Vibrational spectroscopy of group-II-acceptor–hydrogen complexes in GaP

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Using infrared absorption spectroscopy, we have observed the local vibrational modes (LVM's) of group-II-acceptor–hydrogen complexes in GaP. In addition to the previously observed zinc-hydrogen complexes, we report modes corresponding to beryllium-hydrogen and cadmium-hydrogen complexes. In GaP:Be, we attribute the modes at 2292.2 and 1669.8 cm^{-1} to phosphorus-hydrogen and phosphorus-deuterium bond-stretching modes of complexes adjacent to the beryllium acceptors. In GaP:Cd, we attribute the modes at 2434.0 and 1768.3 cm^{-1} to similar complexes adjacent to the cadmium acceptors. The temperature-dependent shifts of the hydrogen LVM's in GaP:Be and GaP:Zn are shown to be proportional to the lattice thermal energy $U(T)$, a consequence of the anharmonic coupling between the LVM's and the lattice phonons.

Local vibrational mode (LVM) spectroscopy is an important tool for determining the microscopic structure of defects in semiconductors.[1] It is particularly useful for studying hydrogen-related complexes,[2,3] since the vibrational frequencies are typically much higher than the lattice phonon frequencies and the substitution of deuterium for hydrogen results in a significant isotope shift. Following the discoveries that hydrogen plasma passivates donors[4] and acceptors[5] in GaAs, LVM spectroscopy has been used extensively to study hydrogen-related complexes in numerous compound semiconductors.

Although most studies have focused on GaAs and InP,[6] significant work has also been done on hydrogen LVM's in GaP. Clerjaud *et al.* observed the C-H and C-D bond-stretching LVM's (Ref. 7) and the N-H mode[8] in GaP grown by the liquid-encapsulation Czochralski (LEC) technique. LVM's corresponding to hydrogen-defect complexes in LEC-grown GaP have also been observed.[9] McCluskey *et al.*[10] reported LVM's corresponding to zinc-hydrogen complexes in GaP. In this paper, we report modes arising from beryllium- and cadmium-hydrogen complexes and compare them to similar complexes in GaAs and InP. In addition, we propose a simple model that accounts for the temperature dependence of the hydrogen LVM's.

The GaP samples used for this study had a (100) orientation and were n type, with a sulfur concentration of approximately 10^{17} cm^{-3}. GaP:Be samples were obtained by implanting the undoped samples with 40-keV beryllium ions at a dose of 5×10^{14} cm^{-2}, and 100- and 200-keV ions at doses of 1×10^{15} cm^{-2} each, for a total dose of 2.5×10^{15} cm^{-2}. To activate the beryllium acceptors, the implantation was followed by a rapid thermal anneal at 1000 °C for 10 s. To obtain GaP:Zn, the undoped samples were placed in a 100-ml evacuated quartz ampoule with 0.5 g metallic zinc and diffused in a vertical furnace for 10 min at a temperature of 860 °C. After completion of the diffusion, the samples were quenched to room temperature by dropping the ampoule into ethylene glycol. To obtain GaP:Cd, the undoped samples were placed with 200 mg cadmium and $\frac{1}{3}$ atm H_2 ambient in an ampoule and diffused for 22 h at a temperature of 950 °C, followed by a quench to room temperature. Room-temperature Hall-effect measurements with the Van der Pauw geometry indicated sheet carrier concentrations of $p(Be) = 1 \times 10^{15}$ cm^{-2}, $p(Zn) = 5 \times 10^{15}$ cm^{-2}, and $p(Cd) = 2 \times 10^{14} cm^{-2}$.

Some of the samples were then exposed to monatomic hydrogen or deuterium in a remote plasma system as described in Ref. 11. The hydrogenation temperature was 300 °C and the duration of the exposure was 1 h. GaP samples that were doped p type but not H or D plasma exposed were used as reference samples.

Infrared absorption spectra were obtained at liquid-helium temperature with a Digilab 80-E vacuum Fourier transform spectrometer with a KBr beam splitter and an instrumental resolution of 0.25 cm^{-1}. A Ge:Cu photoconductor was used as a detector. For temperatures above 10 K, spectra were obtained with a Bomem DA8 spectrometer with a KBr beam splitter and external mercury-cadmium-telluride detector. The instrumental resolution for the variable temperature measurements ranged from 0.5 to 1 cm^{-1}.

