Theory of Multiple Spin-Flip Raman Scattering in Semiconductors*

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Considering the lowest-order electron-light coupling, we present a theory of multiple spin-flip ($\Delta S = n$; $n = 2, 3, \cdots$) Raman scattering based on the interaction of impurity spin states with virtual bound exciton states. The strength for the $\Delta S = n$ process is strongly magnetic field dependent and becomes comparable to the $\Delta S = 1$ case at low fields. The $\Delta S = n$ peak is at slightly lower energy than the nth overtone energy. These predictions may be checked experimentally.

In this Letter we consider the theory of multiple spin-flip Raman scattering in semiconductors, with particular emphasis on recent results on CdS. Spin-flip scattering in CdS has been studied in detail by Hopfield and Thomas.[1] They observed a very strong peak in CdS corresponding to a transition of an impurity electron from one magnetic state to the other ($\Delta S = 1$), the change in energy being $\pm g\mu H$, where g is the g factor and H is the applied magnetic field. The spin-flip transition is allowed because of the following considerations. In the absence of a magnetic field the spins are taken to be quantized along the c axis. As the field is turned, however, the impurity spins follow the field, whereas the valence-band states remain frozen because of spin-orbit coupling (the spin-orbit splitting in CdS is 70 meV $\gg g\mu H$).

Recently Scott and Damen[2] have observed strongly field-dependent multiple spin-flip scattering from CdS. The latter data show that the $\Delta S = 1$ intensity is field independent as expected,[1] but the multiple spin-flip strength decreases rapidly with increasing magnetic field. Another anomalous feature of the Scott-Damen data is the shift of the $\Delta S = 2$ peak energy slightly below $2g\mu H$.[2]

The above Raman structure near $2g\mu H$ cannot be explained in terms of higher-order electron-light scattering processes: Such processes would be expected to give a very small cross section for the $\Delta S = 2$ transition, provided that the scattering is in the spontaneous regime as in the above CdS studies. Furthermore, such second Stokes processes would give a field-independent intensity for the $\Delta S = 2$ transition, in contrast to the experimental observation.[2]

In Fig. 1 we show the energy-level diagram and schematic illustration of the single spin-flip process studied by Hopfield and Thomas.[1] The incoming light excites an electron- [spin down (↓)] hole pair,[3] which forms an exciton state bound to a neutral donor site.[1] Then the electron [spin up (↑)], at the same site, drops into the hole in the valence band, accompanied by the emission of light whose frequency is shifted by $\Delta\omega = \epsilon_\downarrow - \epsilon_\uparrow = g\mu H$.

In Fig. 2 we present Feynman diagrams for the spin-flip Raman processes. The simplest case [Fig. 2(a)] represents incoming light creating an electron-hole pair which is assumed to be noninteracting; subsequently, the hole state is filled by an electron from the $\epsilon_\uparrow$ state and light is emitted.[4] As mentioned above, the situation in CdS is more complex because the electron-hole pair interact strongly to form an exciton which in turn is bound to the impurity site. These intermediate state interactions are denoted by the

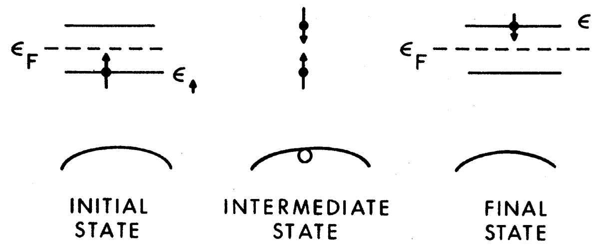

FIG. 1. Schematic illustration of the energy levels involved in the spin-flip transition. ϵ_F is the Fermi energy measured relative to the valence band. Incoming light is absorbed and creates an intermediate electron- (↓) hole pair (exciton) state bound at a neutral impurity site. The spin-up (↑) electron at the same site fills the vacant valence state, leaving only a spin-down (↓) electron, and emits light.

