Breakdown of Selection Rules in Resonance Raman Scattering

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Large 1LO Raman scattering near resonance in CdS is observed in the diagonal components of the Raman tensor $R^{\alpha\alpha}$ independent of crystal-symmetry selection rules. The data support the interpretation as an intrinsic bulk effect dependent on the finite wavelength of light.

Recently there have been a number of Raman-scattering experiments[1-4] in solids using light near resonance with fundamental electronic transitions. The experiments have verified qualitatively the enhancement of the cross section predicted by several authors.[5-8] The present Letter reports observation and interpretation[9] of large "forbidden" 1LO scattering near resonance in CdS.

The breakdown in selection rules is not a surface effect,[10] since the scattering occurs deep in the bulk, but must be caused by (1) impurity states near the band gap as has been proposed,[2,3] or (2) an intrinsic bulk effect dependent upon the finite wavelength of light as is proposed here.

The Raman cross section for one-phonon Stokes scattering at low temperature as a function of the incident light frequency ω_i can be written

$$\sigma(\omega_i) \propto |R^{\alpha\beta}\epsilon_i{}^{\alpha}\epsilon_s{}^{\beta}|^2,$$

$$R^{\alpha\beta} = \sum_{ij} \frac{P_{0j}{}^{\alpha *} M_{ji} P_{i0}{}^{\beta}}{(E_j - \omega_i + \omega_0)(E_i - \omega_i)}, \qquad (1)$$

where i and j denote excited electronic states of energy E_i and E_j, $\vec{P}_{0i}$ is the momentum matrix element with the ground state 0, M_{ji} the phonon scattering matrix element, ω_0 the phonon frequency, and $\vec{\epsilon}_i$ and $\vec{\epsilon}_s$ the incident and scattered photon polarizations. In (1) both electron-photon and electron-phonon interactions have been treated in perturbation theory which is sufficient for our purposes.[11]

Selection rules[12] are derived by expanding the matrix elements in powers of the photon wave vectors $\vec{k}_i$ and $\vec{k}_s$. "Allowed" terms are those which are independent of $\vec{k}_i$ and $\vec{k}_s$, i.e., independent of scattering angle. For intrinsic bulk scattering in which a phonon of wave vector $q = \vec{k}_i - \vec{k}_s$ is created, there is a unique expansion of (1) in powers of $\vec{q}$ with selection rules for all orders determined by the crystal symmetry. Each successive order of forbidden scattering is reduced in intensity by a factor $\sim(qa)^2$ where a is a characteristic length of the excited state and $q \sim$ wave vector of light. Thus forbidden lines are strong only if a is much larger than the lattice constant and the electron-phonon interaction is large. These conditions may be satisfied for large Wannier excitons coupled to phonons via the intraband Fröhlich interaction[6,8,13]; thus we expect forbidden scattering only for LO phonons and with a more pronounced resonance enhancement than for allowed scattering, since only near resonance are large-radius excitons dominant intermediate states.

The magnitude of the forbidden scattering is readily calculated for hydrogenic excitons. For example, for $1s$ scattering we find[13]

$$M^F(q) = (\gamma/q)\{[1+(\alpha_h q a_0)^2]^{-2} - [1+(\alpha_e q a_0)^2]^{-2}\}, \qquad (2)$$

where $\alpha_e = \frac{1}{2} m_e{}^*/(m_e{}^* + m_h{}^*)$, $\alpha_h = \frac{1}{2} - \alpha_e$, γ is the coupling constant, and a_0 the radius. $M^F(q)$ is shown in the insert in Fig. 1 for $m_e{}^*/m_h{}^* = 0.2$ which is appropriate to CdS. In the experiments discussed below, $qa_0 \approx 0.15$. The resonance enhancement has been calculated[9] by summing over all exciton states, discrete and continuum, with the results shown in Fig. 1. The calculated Raman efficiency at $(E_{1s} - \omega_i)/\omega_0 = 1.8$ in CdS is $s = 1.3 \times 10^{-7}$/cm sr. Note that because the excitons are isotropic and the scattering is intraband, only $\vec{\epsilon}_i \| \vec{\epsilon}_s$ forbidden scattering is large independent of crystal symmetry.

