of the squared components of the eigenvector corresponding to the atoms in the first five shells around the defect is larger than 0.3.

We obtained a sufficient agreement with the experimental values for an expected negative scaling factor of $s = -0.1$. The negative scaling factor indicates a softening of the forces at Ti in GaN. The vibration amplitudes of LVMS of the Fe-defect in AlN are shown in Fig. 6 and of the Fe-defect in GaN in Fig. 7.

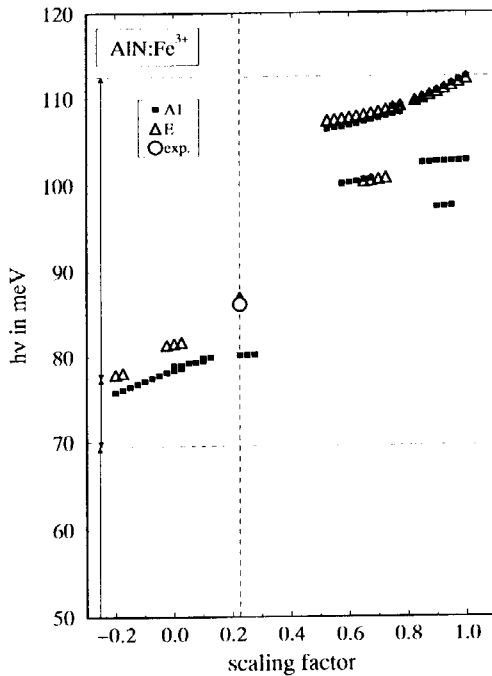


Figure 4: LVMs of AlN:Fe^{3+} in dependence on the scaling factor

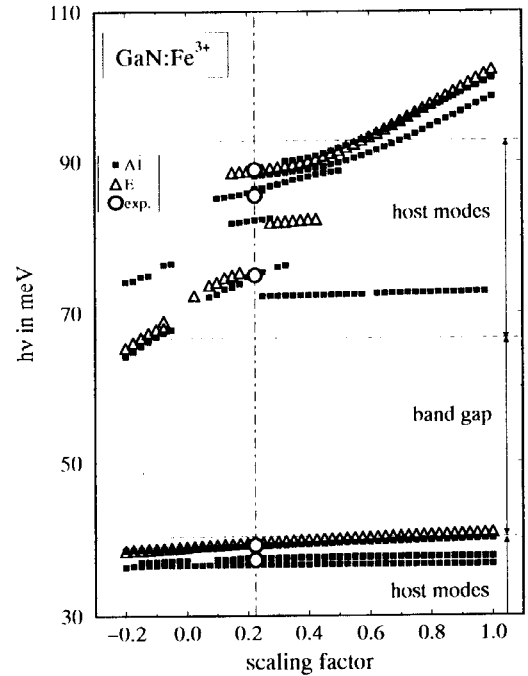


Figure 5: LVMs of GaN:Fe^{3+} in dependence on the scaling factor

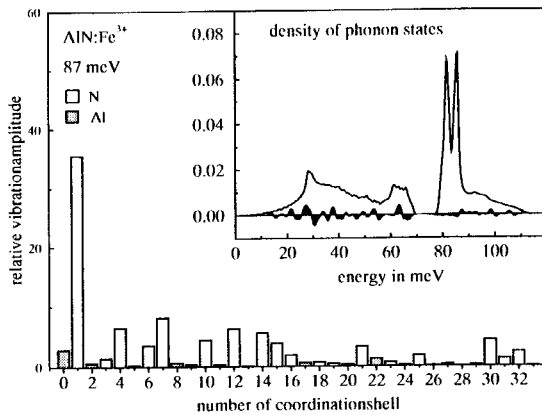


Figure 6: Vibration amplitudes of the LVM with E -symmetry at 87.0 meV of hexagonal AlN and density of phonon states.

The bars indicate the sum of the squares of the vibration amplitudes of all the atoms in the various coordination shells, having the same distance to the central defect. The coordination shells are numbered zero for the TM to 33. The insets show the density of phonon states of the perfect crystals. The difference between the density of phonon states of the unperturbed and of the perturbed crystal multiplied by two is shown black filled. There are two effects responsible for the occurrence of LVMs. A larger mass of the impurity leads to a shift of to lower energies and the modified binding properties of the defect give an additional shift of the energy. LVMs are expected to occur mainly in the energy region, where the density of phonon states of the perfect crystal is low. Due to hybridization, the localization of the LVMs decreases with the scaling factor if its energy is shifted from regions of low density of phonon states into regions of high density of phonon states.

The vibration amplitudes of the LVM at 87 meV of AlN:Fe^{3+} are shown in Fig. 6. The hybridization effects lead to a delocalisation of this mode. In contrast to this the Fig. 7 shows a

strong localized LVM of GaN:Fe³⁺ with an energy of 39.5 meV. Very large vibration amplitudes are found within the first three shells around the defect.

