

IV. OPTICAL AND INFRARED SPECTROSCOPY*

Academic and Research Staff

Prof. C. H. Perry

Graduate Students

T. G. Davis
Jeanne H. Fertel

D. J. Muehlner

J. F. Parrish
N. E. Tornberg

A. OPTICAL PHONONS IN $\text{CdS}_x\text{Se}_{1-x}$ MIXED CRYSTALS

1. Introduction

The infrared transmittance and reflectance of pure crystals of CdS and CdSe have been reported several years ago.¹⁻⁴ More recently, the infrared reflectance of the hexagonal mixed crystals of CdS/CdSe have been reported.^{5,6} The reflection spectra of $\text{CdS}_x\text{Se}_{1-x}$ for several values of x have been remeasured and are reported here. The Raman spectra of these crystals have been measured at 300°K and 80°K in collaboration with Brafman, Chang and Mitra at the University of Rhode Island and are reported for the first time. The transmission spectra of several more of the mixed crystals initially discussed in a previous report⁷ have been measured at 300°K, 80°K and 10°K.

It is evident that in the reststrahlen spectra of $\text{CdS}_x\text{Se}_{1-x}$ the infrared active phonons occur in two main bands with frequencies near those of pure CdS and pure CdSe, which is characteristic of a system in which short-range forces influence the lattice dynamics.⁵ In this respect the present system neither behaves as ionic mixed crystals nor entirely as covalent mixed crystals. In mixed systems composed primarily of ionic crystals,⁸ for example, $\text{Ni}_x\text{Co}_{1-x}$, $\text{KCl}_x\text{Br}_{1-x}$, $\text{Na}_x\text{Rb}_{1-x}\text{I}$, $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$, etc., on account of the presence of long-range Coulomb interactions only a single reststrahlen band occurs, and the long-wavelength longitudinal optic (LO) and transverse optic (TO) modes shift continuously and linearly with concentration. On the other hand, in a mixed system composed of covalent crystals like Ge:Si the triply degenerate $k \sim 0$ optic-mode frequency of Ge shifts slightly downward with increasing Si content,⁹ rather than shifting upward continuously from the heavier to the lighter components' frequency.

The present investigation, which includes Raman measurements, reveals the behavior of both $k \sim 0$ LO and TO phonons as functions of x. At present

*This work was supported principally by the Joint Services Electronics Programs (U.S. Army, U.S. Navy, and U.S. Air Force) under Contract DA 28-043-AMC-02536(E), and in part by the U.S. Air Force (ESD Contract AF19(628)-6066), and the M. I. T. Sloan Fund for Basic Research.

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

$\text{CdS}_x\text{Se}_{1-x}$ constitutes by far the most complete and interesting system studied thus far.

2. Measurements and Results

The $\text{CdS}_x\text{Se}_{1-x}$ system appears to form good mixed crystals with hexagonal unit cells similar to the wurtzite CdSe and CdS structures.⁷ Seven mixed crystals were investigated in the concentration range $0.07 < x < 0.71$. The samples were quantitatively analyzed and found to be stoichiometric with a standard deviation of one mole per cent or less. Power x-ray diffraction measurements revealed unique lattice constants "a" and "c" throughout the concentration range that was studied and varied linearly with x, thereby indicating that the CdS/CdSe system does form a 'good' mixed crystal with a hexagonal lattice.⁷

Since for both CdS and CdSe the anisotropy splitting of the transverse optic phonons is limited^{3,4} to only 6 or 7 cm^{-1} , and that of the LO phonons hardly 1 cm^{-1} , all measurements were made on unoriented crystals.

The reflection spectra were measured with the R.I.I.C. F-S-520 Fourier Spectrometer. The spectra were extracted from the quantized interferograms by taking a discrete phase-corrected Fourier transform of the data with the IBM 7094 computer at the M.I.T. Computation Center. A typical reflection spectrum is shown in Fig. IV-1.

Table IV-1. Raman band positions and their assignments for $\text{CdS}_{.79}\text{Se}_{.21}$.

