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## Optical Phonons of $\text{ZnS}_{1-x}\text{Se}_x$ and $\text{CdS}_{1-x}\text{Se}_x$ Mixed Crystals: Pressure Effects\*

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The ir transmission of the optical phonons for the mixed crystals  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$ , at various concentrations of  $x$ , was studied as a function of pressure up to about 43 kbar. At all concentrations a two-mode behavior was observed. For both systems the high frequency mode exhibits a greater pressure dependence than the low frequency mode. The gap mode observed for the  $\text{ZnS}_{1-x}\text{Se}_x$  mixed crystals at low concentrations of Se is found to be pressure insensitive as contrasted to the  $\text{Cd}_{1-x}\text{Se}_x$  mixed crystals.

INDEX HEADINGS: Pressure studies; Optical phonons; Mixed crystals ( $\text{ZnS}_{1-x}\text{Se}_x$ ,  $\text{CdS}_{1-x}\text{Se}_x$ ); Infrared transmission.

### INTRODUCTION

Binary mixed crystals of simple inorganic crystals can be classified into two groups by studying their long-wavelength ( $\mathbf{k} \sim 0$ , where  $\mathbf{k}$  represents the phonon-wave vector) ir and Raman spectra. In one class of mixed crystals, called the one-mode type, each of the  $\mathbf{k} \sim 0$  optic mode frequencies varies continuously and approximately linearly with concentration from the frequency characteristic of one end member to that of the other end member. The strength of the mode also approximately remains constant. Mixed crystal systems that are known to display this type of behavior are  $\text{Na}_{1-x}\text{K}_x\text{Cl}$ ,  $\text{KCl}_{1-x}\text{Br}_x$ ,  $\text{K}_{1-x}\text{Rb}_x\text{Cl}$ ,  $(\text{Ca}, \text{Ba})_{1-x}\text{Sr}_x\text{F}_2$ ,  $\text{Ni}_{1-x}\text{Co}_x\text{O}$ ,  $\text{GaAs}_{1-x}\text{Sb}_x$ ,  $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ , etc. On the other hand, in the other class of mixed crystals known as the two-mode type, two phonon frequencies for each of the optic modes of the pure crystal are observed to occur at frequencies close to those of the end members. Moreover, the strength of each phonon mode of the mixed crystal is approximately proportional to the mole fraction of the component it represents. Examples are  $\text{K}_{1-x}\text{Rb}_x\text{I}$ ,  $\text{Si}_x\text{Ge}_{1-x}$ ,  $\text{InP}_{1-x}\text{As}_x$ ,  $\text{GaP}_{1-x}\text{As}_x$ ,  $\text{CdS}_{1-x}\text{Se}_x$ , and  $\text{ZnS}_{1-x}\text{Se}_x$ . The crystals belonging to either class are true mixed crystals in the x-ray crystallographic sense; i.e., they display a structure identical with that of the end members with a lattice constant (or lattice constants in case of less symmetric structures) that approximately follows the Vegard law in its dependence on concentration.<sup>1</sup>

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Whether a mixed crystal  $AB_{1-x}C_x$  will exhibit one-mode or two-mode behavior type depends almost entirely on the relative masses of the atoms  $A$ ,  $B$ , and  $C$ , and perhaps to a lesser extent on the strength and nature of binding. Based on a pseudo-unit cell model of the mixed crystals, Chang and Mitra<sup>2</sup> have derived a criterion relating the masses for the determination of the one-or two-mode behavior type. If the relative masses are the determining factors then an external effect as pressure, which can substantially modify the force constants, but keep the masses unaltered, should not change the one-mode type mixed crystal to a two-mode type and vice versa. We have previously reported<sup>3</sup> the effect of pressure on the ir eigenfrequency of the mixed crystal system  $\text{KCl}_{1-x}\text{Br}_x$ . Up to a pressure of about 18 kbar, the system for any value of  $x$  remained a one-mode type, although the eigenfrequencies changed considerably with pressure. In this paper we describe the results of such a study on two-mode type crystals, viz.,  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$ .

The ir reflection and Raman spectra of  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$  at ambient pressure have been reported recently.<sup>4,5</sup> In this communication we report the results of ir transmission measurements on these mixed crystals as a function of pressure up to about 43 kilobar.

