Raman investigation of InSe doped with GaS


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Abstract

The Raman spectrum of InSe doped with GaS exhibits appreciable changes at low doping densities indicating considerable changes on introducing GaS. The photoluminescence as well as resonance Raman study shows that the exciton energy is shifted towards higher energy as a result of doping. At resonance, both the one- and two-phonon polar modes are observed, although considerably broadened. This indicates that the GaS-doped InSe develops significant topological disorder. Resonance Raman study shows that increasing the dopant broadens the resonance but the excitonic energy does not change as a result of the increase in the GaS in InSe. The scattering also exhibits considerable temperature dependence, so that it is possible to temperature tune the resonance in the doped samples at low temperatures.

Keywords: Resonant Raman scattering; Layer structure; Indium selenide

1. Introduction

InSe is a layered material [1-11] and belongs to the III-VI family. It consists of two-dimensional Se-In-Se layers bound together by weak van der Waal’s forces. Indium selenide has attracted [7,11-13] significant interest as an intercalation compound owing to its capacity to accept lithium in its van der Waals gap. The insertion of lithium atoms into layered compounds produces structural changes observable in lattice dynamics and band structure modification of the host [11,13].

Light scattering is a powerful technique to monitor the structural changes induced in the layered compound by intercalation or doping. This can be done by monitoring the polar and non-polar modes in InSe. Kuroda and Nishina [1,2] have measured resonant Raman scattering from optical phonons in InSe at 2 K and have attributed the resonance enhancement to the $E_1$ exciton at 2.531 eV at 77 K. Balkanski [11] has studied the effect of Li intercalation on InSe and has found that for low lithium concentrations the Raman spectrum is modified by the splitting of the valence band. For higher concentrations plasmon coupling has been observed in the Raman spectra. Resonant Raman effects at the indirect band gaps of GaS were studied [14] using excitation energies which ranged from the transparent region up to above the fundamental indirect band gap $\Gamma-\Sigma$ and the $\Gamma-\Sigma$ indirect transition.

Of broader interest is the behaviour of doping impurities in InSe, where there are arguments for impurity segregation in the interlayer spacing of InSe. It has been recently demonstrated that the weakness of binding forces in InSe gives rise to planar defects which do not affect the carrier mobility along the layers [15-22]. These planar defects may be either stacking faults or interlayer precipitates. Even for a rather high concentration of doping impurities, the effective number of charge carriers never exceeds $10^{16}$ cm$^{-3}$, which is very close to the concentration for the pure material.

Many experiments have been carried out to clarify this puzzling effect; high field cyclotron resonance [21], transport [16-19] and magnetotransport [22], electron microscopy [19] and electron paramagnetic resonance (EPR) [15]. From these, various workers have concluded that optical, transport and magnetotransport
properties of doped InSe can be explained with a model of doping impurities in the interlayer spacing of the layered structure.

Direct evidence for the existence of interlayer precipitates has been obtained by electron microscopy and X-ray microprobe analysis in indium selenide [20]. High field cyclotron resonance behaviour, among others, can be accounted for by two-dimensional accumulation layers in the vicinity of these defects [21]. This accounts for the unique behaviour of the layer compounds which exhibit intrinsic features (low apparent carrier density, high mobilities) even with high (100 ppm) initial doping levels. Evidence of interlayer precipitates has been also obtained by EPR measurements on Mn-doped InSe [15]. It has been shown [15] that impurity segregation coefficients have a very high value in InSe. This indicates that the InSe interlayer spacing constitutes privileged host sites for dopant impurities.

