Frequency and temperature dependence of the TO phonon-polariton decay in GaP

A. G. Stepanov,* J. Hebling,† and J. Kuhl
Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany
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The temperature and frequency dependence of the decay time of the transverse optical (TO) phonon polariton in GaP has been measured by impulsive stimulated Raman scattering with 25-fs optical pulses. Tuning of the polariton frequency from 365 to 361 cm^{-1} reveals drastic changes of the polariton decay time with temperature. This result is explainable by third-order anharmonic decay of polaritons into two acoustic phonons taking into account the temperature-dependent shift of the van Hove singularity in the two-phonon density of states of the acoustic phonons at the edge of the Brillouin zone. The frequency dependence of the TO phonon-polariton decay times measured at different temperatures allows one to directly observe the shift of this singularity with temperature.

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I. INTRODUCTION

Unusual properties of the TO phonon in GaP have attracted attention for a long time.[1–4] The TO phonon line measured in Raman backscattering geometry is very broad compared to the LO phonon line of GaP and optical phonon lines in many other III-V semiconductors, the line shape is asymmetric and deviates remarkably from an ordinary Lorentzian profile, and the TO Raman linewidth reveals only very little change with temperature. Early on Barker[1] has suggested that the frequency dependence of the phonon damping due to a coincidence of the TO phonon energy with the sum of $TA(X)+LA(X)$ phonon energies is the origin of the TO phonon line asymmetry. Weinstein found that hydrostatic pressure leads to a pronounced line narrowing and decreasing asymmetry.[3] He proposed that this results from tuning of the TO phonon frequency relatively to the van Hove singularity in the acoustic two-phonon density of states (DOS) at the edge of the Brillouin zone. Recently F. Widulle *et al.* have investigated Raman spectra of isotopically enriched samples enabling fine tuning of the phonon frequency.[4] They have resolved a double peak structure in the TO Raman phonon line of natural GaP at low temperature which could be reproduced by first-principles calculations.[5] Additionally they have shown that the phonon line shape distinctly varies with isotope composition of the sample. The authors[4] explained their findings by a kink in the two-phonon density of states in the vicinity of the TO phonon frequency which is shifting with isotope substitution thus strongly influencing the third-order anharmonic phonon decay. Whereas the measured[2,6,7] temperature dependence of the TO phonon Raman linewidth in GaP does not agree with *ab initio* calculations based on the simple anharmonic decay into two acoustic phonons,[8] TO phonon-polariton lifetimes for modes with frequencies (345 cm^{-1} in Ref. 9 and 354 cm^{-1} in Ref. 10) which are significantly detuned against the phonon frequency (366 cm^{-1}) are well described by the temperature dependence theoretically predicted for that third-order anharmonic decay.[11,12] In previous papers, deviations between measured phonon linewidths and the theoretical temperature dependence predicted for the third-order anharmonic decay have been attributed to either four phonon interaction processes[13] or sample disorder.[14] In this paper, we present investigations of the TO phonon-polariton decay time $T_2(\omega,T)$ in GaP as a function of temperature T and polariton frequency ω measured directly in the time domain by impulsive stimulated Raman scattering (ISRS). $T_2(\omega,T)$ as a function of T changes drastically if ω is tuned from 361 to 365 cm^{-1}. The experimental data clearly show a shift of a van Hove singularity in the two-phonon DOS corresponding to acoustic phonons from 365 to 361 cm^{-1} if T is raised from 10 to 250 K. If this shift is taken into account, the puzzling temperature dependence of T_2 can be well described by a third-order anharmonic decay. Thus our finding confirms the explanation for the unusual temperature dependence of the TO Raman linewidth suggested in Ref. 6.

II. EXPERIMENTAL TECHNIQUE

The experimental setup utilized a forward-folded boxcar four-wave mixing geometry with two pump pulses and one probe pulse delivered by a Kerr-lens mode-locked Ti:sapphire laser. The pulses had a duration of 25 fs corresponding to a spectral bandwidth of 500 cm^{-1}, a central wavelength of 810 nm, and a repetition rate of 76 MHz. The diffracted probe was detected by a standard photodiode as a function of the delay $\Delta\tau$ between the pump and probe pulses. The delay was periodically varied at a frequency of 70 Hz by a rapid scan system. The photodiode output was fed via a fast analog-to-digital (AD) converter into a computer for efficient signal averaging. This detection scheme provided a signal-to-noise ratio of approximately 10^6. The measurements were performed on a high-purity (unintentional doping $<3\times10^{15}$ cm^{-3}) $\langle110\rangle$ oriented GaP bulk crystals. The sample was wedge shaped with a wedge angle of 10° between front and back surface and approximately 200-μm thickness at the measurement spot.

