The long-wavelength longitudinal optic mode (LO) frequency of a crystal is related to the TO mode frequency by the Lyddane–Sachs–Teller relation,[11]

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

where ϵ_0 and ϵ_∞ 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[3] 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[3] quite well with the predictions of the virtual ion model.[2] For a multimode crystal a modified Lyddane–Sachs–Teller relation had been proposed[12]

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

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[2] have given the following semiempirical relations for this purpose:

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

and

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

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[4] 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 $x \simeq 1$. 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 ($\mathbf{k} \sim 0$ 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 $x \simeq 0$. This triply degenerate
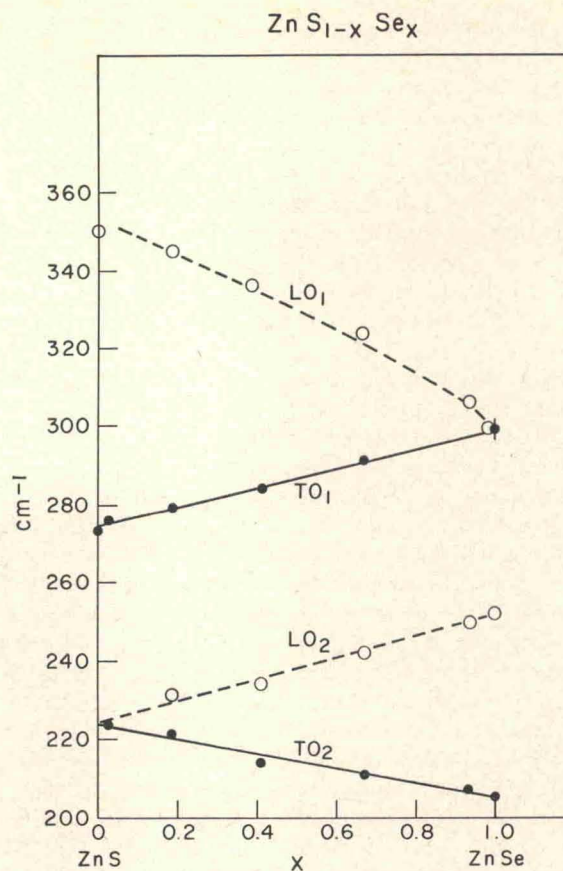

Zn S$_{1-x}$ Se$_x$

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.[13]

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[14] 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 $S \simeq 0$ ($x \simeq 1$), could not be investigated as a function of pressure.

The low frequency modes of $ZnS_{1-x}Se_x$ and $CdS_{1-x}Se_x$ also have linear pressure dependence (Figs. 2 and 4). For $x \geqslant 0.41$ in the case of $ZnS_{1-x}Se_x$, and for all values of x in the case of $CdS_{1-x}Se_x$, the low frequency mode (TO_2) retains its ZnSe- or CdSe-like character. However, for $x=0.19$ and 0.03 in the case of $ZnS_{1-x}Se_x$, 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 $CdS_{1-x}Se_x$ 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 $m_{Br} > m_K, m_{Cl}$. As a result the system $KCl_{1-x}Br_x$ shows one-mode behavior.[2,3] For the cases under consideration, however, $m_{Cd}/m_S = 3.51$ and $m_{Zn}/m_S = 2.01$, 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 CdS[15] and ZnS[16] also confirm this. The calculated bandgaps expressed in the dimension-less unit $\Delta \nu/\nu_{TO}$ are ~ 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.

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