

## Infrared Absorption Spectra due to Localized Vibration in the II-VI Compounds

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The infrared absorption spectra due to localized vibration of Al in ZnS, ZnSe and ZnTe, Be and Mg in ZnSe, and Li in ZnSe and CdS are measured. Aluminium shows five or six bands in zinc chalcogenides. This complexity arises from the charge compensation mechanism of Al donors in the host crystals. From the measurements of concentration dependency, of doubly doped crystal (e.g. ZnSe:Al, Li) and of heat treatment effect one of the bands is assigned to the localized mode of the unassociated Al donor: 438 (ZnS:Al), 359 (ZnSe:Al) and 313  $\text{cm}^{-1}$  (ZnTe:Al). The remaining bands are due to aluminium-defect (presumably Zn vacancy) complexes, but a definite model of the complexes is yet to be determined.

No such complexity arises for Be and Mg and the localized mode bands are observed at 450 for ZnSe:Be, 352, 345 and 334  $\text{cm}^{-1}$  for  $^{24}\text{Mg}$ ,  $^{26}\text{Mg}$  and  $^{28}\text{Mg}$  in ZnSe respectively. Lithium in CdS shows a very broad band at 474 ( $^6\text{Li}$ ) and 457  $\text{cm}^{-1}$  ( $^7\text{Li}$ ).

Lithium acts as an acceptor in doubly doped crystal: ZnSe:Al, Li. When the concentration of Li is much smaller than that of Al, the spectrum is simply the superposition of Al bands and Li band. The localized mode band of the unassociated Li acceptor appears at 412 ( $^6\text{Li}$ ) and 383  $\text{cm}^{-1}$  ( $^7\text{Li}$ ) respectively. As the concentrations of both impurities become comparable, the charge compensation is established between Al donors and Li acceptors and the spectrum changes drastically. This result can be interpreted by considering the pair formation between the Al donor and the Li acceptor.

The heat-treatment effect on some of the doped crystals are also described.

### §1. Introduction

There has been considerable interest in the impurity-induced lattice infrared spectra. The most extensively studied materials are alkali halides<sup>1)</sup> and silicon.<sup>2)</sup> Some measurements have been reported on the III-V compounds.<sup>2)</sup>

The impurity plays an important role in the II-VI compounds as the luminescent center and the behavior of various impurities has been studied by E.S.R., optical emission and absorption spectra and others.<sup>3)</sup> The study of the impurity-induced infrared spectra could be one of the useful tool in studying the behavior of the impurity centers.

Only a few experimental and theoretical results on the II-VI compounds have been reported. Hayes and others<sup>4)</sup> have recently made the experimental

and theoretical study of CdTe : Be. They have observed the localized mode at  $391\text{ cm}^{-1}$  and the resonance mode at  $61\text{ cm}^{-1}$  and compared the results with the shell model calculation. The impurity modes in CdS:Se, CdSe:S, CdTe:Se, CdTe:Li, ZnSe:S, ZnSe:Mn, ZnSe:Te and ZnTe:S have been observed by Balkanski and others,<sup>6)</sup> and preliminary calculation of the local mode in CdS has also been reported.<sup>6)</sup>

This paper presents the results of a series of studies on the localized vibrations due to several light impurities in zinc chalcogenides. A part of the results has already been published elsewhere.<sup>7-9)</sup> The most extensively studied impurity is aluminium. As the valency of the impurity is different from that of the replaced ion of the host lattice, the observed spectrum is inevitably complex. Other light impurities studied are beryllium and magnesium in ZnSe and lithium in CdS. In §3·1 the theoretical estimate of the localized mode frequencies of several light impurities in ZnSe lattice is made, and the experimental result is presented in §3·2. The infrared spectra of doubly doped impurities (ZnSe:Al, Li and ZnS:Al, Cu) are discussed in §3·3. The effect of heat-treatment on ZnSe:Al, ZnTe:Al and ZnSe:Al, <sup>7</sup>Li in different atmospheres is described in §3·4 and the concluding remark is given in §4.

## §2. Experimental

The crystals were grown by the Bridgeman method in argon atmosphere under high pressure and high temperature.<sup>10)</sup> As the infrared absorption bands due to localized modes appear in the fairly strong two-phonon region of the host crystal, the measurements were made with thin specimens ( $\sim 0.3$  mm) of relatively high doping amount ( $\gtrsim 10^{18}\text{ cm}^{-3}$ ) at liquid nitrogen temperature.

