Near-forward Raman study of a phonon-polariton reinforcement regime in the Zn(Se,S) alloy

R. Hajj Hussein, O. Pagès, F. Firszt, A. Marasek, W. Paszkowicz, A. Maillard, L. Broch

To cite this version:


HAL Id: hal-01516065
https://hal.univ-lorraine.fr/hal-01516065
Submitted on 11 May 2017
Near-forward Raman study of a phonon-polariton reinforcement regime in the Zn(Se,S) alloy

R. Haj Hussein, O. Pagès, F. Firszt, A. Marasek, W. Paszkowicz, A. Maillard, and L. Broch

Citation: Journal of Applied Physics 116, 083511 (2014); doi: 10.1063/1.4893322
View online: http://dx.doi.org/10.1063/1.4893322
View Table of Contents: http://aip.scitation.org/toc/jap/116/8
Published by the American Institute of Physics
Near-forward Raman study of a phonon-polariton reinforcement regime in the Zn(Se,S) alloy

R. Hajj Hussein,1 O. Pagès,1,a) F. Firszt,2 A. Marasek,2 W. Paszkowicz,3 A. Maillard,4 and L. Broch1

1LCP-A2MC, Institut Jean Barriot, Université de Lorraine, 1 Bd. Arago, 57078 Metz, France
2Institute of Physics, N. Copernicus University, 87-100 Toruń, Poland
3Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Poland
4LMOPS, Université de Lorraine – Sup’lec, 2, rue Edouard Belin, 57070 Metz, France

(Received 25 June 2014; accepted 5 August 2014; published online 27 August 2014)

We investigate by near-forward Raman scattering a presumed reinforcement of the (A-C,B-C)-mixed phonon-polariton of a A1-xBxC zincblende alloy when entering its longitudinal optical-like (LO-like) regime near the Brillouin zone centre Γ, as predicted within the formalism of the linear dielectric response. A choice system to address such issue is ZnSe0.68S0.32 due to the moderate dispersion of its refractive index in the visible range, a sine qua non condition to bring the phonon-polariton insight near Γ. The LO-like reinforcement regime is actually accessed by using the 633.0 nm laser excitation, testified by the strong emergence of the (Zn-Se,Zn-S)-mixed phonon-polariton at ultimately small scattering angles. © 2014 AIP Publishing LLC.

I. INTRODUCTION

Due to the polarity of the chemical bonding in such an ionic crystal as a zincblende AB semiconductor compound, the long-wavelength (Γ-like, \( q \sim 0 \)) transverse optical (TO) phonon, corresponding to anti-phase displacement of the intercalated A-like and B-like fcc sublattices (mechanical character), is likely to be accompanied by a macroscopic electric field. The latter is transversal to the direction of propagation, thus identical in nature to that carried by a pure electromagnetic wave, namely a photon. Now, due to the quasi vertical “\( \omega \) vs. \( q \)” dispersion of a photon at the scale of the Brillouin zone, the electromagnetic character of a TO mode can only emerge very close to Γ. The concerned \( q \) values are of the order of one per ten thousands of the Brillouin zone size.2 At this limit, the electromagnetic and mechanical characters combine, conferring on a TO mode the status of a so-called phonon-polariton (PP). For certain \( q \) values, the PP might acquire a dominant electromagnetic character, thus propagating at lightlike speeds. This stimulates interest in view of ultrafast (phonon-like) signal processing at THz (phonon-like) frequencies.3

The “\( \omega \) vs. \( q \)” dispersion of PP’s propagating in the bulk of various AB zincblende compounds have been abundantly studied, both experimentally and theoretically.2,4–9 In a nutshell, it can be grasped within four asymptotic behaviors, i.e., two photon-like ones (\( \omega \)-related) and two phonon-like ones \( (q \)-related). For large \( q \) values, i.e., falling within few percent of the Brillouin zone size, as routinely accessible in a conventional backscattering Raman experiment (schematically operating in a “reflection mode,” see below), a transverse electric field cannot propagate at THz (phonon-like) frequencies. This is because the considered \( (\omega,q) \)-domain falls far away from the natural “\( \omega \) vs. \( q \)” dispersion of a photon (quasi vertical). In such so-called \( q_{\infty} \)-regime, a TO mode thus reduces to a purely mechanical oscillator (abbreviated PM-TO hereafter, deprived of electric field), whose frequency, noted \( \omega_{\mathrm{TO}} \), constitutes the first phonon-like asymptote, i.e., away from Γ. The frequency of the non-dispersive longitudinal optical (LO) mode, noted \( \omega_{\mathrm{LO}} \), larger than \( \omega_{\mathrm{TO}} \), defines the second phonon-like asymptote, near Γ then, taking into account that the TO and LO modes are degenerate strictly at Γ.11 Two remaining photon-like asymptotes determine limit PP-behaviors away from the (PM-TO)-LO resonance, as dictated by the static \( \varepsilon_0 \) (\( \omega \ll \omega_{\mathrm{TO}} \)) and high-frequency \( \varepsilon_\infty \) (\( \omega \gg \omega_{\mathrm{TO}} \)) relative dielectric constants of the crystal. The strong PP coupling occurs when the quasi vertical photon-like asymptotes cross the horizontal PM-TO phonon-like ones. This gives rise to an anticrossing, resulting in two distinct PP branches. The upper branch is phonon-like (LO) when \( q \rightarrow 0 \) and photon-like (\( \omega = q c e^{-1} \)) at \( q \gg \omega_{\mathrm{TO}} \), while the lower branch is photon-like (\( \omega = q c e^{-1} \)) at \( \omega \ll \omega_{\mathrm{TO}} \) and phonon-like in the \( q_{\infty} \)-regime (PM-TO). Note that the (PM-TO)-LO band is forbidden for the propagation of bulk PP’s, only surface PP’s can propagate therein.