Coherent TO phonon-polaritons were excited by difference-frequency mixing of appropriately separated spectral components of the pump pulses. The polariton's wave vector and concomitantly its central frequency were tuned in the range from $q=16\,000$–$45\,800$ cm^{-1} and $\omega=357.3$–365.1 cm^{-1}, respectively, by varying the angle between the pump pulses (measured outside of the crystal)

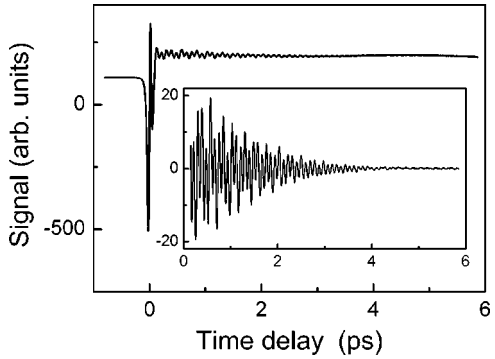

FIG. 1. Experimental signal for a ⟨110⟩ GaP crystal at room temperature as a function of the delay time between the probe pulse and the pump pulses. The angle between the pump beams in free space is 14°. The inset shows the oscillatory part of the signal on an enhanced scale and for a baseline straightened by Fourier filtering.

from 10.5 to 32°. The pump pulses were polarized parallel to each other and perpendicular to the probe pulse and the signal was detected for polarization parallel to the probe. The sample which was mounted on the cold finger of a variable temperature cryostat was oriented so that the [111] direction is perpendicular to the pump pulse polarization since LO phonon contributions to the signal which would render the data analysis more difficult are suppressed in this configuration.

III. EXPERIMENTAL RESULTS

Figure 1 illustrates a typical experimental signal as a function of the time delay between the two pump and the probe pulses recorded at room temperature. The strong oscillation near zero delay time is due to interaction of the three overlapping pulses via the electronic Kerr nonlinearity of GaP. This peak has been rejected before the analysis of the experimental data. The inset of Fig. 1 depicts the signal on an enhanced scale and for a baseline straightened by Fourier transform filtering.

The normalized Fourier power spectrum of the time domain data (inset of Fig. 1) is presented in Fig. 2. The spectrum consists of two main lines at 4.1 and 10.9 THz labeled by CA and TO. The line at 10.9 THz presents the coherent TO phonon-polariton line of GaP. As shown in Refs. 15 and 16 phonon-polariton oscillations appear in the time-domain signal due to heterodyne detection obtained by interference of Raman and Rayleigh scattered parts of the probe pulse. In this case, the decay time of the oscillation amplitude is equal to T_2. Since the finite resolution of the Fourier spectrum in Fig. 2 inhibits an accurate determination of the polariton mode frequency, we have first calculated the polariton wave vector q from the beam configuration and then the frequency was determined using the temperature-dependent polariton dispersion relation in GaP. It is important to mention that determination of q for high-frequency polaritons as studied in our experiments necessitates use of the accurate formula

$$q=(k_L^2+k_S^2-2k_Lk_S\cos\Theta)^{1/2}, \tag{1}$$

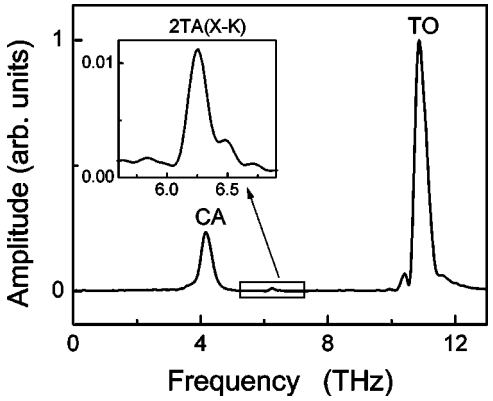

FIG. 2. Normalized Fourier power spectrum of the time domain data presented in the inset of Fig. 1. TO labels the phonon-polariton line. CA is a line attributed to a coherent artifact originating from the interaction of the probe with the pump pulses reflected at the back surface of the sample. The 2TA(X-K) line (shown in the inset on an enhanced scale) is due to excitation of a two-phonon state in a second-order Raman process.

