Vibrational Lifetimes and Frequency-Gap Law of Hydrogen Bending Modes in Semiconductors

B. Sun,[1] G. A. Shi,[2] S. V. S. Nageswara Rao,[3] M. Stavola,[2] N. H. Tolk,[3] S. K. Dixit,[3] L. C. Feldman,[3] and G. Lüpke[1]

[1]*Department of Applied Science, the College of William and Mary, Williamsburg, Virginia 23187, USA*
[2]*Department of Physics, Lehigh University, Bethlehem, Pennsylvania, Pennsylvania 18015, USA*
[3]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

(Received 30 August 2005; published 23 January 2006)

Vibrational lifetimes of hydrogen and deuterium related bending modes in semiconductors are measured by transient bleaching spectroscopy and high-resolution infrared absorption spectroscopy. We find that the vibrational lifetimes follow a universal frequency-gap law; i.e., the decay time increases exponentially with increasing decay order, with values ranging from 1 ps for a one-phonon process to 265 ps for a four-phonon process. The temperature dependence of the lifetime shows that the bending mode decays by lowest-order multiphonon process. Our results provide new insights into vibrational decay and the giant isotope effect of hydrogen in semiconductor systems.

DOI: 10.1103/PhysRevLett.96.035501 PACS numbers: 63.20.Pw, 78.47.+p

Hydrogen passivation of defects is a standard processing step in the production of metal-oxide-semiconductor (MOS) electronic devices. This process reduces the density of P_b centers, the most abundant electrically active defect at the $\mathrm{Si/SiO_2}$ interface, by 3 orders of magnitude [1]. Recently, an isotope effect of Si-H and Si-D bonds has been observed during this passivation process. By using deuterium instead of hydrogen to passivate the Si dangling bond of the P_b center at the $\mathrm{Si/SiO_2}$ interface, Lyding *et al.* found that the hot-electron degradation of MOS transistors was reduced by factors of 10–50 [2]. This reduction increased the operational lifetime of a silicon chip. A similar isotope effect has been observed in a study of the dissociation kinetics of Si-H and Si-D complexes in GaAs. Chevallier *et al.* observed that, for a given incident ultraviolet (UV) photon density, the concentration of dissociated Si-D complexes is 10–20 times below the concentration of dissociated Si-H complexes [3]. The isotope effect of H and D implies that Si-D bond-breaking is slower than for Si-H.

The origin of this isotope effect is not well established and many possible mechanisms have been proposed [2,4–6]. The key feature is that the electronic properties of Si-H and Si-D are identical, and only their vibrational properties are different. It is believed that the dissociation of Si-H and Si-D bonds is caused by inelastic electron scattering, which excites the bond to either a dissociative electronic state or to excited vibrational states [4,7,8]. Si-H bonds can be excited to a more energetic vibrational state by nonradiative electron-hole recombination or by hot electrons at $\mathrm{Si/SiO_2}$ interface. If the excited Si-H oscillation can be sustained, H can be emitted over the barrier to a mobile transport state, causing the Si-H bond to dissociate [9]. Within this model, the vibrational lifetime T_1 is an important parameter that affects the dissociation rate of Si-H or Si-D bonds. Van de Walle *et al.* proposed that the carrier-enhanced dissociation mechanisms are most likely controlled by the Si-H bending mode [10]. Based on their calculations by density functional theory, the bending mode at antibonding sites provides a more favorable dissociation path than the Si-H stretch mode [11]. The vibrational frequency of the bending mode for Si-H was calculated to be around 650 $\mathrm{cm^{-1}}$, and the estimated frequency for Si-D is around 460 $\mathrm{cm^{-1}}$, which is close to the frequency of bulk TO phonon states at the X point (463 $\mathrm{cm^{-1}}$). One may therefore expect that the coupling of Si-D bending modes to Si bulk phonons results in an efficient channel for deexcitation. Evidence for the coupling between Si-D bending modes and Si-Si lattice vibrations was found at the $\mathrm{Si/SiO_2}$ interface [12] and in deuterated amorphous silicon [13]. However, to our knowledge the vibrational lifetimes of Si-H and Si-D bending modes in Si have never been measured and vibrational dynamics of bending modes is essentially unknown.