An interesting question is how such PP picture modifies for a multi-oscillator system such as a AB\( _{1-x} \)C\( _x \) zincblende alloy (A standing indifferently for a cation or an anion)? Bao and Liang provided a pioneering theoretical insight into the “\( \omega \) vs. \( q \)” PP-dispersion of various AB\( _{1-x} \)C\( _x \) zincblende alloys.12,13 As a starting point they assumed a basic two-mode \( [1 \times (A-C), 1 \times (B-C)] \) PM-TO pattern behind the PP’s, as explained within the well-known modified-random-element-isodisplacement (MREI) model.14 Besides the lower (noted LP) and upper (noted UP) PP branches, assimilating to those of a pure compound as described above,2,4–9 an
intermediary (A-C, B-C)-mixed PP branch (noted MP, in abbreviation of medium phonon-polariton) was predicted by Bao and Liang. The latter MP branch is distinct in nature from the former (LP,UP) parent-like ones in that it exhibits an overall S-like shape governed by two phonon-like (horizontal) asymptotes only, i.e., the higher PM-TO frequency in the \( q_{\alpha} \)-regime, say the BC-like one, and the lower LO frequency near \( \Gamma \), the AC-like one then, with a photon-like regime in between approximately corresponding to the inflexion of the S-like branch.\(^{12,13}\) As such, its dispersion covers the gap between the natural A-C and B-C vibration frequencies, possibly a considerable one depending on the alloy.

An example of such “\( \omega \) vs. \( q \)” MREI-like (two PM-TO’s) PP-dispersion, concerning the particular ZnSe\(_{0.68} \)S\(_{0.32} \) zincblende alloy, of interest in this work (see below), is given in Fig. 1, to fix ideas. The whole picture is governed by the PM-TO frequencies of the two Zn-Se and Zn-S oscillators, taken at \( \sim 210 \) and \( \sim 285 \) cm\(^{-1} \), respectively (see below), from recent estimates by Vinogradov et al. (Ref. 15, see Fig. 3 therein). Besides, a basic rule is applied that the amount of oscillator strength available per bond at a given alloy composition scales as the corresponding bond fraction, i.e., as 0.68 for Zn-Se and as 0.32 for Zn-S for the considered alloy. The Zn-Se and Zn-S LO frequencies are accordingly noted \( \omega \), \( \theta \), and \( \theta_{\alpha} \), of interest in this work (see below), from recent estimates by Vinogradov et al. (Ref. 15, see Fig. 3 therein). Besides, a basic rule is applied that the amount of oscillator strength available per bond at a given alloy composition scales as the corresponding bond fraction, i.e., as 0.68 for Zn-Se and as 0.32 for Zn-S for the considered alloy. The Zn-Se and Zn-S LO frequencies are accordingly derived. Further detail concerning the method used to calculate the PP-dispersion and the input parameters needed to implement such calculation is given below, at the occasion of a more adequate (three PM-TO’s) description of the ZnSe\(_{0.68} \)S\(_{0.32} \) PP-dispersion.

We have refined the description of the “\( \omega \) vs. \( q \)” PP dispersion of an alloy beyond the MREI scheme at the occasion of a recent near-forward Raman study (schematically operating in a “transmission mode,” see below) of the Zn\(_{0.67} \)Be\(_{0.33} \)Se zincblende alloy, characterized by a three-mode \( \{1 \times \) (Zn-Se), \( 2 \times \) (Be-Se)\) PM-TO pattern in the \( q_{\alpha} \)-regime. Such three-mode pattern falls out of the scope of the MREI scheme, by construction. It was explained by introducing the phenomenological percolation model.\(^{16}\) In brief, this model distinguishes between the vibrations of the short (Be-Se) bonds depending on whether their local environment is more rich of one or the other (Zn-Se or Be-Se) species (1-bond→2-mode behavior).\(^{17}\) In this study, two intermediary (Zn-Se,Be-Se)-mixed MP’s were revealed, and not only one as predicted within the MREI scheme. Each MP relates to a particular Be-Se-like PM-TO in the \( q_{\alpha} \)-regime, and collapses with an S-like shape onto the LO immediately underneath near \( \Gamma \), consistently with the basic MREI trend (refer to Fig. 1). In particular, the lower MP, noted \( MP^- \), attracts attention, for two reasons. First, in contrast with the upper MP, noted \( MP^+ \), which remains confined within the upper doublet of PM-TO’s (Be-Se-like in this case), \( MP^- \) may exhibit a considerable dispersion (covering the gap between the Zn-Se and Be-Se vibration frequencies in this case), as discussed above within the MREI scheme. Second, as soon as entering the PP regime, \( MP^- \) becomes dominant over \( MP^+ \).\(^{16}\)