Raman Band position (cm^{-1})	Assignment
41*	$E_2(\Gamma)$
87*	Multiphonon
137	?
182	$E_1, A_1(\Gamma)$ TO(CdSe)
196*	LO(CdSe) (Γ)
213	Multiphonon
242	$E_1, A_1(\Gamma)$ TO(CdS)
256	$E_2(\Gamma)$
298*	LO(CdS) (Γ)
335	Multiphonon
360	Multiphonon
413	?
390*	2LO(CdSe)
493*	LO(CdSe) + LO(CdS)
595*	2LO(CdS)

* Relatively strong bands

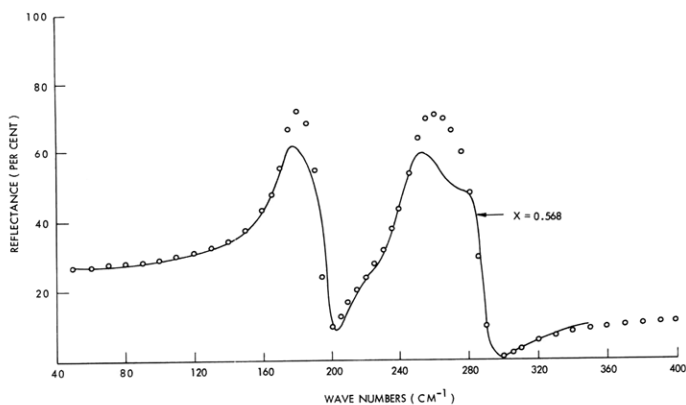


Fig. IV-1. Reststrahlen spectrum of $\text{CdS}_{.568}\text{Se}_{.432}$. Solid line: measured curve. Circles: two-resonance damped oscillator fit. ($\epsilon_{\infty} = 5.7$, $\nu_1 = 175 \text{ cm}^{-1}$, $\nu_2 = 248 \text{ cm}^{-1}$, $\rho_1 = 0.2$, $\rho_2 = 0.12$, $\gamma_1 = 0.045$, $\gamma_2 = 0.045$).

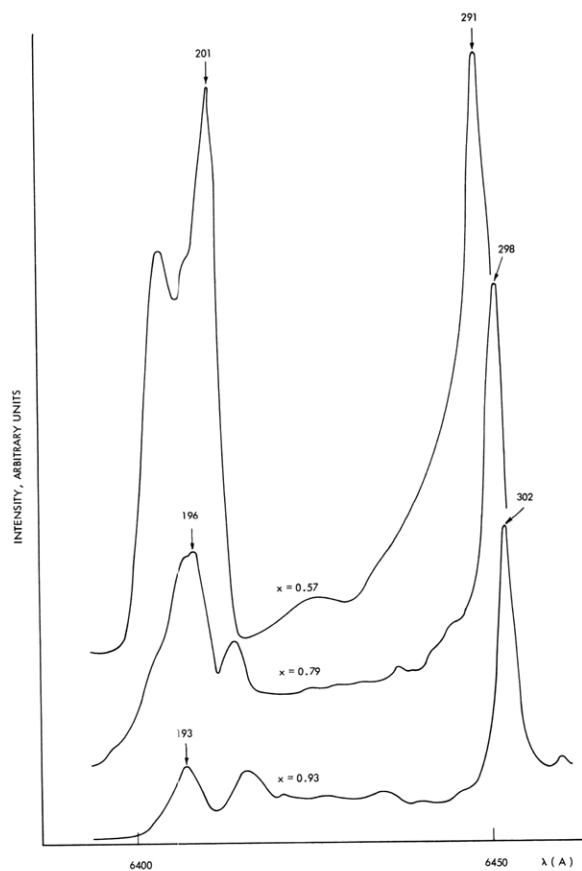


Fig. IV-2. A portion of the Raman spectrum for 3 concentrations: $x = 0.57$; $x = 0.79$; $x = 0.93$. [Brafman, Chang and Mitra, private communication.]

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

The Raman spectra observed by Brafman, Chang, and Mitra were excited with a He-Ne laser (6328 \AA) in the perpendicular scattering mode and were analyzed by means of a Spex 1400 double monochromator. Measurements were also made with the Cary 81 Raman Spectrophotometer in the Spectroscopy Laboratory, M.I.T., in the back-scattering (180°) configuration, with identical band positions but with occasionally altered relative intensities. The Raman spectrum at each concentration contained many bands. An example is shown in Table IV-1, which lists the Raman bands observed with $\text{CdS}_{0.79}\text{Se}_{0.21}$. An interesting portion of the Raman spectrum for three intermediate x-values is shown in Fig. IV-2.