We present here the first lifetime measurement of a H-related bending mode in Si. The lifetime of the $\mathrm{H_2}^*$ bending mode in Si at 817 $\mathrm{cm^{-1}}$ is measured to be $T_1 = 12.2 \pm 0.8$ ps by transient bleaching spectroscopy. The temperature dependence of the lifetime and calculations of multiphonon density of states indicate that the bending mode decays into two phonons (LA + TO phonons). The vibrational lifetimes of other H-related bending modes are estimated from their infrared absorption linewidths. We find the surprising result that the vibrational lifetimes of H and D-related bending modes in semiconductors can vary by orders of magnitude, and that this variation in lifetime can be explained by a simple frequency-gap law; i.e., the decay time increases exponentially with increasing decay order. The potential implications of the results on the physics of electronic device degradation are discussed.

The Si sample used for the lifetime measurement of $\mathrm{H_2}^*$ bending mode consists of a 2 mm thick disk cut from single crystalline high-resistivity Si. A uniform H concentration of 1.7×10^2 ppm was formed from the surface to a depth of 47 μm by variable-energy implantation at 80 K as described in Refs. [14,15]. The Si samples used for linewidth measurements are 15 mm thick, grown by the float-zone method, and prepared by electron irradiation, which is described in Ref. [14]. In addition, a Ge sample was prepared by hydrogen implantation at 80 K at a concentration of 10 ppm in a 18 μm thick layer on both sides of the sample. The IR absorbance spectra are measured using a Bomen DA 3.16 Fourier transform infrared spectrometer with a resolution of 0.1 cm^{-1} for Si and 0.04 cm^{-1} for the Ge sample. The IR pump-probe setup is described in Ref. [16].

Figure 1(a) shows a plot of the transient bleaching signal, S_b, versus time delay measured at 10 K with the laser frequency centered at 817 cm^{-1}. The signal decreases with a time constant $T_1 = 12.2 \pm 0.8$ ps. Measurements of S_b vs wavelength show that the transient bleaching signal originates from the 817 cm^{-1} mode. The inset shows the defect structure: 1 H is close to the bond-center site and the other near the antibonding site. The 817 cm^{-1} line corresponds to the bending mode of H at the antibonding site [17].

The vibrational lifetime of the excited state of a local vibrational mode can be estimated from $T_1 = 1/(2\pi c\Gamma_0)$, where Γ_0 corresponds to the natural linewidth of the absorption [14–16,18]. Linewidth measurements must be performed at low temperature (~ 10 K) using samples with very low defect concentrations (~ 1 ppm). Figure 1(b) shows the absorption spectrum of $\mathrm{H_2}^*$ measured at 5 K using samples with H concentration of $\sim 10^{16}\ \mathrm{cm}^{-3}$. The line shape of $\mathrm{H_2}^*$ is fitted by a Lorentzian with a FWHM of 0.42 cm^{-1}, which corresponds to a lifetime of 12.6 ps, i.e., exactly consistent with the one obtained in the time domain.

Since the lifetime of the bending mode of $\mathrm{D_2}^*$ is difficult to measure due to the weak laser pulses at $\sim 17\ \mu$m, we obtained the lifetime of D-related bending mode at 588 cm^{-1} by measuring its linewidth. The silicon sample containing $\mathrm{D_2}^*$ is prepared in the same way as the $\mathrm{H_2}^*$ complex. Figure 1(c) shows the absorption line with a width of 0.51 cm^{-1} corresponding to a lifetime $T_1 =$ 9.8 ps. For this special case, it is very interesting to find that the lifetimes of $\mathrm{H_2}^*$ and $\mathrm{D_2}^*$ bending modes are almost the same. In the following, we will show that this result can be explained by a frequency-gap law; i.e., both modes fall into the two-phonon band of Si. Further insight arises from identification of the relaxation channel and decay mechanism.