The \( q \)-dependence of the \( MP^+ \) Raman intensity constitutes per se an interesting issue. Though this mode has a basic TO character throughout its whole dispersion, we anticipate variations in its Raman activity depending on whether \( MP^- \) is more phonon-like, in reference to both asymptotic regimes, presumably corresponding to a large Raman activity, or more photon-like, in reference to the intermediary regime, in which the Raman activity is expected to be small-negligible. Based on our recent near-forward Raman study of Zn\(_{0.67} \)Be\(_{0.33} \)Se limited to the early stage of the PP regime (a moderate \( MP^- \) red-shift of \( \sim 15 \) cm\(^{-1} \) was detected, representing less than ten percent of the total \( MP^- \) dispersion), we already know that the initial \( q \)-induced softening of \( MP^- \) goes with a progressive collapse of this mode, the sign that \( MP^- \) progressively enters the intermediary photon-like regime.\(^{16}\) With further reduction in \( q \) the photon-like character should be lost at a certain stage, and near \( \Gamma \), where \( MP^- \) eventually assimilates to a LO,\(^{12,13,16}\) the Raman scattering should reactivate, in principle. Summarizing, when progressing towards \( \Gamma \), we expect that the initial (PM-TO → photon) collapse of \( MP^- \) should be relayed by a (photon → LO) reinforcement at a certain stage. This points to a specific PP feature of an alloy, yet unexplored, neither experimentally nor theoretically.

Interestingly, such a dependence of Raman efficiency in polaritons from matter-like to photon-like and again to matter-like has recently been observed for the LO Raman scattering mediated via exciton-polaritons in a pure compound.\(^{18}\) However, in the cited work the Raman efficiency increases in the strong coupling regime (more photon-like) and decreases when the polariton takes a dominant excitonic (matter-like) character. Basically, we expect the opposite “matter vs. photon” interplay for the Raman efficiency in our case of a TO-like Raman scattering by the lower-medium phonon-polaritons branch of an alloy.

In this work we tackle such issue both theoretically—within the formalism of the linear dielectric response, and experimentally—by applying the near-forward Raman scattering to the ZnSe\(_{0.68} \)S\(_{0.32} \) zincblende alloy. Due to large optical gaps of ZnSe (2.7 eV) and ZnS (3.6 eV),\(^{19}\) ZnSe\(_{0.68} \)S\(_{0.32} \) is transparent to visible laser lines, thus well-suited in view of a near-forward Raman study. Besides, the frequency gap

![Fig. 1. ZnSe\(_{0.68} \)S\(_{0.32} \) ‘\( \omega \) vs. \( q \)” PP dispersion calculated from Eq. (3) on the basis of a two-mode \( \{1 \times \) (Zn-Se), \( 2 \times \) (Be-Se)\) MREI-like description of the PM-TO’s (abbreviated TO) in the \( q_{\alpha} \)-regime, giving rise to a three-mode (lower-\( q \), medium-\( q \), upper-\( q \)-LP,UP) phonon-polariton pattern. The LO asymptotes near \( \Gamma \) (LO labeling) and the photon ones (thin lines) far beyond (a) and far below (b) the (PM-TO)-LO phonon resonances are specified, for reference purposes. A more refined three-mode \( \{1 \times \) (Zn-Se), \( 2 \times \) (Zn-S)\} description is given in Fig. 7.](image-url)
basically, our aim is to penetrate deep into the bold) and experimental (underlined) limits are emphasized in the reported

between the PM-TO’s of its Zn-Se and Zn-S constituting bonds is narrow (235–285 cm⁻¹, see below), with concomitant impact on the magnitude of the MP⁻ dispersion (refer to the MP branch in Fig. 1). This offers an opportunity to explore the MP⁻ dispersion in a different context than was earlier done with Zn₀.₆₇Be₀.₃₃Se, the latter alloy being characterized by a comparatively huge MP⁻ dispersion (250–450 cm⁻¹). Basically, our aim is to penetrate deep into the MP⁻ dispersion of ZnSe₀.₆₈S₀.₃₂ so as to address minimal q values likely to fall into the LO-regime of MP⁺, near Γ.