### I. EXPERIMENTAL

Both  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$  systems appear to form good mixed crystals, the former with cubic unit cells similar to the zinc blende  $\text{ZnS}$  and  $\text{ZnSe}$  structures, and the latter with hexagonal unit cells similar to the wurtzite  $\text{CdSe}$  and  $\text{CdS}$  structures. Polycrystalline samples of  $\text{ZnS}_{1-x}\text{Se}_x$  were prepared by Eastman Kodak Company by hot pressing, a method developed by them for manufacturing Irtran filters. Single crystals of  $\text{CdS}_{1-x}\text{Se}_x$  were grown from the melt by D. C. Reynolds of ARL, Wright-Patterson AFB. Five mixed crystals of  $\text{ZnS}_{1-x}\text{Se}_x$  in the concentration range of  $0.03 \geq x \geq 0.93$  and six mixed crystals of  $\text{CdS}_{1-x}\text{Se}_x$  in the concentration range of  $0.085 \geq$

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$x \geq 0.67$  were investigated. They were quantitatively analyzed and were found to be stoichiometric with a standard deviation of one mole percent or less. Powdered x-ray diffraction measurements revealed a unique lattice constant for  $\text{ZnS}_{1-x}\text{Se}_x$  system and unique values of  $a$  and  $c$  for  $\text{CdS}_{1-x}\text{Se}_x$  system throughout the concentration range studied and varied linearly with  $x$ .

Infrared spectra were obtained using a Perkin-Elmer model 301 far ir spectrophotometer containing a modified  $6\times$  beam condenser and a high pressure opposed diamond anvil cell. The experimental details have been reported earlier,<sup>6,7</sup> and will not be repeated here.

Crystals studied were formed from finely powdered material in the diamond cell by the slow application of pressure and alternately increasing and decreasing the pressure several times, and then leaving the material under pressure (approx. 10 kbar) for a few hours. Spectra were obtained at ambient pressure and at intermediate pressures up to  $\sim 43$  kbar. The pressure was then released and a final spectrum obtained at ambient pressure. Calibration of the pressures obtained has been described previously.<sup>6,7</sup> The pressure gradient existing across the diamond faces, coupled with the sluggishness of the system and friction in the cell, prevented any determination of the half-band width of the observed bands. For these reasons the pressures measured in this study are considered to be only average pressures.

## II. RESULTS

Each of the crystals studied showed two absorption features except for very low or high values of  $x$ . The pressure dependence of the peak positions was measured for each value of  $x$ . The data on  $\text{ZnS}_{1-x}\text{Se}_x$  are presented in Table I, along with available literature data. The same data are plotted in Figs. 1 and 2.

Table I. Optical phonon frequencies ( $\text{cm}^{-1}$ ) as a function of pressure in mixed crystals  $\text{ZnS}_{1-x}\text{Se}_x$ .  $x$  is the mole fraction,  $p$  the pressure in kilobars.

$x/p$	Lit. values at atmospheric pressure							
	0.001	8.5	17.0	25.5	34.0	42.5	a	b
0.00	278	278	281	284	288	292	271	274
0.03	276	278	279	282	287	290	...	...
	224	224	225	226	226	226	...	...
0.19	279	280	283	289	295	300	274	...
	221	221	222	223	224	225	223	...
0.41	284	288	292	295	300	305	280	...
	214	217	220	223	225	227	215	...
0.64	291	293	299	303	306	310	287	...
	211	213	216	219	222	224	211	...
0.93	207 <sup>c</sup>	209	211	214	217	220	...	...
1.00	205	206	210	211	215	218	205	207

<sup>a</sup> O. Brafman, I. F. Change, G. Lengyel, and S. S. Mitra, *Localized Excitations in Solids*, R. F. Wallis, Ed. (Plenum Press, Inc., New York, 1968).

<sup>b</sup> S. S. Mitra, *J. Phys. Soc. (Japan)* 21 (Suppl.), 61 (1966). O. Brafman and S. S. Mitra, *Phys. Rev.* 171, 931 (1968).

<sup>c</sup> High frequency peak was very weak and was difficult to follow with pressure.

