Submitted to Solid State Communications

LBL-4587
Preprint c.

# RESONANT RAMAN SCATTERING IN MIXED $GaS_xSe_{1-x}$ CRYSTALS

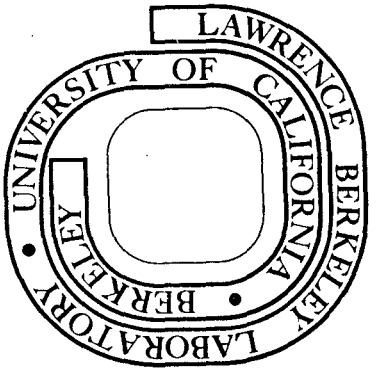
T. C. Chiang, J. Camassel, Y. R. Shen, and
J. P. Voitchovsky

January 1976



Prepared for the U. S. Energy Research and Development Administration under Contract W-7405-ENG-48





## DISCLAIMER

To be Submitted to Solid State Communications LBL-4587

UNIVERSITY OF CALIFORNIA

Lawrence Berkeley Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

# RESONANT RAMAN SCATTERING IN MIXED $GaS_xSe_{1-x}$ CRYSTALS

T. C. Chiang, J. Camassel*, Y. R. Shen, J. P. Voitchovsky†
Physics Department, University of California
Berkeley, California

JANUARY 1976

# RESONANT RAMAN SCATTERING IN MIXED $GaS_xSe_{1-x}$ CRYSTALS

T. C. Chiang, J Camassel*, Y. R. Shen, J. P. Voitchovsky†
Department of Physics, University of California, and
Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

## ABSTRACT

One- and two-phonon resonant Raman scattering around the absorption edge in mixed $GaS_xSe_{1-x}$ crystals with $0 \leqslant x < 0.23$ has been measured. The results can be explained by a simple theory in which the dispersion of RRS is dominated by exciton resonances.

*On leave from University of Montpellier; partially supported by a N.A.T.O. fellowship.

†Swiss National Science Foundation Fellow.

In recent years, there have been extensive studeies on resonant Raman scattering (RRS) around excitonic transitions in solids.[1] Work is however limited to crystals of a single component. No such study on mixed crystals or alloys has yet been reported. In this paper, we present the results of our recent RRS work on $GaS_xSe_{1-x}$ mixed crystals with $0 \leqslant x \leqslant 0.23$.

The layer compounds GaS and GaSe form a continuous series of mixed crystals $GaS_xSe_{1-x}$ with $0 \leqslant x \leqslant 1$.[2] The structures of these crystals with three types of stacking of the layers have been described in the literature.[3] Optical studies of these crystals including absorption[2,4], reflection,[5] and photoluminescence,[2,6] have been made recently. It was found that in each mixed crystal $GaS_xSe_{1-x}$, there exist a direct exciton at[7]

$$\omega_{dx}(x) = 2.100 + 0.728x \text{ eV} \qquad (1)$$

with a binding energy of 20 meV, and an indirect exciton at[7]

$$\omega_{ix}(x) = 2.064 + 0.520x \text{ eV} \qquad (2)$$

with a binding energy of 36 meV. For $0 \leqslant x \leqslant 0.25$, these exciton transitions fall within the tuning range of rhodamine 6G, rhodamine 110 and Coumarine 6 dye lasers and hence RRS measurements around these transitions can be done fairly easily.

The phonon modes of $GaS_xSe_{1-x}$ have been studied by both 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 phonon modes behave in Raman resonant enhancement as the exciting laser frequency varies around the excitonic transitions. Such study has already been carried out in pure GaSe crystals.[10,11] Unfortunately, in both pure GaSe and mixed crystals, presumably because of strong Fröhlich interaction, only the $E'^{(2)}(LO)$ and $A_2''^{(2)}(LO)$ modes (unresolved in mixed crystals with $x \geq 0.1$)show strong resonant enahncement. The other modes either how strong anti-resonance effect or are too weak to be properly measured around excitonic transitions because of strong optical absorption. Here, we shall present and discuss only the one-and two-phonon RRS results of the $E'^{(2)}(LO)$ mode at ~250 $cm^{-1}$.

