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EXCITON ENHANCED RAMAN SCATTERING OF LO PHONONS IN TRIGONAL Se*

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Resonance enhancements in the Raman cross-section of longitudinal optical (LO) phonons in trigonal Se have been measured around its excitonic absorption edge at low temperatures. Our results are explained in terms of resonant scattering of LO phonons via the Fröhlich interaction.

Resonant Raman scattering (RRS) has been recently applied successfully to study properties of phonons [1], electrons [2], and their interaction with each other in solids [3]. In particular, LO phonons have been found to show strong enhancement at excitons due to Fröhlich-type exciton-phonon interaction [4]. In this paper, we report observation of resonant scattering of LO phonons in Se at its direct excitonic absorption edge.

The vibrational and electronic properties of trigonal Se have been studied quite extensively [5]. To summarize, Se has six zone-center optical phonons of symmetry [6]: A_2 (112 cm^{-1}, infrared-active only); $E^{(1)}$ (147 cm^{-1}, both infrared and Raman active); $E^{(2)}$ (232 cm^{-1}) and A_1(235 cm^{-1}, Raman active only). Of the infrared active phonons, only the A_2 and $E^{(1)}$ modes have appreciable effective charge and hence a strong electric field associated with their LO components [7]. The reflectivity and the modulated reflectivity of Se in the region of interest are shown in Figure 1(a) and (b). The position of the excitonic structures a, b, c, and d observed in electroreflectance [8] are indicated by arrows. According to Weiser and Stuke [8],

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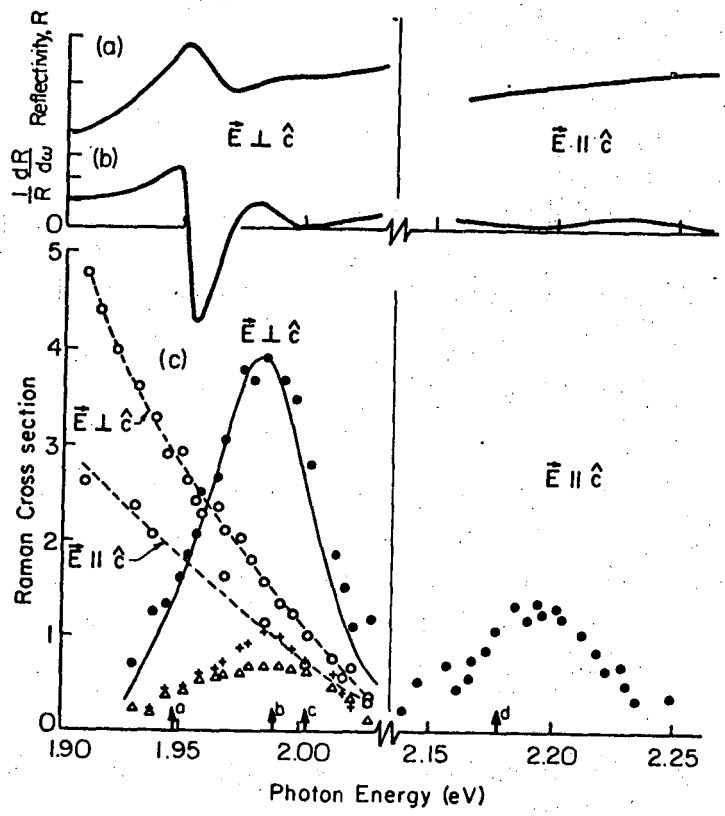

FIG. 1: (a) Reflectivity at 4.2°K; (b) logarithmic derivative of reflectivity at 4.2°K; (c) resonant Raman curves at 1.6°K for trigonal Se. The results for the various Raman modes are + for 114 cm^{-1}, ● for 151 cm^{-1}, ○ for 232 cm^{-1}, and Δ for 303 cm^{-1}. The solid curve is the theoretical curve from Eq. (1).

these excitons are formed from the same conduction band but different valence bands located at the H-point of the Brillouin zone.

Our measurements were performed at 1.6°K with a cw dye laser (tuning range 1.90-2.25 eV) and a conventional Raman spectrometer on melt-grown single crystals of trigonal Se cleaved parallel to the c-axis. Figure 2(a) and (b) give the Raman spectra of Se when the incident photon energy ω_i is close to the excitons a and b respectively. Comparison of the two spectra clearly shows resonant enhancement of some of the peaks.

We present in Fig. 1(c) the variation of the Raman cross-sections of some of the stronger Raman modes of Se with ω_i. The resonant peak around 2.0 eV was observed only for polarizations of incident and scattered radiation both perpendicular to the c-axis, while the peak around 2.2 eV was observed only for

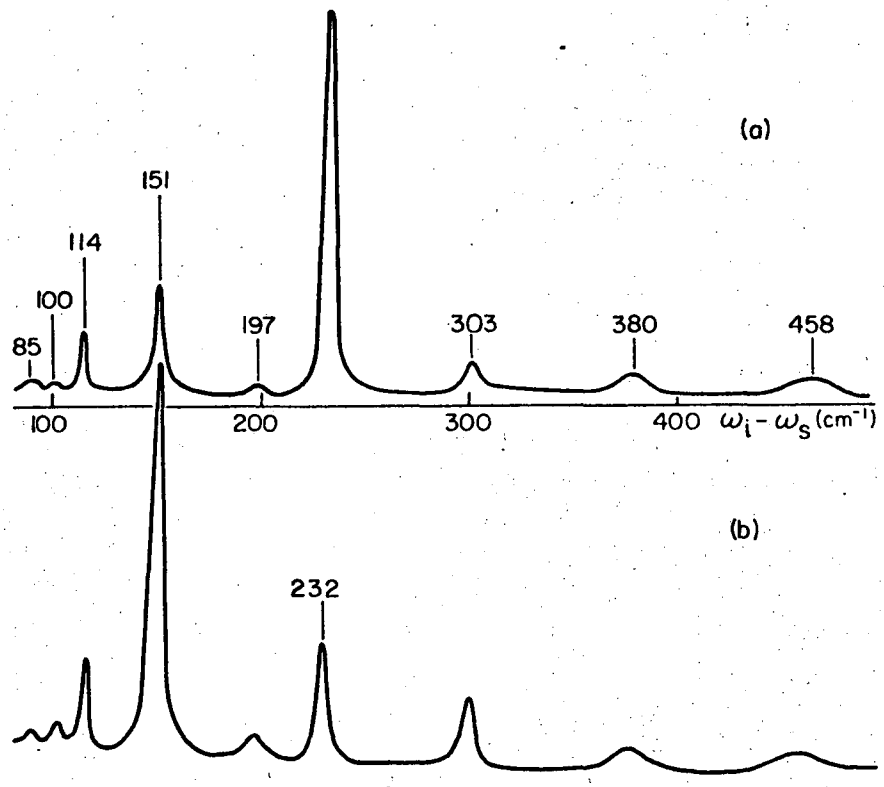

FIG. 2: Raman spectra of trigonal Se at 1.6°K. (a) ω_i = 1.943 eV (6380 Å) (b) ω_i = 1.987eV(6240 Å).

both polarizations parallel to the c-axis. For both polarization configurations, the 232 cm^{-1} $A_1 + E^{(2)}$ mode showed strong resonant enhancement towards lower ω_i, in qualitative agreement with the room-temperature measurements of Richter [9].

We assign the 114, 151, and 303 (± 1) cm^{-1} lines respectively as the LO components of the modes A_2, $E^{(1)}$, and the overtone of $E^{(1)}$. Their resonant behavior is very different from the $A_1 + E^{(2)}$ mode. It can be explained by the strong electric field associated with these LO phonons which couple strongly to the excitons via the Fröhlich interaction [4]. The frequencies of A_2 and $E^{(1)}$ we observed are respectively 2 and 4 cm^{-1} higher than those reported by Mooradian [6]. It could be that Mooradian's off-resonance measurements detected only the TO components. The LO-TO splittings of A_2 and $E^{(1)}$ deduced from infrared measurements are 4 and 6 cm^{-1} respectively [7].

We can explain quantitatively the Raman resonance around 2 eV. Consider the $E^{(1)}$ mode as an example. We assume the dominant intermediate states in the Raman scattering process are the 1s Wannier excitons a and b with damping

constants Γ_a and Γ_b respectively. The contribution of non-resonant processes is neglected since our results do not show a strong constant background. We also assume the inter-exciton Fröhlich interaction dominates. Then, the resonant Raman scattering processes involved are shown in Fig. 3. The

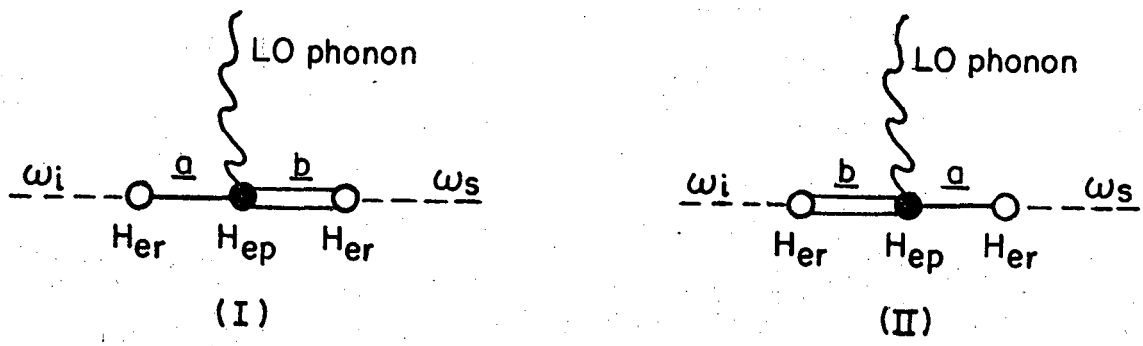

FIG. 3: Inter-exciton resonant Raman scattering by LO phonons. H_{er} and H_{ep} stand for exciton-photon and exciton-phonon interactions respectively

corresponding Raman cross-section is

$$R(\omega_i) \sim \left| \frac{\langle 0|H_{er}|b\rangle\langle b|H_{ep}|a\rangle\langle a|H_{er}|0\rangle}{(\omega_i-\omega_b-i\Gamma_b)(\omega_s-\omega_a-i\Gamma_a)} + \frac{\langle 0|H_{er}|a\rangle\langle a|H_{ep}|b\rangle\langle b|H_{er}|0\rangle}{(\omega_i-\omega_a-i\Gamma_a)(\omega_s-\omega_b-i\Gamma_b)} \right|^2 . \quad (1)$$

We obtain the exciton energies ω_a and ω_b from ref. 8, and treat the damping constants Γ_a and Γ_b as adjustable parameters. As usual, the matrix elements are assumed to be energy-independent. The solid curve in Figure 1(c) is a plot of Eq. (1) with $\Gamma_a = 250\ cm^{-1}$; $\Gamma_b = 200\ cm^{-1}$. The agreement with experiment is quite satisfactory. The value of Γ_a obtained is somewhat larger than the value estimated from the reflectivity ($\Gamma_a \sim 150\ cm^{-1}$). This could have been caused by local heating of the sample induced by the laser beam.

We are still in the process of carrying out the complete theoretical analysis of our experimental results, including the observed polarization dependence. The work will be published elsewhere.

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