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RESONANT RAMAN SCATTERING IN GaSe AND $GaS_x Se_{1-x}$*

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SUMMARY

Multiphonon resonant Raman scattering up to four phonons in Ga Se and one and two phonon resonant Raman scattering in the mixed Ga S_x Se_{1-x} crystals with $x \leqslant 0.23$ have been investigated. The results can be explained by a simple theory in which the dispersion of the resonance behavior is mainly dominated by resonances with the 1s direct exciton state.

I - INTRODUCTION

Resonant Raman scattering (RRS) around excitonic transitions in solids has been a subject of extensive investigation in recent years (1). Among the various semiconductors, the layered GaSe and mixed GaS_x Se_{1-x} crystals seem to be particularly worth studying. They have direct as well as indirect exciton states near the band gap with relative positions varying with x. In this paper, we present : i) recent measurements on multiphonon RRS up to four phonons in pure GaSe and ii) one and two phonons RRS in GaS_x Se_{1-x} with $x < 0.23$.

The layered compounds GaS and GaSe form a continuous series of mixed crystals GaS_x Se_{1-x} with $0 \leq X \leq 1$ (2). The crystals structure show three different types of stacking of the layers which have been described in the literature (3).

Optical studies including absorption (2) (4), reflection (5) and photoluminescence (2) (6) have been reported recently. It was found that in each mixed crystal $GaS_x\ Se_{1-x}$ at liquid N_2 temperature, there exist a direct exciton at (7) :

$$(1) \qquad \omega_{dx}\ (X) = 2.102 + 0.728\ X \quad (eV) \qquad 0 < X \leq 0.2$$

with a binding energy of 20 meV, and an indirect exciton at (7) :

$$(2) \qquad \omega_{ix}\ (X) = 2.064 + 0.520\ X \quad (eV) \qquad 0 < X \leq 0.2$$

with a binding energy of ~ 35 meV. For $0 < X \leq 0.25$, these excitonic transitions fall within the tuning range of rhodamine 6 G, rhodamine 110 and coumarine 6 dye lasers and hence RRS measurements around these transitions can be done fairly easily.

The phonon modes of $GaS_x\ Se_{1-x}$ have been studied by infrared (8) and non-resonant Raman spectroscopy (8)(9). Corresponding to change in composition of the mixed crystals, some phonon modes show the two-mode behavior, while others show either the one mode or the local mode behavior (9). It is interesting to see how the various modes behave as the exciting laser frequency varies around the excitonic transitions. Such study has already been reported in pure GaSe crystals (10). The $A_1'^{(2)}$ (LO) mode at 247 cm^{-1} and $E'^{(2)}$ (LO) mode at 255 cm^{-1} respectively show a strong resonance enhancement while the two A_1' modes at 135 and 310 cm^{-1} show much less apparent resonant behavior as the exciting laser frequency approaches the direct exciton. The strong enhancement of the two LO modes (unresolved in mixed crystals with $X > 0.1$) is presumably due to the Fröhlich interaction between LO phonons and excitons. In particular, the $E'^{(2)}$ (LO) phonon (255 cm^{-1}) appears to couple most strongly with the exciton states. As a result, we were able to observe multiphonon modes up to four phonons involving $E'^{(2)}$ (LO) in pure GaSe and $2E'^{(2)}$ (LO) modes in the mixed crystals.

II - EXPERIMENTS AND RESULTS

Our experimental set up has been described elsewhere (1). Monocrystalline samples of $GaS_x\ Se_{1-x}$ with X=0, 0.05, 0.12, 0.17 and 0.225 were grown by the Bridgman technique. Back scattering from a polished surface parallel to C was used in the measurements because of the larger oscillator strength in this configuration (11). In order to reduce the luminescence background to a tolerable, level without appreciably broadening the exciton linewidths, the samples were immersed in liquid N_2 during the measurements.

Our experimental results are presented in Figs. 1,2 and 3. Figs. 1 and 2 give the RAMAN cross sections of the one and two phonon $E'^{(2)}$ (LO) modes respectively, as functions of laser frequency and sample composition. Fig. 3 gives the Raman cross sections of the $3E'^{(2)}$ (LO); $2E'^{(2)}$ (LO) + A'_1 (310 cm^{-1}); and $4E'^{(2)}$ (LO) modes of pure GaSe. All data points have been corrected for absorption according to the following formula (10).

