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RESONANT RAMAN SCATTERING IN TiO₂

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Abstract. - One investigates the resonant behavior of Raman active phonons in TiO₂ for incident laser energies ranging between 2.0 and 2.75 eV. One finds the enhancement to be dominated by the quadrupolar interaction.

TiO₂ (rutile) is a wide band gap semiconductor which belongs to the D₄₄₄ symmetry group. The fundamental absorption edge has been well characterized from experiments performed at liquid helium temperature(1). The result of both experiments and theoretical calculations(2) concerning the ordering of electronic energy levels at the center of the Brillouin zone is schematically drawn in Fig.1. The lowest absorption edge is associated with a first-order forbidden quadrupolar interaction.

Dipole-allowed transitions correspond to perturbations with Γ₁₂ (E//c) and Γ₅ (E⊥c) symmetry, respectively. If one refers to the crystallographic directions, the polarizability tensor of the first-order non-resonant Raman process corresponds to(3):

\[
\begin{align*}
\alpha_{xx}^{\Gamma_5} & \times \Gamma_5^{\Gamma_5} \rightarrow \Gamma_1 (A_{1g}) + \Gamma_3 (B_{1g}) \\
\alpha_{yy}^{\Gamma_5} & \times \Gamma_5^{\Gamma_5} \rightarrow \Gamma_4 (B_{2g}) \\
\alpha_{zz}^{\Gamma_5} & \times \Gamma_5^{\Gamma_5} \rightarrow \Gamma_1 (A_{1g}) \\
\alpha_{yz}^{\Gamma_5} & \rightarrow \Gamma_5 (E_g)
\end{align*}
\]

We have studied the resonant scattering tuning the incident phonon energy close to the exciton energy of the fundamental gap. In this case, of the six terms contributing to the scattering probability per unit time(4) one becomes the strongest compared to all other terms which can approximated by a constant C. Thus, in resonant Raman scattering (RRS) the scattering probability is written as:

\[
P(\omega_1, \omega_2) \sim \sum_{j,k} \frac{\langle \Gamma_1 | H_3 | k \rangle \langle k | H_2 | j \rangle \langle j | H_1 | \Gamma_1 \rangle}{(\omega_k - \omega_j)(\omega_j - \omega_i)} \delta(\omega_1 - \omega_2 - \Omega)
\]

where |Γ₁⟩ corresponds to the unperturbed ground state of the crystal ; H₁(3) and H₂ are the exciton-radiation and exciton-phonon interactions, respectively ; |j⟩ and |k⟩
denote intermediate states in which excitations are created in the solid; \( \omega_s(\omega) \) is the energy of the incident (scattered) light, \( \hbar \) the energy of the phonon and \( \omega_k(\omega) \) the energy of the intermediate state.

All experiments have been performed using previously described techniques\(^3\). The incident propagation was along the \( c \) axis, the collected one along \( a \). All incident frequencies were provided by i) an argon-ion laser, ii) a C.W. dye laser using R6G in the range 5700-6000 Å, iii) a pulsed dye laser pumped by 1 MWatt nitrogen laser.

\[
\frac{\Gamma(A_{1g})}{2} = 76 \text{ meV/612 cm}^{-1} \text{ Raman-line}
\]

The most resonant electronic process first includes the creation of a direct exciton in an excited state of symmetry \( j_1 = \gamma_3 \) by means of a quadrupolar interaction \( H_1(\gamma_3) \). The exciton is next scattered to the exciton ground state \( |k = \gamma_1 \rangle \) by the \( \gamma_1 \) phonon. Finally the exciton anihilates by a quadrupolar interaction \( H_3(\gamma_3) \). Other processes involving two dipolar interactions from the ground state to higher excited states with symmetry \( \gamma_5 \), are far from resonance. The scattering probability is then given by:

\[
P(A_{1g}) \propto \frac{A^2}{(3.05 + 0.076 - \hbar \omega_q)^2 (3.05 - \hbar \omega_q)^2}
\]

Near resonance:

\[
P(A_{1g}) \propto \frac{A^2}{(3.05 + 0.076 - \hbar \omega_q)^2 (3.05 - \hbar \omega_q)^2}
\]

The solid line in Fig.2 has been calculated using \( A^2 = 0.16 \) and accounts satisfactorily for the dispersion of experimental cross section.

\[
\frac{\Gamma_5(E_g)}{2} = 56 \text{ meV/449 cm}^{-1} \text{ Raman-line}
\]

The different excitation processes involve different immediate states. Two of them are summarized in the expression of the scattering probability:

\[
P(E_g) \propto \left[ \frac{\langle \Gamma_1 | H_3(\gamma_3) | \Gamma_3 \rangle \langle \Gamma_3 | H_2(\gamma_1) | \Gamma_1 \rangle \langle \Gamma_3 | H_1(\gamma_3) | \Gamma_1 \rangle}{(5 + 0.056 - \hbar \omega_1) (3.05 - \hbar \omega_1)} \right]^2 + \left[ \frac{\langle \Gamma_1 | H_3(\gamma_3) | \Gamma_3 \rangle \langle \Gamma_3 | H_2(\gamma_3) | \Gamma_1 \rangle \langle \Gamma_5 | H_1(\gamma_5) | \Gamma_1 \rangle}{(5 + 0.056 - \hbar \omega_1) (3.05 - \hbar \omega_1)} \right]^2
\]

The first contribution is semiresonant (only one energy denominator cancels) and the second is not. Then the scattering probability can be written:

\[
P(E_g) \propto \frac{B^2}{(5 - \hbar \omega_1)^2 (3.05 - \hbar \omega_1)^2}
\]
The solid curve in Fig. 3 has been calculated using $B^2 = 1.75$ and, again, compares satisfactorily with the experimental results.

$$\Gamma_3(B_{1g}) : 18 \text{ meV/143 cm}^{-1} \text{ Raman-line}$$

We did not find a process which permits the enhancement of phonons with symmetry $\Gamma_3$ with quadrupolar-allowed transitions. The allowed process with lowest exciting energy includes two dipolar interactions with excited states of symmetry $\Gamma_5$:

$$\mathcal{P}(\Gamma_3) \propto \left[ \frac{\langle \Gamma_1 | H_3 (r_{51}^\dagger) | \Gamma_5 \rangle \times \langle r_{51}^\dagger | H_2 (r_{51}^\dagger) | \Gamma_5 \rangle \times \langle \Gamma_5 | H_1 (r_{51}^\dagger) | \Gamma_1 \rangle}{(5 - \hbar \omega_1)(5 - \hbar \omega_1)} + C \right]^2$$

In agreement with experimental data, the solid line in Fig. 4 displays a negligible dispersion in our range of investigation.

References: