

II-3. Optically-Active Multiphonon Processes in II-VI Semiconductors*

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The infrared reflection and transmission spectra and the Raman spectrum of monocrystalline and hot pressed pellets of ZnSe were investigated. Critical point phonon frequencies were obtained from the analysis of the spectra. The reflectivity of monocrystalline CdSe was studied with linearly polarized light. A shift of 3.5% in the infrared eigen-frequency was found due to anisotropy splitting. Transmission measurements yielded several multiphonon peaks, which were interpreted in terms of four representative Brillouin zone boundary phonon frequencies. The Raman spectrum of ZnO is reported. Raman-active multiphonon bands of CdS are assigned.

§ 1. Introduction

Considerable interest has been evidenced in recent years on the lattice vibrational properties of II-VI semiconductors such as ZnS, CdS, CdSe, ZnSe, etc. These materials crystallize in the cubic zincblende or hexagonal wurtzite structures. A few of them are available in both modifications. Optical investigations of lattice vibrations of these crystals have usually consisted in the measurements of the reflection coefficient in the region of the reststrahlen band, absorption measurements in the two- and three-phonon summation band, and difference band regions. Raman spectra of a few have also been reported.

Mitra and Marshall¹⁾ had reviewed the existing data on the optically-active lattice vibrations in the II-VI semiconductors. They²⁾ have also indicated certain regularities among the phonon frequencies of the zincblende and wurtzite type crystals. Marshall and Mitra³⁾ and Balkanski and co-workers^{4,5)} have analyzed the extensive multiphonon infrared spectra of ZnS and CdS. Mitsuishi⁶⁾ has recently remeasured the reststrahlen spectra of ZnS, ZnSe, ZnTe, CdS, CdSe and CdTe. He has also given an assignment of the multiphonon spectrum of CdTe in terms of critical point phonon frequencies. New results on the lattice infrared and Raman spectra of some II-VI semiconductors are presented here.

§ 2. Infrared and Raman Spectra of ZnSe

Samples used for these investigations were

either single crystals or hot pressed pellets. The two differed very little in spectral characteristics when examined under similar conditions, except for one known impurity band present in the hot pressed samples.

The reflection spectrum of hot pressed ZnSe was measured at room temperature by a Perkin-Elmer model 12 C single beam spectrophotometer equipped with CsI optics. For low frequencies the spectrum was studied by means of a Fourier interference spectrophotometer, FS 520. The reflection spectra of annealed and unannealed samples are shown in Fig. 1. A single resonance damped oscillator calculation⁷⁾ yields the following parameters: $\nu_0(TO \text{ at } k \approx 0) = 209 \text{ cm}^{-1}$, $\epsilon_\infty = 6.10$, $\gamma = 0.035$ and $\epsilon_0 = \epsilon_\infty + 4\pi\rho = 9.20$, where the symbols have their usual meanings. The measured⁸⁾ refractive index of ZnSe at 6440 Å is about 2.50 giving $\epsilon_\infty = 6.3$ in agreement with our value. The $k \approx 0$ longitudinal mode frequency calculated from the Lyddane-Sachs-Teller formula⁹⁾ is $LO(k \approx 0) = \nu_0 (\epsilon_0/\epsilon_\infty)^{1/2} = 257 \text{ cm}^{-1}$.

A direct determination of the $k \approx 0$ TO and LO modes are possible from a measurement of the Raman spectrum. The Raman spectrum of a single crystal of ZnSe was obtained by means of a 2 mw CW He-Ne laser working at 6328 Å. A grating monochromator with photomultiplier detection was used for the analysis of the spectrum. The spectrum is shown in Fig. 2. Only two bands are observed, one at 205 cm^{-1} and the other at 253 cm^{-1} , which can be obviously identical with the TO and LO modes at $k \approx 0$. These values are in excellent agreement with those obtained from the analysis of the reflection spectrum.