The far infrared transmission spectra of several unoriented slices of the mixed crystal samples were measured at several temperatures by means of Perkin-Elmer spectrophotometers (Model 301 and Model 521) and also by an R.I.I.C. FS-520 Fourier

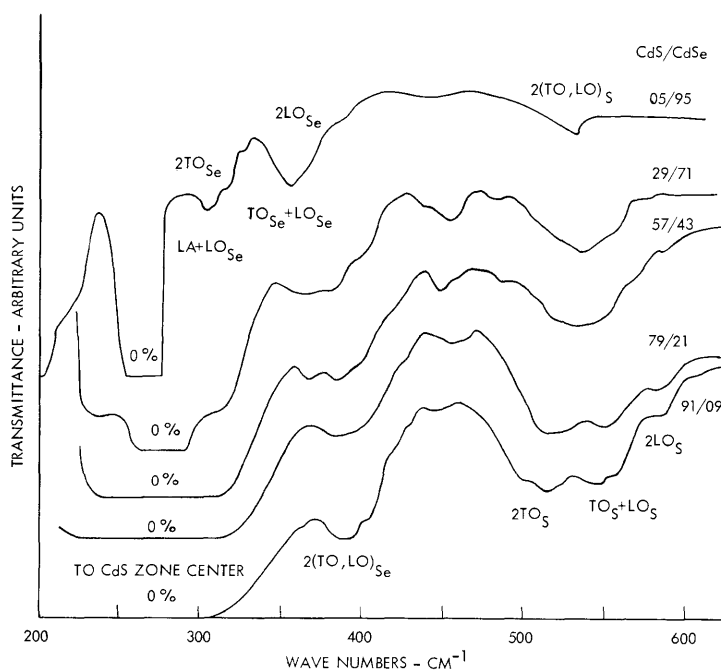


Fig. IV-3. Room temperature infrared transmission spectrum (200 cm^{-1} - 650 cm^{-1}) of $\text{CdS}_x\text{Se}_{1-x}$ for 5 values of x.

spectrophotometer. Figure IV-3 shows the room temperature spectra of 5 of the samples from 200 cm^{-1} to 650 cm^{-1} . Since the frequencies change very little with temperature, in this report we shall discuss primarily the room temperature data.

3. Discussion

Information about the long-wavelength TO modes of the mixed crystals is contained in the reflection spectra. Kramers-Kronig analyses of the room-temperature spectra

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

were performed to obtain the real (ϵ') and imaginary (ϵ'') parts of the complex dielectric constant and other optical constants. A typical result is shown in Fig. IV-4. In all