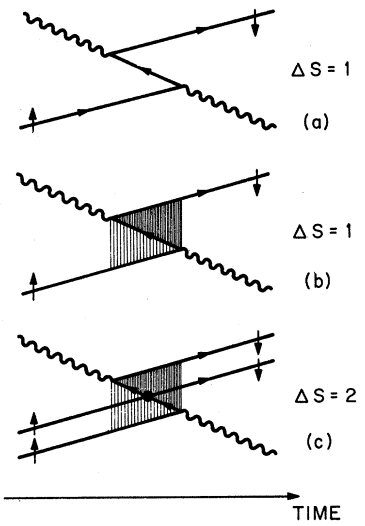

FIG. 2. Feynman diagrams for the spin-flip Raman scattering processes discussed in the text. Wavy lines represent light, solid lines propagating forward (backward) in time denote electron (hole) states, the solid dot denotes the interaction V between the mixed-spin valence hole with an impurity electron (as modified because of the presence of the spin-down electron), and the shaded regions represent electron-hole interactions (see text). (a) Incoming light creates an electron-hole pair; subsequently, the hole state is filled by an electron from the $\epsilon_\uparrow$ state and light is emitted. (b) Scattering process pertinent to CdS where the intermediate state interactions are important. The spin-down electron state is coupled to the hole state, forming an exciton, which in turn is bound at the impurity site of the initial spin-up electron. (c) The double spin-flip process in CdS involves an additional spin-flip at a neighboring site (middle electron line) by an exchange interaction between the spin-down electron of the bound exciton (upper electron line) and the electron at the adjacent impurity site.

shaded regions of Fig. 2(b). Since the valence-band state with spin along the c axis acts as an intermediate state, the transition amplitude depends on the projection of the impurity electron spin states on the c axis. Thus the intensity exhibits an angular dependence of the form $I(\Delta S=1) \propto \sin^2\theta$, where θ is the angle between the field and the c axis.[1]

The physical mechanism we propose for the multiple spin-flip scattering is shown diagrammatically in Fig. 2(c) for the case $\Delta S = 2$. It is apparent that all of the spin-flip processes shown in Fig. 2 are of the same lowest order in the electron-light coupling. The incoming light excites an electron- (↓) hole pair which forms an exciton bound to a neutral impurity site just as in the $\Delta S = 1$ process. In contrast to the single-spin-flip transition, however, the double-spin-flip ($\Delta S = 2$) process involves a spin-flip interaction of the intermediate bound exciton state with an electron at a neighboring impurity site. This interaction between the impurity electron and the electron constituent of the exciton is due to the exchange coupling. In estimating this interaction, however, one should take into account the overlap of the exciton wave function with the nearby impurity site.

Clearly the intermediate exciton state can have a spin-flip interaction with more than one neighboring impurity electron and therefore give rise to even higher-order spin-flip processes such as $\Delta S = 3$. The above mechanism suggests that the multiple spin-flip processes should exhibit the same selection rules as the $\Delta S = 1$ case.

As indicated above, the multi-spin-flip process involves interactions between the bound exciton and an electron at a nearby impurity site. The strength of these interactions cannot be calculated accurately. Therefore we introduce a parameter V to represent this interaction; we discuss an order-of-magnitude estimate of V below.

A very unusual feature of the Scott-Damen[2] results is the shift of the $\Delta S = 2$ peak below twice the $\Delta S = 1$ peak energy by an amount $E_B = 0.1$ cm^{-1}. A possible explanation for this shift is the exchange interaction J between spin states at adjacent impurity sites. We give below an estimate of J taking into account overlap of the impurity wave functions which is of the same order of magnitude as E_B.

Starting with the spin-dependent part of the Hamiltonian $H = -\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - g\mu \vec{H}\cdot\sum_i \vec{S}_i$ in terms of the applied field H along the z direction, one can see that the energy difference corresponding to a one-spin-flip process is

$$\Delta\epsilon_1 = g\mu H + J_T,$$

where

$$J_T = \sum_{i\neq 1} J_{1i}$$

is the total exchange interaction at site 1. On the other hand, in the $\Delta S = 2$ process involving spin flips at two *adjacent* impurity sites (1 and 2) the energy difference should be

$$\Delta\epsilon_2 = 2g\mu H + \sum_{i\neq 1,2} (J_{1i} + J_{2i}) = 2\Delta\epsilon_1 - 2J_{12}. \qquad (1)$$