II. EXPERIMENT

Generally, the wavevector $\vec{q}$ of a TO mode (a PP one near Γ or the corresponding PM-TO one in the $q_\infty$-regime)

accessible in a Raman experiment is governed by the conservation rule $\vec{q} = \vec{k}_i - \vec{k}_s$ in which $\vec{k}_i$ and $\vec{k}_s$ are the wavevectors of the incident laser beam and of the scattered light, respectively, both taken inside the crystal, forming an angle θ therein. In a standard backscattering geometry $\vec{k}_i$ and $\vec{k}_s$ are (nearly) antiparallel ($θ \approx 180^\circ$), so that $q$ is maximum, falling deep into the $q_\infty$-regime. Minimum $q$ values, i.e., those likely to address the PP-regime, are achieved by taking $\vec{k}_i$ and $\vec{k}_s$ (nearly) parallel ($θ \approx 0^\circ$), using a non-standard near-forward Raman setup. From the above conservation rule,

$$q = c^{-1} \times \left\{ n^2(ω_i,x) \times ω_i^2 + n^2(ω_s,x) \times ω_s^2 - 2 \times n(ω_i,x) \times n(ω_s,x) \times ω_i \times ω_s \times \cos θ \right\}^{0.5}, \quad (1)$$

where $ω_i$ and $ω_s$ are the frequencies of the incident and scattered lights, respectively, and $n(ω_i,x)$ and $n(ω_s,x)$ the corresponding refractive indexes of the considered AB₁₋ₓCx alloy. If we refer to pure ZnSe and pure ZnS, the refractive index of ZnSe₁₋ₓSₓ is expected to decrease with the frequency in the visible range. Accordingly one cannot achieve $q=0$ (Γ) in practice. Indeed the minimum $q$ value, accessed in a perfect forward scattering experiment ($θ=0^\circ$), i.e., $q_{\text{min}}=|n(ω_i,x) \times ω_i - n(ω_s,x) \times ω_s|$, remains finite because the difference in frequencies is augmented by the difference in refractive indexes. Optimum conditions are thus reached by minimizing the dispersion of the refractive index around the used laser excitation. The alloy composition ($x=0.32$) as well as the laser excitation ($ω_i$) used, were selected in this spirit, as discussed below.

The ZnSe₀.₆₈S₀.₃₂ sample considered in this work was grown from the melt as a single crystal (cylinder, ~3 mm high and ~8 mm in diameter) by using the high-pressure Bridgman method (see detail, e.g., in Ref. 20). The selected alloy corresponds to the highest achievable S incorporation by the Bridgman method. This provides optimal conditions with respect to the dispersion of the refractive index, since the latter is larger for ZnSe than for ZnS in the visible range. In fact, the wavelength ($λ$) dependence of the ZnSe₀.₆₈S₀.₃₂ refractive index ($n$) measured by ellipsometry throughout the visible range, transposed into a wavenumber ($ω$) dependence in Fig. 2, can be accurately fitted to the Cauchy dispersion formula,

$$n(λ) = X + Y \times λ^2 \times 10^4 + Z \times λ^{-4} \times 10^9 \quad (2)$$

using ($X,Y,Z$) values of (3.1638 ± 0.0007, 1.2380 ± 0.0536, 14.0485 ± 0.1056), where $X$ is dimensionless, $Y$ and $Z$ are constants with units of nm² and nm⁴, respectively, and $λ$ is in nm. The minimum dispersion of the ZnSe₀.₆₈S₀.₃₂ refractive index is further achieved by shifting the Raman analysis to the less energetic end of the visible spectral range. We accordingly use the 633.0 nm line from a He-Ne laser to record the ZnSe₀.₆₈S₀.₃₂ near-forward Raman spectra, instead of the 514.5 nm and 488.0 nm Ar⁺ ones earlier used with Zn₀.₆₇Be₀.₃₃Se, notwithstanding its inferior Raman efficiency. Along the same line, the Stokes experiment ($ω_i > ω_s$) was preferred against the anti-Stokes one ($ω_i < ω_s$), not to mention that the Stokes process is, further, more efficient. The near-forward and backward Raman spectra are taken

![FIG. 2. Ellipsometry measurement of the wavenumber (ω) dependence of the refractive index (n) of the ZnSe₀.₆₈S₀.₃₂ alloy throughout the visible range. The local dispersion of the refractive index around the laser excitations 488.0, 514.5 and 633.0 nm are indicated by the corresponding 'n vs. ω' slopes, as schematically represented by double arrows.](image-url)
along the [110]-growth axis of the sample, corresponding to a nominal \((TO\text{-}allowed, LO\text{-}forbidden)\) geometry, after optical polishing of the opposite \((110)\) faces to optical quality until quasi parallelism was achieved.

