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ABSTRACT

Using infrared absorption spectroscopy of hydrogen passivated β -Ga₂O₃ the temperature dependence of the dominant O – H vibrational line was measured between 5 and 300 K. With increasing temperature, the vibrational line shifts by $\Delta\omega = 7.8 \text{ cm}^{-1}$ to lower frequency. This is accompanied by a broadening of the vibrational line from $\Gamma = 0.61$ to 8.18 cm^{-1} . The data are discussed in terms of elastic and inelastic phonon scattering and exchange coupling. Moreover, the perturbation of the hydrogen potential is evaluated.

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Wide band-gap semiconductors such as β -Ga₂O₃ have been attracting attention for high power devices, deep UV, and solar-blind photodetectors and transparent conducting oxides (TCO), recently.^{1–3} This is mainly attributed to its large band-gap of about 4.5 – 4.9 eV^{3,4} that favors break-down fields as high as 5 to 9 MV/cm.⁵ This value is susceptible to be further increased since it depends sensitively on the intrinsic defect concentrations and controlled doping of the host lattice. In the past, it has been shown that hydrogen can affect both, doping and defect levels, in almost all semiconductors.^{6–9} Previously, it was observed that undoped β -Ga₂O₃ exhibits n-type conductivity with free carrier concentrations around 10^{18} cm^{-3} , which originally was attributed to oxygen vacancies.¹⁰ However, based on ab-initio calculations it has been suggested that the source of this unintentional doping effect are hydrogen atoms.¹¹

Recently, the main hydrogen related center in β -Ga₂O₃ has been identified as an O – H complex with a dominant vibrational line at a wave number of 3437 cm^{-1} .¹² Based on polarization experiments combined with theory it was suggested that the microscopic structure of the H complex is a relaxed Ga vacancy with two hydrogen atoms, V_{Ga} – 2H, along the [102] crystallographic direction.¹² Although additional H-related vibrational modes have been observed recently, they are less stable and disappear after annealing at modest temperatures.^{13–15}

In this paper we present a detailed investigation on the thermal properties of the O – H complex in β -Ga₂O₃. The hydrogen local vibrational mode (LVM) was measured as a function of temperature. A detailed analysis of the experimental results suggests that the observed temperature dependence of the vibrational-mode data can be described with a simple model where the O – H LVM couples to one low-frequency mode.

The samples used for this paper were single crystal β -Ga₂O₃. The crystals were grown by the floating zone technique using 6N purity gallium oxide powders in order to suppress the influence of Si impurities. Hydrogen was incorporated by an ampoule passivation step. For this procedure small pieces with a size of up to $1 \times 1 \text{ cm}^2$ were sealed into quartz ampoules with 800 mbar of hydrogen gas. Then, the sealed ampoules were annealed at a temperature of 900 °C for 2 hours and subsequently quenched to room temperature by immersion in water. Information on hydrogen bonding was obtained by measuring infrared absorption using a Fourier transform infrared (FT-IR) spectrometer with a spectral resolution of 0.2 cm^{-1} . FT-IR measurements were performed as a function of temperature between $T = 5$ and 300 K using a continuous flow cryostat.

The temperature dependence of the O – H vibrational mode was measured between 5 and 300 K. Fig. 1 depicts the FT-IR spectra at three different temperatures, showing the dominant O – H

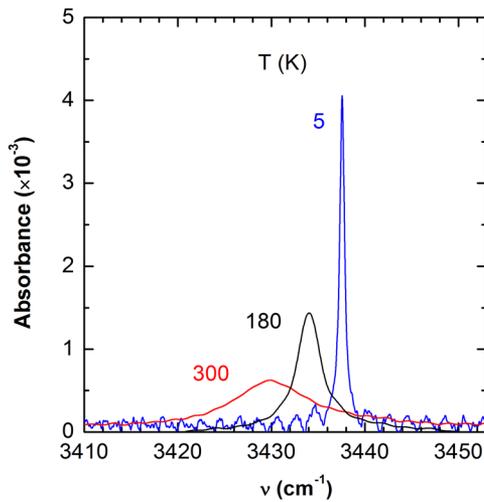


FIG. 1. Infrared absorption spectra of the O – H mode in $\beta\text{-Ga}_2\text{O}_3$ at $T = 300$ K (red curve), 180 K (black curve), and 5 K (blue curve). The spectra were measured with a spectral resolution of 0.2 cm^{-1} .