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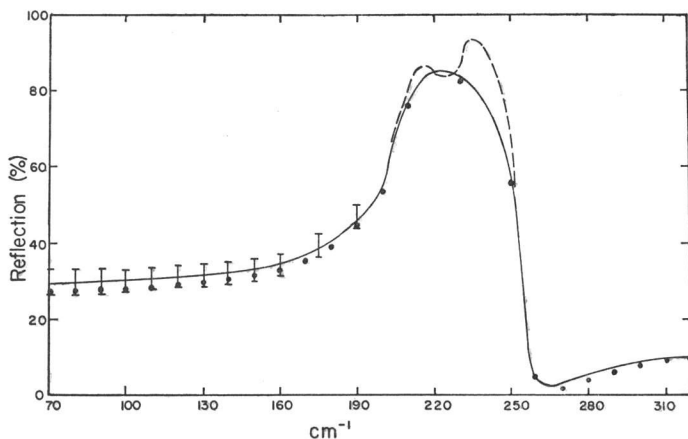


Fig. 1. Reststrahlen spectrum of ZnSe.
 --- before anneal; — annealed; ●●● computed for
 a damped oscillator (for parameters see text).

No second order spectrum could be recorded with the present setup. For the zincblende structure both the $k \approx 0$ LO and TO modes are active in the Raman spectrum. The LO mode, however, is expected in the Raman spectrum to be some ten times more intense than the TO mode.¹⁰⁾ This prediction is borne out by our measurements.

The transmission spectrum of ZnSe was investigated by means of Perkin-Elmer model 521 and model 301 spectrophotometers. The low temperature (80°K) spectrum was recorded by the latter instrument using a dewar with polyethylene windows. Depending on the region, sample thickness ranged from 70μ to 2.5 cm. In some cases the true absorption coefficient was obtained after correcting for the reflection losses.⁷⁾ The absorption coefficient from 80 to 350 cm^{-1} is shown in Fig. 3. The spectrum from 340 cm^{-1} to 480 cm^{-1} is given in Fig. 4. In

Table I all the observed band positions are listed.

The selection rules for the zincblende structure have been worked out by Birman.¹¹⁾ The as-

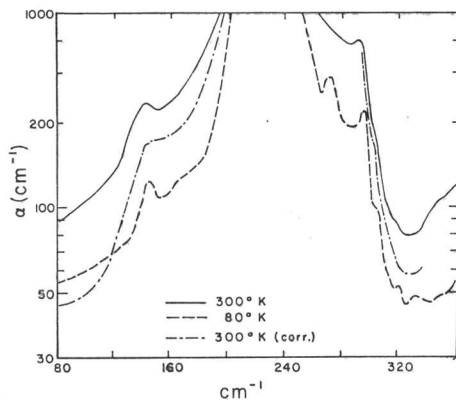


Fig. 3. Absorption spectrum of ZnSe from 80 to 360 cm^{-1} .

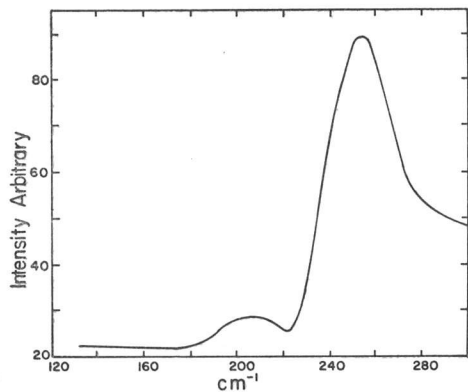


Fig. 2. Raman spectrum of ZnSe.

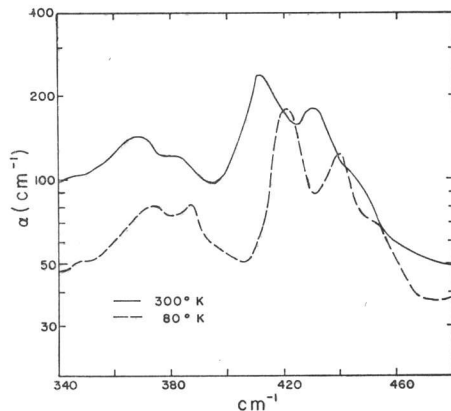


Fig. 4. Absorption spectrum of ZnSe from 340 to 480 cm^{-1} .

Table I. Two- and Three-Phonon Infrared-Active Combinations in ZnSe.

