

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

J. R. Ferraro, S. S. Mitra,[†] C. Postmus, C. Hoskins,[‡] and E. C. Siwiec[§]

Argonne National Laboratory, Argonne, Illinois 60439

(Received 5 December 1969; revision received 22 December 1969)

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.¹

* Based on work performed under the auspices of the U. S. Atomic Energy Commission and also partially supported by the U. S. Air Force In-House Laboratory, Independent Research Fund under Contract No. AF 19(628)-6042.

[†] Consultant to Argonne National Laboratory from University of Rhode Island, Department of Electrical Engineering, Kingston, R. I.

[‡] CSUI Student from University of Kentucky, Department of Chemistry, Lexington, Ky., September–December 1968. Present address: Massachusetts Institute of Technology, Chemistry Department, Cambridge, Mass.

[§] CSUI Student from St. Joseph's College, Brooklyn, N. Y., February–May 1969. Present address: Ohio State University, Chemistry Department Columbus, Ohio.

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 Mitra² 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 reported³ 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.^{4,5} 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 ZnS and ZnSe structures, and the latter with hexagonal unit cells similar to the wurtzite CdSe and 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 $0.085 \geq$

$x \geq 0.67$ 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,^{6,7} 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 ~ 43 kbar. The pressure was then released and a final spectrum obtained at ambient pressure. Calibration of the pressures obtained has been described previously.^{6,7} 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 (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 ^a	209	211	214	217	220
1.00	205	206	210	211	215	218	205	207

^a 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).

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

^c High frequency peak was very weak and was difficult to follow with pressure.

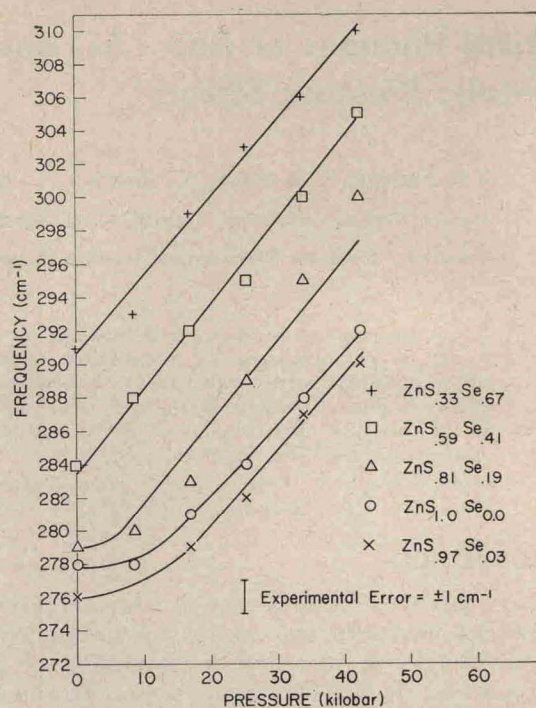


Fig. 1. Pressure dependence of high frequency mode in $\text{ZnS}_{1-x}\text{Se}_x$.

All modes shift to higher frequencies with pressure. In the case of pure ZnS and pure ZnSe, the shifts are comparable (14 and 13 cm^{-1} , respectively, for a pressure change of ~ 43 kbar) and agree well with previous pressure data on ZnS.⁸ 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

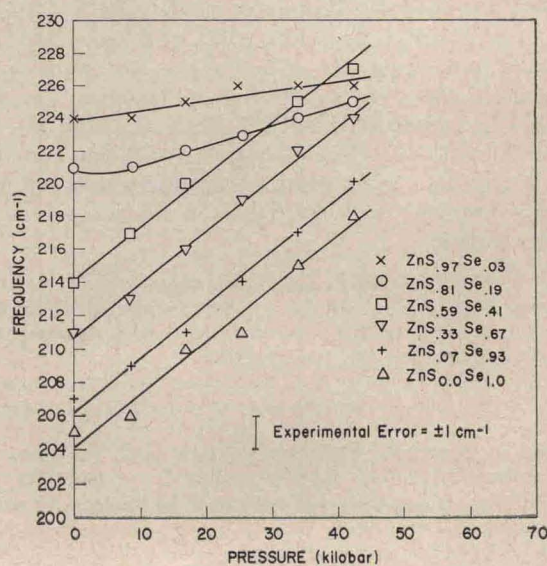


Fig. 2. Pressure dependence of low frequency mode in $\text{ZnS}_{1-x}\text{Se}_x$.