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Infrared Absorption of Localized Vibration Due to Lithium in Zinc Selenide and Cadmium Sulfide

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The infrared spectra of undoped and lithium doped ZnSe and CdS were measured. Localized mode bands originating from relatively light lithium ions were identified by the use of isotope. Four distinct local mode bands were observed in ZnSe: Li^7 but only one Li-band was observed in CdS: Li. The definite assignment of each band to possible Li sites in the crystal is yet to be made.

§1. Introduction

II-5.

Recently there has been considerable interest in impurity activated infrared lattice vibration spectra. Impurities are known to affect the lattice vibration spectra in two ways resulting the two types of infrared absorption; (i) localized modes absorption in the frequency range above the top of the optical branch or in the gap of the optical and the acoustic branch, (ii) resonance and band mode absorption in the range of the fundamental lattice modes of the host crystal. Extensive studies on the existence of these bands have been reported for alkali halides and silicon and some III-V compounds. To the authors knowledge there seems to be no investigation for II-VI compounds.

Lithium, as a light impurity mass, is expected to produce a localized mode above the top of the optical branch of the host lattice in most ionic and semiconducting compounds. The optical measurements have been reported for KBr: Li,¹⁾ GaAs: $\text{Li}^{2)}$ and Si: Li, B.³⁾ For the latter two compounds, the absorption bands due to localized modes of Li were observed with some complications arising from association. For KBr: Li a resonance mode at very low frequency was found and great reduction of the binding force was assumed to interprete the band.

In this respect the measurement of the II-VI compounds doped with Li may be of interest and some experimental results on ZnSe: Li and CdS: Li are reported in this paper.

§2. Experimental

The crystals of ZnSe were grown by the

Bridgeman method in argon atmosphere under the pressure of 95 atm and the temperature of 1600°C. Lithium-doped crystals were prepared by adding LiCl powder in ZnSe powder at a rate of 0.01 gram mole per 1 gram mole ZnSe. The mixed powder was heated at 740°C for 2 hours in argon atmosphere before growing the crystal.

The crystals of CdS were made by the method described by Greene and coworkers.⁴⁾ Lithium was doped by adding the proper amount of Li_2CO_3 powder in the original charge.

The spectral measurement was made by a vacuum grating spectrometer⁵⁾ at room, dry ice and liquid nitrogen temperature. Unwanted higher order radiation was removed by suitable combinations of reststrahlen filter, grating filter and powder filter. The absorption bands due to lithium were situated in the two phonon band region of the host compounds and in most cases the bands were only observable at liquid nitrogen temperature with the sample thickness of around 0.3 mm.

\S 3. Experimental Results and Discussion

(a) ZnSe:Li

Figure 1 shows the absorption spectra of undoped (dotted curve), Li^6 doped (chain curve), and natural Li doped ZnSe (full curve) in the spectral region between 20 μ and 33 μ . By comparing the three curves, two phonon bands of host ZnSe crystal and the localized mode bands due to Li^6 and Li^7 can be identified and the wavenumber of the four distinct Li^7 bands and the two distinct Li^6 bands are given in Table I. It is interesting to note that the two phonon



Fig. 1. The infrared absorption of undoped and Li-doped ZnSe at liquid nitrogen temperature.

Table I. Wavenumbers of the local vibrations of Li^{6} and Li^{7} in ZnSe at liquid nitrogen temperature.

ν(Li ⁶)	ν(Li ⁷)	$ u(\text{Li}^6)/\nu(\text{Li}^7) $
_	353	
350	336	1.04
341	328	1.04
_	318	—

bands are enhanced by the presence of lithium impurity. The Li⁶ bands at 350 cm⁻¹ and 341 cm⁻¹ correspond to the Li⁷ bands at 336 cm⁻¹ and 328 cm⁻¹. The frequency ratio of $\nu(Li^6)$ to $\nu(Li^7)$ is 1.04 for both bands. If the impurities were vibrating independently, the ratio should be 1.08. The Li⁶ bands corresponding to the Li⁷ bands at 353 cm^{-1} , 318 cm^{-1} could not be observed as the Li⁶ concentration was not high enough (from spectrochemical analysis Li content of about 0.001 weight percent was indicated). The Libands became too broad at temperatures higher than that of liquid nitrogen and no quantitative measurement of the temperature dependence of the band peak position and the half width could be made.

The behavior of Li in ZnSe is not well known. Lander⁶ showed that lithium in ZnO could occupy interstitial sites as donors and/or substitutional sites as acceptors by the proper treatment. Hayes² observed five Li-bands in GaAs and, by co-doping Zn or Te, two of them were definitely assigned to the local modes of unassociated Li at interstitial site and at substitutional site (both sites have T_d local symmetry) respectively. Among the remaining three bands two were tentatively assigned to the splitted bands originating from Li⁺-vacancy pair of axial sym-

metry and one to Li-oxygen complex. As ZnSe is iso-electronic compound to GaAs with the same crystal structure and almost equal lattice constant, the Li-bands in ZnSe may be assigned to the local modes due to unassociated interstitial and substitutional Li and some complexes such as Li-vacancy pairs, and closer similarity may be expected. Inspection of both spectra showed no correspondence of the bands (as to relative position and intensity) and no definite assignment of the observed bands could be made. To help the assignment the measurement on the co-doped specimen (ZnSe: Li, Al, ZnSe: Li, Cu and others) are under way. Preliminary result on ZnSe : Li, Al showed slight shifting and splitting of some Li-bands and it is hoped to obtain the useful information on the behavior of Li from these experiments.

(b) CdS:Li

The spectra of Li⁶-doped CdS at room and liquid nitrogen temperature are shown in Fig. 2 together with the one for pure CdS at room



Fig. 2. The infrared spectra of pure CdS at room temperature and Li⁶-doped CdS at room and liquid nitrogen temperature.



Fig. 3. The infrared spectra of pure and Li-doped CdS at liquid nitrogen temperature.

temperature (The measurement was made by Perkin-Elmer Model 221 spectrophotometer). A broad absorption band centered at 474 cm^{-1} at liquid nitrogen temperature is produced by the Li impurity. The band becomes weak and broad at room temperature as is shown in Fig. 2. Similar result is obtained for Li⁷-doped crystal and the Li⁷-band was centered at 457 cm⁻¹ at liquid nitrogen temperature as is given in Fig. 3. The frequency ratio of $\nu(\text{Li}^6)$ to $\nu(\text{Li}^7)$ was again 1.04. Many sharp two phonon bands were also observed.

The spectra of CdS: Li is very much different from that of ZnSe: Li and this may partly be due to the difference in crystal growing method and in the crystal structure. The location of Li in the crystal lattice is not well known and the band may be originating from the localized vibration of interstitial Li⁺ or substitutional Li⁻ or lithium-oxygen complex. The latter possibility cannot be ruled out as Li was added in the form of Li₂CO₃, but usually the frequency ratio of the complex is relatively small $(1.02 \text{ in } \text{GaAs}^2)$ and 1.03 in Si⁷). The reason for the broadening of the band is not clear. The measurement with the polarized radiation on the well oriented single crystal and co-doped specimens will be made in the near future.

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