where k_L and k_S are the wave vectors of the two pump beams and Θ is the angle between these beams in the crystal. The approximation

$$q=4\pi\sin(\Theta/2)\lambda^{-1} \tag{2}$$

(λ is the center wavelength of the pulses) which has been applied by many groups and worked satisfactorily for low-frequency polaritons leads to unacceptable errors in our case. The line at 4.1 THz in Fig. 2 is a coherent artifact due to the interaction of the probe pulse with counter propagating pump pulses created via reflection of the incident pump pulses at the back surface of the sample. The interaction has to be attributed to coupling of the reflected pump pulses with the probe pulse via the strong third-order electronic susceptibility. If the sample is wedge-shaped (or if a plane parallel sample is tilted with respect to the incident pulses) this second pair of pump pulses propagates under some angle with respect to the probe pulse direction as illustrated in Fig. 3. Variation of the delay $\Delta\tau$ between pump and probe pulses modulates the phase of the grating since the interference pattern of the two reflected pump beams is continuously shifted

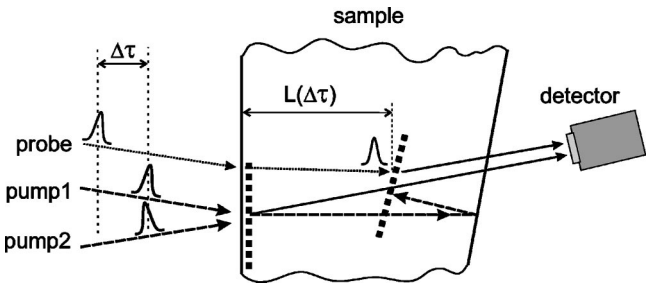

FIG. 3. Schematic illustration of the origin of the coherent artifact (CA). $\Delta\tau$ is the delay time between pump (dashed lines) and probe pulses (dotted lines). $L(\Delta\tau)$ is the distance of the interaction region of the probe and the pump beams reflected by the back surface of the sample measured from the front surface. The solid lines are the phonon signal and the CA.

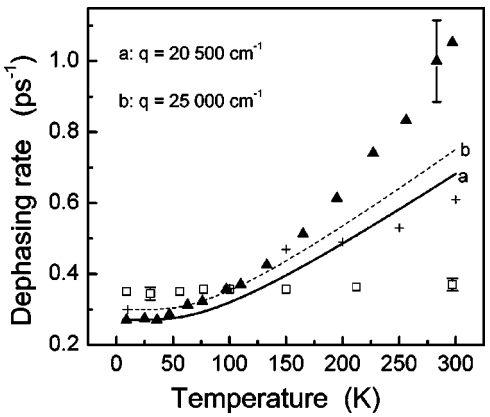

FIG. 4. Temperature dependence of the TO phonon-polariton dephasing rate in pure GaP at $q=20\,500$ cm^{-1} (triangles), 25 000 cm^{-1} (crosses), and 45,800 cm^{-1} (squares). The solid and dashed lines are fits using the usual expression for third-order anharmonic decay (details are given in the text).

perpendicularly to the probe beam direction. This effect creates a phase modulation of the diffracted signal with increasing $\Delta\tau$ which is converted into amplitude modulations by the heterodyne detection process. The low-frequency modulation suddenly vanishes when the delay is equal to twice the sample thickness since the reflected pump beams and the probe pulse do no longer overlap inside the sample. This explanation for the origin of the CA is corroborated by the experimentally observed dependence of its frequency on the angle between the probe beam and the reflected pump beams (which can be easily varied by tilting of the sample) as well as on the angle between the pump pulses. In the experiments, the frequency of the CA line could be tuned between 1 and 6 THz. Finally it should be mentioned that this artificial signal was detectable even when the probe pulse was shifted with respect to the focal spot of the pump pulses by 50–100 μm.

