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RESONANT RAMAN SCATTERING AT THE EXCITON-POLARITON IN TlBr

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Resonant Raman scattering at the exciton-polariton in TlBr is reported. The cross-section for forbidden 1LO(Γ) scattering is analysed within a polariton model, from which we determined the L-T splitting of the B-exciton. We observe strongly resonant forbidden TO(Γ) scattering, for which possible mechanisms are discussed. Two-phonon scattering processes involving M-point phonons prove the existence of phonon intervalley scattering between non-equivalent X-points.

Thallium halides exhibit various properties that make them outstanding materials to study light scattering of exciton-polaritons and their phonon interactions. The lowest (X_6^+,X_6^-) exciton [1] consists of two dipole allowed 1s-states (E_A^T,E_B^T) constructed out of electrons and holes from non-equivalent X-valleys, the splitting resulting from intervalley interactions [2]. The strong exciton-phonon coupling, reflected in the existence of an exciton-phonon-quasi-bound state (EPQBS) observed in absorption [3] should result in enhanced resonant Raman scattering (RRS).

We have investigated the resonance behaviour of several Raman processes in TlBr at 1.8K for incident photon energies around E_A^T = 3.0089 eV and E_B^T = 3.0104 eV. The experimental details have been published elsewhere [4]. Special care was taken in preparing strain-free surfaces of the unoriented sample. The scattering intensity (spectral resolution 0.5 meV) was measured normalized to the incident laser power and is given in consistent units. A series of RRS spectra is shown in Fig.(1). The excitation photon energies cover a range of three LO-phonon energies around the direct exciton states.

The following processes are identified:

1. LO(Γ)-Phonon Scattering

Most dominant are the equidistant LO scattering peaks from which we deduce a LO(Γ) energy of 14.5 meV. The occurrence of the symmetry-forbidden 1LO process strongly in resonance with the exciton states shows that the $\vec{q}$-dependent Fröhlich coupling is responsible for this scattering process. The strength of this interaction is documented by strong multiple LO scattering. Depending on the excitation energy we have observed up to ten LO lines, their maximum enhancement occurring for the scattered photon energy in resonance with the exciton. For the 1LO processes, Fig.(2) illustrates the energy dependence of the scattered intensity. The experimental data are corrected for absorption using the optical constants measured on crystals of the same source. The full line represents a calculation of the cross-section based on an undamped polariton model. In computing the cross-section we proceeded in the following way [5]: a) evaluation of the transmission factors of the incident and scattered photons outside into polaritons inside the crystal with the help of additional boundary conditions (ABC); b) calculation of the polariton scattering cross-section using the "golden rule"; and c) summation over all possible polariton scattering processes giving rise to the same Raman shift neglecting interference effects between different channels.

In backscattering geometry we obtain the following expression for the Raman cross-section:

$$S^{180}(E_o, E_s) \sim \sum_{\alpha\ \beta} \frac{k_s^2}{V_o V_s} \, |P_\alpha(\vec{k}_o)|^2 |P_\beta(\vec{k}_s)|^2 |f^{Ex}(\vec{q})|^2 . \qquad (1)$$

Here E, $\vec{k}$, V and P denote the energy, wavevector, group velocity and exciton polarization, respectively, for the incident (subscript o, branch α) and scattered polaritons (s,β). $f^{Ex}(\vec{q})$ with $\vec{q} = \vec{k}_s - \vec{k}_o$ is the exciton-phonon Fröhlich interaction matrix element.

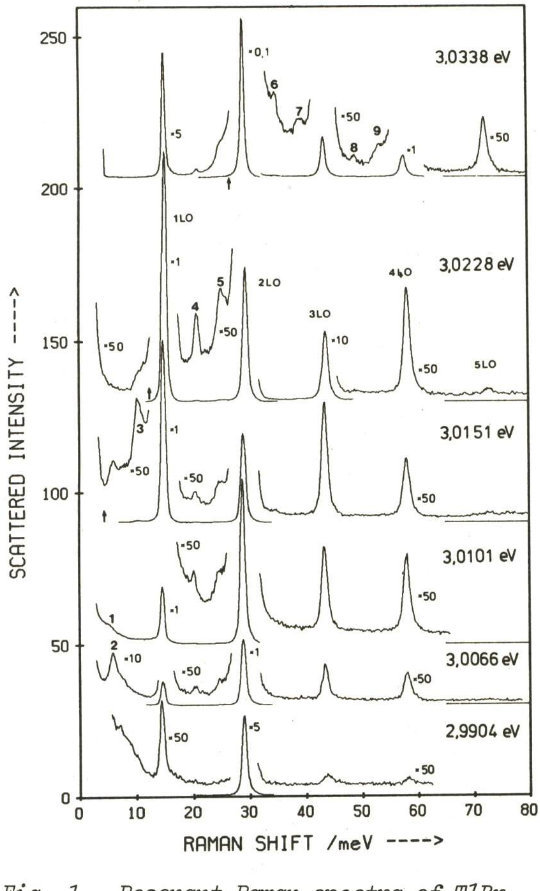

Fig. 1 Resonant Raman spectra of TlBr at T = 1.8K for excitation energies as shown: Arrows mark E_B^T

The polariton dispersion, necessary to calculate the different quantities, is obtained using the exciton transverse energies E_A^T and E_B^T, the effective masses $M_A^* = M_B^* = 1\ m_e$, the background dielectric constant $\varepsilon_o = 8$, and the ratio of exciton photon coupling constants for B and A exciton equal to 2.