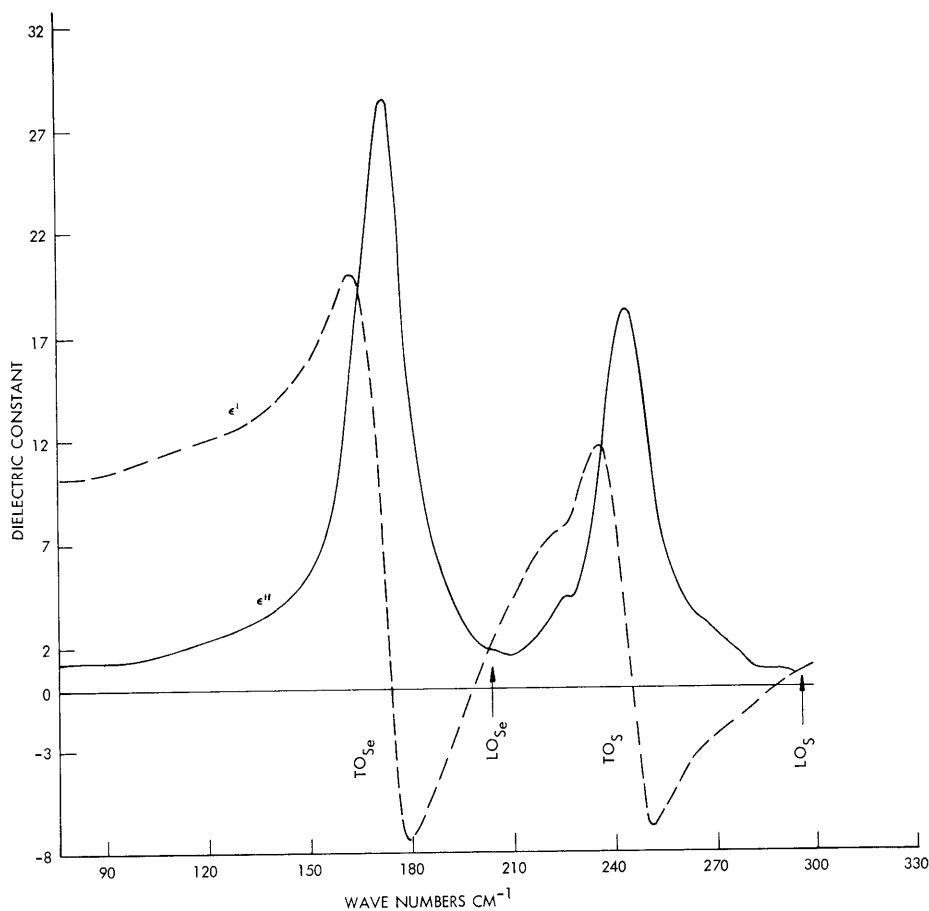


Fig. IV-4. Kramers-Kronig analysis of the reflection spectrum of Fig. IV-1, giving the real and imaginary parts of the dielectric constant.

cases, only two distinct peaks with occasional minor structures were noted in the curves for extinction coefficient, conductivity or ϵ'' vs frequency. The peak frequency of the conductivity curves are assigned to TO(CdS) and TO(CdSe), the assignment depending on their positions. Verlur and Barker,⁶ on the other hand, have used a model of lattice dynamics, which utilizes 7 distinct TO phonons at $k \sim 0$. A closer inspection of their values reveals that for each mixed crystal studied, 2 of the 7 modes considered stand out in strength over the rest. Moreover, a two-resonance damped oscillator can be made to fit our room-temperature reststrahlen spectra, as shown in Fig. IV-1.

In the absence of direct measurement, the $k \sim 0$ LO mode frequency for a single

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

oscillator may be inferred either from the Lyddane-Sachs-Teller (LST) relation or from Drude's rule (the frequency at which $\epsilon' = 0$ or $n = k$). For multiple oscillators, although a generalized LST relation involving all of the modes holds good,¹⁰ it does not, however, yield the LO mode frequencies individually. Often Drude's rule has been invoked for the multiresonance oscillators also,¹¹ although without any theoretical justification. Furthermore, in some cases, for example, when one of the oscillators is much weaker than the others (for low and high values of x in the present case, the n and k curves may not cross and therefore the application of the Drude's rule is impractical. Chang and Mitra¹² have shown that it is possible to obtain the LO frequencies individually as functions of