On the other hand, impurity states modify the selection rules because they break the translational and point symmetry. If large-radius bound excitons are the important impurity states,[3] one also finds that forbidden scattering may be large

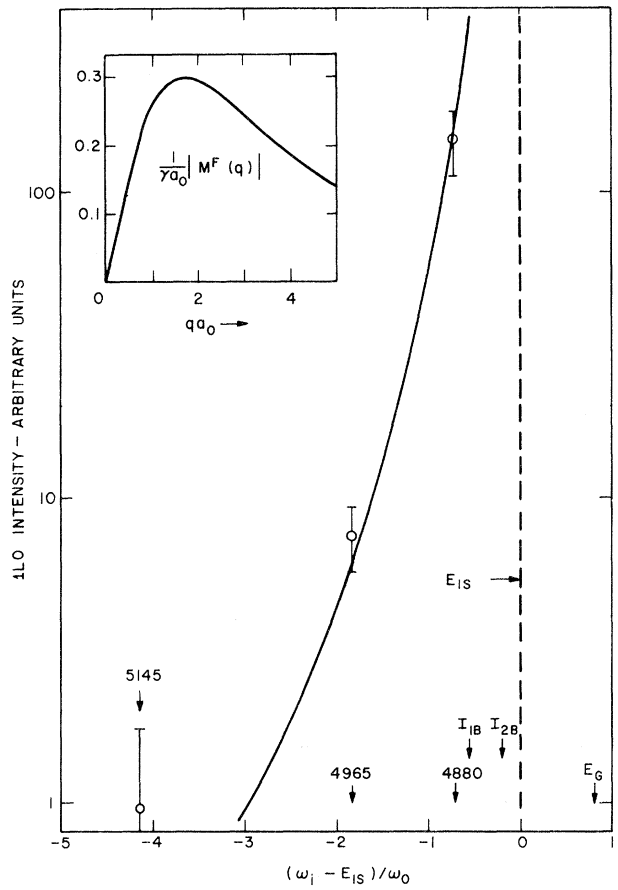

FIG. 1. Relative enhancement of the forbidden $x(zz)y$ 1LO scattering intensity in CdS as a function of the incident light frequency ω_i: solid line, calculated; points, experiment. The gap E_G and bound excitions I_1 and I_2 are indicated and $\omega_0 = 37$ meV is the LO frequency. The insert gives the matrix element $M^F(q)$ of Eq. (2) as a function of qa_0 for CdS.

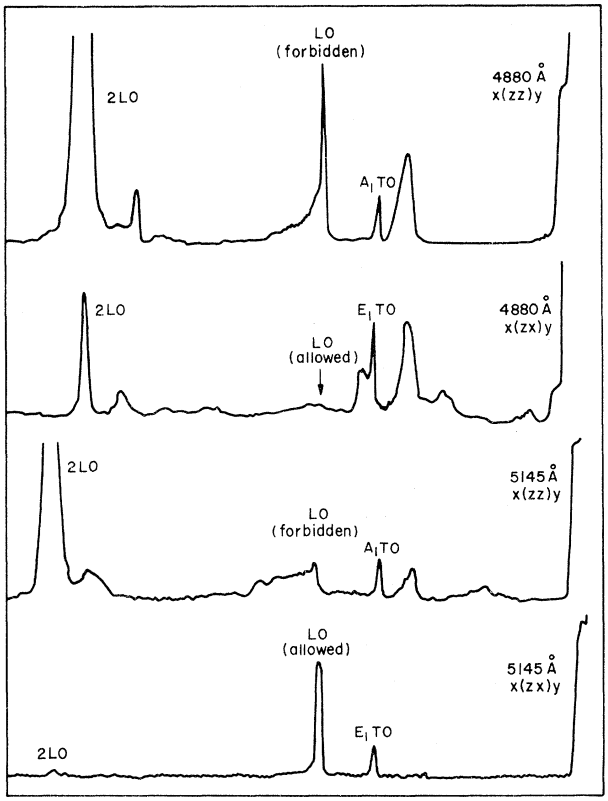

FIG. 2. Uncorrected experimental traces of the Raman scattered light near resonance in CdS for various incident frequencies and polarizations. Note that near resonance the allowed $x(zx)y$ 1LO line is weak whereas the forbidden $x(zz)y$ line is very strong.

only for LO phonons and $\vec{\epsilon}_i \| \vec{\epsilon}_s$. The differences from intrinsic forbidden scattering are that impurity-induced scattering (1) is independent of scattering angle and (2) should lead to dispersive broadening of the one-phonon line since the phonon momentum is not fixed.

