

Table II. Optical phonon frequencies (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 ^a	264			266		268			269		272				272
	175	176			177		178			180		181				181
1.00	170	171			172		174			175		176		177		

^a 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 limited⁹ to only 6 or 7 cm^{-1} , and that of the LO phonons hardly 1 cm^{-1} . As all measurements were done with un-

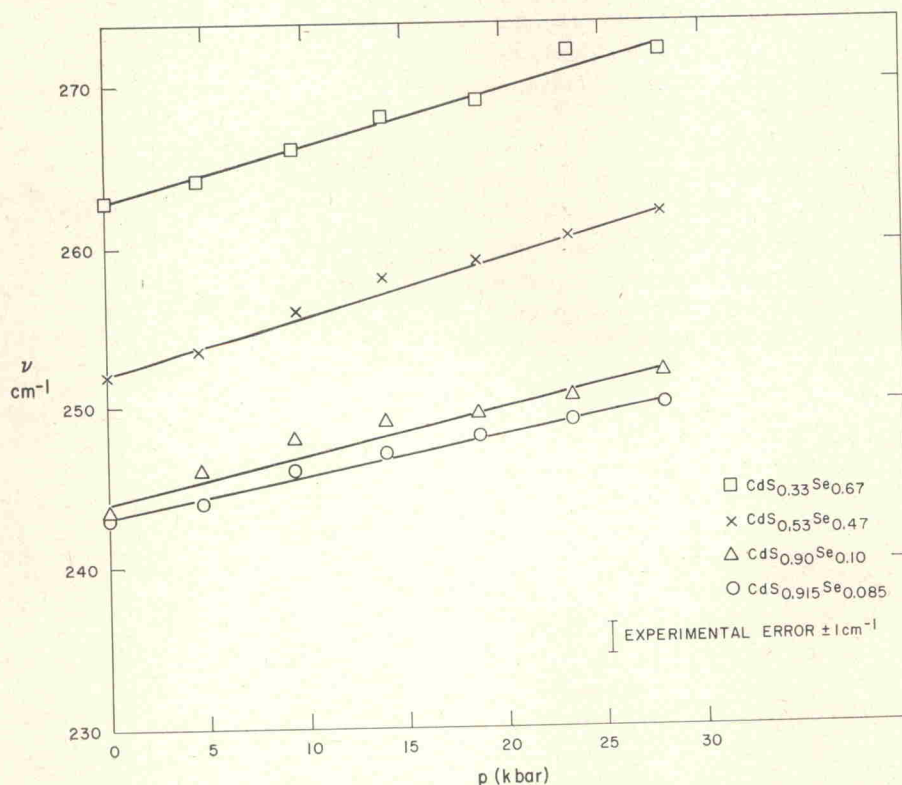


Fig. 3. Pressure dependence of high frequency mode in $\text{CdS}_{1-x}\text{Se}_x$.