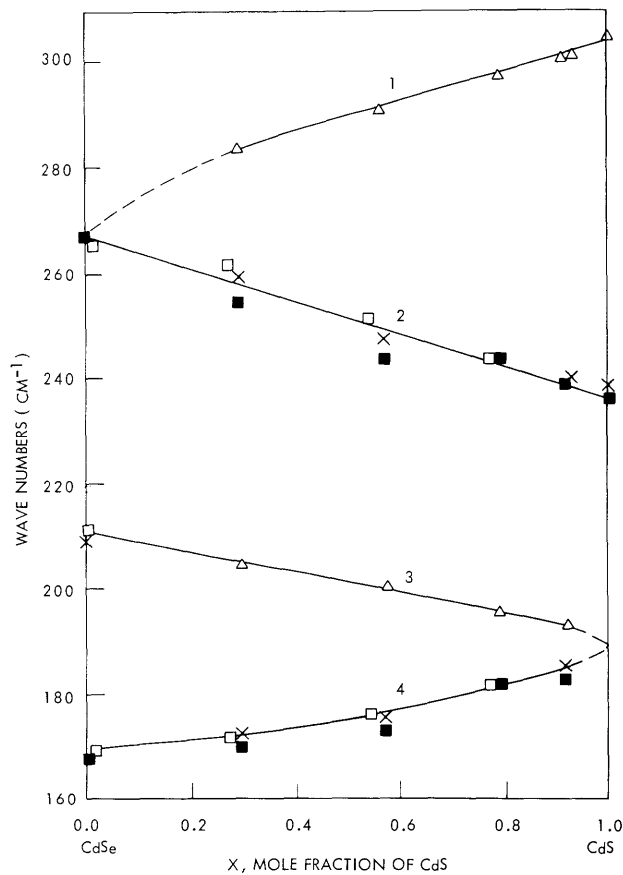


Fig. IV-5. $k \sim 0$ optical phonons of $\text{CdS}_x\text{Se}_{1-x}$ as functions of x .
 1: LO(CdS); 2: TO(CdS); 3: LO(CdSe); 4: TO(CdSe);
 O – Raman (80°K); Δ – Raman (300°K); \square – Kramers-Kronig analysis, using present reflectivity data; \square – Kramers-Kronig analysis, using data of Verlur and Barker⁶; x – Two-resonance damped oscillator fit of the present reflectivity data.

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

oscillator parameters. They have also shown that Drude's rule holds only under certain conditions, viz., the LO frequencies are obtainable only if $\epsilon' = \epsilon'' = 0$ occurs at the same frequency. The LO mode frequencies for a few of the mixed crystals have been determined in this fashion. Thus, for each TO frequency we obtain one LO frequency. Experimental determination of the LO modes is possible by Raman scattering measurements. The two strongest bands in the Raman spectra of each crystal were identified with the LO phonons at $\underline{k} \sim 0$. Their positions showed excellent agreement with those obtained from the modified Drude's rule.¹² The two LO and the two TO modes for each mixed crystal also followed the generalized LST relation¹⁰ within the limits of experimental accuracy.

The one-phonon optic frequencies are plotted as functions of the mole fraction x of