A far infrared vacuum grating instrument<sup>11)</sup> was used to measure the spectral region from  $500\text{ cm}^{-1}$  down to the wavenumber below which the strong reststrahlen absorption makes the transmission measurement impossible. The optical properties of the undoped II-VI compounds in the far infrared region have been reported previously.<sup>12)</sup>

## §3. Experimental results and discussion

### 1) Estimate of localized mode frequencies in ZnSe

When the eigenvectors and the normal mode frequencies of the host lattice are known, the localized mode frequency of an isotopic mass defect can be calculated from the following expression:<sup>13)</sup>

$$\frac{1}{\epsilon_{\alpha}} = \frac{\omega^2}{3N} \sum_{i,j} \frac{|W(\kappa | \frac{q}{j})|^2}{\omega^2 - \omega_j^2(q)}. \quad (1)$$

Here  $\epsilon_{\kappa}=1-M'_{\kappa}/M_{\kappa}$ ,  $M'_{\kappa}$  is the mass of the impurity which replaces the  $\kappa$ -th host ion of the mass  $M_{\kappa}$ ,  $\omega_j(q)$  and  $W(\kappa|q)$  are the frequency and the eigenvector of the normal mode of the wave vector  $q$  of the  $j$ -th branch. As there seemed to be no reliable lattice dynamical model for the II-VI compounds to perform this elaborate calculation, a simpler method<sup>14)</sup> was used to estimate the normal mode frequencies of several light impurities in ZnSe which is the most extensively studied host lattice. Firstly the zinc blende lattice is approximated by the diamond lattice. Then the Eq. (1) is reduced to the following expression for the isotopic mass defect:<sup>13)</sup>

$$\frac{1}{\epsilon_{\kappa}} = \omega_L^2 \int_0^{\omega_M} \frac{g(\omega)}{\omega_L^2 - \omega^2} d\omega, \tag{2}$$

where  $g(\omega)$  is the phonon density of state of the host lattice,  $\omega_L$  is the localized mode frequency, and  $\omega_M$  is the maximum lattice frequency. Secondly the density of state  $g(\omega)$  of ZnSe is approximated by the known  $g(\omega)$  of the other compounds of the same crystal structure. The density of state of GaAs<sup>15)</sup> renormalized to ZnSe was used for this purpose. Later the paper by Hayes and others<sup>4)</sup> on CdTe:Be came to our attention and  $g(\omega)$  of CdTe was also used. Both results show a slight difference. In Fig. 1 the former result is given. The coincidence between the calculated values and the experimental ones described later is not satisfactory as is clear from Fig. 1 and Table I. This discrepancy is due to the approximation assumed above. For the impurities of the different valency (Al and Li) the difference is larger and the proper force model which takes into account the coulomb interaction should be considered.

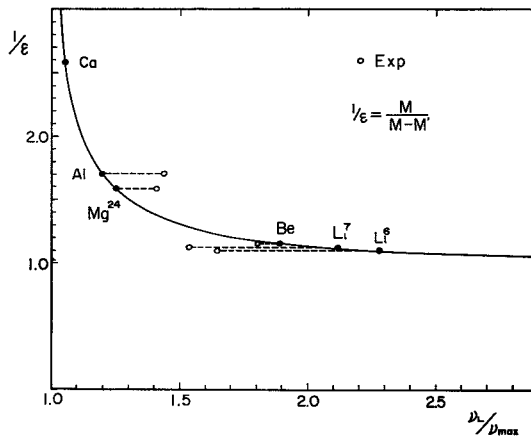


Fig. 1. The calculated localized mode frequency as the function of impurity mass in ZnSe (see Eq. (2)).

Table I. The calculated and observed localized mode frequencies of several light impurities in ZnSe.

Impurity	$1/\epsilon$	$\nu_L[\text{CdTe}]^{*)}$ ( $\text{cm}^{-1}$ )	$\nu_L[\text{GaAs}]^{**})$ ( $\text{cm}^{-1}$ )	Obs. ( $\text{cm}^{-1}$ )
$^6\text{Li}$	1.101	581.0	570.0	412
$^7\text{Li}$	1.120	540.0	530.0	383
Be	1.160	481.0	472.5	450
$^{24}\text{Mg}$	1.580	313.8	312.8	352
$^{25}\text{Mg}$	1.619	308.8	308.0	345
$^{26}\text{Mg}$	1.660	303.8	303.0	334
Al	1.703	300.0	297.5	359

\*) Calculated values using the phonon density of state of CdTe.

\*\*) Calculated values using the phonon density of state of GaAs.

## 2) The localized modes of aluminium, magnesium, beryllium and lithium

The infrared absorption spectra of ZnSe:Al of three different concentrations are shown in Fig. 2. At the lowest concentration (dotted curve) the band at  $359\text{ cm}^{-1}$  is dominant and there are two groups of bands at both sides of this band. In all, six bands are observed. As the concentration is increased, the intensity of all the bands increases as is seen in Fig. 2, but the intensity of the two groups of bands increases much more strongly than that of the  $359\text{ cm}^{-1}$  band which is dominant at the lowest concentration. This fact is more clearly shown in Fig. 3. Here the bands are resolved assuming the Lorentzian form for the band shape and the integrated intensity