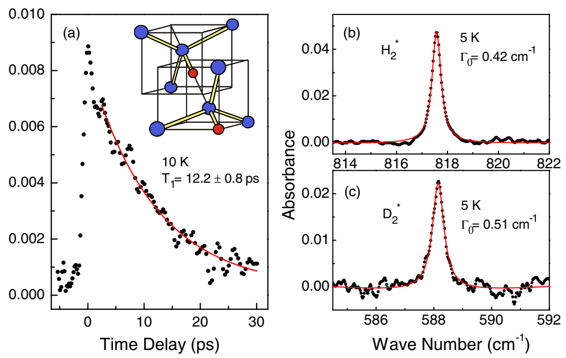

FIG. 1 (color online). (a) The transient bleaching signal S_b decays exponentially with a time constant $T_1 = 12.2 \pm 0.8$ ps for the bending mode of $\mathrm{H_2}^*$ in Si. The structure of $\mathrm{H_2}^*$ is shown in the inset. (b), (c) show the IR absorbance spectra of *e*-irradiated, H- and D-containing Si, respectively.

Previous studies of the vibrational lifetime of H-related defects in Si have focused on the stretch mode [14,15,18]. The exact nature of the accepting modes of H-related stretch modes is unknown. They can be Si-H bending modes, pseudolocalized modes, and/or phonon modes. In contrast, the decay channel of the bending modes may be less complicated because they are low-frequency modes and may decay directly into the phonon bath. Nitzan *et al.* developed a theory of vibrational energy relaxation in solids [19]. The total decay rate (inverse lifetime) is given as the sum of the rates of all of the decay channels:

$$\frac{1}{T_1} = \frac{2\pi}{\hbar^2}\sum_{\{\nu\}}|G_{\{\nu\}}|^2 n_{\{\nu\}}\rho_{\{\nu\}}, \tag{1}$$

where each channel $\{\nu\}$ is characterized by the set $\{\omega_1^{(\nu)}, \omega_2^{(\nu)}, \ldots, \omega_{N_\nu}^{(\nu)}\}$ of accepting mode frequencies. Energy is conserved in the decay process, $\omega = \sum_{j=1}^{N_\nu} \omega_j^{(\nu)}$, where ω is the frequency of the local vibrational modes (LVM). The decay rate of each channel is given by the temperature-independent coupling strength $G_{\{\nu\}}$ of the channel, the function $n_{\{\nu\}}$ describing the temperature dependent population of the receiving modes:

$$n_{\{\nu\}} = \frac{\exp(\hbar\omega/k_BT) - 1}{\prod_{j=1}^{N_\nu}[\exp(\hbar\omega_j^{(\nu)}/k_BT) - 1]}, \tag{2}$$

and the compound many-phonon density of accepting states $\rho_{\{\nu\}}$ which can be expressed in terms of a convolution of single phonon densities of states

$$\rho_{\{\nu\}} = \int d\omega_1^{(\nu)} \int d\omega_2^{(\nu)} \ldots \int d\omega_{(N_\nu - 1)}^{(\nu)} \rho(\omega_1^{(\nu)}) \times \rho(\omega_2^{(\nu)}) \ldots \rho(\omega_{N_\nu}^{(\nu)}). \tag{3}$$

Figure 2(a) shows T_1 versus temperature for the bending mode of $\mathrm{H_2}^*$ at 817 cm^{-1} in Si. T_1 is nearly constant up to 130 K. The lifetime measured above 130 K is not reliable due to the low signal-to-noise ratio. The solid line in Fig. 2(a) shows a fit using Eq. (2) with the vibrational relaxation channel of the 817 cm^{-1} mode represented by two accepting modes 460 and 357 cm^{-1}, which correspond to the combination of TO + LA phonons. The dashed line is a fit using three accepting modes 517, 150, and 150 cm^{-1} corresponding to one optical phonon at the Γ point and two TA phonons. It is clear that the bending mode at 817 cm^{-1} decays via a two-order process. The phonon decay channels are not uniquely determined by the temperature dependence of the lifetime. However, a three-order process will not fit the data points. Since both $\mathrm{D_2}^*$