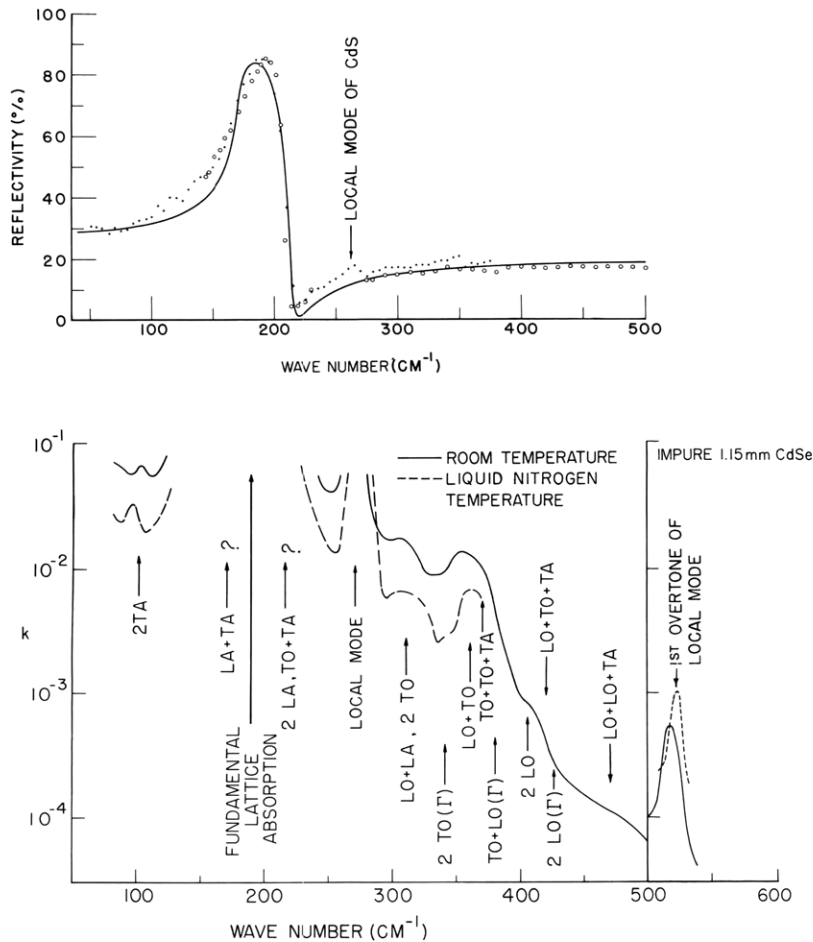


Fig. IV-6. Local mode spectrum of S impurity in CdSe. (a) Reflection spectrum. (b) Absorption spectrum at two temperatures showing the local mode fundamental. (c) First overtone of the local mode.

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

CdS in Fig. IV-5. It may be noted that the LO frequency of CdS monotonically decreases, while the TO frequency increases with increasing concentration of CdSe. These two lines intersect at a point in the region of 100% CdSe. This triply degenerate phonon at 268 cm^{-1} may be considered the quasi-localized mode of S in CdSe. The local mode frequency may be approximately evaluated⁶ by using the Dawber and Elliott theory.¹³ A value of 285 cm^{-1} is obtained for the local-mode frequency, a value not too different, considering the approximations involved, from the value predicted from the behavior of the mixed crystals. Perry, Geick, and Young¹⁴ have noted the presence of this local mode at 268 cm^{-1} in the reflection spectrum of CdSe with a nominal amount of S impurity, which is shown in Fig. IV-6. Verlur and Barker's⁶ spectrum of $\text{CdS}_{.015}\text{Se}_{.985}$ confirms this observation. The local mode spectrum is best demonstrated by the transmission spectrum of a CdSe single crystal with S impurity as presented in Fig. IV-6. The local mode and its first overtone show the characteristic absorption and temperature dependence.

The behavior of the long-wavelength optic modes of the heavier component may be summarized as follows. The LO of CdSe decreases and its TO increases with increasing concentration of CdS. The point of intersection occurring in the region of 100% CdS may likewise be regarded as a resonant gap mode of Se in CdS. This triply degenerate phonon occurs at 188 cm^{-1} . An approximate estimate of the gap mode may be made by applying Jaswal's¹⁵ model on NaI to the present case. Using the phonon assignment of Marshall and Mitra² for CdS, we have obtained a value of 191 cm^{-1} for the gap-mode frequency.

A sum rule pertaining to the optic phonons of mixed zincblende crystals was discovered¹⁶ in connection with the system $\text{ZnS}_x\text{Se}_{1-x}$. We find that the sum rule also holds good for the present system. It has been found that the sum of one-phonon optic-mode frequencies at any concentration, properly weighted for degeneracy (1 for an LO, 2 for a TO, and 3 for a local or a gap mode) is a constant. The 'average' one-phonon frequency of the mixed system, which occurs at $225 \pm 2 \text{ cm}^{-1}$, is to a very good approximation halfway between the quasi-local mode frequency of S in CdSe (268 cm^{-1}) and the resonant gap mode of Se in CdS (188 cm^{-1}). Another consequence of this sum rule is that in the mixed-crystal system $\text{AB}_x\text{C}_{1-x}$ ($m_B < m_C$) the sum of the local mode of B in AC and the gap mode of C in AB can be predicted from the $k \sim 0$ optic phonons of the pure crystals AB and AC alone:

$$\text{Local mode} + \text{gap mode} = \left(\frac{2\text{TO} + \text{LO}}{3}\right)_{\text{AB}} + \left(\frac{2\text{TO} + \text{LO}}{3}\right)_{\text{AC}} \dots \dots \quad (1)$$

In the case of $\text{CdS}_x\text{Se}_{1-x}$, the left-hand side of Eq. 1 is 456 cm^{-1} , whereas the right-hand side is 446 cm^{-1} . The sum rule is apparently obeyed rigorously by the $\text{ZnS}_x\text{Se}_{1-x}$ system.¹⁶ The relatively less exact agreement noted in the present case

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

may be attributed (i) to the exclusion of some of the other allowed $k \sim 0$ optic phonons for the wurtzite structure, and (ii) to the fact that, although $\text{CdS}_x\text{Se}_{1-x}$ is hexagonal for all values of x , the expected anisotropy splitting has been neglected here.