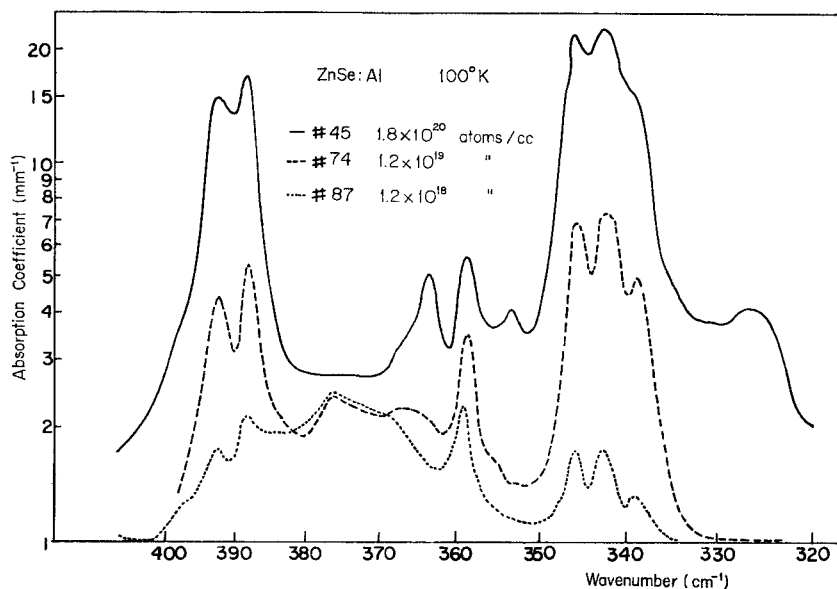


Fig. 2. The infrared absorption spectra of ZnSe:Al of three different concentrations.

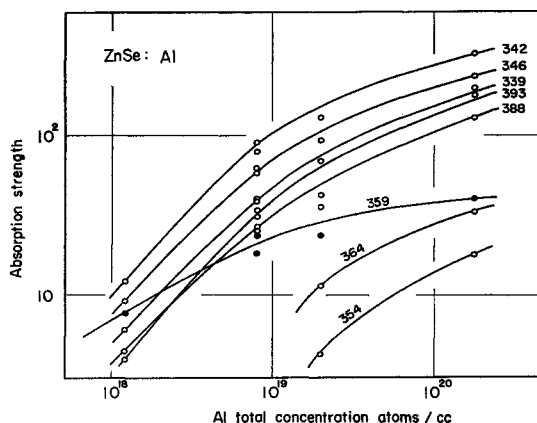


Fig. 3. The concentration dependency of the Al bands in ZnSe.

of each band is taken as the ordinate and the concentration of aluminium impurities as abscissa. It is clearly shown that the  $359\text{ cm}^{-1}$  band shows the different behavior to the remaining five bands, indicating that the band has the different origin to the others. At the highest concentration three new bands are observed at  $364$ ,  $354$  and  $325\text{ cm}^{-1}$ .

From these results it may be assumed that the  $359\text{ cm}^{-1}$  band is due to the localized mode of unassociated aluminium, that is an aluminium ion which is far away from any other impurity or defect and the remaining ones due to aluminium-defect complexes. The most simple aluminium-defect complex is an aluminium ion associated with a zinc vacancy which is situated at a next nearest neighbor site. As an aluminium ion replaces a Zn ion and the charge compensation is maintained by the presence of Zn vacancies, the presence of this complex is highly possible. Actually the presence of this complex is definitely shown by EPR experiment and optical experiment, and the complex is labeled as the A center.<sup>3)</sup> As the local site symmetry of the complex is  $C_2$ , and the perturbing Zn vacancy situates at the next nearest neighbor site to the Al impurity which has otherwise  $T_d$  site symmetry, the three split lines the separation of which would not be too large, should be expected for the localized vibration for this type of the associated aluminium. The number of the observed bands which are to be assigned is five and the experimental result cannot be interpreted with this model alone and more involved model should be taken into account.

The results for ZnTe:Al and ZnS:Al are shown in Fig. 4 and Fig. 5 respectively. The general feature is the same as for ZnSe:Al. There are a sharp band at  $313\text{ cm}^{-1}$  for ZnTe:Al and at  $438\text{ cm}^{-1}$  for ZnS:Al and two groups of bands in both sides of these bands. The concentration dependency of the band intensity in ZnTe:Al shows the same tendency as in ZnSe:Al.

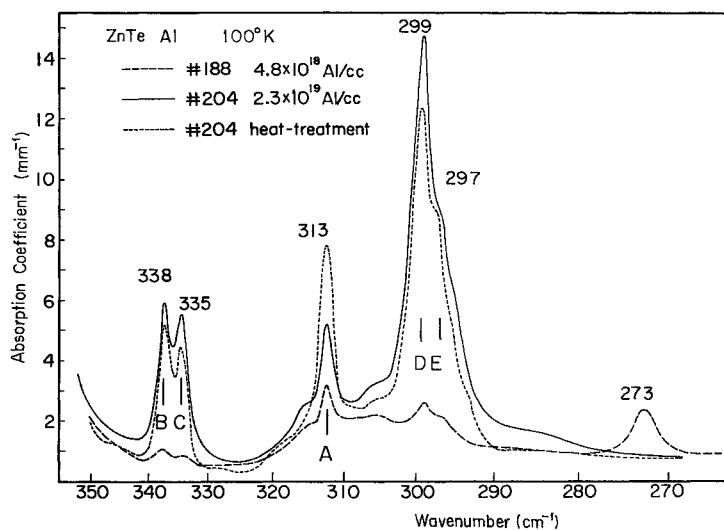


Fig. 4. The infrared spectra of ZnTe:Al of the two specimens (#188 and #204) and the heat treatment effect on #204 in zinc atmosphere.

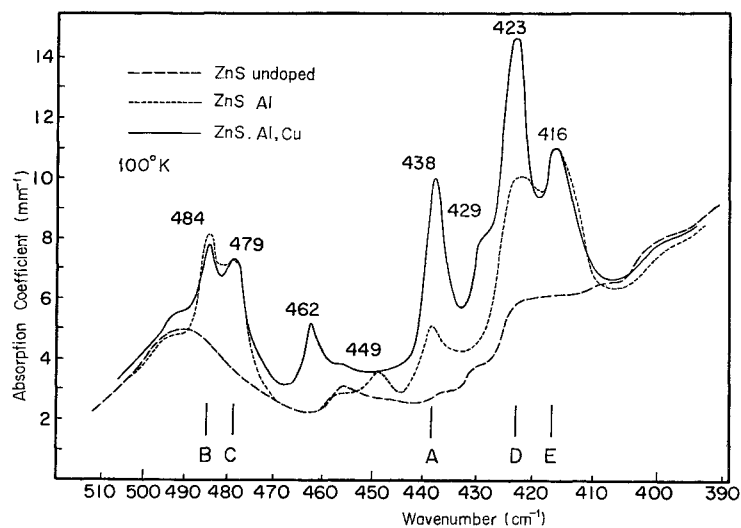


Fig. 5. The infrared spectra of ZnS:Al and ZnS:Al, Cu.

The band position of the localized modes due to Al-doping in zinc-chalcogenides is shown in Fig. 6 in the reduced wavenumber scale. The central band designated A can be assigned to the localized vibration of an unassociated aluminium. The relative intensity of the two groups of the bands B, C, D, E and F at both sides of the central band is different for the different host materials. To obtain the further information as to these bands which may be due to the localized vibration of aluminium-defect (presumably Zn

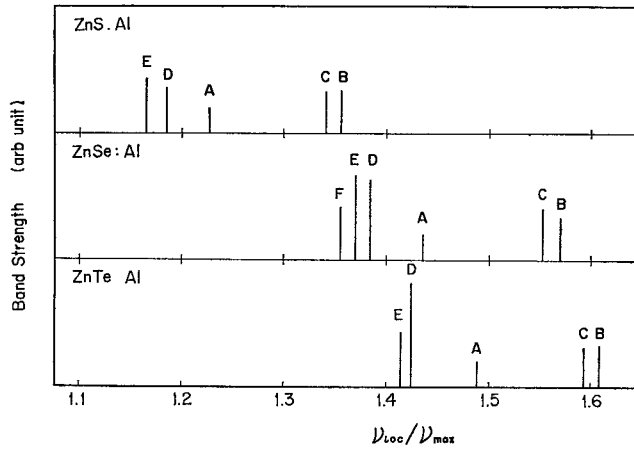


Fig. 6. The band positions of the Al bands in zinc-chalcogenides in reduced wavenumber scale.  $\nu_{\max}$  is the highest band mode frequency of the host lattice.

vacancy) complexes, the infrared spectrum of doubly doped crystals and heat-treated ones have been measured and the results are described later.

The infrared spectrum of ZnSe:Mg is shown in Fig. 7. Magnesium has three isotopes,  $^{24}\text{Mg}$  (76.60%),  $^{26}\text{Mg}$  (10.11%) and  $^{28}\text{Mg}$  (11.29%). As magnesium replaces zinc in ZnSe and has the same valency to the replaced ion, there arises no complication originating in the charge compensation. The three bands observed at 352, 345 and 334  $\text{cm}^{-1}$  are due to the localized vibration of Mg isotopes.

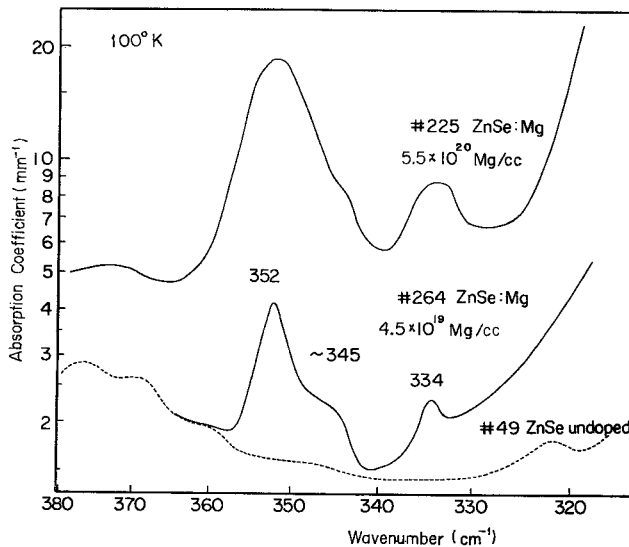


Fig. 7. The infrared absorption of Mg in ZnSe.