Our experimental setup has been described elsewhere.[1] Monocrystalline samples of $GaS_xSe_{1-x}$ with x = 0, 0.05, 0.12, 0.166, and 0.225 were grown by the Bridgman technique. Back scattering from a polished surface paralell to $\hat{c}$ was used in the resonant Raman measurements. In order to reduce the luminescence background to a tolerable level without appreciably broadening the exciton linwidths, the samples were kept at liquid $N_2$ temperature during the measurements.

Our RRS results on the one- and two-phonon $E'^{(2)}(LO)$ modes are shown in Figs. 1 and 2 respectively. The data have been corrected for absorption in the same way as has been described earlier.[11] 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, 0.166, 0.225 are 255, 254, 251, 250, 249, and 510, 509, 504, 500, 499 respectively within $\pm 1$ $cm^{-1}$ accuracy.

We use a simple theory to explain our results. For the one-phonon mode, we consider the following resonant Raman processes. The laser photon at $\omega_\ell$ excites either a direct exciton or an electron-hole (e-h) pair into the continuum. The exciton or e-h pair then makes a transition (real or virtual) among the exciton and continuum states by emitting a phonon at $\omega_{ph}$. Finally, the exciton or e-h pair recombines and emits a Stokes photon at $\omega_s$. Since the absorption curves of these mixed crystals are rather flat immediately beyond the direct exciton absorption peak, we assume that the dispersion of the above RRS processes comes mainly from $\omega_\ell$ and $\omega_s$ resonances with the direct exciton ground state. The one-phonon resonant Raman cross-section can therefore be written as

$$\sigma_R(\omega_{ph}) = A_1[\alpha(\omega_\ell) + B_1][\alpha(\omega_s) + C_1] \qquad (3)$$

where $\alpha(\omega)$ describes the direct exciton absorption peak and $A_1$, $B_1$, and $C_1$ are constants independent of $\omega_\ell$ and $\omega_s$. The solid curves in Fig. 1 were actually obtained from Eq. (3) using $A_1$, $B_1$, and $C_1$ as adjustable parameters. They fit the experimental data points very well. Note that we have used the log scale for Raman cross-section in Figs. 1 and 2.

For the two-phonon mode, we use the model given in Ref. 11 to describe the resonant processes. We then have

$$\sigma_R(2\omega_{ph}) = A_2[(\omega_\ell - \omega_{dx} - 2\omega_{ph})^2 + \Gamma_{do}^2]^{-1} + B_2 F(\omega_\ell - \omega_{dx} - \omega_{ph}, \Gamma_d) + [C_2 F(\omega_\ell - \omega_{ix} - \omega_{ph}, \Gamma_i) + D_2][(\omega_\ell - \omega_{dx})^2 + \Gamma_{do}^2]^{-1} \quad (4)$$

where $A_2$, $B_2$, $C_2$, and $D_2$ are constants to be used as adjustable parameters, $\Gamma_d$ and $\Gamma_i$ are the damping constants for direct and indirect excitons respectively with $\Gamma_{do}$ reserved for the direct exciton at $k = 0$, and the function $F(\Delta\omega,\Gamma)$ describes the intermediate resonances of $\omega_\ell - \omega_{ph}$ with the direct or indirect exciton states.

$$F(\Delta\omega,\Gamma) = \int_0^{y_c} \frac{1}{2} y^2 [(\Delta\omega - y)^2 + \Gamma^2]^{-1} dy \quad (5)$$

where $y_c$ is somewhat arbitrarily chosen as 3/2 times the exciton binding energy. The solid curves in Fig. 2 were obtained from Eq. (4) with $A_2$, $B_2$, $C_2$, and $D_2$ as adjustable parameters, $\Gamma_{do}$ deduced from the absorption curves, and $\Gamma_d$ and $\Gamma_i$ taken to be $2\Gamma_{do}$. (Dependence of theoretical curves on $\Gamma_d$ and $\Gamma_i$ 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. (4). For the mixed crystals, it is however more appropriate to drop the $C_2$ term.