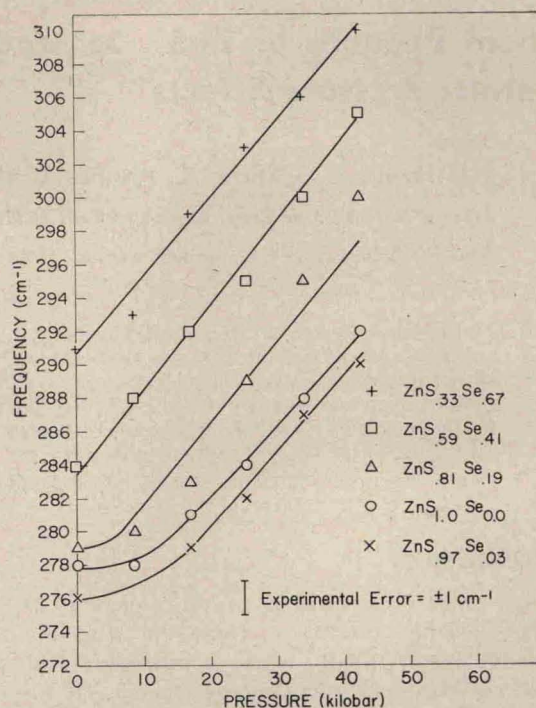


FIG. 1. Pressure dependence of high frequency mode in  $\text{ZnS}_{1-x}\text{Se}_x$ .

All modes shift to higher frequencies with pressure. In the case of pure ZnS and pure ZnSe, the shifts are comparable (14 and 13  $\text{cm}^{-1}$ , respectively, for a pressure change of  $\sim 43$  kbar) and agree well with previous pressure data on ZnS.<sup>8</sup> For the mixed crystals, on the other hand, the high frequency mode which, for all values of  $x$ , occurs at a frequency near that for pure ZnS, shows somewhat greater pressure dependence than the low frequency mode which occurs at frequency near that for pure ZnSe.

The data on  $\text{CdS}_{1-x}\text{Se}_x$  are given in Table II and Figs. 3 and 4. Here again the high frequency CdS-like

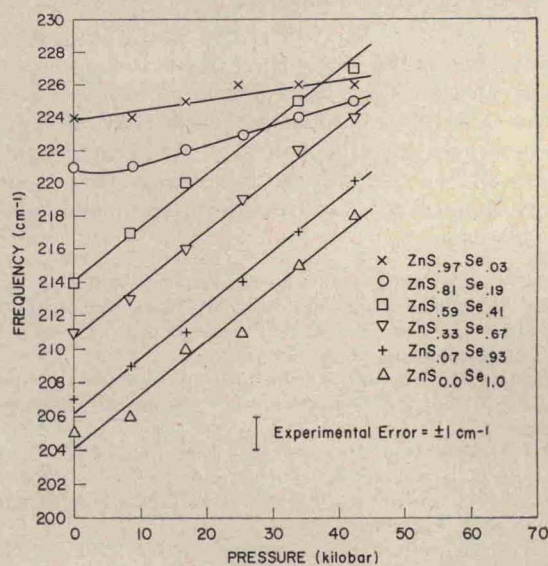


FIG. 2. Pressure dependence of low frequency mode in  $\text{ZnS}_{1-x}\text{Se}_x$ .



Table II. Optical phonon frequencies ( $\text{cm}^{-1}$ ) as a function of pressure in mixed crystals  $\text{CdS}_{1-x}\text{Se}_x$ .  $x$  is the mole fraction,  $p$  the pressure in kilobars.

$x/p$	.001	4.7	5.7	8.3	9.4	11.3	14.0	16.8	17.0	18.7	22.7	23.4	24.9	28.1	28.3	33.7
0.00	239			244				247					249			248
0.085	243	244			246		247			248		249		250		
	184	185			186		187			187		187		188		
0.10	244	246			248		249			250		251		252		
	184	185			186		187			189		190		191		
0.21	243	245			247		248			249		250		252		
	180	181			181		182			182		183		185		
0.47	252	254			256		258			259		261		262		
	177	178			179		180			181		181		182		
0.64	262		262			268			270			271				274
	173		174			176			178			178				181
0.67	263 <sup>a</sup>	264			266		268			269		272				272
	175	176			177		178			180		181				181
1.00	170	171			172		174			175		176				177

<sup>a</sup> S. S. Mitra, in *Optical Properties of Solids*, S. Nudelman and S. S. Mitra, Eds. (Plenum Press, Inc., New York, 1968), pp. 413-417.

mode shows a somewhat greater pressure dependence than the low frequency CdSe-like mode.