The weak line at 6.3 THz (shown on an enhanced scale in the inset of Fig. 2) presents a two-phonon state excited by second-order Raman scattering.[17,18] This nonclassical state involves a continuum of TO modes that leads to oscillations associated with the frequency of a van Hove singularity in the phonon DOS. In our case, the frequency of the two phonon oscillation is equal to twice the TA phonon at the *X*-*K*(lower branch) points of the Brillouin zone.[19]

IV. ANALYSIS AND DISCUSSION

The polariton decay time can be evaluated from our experimental data by fitting of the time-domain data (Fig. 1) with exponentially decaying oscillatory functions. Direct fitting of the raw data is complicated due to the presence of the CA modulation which obviously decays nonexponentially. Therefore the CA oscillations are reduced by Fourier transform filtering and then the oscillation maxima and minima of the filtered curves are fitted. The TO phonon-polariton decay time has been measured for several modes in the frequency range from 357 to 365 cm^{-1} at various temperatures between 10 and 250 K. Figure 4 presents as examples plots of the dephasing rate $\Gamma=(T_2)^{-1}$ measured at $q=45\,800$ cm^{-1} (squares), 25 000 cm^{-1} (crosses), and 20 500 cm^{-1} (triangles) vs T. The curves demonstrate that slight tuning of ω near the TO phonon frequency leads to drastic changes of the temperature dependence of Γ. The solid and dashed line in Fig. 4 represent theoretical curves for the modes at 20 500 and 25 000 cm^{-1}, respectively, obtained from the usual expression for the third-order anharmonic decay of an optical phonon into two acoustic phonons:

$$\Gamma(\omega,T)=|V_3|^2\rho(\omega)[1+n(\omega_1,T)+n(\omega_2,T)], \qquad (3)$$

where $\Gamma(\omega,T)$ is the inverse lifetime of the initially excited optical phonon, $|V_3|$ is the effective third-order anharmonic coupling constant, $n(\omega_{1,2},T)=[\exp(h\omega_{1,2}/k_BT-1]^{-1}$ are the Bose-Einstein occupation numbers of the acoustic phonons with frequencies $\omega_{1,2}$ ($\omega=\omega_1+\omega_2$), $\rho(\omega)$ is the two-phonon DOS at $\omega=\omega_1+\omega_2$. The term $|V_3|^2\cdot\rho(\omega)$ was used as a temperature-independent fitting parameter. Recently we have shown that the TO phonon polariton in the investigated frequency range decays into a TA (upper branch) plus a LA phonon at the *K* point of the Brillouin zone.[20] Accordingly the values of ω_1 and ω_2 were chosen to be 153 and 212 cm^{-1}, respectively. The experimental data for the $q=20\,500$-cm^{-1} and the 25 000-cm^{-1} mode exhibit either a systematically higher (20 500 cm^{-1}) or lower (25 500 cm^{-1}) dephasing rate than calculated by Eq. (3). Finally the decay time of the polariton mode at $q=45\,800$ cm^{-1} exhibits no significant temperature dependence between 4 and 300 K in accordance with previous data for the TO-phonon lifetime in GaP derived from Raman linewidth measurements.[2,6,7] [The Raman linewidth σ_ω is equal to $(\pi\cdot T_2)^{-1}$.] This extraordinary behavior can be attributed to a temperature-dependent shift of a narrow peak (width of a few cm^{-1}) in the two-phonon DOS. For natural GaP, a kink at 366 cm^{-1} has been detected at 10 K (Ref. 4). If this kink shifts to lower frequencies with rising temperature more strongly than the TO phonon, as supposed in Refs. 1, 6, and 7, $\rho(\omega_{\rm TO})$ in Eq. (3) becomes considerably temperature dependent. A plot of the frequency dependence of the dephasing rate $\Gamma=(T_2)^{-1}$ experimentally determined for various temperatures in the range between 10 and 250 K and depicted in Fig. 5 shows a pronounced peak of $\Gamma(\omega)$ which moves from 365 to 361 cm^{-1} with increasing temperature. This peak in $\Gamma(\omega)$ has to be attributed to $\rho(\omega)$ if we assume that the frequency dependence of $|V_3|^2$ and $[1+n(\omega_1,T)+n(\omega_2,T)]$ is negligible in the region 357–366 cm^{-1}.