Peak Position cm ⁻¹	Assignment #1	Calculated cm ⁻¹	Assignment #2	Calculated cm ⁻¹
140	2TA(X); LA(L) + TA(L)	140; 142	2TA(L)	142
268	TO(X) + TA(X)	269	LO(X) + TA(X)	270
292	2LA(X)	294	TO(X) + TA(X)	293
303	TO(X) + LA(X)	303	TO(X) + LO(X) - TA(X)	299
318	LO(X) + LA(X)	317	LO(X) + LA(X)	316
334	2TO(L)	336	2LA(L)	336
351	2TA(X) + LO(X)	353	TO(X) + LA(X)	351
366	LO(L) + LA(L)	364	2TO(L)	366
384	LO(L) + TO(L)	385	LO(L)+LA(L); TO(X) + LO(X)	384; 387
412	LO(X) + TO(X)	412	2TO(X)	410
432	2LO(L)	434	2LO(L)	432
444	TA(L) + LA(L) + TO(X)	441	TO(X) + LA(L) + TA(L)	444
475	TO(L) + TA(L) + LO(X)	476	LO(X) + TO(X) + TA(X)	475
530	TO(L) + LA(L) + LO(X)	528	LO(L) + TO(L) + LA(X)	533
580	LO(L) + LA(L) + LO(X)	577	LO(L) + TO(L) + LO(X)	581
612	2TO(X) + LO(X)	611	3TO(X)	615

signment of the observed bands to multiphonon transitions is shown in Table I. As evident, two sets of critical point (c.p.) phonon frequencies are reasonably consistent with the observed data. The c.p. phonon frequencies for ZnSe are listed in Table II along with the Brout sums¹²⁾ at various c.p.s.. As expected the Brout sum remains reasonably constant at the various points in the first Brillouin zone. Langer and Richter¹³⁾ from the analysis of vibronic spectrum of ZnSe: Mn lists five principal phonon frequencies con-

tributing to the structure. These are 70, 94, 160, 209 and 242 cm⁻¹ in reasonable agreement with the c.p. phonons listed in Table II.

§ 3. Lattice Infrared Spectrum of CdSe

Reflection and transmission measurements on hexagonal CdSe have been made at 300°K and 80°K in the region from 70 cm⁻¹ to 600 cm⁻¹ by means of Perkin-Elmer model 521 and Fourier interference FS 520 spectrophotometers.

The reflectivity of a monocrystalline sample was measured with linearly polarized light. The results for 80°K are shown in Fig. 5. Single resonance damped oscillator calculations yield the following parameters:

(a) $E//c$, 300°K

$$\epsilon_{\infty}=6.30 \quad \epsilon_0=10.16$$

$$TO(k \approx 0)=166 \text{ cm}^{-1} \quad LO(k \approx 0)=211 \text{ cm}^{-1}$$

$$\gamma=0.048$$

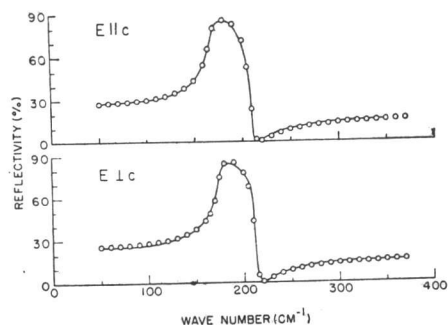


Fig. 5. Polarized reststrahlen spectrum of CdSe at 80°K. Experimental data: solid line; calculated for a damped oscillator: circles.

Table II. Critical point phonon frequencies (in cm⁻¹) of ZnSe.
Assignment Number 1

	Γ	L	X
LO	254	217	213
TO	205	168	199
LA		147	104
TA		95	70
$\sum_{i=1}^6 \nu_i^2 (\text{cm}^{-2} \times 10^{-4})$	14.86	14.32	14.52

Assignment Number 2

	Γ	L	X
LO	254	216	182
TO	205	183	205
LA		168	134
TA		71	88
$\sum_{i=1}^6 \nu_i^2 (\text{cm}^{-2} \times 10^{-4})$	14.86	15.19	15.06