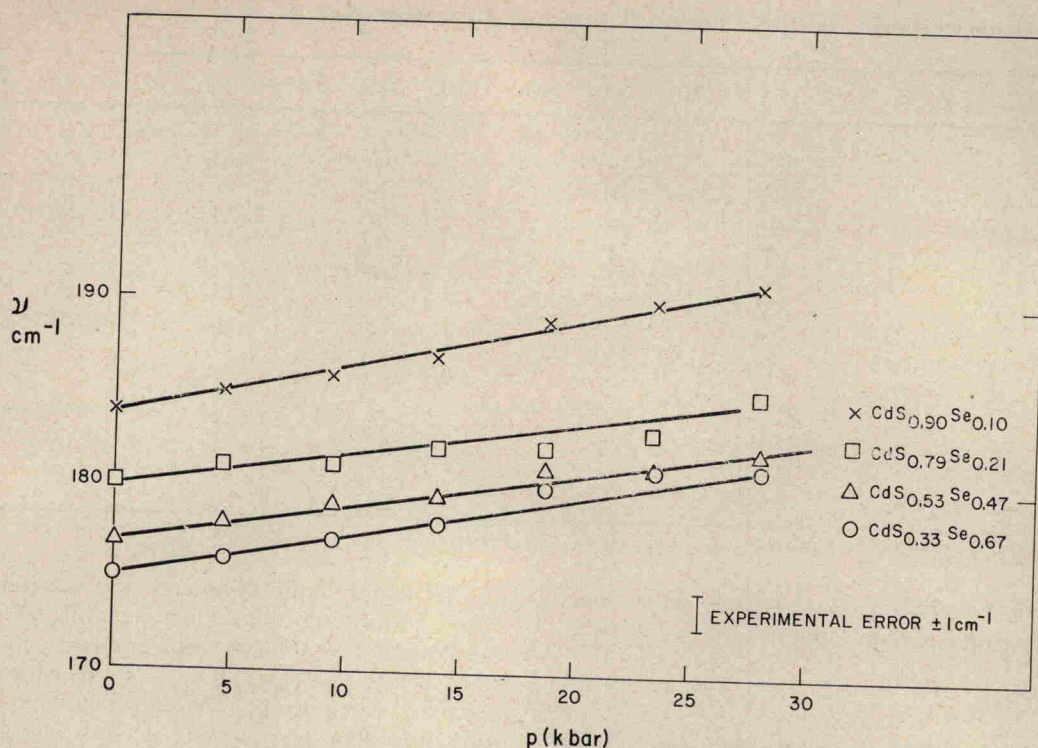


Fig. 4. Pressure dependence of low frequency mode in $\text{CdS}_{1-x}\text{Se}_x$.

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 μ_{AC} the reduced mass per Bravais unit cell of AC . The two observed transmission minima for each value of x are thus labeled TO_{AB} and 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^{4,5} 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.¹⁰ The

present experimental data are compared with those calculated from the Chang and Mitra² theory in Fig. 6.

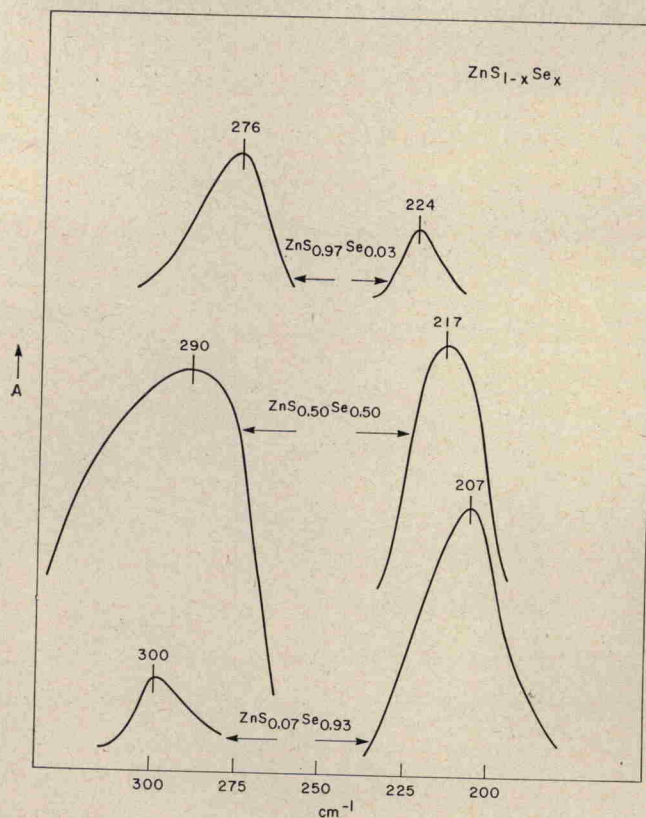


Fig. 5. The high frequency and low frequency modes of $\text{ZnS}_{1-x}\text{Se}_x$ at several mole fractions.