### III. RESULTS AND DISCUSSION

Preliminary insight as to whether there is any chance to access experimentally the presumed \(LO\)-like \(MP^\text{-}\) reinforcement with \(\text{ZnSe}_{0.68}\text{S}_{0.32}\) in a near forward Raman scattering experiment using the 633.0 nm laser excitation is achieved by calculating the related multi-\(PP\) near-forward Raman cross section \((RCS)\) in its \((q,\theta)\)-dependence. For doing so we use the generic \(RSC\) expression established in Ref. 16 which we reproduce hereafter in its specific form applying to multi-\(PP\)’s propagating in the bulk of an alloy containing \(p\) oscillators (in reference to the multi \(PM\text{-}TO\)’s of the \(q_{\infty}\text{-regime}\) behind the \(PP\)’s),

\[
RCS(\omega, q, x) \sim \text{Im}\left\{ -[\varepsilon_\infty(\omega, x) - q^2 \times c^2 \times \omega^2]^{-1} \times \left[1 + \sum_p C_p^2(x) \times L_p(\omega, x)^2 \right] + \sum_p C_p^2(x) \times \omega^2_j \times \omega^2_j \times L_p(\omega, x)^2 \times S_{\infty}^{-1}(x) \times \varepsilon_{\infty,p}^{-1} \times \omega_p^{-2} \right\}. \tag{3}
\]

\(\varepsilon_\infty(\omega, x)\) is the relative dielectric function of the \(AB_1x\text{C}_x\) alloy taken in its classical form, including, on the one hand, the electronic contribution, \(\varepsilon_\infty(x)\), varying linearly with \(x\) between the parent values and, on the other hand, a summation over the \(p\) ionic oscillators present in the crystal, each represented by a damped Lorentzian resonance \(L_p(\omega, x) = \omega_p^2(x) \times \omega_p^2(x) \times \omega_p^2(x) \times \omega_p^2(x) \times \omega_p^2(\omega, x)^{-1}\) at the relevant \(PM\text{-}TO\) frequency \(\omega_p(x)\) in the \(q_{\infty}\text{-regime}\). The damping parameter \(\gamma_p(\omega, x)\), which determines the Raman linewidth, is sample-dependent. \(C_p(x)\) and \(S_{\infty}(x)\) are the \(p\)-related Faust-Henry coefficient and oscillator strength, monitoring the Raman intensity and the \((PM\text{-}TO)\text{-LO}\) band of oscillator \(p\), respectively. Both parameters scale linearly with the fraction of oscillator \(p\) in the crystal. The \((C_p, S_{\infty}, \omega_p, \varepsilon_{\infty,p})\) values of the pure \(\text{ZnSe}\) or \(\text{ZnS}\) compound related to oscillator \(p\) are \((-0.7, 2.92, 254.5\text{ cm}^{-1}, 5.75)\)\(^{16}\) and \((-0.45, 2.57, 2377.0\text{ cm}^{-1}, 5.20)\)–\(^{15}\) respectively. Remaining alloy-related input parameters are the number \(p\) of oscillators per alloy, the corresponding \(\omega_p(x)\) frequencies and the fractions \(f_p(x)\) of such oscillators at a given composition \(x\). Such \([p, \omega_p(x), f_p(x)]\) parameters refer to the \(q_{\infty}\text{-regime}\) and are thus directly accessible from a pure-\(TO\) backscattering Raman insight, or by infrared absorption.

Vinogradov et al. have revealed a well-resolved three-mode \([1 \times (\text{Zn-Se}), 2 \times (\text{Zn-S})]\) \(PM\text{-TO}\) pattern \((p=3)\) for \(\text{ZnSe}_{1-x}\text{S}_x\) in their recent exhaustive infrared study.\(^{15}\) The question as to whether the \(\text{Zn-S}\) doublet falls into the scope of the 1-bond\(\rightarrow\)2-mode percolation scheme, or not, will be debated elsewhere. For our present use, we may only retain that the two \(\text{Zn-S} \text{ PM-TO’s}\), presently labelled as \(TO_{\text{Zn-S.1}}\) and \(TO_{\text{Zn-S.2}}\) show up distinctly in the backscattering Raman spectrum of \(\text{ZnSe}_{0.68}\text{S}_{0.32}\), being characterized by comparable Raman intensities (a direct insight is given below). This means that the available \(\text{Zn-S}\) oscillator strength, which scales as the \(\text{Zn-S}\) bond fraction, equally shares between the two \(\text{Zn-S}\) sub-modes, leading to \(f_{\text{Zn-S.1}} = f_{\text{Zn-S.2}} = 0.16\). As for the unique \(\text{Zn-Se}\) mode, its oscillator strength directly scales as the \(\text{Zn-Se}\) bond fraction, so that \(f_{\text{Zn-Se}} = 0.68\). Besides, the three \([TO_{\text{Zn-Se}}, TO_{\text{Zn-S.1}}, TO_{\text{Zn-S.2}}]\) \(PM\text{-TO’s}\) emerge at the \(\omega_p(x)\) Raman frequencies of \((-210, 285, 303)\) cm\(^{-1}\), correspondingly.

The theoretical \(q\)-dependent near-forward multi-\(PP\) Raman lineshapes derived for \(\text{ZnSe}_{0.68}\text{S}_{0.32}\) via Eq. (3) using the above \([p, \omega_p(x), f_p(x)]\) input parameters are shown in Fig. 3, taking a uniform phonon damping of \(1\) cm\(^{-1}\), for optimum resolution of the individual features. In fact, instead of \(q\) we conveniently use the dimensionless parameter \(y = q \times c \times \omega_1^{-1}\), arbitrarily taking \(\omega_1\), the \(PM\text{-TO}\) frequency of the pure \(\text{Zn-Se}\) crystal in the \(q_{\infty}\text{-regime}\), for the change of variable. As anticipated, in the theoretical \(RCS(y)\) curves the initial \(MP^\text{-}\) collapse at large \(y\) values is relayed by a \(LO\)-like \(MP^\text{-}\) reinforcement at moderate-to-small \(y\) values (refer to the dotted box). Interestingly, a moderate penetration into the \(MP^\text{-}\) dispersion curve, not exceeding one third of the total dispersion (covering the \(LO_{\text{Zn-Se}} - TO_{\text{Zn-S.1}}\) band, see Fig. 3), seems sufficient to access the \(LO\)-like reinforcement regime. The crucial question is whether the latter regime can be accessed experimentally, or not. Basically this depends on the dispersion of the refractive index around the used laser excitation, as already discussed (see Sec. II). For a direct insight we indicate in front of a given theoretical \(MP^\text{-}\) peak in Fig. 3 (in reference to the dotted box therein), corresponding to a certain \(\omega = |\omega_1 - \omega_3|\) frequency at a certain \(y\) value, the relevant \(\theta\) angle for the used 633.0 nm laser excitation, as directly inferred from Eq. (1) via Eq. (2). As apparent in Fig. 3 the minimum accessible \(y\) value with the latter laser line, corresponding to \(\theta=0^\circ\), hopefully falls into the \(MP^\text{-}\) reinforcement regime. This is encouraging in view of a possible detection by near-forward Raman scattering using the 633.0 nm excitation.

We turn to experiment. For reference purpose, we show at the top of Fig. 4 (thick spectrum) the nominally pure-\(TO\) Raman spectrum taken in a backscattering geometry along the [110]-growth crystal axis using the most energetic laser line at hand, namely the 488.0 nm one. This line is more absorbed than the 633.0 nm one in our sample. The spurious near-forward Raman signal due to reflection of the incident laser at the back surface of the (quasi) transparent sample is thus minimized. Along with the nominal triplet \((TO_{\text{Zn-Se}}, TO_{\text{Zn-S.1}}, TO_{\text{Zn-S.2}})\) of \(PM\text{-TO’s}\) described above, several theoretically forbidden features are observed, such as the \(LO_{\text{Zn-Se}}\) and \(LO_{\text{Zn-S}}\) modes at \(~245\) and \(~322\) cm\(^{-1}\), respectively, and also the so-called \(A\)-band around 165 cm\(^{-1}\), reflecting the acoustical two-phonon density of states. We mention that the emergence of theoretically forbidden optic modes or acoustic bands is a common feature of alloys, due to a partial breaking of the wavevector conservation rule \([\text{i.e., Eq. (1)}]\) by the alloy disorder. As for the minor \(LO_{\text{Zn-S}}\) mode of the \(\text{Zn-S}\) doublet, this remains screened by the nearby \(TO_{\text{Zn-S.1}}\) and \(TO_{\text{Zn-S.2}}\) \(PM\text{-TO’s}\) (see Fig. 3). Satisfactory contour modeling of the nominal three-mode \(PM\text{-TO}\) pattern (top thin curve of Fig. 4) is achieved both in the \(\text{Zn-Se}\) (not shown)
and Zn-S (thin line) spectral ranges by injecting the selection of input parameters specified above into the asymptotic form of Eq. (3) valid in the $q_1$-regime (backscattering-like), in fact reduced to its second term, taking the same $c_p(x)$ value of 24 cm$^{-1}$ for the two Zn-S sub-modes.

Now, we change the Raman setup from backscattering to near-forward scattering. A representative series of near-forward Raman spectra taken at different $\theta$ angles with respect to the [110]-growth axis of the ZnSe$_{0.68}$S$_{0.32}$ ingot using the 633.0 nm laser line are shown in Fig. 4 (thin spectra). The intensities, normalized to the $\theta$-insensitive A-band, are directly comparable. In each spectrum the near-forward Raman signal ($MP^-$-labeling in Figs. 3 and 4) is partially obscured by the $\theta$-insensitive backscattering one ($TO^-$ labeling in abbreviation of $PM$-$TO$) generated after reflection of the laser beam at the top surface (detector side) of the sample. As $MP^+$ is located within the Zn-S doublet of parasitical $PM$-$TO$’s (see Fig. 3), it remains partially obscured at any angle. The best resolved $PP$ feature is $MP^-$, because it falls outside the doublet (refer to the dotted box in Fig. 3). Its $(q,\theta)$-dependence is discussed in detail hereafter.

