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Phonon transport unveils the prevalent point defects in GaN

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Determining the types and concentrations of vacancies present in intentionally doped GaN is a notoriously difficult and long-debated problem. Here we use an unconventional approach, based on thermal transport modeling, to determine the prevalence of vacancies in previous measurements. This allows us to provide conclusive evidence of the recent hypothesis that gallium vacancies in ammonothermally grown samples can be complexed with hydrogen. Our calculations for O-doped and Mg-O co-doped samples yield a consistent picture interlinking dopant and vacancy concentration, carrier density, and thermal conductivity, in excellent agreement with experimental measurements. These results also highlight the predictive power of *ab-initio* phonon transport modeling, and its value for understanding and quantifying defects in semiconductors.

GaN has revolutionized the fields of solid-state lighting and power electronics^{1–5}. In these applications the material’s performance is critically dependent on its defects. However, understanding GaN’s defects has turned out to be a very challenging problem^{6–8}. In the endeavor to clarify it, theory has greatly helped to resolve long-lasting controversies and reconcile seemingly conflicting results^{9–14}. Examples are the intrinsic *n*-type character of carriers, originally attributed to nitrogen vacancies but later shown to be the result of residual hydrogen and oxygen impurities^{7,15–17}, or the explanation of the photoluminescent signatures of Mg-doped samples^{10,18}. A presently open debate concerns the interdependence between external doping, vacancies, and carrier concentration. Based on positron annihilation experiments a relation has recently been suggested between the concentration of oxygen doping, Ga vacancies, and hydrogen associated to them¹⁹. We provide independent evidence supporting this hypothesis from an unusual source, namely thermal transport.

The thermal conductivity (κ) is a rich and largely unexplored source of information on defects in materials. Each defect type has a signature on thermal transport. Therefore by combining measurements and novel *ab-initio* thermal conductivity techniques, it may be possible to decipher the type and concentration of native defect types present in the material^{20–22}, even without the use of more involved defect characterization techniques such as secondary ion mass spectrometry, positron annihilation or carrier lifetime spectroscopy^{23–26}. Thus a fundamental question is whether one can elucidate the types and concentrations of vacancies in GaN by using the calculated thermal transport signatures of the different defects. We provide the answer here. In what follows, we present *ab-initio* calculations of GaN’s thermal conductivity under Mg and O doping in the presence of different vacancies, and compare them with measurements on ammonothermally grown samples from ref. 27. The resulting picture coherently relates thermal conductivities, extrinsic and intrinsic defect concentrations, and carrier densities, yielding excellent agreement between theory and experiment.

In the decade elapsed since its initial demonstration²⁸, the ability to predict the thermal conductivity of single crystals in a parameter-free fashion has rapidly evolved to become a recognized computational tool, implemented in several software packages^{29–33}. In contrast, predicting the thermal conductivity of materials with vacancies is not mainstream, and it has been achieved only recently^{20–22}. The theory and implementation of *ab-initio* scattering by defects is considerably more involved than the often used formulas for mass-defect scattering^{34,35}. It requires the symmetrization of the *ab-initio* force constants around the vacancy, and a t-matrix formulation of the scattering by isolated defects^{20,22,36}, as implemented in our program almaBTE²⁹. The lattice thermal conductivity (κ) is given by^{29,30},

$$\kappa_{\mu\nu} = \frac{1}{k_B T^2 \Omega} \sum_j \int d\mathbf{q} \, n_{0j\mathbf{q}} (n_{0j\mathbf{q}} + 1) (\hbar \omega_{j\mathbf{q}})^2 v_{j\mathbf{q}}^\mu v_{j\mathbf{q}}^\nu \tau_{j\mathbf{q}} \quad (1)$$

where μ and ν specify Cartesian components of the κ tensor, T is the temperature and Ω is the unit cell volume. The phonon mode $j\mathbf{q}$ (j branch and $\mathbf{q}$ wave vector) dependent quantities ω , v , n_0 and τ correspond to the phonon frequencies, group velocities, equilibrium occupancy and relaxation time, respectively. The total mode-specific scattering rate $\tau_{j\mathbf{q}}^{-1}$ is determined as the sum of different scattering contributions: phonon-phonon (anharmonic) scattering τ_{anh}^{-1} , phonon-isotope scattering τ_{iso}^{-1} , phonon-defect scattering τ_{def}^{-1} , and so on^{20,21}. τ_{anh}^{-1} is computed using the *ab-initio*-calculated second- and third-order interatomic force constants (IFCs) for GaN^{30,37}. τ_{iso}^{-1} is calculated using phonon spectrum and isotope concentrations following Refs. 34 and 35. τ_{def}^{-1} is calculated as,^{20–22,38}

$$\tau_{j\mathbf{q},\text{def}}^{-1} = -\chi_{\text{def}} \frac{\Omega}{V_{\text{def}}} \frac{1}{\omega_{j\mathbf{q}}} \Im \{ \langle j\mathbf{q} | \mathbf{t} | j\mathbf{q} \rangle \}. \quad (2)$$

where χ_{def} represents the number fraction of defects, V_{def} the volume of a defect and Ω the volume for normalizing

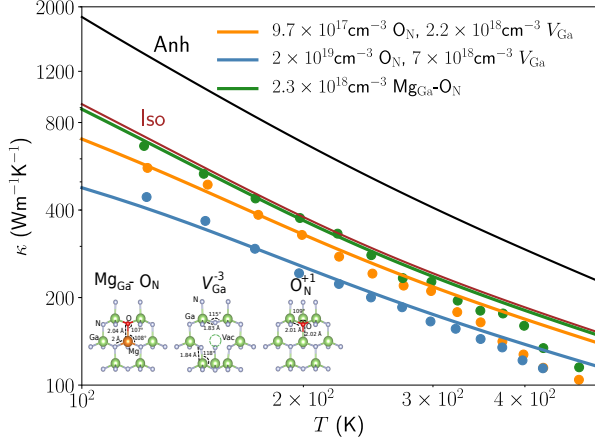


FIG. 1: Lattice thermal conductivity of GaN with O_N , $Mg_{Ga}-O_N$ defects. O-doped samples also contain gallium vacancies (V_{Ga}), which are included in our calculations. The vacancy concentrations of the respective samples are obtained from the positron annihilation experiments in ref. 19. The calculated thermal conductivity results with different concentrations of defects are in good agreement with corresponding measurements from ref. 27. The inset shows the local structure of GaN with $Mg_{Ga}-O_N$, O_N and V_{Ga} defects. Defective GaN structures are also included in the SI³⁹.

$|j\mathbf{q}\rangle$. The $\mathbf{t}$ matrix in Eq. (2) is defined as,

$$\mathbf{t} = (\mathbf{I} - \mathbf{V}\mathbf{g}^+)^{-1} \mathbf{V} \quad (3)$$

where $\mathbf{V}$ is the *ab-initio* calculated defect perturbation matrix, $\mathbf{g}^+$ the casual Green's function for the pristine structure, and $\mathbf{I}$ the identity matrix. The different contributions to phonon scattering rates and the thermal conductivity for GaN are calculated with almaBTE package²⁹, where an in-built iterative scheme is used to solve the BTE. More details about the methodology and *ab-initio* calculations are presented in the Supporting Information (SI)³⁹.

First of all, we have verified that our calculations for the isotopically pure and natural single crystals (black and brown solid curves in Fig. 1) agree with previous calculations⁴¹ (the plot displays the isotropic component of the conductivity as $\kappa = \frac{1}{3} \text{Tr}(\boldsymbol{\kappa})$). Such a high thermal conductivity denotes a very weak anharmonic phonon scattering in GaN. This stems from its large acoustic-optic phonon gap due to the large atomic mass difference between Ga and N ($\frac{m_{Ga}}{m_N} \sim 5$)^{41,42}. The acoustic-optic gap in GaN is plotted in Fig. 2, which shows good quantitative agreement with the inelastic X-ray scattering experiments⁴⁰.

We now proceed to determine the thermal transport signature of the different defect types, focusing on the three systems whose thermal conductivities have been measured by ref. 27: one semi-insulating Mg-O co-doped

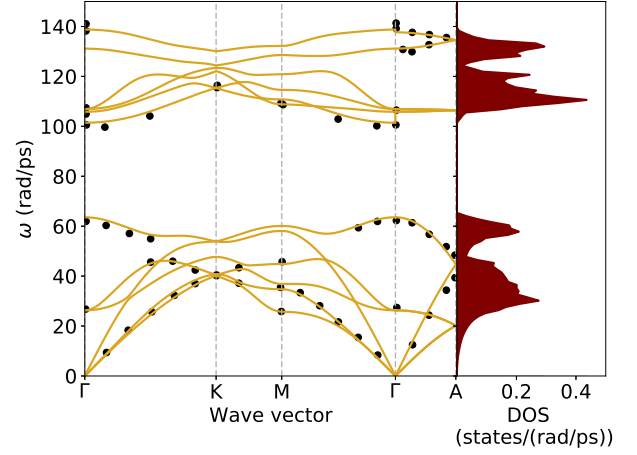


FIG. 2: Phonon dispersion and density of states for wurtzite GaN. The calculated results are in excellent agreement with the inelastic X-ray scattering results from ref. 40.

and two *n*-type O-doped samples. To best compare the relative effect of each defect type, we plot their scattering rates (τ_{def}^{-1}) at a hypothetical concentration (c) of 10^{20} cm^{-3} . We consider the effect of single substitutionals and vacancies, and also that of coupled dopant-vacancy and dopant-dopant complexes, including the charged states reported as most stable by refs. 6 and 7.