Diffusion perpendicular to the plane of the lamellar compounds has not been observed [20,23]. It has been shown [24] that in III-VI materials d electrons prevent the rotation of metal atoms and stabilize the Se-In pattern in the eclipsed configuration. As a rule, doping of the melt yields crystals with a remarkably small number of carriers (10^15) and no relation is found, except for Sn, between the initial composition and the final apparent number of free carriers. This is consistent with the stability of intralayer bonds in layer compounds which precludes substitution within the layer [23]. Chevy [23] has shown that with dopant concentrations up to 10^20 cm^-3 the number of apparent carriers remains in the range of 10^16 cm^-3. This indicates that the dopant precipitates in interlayer sites as excess indium does. Far-IR spectra of InSe doped with InS (150 ppm), GaS (100 ppm), Sn (3000 ppm) and Zn (1000 ppm) are given in Fig. 10 of Ref. [25]. These spectra show that only for the case of sulphur-doped samples is there a free carrier contribution at low frequency from which one could conclude that GaS is in the molecular form in the InSe crystal lattice. Moreover, InSe and GaS have melting points of 640 °C [26] and 1020 °C [27] respectively.

In view of the above, it is natural to think of GaS, which could be segregated, as a doping impurity in the van der Waal’s gap of InSe. High resolution X-ray diffraction data for our samples were obtained on a four-circle Siemens diffractometer to ascertain c axis modification on introduction of GaS in InSe. These data show that the c axis parameter is again 24.84 Å, indicating that there is no c axis modification on introduction of GaS. However, this negative result may be due to a very low concentration of GaS. Furthermore, no supplementary peaks of GaS are seen in the X-ray data, which may again be due to the small concentration of GaS. Therefore one may assume that the interlayer spacing is not affected by the presence of GaS, which may therefore be regarded as a doping impurity.

The purpose of this paper is to report a Raman study of changes produced in the Raman spectrum of InSe due to doping with GaS. In addition to doping effects, the temperature and excitation wavelength dependence of the one-phonon and two-phonon scattering is also studied. After doping, the damping of the non-polar, polar and two-phonon modes is particularly important and this reflects changes in InSe spectrum on introducing GaS. This study shows that there are two effects on introducing the GaS into InSe crystals. Firstly, there is a shift in the excitonic energy level towards higher energies and this is manifested by a change in the peak position of the photoluminescence of the doped samples with respect to pure InSe. This effect is also seen in the Raman scattering where at 2.41 eV one has resonant scattering for pure InSe at room temperature and one sees polar modes in addition to non-polar modes. This situation changes considerably on doping where polar mode scattering almost disappears indicating a shift of the exciton resonance. Secondly, in addition to the shift in the exciton energy we also observed the broadening of the phonon modes which we attribute to topological disorder due to GaS dopant. For further evidence of this we have tried to consider resonance Raman scattering (RRS) of the non-polar A1 mode for both pure and doped samples. The RRS experimental results have been justified by taking the same reduction in the binding energy of the exciton compared with the pure InSe for different concentrations of GaS dopant. This is because of the observation of the same shift in the peak position of the photoluminescence experiments for different concentrations of GaS dopant with respect to the pure InSe. Then, the value of the damping constant was changed to obtain the best fit. The results so obtained support the above-mentioned two effect. i.e. doping InSe with GaS causes the exciton energy shift towards the higher energy values, and secondly there is a broadening of the phonon modes which increases as dopant concentration increases.

The temperature study of the pure InSe has shown that the resonance occurs with laser excitation at 2.54 eV and 77 K [1,3,6]. Our doped InSe samples with various densities of GaS dopant also exhibit the resonance enhancement with laser excitation at 2.54 eV and 77 K. This is because, in this temperature range, the temperature coefficient of the band gap yields low temperature exciton energies in the proximity of 2.54 eV.

2. Experimental procedure

2.1. Crystal growth

Single crystals of InSe were grown by using the modified Bridgman technique from a non-stoichiometric In_{1.12}Se_{0.88} melt [15,26]. This method provides crys-
tals having the $\gamma$ modification with a rhombohedral (3R) structure. The GaS dopant was introduced in the preparation of the polycrystalline melt before the crystal growth. In this work we used samples with concentrations of GaS of 0.7, 2.5, 10, 20 and 100 ppm. These values refer to the concentration included in the polycrystalline powder before synthesis. Chemical analysis [15] shows that the actual “doping agent” concentration in the InSe monocrystal is much lower owing to the high value of the impurity segregation coefficient in InSe [15]. A large proportion of the impurity atoms are rejected towards the end of the ingot, and some remains in the form of interlayer precipitate planes [28].