### III. DISCUSSION

ZnS and ZnSe belong to the cubic zinc blende ( $T_d^2$ ) structure with two particles per Bravais unit cell. Thus the use of group theory predicts one triply degenerate optic mode at  $\mathbf{k} \approx 0$ , which is split into a nondegenerate longitudinal optic (LO) and a doubly degenerate transverse optic (TO) mode as a result of the partially ionic nature of the solids. CdS and CdSe,

on the other hand, belong to the wurtzite structure ( $C_{6v}^4$ ) containing four atoms per unit cell. The wurtzite structure is uniaxial but is closely related to the zinc blende structure. Due to anisotropic splitting, however, each of the TO and LO modes is further split into TO ( $A_1$ ), TO ( $E_1$ ) and LO ( $A_1$ ), LO ( $E_1$ ) depending on whether the particle displacements are parallel ( $A_1$ ) or perpendicular ( $E_1$ ) to the  $c$  axis of the crystal. As remarked earlier, for both CdS and CdSe, the anisotropic splitting of TO phonons is limited<sup>9</sup> to only 6 or 7  $\text{cm}^{-1}$ , and that of the LO phonons hardly 1  $\text{cm}^{-1}$ . As all measurements were done with un-

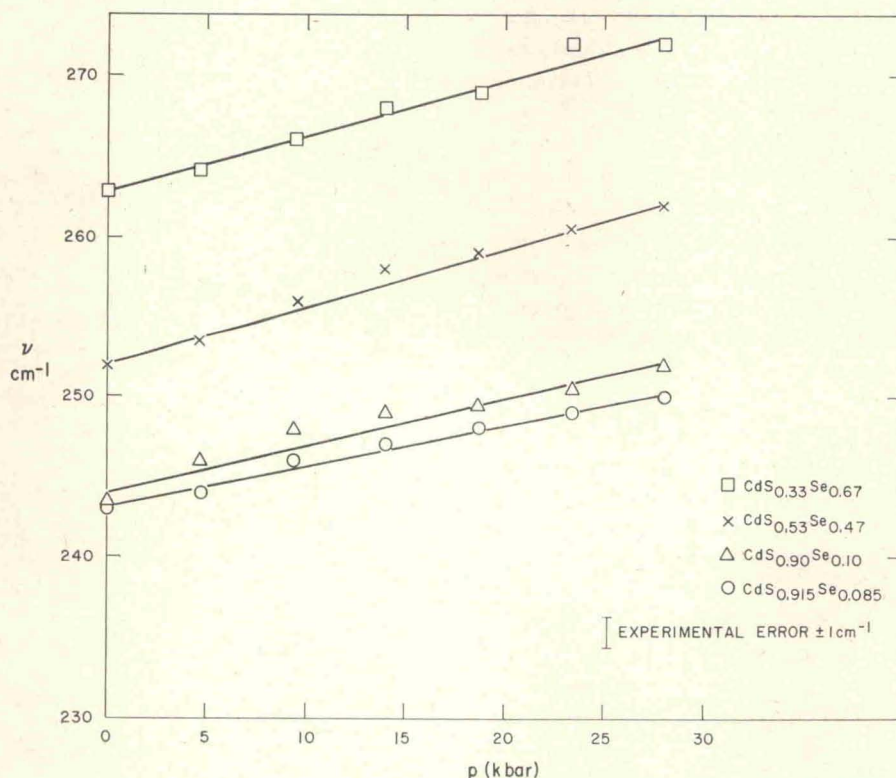


Fig. 3. Pressure dependence of high frequency mode in  $\text{CdS}_{1-x}\text{Se}_x$ .