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 functions in Eqs. (4) and (5) by the observed lineshape $\alpha(\omega,\Gamma)$ of the direct exciton absorption peak, with $\Gamma$ still being the halfwidth, the theoretical curves remain essentially unchanged for $\omega_\ell > \omega_{dx}$, but change into the dashed curves for $\omega_\ell < \omega_{dx}$. The agreement between theory and experiment is then very good. The near-Gaussian lineshape of excitonic transitions could be due to inhomogeneous broadening.

The theoretical curve for $GaS_{0.225}Se_{0.775}$ in Fig. 2 was obtained from Eq. (6) with the superposition of another Lorentzian-type resonance at $\omega_\ell = \omega_{ix}$ with $\Gamma_{io}$ = 24 meV. 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 $\omega_\ell = \omega_{ix}$ was seen in the raw data of RRS in the other crystals[11], 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.[11] The $\omega_\ell \sim \omega_{ix}$ resonance should also appear in the one-phonon RRS in $GaS_xSe_{1-x}$. It was indeed observed in the raw data as a shoulder on the strong resonance tail, but became invisible after absorption correction.

In conclusion, we have shown that the strong Raman resonance enhancement of the $1E'^{(2)}(LO)$ and $2E'^{(2)}(LO)$ modes near the absorption edge in $GaS_xSe_{1-x}$ can be explained satisfactorily by a simple theory with dispersion dominated by exciton resonances.

We acknowledge collaboration in the growth of the crystals with the members of the Laboratorie de Physique Applique in Lausanne, Switzerland. This work was supported by the U. S. Energy Research and Development Administration.

REFERENCES

1. See, for example, P. Y. Yu and Y. R. Shen, Phys. Rev. B12 , 1377 (1975), and references therein; N. M. Amer, T. C. Chiang, and Y. R. Shen, Phys. Rev. Lett. 34, 1454 (1975).

2. A. Mercier, E. Mooser, and J. P. Voitchovsky, J. Lum. 7, 241 (1973) and references therein.

3. K. Schubert, E. Dörre, and M. Kluge, Z. Metallk. 46, 216 (1955); F. Jellinek and H. Hahn, Z. Naturf. 16B, 713 (1961).

4. J. L. Brebner, J. Phys. Chem. Solids 25, 1427 (1964); E. Aulich, J. L. Brebner, and E. Mooser, Phys. Status Solidi 31, 129 (1969).

5. M. Schlüter, J. Camassel, S. Kohn, J. P. Voitchovsky, Y. R. Shen and M. L. Cohen, Phys. Rev. (to be published).

6. A. Mercier, E. Mooser, and J. P. Voitchovsky, Phys. Rev. B12, 4307 (1975).

7. Equations (1) and (2) were deduced from the experimental data of J. P. Voitchovsky.

8. T. J. Wieting and J. L. Verble, Phys. Rev. B5. 1473 (1972).

9. M. Hayek, O. Brabman, and R. M. A. Lieth, Phys. Rev. B8, 2772 (1973); A. Mercier and J. P. Voitchovsky, Solid State Comm. 14, 757 (1974).

10. R. M. Hoff and J. C. Irwin, Phys. Rev. B10, 3464 (1974); J. Reydellet and J. M. Besson, Solid State Comm. 17, 23 (1975).

11. J. Camassel, T. C. Chiang, Y. R. Shen, J. P. Voitchovsky, and N. M. Amer, Solid State Comm. (to be published).

FIGURE CAPTIONS

Fig. 1 Raman cross section of the $E'^{(2)}(LO)$ mode as a function of laser frequency. O, Δ, □, O and Δ are data points for $GaS_xSe_{1-x}$ with x = 0, 0.05, 0.12, 0.166 and 0.225 respectively. Solid curves are obtained from theory in the text.

Fig. 2 Raman cross section of the two-phonon $2E'^{(2)}(LO)$ mode as a function of laser frequency. O, Δ, □, O and Δ are data points for $GaS_xSe_{1-x}$ with x = 0, 0.05, 0.12, 0.166 and 0.225 respectively. Solid and dashed curves are obtained from theory in the text.