2.2. Raman set-up

The Raman experiments were performed in the backscattering geometry using a 120 $\mu$m focused spot of a continuous wave argon ion laser beam at a reduced power density of 0.40 kW cm$^{-2}$ to avoid sample heating effects as a light source. The Raman set-up used for this work consists of a RAMANOR double monochromator, photon-counting electronics, and argon ion laser.

RRS near the excitonic transition energy was studied using various lines of an argon-ion laser. For room and low temperature study the samples, together with silicon, which is used as a reference scatterer, were mounted on the cold finger of a variable-temperature liquid helium cryostat where low temperatures were obtained by conduction cooling and measured with a calibrated gold chromel thermocouple. The normalized Raman signals were obtained by finding for each laser excitation energy the ratio of intensity of the studied samples to the intensity of the 520 cm$^{-1}$ line of the silicon. Since Si has an indirect and direct band gap of about 1.1 eV and about 3.4 eV respectively at room temperature the 520 cm$^{-1}$ Si line is far away from resonance in the range of interest to us (2.4 - 2.7 eV); therefore its efficiency in this region is proportional to the incident photon energy. The absorption was corrected for by obtaining the ratio of the sum of the absorption coefficients for incident and scattered energies for the samples under study to the sum of the absorption coefficients for incident and scattered energies for Si. Then, multiplying this ratio with that obtained from normalization procedure described above, we obtained the absorption-corrected Raman efficiency normalized to the silicon. It should be mentioned in the above procedure for absorption correction we have used absorption coefficient data of pure InSe taken from Refs. [29] and [30] because of the non-availability of absorption data for doped samples. This may not be a poor approximation since the percentage of doping is rather small. For Si we used the absorption coefficient of Ref. [31] for room temperature and 77 K. For lower temperatures we shifted 77 K data linearly towards the higher energy values with temperature coefficient $\Delta E/\Delta T \approx -2.2 \times 10^{-4}$ eV K$^{-1}$.

3. Experimental results and discussion

3.1. Doping dependence

Fig. 1, spectrum a, is a typical room temperature (282 K) near-resonance Raman spectrum for InSe with an incident photon energy of 2.41 eV in the backscattering geometry. This is in agreement with the Raman spectra of InSe reported by Kuroda and Nishina [1,3]. The main features observed here are at 117, 177, 199,
210, 225, 402, 416 and 423 cm\(^{-1}\). First-order phonons are observed between 100 cm\(^{-1}\) and 230 cm\(^{-1}\) and the second-order spectrum extends from 380 cm\(^{-1}\) to 450 cm\(^{-1}\). The modes at 117, 177, 225 cm\(^{-1}\) are the non-polar modes while those at 199, 210, 416 and 423 cm\(^{-1}\) are polar. The features at 199 and 210 cm\(^{-1}\) were originally assigned to \(\tilde{E}(\text{TO})\) and \(\tilde{E}(\text{LO})\) modes. The resonant behaviour of the 199 and 210 cm\(^{-1}\) modes can be understood using the theory of Martin and the experimental observations reported on forbidden modes that, near resonance, when \(q\)-dependent scattering predominates, \(\tilde{E}\)-active modes that are normally forbidden can become Raman active. In InSe the \(\tilde{E}(\text{LO})\) and \(\tilde{E}(\text{TO})\) phonon modes are examples of forbidden phonon modes that become active when resonance is approached and \(q\)-dependent scattering predominates. Such a selection rule breakdown has been predicted by Martin and observed previously in other compounds. InSe is a polar semiconductor and our experimental results show that the polar modes are present only near resonance whereas non-polar modes are allowed by selection rules in the off-resonance condition. At room temperature the 2.41 eV laser excitation energy is near the exciton energy \(E_x\). Therefore, we observe the polar as well as the non-polar modes in the Raman spectrum shown in Fig. 1, spectrum a.

Spectra b and c of Fig. 1 are the room temperature Raman spectra of InSe doped with 0.7 ppm and 2.5 ppm of GaS respectively. In Fig. 1, spectrum b, we observe the decrease in Raman intensity of all modes in comparison with their counterparts in pristine InSe. Furthermore, the structure corresponding to the polar mode at 210 cm\(^{-1}\) disappears. In Fig. 1, spectrum c, the effect of doping in InSe is larger in comparison with that in Fig. 1, spectrum b. The Raman intensities of all the non-polar, polar and second-order modes are much weaker in Fig. 1, spectrum c. The peak positions of the non-polar modes at 117 cm\(^{-1}\) and 177 cm\(^{-1}\) also change to 114 cm\(^{-1}\) and 174 cm\(^{-1}\) respectively as a result of doping.

Fig. 2 shows the off-resonance room temperature Raman spectra of the same samples using an argon ion laser excitation energy of 2.54 eV. As the photon energy of the laser beam increases, the Raman intensity of every line decreases sharply and the polar modes at 199 cm\(^{-1}\) and 210 cm\(^{-1}\) disappear. After doping with GaS (0.7 ppm), the Raman spectrum is modified as shown in Fig. 2, spectrum b. The two-phonon scattering becomes weaker and a maximum appears at 418 cm\(^{-1}\). Furthermore, on increasing dopant amount to 2.5 ppm, the results reveal the total disappearance of the two-phonon scattering in Fig. 2, spectrum c.

The effect of doping InSe with GaS can be followed by systematic changes in the Raman spectra. The main observations are (a) the decreases in the Raman intensity, which are found for one- and two-phonon modes and are probably due to changes in the excitonic energy levels since the resonance enhancement would be strongly dependent on the energy and the broadening of the intermediate state, and (b) that all the modes are heavily damped as a result of topological disorder due to GaS doping. At room temperature the excitonic transition almost appears in coincidence with incident laser photon energy of 2.41 eV and then vibrational modes are strongly in resonance [3]. The introduction of GaS in InSe results in electron transfer to the conduction band, screening the excitons. The persistence of excitonic transitions \(E_x\) after doping with GaS implies that the exciton screening is only partial but causes the exciton levels to move towards higher energies. Thus, the incident photon energy 2.41 eV is no longer in coincidence with the exciton energy, resulting in a diminution of the resonance enhancement. Coupled with this is the broadening of the phonon modes due to the topological disorder on doping. Both of these effects show up in Fig. 1.
The shift in the electronic energy levels due to electron transfer to the conduction band can also be studied using photoluminescence techniques. We restrict consideration to the range of interest to us (2.50-2.60 eV) since pure InSe has a broad photoluminescence peak located at 2.42 eV at room temperature. The displacement of the photoluminescence peak gives us direct evidence of change in the exciton energy. The experimental results at 10 K are given in Fig. 3, spectra a and b, for pristine InSe and InSe doped with 2.5 ppm GaS respectively. Here the luminescence of the doped sample shifts towards higher energies, contrary to the effect in lithium intercalation where one has a low energy shift of 7.9 meV. The results for other samples are the same as for the sample with 2.5 ppm GaS, that is there is a shift towards higher energies and within the experimental error the shifts have the same value of 6.8 meV. The luminescence in InSe and GaS-doped InSe is probably due to donor acceptor transitions, which changes on introducing GaS. The donor level moves towards the conduction band for the same reason responsible for screening the exciton.

### 3.2. Temperature dependence

#### 3.2.1. One-phonon Raman scattering

It has been observed that it is possible to temperature tune the exciton resonance for various wavelengths by lowering the temperature for InSe [6]. It is therefore also of interest to see a similar effect on doping with GaS. Assuming the same temperature coefficient of pure InSe for GaS-doped InSe and taking into account the shift in excitonic energy level observed by photoluminescence experiments one expects to have resonance enhancement at 77 K. Our results which follow confirmed this assumption.