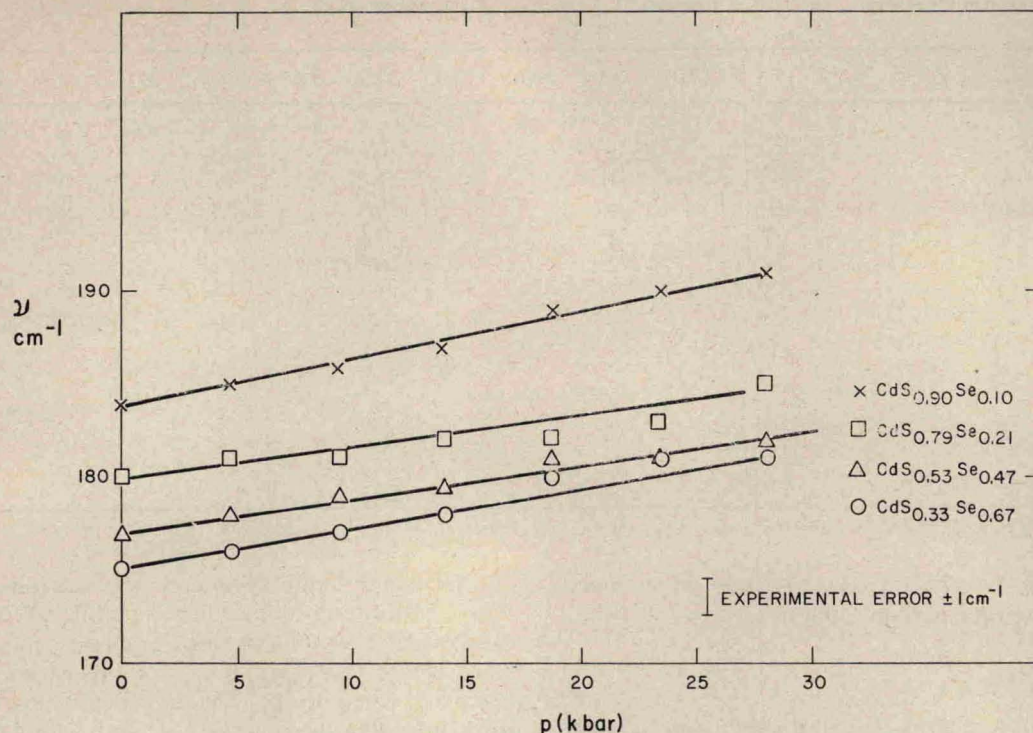


FIG. 4. Pressure dependence of low frequency mode in  $\text{CdS}_{1-x}\text{Se}_x$ .

oriented polycrystals in unpolarized radiation, we were unable to resolve the anisotropic splitting. Thus for  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$  only two absorption features were observed for each value of  $x$ . Since  $\sim 1 \mu$  thick samples were used, the transmission minima are to be associated with long-wavelength TO-type modes.

The mixed crystal systems  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$  both obey the necessary inequality of the pseudo-unit cell model,  $m_B < \mu_{AC}$  where in a crystal  $AB_{1-x}C_x$ ,  $m_B$  represents the mass of the atom  $B$ , and  $\mu_{AC}$  the reduced mass per Bravais unit cell of  $AC$ . The two observed transmission minima for each value of  $x$  are thus labeled  $\text{TO}_{AB}$  and  $\text{TO}_{AC}$  since they occur with frequencies near those of pure  $AB$  and pure  $AC$ , and with intensities approximately dependent on the mole fraction of each component present, and this is indicated in Fig. 5.

Previous studies<sup>4,5</sup> on the  $\text{ZnS}_x\text{Se}_{1-x}$  and  $\text{CdS}_x\text{Se}_{1-x}$  at ambient pressure were done by ir reflection and Raman scattering measurements. The TO modes were inferred from the maxima in the imaginary part of the dielectric constant derived from the reflection data by a damped-Lorentz-oscillator fit or by Kramer-Kronig dispersion analysis. The present data, on the other hand, constitute the first direct observation of two-mode behavior by transmission measurements on crystalline samples. The TO mode frequencies of  $\text{ZnS}_{1-x}\text{Se}_x$  obtained by the two methods are compared in Table I. The slight discrepancies between the two data may be attributable to the different methods of obtaining them and the sample-size effect.<sup>10</sup> The

present experimental data are compared with those calculated from the Chang and Mitra<sup>2</sup> theory in Fig. 6.