(b) $E \perp c$, 300°K

$$\begin{aligned}\epsilon_\infty &= 6.20 & \epsilon_0 &= 9.29 \\ TO(k \simeq 0) &= 172 \text{ cm}^{-1} & LO(k \simeq 0) &= 210 \text{ cm}^{-1} \\ \gamma &= 0.041\end{aligned}$$

(c) $E // c$, 80°K

$$\begin{aligned}\epsilon_\infty &= 6.30 & \epsilon_0 &= 9.91 \\ TO(k \simeq 0) &= 168 \text{ cm}^{-1} & LO(k \simeq 0) &= 210 \text{ cm}^{-1} \\ \gamma &= 0.036\end{aligned}$$

(d) $E \perp c$, 80°K

$$\begin{aligned}\epsilon_\infty &= 6.20 & \epsilon_0 &= 9.15 \\ TO(k \simeq 0) &= 175 \text{ cm}^{-1} & LO(k \simeq 0) &= 212 \text{ cm}^{-1} \\ \gamma &= 0.029\end{aligned}$$

The results for 300°K are in reasonable agreement with previous results. Measurements of the refractive index¹⁴⁾ in the near infrared yield $\epsilon_\infty = 6.30$ for $E // c$ and $\epsilon_\infty = 6.20$ for $E \perp c$, while Kostyshin¹⁵⁾ obtained $\epsilon_\infty = 7.02$ with unpolarized light. Halsted, Lorenz and Segall¹⁶⁾ have obtained a value of 217 cm^{-1} for the long wavelength LO frequency from the analysis of the band-edge emission of CdSe. The Szigeti effective ionic charge¹⁷⁾ calculated from data at 300°K are $q^* = 0.86$ for $E // c$ and $q^* = 0.80$ for $E \perp c$.

Transmission spectrum was measured between 90 cm^{-1} and 500 cm^{-1} . Six minima were noted and are listed in Table III. These were assigned to combinations of four representative phonon frequencies ($LO = 202 \text{ cm}^{-1}$, $TO = 155 \text{ cm}^{-1}$, $LA = 110 \text{ cm}^{-1}$ and $TA = 60 \text{ cm}^{-1}$) belonging to the Brillouin zone boundary. The assignment is also shown in Table III. A critical point analysis of spectrum was unwarranted because of the paucity of data.

Table III. Infrared-active multiphonon peaks in CdSe.

Observed cm^{-1}	Assignment	Calculated cm^{-1}
95	2 TA	120
260-280	$LO + TA$; $TO + LA$	262; 265
310	2 TO; $LO + LA$	310; 312
360	$LO + TO$; 2 $TO + TA$	357; 370
405	2 LO	404
470	2 $LO + TA$	464
$\sum_{i=1}^6 v_i^2(k \simeq 0) = 10.2 \times 10^4 \text{ cm}^{-2}$		
$\sum_{i=1}^6 v_i^2(k_{\text{max}}) = 10.8 \times 10^4 \text{ cm}^{-2}$		

§ 4. Raman Spectrum of CdS and ZnO

The analysis of Raman spectrum of uniaxial crystals obtained by conventional techniques may be quite involved and may often predict inaccurate results. The use of lasers as excitation source, simplifies the matter, especially extensive angular-dependence and polarization measurements make unambiguous identification of symmetry character of the Raman-active lattice modes possible. Recently such measurements on CdS and ZnO, both of which belong to the wurtzite structure, have been made.

The Raman spectrum of CdS was measured by Poulet and Mathieu¹⁸⁾ by conventional excitation. Tell, Damen and Porto,¹⁹⁾ on the other hand, have recently measured the Raman spectrum of this crystal excited by a He-Ne laser (6328 Å) and an argon laser (5145 Å). Their data on angular dependence and polarization measurements do not agree with Poulet and Mathieu's assignment. Tell *et al.*'s assignment of the Raman-active $k \simeq 0$ modes are 44 cm^{-1} (E_2), 252 cm^{-1} (E_2), 235 cm^{-1} (E_1 transverse), 228 cm^{-1} (A_1 transverse), 305 cm^{-1} (E_1 , A_1 longitudinal). They have also observed seven multiphonon transitions in the Raman spectrum which are listed in Table IV.

