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Cascade Theory of Inelastic Scattering of Light

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Scattering of light from solids with incident frequency above the band gap is shown to occur as a cascade process in which the electron (hole) makes successive transitions between real states with a small probability of radiative recombination at each step. This gives rise to multiple LO-phonon Stokes-shifted lines in agreement with experimental results.

Light-scattering experiments[1-5] in semiconductors using incident frequency near resonance with fundamental electronic transitions show an increase in the cross section over those measured away from resonance. The increase is especially striking for Stokes lines shifted by multiples of the longitudinal-optical (LO) phonon energies. The most dramatic results[2-5] have been obtained when both incident- and scattered-photon energies (ω_i and ω_s) are above the band gap E_g; in such cases it has been possible to observe LO-shifted lines to seemingly arbitrary order. Indeed, Leite, Scott, and Damen[2] have observed ninth order Stokes lines in CdS. Since the electron-phonon coupling constant α is only about 0.7, the origin of such high-order processes is both puzzling and interesting.

We show here that for photons above E_g, inelastic scattering of light occurs via a cascade process in which the electron-hole pair centered by the photon scatters successively to real states separated by the LO-phonon energy ω_0 (neglecting phonon dispersion). From each state there is a small probability of radiative decay at frequencies shifted from the incident frequency by an integral number of LO-phonon energies. The result of such a cascade process is that so long as $\omega_i, \omega_s > E_g$, the relative intensities of the various Stokes-shifted lines are independent of the coupling constant α and depend only on the dispersion curves of the electron and hole bands. This behavior contrasts with Raman scattering for $\omega_i < E_g$ where the intensity of the nth order line varies as α^n.

To elaborate on these remarks, consider the processes that occur when a photon resonant with a line in the continuum of electronic states is incident on the crystal. Real absorption is the dominant process on the time scale of recombination, and an electron-hole pair of momentum $\vec{k}_i \simeq 0$ is created. We classify the processes that can occur with the electron-hole pair thus created as (i) LO-phonon emission; (ii) radiative recombination; (iii) other processes, elastic or inelastic, involving scattering with impurities, acoustic phonons, transverse-optic phonons, etc. For $\alpha \lesssim 1$ it is a good approximation to neglect processes in which more than one LO phonon is emitted simultaneously. The lifetime τ_{LO} for a real transition of the electron (hole) to a state of energy ω_0 below the initial state is $O(10^{-13}$ sec); the lifetime of (ii) and (iii) together is much longer, $O(10^{-9}$ sec) [the lifetime due to (ii) is discussed in more detail below]. We thus conclude that the electron-hole pair successively occupies real states of energy $n\omega_0$ ($n = 1, 2, \cdots$) below the initial state as shown in Fig. 1. Since a negligible number of electrons are lost from the cascade due to (ii) and (iii), the probability per absorbed photon of radiative recombination from the nth step is simply the branching ratio

$$S_n = \tau_R^{-1}(n)/\tau_{LO}^{-1}(n), \qquad (1)$$

where $\tau_R(n)$ is the radiative lifetime at the nth

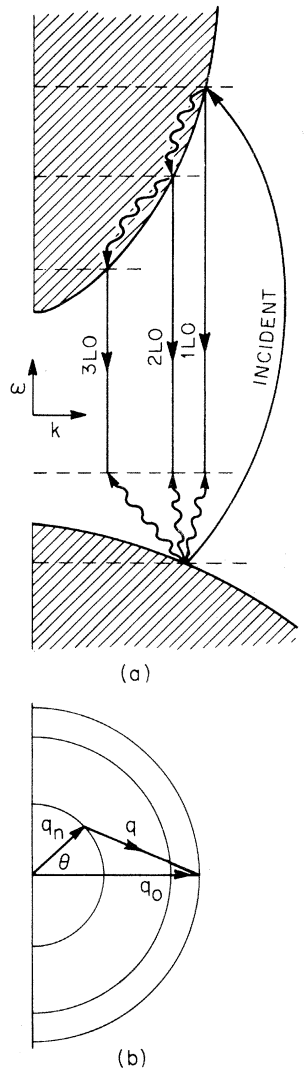

FIG. 1. Schematic illustration of the cascade process of light scattering. (a) Isotropic dispersion curves; the dashed lines are determined by the incident frequency and are separated by the optical-phonon frequency. The vertical lines denote photon emission and the wavy lines phonon emission. For recombination, a virtual transition is required in each order (shown as occurring only in the hole band for simplicity). (b) Shells of momentum whose magnitude is fixed at each step of the cascade by the energies in (a). $\vec{q}_0$ and $\vec{q}_n$ are the vector momenta at the zeroth and nth step, and $\vec{q}$ the phonon momentum required for recombination.

step.

