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Equivalence of Resonance Raman Scattering in Solids with Absorption followed by Luminescence*

Miles V. Klein

Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

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The method used in a recent paper by Yu, Shen, Petroff, and Falicov to analyze successfully their data on two-phonon resonance Raman scattering in Cu_2O illustrates the principle that resonance scattering is often equivalent to absorption into a resonant state followed by luminescence from that state. It is shown explicitly for the case considered by Yu *et al.* that the two descriptions are the same. Other examples from the literature are discussed. It is also shown that the maximum smallness of the resonant-energy denominator is unaffected by the widths of the relevant phonon states.

The recent paper by Yu *et al.*, "Resonance Raman Scattering at the Forbidden Yellow Exciton in Cu_2O,"[1] illustrates the general principle that resonance scattering is equivalent to absorption into the resonant state followed by spontaneous emission—provided that interferences with nonresonant amplitudes can be neglected.[2] Their process can also be referred to as "hot luminescence," that is, luminescence from "hot" excitons, not in thermal equilibrium.

It will be shown explicitly that the assumptions made by Yu *et al.* lead to an expression for the scattering efficiency that is identical to that obtained by considering absorption followed by emission. The scattering efficiency into unit solid angle will be shown to be equal to the absorption coefficient multiplied by the quantum yield for hot-luminescence emission into unit solid angle.

The notation is the same as that of Ref. 1. The resonant scattering process is illustrated in Fig. 1. State $|o)$ is the initial state involving n_i initial monochromatic photons per unit volume. State $|f)$ is the final state containing phonons of momenta $\vec{q}$ and $-\vec{q}-\vec{s}$, plus a photon of momentum $\vec{s}$. State $|a)$ is the resonant intermediate state consisting of an exciton α of momentum $-\vec{q}$ and a phonon of momentum $\vec{q}$ and energy ω_o. It is reached via the first intermediate state $|b)$ consisting of exciton β having essentially zero momentum. The transition from $|a)$ to $|f)$ goes via $|c)$, which consists of exciton β having momentum $\vec{s}$ and the two phonons of momenta $\vec{q}$ and $-\vec{q}-\vec{s}$. In the presence of perturbing Hamiltonians H'_{rad} and $H'_{e\text{-}l}$, representing, respectively, the coupling of the β exciton to the electromagnetic field and the exciton-phonon interaction, the matrix element for the process of Fig. 1 becomes ($\hbar = 1$ here)

$$(f|M|o) = \frac{(f|M_{\mathrm{em}}|a)(a|M_{\mathrm{abs}}|o)}{\omega_\alpha(q) + \frac{1}{2}i\gamma + \omega_o - \omega_i}\ , \tag{1}$$

where

$$(f|M_{\mathrm{em}}|a) = \frac{(f|H'_{\mathrm{rad}}|c)(c|H'_{e\text{-}l}|a)}{\omega_\beta - \omega_i + 2\omega_o} \tag{2}$$

and

$$(a|M_{\mathrm{abs}}|o) = \frac{(a|H'_{e\text{-}l}|b)(b|H'_{\mathrm{rad}}|o)}{\omega_\beta - \omega_i}\ . \tag{3}$$

In Eq. (1) γ is the reciprocal of the lifetime of the α exciton. The scattering efficiency $dR/d\Omega$ is the scattering cross section per unit volume per unit solid angle. To calculate it we use the "golden rule." The final states to be summed over will be represented by q and s. The sum over s introduces the final photon density of states per unit solid angle

$\frac{1}{4\pi}\frac{dN_s}{d\omega_s}$ with $\omega_s = \omega_i - 2\omega_o$.