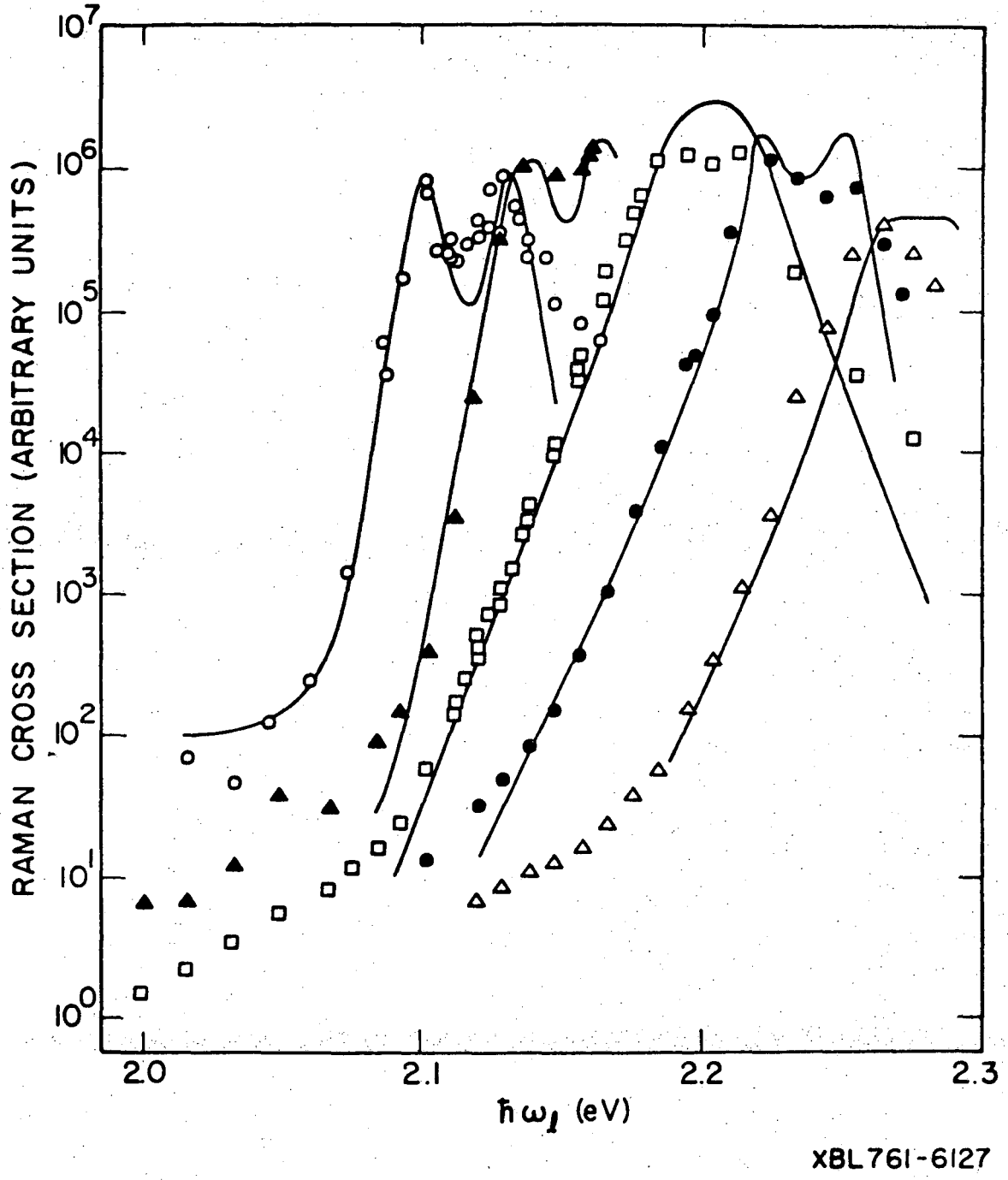



Fig. 1

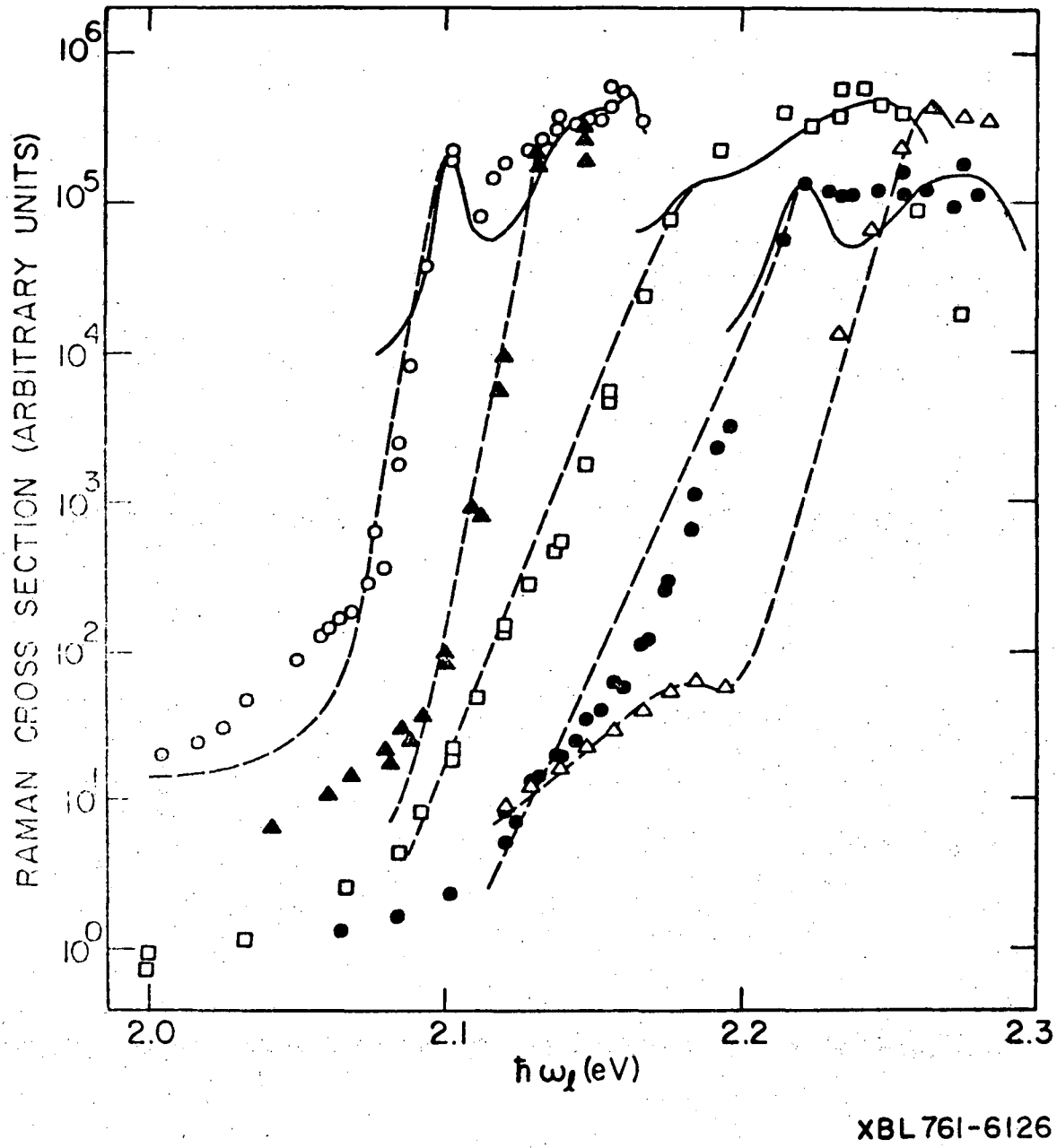

RAMAN CROSS SECTION (ARBITRARY UNITS)
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
2.0
2.1
2.2
2.3
$\hbar\omega_l$ (eV)
XBL761-6126

Fig. 2

*TECHNICAL INFORMATION DIVISION*
*LAWRENCE BERKELEY LABORATORY*
*UNIVERSITY OF CALIFORNIA*
*BERKELEY, CALIFORNIA 94720*