local vibrational mode in $\beta\text{-Ga}_2\text{O}_3$ that has been ascribed to a relaxed $V_{\text{Ga}}\text{-2H}$ center.¹² At room temperature the maximum of the O – H LVM is located at a wave number of $\nu = 3429.8\text{ cm}^{-1}$. As the specimen is cooled down the vibrational mode shifts towards higher wave numbers, to $\nu = 3434.0\text{ cm}^{-1}$ at $T = 180$ K, and finally, to $\nu = 3437.6\text{ cm}^{-1}$ at $T = 5$ K. The position of low-temperature IR absorption line is in agreement with previous reports.^{12,13}

The frequencies and line widths of the spectra were obtained by fitting the data to Lorentzian functions. The temperature dependence of the wave number and the line width, Γ , of the O – H vibrational mode are shown in Fig. 2(a) and (b), respectively. With increasing temperature, the position of the O – H vibrational mode exhibits a shift of $\Delta\omega = 7.8\text{ cm}^{-1}$ to smaller wave numbers [Fig. 2(a)]. This is accompanied by a broadening of the line width from $\Gamma = 0.61\text{ cm}^{-1}$ at 5 K to $\Gamma = 8.18\text{ cm}^{-1}$ at 300 K [Fig. 2(b)]. In the past, such a behavior has been observed for a number of hydrogen complexes in different semiconductors such as Ga – H and Al – H in Si,¹⁶ Be – H and Zn – H in GaP,¹⁷ and Se – H and Te – H in GaAs.¹⁸

To first order, a change of the sample temperature will influence the local vibrational modes due to thermal expansion or compression of the host lattice and due to coupling of the LVM to lattice phonons. The first contribution is small and has been estimated from uniaxial stress measurements to result in line shifts of less than 0.1 cm^{-1} .^{17,18} The second process could involve a phonon emission process where the local mode couples inelastically to lattice phonons. For this process to be efficient the frequency of the LVM should not exceed the phonon frequency by more than a factor of two or three. In case of $\beta\text{-Ga}_2\text{O}_3$ the highest phonon frequency amounts to about 768 cm^{-1} .¹⁹ Hence, for de-excitation of the O – H vibrational mode would require more than 4 lattice phonons to conserve energy. This process has a very low probability and therefore can be neglected. On the other hand, elastic phonon scattering can reduce the lifetime of the vibrational mode that results in a temperature dependent line width and a decrease of the frequency with increasing temperature.

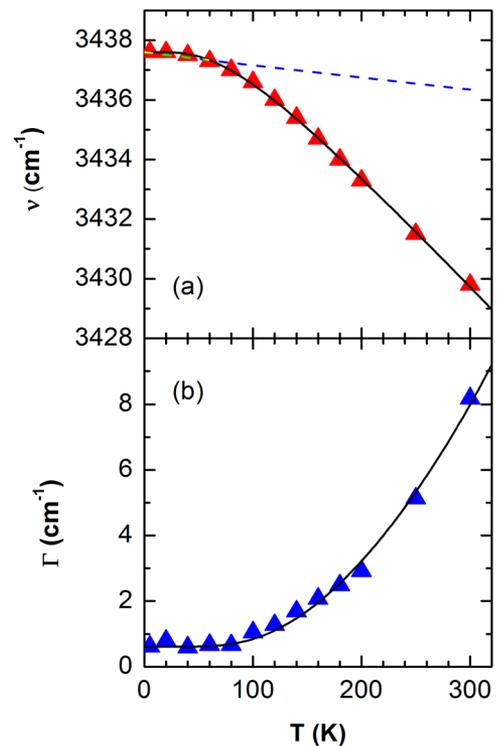


FIG. 2. Wave number of the O – H vibrational mode (a) and line width, Γ , (b) as a function of temperature. The triangles were obtained from least-squares fits of the data to Lorentzian functions. The solid lines are fits to Eqs. (1) and (2) and the dashed line represents a fit to Eq. (7). Details are described in the text.