The variation of the long-wavelength optic phonon frequencies with concentration, as presented in Fig. IV-5, is unique, in the sense that it is different from either that of the ionic⁷ or the covalent⁸ crystals. Yet, in some respects, it reflects the pertinent features of either type of solid. The lines (1) and (4) in Fig. IV-2 are in some ways reminiscent of ionic crystals,⁸ whereas lines (2) and (3) are similar to those found for covalent crystals. The II-VI compounds may thus be regarded in many ways as behaving as ionic crystals (for example, the separation of the LO and TO branches at $k \sim 0$), yet in some other respects they are like covalent crystals (for example, the short-range forces that give rise to characteristic frequencies for both the components in the mixed crystal, Ge:Si).

Besides the TO and LO modes discussed here, the wurtzite structure has two additional Raman-active optical modes of the E_2 type. In pure CdS these occur¹⁷ at 44 cm^{-1} and 252 cm^{-1} . In some of the S-rich mixed crystals these modes have been noted. But since these were not followed through the entire concentration range, they could not be included in the present discussion. Tell, Damen, and Porto,¹⁷ in their study of the Raman spectrum of CdS, have reported 7 multiphonon bands. These have been assigned to various phonon combinations by Mitra¹⁸ and by Nusimovici and Birman.¹⁹ Most of these bands are also observed in the mixed crystals and may be similarly assigned. In both zincblende and wurtzite structures the second harmonic of the Brillouin zone center LO modes are allowed in the Raman spectrum. What is noteworthy here is that in the Raman spectrum of $\text{CdS}_x\text{Se}_{1-x}$ we not only find bands corresponding to 2 LO (CdS) and 2 LO (CdSe) but also a combination band of the type LO (CdS) + LO (CdSe). The observed Raman bands and their assignments for $\text{CdS}_{.79}\text{Se}_{.21}$ have been presented in Table IV-1 as an example.

The strongest two-phonon infrared-active bands above the fundamental lattice vibrations have been given in Fig. IV-3 for a number of x -values. In hexagonal crystals of pure CdS or CdSe, the strongest two-phonon absorption bands are due only to combination of phonons from critical points at the end of the Brillouin zone. Two-phonon transitions involving the zone-center critical points are excluded by group theory and occur as cutoffs in the absorption spectrum. Although a classical Brillouin zone is not well defined for these mixed crystals, the two-phonon absorption spectrum still behaves as if it were due only to critical points at the edge of a pseudo Brillouin zone. No overtones of the observed zone center frequencies have been seen. Moreover, the absorption spectrum, like the reflection spectrum, appears to be due to nearly independent contributions from both the CdS and the CdSe in each mixed crystal.

Figure IV-7 is a plot, as a function of the mole fraction of CdS in the mixed crystal

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

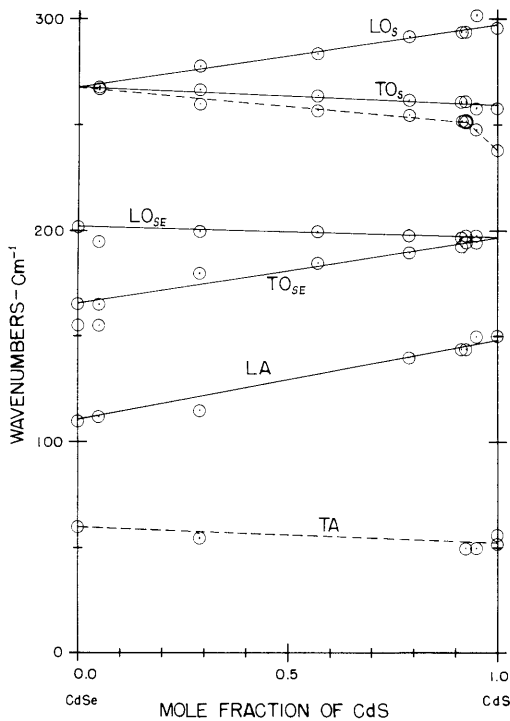


Fig. IV-7.