The incident photon flux is $n_i v_i$, where v_i is the group velocity of the incident photon. (For cases of strong resonant absorption one should use the velocity of energy transport.) We then find

$$\frac{dR}{d\Omega} = \frac{2\pi}{n_i v_i}\sum_q |(f|M|o)|^2 \frac{1}{4\pi}\frac{dN_s}{d\omega_s} . \tag{4}$$

Let

$$\omega_\alpha(\vec{q}) = \omega_1 + K ,$$

where ω_1 is the energy at the bottom of the α-exciton band and K is the kinetic energy of the α exciton. The square of the absolute value of the resonant-energy denominator in Eq. (1) is then treated as in Ref. 1:

$$[(\omega_\alpha + \omega_o - \omega_i)^2 + \tfrac{1}{4}\gamma^2]^{-1} = 2\pi\delta(\omega_1 + K + \omega_o - \omega_i)/\gamma(K) \tag{5}$$

This means that only real, i.e., resonant, intermediate states are allowed to contribute to the scattering. Nonresonant states are neglected. This is the key assumption.

If dispersion of the phonon frequency ω_0 is neglected, the sum over q in Eq. (4) goes over into an integral involving the density of α-exciton states of kinetic energy $K = \omega_i - \omega_1 - \omega_o$:

$$\sum_q \delta(\omega_i + K + \omega_o - \omega_i) \to \frac{dN_\alpha}{dK} ,$$

and Eq. (4) becomes

$$\frac{dR}{d\Omega} = \left(\frac{2\pi}{n_i v_i}|(a|M_{abs}|o)|^2 \frac{dN_\alpha}{dK}\right)\frac{2\pi}{\gamma(K)} \times \frac{|(f|M_{em}|a)|^2}{4\pi}\frac{dN_s}{d\omega_s} . \tag{6}$$

The term in large parentheses in Eq. (6) represents $K_{abs}(\alpha)$, the contribution of exciton state α to the (indirect) absorption coefficient.

The radiative decay rate out of the resonant exciton state into unit solid angle of final photon states is

$$\frac{d\gamma_R(\alpha)}{d\Omega} = 2\pi\frac{|(f|M_{em}|a)|^2}{4\pi}\frac{dN_s}{d\omega_s} .$$

Thus we have

$$\frac{dR}{d\Omega} = K_{abs}(\alpha)\frac{1}{\gamma(K)}\frac{d\gamma_R(\alpha)}{d\Omega} . \tag{7}$$

The total scattering efficiency is therefore

$$R = K_{abs}(\alpha)\tau/\tau_R , \tag{8}$$

where

$$\tau_R = \gamma_R(\alpha)^{-1}$$

is the radiative lifetime of exciton α, and where

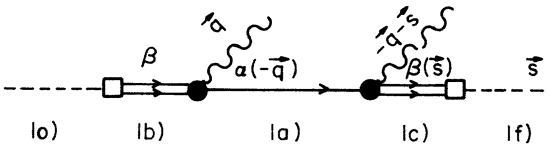

FIG. 1. Two-phonon resonance scattering process considered in Ref. 1.

$$\tau = \gamma(K)^{-1}$$

is the net lifetime of the exciton due to both radiative and nonradiative processes. For the experimental situation of Ref. 1 τ is dominated by nonradiative phonon-emission processes.

In Ref. 1 strong evidence is presented for the validity of the line of reasoning presented above. The scattering efficiency as a function of the energy ω_i of the incident photon is dominated by a dependence on $1/\gamma(K)$, as stated in Eq. (7), with K given by

$$K = \omega_i - \omega_1 - \omega_o .$$

One can find other examples in the solid-state-physics literature where resonance absorption followed by emission dominates a "resonant" Raman-scattering situation. For instance, in CdS Gross and co-workers have observed such a resonance-absorption process, where the resonant state is a "hot" excitonic polariton and the reemitted photon is downshifted in energy by the energy of one or two LO phonos.[3] The proof that the excitonic polariton exists as a real well-defined intermediate state lies in the dependence of the 1-LO scattering efficiency on the radiative transition rate $\gamma_R(\alpha)$ in Eq. (7). This rate is proportional to the square of the polariton's wave vector, and the latter is known from energy conservation, once the dispersion curve of the polariton has been parametrized.[4]

Martin and Varma have shown that the multiple-LO-phonon "resonance Raman effect" observed for incident photon energies above the band gap in CdS and other II-VI compounds can be explained in terms of absorption into resonant electron-hole pair states followed by photon emission from a series of such states lower in energy than the initial state by an integral multiple of the LO-phonon energy.[5] They call this a multiple-phonon-"cascade" process.