Experimental observation of forbidden lines near resonance has been carried out on pure ($\lesssim 10^{16}$ impurity concentration) CdS using a polished 5-mm cube and a 1-mm slab for which absorption corrections were measured directly.[1] In Fig. 2 are shown typical traces of the Raman spectrum for right-angle scattering with different polarizations and frequencies. For $x(zz)y$ geometry ($\vec{k}_i = \hat{x}, \vec{\epsilon}_i = \hat{z}, \vec{\epsilon}_s = \hat{z}, \vec{k}_s = \hat{y}$), 1LO scattering is forbidden[12] whereas for $x(zx)y$ it is allowed.[12] We see that the forbidden LO line is weak away from resonance but increases dramatically near resonance, becoming much larger than any allowed one-phonon line.[14] Quantitative measurements of the $x(zz)y$ intensities and absorption coefficients α were made on the 1-mm sample at 6°K with small detector aperture ($f25$) with the results listed in Table I. Error limits are estimated to be ~25%.

The experimental results are in good agreement with the calculated enhancement as shown in Fig. 1. (Since the photons are polarized paral-

Table I. Experimental LO/TO ratios for CdS in $x(zz)y$ geometry and the LO enhancement corrected for laser intensity and absorption as discussed in Ref. 1. The measured extinction coefficient α is also listed.

Wavelength (Å)	LO/TO $x(zz)y$	α (cm^{-1})	LO corrected
5145	0.5	3.3	1.0
4965	1.1	5.8	7.4
4880	4.5	24.	150.

lel to the c axis, the resonance is with the B exciton series in which $E_{1s} = 2.569$ eV.) The Raman efficiency of the forbidden 1LO at 4965 Å $[(E_{1s} - \omega_i)/\omega_0 = 1.8]$ may be found from Table I and absolute measurements[15] of the A_1 TO intensity at 5145 Å to be 0.6×10^{-7}/cm sr in excellent agreement with the theory.

Consider now the alternative interpretation based on extrinsic bound excitons. For I_1 or I_2 type impurity states one expects 1LO to be greatly broadened (~2LO width); this has been observed by Colwell and Klein.[3] In the present work, however, the 1LO width is invariant (2 ± 0.2 cm^{-1}) for allowed or forbidden lines at all reported ω_i. Our data could be explained (including the resonance enhancement) by a very shallow unknown impurity state of radius ~100 Å, but it would be unlikely that a state with such large oscillator strength would escape detection in absorption and luminescence. Forward scattering measurements which would also distinguish between intrinsic and extrinsic processes have not been made because of difficulties in analyzing measured intensities.

In conclusion, large forbidden 1LO Raman scattering has been observed near resonance in good agreement with theoretical calculations in which the resonant intermediate states are intrinsic hydrogenic excitons. All theoretical results are independent of crystal symmetry; consequently large forbidden 1LO lines near resonance are expected in a wide range of crystals, including many for which 1LO is completely inactive and cannot be detected in any geometry far from resonance.

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Observation of Electron Standing Waves in a Crystalline Box

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We have observed electron standing-wave states in thin Pb films by electron tunneling. The simple theory includes the important fact that oriented crystalline films will vary in thickness only by discrete steps. As a result, certain "commensurate" energy levels play an important role in the experiment.

The description of a particle confined to a box of finite dimensions is a basic problem in quantum mechanics. As is well known, the particle has available to it a series of energy levels whose spacing varies with the size of the box. This Letter reports a direct observation and study of these states in crystalline Pb, in the form of thin films. The term crystalline is used to emphasize that, while real metal films are not perfectly smooth, they nevertheless may vary in thickness only by discrete steps. This fact has very significant experimental consequences related to the observability of the box-quantized energy levels in Pb films. Briefly, the energy-level structure of these crystalline films is found to possess special "commensurate" lev-