The case of single defects is shown in Fig. 3. The scattering rates for gallium and nitrogen vacancies are remarkably stronger than those for the substitutional impurities. Regarding the latter, Mg_{Ga} scatters phonons more strongly than either O_N or isotope impurities, both of which have similarly weak rates. An important consequence of this is that any noticeable decrease in the thermal conductivity of GaN upon oxygen doping is most likely not due to direct phonon scattering by the O atoms, but rather by an associated change in the compensating vacancy concentration. Furthermore, this explains why the thermal conductivity is higher for the magnesium-oxygen co-doped sample in Fig. 1 than for the oxygen-only doped cases, even when the oxygen concentrations in the latter are lower. In the case of coupled defects, the scattering rate comparison reveals another important fact: phonon scattering due to the coupled defect is very similar to the added separate contributions of the two single defects. This is shown in the SI for vacancy-oxygen and magnesium-oxygen complexes along with their corresponding local defective structures³⁹.

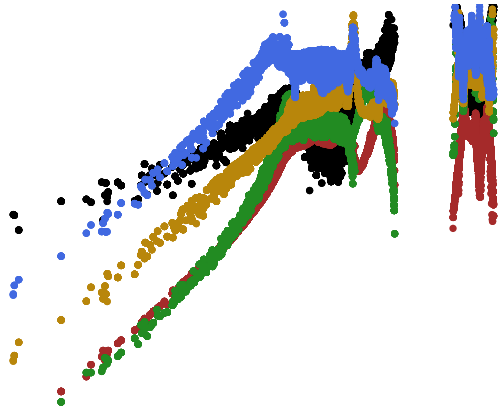
The above comparison of scattering rates indeed ascertains that it is not the oxygen, but the associated magnesium or vacancy defect that will have a significant impact on the thermal conductivity. However, the concentration of these associated defects, especially in the case of vacancies, is not trivial to find. For the case of magnesium-oxygen defects, only $Mg_{Ga}-O_N$ pair complexes form⁴³. Simon *et al.*²⁷ measured equal concentrations of mag-

nesium and oxygen in their co-doped sample. Using the given concentrations for the magnesium-oxygen co-doped sample in ref. 27, we get a very good agreement between our calculated thermal conductivity and experiment up to room temperature, as seen in Fig. 1.⁴⁴ In turn, for the case of vacancy-oxygen defects there are different opinions on whether $V_{\text{Ga}}\text{-O}_{\text{N}}$ pairs or $V_{\text{Ga}}\text{-(O}_{\text{N}})_3$ clusters are more favorable^{27,45}. A few studies suggest that hydrogen is also present in such samples and tends to form complexes with the vacancies and oxygen defects^{46,47}. Recent *ab-initio* studies support this finding based on calculated lower defect formation energies for $V_{\text{Ga}}\text{-H}$ and several $V_{\text{Ga}}\text{-H-O}_{\text{N}}$ complexes than for single isolated defects^{6,47}. The theoretically predicted defect levels are confirmed experimentally^{48,49}. However, they do not provide any evidence of actual concentrations of the prevalent hydrogen defects and vacancies.

Analysis of the growth process of these samples provides relevant information about the existing defects. Samples in ref. 27 are grown by the ammonothermal technique⁵⁰. This growth process, performed at low temperatures and pressures, is known to produce samples with very low dislocation density^{19,50,51}. However, higher content of point defects, mainly vacancies, is found^{19,52}. Tuomisto *et al.*¹⁹ report very high concentrations of vacancies and hydrogens in their different O-doped GaN samples and, based on their positron annihilation measurements, reveal the formation of vacancy-hydrogen complexes too¹⁹. Furthermore, another very interesting fact seen in their samples is that the concentrations of hydrogen, which also acts as a donor, are generally higher than those of oxygen, yet the free carrier concentration is low. This implies a high compensating vacancy content in the ammonothermally grown samples.

As the hydrogen concentrations are not specified for the ammonothermally grown samples in ref. 27, we extract this information from ref. 19. Sample-1 and sample-3 grown by Tuomisto *et al.*¹⁹ correspond to the oxygen-doped cases in ref. 27. Thus, we use the hydrogen concentrations from the above mentioned two samples in ref. 19 and determine the vacancy concentrations by balancing the free charge carriers (n_e) as $c_{V_{\text{Ga}}} = \frac{1}{3}(c_{\text{O}_{\text{N}}} + c_{\text{H}} - n_e)$, to calculate the thermal conductivity. We do not include the scattering contributions from hydrogen as they can be shown to be negligible (see SI³⁹). Hydrogen atoms bond with the nitrogen atoms surrounding the gallium vacancy,⁶ and their negligible contribution to phonon scattering can be rationalized as if N^{15} isotopes were present. The calculated thermal conductivity using these concentrations show remarkable agreement with the experiments for both O-doped samples, as shown in Fig. 1 and Table. I. Thus, our calculation consistently relates the results of the two separate experiments in refs. 19 and 27, and lends strong support to the hydrogen hypothesis put forth in ref. 19.

One can check that, if residual hydrogen is not considered, the measured thermal conductivity cannot be explained based on the presence of oxygen substitutionals



```
ERROR:
invalidrestore
OFFENDING COMMAND:
restore
STACK:
--nostringval--
--nostringval--
```