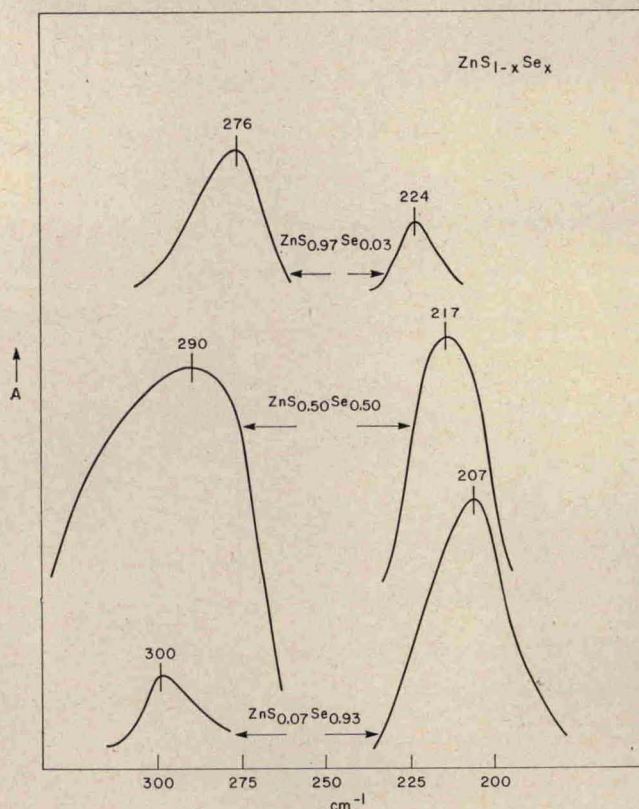


FIG. 5. The high frequency and low frequency modes of  $\text{ZnS}_{1-x}\text{Se}_x$  at several mole fractions.



The long-wavelength longitudinal optic mode (LO) frequency of a crystal is related to the TO mode frequency by the Lyddane-Sachs-Teller relation,<sup>11</sup>

$$\nu_{LO}/\nu_{TO} = (\epsilon_0/\epsilon_\infty)^{1/2}, \quad (1)$$

where  $\epsilon_0$  and  $\epsilon_\infty$  represent the low and high frequency dielectric constants. Equation (1) holds for a cubic diatomic crystal. For the mixed crystal system  $KCl_{1-x}Br_x$  which exhibit a one-mode behavior, Eq. (1) was used<sup>3</sup> to obtain the LO mode frequency, assuming that the dielectric constants vary linearly with  $x$ . Longitudinal optical modes of  $KCl_{1-x}Br_x$  thus calculated agreed<sup>3</sup> quite well with the predictions of the virtual ion model.<sup>2</sup> For a multimode crystal a modified Lyddane-Sachs-Teller relation had been proposed<sup>12</sup>

$$\pi_i(\nu_{LO_i}/\nu_{TO_i}) = (\epsilon_0/\epsilon_\infty)^{1/2} \quad (2)$$

and should also apply to mixed crystals displaying two-mode behavior. However, this relation is inadequate for obtaining individual  $LO_1$  and  $LO_2$  frequencies of a crystal  $AB_{1-x}C_x$ , when their  $TO_1$  and  $TO_2$  frequencies are known. Chang and Mitra<sup>2</sup> have given the following semiempirical relations for this purpose:

$$\nu_{LO_1} = \nu_{TO_1} \{1 + [4\pi\rho_1/\epsilon_\infty(AB)]\}^{1/2}, \quad (3)$$

and

$$\nu_{LO_2} = \nu_{TO_2} \{1 + [4\pi\rho_2/\epsilon_\infty(AC)]\}^{1/2}, \quad (4)$$

where

$$4\pi\rho_1 = (1-x)[\epsilon_0(AB) - \epsilon_\infty(AB)]$$

and

$$4\pi\rho_2 = x[\epsilon_0(AC) - \epsilon_\infty(AC)].$$

Longitudinal optical frequencies for  $ZnS_{1-x}Se_x$  obtained from present TO frequency data using Eqs. (3) and (4) are shown in Fig. 6. Experimental values of LO frequencies for the mixed crystal were measured<sup>4</sup> by Raman scattering and are also shown in Fig. 6. The comparison appears excellent. Similar results were also indicated for the  $CdS_{1-x}Se_x$  system.

Observation of Fig. 6 will show that as the mole fraction  $x$  of ZnSe increases the ZnS-like LO mode frequency ( $LO_1$ ) decreases and the ZnS-like TO mode frequency ( $TO_1$ ), on the other hand, increases, the two lines meeting in the region of  $x \approx 1$ . This triply degenerate mode is termed the localized vibrational mode of  $S$  in ZnSe. Ideally, such a mode should be operative at an infinite dilution of a light impurity ( $B$ ) in a crystal  $AC$  such that  $m_B < m_A, m_C$ , and will occur in a frequency region above the highest optic phonon frequency ( $k \sim 0$  LO) of the host lattice ( $AC$ ). The local mode peak position observed with a crystal of ZnSe about 1 mm thick and 1 in. diameter with about 1% substitutional  $S$  impurity is presented in Fig. 6. Such a spectrum could not be observed with the diamond cell because of necessarily thin samples used in such a cell. Now turning to the ZnSe modes, one observes that the  $LO_2$  mode frequency increases and the  $TO_2$  mode frequency decreases with  $x$ . The two lines meet in a region of  $x \approx 0$ . This triply degenerate

