Pressure-Raman study of resonant TO(Γ)–two-phonon decay processes in ZnS: Comparison of three isotope compositions

R. E. Tallman[1], **J. Serrano**[2], **A. Cantarero**[3], **N. Garro**[3], **R. Lauck**[2], **T. M. Ritter**[4], **B. A. Weinstein**[*, 1], and **M. Cardona**[2]

[1] Department of Physics, SUNY at Buffalo, NY 14260-1500, USA
[2] Max Plank Institut für Festkörperforschung, 70569 Stutgart, Germany
[3] Institut de Ciencia dels Materials, Universtitat de Valencia, E-46071 Valencia, Spain
[4] Department of Chemistry and Physics,UNC Pembroke, North Carolina 28372, USA

Pressure-Raman studies (to 15 GPa, at 300 K and 16 K) are reported on $^{64}Zn^{34}S$, $^{68}Zn^{32}S$, and natural ZnS to compare the effects of resonant 3-phonon mixing on the TO(Γ) phonons for the different isotope compositions. Under pressure the TO(Γ) Raman profiles exhibit several distinct features, and a sharp Lorentzian TO(Γ) peak eventually emerges at a threshold pressure P_{Th} that differs for each isotope composition. These effects are due to resonant mixing of the TO(Γ) phonon with TA + LA combination modes. Calculations based on a bond-charge model and perturbation theory reproduce the observed pressure variations in the shape and the width of the TO(Γ) peaks. It is shown that these changes relate to singularities in the TA + LA density of states. Mass scaling of the TO(Γ) and TA + LA modes explains the isotope effect on P_{Th}, and leads to the estimate $\gamma_{LA(W)} \sim 1.2$.

1 Introduction

Anharmonic effects in semiconductors can usually be understood within the quasiparticle approximation in which the spectral function is represented by a Lorentzian with a frequency independent complex self energy [1]. However, this quasiparticle approach must be modified whenever accidental degeneracies occur between quasiharmonic phonons and singularities in the two-phonon density of states (DOS). Prior work has found that the line-shapes of the TO(Γ) Raman peaks in GaP, [2, 3] CuCl, [4, 5] and ZnS [6, 7] are profoundly altered by resonant mixing between the TO(Γ) mode and Brillouin Zone boundary (ZB) TA + LA combinations. In fact, this mixing is sufficiently large in CuCl and ZnS at room temperature (RT) and 1 atm. pressure, that it is difficult to define the TO(Γ) normal mode frequency. Similar anharmonic interactions strongly modify the E_2^{high} and A_1^{TO} modes in wurtzite-structure ZnO [8]. The reader is referred to the review by M. Cardona in the present Proceedings for a survey of these and related effects.

The strengths of resonant anharmonic processes are sensitive to changes in both applied pressure and isotope composition, which can tune the degeneracy of the interacting modes *via* the different pressure and/or mass dependences of their frequencies. In previous work on ZnS, the authors have used either the isotope effect (at 1 atm.) or applied pressure (in $^{68}Zn^{32}S$) to explore the impact of the TO(Γ) $\Leftrightarrow$ TA + LA interaction on the TO(Γ) Raman line-shape [6, 7]. Here, we present pressure-Raman results on three different isotopic compositions – natural ZnS, $^{64}Zn^{34}S$, and $^{68}Zn^{32}S$. The measurements are analyzed using bond-charge-model (BCM) calculations of the DOS. Our findings underscore the shortfalls in

* Corresponding author: e-mail: phyberni@acsu.buffalo.edu

treatments of the optical phonons as Lorentzians with frequency independent widths and anharmonic shifts in several common semiconductors.

2 Experimental details

High quality bulk crystals of cubic ZnS were grown for this study at temperatures below 800 °C by chemical vapor transport using an iodine as transparent medium and pre-purified ^{68}Zn, ^{64}Zn, ^{nat}Zn (M_{av} of 65.4), ^{34}S, and ^{nat}S (M_{av} of 32.1) starting materials [7, 9]. Specimens for our high pressure experiments were prepared by cleaving under acetone and selecting unoriented crystals of $\sim 70 \times 70 \times 30 \ \mu m^3$ size. The 300 K and 16 K diamond-anvil cell (DAC) measurements reported here employ alcohol (4:1 methanol:ethanol) and He pressure media, respectively, with Inconel gaskets, and pressures determined via the standard Ruby method. Raman spectra are recorded as a function of applied pressures $P \leq 15$ GPa using a 1m double monochromator with multichannel or photomultiplier detection. The spectra are excited by ~ 20 mW 514.5 nm Ar-ion laser-light focused to a $\sim 20 \ \mu m$ diameter spot on the sample inside the DAC. Detailed procedures are described elsewhere [10].