The above description of the spin-flip processes implies an associated line broadening due to the random distribution of both J_T and J_{12}. Note, however, that the $\Delta S = 1$ process should give rise to a narrow line in the Raman spectrum because of the averaging over all neighboring impurity sites. On the other hand the $\Delta S = 2$ peak should have a larger width since the process involves only adjacent impurities. To a first approximation we expect the latter width to be of the order of the observed shift E_B. It is interesting to note that the closest allowed (see below) impurities would dominate the double spin-flip process and therefore the sites with the largest J_{12} would be favored. Consequently the line should be asymmetric and weighted towards the largest energy shift ($\sim E_B$). The observed line shapes[2] are consistent with the above considerations. A quantitative calculation of the line shape requires a careful study of the probability distribution of the impurity sites, which would yield a distribution of J values. Further experimental line-shape studies are needed in order to check the detailed predictions of the above mechanism. Similar considerations apply for the higher multiple spin-flip processes.

The Raman scattering cross section for the $\Delta S = 1$ process is given by the well-known expression[1,4]

$$(d\sigma/d\Omega)_{\Delta S=1} \propto (\omega_1 - \omega_0)^{-2}, \quad \Delta\omega = \Delta\epsilon_1, \tag{2a}$$

where ω_1 is the incoming light frequency, ω_0 denotes the energy of the intermediate bound exciton state (see Fig. 1), and $\Delta\omega$ is the frequency shift of the scattered light. The $\Delta S = 2$ process involves an additional intermediate state in which the spin of an adjacent impurity site is flipped. The Raman cross section for the latter case can be obtained by standard perturbation theory[5] and is of the form

$$\left(\frac{d\sigma}{d\Omega}\right)_{\Delta S=2} \propto \frac{1}{(\omega_1 - \omega_0)^2}\,\frac{V^2}{(\omega_1 - \omega_0 - g\mu H)^2}, \qquad \Delta\omega = 2\Delta\epsilon_1 - 2J_{12}, \tag{2b}$$

where we have omitted the small energy shift of the intermediate state due to the exchange coupling. This shift is much smaller than $g\mu H$. Similar expressions can be obtained for the higher-order spin-flip processes by a straightforward extension of the above discussion.

Our results [Eq. (2b)] show a strong field dependence for the multiple spin-flip cross section provided that the incident light is nearly resonant with ω_0, i.e., the intensity of the $\Delta S = 2$ peak varies as $(\omega_1 - \omega_0 - g\mu H)^{-2}$. Such a dependence is consistent with the available data[2] and suggests $\omega_0 - \omega_1 \sim 10$ cm^{-1} in CdS. Experimental studies of the field dependence of the $\Delta S = 2$ processes may provide accurate determinations of the intermediate state energies. It should be noted that the above estimate is consistent with the estimate given in Ref. 1.

To estimate the exchange parameters J and V we consider a typical impurity concentration $n \sim 10^{17}$ cm^{-3} which gives an average impurity separation $R_0 \simeq 120$ Å. Following Toyozawa[6] we obtain $J_{12} \cong 1.3U[(1+\alpha R_0)e^{-\alpha R_0}]^2$, where U is the intra-atomic Coulomb repulsion and α^{-1} is the hydrogenic radius of the impurity wave function. Using an effective mass $m_e = 0.2m$ and dielectric constant $K = 8$ for CdS,[7] we estimate $\alpha^{-1} = 20$ Å, $U \cong 500$ cm^{-1}, and therefore $J_{12} \cong 0.2$ cm^{-1} which is of the required order of magnitude ($E_B \simeq 0.1$ cm^{-1}).

A proper estimate of V requires detailed knowledge of the bound exciton wave function. Although it is generally accepted that the exciton moves as a unit weakly bound to the neutral donor,[1,8] detailed information for the wave function is not presently available. Utilizing the above physical picture of the bound exciton we expect V to depend on the overlap of the bound exciton wave function with the adjacent impurity site. Thus, we obtain $V = 1.3U[(1+\alpha R)e^{-\alpha R}]^2\gamma$, where $R = R_0 - R_{\text{exc}}$; $\gamma \sim 0.04$ takes into account the normalization of the excitonic wave function relative to the impurity wave-function normalization; here R_{exc} is the radius of the orbit traced by the exciton around the donor impurity to which it is bound. Furthermore in the formula for V we have considered the decay of the excitonic wave function to be the same as that of the impurity in accord with the estimates in Ref. 8. Taking $R_{\text{exc}} \simeq 40$ Å,[9] we obtain $V \simeq 0.2$ cm^{-1}, corresponding to a typical impurity separation $R_0 = 120$ Å. In view of the uncertainty in our knowledge of the exciton wave function, the above value for V is at best an order-of-magnitude estimate. Nevertheless the above value is consistent with experiment.