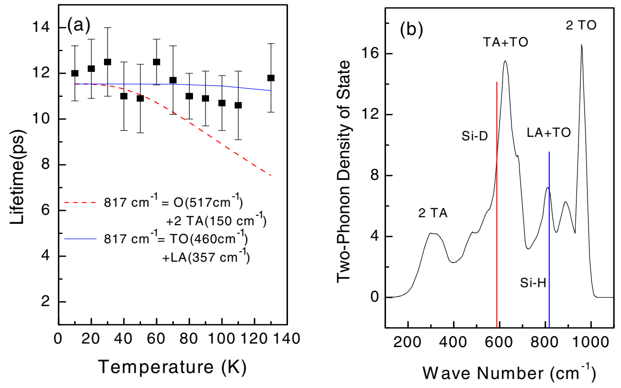

FIG. 2 (color online). (a) Temperature dependence of T_1 of the 817 cm^{-1} mode of $H_2{}^*$ obtained by transient bleaching spectroscopy. The dashed and solid lines are theoretical predictions for decay into three phonons {517, 150, 150} and two phonons {460, 357} cm^{-1}, respectively. (b) Two-phonon density of states in Si. The $H_2{}^*$ bending mode at 817 cm^{-1} coincides with LA + TO phonons, whereas the $D_2{}^*$ bending mode at 588 cm^{-1} lies in the TA + TO phonon band.

and $H_2{}^*$ fall into the two-phonon band of Si, we would expect that $D_2{}^*$ also decays via a two-order process. Figure 2(b) shows the calculation of the two-phonon density of states by straightforward convolution of the one-phonon density of states according to Eq. (3). The $H_2{}^*$ bending mode at 817 cm^{-1} falls on the peak of the TO + LA phonon combination, whereas the $D_2{}^*$ bending mode at 588 cm^{-1} coincides with the TA + TO phonon combination. The two-phonon decay channels of $H_2{}^*$ and $D_2{}^*$ are infrared active and therefore they are allowed [16].

The relaxation rate is determined by the magnitude of the coupling terms between the LVM and accepting modes. As $|G_{\{\nu\}}|$ is expected to exhibit a very strong dependence on N_ν, the relaxation rate can be approximately expressed by the dominant contribution. The largest term in Eq. (1) is determined by the collection of phonon states $\{\nu\} = 1, 2, \ldots, N_\nu$, where N_ν is the smallest number of phonons that can result in a vibrational relaxation process subjected to energy conservation [19]. The approximate expression for the vibrational relaxation rate is now $\gamma = 2\pi/\hbar |G_{\{\nu\}}|^2 n_{\{\nu\}} \rho_{\{\nu\}}$. To a good approximation [19], the coupling term can be written as $G_{\{\nu\}} \cong C\delta^N$, where C is a constant, $0 < \delta \ll 1$, and the decay order N is determined by the frequency gap between the LVM and accepting phonon modes, that is, the number of (maximum frequency) phonons required to conserve energy. Such a relation together with Eq. (1) implies that $\gamma \propto \delta^{2N}$ (at constant temperature). It is generally believed that the relaxation rate decreases exponentially as the frequency gap is increased. The frequency-gap law can be expressed by [19,20]

$$T_1 = Ae^{BN}, \tag{4}$$

where A and B are two parameters which depend on the coupling constants between the LVM and accepting modes.

Figure 3 shows a plot of the vibrational lifetimes of H (D)-related bending modes vs decay order N for various defects in different semiconductors. As a first test of Eq. (4), we measured the linewidth of the bending mode of $H_2{}^*$ in Ge. The maximum phonon frequency in Ge is ~306 cm^{-1}, and the bending mode at 765 cm^{-1} is expected to decay into 3 phonons. The bending mode exhibits a linewidth of 0.065 cm^{-1} at 5 K, which corresponds to a lifetime of ~80 ps. This is much longer than in Si, strongly supporting the frequency-gap law.

The solid line in Fig. 3 shows that as a general trend the vibrational lifetime of H (D)-related bending modes does follow closely a frequency-gap law. The data points in Fig. 3 are fitted with the values $A = 0.15$ ps and $B = 2.01$ in Eq. (4). A is determined by the time scale of the first-order decay and B only depends logarithmically on the coupling constant and on N [19]. A similar value of $B = 1.93$ was obtained for the lifetime of the CN$^-$ stretch mode in silver halides, which also follows the frequency-gap law