Figure 5 clearly demonstrates that the shift of the peak in $\rho(\omega)$ with T can result in a dramatically different temperature dependence of the dephasing time of polaritons with only slightly different frequencies (see Fig. 4). Let us consider for example the polariton at 365 cm^{-1}. At low temperature the peak of $\rho(\omega)$ appears at this frequency. For increasing temperature the phonon occupation numbers increase. According to Eq. (3) this should imply an increase of $\Gamma(\omega)$. However, this increase is compensated by a decrease of $\rho(\omega)$ associated with the shift of the peak to lower frequency. This leads to an almost temperature-independent dephasing rate (see Fig. 4). The peak of $\rho(\omega)$ moves below 363 cm^{-1} only for temperatures higher than 150 K. As a

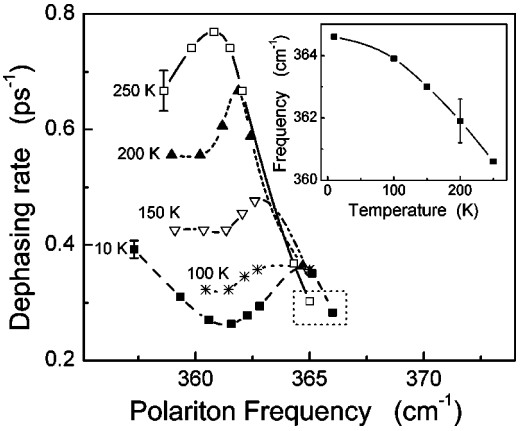

FIG. 5. Frequency dependence of the TO phonon-polariton dephasing rate in GaP measured at 10, 100, 150, 200, and 250 K. $\Gamma(\omega)$ for 250 K agrees fairly well with previous data (Ref. 20) obtained at room temperature. Two points in the dashed square at the bottom-right corner have been determined by analysis of the TO-phonon linewidth measured by spontaneous Raman scattering (Ref. 7). The lines are guides to the eye. The inset shows the shift of the maximum in the dephasing rate [related to the peak in $\rho(\omega,T)$] with temperature.

result (see Fig. 4) the decay rate of the polariton at 363 cm^{-1} approximately follows Eq. (3) in the 10–150-K range, but deviates to values smaller than predicted for temperatures above 150 K. Finally, the mode at 361 cm^{-1} exhibits a minimum in the dephasing rate (see Fig. 5) and accordingly in $\rho(\omega)$ at low temperature. The shift of the peak in $\rho(\omega)$ to this position causes a considerably stronger (up to 50%) rise of the dephasing rate than expected for the change in the occupation numbers (see solid line in Fig. 4).

Thus we believe that the puzzling temperature dependence of $\Gamma(\omega)$ for polariton modes with slightly different frequencies (see Fig. 4) can be satisfactorily explained if the temperature dependence of both the acoustic phonon occupation numbers and the position of the peak in $\rho(\omega,T)$ are taken into account. There is no need to consider higher-order anharmonic decay process. The inset of Fig. 5 displays the measured temperature dependence of the relative maximum of the dephasing rate caused by a shift of the peak of $\rho(\omega,T)$. The data confirm the behavior suggested in Ref. 4. The shift of 4 cm^{-1} (equivalent to approximately 1% change) is at least two times larger than measured values for the shift of the TO frequency[2,4] in the same temperature range. This stronger shift of the peak in the two-phonon DOS as compared to the TO-phonon frequency is the origin of the extraordinary variation of $\Gamma(\omega)$ with T. To the best of our knowledge, there exist no reliable literature data for the temperature dependence of the acoustic phonon frequency in GaP. Our technique allows observation of 2TA(X-K) oscillations due to second-order Raman scattering (Fig. 2), and

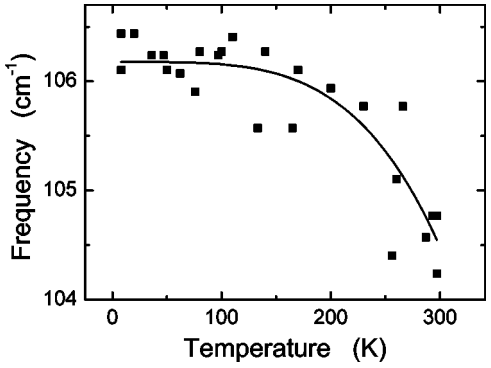

FIG. 6. Temperature dependence of the TA(X-K) phonon energy measured by second-order Raman scattering. Squares represent experimental points, the solid line is a guide to the eye.

temperature-dependent measurements of the TA(X-K) line (Fig. 6) demonstrate that the TA(K-X) frequency decreases with rising temperature. The relative shift of the TA phonon by approximately 1% between 10 and 250 K agrees very well with the shift of $\rho(\omega,T)$ in the inset of Fig. 5. It should be noticed, however, that this measurement concerns TA phonons on the lower branch at the K point whereas TA phonons on the upper branch are involved in the decay of the TO phonon-polariton in the studied wave-vector range.