Mathematically, the interaction is described by a sum over all lattice phonons that are coupling to the local vibrational mode. Using the Debye approximation, McCumber and Sturge²⁰ described the temperature dependence of the peak position of the vibrational mode by

$$\Delta\omega = A \left(\frac{T}{\Theta_C} \right)^4 \int_0^{\Theta_C/T} \frac{y^3}{e^y - 1} dy, \quad (1)$$

and the temperature dependence of the line width by

$$\Delta\Gamma = B \left(\frac{T}{\Theta_C} \right)^7 \int_0^{\Theta_C/T} \frac{y^6 e^y}{(e^y - 1)^2} dy. \quad (2)$$

Here A and B are empirical constants and $k\Theta_C$ is an effective Debye energy. Eqs. (1) and (2) were used to fit the temperature dependence of ω and Γ . The fits are in excellent agreement with the data (solid lines in Fig. 2) and the fitting parameters are summarized in Table I.

Based on first-principles calculations the Debye temperature was predicted to $\Theta = 872\text{ K}$.²¹ From an experimental point of view a lower value of $\Theta = 738\text{ K}$ was derived from heat capacity measurements in the temperature range from 123 to 748 K.²² However, both values are considerably larger than the fitting value of $\Theta_C = 305.5\text{ K}$ obtained from the temperature dependence of the O – H vibrational frequency. On the other hand, the Debye temperature derived from

TABLE I. Fitting parameters A , B , and Θ_C . The values were obtained from least-squares fits of the temperature dependent shift of the vibrational line and broadening of the O – H vibrational mode to Eqs. (1) and (2).

LVM	$\Delta\omega$		$\Delta\Gamma$	
	A (cm ⁻¹)	Θ_C (K)	B (cm ⁻¹)	Θ_C (K)
O – H	36.0	305.5	152.2	552.5

the line broadening of the O – H vibration mode is much closer to Θ obtained from heat capacity measurements. Because of the large discrepancy of the Debye temperature it is unlikely that elastic phonon scattering is causing the temperature dependence of the O – H LVM.

On the other hand, it is conceivable that the O – H LVM interacts with one low-frequency mode, ω_0 , primarily. Such an anharmonic coupling was investigated by Persson and Ryberg for chemisorbed CO molecules on a Ni (111) surface.²³ Due to damping, the low-frequency mode has the width η and couples with the magnitude $\delta\omega$ to the high-frequency mode, which in our case is the O – H stretching vibration. The low-frequency mode can be a vibrational mode of the host lattice or another mode of the O – H LVM.²³ Analytical expressions can be derived for two cases: (i) weak coupling between the high- and low-frequency mode ($\delta\omega \ll \eta$), and (ii) for the low temperature limit where $kT < \hbar\omega_0$. In case of (i) the change of the frequency and line width with temperature are given by²³

$$\Delta\omega = \frac{\delta\omega}{e^{\hbar\omega_0/kT} - 1}, \quad (3)$$

and

$$\Delta\Gamma = \frac{e^{\hbar\omega_0/kT}}{(e^{\hbar\omega_0/kT} - 1)^2} \frac{2\delta\omega^2}{\eta}, \quad (4)$$

where k is the Boltzmann constant and T is the temperature. Using these equations to fit the temperature dependence of the O – H frequency and line width yields $\delta\omega/\eta = 1.13$. This value indicates that the constraint for weak coupling is not fulfilled. On the other hand, for the low-temperature approximation the temperature dependence of $\Delta\omega$ and $\Delta\Gamma$ are given by²³

$$\Delta\omega = e^{-\hbar\omega_0/kT} \delta\omega \frac{\eta^2}{\delta\omega^2 + \eta^2}, \quad (5)$$

and

$$\Delta\Gamma = e^{-\hbar\omega_0/kT} 2\eta \frac{\delta\omega^2}{\delta\omega^2 + \eta^2}. \quad (6)$$