As reported in Ref. 7, hydrogenated and deuterated GaP:Zn samples have infrared absorption peaks at 2379.0 and 1729.4 cm^{-1}, respectively [Fig. 1(b)]. The isotopic ratio of these frequencies $r = \nu_H/\nu_D$, is 1.3756. By way of comparison, hydrogenated InP:Zn has a bond-stretching mode at 2287.7 cm^{-1} and isotopic ratio $r = 1.3744$.[12] The bond-stretching mode has been attributed to a P-H complex oriented along a [111] bond-centered direction, adjacent to the zinc acceptor, with the zinc relaxed into the plane of phosphorus atoms (Fig. 2). Since the LVM's
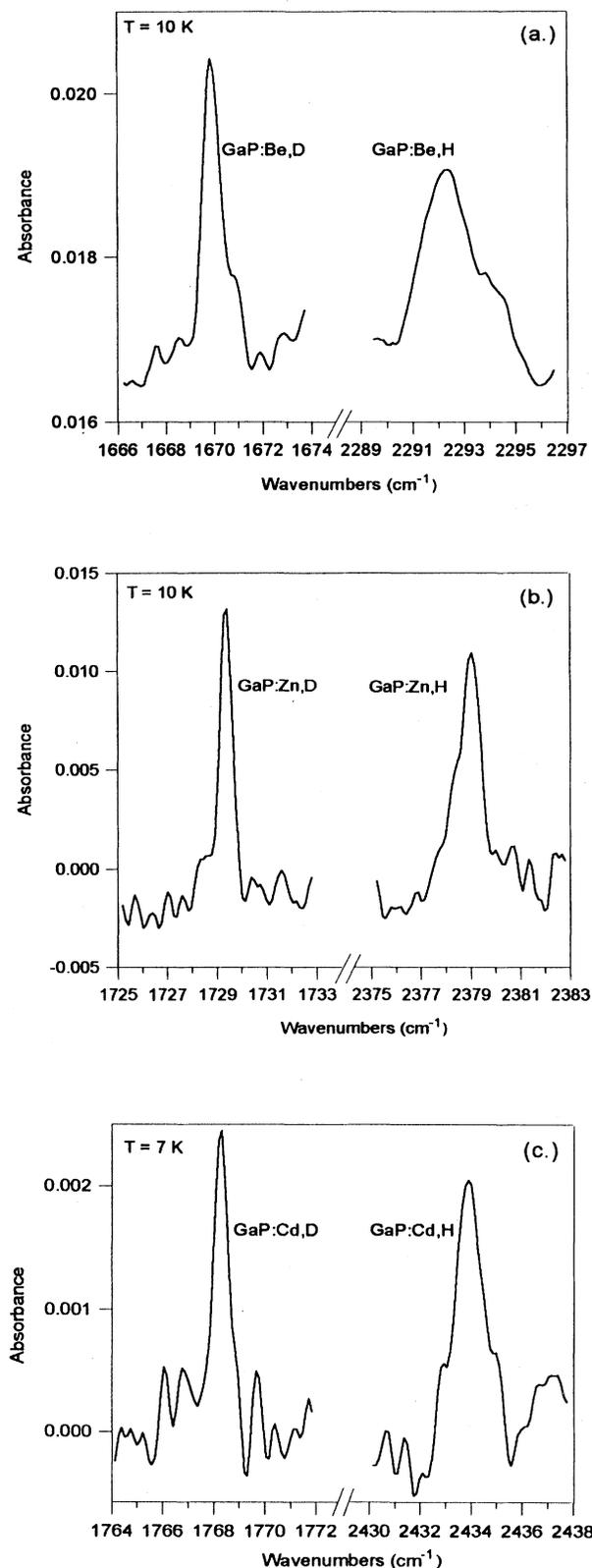
FIG. 1. Infrared absorption spectra of deuterated and hydrogenated (a) GaP:Be, (b) GaP:Zn, and (c) GaP:Cd. The vibrational modes are associated with P-H (P-D) complexes adjacent to the group-II acceptors.
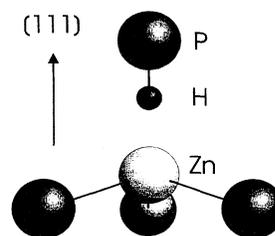

FIG. 2. Model for H passivation of the Zn acceptor with the H atom attached to a P atom in a bond-centered orientation. This model applies for all observed group-II-acceptor–hydrogen complexes in GaP and InP.

and the r factor for GaP:Zn are similar to the corresponding values for InP:Zn, we assume that the structures are the same. The P-H model receives further support from the observation that the Zn-H bond-stretching frequency is 1600 cm^{-1}, whereas the P-H bond-stretching mode of phosphine is 2328 cm^{-1}.