$$(3) \qquad \sigma_R = \frac{\alpha_l + \alpha_s + 3.93\ cm^{-1}}{1 - e^{-(\alpha_l + \alpha_s + 3.93\ cm^{-1})\,d}}\ (1 - R_l)^{-1}\ (1 - R_s)^{-1}\ \sigma$$

where σ_R is the corrected Raman cross section, σ the uncorrected Raman cross section normalized over the laser power ; α_l, R_l, α_s, R_s are the absorption coefficients and sample reflectances at the laser frequency and the scattered photon frequency respectively ; d is the sample thickness. The factor 3.93 cm^{-1} takes account of the finite collecting depth of our lens. The absorption curve for GaSe was taken from Ref. (10) and those for the mixed crystals were measured in our laboratory. The observed Raman shifts of the $1E'^{(2)}$ (LO) and $2E'^{(2)}$ (LO) modes for X = 0, 0.05 0.12, 0.17, 0.225 and the shifts of the $3E'^{(2)}$ (LO), $2E'^{(2)}$ (LO) + A_1' (310 cm^{-1}) and 4E' (LO) modes for pure GaSe are given in Table 1. All numbers are within ± 1 cm^{-1} accuracy.

III - THEORY

To explain our results, we use a simple cascade theory (12). We assume (13) the following absorption emission processes (in decreasing order of importance) dominating in the n-phonon RRS :

1) Incoming photon at ω_l excites an electron hole (e - h) pair in the band continuum. The e-h par then decays into the k= 0 1s direct exciton by successively emitting n phonons. The direct exciton finally recombines and emits a Stokes photon at ω_s.

2) Incoming photon excites an e-h pair in the band continuum. The e-h pair decays into a k ≠ 0 1s direct exciton state by successively emitting m (1 ≤ m ≤ n - 1) phonons. The direct exciton then recomibnes by an (n - m) phonon-assisted transition and emits a Stokes photon.

3) Incoming photon excites the k = 0 1s direct exciton. The direct exciton then either recombines by an n phonon-assisted transition or decays into the 1s indirect exciton by emitting a phonon and the resulting indirect exciton recombines by an (n-1) phonon assisted transition.

Since the absorption curves of these crystals are rather flat immediatly beyond the direct exciton absorption peak, we can assume the dispersion of the RRS curves is mainly due to resonances with the exciton states. The one-phonon cross section can therefore be written approximatly as a direct product of 2 resonant terms for i) the incident and ii) the scattered photon energies:

$$(4) \qquad \sigma_R(\omega_{ph}) = A_1 \left[a(\omega_l) + B_1\right] \cdot \left[a(\omega_s) + C_1\right]$$

a(ω) describes the direct exciton absorption peak deduced from the absorption measurements and A_1, B_1 and C_1 are constants. The solid curves in Fig. 1 were actually obtained from Eq. (4) using A_1, B_1 and C_1 as adjustable parameters. The non-resonant terms B_1 and C_1 were set equals to 650 cm^{-1} and 500 cm^{-1} respectively for all the five crystals ; A_1 is merely a normalizing constant. Our curves fit the experimental data points very well and "a posteriori" confirm the domination of the 1s direct exciton.

By assuming all resonances have the Lorentzian lineshape, we can also write down the approximate analytical expression for the two phonon Raman cross section as :

$$(5)\quad \sigma_R\,(2\omega_{ph}) = A_2\left[(\omega_l - \omega_{dx}) - 2\omega_{ph})^2 + \Gamma_{do}^{\;2}\right]^{-1} + B_2\,F\,(\omega_l - \omega_{dx} - \omega_{ph}, \Gamma_d)$$

$$+ \left[C_2\,F\,(\omega_l - \omega_{ix} - \omega_{ph}, \Gamma_i) + D_2\right]\left[(\omega_l - \omega_{dx})^2 + \Gamma_{do}^{\;2}\right]^{-1}$$

For 3 phonon RRS, we have :

$$(6)\quad \sigma_R\,(2\omega_{ph} + \omega'_{ph}) = A_3\left[(\omega_l - \omega_{dx} - 2\omega_{ph} - \omega'_{ph})^2 + \Gamma_{do}^{\;2}\right]^{-1}$$

$$+ B_3\,F\,(\omega_l - \omega_{dx} - 2\,\omega_{ph}, \Gamma_d) + C_3\,F\,(\omega_l - \omega_{dx} - \omega_{ph}, \Gamma_d)$$

For 4 phonon RRS, we have :

$$(7)\quad \sigma_R\,(4\omega_{ph}) = A_4\left[(\omega_l - \omega_{dx} - 4\omega_{ph})^2 + \Gamma_{do}^{\;2}\right]^{-1}$$

$$+ B_4\,F\,(\omega_l - \omega_{dx} - 3\omega_{ph}, \Gamma_d) + C_4\,F\,(\omega_l - \omega_{dx} - 2\,\omega_{ph}, \Gamma_d)$$