Beryllium in ZnSe shows a single sharp band at  $450\text{ cm}^{-1}$  at liquid nitrogen temperature as is shown in Fig. 8. The bands at the lower wavenumber side are all due to the two phonon process. The second overtone of the localized mode is observed at  $894\text{ cm}^{-1}$ . A sharp band at  $490\text{ cm}^{-1}$  is also observed in ZnS:Be. Beryllium is an interesting impurity, because it shows the localized mode at the highest edge of the two-phonon band region and enables the observation of the antistokes side bands originating from the combination with band modes of the host lattice as is shown by Hayes and others for CdTe:Be.<sup>4)</sup> Detailed work on this impurity in different host crystals is under way and will be reported later.

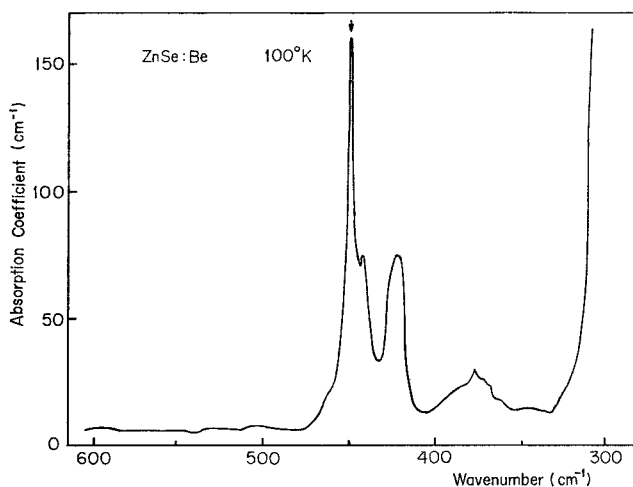


Fig. 8. The infrared absorption of ZnSe:Be. The band indicated by the arrow is due to the localized mode. The other bands are due to the two-phonon process.

Figure 9 shows the absorption band of Li-doped CdS. Contrary to the previous cases, the absorption band is very broad even at liquid nitrogen temperature (half width is about  $40\text{ cm}^{-1}$  compared with  $\lesssim 5\text{ cm}^{-1}$  of the other impurities in zinc chalcogenides). The band shows the isotope shift; the band center in CdS:<sup>7</sup>Li is at  $457\text{ cm}^{-1}$  and that of CdS:<sup>6</sup>Li at  $474\text{ cm}^{-1}$ . The ratio of the wavenumber  $\nu(^6\text{Li})/\nu(^7\text{Li})$  is 1.04 which is fairly small compared with 1.08, the square root of the mass ratio of the lithium isotopes. The band is perfectly polarized parallel to the *c*-axis of the hexagonal crystal. According to the calculation by Pfeuty and Elliott under the assumption of the simple substitutional mass defect,<sup>9)</sup> the localized mode of <sup>7</sup>Li in CdS will appear at  $615\text{ cm}^{-1}$  for the mode polarized parallel to the *c*-axis and  $665\text{ cm}^{-1}$  for the one polarized perpendicular to the *c*-axis. As the observed band shows the isotope shift, it is obvious that the lithium ion takes part in the vibration responsible to this mode but a definite model is yet to be determined. Recently Balkanski and others<sup>9)</sup> have measured Li-doped CdTe and observed



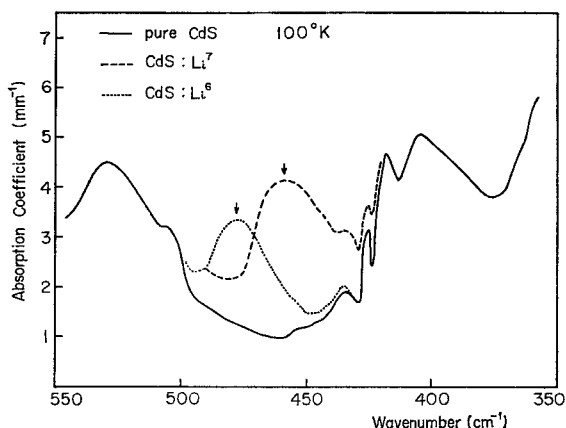


Fig. 9. The infrared absorption bands of Li doped CdS.

also very broad band whose half width is about  $35\text{ cm}^{-1}$ . It is unlikely that the band is due to the localized vibration of an unassociated lithium ion at a substitutional or an interstitial site.

Contrary to CdS:Li the infrared spectrum of ZnSe:Li showed many bands which could not be interpreted definitely.<sup>7)</sup> Further work will be interesting in understanding the behavior of lithium in the II-VI compounds.

In Fig. 1 and Table I the observed values of the localized vibrations of the unassociated impurities in ZnSe are given.

### 3) *Doubly doped crystal*

When Al and Li are doped together in ZnSe, Al acts as a donor and Li acts as an acceptor, both replacing Zn. When the concentrations of both impurities are the same, the charge compensation is mainly maintained between donors and acceptors without recourse to Zn vacancies, and the infrared spectrum may provide the useful information in distinguishing the band character of ZnSe:Al described above.