This approximation is valid for $T \leq 200$ K. Hence, Eqs. (5) and (6) were used to fit the temperature dependence of the frequency and line width (solid lines in Fig. 3). The fits are in excellent agreement with the data for $T \leq 200$ K and the fitting parameters are summarized in Table II. It is important to note that the least-squares fits yield a low-frequency mode located at 1257 and 1591 cm⁻¹ for the temperature dependence of the O – H frequency and the line width, respectively. Both values are much higher than typical phonon frequencies of β -Ga₂O₃. However, Raman backscattering measurements reveal the presence of vibrational modes at $\nu = 1344$ and 1497 cm⁻¹ (see arrows in Fig. 4). It is likely that one of these

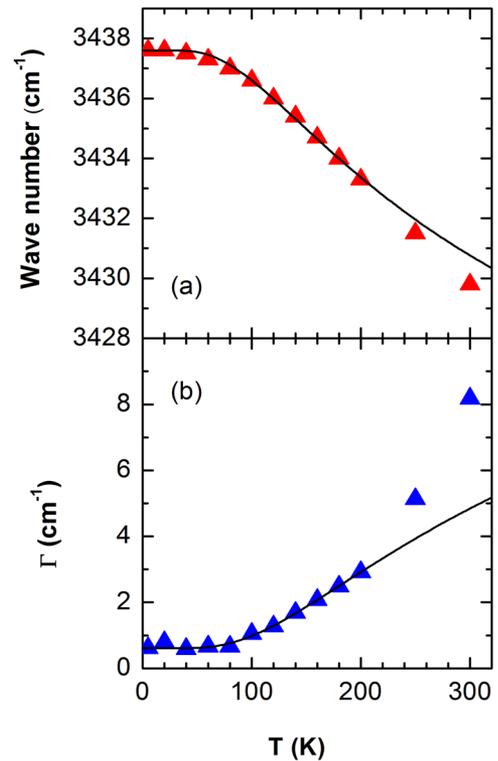


FIG. 3. Wave number of the O – H vibrational mode (a) and line width, Γ , (b) as a function of temperature. The solid lines are fits to Eqs. (5) and (6) that represent the low-temperature case from the exchange coupling model by Persson and Ryberg.¹⁸ Details are described in the text.

modes preferentially couples to the LVM of O – H. Hence, this indicates that the observed temperature dependence is caused by exchange coupling.

Compared to an undisturbed O – H bond like in a water molecule, the nearest neighbor atoms of H in β -Ga₂O₃ cause a perturbation of the hydrogen potential. The influence of this perturbation on the temperature dependence of the local vibrational mode has been described quantitatively by Elliot et al.²⁴ for H and D in alkali halides. In this model, the shift of the LVM is proportional to the mean-vibrational energy, $U(T)$, of the crystal,¹⁷

$$\Delta\nu = C \frac{U(T)}{N_A}, \quad (7)$$

TABLE II. Fitting parameters $\delta\omega$, ω_0 , and η . The values were obtained from least-squares fits of the temperature dependent shift of the vibrational line and broadening of the O – H vibrational mode to Eqs. (5) and (6).

LVM	$\Delta\omega$		$\Delta\Gamma$	
	$\delta\omega/\eta$	ω_0 (cm ⁻¹)	$\delta\omega/\eta$	ω_0 (cm ⁻¹)
O – H	0.64	1257	2.78	1591

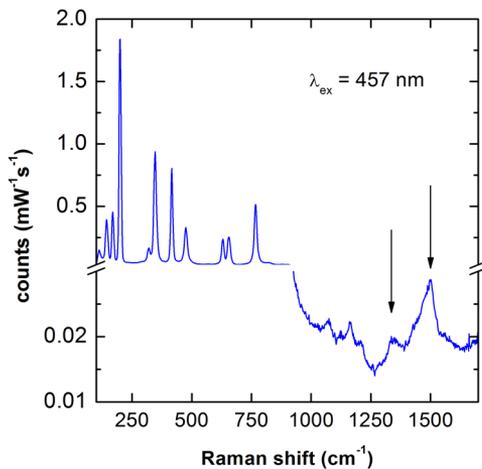


FIG. 4. Raman backscattering spectrum of β -Ga₂O₃ at $T = 300$ K. For the excitation an Ar⁺ ion laser emitting at a wave length of $\lambda = 457$ nm was used.