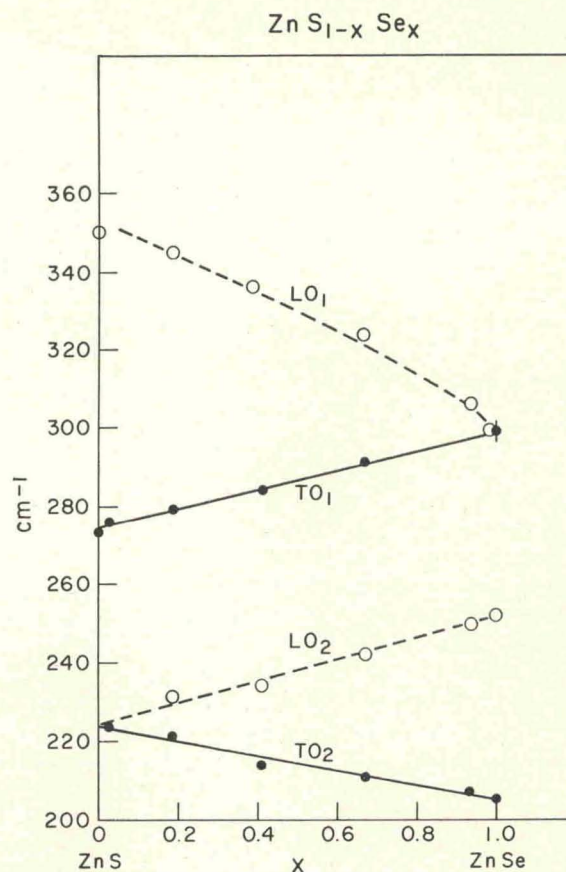


Fig. 6. Long-wavelength optic phonon frequencies of  $ZnS_{1-x}Se_x$  at 1 atm pressure as functions of  $x$ . The various symbols are as follows: ● infrared transmission data obtained with diamond cell; ● local mode frequency of  $S$  in ZnSe obtained from transmission measurement on a thicker and larger sample (see text); ○ Raman data (Ref. 4); — Chang and Mitra theory (Ref. 2); --- Calculated LO data using present experimental TO data.

mode is termed the gap mode, and is observed when a nominal amount of a heavy impurity (Se) is introduced in a crystal in which a frequency gap occurs between the optic and acoustic bands in its phonon spectrum. The local and gap modes are known to be quite temperature sensitive.<sup>13</sup>

Next, we consider the effect of pressure. A precise measurement of shift of frequency of the LO and TO modes of ZnSe has recently been made<sup>14</sup> using a hydrostatic pressure cell over only a small pressure range (9 kbar). The present data on the TO of ZnSe agree qualitatively with the data of Ref. 14. But the uncertainty in the present data, chiefly because of difficulties in accurate pressure calibration and presence of pressure gradient in the diamond cell, makes a quantitative comparison difficult.

The results of the present experiment establish that up to the pressure range investigated both  $ZnS_{1-x}Se_x$  and  $CdS_{1-x}Se_x$  remain two-mode systems. Since dielectric constants of the end members are not known as functions of pressure, the LO modes at higher pressures could not be determined. Nevertheless, extrapolation of the  $TO_1$  branch to  $x=1$  and  $TO_2$  branch to  $x=0$  enables one, in principle, to obtain



the local and gap mode frequencies as functions of pressure.

As may be seen from Figs. 1 and 3, the position of the high frequency mode varies linearly with pressure; the slopes for the various mixtures do not differ appreciably, indicating that they retain their ZnS or CdS character. For both the systems, the lowest S concentration studied corresponded to 0.33 mole fraction of ZnS or CdS ( $x=0.67$ ). Thus, the local mode, which corresponds to a concentration of  $S \approx 0$  ( $x \approx 1$ ), could not be investigated as a function of pressure.

The low frequency modes of  $\text{ZnS}_{1-x}\text{Se}_x$  and  $\text{CdS}_{1-x}\text{Se}_x$  also have linear pressure dependence (Figs. 2 and 4). For  $x \geq 0.41$  in the case of  $\text{ZnS}_{1-x}\text{Se}_x$ , and for all values of  $x$  in the case of  $\text{CdS}_{1-x}\text{Se}_x$ , the low frequency mode ( $\text{TO}_2$ ) retains its ZnSe- or CdSe-like character. However, for  $x=0.19$  and  $0.03$  in the case of  $\text{ZnS}_{1-x}\text{Se}_x$ , very little frequency shift with pressure is observed. Repeated measurements have given assurance that this apparently anomalous behavior for the low Se concentrations is real. Such a situation does not, however, exist for the  $\text{CdS}_{1-x}\text{Se}_x$  system.