The cascade process must go on until the electron arrives close to the bottom of the conduction band. For energies $\sim kT$ near the band gap, the absorption of phonons is significant, i.e., the electrons and the phonons will come to mutual thermal equilibrium. As a result of process (iii) a continuous electron distribution will be achieved, while process (i) will lead to the occupation centered around discrete levels which is superposed on the continuous background. The above arguments would predict that the light emitted in the continuum close to E_g is $O(\tau_{LO}/\tau_R) \approx 10^6$ times that in a discrete line. Experimentally the luminescence near E_g is found to vary enormously with surface conditions; in the best samples the observed results are consistent[6] with this prediction.

The above description of the time development of the electron depends only on the assumption that LO-phonon scattering is the predominant mode of decay. For a large number of heteropolar crystals, this is supported by a variety of experiments including induced photoconductivity[7] as a function of photon energy which oscillates with period ω_0, LO-phonon–assisted luminescence,[8] and phonon generation due to Landau-level–LO-phonon coupling.[9]

The approximation in the above discussion is the replacement of the actual time development of the electron-hole pair by a characteristic time τ_{LO} to make real transitions to the next state. The real states are eigenstates of momentum and have an energy uncertainty $\Gamma_n \simeq 2\pi\hbar/\tau_{LO}(n)$ due to the lifetime to decay in turn to the next step. The weak interaction with photons is then calculated separately for each step in the cascade. The approximation is justified because for purposes of calculating the recombination spectra, the real states and the virtual states share two important features. The width Γ_n plays the same role as the energy denominator for virtual processes, viz. it fixes the volume in phase space available for recombination. Conservation of momentum requires that, as for virtual states, each real state has a definite spatial correlation with the initial state. This ensures that as in the usual Raman scattering theory[10] the line shape of the scattered light is determined solely by intrinsic phonon dispersion. We note that typically the broadening introduced by (iii) is negligible compared to the intrinsic effects.

Turning to the calculation of τ_R we note that in general, momentum conservation requires at least one virtual intermediate state. [Hence recombination from step n gives rise to photons Stokes shifted by $(n+1)\omega_0$.] Consider the case where the virtual intermediate step occurs in recombination, in either the hole (shown in Fig. 1) or electron bands. For simplicity we consider

only spherical simple bands with $m_h \gg m_e$ so that no real hole transitions are possible. Assuming that each state of momentum $\vec{q}$ at the nth step has a width Γ_n, and treating the transition probability as uniform in this range, we find[11] for $\Gamma_n \ll n\omega_0$.

$$\tau_R^{-1}(n) = \frac{2\pi}{\hbar} \frac{\Gamma_n^2}{\hbar\omega_i - E_g} \rho_n \rho_F \int_0^\pi d\theta f^{(n)}(\theta) \frac{q_n(q_n+q)^2}{q} |M(q)|^2. \quad (2)$$

Here $q = q(\theta)$, and $M(q)$ is the matrix element for creation of a phonon and photon by the Fröhlich interaction $H_L(q) \propto 1/q$ and the photon interaction H_R:

$$M(q) = \frac{H_L(q) H_R}{\hbar\omega_{LO}} \left[\frac{1}{n+1} - \frac{1}{1 - nm_e/m_h} \right], \quad (3)$$

where the two energy denominators arise from virtual electron and hole transitions, respectively, and ρ_n and ρ_F are the densities of states, respectively, for the conduction band at step n and for the final photon states. The angles and wave vectors are defined in Fig. 1(b) and $f^{(n)}(\theta)$ is the *normalized* angular distribution in shell n of an electron that started at $\theta = 0$ initially. Implicit in deriving Eq. (2) is the approximation that each broadened real state has a sharp cutoff at $\pm\Gamma$; other line shapes such as a Lorentzian would merely modify the numerical coefficient in Eq. (2).

In addition to the order of steps considered above, there are others, such as a modification of Fig. 1 in which the virtual state occurs in absorption, which must be added coherently. There is cancelation among the different channels making quantitative calculations very involved. We report below the calculations using (2) alone to illustrate the new ideas presented here.

We have calculated $f^{(n)}(\theta)$ by summing numerically over the weighted probabilities for real transitions for all possible paths to shell n. The resulting relative Raman efficiencies from (1) and (2) for $n = 2, \cdots, 5$ are listed in Table I for comparison with experiment[2] on CdS. We have used $\omega_i - E_g = 6\omega_0$, $m_e = 0.18$, $m_h = 1.2$ (isotropic), and $\alpha_e = 0.7$. Since $\Gamma_n \sim \omega_0$, our approximations are not reliable for the 2LO line. For this reason we have normalized the results to 3LO in Table I. The absolute efficiency integrated over scattering angles is calculated to be $\sim 10^{-6}$ for the 3LO line.

Table I. Calculated and experimental relative intensities (normalized to the third-order line) of the Stokes-shifted lines. The experimental numbers are from Ref. 2.