V. CONCLUSION

The temperature and frequency dependence of the (TO) phonon-polariton decay time T_2 in GaP has been measured by ISRS spectroscopy. Tuning of the polariton frequency from 361 to 365 cm^{-1} has been shown to create drastic changes of the temperature dependence of T_2. These observations can be explained in terms of anharmonic decay of the TO phonon polariton into two acoustic phonons taking into account a variation of the two-phonon DOS with temperature. The unusual temperature dependence of T_2 found for modes with energies between 365 and 361 cm^{-1} is caused by a shift of a van Hove singularity in the two phonon DOS at $(TA+LA)_K$ with temperature. Measurements of the temperature and frequency dependence of the TO phonon-polariton decay time allowed us to observe the shift of the singularity directly. The temperature dependence of the TA(X-K) two-phonon energy has been measured by second-order ISRS.

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*Permanent address: Institute of Spectroscopy, Russian Academy of Sciences, 142092 Troitsk, Moscow Region, Russia.
†Permanent address: Experimental Physics Department, University of Pecs, H-7624 Pecs, Hungary.

[1] A.S. Barker, Jr., Phys. Rev. **165**, 917 (1968).
[2] B.Kh. Bairamov, Yu.E. Kitaev, V.K. Negoduiko, and Z.M. Khashkhozhev, Fiz. Tverd. Tela (Leningrad) **16**, 2036 (1974) [Sov. Phys. Solid State **16**, 1323 (1975)].

[3] B.A. Weinstein, Solid State Commun. **20**, 999 (1976).
[4] F. Widulle, T. Ruf, A. Göbel, E. Schönherr, and M. Cardona, Phys. Rev. Lett. **82**, 5281 (1999).
[5] A. Debernardi, Solid State Commun. **113**, 1 (2000).
[6] W.E. Bron, J. Kuhl, and B.K. Rhee, Phys. Rev. B **34**, 6961 (1986).
[7] F. Widulle, T.Ruf.E. Schönherr, and M. Cardona, Phys. Status Solidi B **215**, 131 (1999).
[8] A. Debernardi, Phys. Rev. B **57**, 12 847 (1998).
[9] S. Ushioda, J.D. McMullen, and M.J. Delaney, Phys. Rev. B **8**, 4634 (1973).
[10] T. Juhasz and W.E. Bron, Phys. Rev. Lett. **63**, 2385 (1989).
[11] P.G. Klemens, Phys. Rev. **148**, 845 (1966).
[12] J. Menéndez and M. Cardona, Phys. Rev. B **29**, 2051 (1984).
[13] M. Balkanski, R.F. Wallis, and E. Haro, Phys. Rev. B **28**, 1928 (1983).
[14] T.N. Zavaritskaya, A.V. Kvit, N.N. Mel'nik, and V.A. Karavanskii, Semiconductors **32**, 213 (1998).
[15] H.M. Perry and T.P. Dougherty, Phys. Rev. B **55**, 5778 (1997).
[16] H.J. Bakker, S. Hunsche, and H. Kurz, Rev. Mod. Phys. **70**, 523 (1998).
[17] G.A. Garrett, A.G. Rojo, A.K. Sood, J.F. Whitaker, and R. Merlin, Science **275**, 1638 (1997).
[18] A. Bartels, T. Dekorsky, and H. Kurz, Phys. Rev. Lett. **84**, 2981 (2000).
[19] B.A. Weinstein, J.B. Renucci, and M. Cardona, Solid State Commun. **12**, 473 (1973).
[20] T.E. Stevens, J. Hebling, J. Kuhl, and R. Merlin, Phys. Status Solidi B **215**, 81 (1999).