We offer a tentative explanation for this behavior. Both ZnS and CdS crystals have forbidden gaps in their phonon spectrum. Absorption spectra of specimens containing nominal quantities of Se in ZnS or CdS are thus true gap modes. The frequency range of the frequency gap found in a diatomic crystal  $AB$  depends primarily on the mass ratio  $m_A/m_B$ . If the two masses are nearly equal, no gap exists, e.g., KCl. Consequently, no gap mode is observed for a Br impurity in KCl although  $m_{\text{Br}} > m_{\text{K}}, m_{\text{Cl}}$ . As a result the system  $\text{KCl}_{1-x}\text{Br}_x$  shows one-mode behavior.<sup>2,3</sup> For the cases under consideration, however,  $m_{\text{Cd}}/m_{\text{S}} = 3.51$  and  $m_{\text{Zn}}/m_{\text{S}} = 2.01$ , and thus it is expected that the forbidden frequency gap in CdS will be considerably larger than that in ZnS. Recent lattice dynamical calculations on  $\text{CdS}^{15}$  and  $\text{ZnS}^{16}$  also confirm this. The calculated bandgaps expressed in the dimension-

less unit  $\Delta\nu/\nu_{\text{TO}}$  are  $\sim 0.05$  and  $0.14$ , for CdS and ZnS, respectively. Because of the limited range of a gap that can exist in the frequency spectrum of a crystal, the gap modes are expected to be relatively less pressure sensitive in comparison to local modes which occur in a free region above the optic band. Furthermore, for crystals with relatively smaller gaps, the gap mode will be expected to exhibit less pressure dependence as in the case with ZnS:Se vis-à-vis CdS:Se.

1. L. Vegard, *Shrifter Norsk Videnskaps. Akad. Oslo, Mat. Naturv. Klasse 1*, 88 (1947). *Chem. Abstracts* **43**, 4073h (1949).
2. I. F. Chang and S. S. Mitra, *Phys. Rev.* **172**, 924 (1968).
3. J. R. Ferraro, C. Postmus, S. S. Mitra, and C. J. Hoskins, *Appl. Opt.* **9**, 5 (1970).
4. O. Brafman, I. F. Chang, G. Lengyel, S. S. Mitra, and E. Carnall, Jr., *Phys. Rev. Letters* **19**, 1128 (1967).
5. J. F. Parrish, C. H. Perry, O. Brafman, I. F. Chang, and S. S. Mitra, *Proceedings of the International Conference on Physics of II-VI Semiconductors* (W. A. Benjamin, New York, 1967), pp. 1164-84.
6. J. R. Ferraro, S. S. Mitra, and C. Postmus, *Inorg. Nucl. Chem. Letters* **2**, 269 (1966).
7. C. Postmus, J. R. Ferraro, and S. S. Mitra, *Inorg. Nucl. Chem. Letters* **4**, 55 (1968).
8. S. S. Mitra, C. Postmus, and J. R. Ferraro, *Phys. Rev. Letters* **18**, 455 (1967).
9. R. Geick, C. H. Perry, and S. S. Mitra, *J. Appl. Phys.* **37**, 1994 (1966); H. N. Verlur and A. S. Barker, Jr., *Phys. Rev.* **155**, 750 (1967).
10. M. Hass, *Phys. Rev. Letters* **13**, 429 (1964).
11. R. H. Lyddane, R. B. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).
12. W. Cochran, *Z. Krist.* **112**, 465 (1959).
13. L. Genzel, in *Optical Properties of Solids*, S. Nudelman and S. S. Mitra, Eds. (Plenum Press, Inc., New York, 1969).
14. S. S. Mitra, O. Brafman, W. B. Daniels, and R. K. Crawford, *Phys. Rev.* **186**, 942 (1969).
15. M. A. Nusimovici and J. L. Birman, *Phys. Rev.* **156**, 925 (1967); P. Pfeuty, J. L. Birman and M. A. Nusimovici, in *Localized Excitations in Solids*, R. F. Wallis, Ed. (Plenum Press, Inc., New York, 1968), p. 210.
16. J. F. Vetelino, S. S. Mitra, O. Brafman, and T. C. Damen, *Solid State Comm.* **1**, 1809 (1969).