The lattice modes of CdS belonging to the edge of the first Brillouin zone were derived by Marshall and Mitra³⁾ from the analysis of the infrared spectrum of the crystal. Balkanski, Besson and LeToullec⁴⁾ have also investigated the infrared spectrum of CdS. Their results are essentially in agreement with those of Marshall and Mitra. However, Balkanski *et al.*'s more extensive data make possible more accurate determination of the acoustic mode frequencies. The polarized infrared spectrum between 80 and

Table IV. Assignment of Raman-active multiphonon processes in CdS.

Raman shifts (cm^{-1}) Observed ^a	Assignments	Calculated (cm^{-1})
97	2 TA_2 ; $LA_1 - TA_{1,2}$	102; 95; 100
207	$LA_1 + TA_1$; $TO_1 - TA_2$	207; 208
328	$TO_1 + TO_3$	328
347	$LO_1 + TA_2$	348
364	$LO_1 + TO_3$	366
556	$LO_1 + TO_1$	556
604	2 LO_1	594

^a from ref. 19).

600 cm^{-1} consists of about 35 bands, which are satisfactorily explained as multiphonon combinations of ten representative zone edge modes (in cm^{-1}): $LO_1=297$, $TO_1=259$, $TO_1'=238$, $LO_2=277$, $TO_2=199$, $TO_2'=208$, $TO_3=69$, $LA_1=151$, $TA_1=56$ and $TA_2=51$. The Raman bands not assigned to allowed $k \approx 0$ fundamentals may also be explained as multiphonon combinations of the above zone edge modes. The assignment is shown in Table IV. The temperature dependence of the 97 cm^{-1} and 207 cm^{-1} bands as measured by Tell *et al.* tends to indicate them as difference bands supporting the second assignment of Table IV in each case.

The Raman spectrum of single crystal ZnO was first reported by Mitra and Bryant,²⁰⁾ who used excitation by a Hg arc source. Damen, Porto and Tell²¹⁾ have subsequently obtained the Raman spectrum using laser radiation. They give the following assignments for the $k \approx 0$ Raman-active fundamentals: 101 cm^{-1} (E_2), 437 cm^{-1} (E_2), 407 cm^{-1} (E_1 transverse), 380 cm^{-1} (A_1 transverse), 583 cm^{-1} (E_1 longitudinal) and 574 cm^{-1} (A_1 longitudinal). They have also observed a few multiphonon bands. Using a Cary 81 Raman spectrophotometer, extensive multiphonon Raman bands have been recorded by us. These along with Damen *et al.*'s data are listed in Table V.

Table V. Multiphonon Raman bands of ZnO.

Present study shifts in cm^{-1}	Strength	Damen <i>et al.</i> ^a shifts in cm^{-1}
60	very weak	
85	very weak	
120	very weak	
146	very weak	
180	weak	
		208
333	weak	334
480	weak	
538	weak	540-670
660	weak	Broad Band
820	medium	
		986
		1084
1160	medium	1149

^a from ref. 21).

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DISCUSSION

Cardona, M.: Since the splitting of the reststrahlen bands between $E_{||c}$ and $E_{\perp c}$ for CdSe is so small, I would like to ask what your estimated limit of error is and whether the splitting is beyond this limit of error.

Mitra, S. S.: Our estimated limit of error is better than 0.5 cm^{-1} , hence a splitting of 6 or 7 cm^{-1} is well within the accuracy of measurement.

Stierwalt, D. L.: One of the criteria we have used in making assignments of the acoustic phonon energies was that the ratio of the energies of the longitudinal and the transverse phonons should be about the same as the ratio of the elastic constants. Are the elastic constants available for zinc selenide so that one might decide between your two alternative assignment schemes?

Mitra, S. S.: What you say seems to be a good criterion. Off hand I do not know, if the elastic constants of ZnSe are available. I shall definitely look into the matter.

Rodot, M.: Do you know the origin of the anomaly in non-annealed samples?

Mitra, S. S.: Barker in his paper on Al_2O_3 has discussed this point in some detail. Broken bonds at the surface during the process of polishing may give rise to new modes or may violate the one-phonon selection rules. Annealing supposedly restores these broken bonds, hence the spectrum appears normal again.