Fig. 4 shows the one-phonon Raman spectra for InSe doped with GaS (2.5 ppm) using an incident photon energy of 2.54 eV at temperatures ranging from 282 K to 25 K. The non-polar modes at 114, 174 and 224 cm\(^{-1}\) are seen in Fig. 4, spectrum a, at room temperature. As the temperature is lowered from 282 K to 180 K, the polar modes appear at 201 cm\(^{-1}\) and 208 cm\(^{-1}\) and the non-polar mode positions shift from 114 to 116 cm\(^{-1}\), from 174 to 180 cm\(^{-1}\) and from 224 to 230 cm\(^{-1}\) in Fig. 4, spectrum b. The non-polar mode at 116 cm\(^{-1}\) becomes very weak and polar modes shift from 201 to 203 cm\(^{-1}\) and 208 cm\(^{-1}\) to 213 cm\(^{-1}\) at 140 K in Fig. 4, spectrum c. As the temperature is further lowered from 140 K to 100 K in Fig. 4, spectrum d, the very weak non-polar mode at 116 cm\(^{-1}\) at 140 K becomes well defined with a peak at 118 cm\(^{-1}\) at this temperature, and enhancement in the Raman intensity is observed. At the same time the intensity of the Rayleigh tail becomes very high which is probably due to the intense resonant luminescence of the \(E_1\) exciton. As the temperature is further decreased, the Raman intensities of all modes increase and then decrease as shown in Fig. 4, spectra e and f.

The enhancement in the Raman intensity and appearance of polar modes at low temperature can be understood if we consider the band gap temperature dependence of pure InSe. The temperature coefficient \(\Delta E/\Delta T\) of the energy gap is about \(-5.3 \times 10^{-4}\) eV K\(^{-1}\) in the temperature range 300–90 K [10]. With decreasing temperature the laser excitation energy of 2.54 eV comes close to the excitonic energy \(E_1\) and remains almost in resonance from 77 K and down to lower temperatures for pure InSe [2], since in the temperature range 90–15 K the temperature coefficient \(\Delta E/\Delta T\) is much smaller, about [10] \(-2 \times 10^{-4}\) eV K\(^{-1}\). From our results for doped samples, although we see enhancement at 77 K, further decrease in the temperature reduces the Raman intensity as one moves away from the resonance. This, and observations of Figs. 1–3 suggest that excitonic energy has been shifted upward after doping GaS in InSe.

#### 3.2.2. Two-phonon Raman scattering

Fig. 5 shows two-phonon Raman spectra observed at different temperatures from InSe doped with GaS (2.5 ppm). Room temperature experiments do not reveal any structure from 380 cm\(^{-1}\) to 450 cm\(^{-1}\) as shown in Fig. 5, spectrum a. As the temperature is lowered to 230 K, the two-phonon spectrum appears with a maximum at 426 cm\(^{-1}\) in Fig. 5, spectrum b. As the temperature is further decreased, the line shape of the two LO phonon spectrum changes remarkably and the peak position shifts from 426 cm\(^{-1}\) to 431 cm\(^{-1}\). The LO and TO modes also becomes distinguishable in Fig. 5, spectra c–f.

The Raman spectrum of InSe at low temperatures has been studied by many researchers [1,3,6,9]. As the temperature is lowered to 77 K, the polar modes and two-phonon scattering exhibit strong resonant behaviour at the laser energy of 2.54 eV resonating with exciton energy \(E_1\). However, our experiments on InSe doped with GaS show that at room temperature one-phonon scattering is damped and two-phonon scattering is not observed. The results in Fig. 5 shows that here also as the laser excitation energy of 2.54 eV approaches the exciton energy \(E_1\) on tuning the temperature, the Raman scattering increases rapidly. At 77 K, the Raman intensity reaches a maximum owing to resonance with the excitation energy. A further decrease in the temperature reduces the Raman intensity as one moves away from the resonance.