Brillouin zone boundary of $\text{CdS}_x\text{Se}_{1-x}$ as functions of x .

system, of an assignment of the frequencies contributing to the two-phonon absorption spectra. The assignment shown is most consistent with the over-all experimental data. It shows only one clearly defined LA mode and that the zone-boundary optical frequencies and the zone-center optical frequencies associated with a given substance approach each other as the concentration of their contributor becomes very small. Near zero concentration they approach the local mode of that substance in the host lattice. The TA frequencies are also shown on a single straight line, but there were insufficient data to locate the TA mode for all samples.

We are grateful to Dr. D. C. Reynolds of Wright-Patterson Air Force Base, Ohio, for supplying some of the samples and to Dr. S. S. Mitra and his co-workers at the University of Rhode Island for their collaboration in this work. We are also

indebted to the Space Optics Branch, NASA (Electronics Research Center) Cambridge, for their keen interest in this work, for supporting Mr. J. F. Parrish as a summer-employee, and for making available to us the Perkin-Elmer Model 301 spectrophotometer.

J. F. Parrish, C. H. Perry

References

1. A. Mitsuishi, H. Yoshina and S. Fujita, *J. Phys. Soc. (Japan)* **13**, 1235 (1958).
2. R. Marshall and S. S. Mitra, *Phys. Rev.* **134**, A1019 (1964).
3. M. Balkanski, J. M. Besson, and R. Le Toullec, *Proc. International Conference on the Physics of Semiconductors, Paris, 1965*, pp. 1091-1099.
4. R. Geick, C. H. Perry, and S. S. Mitra, *J. Appl. Phys.* **37**, 1994 (1966).
5. M. Balkanski, R. Beserman, and J. M. Besson, *Solid State Commun.* **4**, 201 (1966).
6. H. N. Verlur and A. S. Barker, Jr., *Phys. Rev.* **155**, 750 (1967).
7. J. F. Parrish and C. H. Perry, *Quarterly Progress Report No. 85, Research Laboratory of Electronics, M.I.T., April 15, 1967*, pp. 42-47.

(IV. OPTICAL AND INFRARED SPECTROSCOPY)

8. P. J. Gielisse, J. N. Plendl, L. C. Mansur, R. Marshall, S. S. Mitra, R. Mykalajewycz, and A. Smakula, *J. Appl. Phys.* 36, 2446 (1965); A. Mitsuishi in "U.S.-Japan Cooperative Seminar on Far Infrared Spectroscopy," Columbus, Ohio, September 1965 (unpublished); Jeanne H. Fertel and C. H. Perry, a paper presented at the Symposium on Molecular Structure and Spectroscopy, Ohio State University, Columbus, Ohio, September 6-9, 1967; R. M. Fuller, C. M. Randall, and D. J. Montgomery, *Bull. Am. Phys. Soc.* 9, 644 (1964); R. K. Chang, B. Lacina, and P. S. Pershan, *Phys. Rev. Letters* 17, 755 (1966).
9. D. W. Feldman, M. Ashkin, and J. H. Parker, Jr., *Phys. Rev. Letters* 17, 1209 (1966).
10. W. Cochran, *Z. Krist.* 112, 465 (1959).
11. D. R. Renneke and D. W. Lynch, *Phys. Rev.* 138, A530 (1965).
12. I. F. Chang and S. S. Mitra (private communication, 1967).
13. P. G. Dawber and R. J. Elliott, *Proc. Roy. Soc. (London)* A273, 222 (1963); *Proc. Phys. Soc. (London)* 81, 459 (1963).
14. C. H. Perry, R. Geick, and E. F. Young, *Appl. Opt.* 5, 1171 (1966).
15. S. S. Jaswal, *Phys. Rev.* 137, 302 (1965).
16. S. S. Mitra (private communication, 1967).
17. B. Tell, T. C. Daman, and S. P. S. Porto, *Phys. Rev.* 144, 771 (1966).
18. S. S. Mitra, *J. Phys. Soc. (Japan)* 21 (Supplement), 61 (1966).
19. M. A. Nusimovici and J. L. Birman, *Phys. Rev.* 156, 925 (1967).