The relevant $\theta$ angle for each near-forward Raman spectrum of Fig. 4 is determined via a combined adjustment, by using Eq. (3), of both the frequency and the total area (Raman intensity) of the experimental $MP^-$ Raman peak (schematically indicated by arrows). A reliable insight into the latter peak, and more generally into the whole $PP$ signal, i.e., including both $MP^-$ and $MP^+$, requires to remove the parasitical contribution from the backscattering contribution in the spectral range of interest. This is achieved by subtracting to each raw near-forward Raman spectrum (numbered “N”) in Fig. 4, the upper spectrum of the series (numbered “2”), corresponding to the largest reported $\theta$ angle. The resulting series of (“N–2”) $PP$-like difference Raman spectra is shown in Fig. 5. Note that the “1–2” difference spectrum (upper curve) is flat. This indicates that the near-forward Raman spectrum numbered “2” assimilates with the nominal backscattering one, in reference to the upper-thick curve of Fig. 4, even though the analogy between the two spectra is not so obvious. This is due to a difference between the $\gamma_p(x)$ values in the backward ($\sim 24$ cm$^{-1}$, see above) and near-forward (roughly double, see below) scattering geometries.

The best-adjusted $PP$ theoretical Raman lineshapes (thin lines) obtained via Eq. (3) by using the input parameters specified above, are superimposed onto the corresponding $PP$ difference Raman spectra in Fig. 5—and also in Fig. 4 in the particular case of the smallest achievable $\theta$ angle experimentally, for comparison. Globally, the agreement is rather...
fair, especially if we realize that only one adjustable parameter, i.e., the angle $\theta$, governs both the Raman frequencies (indicated by arrows in Fig. 5) and the Raman intensities of both $MP^-$ and $MP^+$. The only remaining adjustable parameter is the phonon damping $\gamma_\nu(x)$, taken identical for both modes. The relevant $\theta$ and $\gamma_\nu(x)$ values per near-forward Raman spectrum are indicated in Fig. 5 (and also in Fig. 4 regarding $\theta$).

Basically, as long as $\theta$ remains larger than $\sim 2.20^\circ$, the near-forward Raman signal of ZnSe$_{0.68}$S$_{0.32}$ approximates to the backscattering one ($\theta \sim 180^\circ$) and remains stable, as already discussed. Below this critical angle, the multi-TO’s enter their PP-regime, signed by a red-shift of $MP^-$ (see arrows in Figs. 4 and 5). Note that the minimum achievable $\theta$ angle remains finite ($\sim 0.32^\circ$), meaning that the near-forward Raman study cannot be fully developed in practice. This, we attribute to slight $\vec{K}$-disorientation inside the crystal due to inherent defects in an alloy. Nevertheless, the accessible $\theta$-domain suffices to reach the LO-like reinforcement regime ($\theta$: $0.60^\circ$--$0.32^\circ$) beyond the initial collapse regime ($\theta$: $3.00^\circ$--$1.20^\circ$), testified by the development of $MP^-$ into a sharp and intense feature at near-normal incidences. An interesting trend regarding $\gamma_\nu(x)$, is that it reduces dramatically with $\theta$. A maximum value of $\sim 48$ cm$^{-1}$ is detected just when departing from the backscattering regime ($\theta = 2.20^\circ$), being roughly reduced by half in the collapse regime, and again roughly by half when penetrating the reinforcement regime, with concomitant impact on the $MP^-$ lifetime (correspondingly increased).

Now, we focus on the $MP^-$ Raman intensity, of central interest in this work. We display in Fig. 6 the experimental (symbols) and theoretical (thin line) ($\nu, \theta$)-dependencies of the $MP^-$ Raman intensities. The reference Raman intensity of the $TO_{2\nu+5}$ mode observed in the backscattering geometry (in reference to spectrum “0” of Fig. 4), from which the $MP^-$ proceeds, is arbitrarily normalized to unity, and also the Raman intensity of the corresponding theoretical feature, for a straightforward comparison of the two data sets. Experimentally, the $MP^-$ Raman intensities are estimated from the (“N – 2”) PP-like difference Raman spectra reported in Fig. 5, after subtraction of the nearby $MP^+$ and $LO_{2\nu-5}^-$ modes, and subsequent integration of the remaining $MP^-$ signal. The experimental data are spoiit by a fixed error bar representing slight differences in the final estimate of the $MP^-$ Raman intensity depending on the option used to remove the nearby $MP^+$ and $LO_{2\nu-5}^-$ features (i.e., by using Lorentzian functions, Gaussian functions or a combination of both). As for the theoretical $MP^-$ Raman intensities, these were obtained by re-calculating the PP Raman lineshapes at the relevant $\theta$ angles by using a phonon damping sufficiently small to generate well-separated $MP^-$ and $MP^+$ features—the remaining input parameters being otherwise kept constants and by performing a selective curve-fitting of the distinct $MP^-$ lines (using a Lorentzian function).