Figs. 4 and 5 also show that the phonons shift towards higher wavenumbers with decreasing temperature.
3.3. Excitation wavelength dependence

Fig. 6 shows the room temperature Raman spectra of InSe doped with GaS (2.5 ppm) as a function of the laser wavelength. The non-polar modes and damped second-order scattering are observed in Fig. 6, spectrum a, as discussed in Section 3.1. As the laser excitation energy is increased from 2.41 eV to 2.54 eV the second-order scattering vanishes as shown in Fig. 6, spectra b–d.

It is well established that for InSe the two-phonon structure is visible with a laser energy of 2.54 eV at room temperature. The situation is quite different after doping when two-phonon scattering is not detected with excitation energy 2.54 eV. The situation remains the same when the laser is excitation is increased above 2.54 eV as shown in Fig. 6. This seems to suggest that the exciton energy $E_x$, which is responsible for resonant Raman scattering in InSe at room temperature as shown in Fig. 1, has changed as a result of doping. Consequently, for doped samples, polar modes and two-phonon scattering are absent.

3.4. Dopant concentration dependence

We have also studied InSe doped with different concentrations of GaS. In this respect the Raman spectra of InSe with different degrees of GaS dopant (2.5 ppm, 10 ppm, 20 ppm and 100 ppm) have been obtained at different temperatures and with different excitation energies of the argon ion laser. The spectra of these samples show that all non-polar and polar modes are damped as the amount of dopant is increased.

The persistence of the excitonic transitions after doping with GaS suggests that not all the GaS electrons transfer to the conduction band, thus transforming the semiconducting InSe into a metal. If we had a metallic transition, the Coulomb interaction between the electron and hole of the exciton would be screened and the excitonic state would be washed out. The persistence of the excitonic transitions in highly doped InSe (100 ppm) suggests that the GaS electrons form a low mobility
impurity band or are efficiently trapped into a localized state.

The resonance curves for the non-polar mode at 117 cm\(^{-1}\) at 20 K as a function of the photon energy of laser beam for various doping densities are given in Fig. 7. Experimental points taken at 77 K are also plotted with a shift of 11 meV in photon energy towards higher values corresponding to the thermal shift of the exciton level. The same shift as in the case of pure InSe was assumed for all impurity concentrations since in the photoluminescence experiment different concentrations have the same shift. From the resonance curves in Fig. 7 we see that there is a shift in peak position towards a higher energy value of 7 meV compared with the pure InSe, this shift being consistent with photoluminescence results. It should be mentioned that in plotting the above resonance curve we have used absorption coefficient data of pure InSe taken from Refs. [29] and [30] because of the non-availability of absorption data for doped samples. This may not be a poor approximation since the doping percentage is rather small. For correction due to absorption we obtained the ratio of the sum of the absorption coefficients for incident and scattered energies for the samples under study to the sum of the absorption coefficients for incident and scattered energies for Si.

We have calculated theoretical curves of resonance behaviour for the \(\text{Mo}_0\) exciton to interpret our experimental results. The resonant Raman tensor at the \(\text{Mo}_0\) exciton for non-polar phonon is obtained from [1]

\[
R(\omega) = \frac{A}{\pi a_0^2 \omega} \left( \sum_{m} \frac{1}{n^3} \left[ n + 1 \right] \left[ \frac{\hbar(\omega + i\eta_D) + E_D/n^2 - E_g}{\hbar(\omega' + i\eta_D) + E_D/n^2 - E_g} \right] \right)
+ \frac{1}{4\hbar \omega E_B} \left\{ \ln \left[ \frac{\hbar(\omega + i\eta_c) - E_g}{\hbar(\omega' + i\eta_c) - E_g} \right] + \left[ \tan^{-1} \left( \frac{\hbar \omega - E_g}{\heta_c} \right) - \tan^{-1} \left( \frac{\hbar \omega' - E_g}{\heta_c} \right) \right] \right\}
+ \pi i [\coth z(\omega) - \coth z(\omega')] \right) \right)
\]