Since the impurities are randomly distributed, a non-negligible number of pairs will have a separation $R < 120$ Å. Clearly these pairs would exhibit a stronger exchange interaction than the above case and therefore would give rise to a larger shift of the $\Delta S = 2$ peak ($E_B > 0.2$ cm^{-1}) as well as substantial broadening of the $\Delta S = 1$ and $\Delta S = 2$ peaks, in contrast to the experimental observations. This discrepancy would be removed if impurities whose separation is smaller than a critical value cannot contribute to the Raman spectrum. A possible explanation for this feature is that an exciton interacting equally strongly with more than one impurity cannot be bound and serve as necessary intermediate state. Using the same parameters as above, i.e., $R_{\rm exc} = 40$ Å and $\alpha^{-1} = 20$ Å, the critical separation would be $R_c \sim 120$ Å; although this estimate is crude, a more accurate determination requires the study of the complex interaction of three neutral entities.

In conclusion we propose further Raman studies of spin-flip transitions at lower magnetic fields to check the detailed field dependence of the multi-spin-flip peaks. It is evident from the discussion following Eq. (1) that the higher-order peaks $\Delta S = 3, 4, \cdots$ may become observable at sufficiently low fields, and exhibit a strong field dependence. Note, however, that our predictions require low temperatures such that $k_B T < g\mu H$. Since the parameters in our theory are very sensitive to the form of the wave functions, the multiple spin-flip experiments may provide a check on future calculations on excitons bound to neutral impurities.

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[1] J. J. Hopfield and D. G. Thomas, *Light Scattering Spectra of Solids* edited by G. Wright (Springer, Berlin, 1969), p. 255, and Phys. Rev. 175, 1021 (1968).

[2] J. F. Scott and T. C. Damen, preceding Letter [Phys. Rev. Lett. 29, 107 (1972)].

[3] For convenience we consider the field direction as the axis of spin quantization.

[4] This is the basic Compton scattering process. See, for example, W. Heitler, *Quantum Theory of Radiation* (Clarendon Press, Oxford, 1936), p. 132; J. J. Sakurai, *Advanced Quantum Mechanics* (Addison-Wesley, Reading, Mass., 1967), p. 215.

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[7] R. M. Martin, in *Proceedings of the Second International Conference on Light Scattering in Solids*, edited by M. Balkanski (Flammarion, Paris, 1972), p. 25.

[8] E. I. Rashba and G. E. Gurgenishvili, Fiz. Tverd. Tela 4, 1029 (1962) [Sov. Phys. Solid State 4, 759 (1962)].

[9] A crude estimate, using the analogy with the neutral hydrogen molecule and taking into account the dielectric constant and electronic effective mass appropriate to CdS, gives $R_{\rm exc} \gtrsim 35$ Å.

Gor'kov-Eliashberg Effect in One-Dimensional Metals?

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We point out the possibility that the potentially important dielectric effect first considered by Gor'kov and Eliashberg for minute metallic particles may well occur in the recently identified one-dimensional metals formed by the mixed-valency planar complex compounds of Pt. Our idea is conditional on the validity of a recently proposed model of interrupted metallic strands.

Following the original work of Kubo[1] on the electronic properties of small metallic particles, Gor'kov and Eliashberg[2] (GE) made in 1965 the most remarkable theoretical prediction that the electronic polarizability of a metallic particle —sufficiently minute that its electronic energy levels are discrete—should be enormously enhanced with respect to the classical polarizability which one would have expected on the basis of elementary electrostatics. The effect should have been observable in electric fields and at absolute temperatures such that the discrete electronic energy levels of the minute particle remain unmixed, i.e., under the physical conditions for which the minute-metallic-particle system could be regarded as a dielectric insulator. Besides the considerable intrinsic physical interest of the effect, such an anomalous enhancement of the electronic polarizability of a minute metallic particle would have important technological application, a fact fully realized by GE.[2] Unfortunately, however, several recent experi-