Order	Relative efficiency	
	Expt	Theory
2	1.6	3.6
3	1	1
4	0.5	0.68
5	0.4	0.46

There are a number of other aspects of the experiment which further corroborate the model presented. The polarization of the scattered photons is the same for all n, which follows from our theory since all steps in the cascade are equivalent. The width of all lines is comparable for the same reason. Further, the narrow lines observed follow from our picture of each step being a resonance (real) scattering. It is to be noted that these features are not present in the usual Raman scattering. We estimate that the 2LO line is broadened by anisotropy and dispersion by ~ 3 cm^{-1}, in good agreement with experiment.[5]

The 1LO and (6 to 9)LO lines have been omitted in our discussion. The 1LO line is "forbidden" by selection rules[12] so that its intensity depends upon photon wavelengths in the crystal, i.e., on the skin depth in the present case, and is not directly comparable with the other lines. The observed sharp lines in the luminescence region are consistent with the cascade scattering theory as discussed earlier. We do not discuss them, since the details of the calculation presented above are limited to the intrinsic bands.

On the basis of the model presented, the following prediction can be made: (1) Since only a small fraction of the electrons decay radiatively, the Stokes lines should be observable to essentially arbitrary order for ω_1 sufficiently above E_g provided there are no strong competing processes. (2) For ω_1 large enough to have real transitions in both the bands there will be well-defined nonmonotonic variations in intensity with order. In particular, very large Raman intensities would result for a case where a near-vertical transition is possible. (3) There is a time delay $\tau_{LO}(n) \sim 10^{-13}$ sec for each successive line. (4) Lifetime processes (iii) should give observable broadening of the lines under appropriate

conditions.

We end on a semantic note. The inelastic scattering of light described here contains aspects of both luminescence and Raman scattering. The scattered light will be delayed in time at successive steps in the cascade because the transitions are real, which is an aspect of luminescence. On the other hand the scattered light is shifted by precise multiples of LO-phonon energies and there is spatial correlation between initial and final states so necessary for sharp lines, which are aspects of Raman scattering.

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Deviation from Matthiessen's Rule in Dilute Nonmagnetic Alloys

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It is shown how the low-temperature deviations from Matthiessen's Rule observed in a wide variety of dilute nonmagnetic alloys are a consequence of phonon drag in the regime where λ, the electron mean free path, is determined by electron-impurity scattering [i.e., $g^2(T/\theta)^3 \ll (k_F\lambda)^{-1}$ where $g^2 \sim v_S/v_F$]. For a spherical Fermi surface $\Delta_T \sim g^2(T/\theta)^3 \times (\lambda k_F)^{-1}\ln(\lambda k_F) + g^4(T/\theta)^5\ln(\rho_0/\rho_T{}^{\text{pure}})$, where $\Delta_T = \rho_T - \rho_0 - \rho_T{}^{\text{pure}}$ with $\rho_T{}^{\text{pure}}$ being the resistivity of the alloy (host) at temperature T. For a cylindrical Fermi surface $\Delta_T \sim g^2(T/\theta)^3\ln(\rho_0/\rho_T{}^{\text{pure}})$. It is also shown that the singular behavior noted by Mills is spurious.

The electrical resistivity of a wide variety of alloys of Al with nonmagnetic impurities has been investigated by Caplin and Rizzuto.[1] They find that there exists a temperature-dependent term in the resistivity, $\Delta_T = \rho_T - \rho_0 - \rho_T{}^{\text{pure}}$ [where $\rho_T{}^{\text{pure}}$ is the resistivity of the alloy (host) at a temperature T], with the following properties: (1) at low T such that $\rho_0 \gg \rho_T - \rho_0$, $\Delta_T = BT^3$; (2) the magnitude B is independent of the impurity species; (3) B is proportional to $\ln(\rho_0/\rho_T{}^{\text{pure}})$; (4) B is related to the coefficient of the linear term (in T) in the high-temperature resistivity. Campbell, Caplin, and Rizzuto[2] have recently suggested that this behavior is very general and represents a "breakdown of momentum conservation in the host metal," and Mills[3] has suggested that the interference between the electron-impurity and electron-phonon interaction provides a concrete mechanism for the justification of such a picture. The specific expression for Δ_T presented by these authors is independent of ρ_0, however, and thus is not in accord with (3) above. Moreover, in order to obtain such a ρ_0-independent result, Mills argued that in the limit $Q_{\max}/k_F \to 0$ (where $Q_{\max}$ is the maximum phonon wave number) the electron-phonon interaction would give rise to a singular behavior of the scattering cross section. We shall show below that such an electron-phonon interaction merely gives rise to an effective temperature-dependent Fermi energy; the resulting Δ_T is linear in ρ_0.

Our main interest, however, is to show that the phonon-drag contribution to the conductivity, in the presence of the electron-impurity scattering and with a cylindrical portion (i.e., $m_1, m_2 \ll m_3$) of the Fermi surface, gives rise to a Δ_T