The infrared spectrum of ZnSe:Al, <sup>7</sup>Li is shown in Fig. 10. When the concentration of Li is much smaller than that of Al (solid line), there exist all of six bands observed in ZnSe:Al (Fig. 1). A new band appears at  $383\text{ cm}^{-1}$  which shows the isotope shift (see Fig. 11) and the band can be assigned to the localized mode of the unassociated Li acceptor. When the concentrations of both impurities are about the same order and high, fairly different spectrum is obtained as is seen from the dotted curve. The five aluminium bands in the solid curve which are attributed to unknown aluminium-defect complexes disappear and four new bands appear at  $350$ ,  $356$ ,  $373$  and  $393\text{ cm}^{-1}$  besides the  $359$  and the  $383\text{ cm}^{-1}$  band which are assigned to an unassociated Al donor and a Li acceptor respectively. The coincidence of the band at  $393\text{ cm}^{-1}$  in both spectra is accidental as becomes clear when

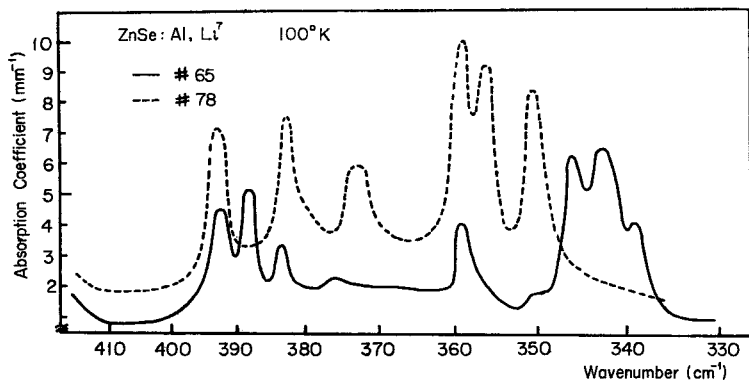


Fig. 10. The infrared absorption spectra of ZnSe:Al,  ${}^7\text{Li}$ . The concentrations of the impurities are as follows ( $\text{cm}^{-3}$ ):

$$\#65: N_{\text{Al}}=1.2 \times 10^{19}, N_{\text{Li}}=6.7 \times 10^{17}$$

$$\#78: N_{\text{Al}}=9.5 \times 10^{18}, N_{\text{Li}}=1.8 \times 10^{19}$$

${}^7\text{Li}$  is replaced by  ${}^6\text{Li}$ .

Figure 11 shows the spectrum of ZnSe:Al,  ${}^6\text{Li}$ . Again when the concentration of aluminium is much greater than that of  ${}^6\text{Li}$  (solid curve), the spectrum is the superposition of the six bands of ZnSe:Al and one band of  ${}^6\text{Li}$  which is isotope-shifted to  $412 \text{ cm}^{-1}$ . In this specimen there are two extra bands at  $350$  and  $373 \text{ cm}^{-1}$  which grow up very strongly when the concentration of  ${}^6\text{Li}$  is increased to the same order to that of aluminium. In the dotted curve where the concentrations of  ${}^6\text{Li}$  and Al are about the same and fairly high, the five bands which are attributed to the unknown aluminium-defect complexes are completely absent and five bands are observed at  $412, 390, 373, 359$  and  $350 \text{ cm}^{-1}$ . Among these bands three bands at  $373,$

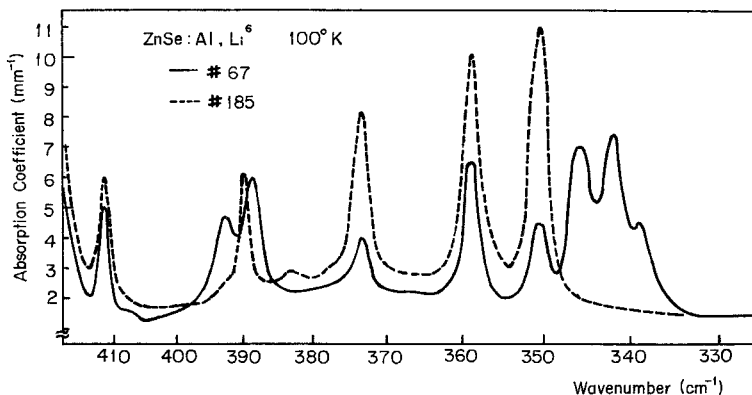


Fig. 11. The infrared absorption spectra of ZnSe:Al,  ${}^6\text{Li}$ .