In the above expressions, A_i, B_i, C_i, D_i are constants to be used as adjustable parameters ; ω_{ph}, ω_{dx}, ω_{ix} are the frequencies of the optical phonon, direct exciton at $k = 0$, and indirect exciton at the bottom of the indirect exciton band respectively ; Γ_d and Γ_i are the damping constants for the direct and indirect excitons respectively with Γ_{do} reserved specifically for the $k = 0$ direct exciton. The function F has the form :

$$(8)\quad F\,(\Delta\omega\,,\,\Gamma) = \int_0^{Y_c} Y^{1/2}\,(\Delta\omega - y)^2 + \Gamma^2)^{-1}\,dy$$

where Y_c is a somewhat arbitrary cut-off chosen as 3/2 times the exciton binding energy. The value of Γ_{do} for each crystal is deduced from the corresponding absorption curve ; Γ_d and Γ_i are taken to be 2 Γ_{do}. (Dependence of theoretical curves on Γ_d and Γ_i is not critical). For pure GaSe, the separation between direct and indirect exciton states is fairly close to the phonon frequency involved. Accordingly, we can drop the non-resonant D_2 term in Eq. (5). For the mixed crystals, it is however more appropriate to drop the C_2 term.

The solid curves in Fig. (2) were obtained from Eq. (5) with $A_2 : B_2 : C_2 : D_2 = 12 : 1 : 10 : 0$; $5 : 1 : 0 : 12$; and $12 : 1 : 0 : 22$ for $X = 0$, 0.12, and 0.17 respectively. The solid curves in Fig. 3 were obtained from Eqs. (6) and (7) with $A_3 : B_3 : C_3 = 12 : 1 : 0.2$ and $20 : 1 : 0.2$ for $3E'^{(2)}$ (LO) and $2E'^{(2)}$ (LO) + A_1' (310 cm^{-1}) modes respectively; and $A_4 : B_4 : C_4 : = 12 : 1 : 0.2$ for the $4E'^{(2)}$ (LO) mode in pure GaSe.

It is seen that the solid theoretical curves in Fig. 2 deviate from the experimental data at the low energy tail. This is because we have assumed a Lorentzian lineshape for all the transitions involved. If we replace the Lorentzian function in Eq. (5) and (8) by the observed lineshape $\alpha(\omega, \Gamma)$ of the direct exciton absorption peak, with Γ still being the halfwidth, the theoretical curves remain essentially unchanged for $\omega_l > \omega_{dx}$, but change into the dashed curves for $\omega_l < \omega_{dx}$. The agreement between theory and experiment is then very good. The near-Gaussian line shape of excitonic transitions could be due to inhomogeneous broadening.

The theoretical curve for $GaS_{0.225}Se_{0.775}$ in Fig. 2 was obtained with the super-position of another Lorentzian type resonance at $\omega_l \simeq \omega_{ix}$ with $\Gamma_{io} = 24$ me It then describes the experimental results satisfactorily. This indicates that direct laser excitation of the indirect exciton is also operative in RRS although the contribution is relatively weak. The same resonance peak at $\omega_l \simeq \omega_{ix}$ was seen in the raw data of RRS in the other crystals, but after absorption correction was masked off by the much stronger direct exciton resonance. This is presumably because the separation between direct and indirect excitons in these crystals is too small. Although momentum conservation forbids the direct excitation of indirect excitons, stacking faults in the crystals can easily induce such a process (10) The $\omega_l \sim \omega_{ix}$ resonance should also appear in the one-phonon RRS in $GaS_s Se_{1-x}$. It was indeed observed in the raw data as a shoulder on the strong resonance tail, but became invisible after absorption correction.

IV - CONCLUSION

The good agreements between theory and experiment in Figs. 1,2 and 3 shows that the dispersion of RRS in $GaS_x Se_{1-x}$ is indeed dominated by resonances with the exciton states. Last the weak evidence found in this work for indirect transitions makes questionable the use of RRS as a probe for indirect gaps when they

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Figure 2. Level scheme for a spin ½ nuclei interacting with each other through the homonuclear dipole-dipole interaction. The representative frequencies given are for protons in adamantane in an external field of 25 Kgauss. The populations of the Zeeman levels are described by the Zeeman spin temperature T_Z or the inverse temperature $\beta_Z = 1/k\ T_Z$. The populations of the dipolar sublevels are given by the dipolar spin temperature T_D or its inverse β_D.