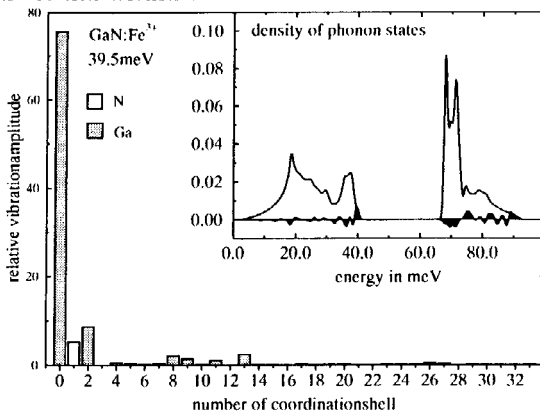


Figure 7: Vibration amplitudes of the LVM with E -symmetry at 39.5 meV of hexagonal GaN and density of phonon states.

| Local Vibrational Modes | | | | Isotope Shifts | | | |
|--|---------------|------------------------|-------|---|---|---|------------|
| | exp. [meV] | $\hbar\omega$ [meV] | | case a [$\frac{\mu\text{eV}}{\text{nucleon}}$] | case b [$\frac{\mu\text{eV}}{\text{nucleon}}$] | case c [$\frac{\mu\text{eV}}{\text{nucleon}}$] | |
| AlN:Fe³⁺ $s = 0.225$ | | 80.2 | A_1 | -7 | -103 | -148 | |
| | | 86.1 | E | -13 | -8 | -18 -370 | |
| GaN:Fe³⁺ $s = 0.225$ $(s = 0.175)$ | | 36.7 | A_1 | -4 | 0 | -1 | |
| | | 37.3 | A_1 | -19 | -1 | -1 | |
| | | 39.2 | A_1 | -49 | -6 | -2 | |
| | | 39.5 | E | -85 | -2 | -12 -2 | |
| | | 75.0 | A_1 | -25 | -692 | -55 | |
| | | | 75.3* | E | | | |
| | | | 82.2 | A_1 | 0 | -105 | -203 |
| | | 85.5 | 86.0 | A_1 | 0 | -406 | -194 |
| | | | 86.4 | A_1 | -1 | -13 | -213 |
| | | | 88.1 | A_1 | -16 | -173 | -122 |
| | 88.9 | 88.8 | E | -21 | -111 | -99 -267 | |
| GaN:Ti²⁺ $s = -0.1$ | | 36.6 | A_1 | -7 | 0 | -1 | |
| | | 38.9 | A_1 | -46 | -1 | -1 | |
| | | 39.3 | E | -99 | -2 | -3 -2 | |
| | | 67.0 | A_1 | -41 | -1218 | -131 | |
| | | 67.8 | 67.9 | E | -11 | -5 | -14 -531 |
| | | 82.2 | 84.5 | A_1 | 0 | -42 | -46 |
| | | 88.2 | E | -10 | -131 | -134 -64 | |

Table 1: Summary of the calculated LVMS in comparison to the experimental values. The isotope shifts due to the three possible isotope effects are also summarized.

In both semiconductors the Fe defect has a LVM in the optical phonon band. The LVM of AlN:Fe³⁺ has E -symmetry, whereas the LVM of GaN:Fe³⁺ has A_1 -symmetry. Because of the similarity of the phonon-dispersion curves we expect in both materials a LVM of the same symmetry. If we regard the LVMS of GaN:Fe³⁺ at a scaling factor of $s=0.175$ we find a LVM of E -symmetry with an energy of 75.3 meV. Considering the uncertainties of the fit of the phonon-dispersion curves of GaN, our calculations are consistent with both E and A_1 modes

AlN and GaN exist also in the cubic modification. We suppose that there is a LVM at about 75 meV with T_2 symmetry in cubic GaN. This gives reason to the assumption that there also exists an A_1 mode at about 87 meV in hexagonal AlN and a LVM of T_2 symmetry in cubic AlN. We did not find the expected LVM of A_1 symmetry. A possible reason is an improper fit of the phonon-dispersion curves of AlN in the energy region between 80 meV and 90 meV. The highest optical phonon branch is about 5 meV too high, which leads to a large density of phonon states in the energy region of 87 meV. We therefore assume that the hybridization of the A_1 mode with host modes is very strong.

Our calculations of the impurity and ligand induced isotope shifts of the LVMs are based on Eq. 1. The results are listed in Table I. There were no isotope shifts observed and the calculated isotope shifts were found to be smaller than 1.2 meV. Because of the dependence of the isotope shift on the vibration amplitude, the isotope shift is strongly affected by hybridization.

Conclusion

We present a detailed experimental and theoretical study of the local vibrational properties of the Fe^{3+} transition metal impurity in wurtzite type GaN and AlN and of the Ti^{2+} defect in hexagonal GaN. In spite of the uncertainties of the phonon-dispersion curves of the perfect crystals, our calculated energies of the LVMs are in good agreement with the results obtained by our photoluminescence and photoluminescence excitation measurements. The Fe^{3+} defect has in both semiconductors, GaN and AlN, a LVM in the optical phonon band which is strongly hybridized with host modes. The calculated isotope-shifts due to the impurity were found to be smaller than 1.2 meV per nucleon and therefore could not be observed because of the experimental linewidth of 1.5 meV.

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