Table II. Optical phonon frequencies (cm^{-1}) as a function of pressure in mixed crystals $CdS_{1-x}Se_x$. 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	243 184	244 185			246 186		247 187			248 187		249 187		250 188		
0.10	244 184	246 185			248 186		249 187			250 189		251 190		252 191		
0.21	243 180	245 181			247 181		248 182			249 182		250 183		252 185		
0.47	252 177	254 178			256 179		258 180			259 181		261 181		262 182		
0.64	262 173		262 174			268 176			270 178		271 178				274 181	
0.67	263[a] 175	264 176			266 177		268 178			269 180		272 181			272 181	
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 $\mathbf{k}\simeq 0$, 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[9] to only 6 or 7 cm^{-1}, and that of the LO phonons hardly 1 cm^{-1}. As all measurements were done with un-

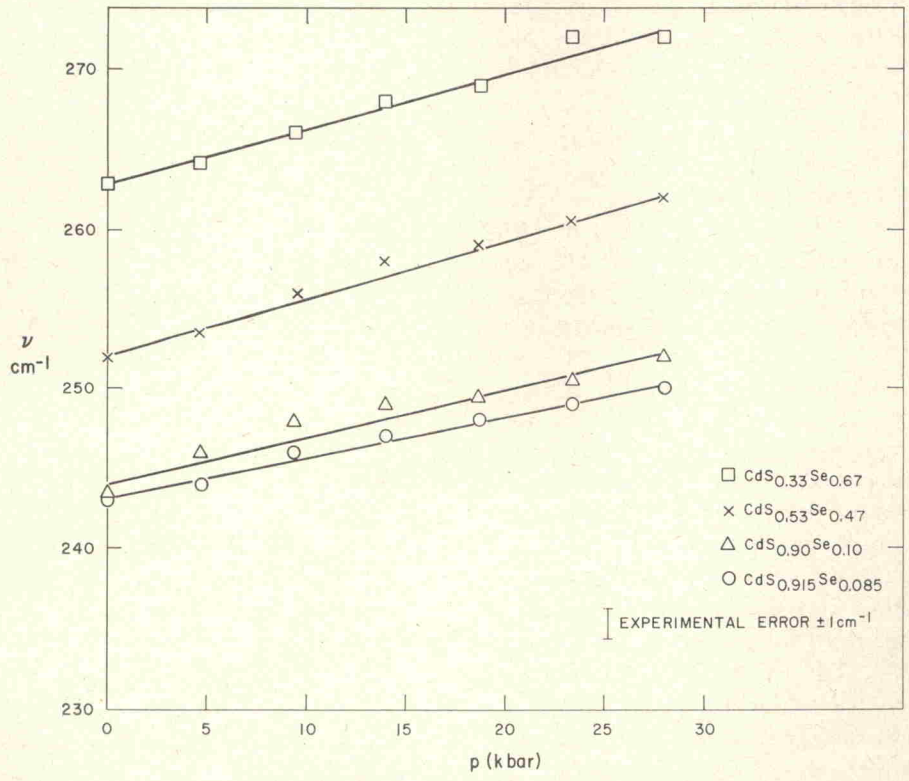

FIG. 3. Pressure dependence of high frequency mode in $CdS_{1-x}Se_x$.

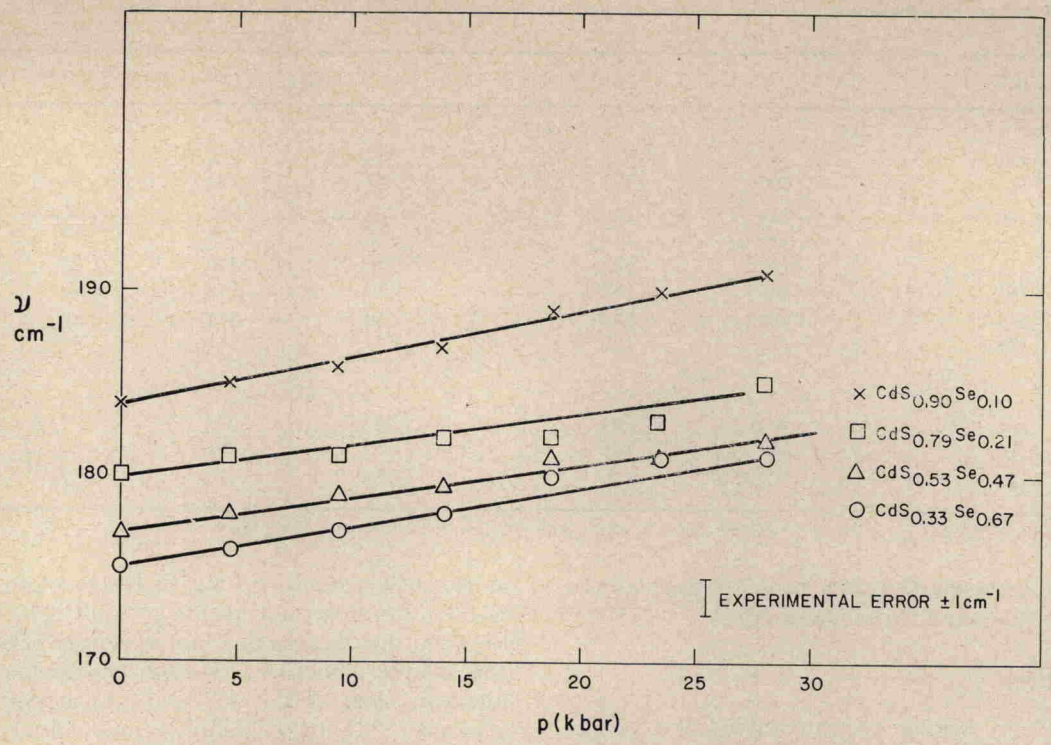

FIG. 4. Pressure dependence of low frequency mode in $CdS_{1-x}Se_x$.

oriented polycrystals in unpolarized radiation, we were unable to resolve the anisotropic splitting. Thus for $ZnS_{1-x}Se_x$ and $CdS_{1-x}Se_x$ 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 $ZnS_{1-x}Se_x$ and $CdS_{1-x}Se_x$ 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 ZnS_xSe_{1-x} and CdS_xSe_{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 $ZnS_{1-x}Se_x$ 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 Mitra[2] theory in Fig. 6.

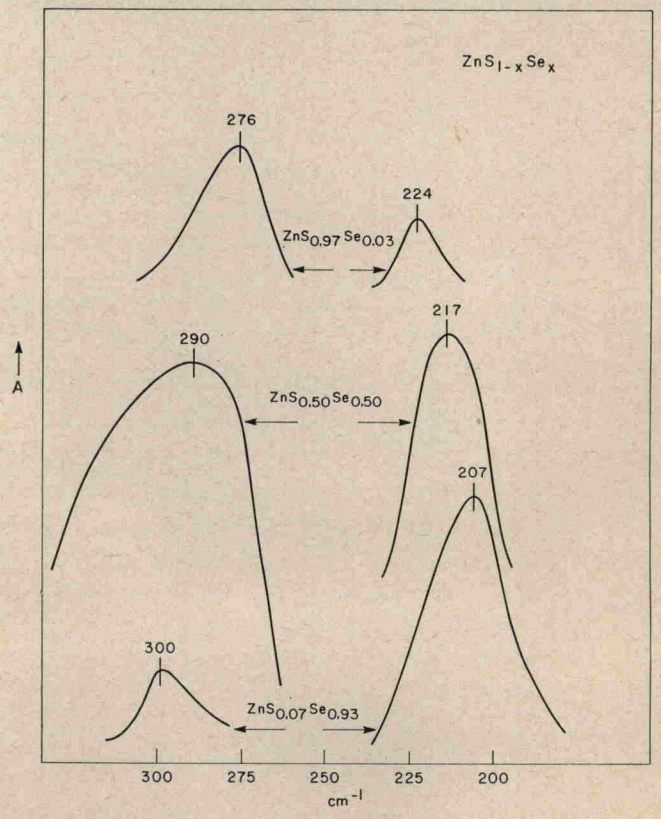

FIG. 5. The high frequency and low frequency modes of $ZnS_{1-x}Se_x$ at several mole fractions.