The hydrogenated and deuterated GaP:Be samples have infrared absorption peaks at 2292.2 and 1669.8 cm^{-1}, respectively, at a temperature of 10 K [Fig. 1(a)]. The isotopic ratio of these frequencies is $r = 1.3727$. Neither peak was seen in GaP:Be, which was not H or D plasma exposed. These values are similar to the corresponding values in InP:Be, which has a P-H bond-stretching mode at 2236.5 cm^{-1} and isotopic ratio $r = 1.3714$. We therefore assume that the absorption peaks arise from a P-H complex, oriented in a bond-centered direction, adjacent to the beryllium acceptor.

The hydrogenated and deuterated GaP:Cd samples have infrared absorption peaks at 2434.0 and 1768.3 cm^{-1}, respectively, at a temperature of 7 K [Fig. 1(c)]. The isotopic ratio of these frequencies is $r = 1.3765$. Although the samples were diffused in a H_2 ambient, GaP:Cd, which was not exposed to a hydrogen plasma, did not have the hydrogen-related absorption peak. Once again, these values are similar to the corresponding values for InP:Cd, which has a P-H bond-stretching mode at 2332.4 cm^{-1} and isotopic ratio $r = 1.3757$. It therefore appears that for all group-II-acceptor–hydrogen complexes in GaAs,[13] InP, and GaP, the hydrogen binds to the host anion in a [111] bond-centered orientation.

The positions and full width at half maximum (FWHM) of the observed peaks are listed in Table I. The FWHM's of the P-D peaks are smaller than those of the P-H peaks. This narrowing effect has been observed in all group-II-acceptor–hydrogen complexes in III-V semiconductors and is correlated with the smaller vibrational amplitude of the deuterium as compared to the hydrogen.

Several additional trends are immediately apparent. First, the P-H modes in GaP are higher than the corresponding P-H modes in InP [Fig. 3(a)]. This could be related to the fact that GaP has a smaller lattice constant than InP. Second, as the size of the group-II acceptor increases, the frequency of the P-H mode increases. The

TABLE I. Frequencies and FWHM of P-H and P-D LVM peaks in group-II-acceptor–hydrogen complexes in GaP and InP.

Compound	P-H stretch mode		P-D stretch mode		
	Peak (cm^{-1})	FWHM (cm^{-1})	Peak (cm^{-1})	FWHM (cm^{-1})	$r = \nu_H/\nu_D$
GaP:Be	2292.2	2.7	1669.8	0.8	1.3727
GaP:Zn	2379.0	1.1	1729.4	0.5	1.3756
GaP:Cd	2434.0	1.2	1768.3	0.6	1.3765
InP:Be[a]	2236.5	0.43	1630.9	0.2	1.3714
InP:Zn[a]	2287.7	0.23	1664.5	0.08	1.3744
InP:Cd[a]	2332.4	0.12	1695.4	0.10	1.3757

[a]See Ref. 12.

significant upward shift in frequency is evidence that the hydrogen is in a bond-centered, rather than an antibonding, orientation. A larger acceptor probably relaxes less and sits closer to the proton, so its repulsive core potential has a more pronounced upward effect on the P-H vibrational mode. Finally, the isotopic ratio $r = \nu_H/\nu_D$ increases with increasing acceptor size [Fig. 3(b)]. This can also be understood in terms of the repulsion between the proton and the acceptor. Since the proton's wave function overlaps the repulsive potential more than the deuteron's, the ratio of the hydrogen to deuterium frequencies increases. Although the GaAs:Be,H complex has been modeled with *ab initio* calculations,[14] the effect of the group-II-acceptor size on the hydrogen LVM's awaits a theoretical treatment.

The temperature dependence of the hydrogen-related LVM's in GaP:Be and GaP:Zn was observed between 7 and 150 K (Figs. 4 and 5). Unfortunately, the small signal-to-noise ratio of the GaP:Cd,H LVM precluded
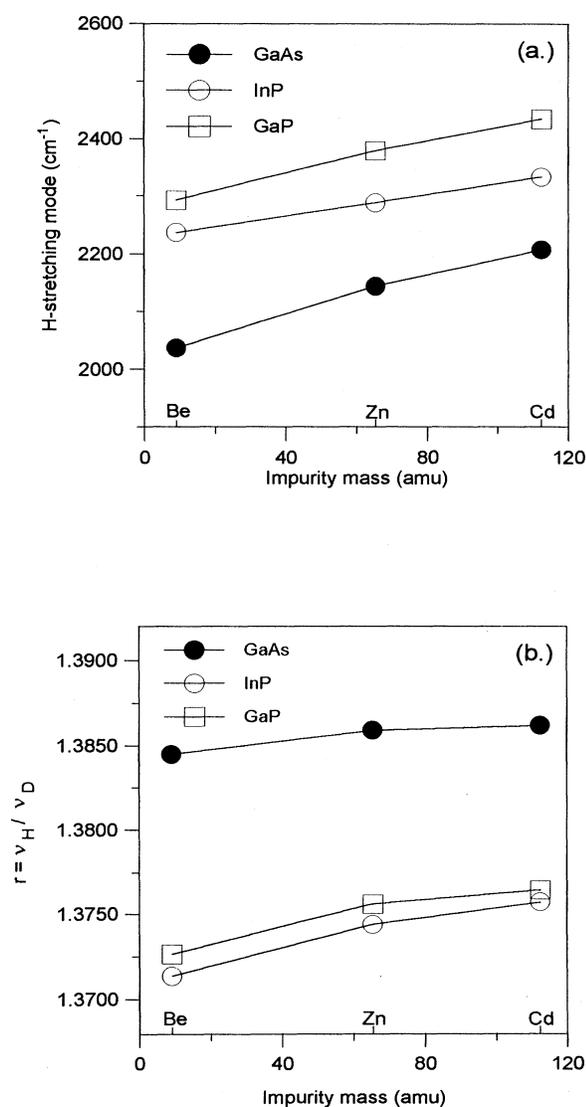

FIG. 3. (a) Hydrogen bond-stretching modes for group-II-acceptor–hydrogen complexes in GaAs (Ref. 13), InP (Ref. 12), and GaP (this work). Note that the LVM frequency shifts upward with increasing acceptor size, evidence that the hydrogen is in a bond-centered orientation. (b) Isotopic ratio $r = \nu_H/\nu_D$. As the size of the acceptor increases, so does the r factor.
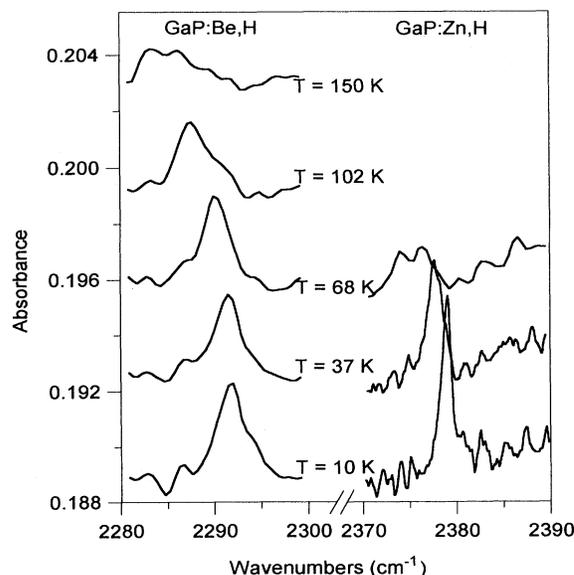
FIG. 4. Variable temperature spectra of GaP:Be,H and GaP:Zn,H LVM's. The LVM shift and linewidth broadening of the GaP:Zn,H mode are much greater than in the GaP:Be,H mode.
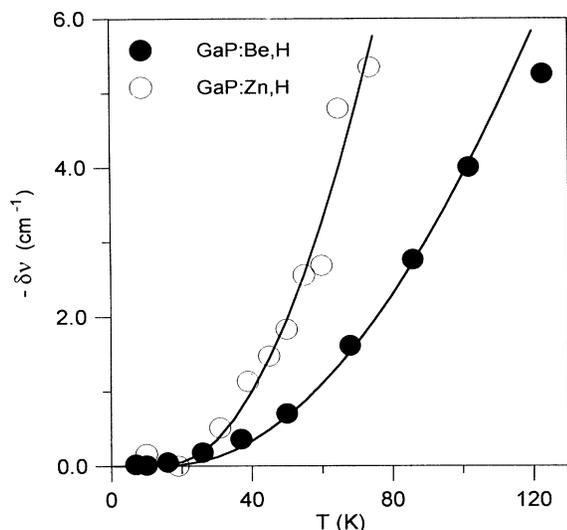
FIG. 5. Shifts of the GaP:Be,H and GaP:Zn,H LVM's as a function of temperature. The solid lines are fits according to Eq. (6), with the β parameters given in Table II.
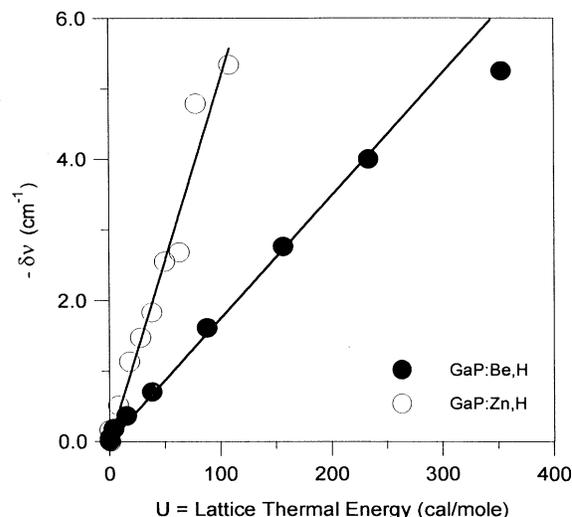