(1)

with

\[
z(\omega) = \pi \left( \frac{E_B}{\hbar \omega + i\eta_c - E_g} \right)^{1/2}
= \pi x e^{i\theta} \quad \text{if} \quad \hbar \omega - E_g \geq 0
= \pi x e^{i\left( \theta + \pi/2 \right)} \quad \text{if} \quad \hbar \omega - E_g < 0
\]

and

\[
x(\omega) = \frac{E_B}{\left| \left( \hbar \omega - E_g \right) + (i\eta_c) \right|^{1/2}}^{1/2}
\theta(\omega) = \frac{1}{2} \tan^{-1} \left( \frac{\heta_c}{\hbar \omega - E_g} \right)
\]

where \(\hbar \omega\), \(\hbar \omega'\) and \(\hbar \omega_0\) are energies of incident photons, scattered photons and emitted phonons respectively, \(E_B\) and \(a_0\) the binding energy and Bohr radius respectively of the first exciton the constant \(E_g\) is the energy gap, and \(\eta_D\) and \(\eta_c\) are phenomenological damping constants for the discrete and continuum exciton levels respectively. The constant \(A\) is the coefficient which involves the momentum matrix element, exciton–phonon deformation potential and other fundamental constants. In order to fit the theory with experimental points for the doped samples we reduced the binding energy because of the shift of the exciton energy towards of the higher energy levels and kept this at the same value for samples of all different concentrations in view of the same shift observed in peak positions of the photoluminescence experiment. Then we changed the values of the damping constant to obtain the best fit. However, we used the same value of energy gap of the pure InSe for the doped samples. In Table 1 we give the parameters used for theoretical calculation.
Fig. 6. Room temperature Raman spectra of InSe:GaS (2.5 ppm) at different excitation energies of the argon ion laser.

As can be seen from Fig. 7 and Table 1 an increase in the amount of dopant causes more damping but there is no shift in peak position towards either the high or the low energy side due to various dopant densities and this may reflect the fact that the effective number of charge carriers remains very close to that of the pure material and there is no functional relation between the impurity concentration and the effective number of charge carriers as already stated in the introduction. It is to be emphasized that the resonance broadens out as the dopant density increases, implying increasing compositional and topological disorder.

4. Concluding remarks

In this paper, we have presented a detailed RRS study of spectral changes in InSe doped with GaS. It was found that on doping there are changes in the spectra of the doped samples compared with that of pure InSe. These changes are as follows. (i) There is a shift in the excitonic energy towards higher energy values, but this shift remains the same for different GaS concentrations. (ii) Modes all exhibit broadening indicating topological disorder. This broadening increases with increasing dopant densities. (iii) At room temperature the Raman spectrum of doped InSe displays almost off-resonance behaviour with the 2.41 eV laser excitation energy as shown in Fig. 1, spectra b and c. In Fig. 2, spectrum e, two-phonon scattering disappears with the laser excitation energy of 2.54 eV. Pure InSe exhibits resonance scattering at 77 K with the 2.54 eV laser line [1,3,6]. A similar effect is seen in our doped samples.

At present one can make some qualitative remarks about the effect of doping InSe with GaS which illustrate the trends on the basis of results obtained so far.

(1) From photoluminescence experiment and resonant Raman study we found that, on doping InSe with GaS, the exciton energy shifts about 7 meV towards higher energies. This result can be substantiated by a temperature study of doped InSe which reveals resonance enhancement at 77 K, in spite of the damped phonon at room temperature. This is because at 300 K the 2.41 eV line is about 10 meV in energy below and at 77 K the 2.54 eV line is about 9 meV in energy above that of \( E_1 \) exciton for pure InSe [1]. Taking the observed shift into consideration for our doped samples, the 2.41 eV line is about 17 meV below the \( E_1 \) exciton at room temperature; hence the decrease in Raman intensities as shown in spectrum c, Fig. 1, for the sample doped with 2.5 ppm. At 77 K, the 2.54 eV line becomes almost coincident with the \( E_1 \) exciton for the doped samples and so there is the resonance enhancement in the Raman lines as shown in Figs. 4 and 5. The Raman lines do, however, shift to lower frequency with increasing temperature owing to anharmonic interactions.