3 Results and discussion

The Raman spectra of ^{68}Zn^{32}S, ^{64}Zn^{34}S, and natural ZnS recorded at several different pressures and room temperature in the frequency region of the TO(Γ) and LO(Γ) phonons are shown in the (a)-panels of Figs. 1, 2, and 3, respectively. Each spectrum is normalized to the intensity of the LO(Γ) peak. It is apparent that the pressure-induced spectral changes are qualitatively similar for the three isotopic compositions. The LO(Γ) peaks exhibit a standard Lorentzian shape and pressure response: They are intense (due to E_0-gap Fröhlich enhancement), relatively narrow (slit-deconvoluted FWHM $\sim 1 - 2$ cm^{-1} at 300 K), and shift with pressure to higher energy at a rate conforming to the ionicity trends in II–VI materials [1].

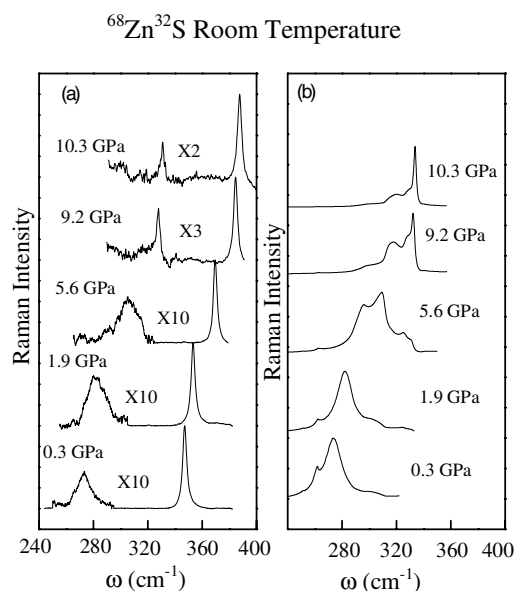**Fig. 1** (a) Raman spectra of ^{68}Z^{32}S at 300 K and several pressures measured without polarization in the region of the TO(Γ) and LO(Γ) phonons. (b) Theoretical TO(Γ) Raman line-shapes obtained for the same conditions *via* a BCM[14] calculation, with adjustments as explained in the text.
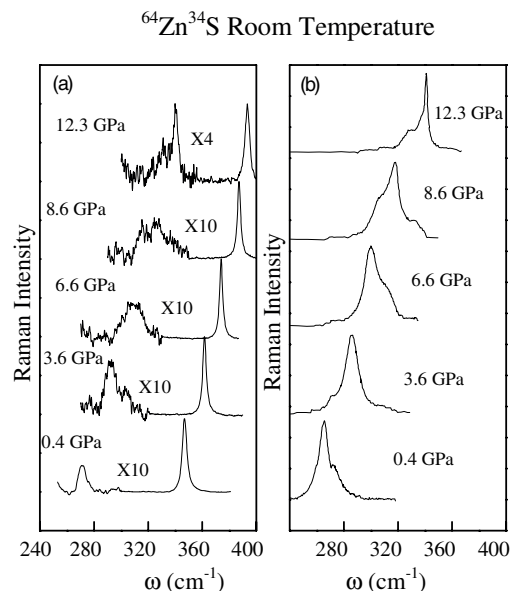
Fig. 2 (a) Effects of pressure on the measured TO(Γ) and LO(Γ) Raman spectra at 300K in ^{64}Zn^{34}S, and (b) corresponding calculated line-shapes, as in Fig. 1.
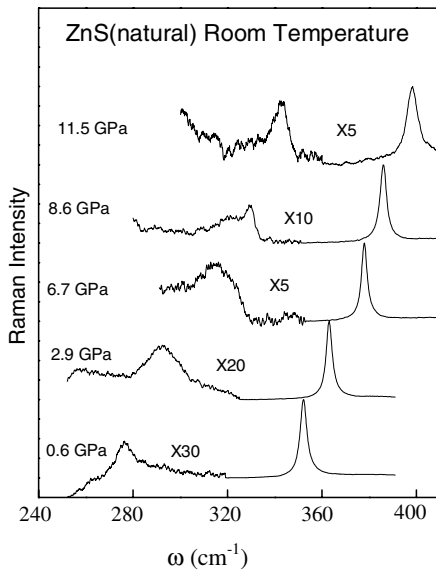
Fig. 3 Effects of pressure on the measured TO(Γ) and LO(Γ) Raman spectra at 300 K in natural ZnS, as in Fig. 1(a) above.