The longitudinal-transverse (L-T) splitting of the B-exciton ΔE_B^{LT} was taken as the only adjustable parameter in the model. As ABC we used those proposed by Sein and Birman [6], extended for the three polariton branches in TlBr. Using $\Delta E_B^{LT} = 1.9$ meV the computed cross-section (full line in Fig.(2)) reproduces the following features of our experimental data:

a) The incident photon shows resonance with both the A and B excitons.

b) The non-Lorentzian lineshape of the resonance is a result of the L-T splitting giving a sharp decrease of the scattering cross-section at E_B^L.

c) The difference in the scattered intensity between the incoming and outgoing resonance can be understood as a result of the spatial dispersion, which in conjunction with the $\vec{q}$-dependent Fröhlich

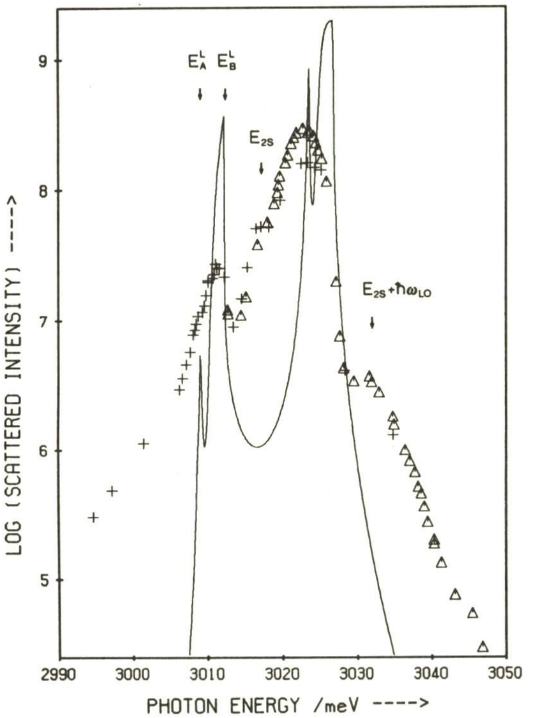

Fig. 2 *1LO(Γ) scattering cross-section. + and Δ: experimental points, straight line: model calculation (see text).*

interaction greatly enhances the scattering of polaritons with large wavevectors.

In contrast, the polariton model cannot explain the observed peak position of the outgoing resonance, occurring at $E_B^L + 0.75\ \hbar\omega_{LO}$. Although this peak nearly coincides with the exciton binding energy, a dominant contribution of free electron-hole pairs can be excluded, since it would imply strong enhancement for the outgoing resonance at $E > E_{2s} + \hbar\omega_{LO}$. From comparison with the LO-assisted 1s absorption spectrum closely related to the Raman cross-section we rather propose to attribute the shift to the influence of an EPQBS [3]. It is observable if an exciton and a LO phonon are created simultaneously in the crystal. In RRS this is just the case, when the energy of the scattered polariton is near the transverse exciton. Then the EPQBS leads to a reduction in exciton-polariton energy showing up as a shift in the resonance peak of the cross-section to lower energies by the same amount.

Two other arguments are in strong favour of this interpretation. First, the in- and outgoing resonances with the 2s exciton state, which is not leading to an EPQBS, are at the expected position at E_{2s} and $E_{2s}+\hbar\omega_{LO}$, respectively. Secondly, the same shift in the outgoing resonance peak position occurs for all scattering processes involving at least one LO-phonon.

2. TO(Γ)-Phonon Scattering

From comparison with the known phonon energies [7], peak 2 in Fig.(1) at 5.8 meV can be attributed to TO(Γ) scattering. Peaks 4, 6 and 8 are multiple LO(Γ) replicas of this process. Considering the energy dependence of the cross-section with maximum at the B-exciton energy, it can be concluded that the intermediate states responsible for this process are exciton-polaritons, while the scattered excitations are bulk TO(Γ) phonons. That rules out any breakdown of wavevector selection rules due to impurities or at the surface.

On the other hand, there is a finite momentum transfer in the scattering process, leading to the possibility of forbidden scattering via $\vec{q}$-dependent interactions. These can result in two ways: First, the deformation potential vanishing for the TO phonon at the Γ-point might contribute in higher order. Secondly, exciton and TO phonon can interact via a mechanism similar to the Fröhlich interaction. The electric field necessary for this type of interaction originates from local electric fields associated with the TO phonon in polar materials. For finite wavevectors these fields do not compensate over an exciton radius. From the scattering cross-section the magnitude of the field can be estimated to be 1/3 to 1/10 of that of the LO(Γ) phonon, in qualitative agreement with the results recently obtained [8] that TO phonons in principle may give rise to electro-optic Raman scattering. In addition, the field might be due to a mixing of TO and LO phonons, occurring for arbitrary directions in $\vec{k}$-space.

3. Intervalley Scattering

The threeforld $\vec{k}$-star degeneracy of the X-point leads to the possibility of intervalley scattering with momentum conserving M-phonons. Peak 1 and 3 are attributed to 2TA(M) and 2LA(M) Raman processes, respectively, the peaks 5, 7 and 9 being multiple LO(Γ) replicas. This assignment again is in good agreement with the known phonon energies. Microscopically the incident polariton is scattered into an intermediate virtual state by M-phonon scattering of the electron or the hole to another X-point, thus forming an exciton at M, and back again into the final polariton state. The existence of M-excitons with energy close to that of the exciton at $\vec{K}=0$ is substantial for the occurrance of the enhancement of M-phonon processes.

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