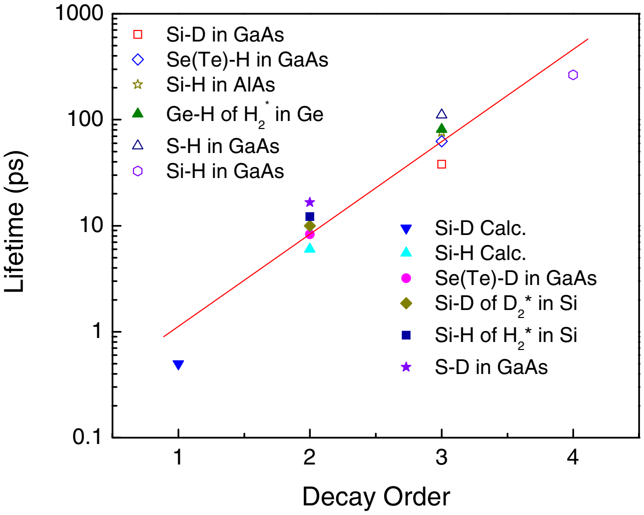

FIG. 3 (color online). Vibrational lifetimes of H-related bending modes via decay order in different hosts. The line is a fit of Eq. (4) with two parameters: $A = 0.15$ ps and $B = 2.01$. Tight-binding molecular dynamics simulations predict a lifetime of 0.3–0.5 ps for Si-D at 460 cm^{-1} in Si ($N = 1$) and 5–6 ps for Si-H at 640 cm^{-1} ($N = 2$) [9]. The linewidth of the Si-H bending mode in Si-doped GaAs at 896 cm^{-1} is ~0.02 cm^{-1} [23], which corresponds to a lifetime of ~260 ps. Since the maximum phonon frequency in GaAs is at 290 cm^{-1}, there must be at least 4 phonons involved in the decay process. The linewidth of the Si-H bending mode at 890 cm^{-1} in Si-doped AlAs is 0.07 cm^{-1} [24], which corresponds to a lifetime of ~75 ps. The maximum phonon frequency of AlAs is 402 cm^{-1}, which leads to $N = 3$. The linewidth of Si-D in GaAs at 641 cm^{-1} is around 0.13 cm^{-1}, corresponding to $T_1 = 40$ ps and $N = 3$ [25]. S(Se,Te)-H modes have almost the same frequencies with linewidths of 0.045–0.09 cm^{-1} corresponding to $T_1 = 55$–110 ps and $N = 3$ [26], whereas the linewidths of the corresponding D modes are broader in the range 0.3–0.6 cm^{-1} ($T_1 = 8$–16 ps) due to their lower-order decay process ($N = 2$).

[21]. In contrast, a much larger value of $A = 50$ ps was found for the CN^- stretch mode [21], which indicates that the phonon coupling strengths vary with impurity. However, our analysis and the results in Ref. [21] show that these coupling parameters do not vary considerably in similar hosts.

The overall agreement between the fit and the data is satisfactory, but by no means perfect. There are possible errors in the lifetime determination of H (D)-related bending modes plotted in Fig. 3. Most of the lifetimes are deduced from the linewidths measured at low temperature, which may include contributions from: (1) inhomogeneous broadening; (2) instrumental broadening, especially for those sharp lines; (3) isotope broadening for the linewidths of Se(Te)-H or D modes in GaAs [22]; and (4) variable coupling constants between hosts, although calculations by Biswas [9] indicate that lifetimes of bending modes are insensitive to the environment.

Our study of H-related bending modes in various semiconductors and analysis of the frequency-gap law shows clearly that the lifetime of the bending mode depends critically on the decay order, i.e., the gap between the local mode and the accepting phonon states. The energy relaxation time can be different by 3 orders of magnitude when the bending mode decays into a different number of phonons. Since the frequency of the calculated bending mode is smaller for deuterium than for hydrogen the former may decay via a lower-order process, which results in a shorter lifetime. This result can explain the giant H (D) isotope effect as indicated by the calculated Si-H (D) data points in Fig. 3 [9] and supports the finding that the difference in the dissociation rate of Si-H and Si-D bonds may be controlled by the dynamics of hydrogen bending modes [10]. The actual rates for this multiple excitation process depend sensitively on the absolute lifetime [23], which are now available via this report.

In conclusion, we have measured the vibrational lifetimes of Si-H and Si-D bending modes of H_2^* in Si and extended this study to many other bending modes in semiconductors. We show that the vibrational lifetime of bending modes can be described by a frequency-gap law. This is experimentally verified in Ge where we show that the H-related bending of H_2^* has a much longer lifetime than in Si due to the lower phonon frequencies. The lifetime increases dramatically with increasing decay order. This result provides new insights into vibrational decay and an important fundamental parameter in the analysis of semiconductor device reliability values.