(2) Our results show that the resonance properties are modified by a small quantity (a few parts per million) of GaS dopant. This means that the band edge singularities are sensitive to a small percentage of GaS dopant. Evidently the band edge singularities are sensitive to interlayer coupling. The electronic band structure of InSe is almost flat in all directions within the layer plane. The uppermost valence bands are derived mainly from the Se 4p state and the bottom of the conduction band is formed mainly from the In s state and has an antibonding character. The In-Se bond is tilted at only 29° out of the layer plane and the the In-In bond is normal to the layer. In these conditions the Se 4p, and Se 4p, electrons have a much greater coulombic interaction with indium cations than the Se 4p, electrons do. Because of such anisotropy of the crystalline field. Se 4p, and Se 4p, states lies well below Se 4p, states [7]. The electronic band structure shows that the states near the gap have \( p_\perp \) character having contributions from both In and Se, whose orbitals overlap strongly in the \( c \) direction. It is clear in this case that the interlayer interaction has a major influence on the band edge energy [35]. Perhaps GaS doping of InSe causes the Se-Se interlayer interaction to be affected by S in GaS. The details of this can be elucidated only when local density approximation band structure calculations become available.
(3) It is well known in polar semiconductors that electrons can also interact with LO phonons via the Fröhlich mechanism [36] leading to a breakdown of selection rules [32]. In this case the Raman tensor is diagonal [37] and the forbidden scattering can be observed in the backscattering configuration. This Raman process is called forbidden because, in the dipole approximation, the contributions of electrons and holes cancel exactly when the wavevector of the phonon is taken to be zero. The finiteness of the photon wavevector and the wavevector conservation law make the process "allowed" in backscattering. At resonance one sees both polar and non-polar modes. This is because of breakdown of selection rules due to the Fröhlich interaction for resonance with an exciton as the intermediate scattering state. A simple theory [1] has been used in Eq. (1) to fit our experiments.

From our results we see there is a shift in the excitonic energy at 2.531 eV at 77 K due to doping of InSe with GaS. No new modes appear in the Raman spectrum of the doped sample. Bourdon et al.'s band structure calculation of InSe [38] shows that the uppermost valence band and the lowest conduction band are mainly determined by the In-In bond and anti bonding orbitals. The 14.5 meV A, Phonon strongly stretches this bond and must be coupled to electrons. The 27.8 meV modes also stretches this bond. but the coupling constant depends inversely on phonon energy and must be lower. Our observations show that the doped GaS atoms do not disturb the intralayer vibrational properties. However, the electronic states are modified mainly in the uppermost valence bands. Therefore, we suggest that there are at least two mechanisms which change the properties of the system on doping: (i) one of crystallographic origin; (ii) one of electronic origin due to the GaS doping. These effects require further study to elucidate changes in the electronic states on doping.

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Figure 7. Resonance curves for the 117 cm⁻¹ non-polar mode at 20 K for various InSe:GaS doping densities. The Raman intensity is normalized with respect to the 520 cm⁻¹ line of silicon and corrected for absorption. Solid lines are the curves obtained using Eq. (1) for various GaS dopant concentrations.

<table>
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<th>Sample</th>
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<th>$\hbar \gamma$ (meV)</th>
<th>$\Delta$ (meV)</th>
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<td>Pure InSe</td>
<td>10.5</td>
<td>10.7</td>
<td>17</td>
</tr>
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<td>InSe:GaS (2.5 ppm)</td>
<td>13.3</td>
<td>12</td>
<td>7</td>
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<tr>
<td>InSe:GaS (10 ppm)</td>
<td>13.3</td>
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<tr>
<td>InSe:GaS (20 ppm)</td>
<td>15</td>
<td>14</td>
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<tr>
<td>InSe:GaS (100 ppm)</td>
<td>17</td>
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<td>7</td>
</tr>
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</table>
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References