$$\#67: N_{\text{Al}}=1.2 \times 10^{19}, N_{\text{Li}}=6.7 \times 10^{17}$$

$$\#185: N_{\text{Al}}=3.6 \times 10^{19}, N_{\text{Li}}=1.1 \times 10^{19}$$

359 and  $350\text{ cm}^{-1}$  are also observed in  $\text{ZnSe:Al, }^7\text{Li}$ . These band positions are not affected by replacing  $^7\text{Li}$  by  $^6\text{Li}$  and the bands can be attributed to the localized mode due to Al donor. The three bands observed at 356, 383 and  $393\text{ cm}^{-1}$  in  $\text{ZnSe:Al, }^7\text{Li}$  show isotope-shift by replacing  $^7\text{Li}$  by  $^6\text{Li}$ . The band at  $356$  and  $383\text{ cm}^{-1}$  of  $^7\text{Li}$  correspond to the bands at 390 and  $412\text{ cm}^{-1}$  of  $^6\text{Li}$  respectively as is clear from the frequency ratio. The band of  $^6\text{Li}$  corresponding to the  $393\text{ cm}^{-1}$  band of  $^7\text{Li}$  should appear at about  $424\text{ cm}^{-1}$ . The strong two-phonon band appears just at this region and makes the observation of the expected  $^6\text{Li}$  band difficult.

These experimental results can be interpreted by considering the pair formation between a Li acceptor and an Al donor. When the concentration of Al impurity is much higher than that of Li impurity, most of the Al ions are compensated by the presence of defects (Zn vacancies) and the spectrum of  $\text{ZnSe:Al, Li}$  is essentially the superposition of the spectrum of  $\text{ZnSe:Al}$  and that of substitutional Li acceptors. As the concentration of Li impurity is increased and becomes nearly the same as that of Al, the charge compensation is established between Al donors and Li acceptors without the help of Zn vacancies and the five bands due to aluminium-defect complex disappear. As there is the coulomb attraction between Al donors and Li acceptors, the number of the next nearest  $\text{Al}^+-\text{Li}^-$  pair will be appreciable. When such pair is formed, the triple degeneracy of the localized mode due to unassociated Al and unassociated Li is completely lifted because of the lowering of the local site symmetry from  $T_d$  to  $C_s$ . Among six bands observed in  $\text{ZnSe:Al, }^7\text{Li}$  (#78), the three bands at  $350$ ,  $359$  and  $373\text{ cm}^{-1}$  remain unchanged when  $^7\text{Li}$  is replaced by  $^6\text{Li}$  and the other three bands at  $356$ ,  $383$  and  $393\text{ cm}^{-1}$  show the isotope shift. The vibration of Al impurity is dominant for the former group of bands and the vibration of Li impurity is dominant for the latter. Thus it may be reasonably considered that these two groups of bands are due to the three split bands of the localized vibration of weakly coupled Al donor and Li acceptor respectively. Similar bands assigned to the pairing of the impurities have been reported in  $\text{Si}^{16)}$  and  $\text{GaAs}^{17)}$

Recently Elliott and Pfeuty<sup>18)</sup> have made the theoretical treatment of the impurity pair in Si. They have considered only nearest neighbor pair, and the direct comparison of the theory with the present result could not be made.

The preliminary measurement on  $\text{ZnS:Al, Cu}$  is shown in Fig. 5. In this case Cu acts as an acceptor replacing Zn ion. The concentration of the impurities is not known, but from the similarity to the case of  $\text{ZnSe:Al, Li}$ , the bands at  $423$ ,  $438$  and  $462\text{ cm}^{-1}$  can be attributed to the three split bands of a donor weakly coupled to a next nearest neighbor Cu acceptor. The mass of Cu is only slightly lighter than that of Zn, and no localized vibration due to Cu can be observed. Further work on the localized modes of paired impurities is under way.

4) *Heat-treatment effect*

The infrared spectra of heat-treated crystals in selenium, tellurium or zinc atmosphere have been measured to obtain further information on the defect model in interpreting the spectra of Al doped crystals.

When ZnSe:Al specimen is heated in saturated zinc atmosphere, it becomes highly conductive and completely opaque in the infrared region concerned. The fact shows that compensation by Zn vacancies is destroyed by the diffusion of Zn atoms into the crystal lattice and Al donors are electron compensated producing shallow impurity level and thermally excited free carriers absorb the infrared radiation.

The effect of heat-treatment of ZnSe:Al in selenium atmosphere of 2 atm. at 900°C for 120 hours is shown in Fig. 12 by dotted curve. Here the band at 359 cm<sup>-1</sup> which is assigned to the localized vibration of the unassociated Al donor remains almost unchanged, but the other bands become very much weak after the heat treatment. One of the possible interpretation for this result is out-diffusion of Al impurities. The unassociated Al donors may be more difficult to diffuse out compared with the associated Al donors (presumably with Zn vacancy) and also there would be the process in which aluminium defect complexes are dissociated by the heat-treatment resulting the unassociated Al donors. Thus the total density of the unassociated Al donors may not change appreciably and the intensity of the central band remains almost unchanged. Anyway this result also shows that the band at 359 cm<sup>-1</sup> has different character from the remaining bands in ZnSe:Al.