When $\theta$ reduces the theoretical trend in Fig. 6 (and also within the hatched box in Fig. 3), corresponding to a dramatic collapse of the $MP^-$ mode until quasi total extinction, relayed by a strong reinforcement at the approach of the near-normal incidence, is apparent in the experimental data as well, as ideally expected. Only, the latter data generally overestimate the theoretical estimates, i.e., by 10–20%. This might relate to an intrinsic inability in our theoretical approach to account for observed asymmetries of the experimental PP Raman lineshapes (as clearly apparent for most $\theta$ values in Fig. 5).

We have checked that the LO-like reinforcement regime of $MP^-$ is likewise accessible with the alternative ZnSe$_{0.78}$S$_{0.22}$ alloy (not shown), corresponding to a smaller S content, meaning that the trend is reproducible. Nevertheless, the emergence of $MP^-$ at the minimum accessible $\theta$ angle with the latter alloy is less pronounced than with the present ZnSe$_{0.68}$S$_{0.32}$ alloy, as expected due to the less favorable dispersion of the refractive index (see Sec. II). In contrast, a similar near-forward Raman study using the 633.0 nm laser excitation performed with the Zn$_{0.67}$Be$_{0.33}$Se alloy, earlier studied in Ref. 16, just falls short of engaging the $MP^-$ reinforcement regime, due to an even less favorable dispersion of the refractive index.

Last, we discuss briefly the Zn-Se signal. At first sight the latter remains $\theta$-insensitive, pinned by a Fano interference with the $A$-band nearby (a characteristic antiresonance is marked by an asterisk in Fig. 4), as earlier discussed for Zn$_{0.67}$Be$_{0.33}$Se. The dramatic weakening of the near-forward Zn-Se signal with respect to the backscattering one (divided by $\sim 5$, see Fig. 4) is attributed to a reinforcement of the Fano interference that occurs when the Zn-Se mode

---

**FIG. 6.** Comparison between the theoretical [thin line, derived from Eq. (3)] and experimental (symbols) $MP^-$ Raman intensities depending on ($\nu, \theta$). The experimental data are spoilt by error bars representing a variation in the estimate of the $MP^-$ Raman intensity depending on the procedure used to remove the $MP^+$ and $LO_{2\nu-5}^-$ features (i.e., by using Lorentzian functions, Gaussian functions or a combination of both) from the PP-like difference Raman spectra reported in Fig. 5, prior contour modeling of the remaining experimental $MP^-$ signal. The Raman intensities of the reference experimental and theoretical $TO_{2\nu+5}$ signals, from which $MP^-$ proceeds, are arbitrarily normalized to unity, for a straightforward comparison of the two data sets.
FIG. 7. Comparison between the theoretical and experimental ‘α vs. q’ multi-PP dispersions of the three-mode [1 × (Zn-Se), 2 × (Zn-S)] ZnSe₀.₆₈S₀.₃₂ alloy, as obtained via Eq. (3) (thick lines) and by near-forward Raman scattering (symbols, with error bars representing the Raman line-shapes in their (q, θ)-dependence within the formalism of the linear dielectric response.

IV. CONCLUSION

Summarizing, we perform a near-forward Raman study of the three-mode [1 × (Zn-Se), 2 × (Zn-S)] ZnSe₀.₆₈S₀.₃₂ alloy in search of the presumed LO-like reinforcement of the (Zn-Se-Zn-S)-mixed MP near θ. The laser excitation as well as the alloy compositions were selected so as to minimize the degree of the refractive index, a prerequisite to penetrate deep into the MP− dispersion in view to address the vicinity of θ. The LO-regime is successfully accessed, as evidenced by the development of MP− into a giant feature at ultimately small scattering angles, solving the raised issue in the positive sense. The discussion is supported by a contour modeling of the ZnSe₀.₆₈S₀.₃₂ multi-PP near-forward Raman lineshapes in their (q, θ)-dependence within the formalism of the linear dielectric response.

ACKNOWLEDGMENTS

We would like to thank P. Franchetti and J.-P. Decruppe for technical assistance in the Raman measurements, C. Jobart for sample preparation, and A. V. Postnikov for useful discussions and careful reading of the manuscript. This work has been supported by the “Fonds Européens de Développement Régional” of Region Lorraine (FEDER Project No. 34619).

3N. S. Stoyanov et al., Nature Mater. 1, 95 (2002).
10In contrast with the TO-like electric field, the LO-like electric field suffers no q-restriction, and remains invariant (non-dispersive) in between θ and the ωα− regime. Therefore at the latter limit the effective force constant of the LO mode is reinforced by a Colombian contribution with respect to the purely-mechanical force constant of the PM-TO mode, meaning that ωLO > ωTO.
11For a given optical mode at θ, one may as well consider that the wavevector, null in fact, is oriented along the atom displacement (LO) or perpendic-