X Shift	0	0.05	0.12	0.17	0.22_5
$E'^{(2)}$ (LO)	255	254	251	250	249
2 $E'^{(2)}$ (LO)	510	509	504	500	499
3 $E'^{(2)}$ (LO)	767				
2 $E'^{(2)} + A'_1$	821				
4 $E'^{(2)}$ (LO)	1018				

TABLE 1 : Raman shift for various one and multiphonon modes in GaS_xSe_{1-x} .

FIGURE CAPTIONS

FIGURE 1 : Raman cross section of the $E'^{(2)}$ (LO) mode as a function of laser frequency. ○ ▲ □ ● and △ are data points for $GaS_x\ Se_{1-x}$ with $x = 0$, 0.05, 0.12, 0.17 and 0.22 respectively. Solid curves are obtained from theory in the text.

FIGURE 2 : Raman cross section of the two phonon $2E'^{(2)}$ (LO) modes as a function of laser frequency. ○ ▲ □ ● and △ are data points for $GaS_x\ Se_{1-x}$ with $x = 0$, 0.05, 0.12, 0.17 and 0.22 respectively. Solid and dashed curves are obtained from theory in the text.

FIGURE 3 : Raman cross sections of the three and four phonons modes of pure GaSe ○ : $3E'^{(2)}$ ● $2E'^{(2)} + A_1$ (310 cm^{-1}) △ $4E'^{(2)}$ Solid curves are obtained from theory in the text.