The effect of heat-treatment of ZnTe:Al in saturated zinc atmosphere at 700°C for 120 hours is given by dotted curve in Fig. 4. The intensity of the 313 cm<sup>-1</sup> band which is assigned to the unassociated Al donor is increased but the remaining bands are weakened. This result agrees with the inter-

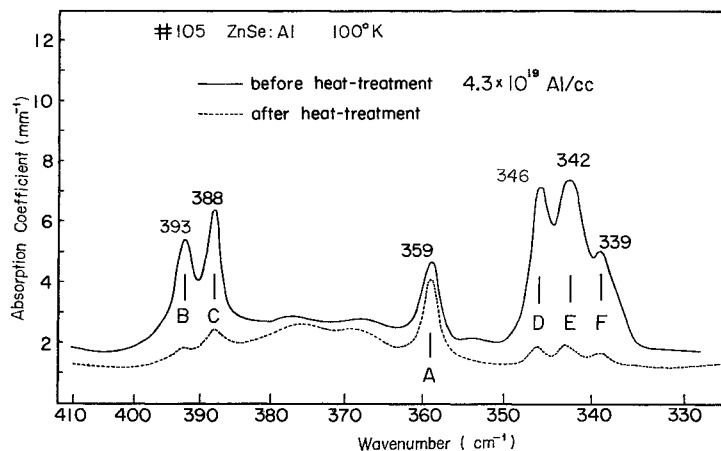


Fig. 12. The heat-treatment effect on #105 ZnSe : Al in saturated Se atmosphere.

pretation described previously that the vacancy compensation is destroyed by the diffusion of zinc. However the effect is not so drastic compared with ZnSe:Al heat-treated in saturated zinc atmosphere. In the latter case free carrier effect becomes dominant. It is suggested<sup>19)</sup> that the Frenkel type disorder on the zinc sublattice is present and controls the diffusion of zinc in highly Al doped ZnTe. The present result does not contradict with this suggestion. Heat-treatment of ZnTe:Al in tellurium atmosphere has not been made yet.

Finally the effect of heat-treatment on one of the doubly doped ZnSe (#75 ZnSe:Al, <sup>7</sup>Li) in saturated selenium atmosphere at 900°C for 120 hours is given in Fig. 13. Among the six bands which are observed before heat-treatment and are assigned to the localized vibration of the loosely coupled next nearest pair of an Al donor and a Li acceptor, the four bands at 393, 373, 356 and 350 cm<sup>-1</sup> are weakened considerably. These bands are attributed to the split bands of the localized modes of Al donor and Li acceptor respectively. The result shows that at least a part of next nearest Al<sup>+</sup>-Li<sup>-</sup> pairs is destroyed by the heat-treatment effect.

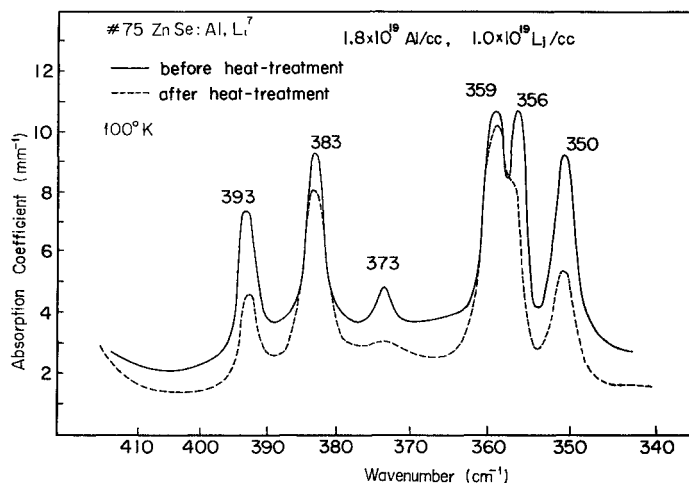


Fig. 13. The heat-treatment effect on #75 ZnSe:Al, <sup>7</sup>Li in saturated Se atmosphere.

#### §4. Concluding remarks

The infrared spectra of the several light impurities (Li, Al, Be, Mg) in some of the II-VI compounds are observed. When the valency of the impurity is different from that of the replaced ion of the host crystal, the complication of the spectrum arises because of the charge compensation mechanism. The detailed studies have been made on aluminium impurity in zinc chalcogenides. Several bands are observed and one of them is assigned

to the localized mode of the unassociated Al donor from the measurements of concentration dependency, of heat-treatment effect and of pairing effect. As to the definite model for the remaining bands of Al impurity which are attributed to the aluminium-defect complexes, no useful information has been obtained from the measurements on ZnSe:Al, Te, ZnSe:Al, Cd, and more systematic studies are necessary.

The infrared spectrum due to localized modes is also useful in the study of the pair formation of the lighter ions in the II-VI compounds. The quantitative measurement and the combined experiments with other techniques (e.g. light irradiation at low temperature producing charge carrier transfer between the impurity levels) will provide more detailed information.

The far infrared spectrum due to the resonance mode will also be interesting in understanding the behavior of the impurities, if they show the resonance mode. Preliminary measurement on ZnS:Ag showed several bands below  $120\text{ cm}^{-1}$  and the measurement will be extended to the other impurities and host crystals.

The authors wish to thank Prof. S. Shionoya and Dr. H. Kukimoto for kindly providing us the doped ZnS crystals.

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