where N_A is the Avogadro constant and C represents the fraction of thermal energy that is transferred from the nearest neighbor atoms to the O – H vibrational mode.

In Fig. 5 the line shift of the O – H vibrational mode (triangles) is plotted as a function of the lattice thermal energy, $U(T)$, which was obtained by numerical integration of the specific heat, C_V , from Ref. 22. For $U < 250$ J/mol the experimental data can be described by a least-squares fit to Eq. (3) with $\beta = 0.012$ (solid line in Fig. 5). The small value for β indicates that the nearest neighbor atoms have only a small influence on the vibrational mode. For $U \geq 250$ J/mol the fit exhibits a pronounced deviation from the experimental data. The fit is also shown by the dashed line in Fig. 2(a). The deviation from the experimental data starts at about 100K. At $T = 300$ K the difference amounts to about 7.4 cm⁻¹, which translates into an energy

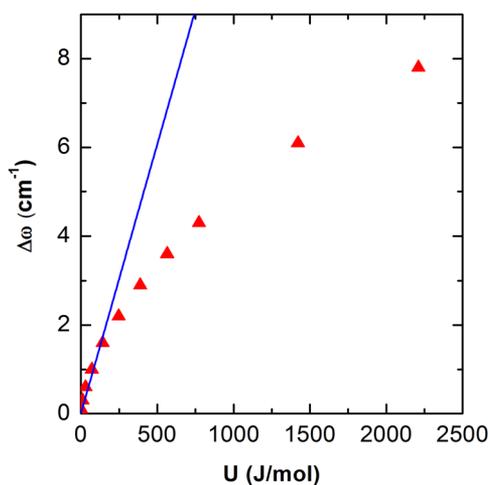


FIG. 5. Shift of the O – H vibrational mode as a function of the lattice thermal energy, $U(T)$. The solid line is a least-squares fit to Eq. (3) for $U < 250$ J/mol.

of ≈ 0.9 meV. Most likely, the reason for the deviation between fit and experimental data is caused by the anharmonicity of the hydrogen potential. Hence, the increase in temperature from 100 to 300 K results in a decrease of the vibrational transition energy by about 0.9 meV due to anharmonicity.

In summary, the temperature dependence of the dominant O – H vibrational mode in β -Ga₂O₃ was measured between 5 and 300 K. With increasing temperature, the vibrational mode shifts from $\omega = 3437.6$ cm⁻¹ to 3429.8 cm⁻¹, while the line width increases from $\Gamma = 0.61$ cm⁻¹ to 8.18 cm⁻¹. To account for the observed temperature dependence two models were employed. (i) elastic phonon scattering where all lattice phonons couple to the local vibrational mode. Employing this model yields an estimate of the Debye temperature of $\Theta_C = 305.5$ K and 552.5 K for $\Delta\omega$ and Γ , respectively. These values differ considerably from literature values. (ii) anharmonic coupling with primarily one low-frequency mode. For the low-temperature approximation of this model two low-frequency modes located at 1257 and 1591 cm⁻¹ were derived from fitting of the T dependence of the frequency and line width of the O – H LVM, respectively. Raman measurements revealed the presence of vibrational modes at 1344 and 1497 cm⁻¹. These results strongly support the idea that the temperature dependence of the O – H LVM is caused by anharmonic coupling with primarily one low-frequency mode. Moreover, the perturbation of the hydrogen potential by neighboring atoms was estimated by fitting the frequency to the mean-vibrational energy, $U(T)$. The large deviation for $T \geq 100$ K indicates that the anharmonicity of the H potential increases by about 0.9 meV.

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