In contrast, the TO(Γ) peaks exhibit unconventional behavior. The scattering in the TO(Γ) region at 1 atm. and low pressure is relatively weak and broad (FWHM ~8–15 cm^{-1} at 300 K). With increasing pressure the line-shape changes, broadening (by as much as a factor of 2) and then narrowing as new features appear to shift through the region, until a sharp peak (FWHM similar to LO(Γ); intensity ~1/4 LO(Γ)) emerges on the high energy side of the TO(Γ) line-shape. The threshold pressures P_{Th} for the appearance of this peak are 7.3 ± 0.5 GPa in $^{68}Zn^{32}S$, 8.5 ± 0.5 GPa in natural ZnS, and 11.5 ± 0.5 GPa in $^{64}Zn^{34}S$.

The line-shape changes in the TO(Γ) peak increase the uncertainty in tracking its position *vs* pressure. However, the upward pressure-shift of the TO(Γ) peak is clearly more rapid than for LO(Γ) (~30% more rapid), and hence, as in most binary semiconductors, compression decreases the transverse effective charge. Table 1 gives the coefficients of the best quadratic fits to the measured pressure dependences of the LO(Γ) and TO(Γ) peak frequencies. The Grüneisen parameters γ for these phonon modes are computed using bulk modulus values of 76.9 GPa [11] and 78.2 GPa [12] for ZnS at room and cryogenic temperatures, respectively. The obtained γ's agree well with prior findings and with trends in the Zn-chalcogenides [1].

The pressure induced changes in the line-shape of the TO(Γ) Raman peak can be explained by considering the interaction of the bare (i.e., quasiharmonic) TO(Γ) mode with the continuum of TA($\mp q$) + LA($\pm q$) combination modes, which has several distinct van Hove singularities at frequencies close to

Table 1 Summary of best-fit pressure coefficients, defined by $\omega(P) = a + bP + cP^2$, with P in GPa, for the LO(Γ) and TO(Γ) phonons in the three isotopic varieties of ZnS measured in this work and in Ref. [7].

		$^{68}Zn^{32}S$		$^{64}Zn^{34}S$		natural ZnS	
		LO	TO	LO	TO	LO	TO
a (cm^{-1})	RT	346 ± 1	272 ± 3	344 ± 1	270 ± 3	350 ± 1	274 ± 3
	16 K	350.6 ± 0.4	275.6 ± 1				
b (cm^{-1}/GPa)	RT	4.7 ± 0.5	7.6 ± 1	5.4 ± 0.5	6.1 ± 1	4.9 ± 0.5	7.4 ± 1
	16 K	4.3 ± 0.4	6.1 ± 0.6				
c (cm^{-1}/GPa^2)	RT	–0.05 ± 0.03	–0.15 ± .15	–0.10 ± 0.05	–0.02 ± 0.05	–0.06 ± 0.03	–0.1 ± 0.1
	16 K	–0.04 ± 0.02	–0.08 ± 0.04				
$\gamma = -\dfrac{\partial \ln \omega}{\partial \ln V}$	RT	1.04 ± 0.12	2.16 ± 0.3	1.21 ± 0.12	1.74 ± 0.3	1.08 ± 0.12	2.08 ± 0.3
	16 K	0.96 ± 0.1	1.73 ± 0.2				