Klein and Colwell have observed a resonant-absorption–hot-luminescence process in CdS for excitation energies below the band gap at finite temperatures.[6] In this case absorption into the resonant intermediate state occurs with the aid of the simultaneous absorption of one or more LO phonons; emission out of the resonant state is accompanied by the emission of one more LO phonons than assisted the absorption. The over-all pro-

cess has the appearance of a one-phonon Raman process, except that the width of the pseudo-one-phonon line is n times greater than the LO-phonon linewidth. Here n is the total number of LO phonons involved. In Ref. 6 a distinction was made between a "true" multiple-phonon resonance Raman process and hot-luminescence process. This is unnecessary, since the arguments given above for the situation of Ref. 1 carry over with only minor changes to the situation of Ref. 6. For instance, when the incident-photon energy in Ref. 6 is less than one LO-phonon energy below resonance, photon absorption occurs mainly with the assistance of one-phonon absorption. Then Eq. (1) of the present paper applies with ω_o replaced by $-\omega_o$ provided that Eq. (2) is modified by the insertion of another matrix element of H'_{e-l} and another energy denominator.

One might ask about the effect on our argument if the phonon lifetime is less than that of the exciton. Should γ in Eq. (1) then be replaced by the decay rate of the phonon? The answer is negative. This can be seen by considering the spectral functions $A_o(q,\omega)$ and $A_\alpha(q,\omega)$ for phonons and α-excitons, respectively. The line representing the α-exciton in Fig. 1 is internal. Thus one must integrate over its spectral function in the expression for the over-all matrix element, which takes the form

$$(f|\,M|\,o)=\int \frac{(f|\,M_{em}|\,a)(a|\,M_{abs}|\,o)}{\bar{\omega}+\omega_o-\omega_i+i0^+} \times A_\alpha(-\vec{q},\bar{\omega})\,d\bar{\omega} \quad . \quad (9)$$

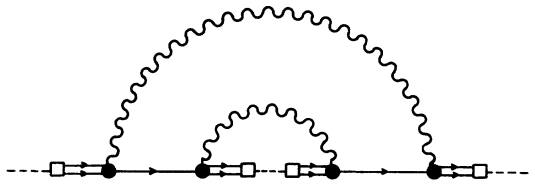

FIG. 2. Diagram representing the proper self-energy for the process of Fig. 1.

This reduces to Eq. (1) when the exciton's spectral function is that of a Lorentzian. On the other hand, the phonon lines are external in Fig. 1. This means that their spectral functions are used only with the full self-energy diagram of Fig. 2. This is equivalent to making the replacement

$$\sum_{q,s}|(f|M|o)|^2 \to \sum_{q,s}\int\int d\omega'\,d\omega''\,|(f|M'|o)|^2 \times A_o(\vec{q},\omega')A_o(-\vec{q}-\vec{s},\omega'') \quad , \quad (10)$$

where $(f|\,M'|o)$ is given by Eqs. (1)–(3) with ω_o in Eq. (1) replaced by ω' and $2\omega_o$ in Eq. (2) replaced by $\omega'+\omega''$. This will affect the spectral shape of the emitted light—indeed, it determines the spectral shape—but if $A_o(q,\omega)$ is strongly peaked about $\omega=\omega_o$, the resulting change in the scattered intensity, as integrated over the final photon energy, will be negligible. Thus the maximum smallness of the energy denominator in Eq. (1) is determined by the width of the exciton state, not by the phonon width.

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