FIG. 6. Shifts of the GaP:Be,H and GaP:Zn,H LVM's as a function of lattice thermal energy $U(T)$. The solid lines are fits according to Eq. (6), with the β parameters given in Table II.

variable temperature measurements. We obtained the frequencies and linewidths of the peaks by fitting the data to Lorentzian functions. The linewidth broadening and shift to lower energy with increasing temperature have been observed in numerous systems and are believed to be caused by anharmonic coupling between the localized mode and the extended lattice phonons. The temperature dependence of hydrogen LVM's in GaAs (Ref. 15) and InP (Ref. 12) has been explained with a model which assumes that the LVM interacts with a *single* phonon mode. In our case, however, we assume that the LVM interacts with *all* the phonons and does not couple preferentially to any one mode.

Elliot *et al.*[16] quantitatively described the temperature dependence of LVM's in alkali halides. In our case, we assume that the hydrogen's potential is perturbed by the neighboring acceptor. The phosphorus-acceptor distance is given by

$$x(t) = x_0 + \delta x(t) , \qquad (1)$$

where x_0 is the equilibrium distance and $\delta x(t)$ is a perturbation due to thermal fluctuation. The resultant shift in the LVM energy can be expanded in a Taylor series about small δx:

$$\delta(\hbar\omega(t)) = a(\delta x) + b(\delta x)^2 + \cdots . \qquad (2)$$

When averaged over time, the linear term does not contribute to the LVM shift. To lowest order, the shift is given by

$$\delta(\hbar\omega) = b\langle(\delta x)^2\rangle . \qquad (3)$$

$\langle(\delta x)^2\rangle$ is calculated by summing the contributions from all the lattice modes q:

$$\langle(\delta x)^2\rangle = \sum_q \langle(\delta x_q)^2\rangle = \sum_q A_q^2/2 , \qquad (4)$$

where A_q is the amplitude of vibration. In this simple model, the lattice modes are assumed to be unperturbed by the defect. Classically, the mean vibrational energy of the crystal is given by

$$U(T) = \frac{N}{2}\gamma \sum_q A_q^2 , \qquad (5)$$

where N is the number of atoms and γ is the nearest-neighbor force constant. From Eqs. (3)–(5), it can be seen that the LVM shift is proportional to the thermal lattice energy $U(T)$. Equation (3) can therefore be written

$$\delta(\hbar\omega) = \frac{\beta}{N_A} U(T) , \qquad (6)$$

where $U(T)$ is given in units of energy per mole, N_A is Avogadro's number, and β is a dimensionless constant.