TO(Γ). The 3-phonon anharmonic interaction TO(Γ) $\Leftrightarrow$ TA($\mp q$) + LA($\pm q$) can be treated theoretically as a Fermi resonance. In thermal equilibrium, one obtains frequency dependent imaginary and real parts of the phonon self energy, given to lowest order in perturbation theory by [2, 13],

$$\Gamma(\omega) = |V_3|^2 \, \rho_+^{(2)}(\omega) \, [1 + n(\omega_1) + n(\omega_2)] \quad \text{and} \quad \Delta(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\omega' \Gamma(\omega')}{(\omega'^2 - \omega^2)} \, d\omega' \, , \tag{1}$$

respectively. Here, V_3 is an effective 3-phonon coupling strength, $\rho_+^{(2)}(\omega = \omega_1 + \omega_2)$ is the 2-phonon density of states (DOS) for TA($\mp q$) + LA($\pm q$) combination modes, and n(ω_i) are Bose–Einstein factors. The standard Lorentzian line-shape, where the width Γ (FWHM) and anharmonic shift Δ are independent of the frequency ω, must now be replaced by

$$I(\omega) \propto \frac{\Gamma(\omega)/2}{[\omega - \omega_0 - \Delta(\omega)]^2 + [\Gamma(\omega)/2]^2} \, . \tag{2}$$

Hence, one expects the line-shape to exhibit structure near distinct singularites in $\rho_+^{(2)}(\omega)$.

Figures 1(b) and 2(b) present calculated results for the TO(Γ) Raman line-shapes of ^{68}Zn^{32}S and ^{64}Zn^{34}S at pressures coinciding with the measured spectra ((a)-panels) for each sample. These theoretical line-shapes are obtained by evaluating Eqs. (1) and (2), with the 2-phonon D0S $\rho_+^{(2)}(\omega)$ computed using the adiabatic bond-charge model of Ref. [14], adjusted at 1 atm to match the existing ZnS neutron scattering data [15], and shifted to higher pressures according to the values of the Grüneisen constants found in prior two-phonon pressure-Raman experiments on ZnS and similar materials [1]. We see that the calculations give a reasonable semi-quantitative account of the observed changes in the TO(Γ) line-shapes. A number of corresponding features can be identified at similar pressures in the measured and calculated spectra, although differences in relative strength are apparent (e.g., see the 9.2 GPa ^{68}Zn^{32}S spectra, and the 8.6 GPa ^{64}Zn^{34}S spectra.) This is probably the best level of agreement that can be expected given the frequency independent coupling strength V_3 employed in the present analysis. In particular, the emergence of the sharp unrenormalized TO(Γ) peak at a threshold pressure P_{Th} that is ~30 kbar higher in ^{64}Zn^{34}S than in ^{68}Zn^{32}S is predicted.

Our calculated result for the DOS of 2-phonon summation modes in the region of the TO(Γ) and LO(Γ) phonons in ^{68}Zn^{32}S is displayed in Fig. 4. The lower arrows assign the significant van Hove singularities, and the upper arrows show how the TO(Γ) Raman peak shifts with pressure in relation to these singularities. The reason for the emergence of the sharp unrenormalized TO(Γ) peak at high pressure is quite clear from this figure. The shift of the TO(Γ) phonon to higher energy with pressure is more rapid than the shifts of the TA + LA modes, which are affected by the softening of the ZB TA phonons [1]. Consequently, above some threshold pressure, the TO(Γ) frequency must emerge into the density of states gap between the TA + LA and the TA + TO (also 2LA) combination bands. According to Eqs. (1) and (2), the TO(Γ) peak should then sharpen substantially, and a more standard Lorentzian line-shape should be established. This is the observed behavior for all three isotopic compositions (see Figs. 1(a), 2(a), and 3).

The isotope dependence of the threshold pressures results from the mass scaling of the mode frequencies – essentially $\propto M_{\text{Zn}}^{-1/2}$ for the ZB TA and LA phonons, and $\propto M_{\text{red}}^{-1/2}$ for the TO(Γ) phonon. The Fig. 4 inset plots the observed P_{Th} values in our samples vs the corresponding calculated results for the separation at 1 atm between the TO(Γ) frequency and the strong DOS maximum at (TA$_2$ + LA)$_W$, (i.e., combinations of phonons from the upper TA and the LA branches near the ZB W-point). The 1 atm frequencies for the different isotope compositions are again obtained using the adjusted BCM [7, 14]. Assuming no isotope effect on the pressure coefficients, one can estimate the Grüneisen constant for LA(W) (which is difficult to measure directly). From the slope of the fitted line through the origin in the Fig. 4 inset, and the established pressure shifts of TO(Γ) and TA(W) (similar to that for TA(K)) [1], we obtain $\gamma_{\text{LA(W)}} \approx 1.2$. This is in line with other estimates for ZnS and similar materials. [See the paper by M. Cardona in these Proceedings.]