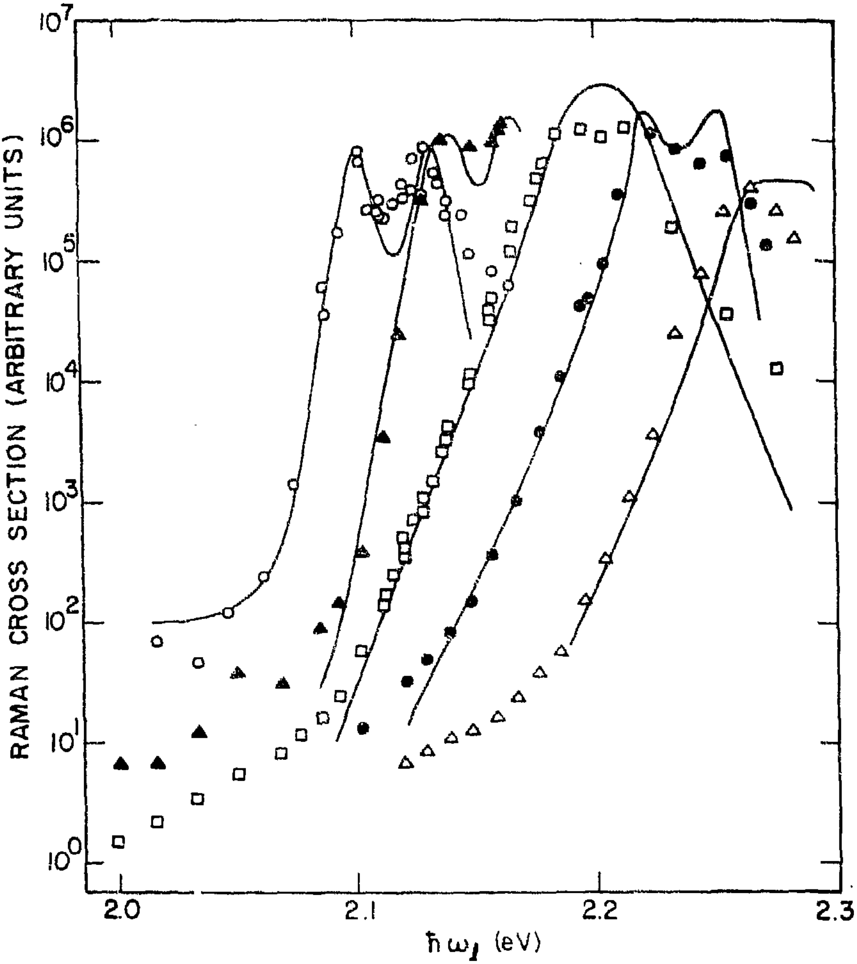

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Fig 1 -

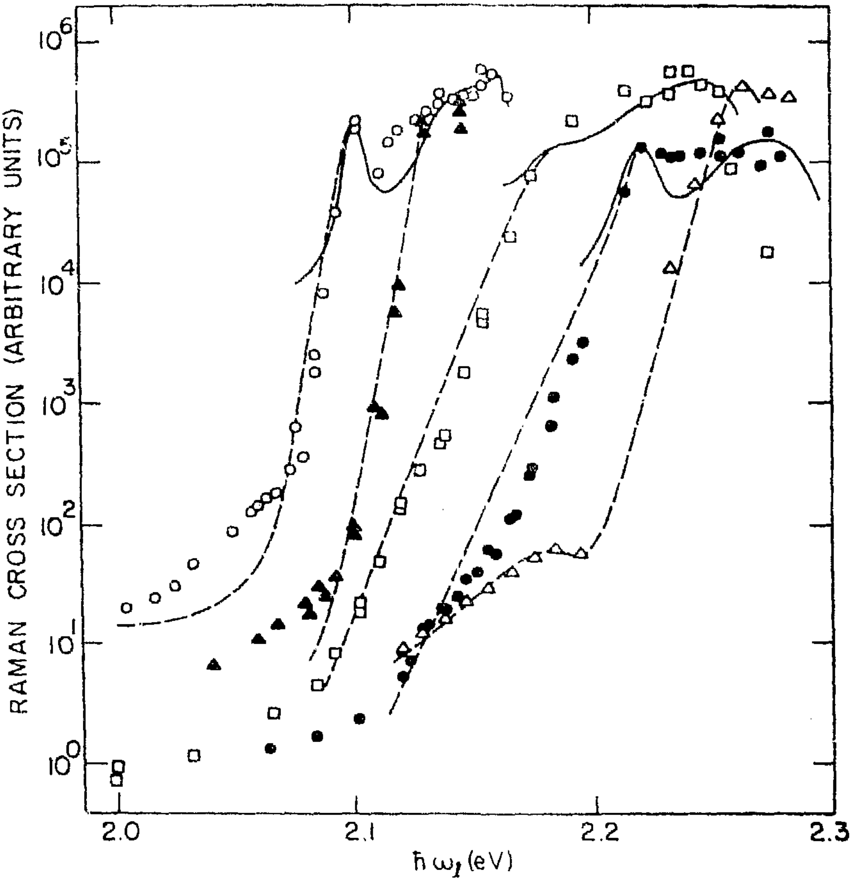

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Fig 2

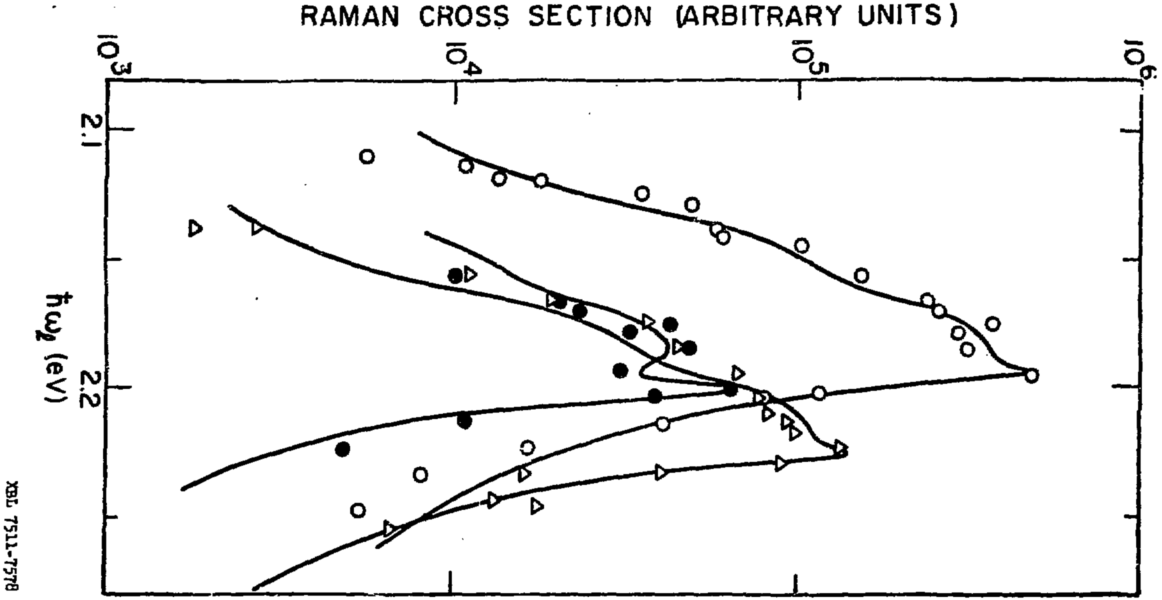
RAMAN CROSS SECTION (ARBITRARY UNITS)
10^3
10^4
10^5
10^6
2.1
2.2
$\hbar\omega_\ell$ (eV)
XBL 7511-7578

Fig 3-