The authors gratefully acknowledge the staff at the TJNAF FEL and W. M. Augustyniak for technical assistance. We are grateful to Michael Budde for helpful discussions. This work was supported in part by DOE through Grant No. DE-FG02-99ER45781 (C. W. M. and V. U.), ONR (C. W. M. and V. U.), NSF through Grants No. DMR-02-42316 (C. W. M.) and No. DMR-04-03641 (L. U.).

[1] A. Stesmans, Phys. Rev. B **61**, 8393 (2000); J. Appl. Phys. **88**, 489 (2000).

[2] J. W. Lyding, K. Hess, and I. C. Kizilyalli, Appl. Phys. Lett. **68**, 2526 (1996).

[3] J. Chevallier, M. Barbé, E. Constant, D. Loridant-Bernard, and M. Constant, Appl. Phys. Lett. **75**, 112 (1999).

[4] T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, Science **268**, 1590 (1995).

[5] Ph. Avouris, R. E. Walker, A. R. Rossi, H. C. Akpati, P. Nordlander, T. C. Shen, G. C. Abeln, and J. W. Lyding, Chem. Phys. Lett. **257**, 148 (1996).

[6] J.-H. Wei, M.-S. Sun, and S.-C. Lee, Appl. Phys. Lett. **71**, 1498 (1997).

[7] K. Hess, L. F. Register, B. Tuttle, J. Lyding, and I. C. Kizilyalli, Physica (Amsterdam) **3E**, 1 (1998).

[8] E. T. Foley, A. F. Kam, J. W. Lyding, and Ph. Avouris, Phys. Rev. Lett. **80**, 1336 (1998).

[9] R. Biswas, Y.-P. Li, and B. C. Pan, Appl. Phys. Lett. **72**, 3500 (1998).

[10] C. G. Van de Walle and W. B. Jackson, Appl. Phys. Lett. **69**, 2441 (1996).

[11] C. G. Van de Walle and R. A. Street, Phys. Rev. B **49**, 14 766 (1994).

[12] Zhi Chen, Jun Guo, and Pangleen Ong, Appl. Phys. Lett. **83**, 2151 (2003).

[13] An Shih, Si-Chen Lee, and Chih ta Chia, Appl. Phys. Lett. **74**, 3347 (1999).

[14] M. Budde, G. Lüpke, E. Chen, X. Zhang, N. H. Tolk, L. C. Feldman, E. Tarhan, A. K. Ramdas, and M. Stavola, Phys. Rev. Lett. **87**, 145501 (2001).

[15] G. Lüpke, X. Zhang, B. Sun, A. Fraser, N. H. Tolk, and L. C. Feldman, Phys. Rev. Lett. **88**, 135501 (2002).

[16] B. Sun, Q. Yang, R. C. Newman, B. Pajot, N. H. Tolk, L. C. Feldman, and G. Lüpke, Phys. Rev. Lett. **92**, 185503 (2004).

[17] J. D. Holbech, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, Phys. Rev. Lett. **71**, 875 (1993).

[18] M. Budde, G. Lüpke, C. Parks Cheney, N. H. Tolk, and L. C. Feldman, Phys. Rev. Lett. **85**, 1452 (2000).

[19] A. Nitzan, S. Mukamel, and J. Jortner, J. Chem. Phys. **60**, 3929 (1974); **63**, 200 (1975).

[20] We note that the "frequency-gap law" has also been referred to as the "energy-gap law" but we have renamed it to avoid any confusion with the band gap in semiconductors.

[21] U. Happek, C. E. Mungan, W. von der Osten, and A. J. Sievers, Phys. Rev. Lett. **72**, 3903 (1994).

[22] The natural isotope of S is dominated by ^{32}S (95.02%) and isotope broadening can be neglected. The isotope broadening is much larger for Se(Te)-H(D) modes due to the comparable abundances.

[23] L. C. Feldman, G. Lüpke, N. H. Tolk, Diffus. Defect Data, Pt. B, Solid State Phenom. **95–96**, 123 (2004).

[24] E. Tuncel and H. Sigg, Phys. Rev. B **48**, 5225 (1993).

[25] B. Pajot (private communication).

[26] J. Vetterhöffer and J. Weber, Phys. Rev. B **53**, 12 835 (1996).