Figure 6 shows the LVM shifts plotted against $U(T)$. We obtained the values of $U(T)$ by numerically integrating the reported experimental values of the specific heat $C_V(T)$,[17] neglecting the zero temperature energy. The data can be approximated by linear least-square fits, with coefficients given in Table II. Evidently, the larger zinc

TABLE II. Parameters from Eqs. (6) and (8), which describe the temperature dependence of the GaP:Be,H and GaP:Zn,H LVM's.

LVM	β	θ_C (K)	A (cm^{-1})
GaP:Be,H	−0.050	400	200
GaP:Zn,H	−0.15	400	4900

acceptor has more influence than the beryllium on the LVM frequency.

The temperature-dependent shift of the linewidth is determined by the lifetime of the mode. It is unlikely that the hydrogen-related LVM's decay via the creation of phonons, since at least six optical phonons would be required to conserve energy. Instead, elastic phonon scattering reduces the lifetime of the overall mode.[18] Schematically,

$$|1\rangle|\ldots n_q, n_{q'}, \ldots\rangle \rightarrow |1\rangle|\ldots n_q+1, n_{q'}-1, \ldots\rangle \, , \qquad (7)$$

where $|1\rangle$ is the LVM and the n_q's are the phonon modes. In the Debye approximation, this process leads to a temperature-dependent linewidth

$$\delta\Gamma = \Gamma(T) - \Gamma(0) = A \left[\frac{T}{\theta_C}\right]^7 \int_0^{\theta_C/T} \frac{z^6 e^z}{(e^z-1)^2} dz \, , \qquad (8)$$

where $k\theta_C/\hbar$ is an effective cutoff frequency and A is an empirical constant. These two parameters have been adjusted to give reasonable fits to the data (Table II). The obtained value of $\theta_C = 400$ K is physically reasonable, since the Debye temperature for GaP ranges from 300 to 500 K as the sample is warmed from 10 to 150 K. The data and the fits are plotted in Fig. 7. Again, it can be seen that the GaP:Zn,H LVM is more sensitive to temperature variation than the GaP:Be,H LVM.

It should be noted that the thermal expansion of the lattice may contribute to the temperature-dependent shifts of the hydrogen LVM's. From 0 to 125 K, however, the lattice constant increases by only $\Delta a/a \sim 10^{-4}$.[19] From hydrostatic pressure measurements done on GaAs:Si,[20] it can be shown that a strain of $-\Delta a/a = 10^{-4}$ yields a LVM shift of less than 0.1 cm^{-1}. It is therefore unlikely that the small lattice expansion from 0 to 125 K plays a dominant role in the LVM shifts.

In conclusion, we have discovered vibrational modes in GaP:Be and GaP:Cd exposed to H and D plasma. It appears that for all observed group-II-acceptor–hydrogen complexes in III-V semiconductors, the hydrogen binds
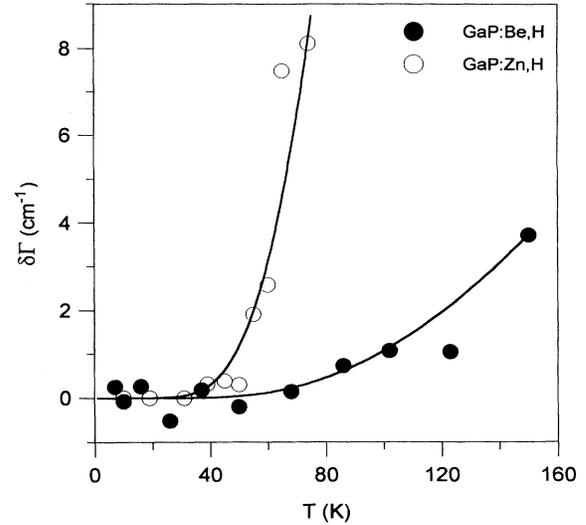

FIG. 7. Temperature-dependent shifts of the linewidth $\delta\Gamma$ for the GaP:Be,H and GaP:Zn,H modes. The solid lines are fits according to Eq. (8), with the θ_C and A parameters given in Table II.

to the host anion in a bond-centered orientation. The temperature-dependent shifts of the LVM's are proportional to the lattice thermal energy $U(T)$, an observation that probably holds for hydrogen LVM's in other semiconductors as well.

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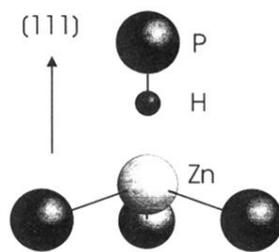
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