The relationship between the pressure-induced changes in line-width of the TO(Γ) Raman peak and the singularities in the TA + LA DOS is more easily seen when thermal broadening is absent. Figure 5
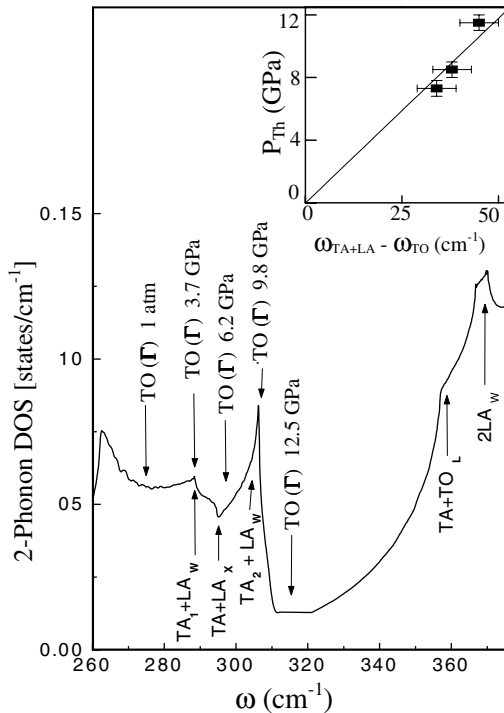
Fig. 4 Theoretical DOS at 1 atm for the summation modes that overlap the TO(Γ) and LO(Γ) peaks in $^{68}Zn^{32}S$ [after Ref. 7]; results computed using a BCM and adjusted to fit 1 atm neutron scattering data. Arrows mark important DOS singularities, and the TO(Γ) frequency at several pressures. Inset plots observed P_{Th} values (emergence pressures for bare TO(Γ) peaks) against the 1 atm separation between TO(Γ) and the W-point $TA_2 + LA$ singularity for the different isotope compositions.
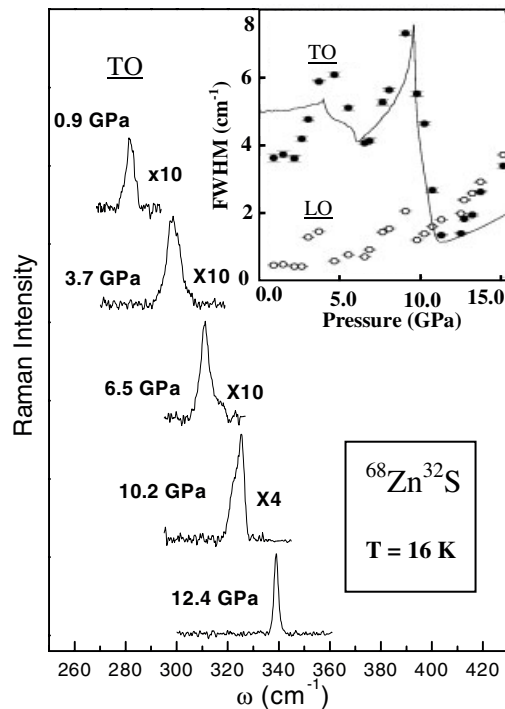
Fig. 5 Measured TO(Γ) Raman peak in $^{68}Z^{32}S$ recorded without polarization at 16 K and several pressures. Inset shows the observed pressure dependence of the TO(Γ) line-width (slit-deconvoluted FWHM) compared to the TA + LA DOS represented as $\rho_+^{(2)}[\omega_{TO(\Gamma)}(P)]$ (solid curve). See discussion in text. Data for the LO(Γ) line-width (spectra unshown) are also given.

shows results for the TO(Γ) Raman peak in $^{68}Zn^{32}S$ measured at 16 K and several different pressures. In the inset, the observed line-widths at this temperature (FWHM corrected for the 1.1 cm^{-1} slit resolution) of both the TO(Γ) and the LO(Γ) peaks are plotted over the full pressure range studied (0–15 GPa). The solid curve is $\rho_+^{(2)}(\omega_1(P) + \omega_2(P) = \omega_{TO(\Gamma)}(P))$, i.e., the calculated two-phonon DOS in Fig. 4 evaluated at $\omega_{TO(\Gamma)}(P)$ for each pressure. As expected from the theory (Eqs. (1)), there is a close correspondence between the variations in the TO(Γ) peak-width and the structure in the two-phonon DOS. Likewise, the gradual increase with pressure in the FWHM of the LO(Γ) peak follows the shape of the TA + TO edge (350–390 cm^{-1}) in the two-phonon DOS. These correspondences are strong evidence in support of our interpretation.

4 Summary

At ambient pressure the TO(Γ) Raman peak in cubic ZnS is anomalously broad and weak compared to the LO(Γ) peak. This effect arises from the resonant anharmonic mixing of the TO(Γ) mode with a co-energetic band of TA + LA combination modes. In the present work, a comparative study of the influence of pressure (applied at 300 K and 16 K up to 15 GPa) on this mixing has been carried out for three isotope compositions: $^{68}Zn^{32}S$, $^{64}Zn^{34}S$, and natural ZnS. The TO(Γ) Raman profiles undergo qualitatively similar changes in the three samples, but at different pressures, with the eventual emergence at

high pressures of a sharp unrenormalized TO(Γ) peak. Line-shape calculations based on a perturbation treatment of the TO(Γ) $\Leftrightarrow$ TA + LA mixing, and employing an adjusted BCM for the 2-phonon DOS, give a reasonable account of the pressure effects. It is shown that the changes in line-shape and line-width are related to tuning of the TO(Γ) frequency through prominent singularities in the TA + LA DOS, and that the different threshold pressures for emergence of the bare TO(Γ) peak are a direct result of the mass-scaling of phonon frequencies with isotope composition. These results in the ZnS system, together with comparable findings in similar I–VII and II–VI compounds, show that the simple Lorentzian description of optical phonon spectra breaks down in a number of important cases.

References

[1] B. A. Weinstein and R. Zallen, in: Light Scattering in Solids, edited by M. Cardona and G. Güntherodt (Springer, Berlin, 1984), Vol. IV, p. 463.

[2] B. A. Weinstein, Solid State Commun. **20**, 999 (1976).

[3] F. Widulle, T. Ruf, A. Gobel, E. Schonherr, and M. Cardona, Phys. Rev. Lett. **82**, 5281 (1999).

[4] M. Krauzman, R. M. Pick, H. Poulet, G. Hamel, and B. Prevot, Phys. Rev. Lett. **33**, 528 (1974).

[5] C. Ulrich, A. Gobel, K. Syassen, and M. Cardona, Phys. Rev. Lett. **82**, 351 (1999).

[6] R. Tallman, T. M. Ritter, B. A. Weinstein, A. Cantarero, J. Serrano, R. Lauck, and M. Cardona, phys. stat. sol. (b) **241**(3), 491 (2004).

[7] J. Serrano, A. Cantarero, M. Cardona, N. Garro, R. Lauck, R. E. Tallman, T. M. Ritter, and B. A. Weinstein, Phys. Rev. B **69**, 014301 (2004).

[8] J. Serrano, A. H. Romero, F. J. Manjon, R. Lauck, M. Cardona, and A. Rubio, Phys. Rev. B **69**, 094306 (2004).

[9] R. Lauck et. al., to be published.

[10] U. D. Venkateswaran, L. J. Cui, B. A. Weinstein, and F. A. Chambers, Phys. Rev. B **45**, 9237 (1992).

[11] D. F. Cline and D. R. Stephens, J. Appl. Phys. **36**, 2869 (1965).

[12] A. Zarembovitch, J. Phys. (Paris) **24**, 1097 (1963).

[13] A. Debernardi, C. Ulrich, M. Cardona, and K. Syassen, phys. stat. sol. (b) **223**, 213 (2001).

[14] B. D. Rajput and D. A. Browne, Phys. Rev. B **53**, 9052 (1996).

[15] N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. **60**, 3613 (1974).