THEORY OF MAGNETICALLY ASSISTED INDIRECT TRANSITIONS IN MAGNETIC SEMICONDUCTORS*

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The optical absorption coefficient for ferromagnetic semiconductors has been calculated for an indirect transition in which spin-fluctuation scattering takes the place of the usual phonon scattering. The resulting absorption coefficient is found to be proportional to $\langle|S_{\vec{Q}z}|^2\rangle$, where $\vec{Q}$ is the wave-vector difference between the valence-band maximum and the conduction-band minimum. The fact that this decreases with decreasing temperature below the Curie point can lead to an apparent blue shift of the absorption edge similar to what is observed in $CdCr_2S_4$.

In materials whose valence-band maximum does not occur at the same wave vector as the conduction-band minimum the optical absorption edge may correspond to an indirect transition in which the momentum difference is taken up by the lattice through phonon emission or absorption.[1] In magnetic semiconductors the local moments provide another degree of freedom which can assist in producing indirect transitions. The purpose of this paper is to investigate the nature of the optical absorption edge associated with indirect transitions involving such local moments.

Let us describe the electron system by a valence band of energy $\epsilon_{1,\vec{k},\sigma}$ and a conduction band of energy $\epsilon_{2,\vec{k},\sigma}$. The ferromagnetic system is characterized by ionic moments $g\mu_B\vec{S}_n$ localized at lattice sites $\vec{R}_n$. When an electron-hole pair is produced by optical absorption, both particles will interact with the local moments through the screened intra-atomic Coulomb interaction which may be expressed as an exchange interaction. For the sake of simplicity let us assume that the interaction between the holes and the local moments is small and can be neglected. The remaining electron–local-moment coupling then has the form

$$\mathcal{H}_2 = -\sum_{\vec{k},\vec{q}} J_{\vec{k},\vec{k}+\vec{q}}\left[S_{\vec{q}z}(c_{2,\vec{k},\uparrow}{}^{\dagger}c_{2,\vec{k}+\vec{q},\uparrow} - c_{2,\vec{k},\downarrow}{}^{\dagger}c_{2,\vec{k}+\vec{q},\downarrow}) + S_{\vec{q}+}c_{2,\vec{k},\downarrow}{}^{\dagger}c_{2,\vec{k}+\vec{q},\uparrow} + S_{\vec{q}-}c_{2,\vec{k}\uparrow}{}^{\dagger}c_{2,\vec{k}+\vec{q},\downarrow}\right], \tag{1}$$

where $c_{n,\vec{k},\sigma}{}^{\dagger}$ is the creation operator for an electron in band n with wave vector $\vec{k}$ and spin projection σ. The interaction of the electrons with the radiation field has the form

$$\mathcal{H}_1(t) = -\sum_i \frac{e}{mc}\vec{A}(\vec{r}_i,t)\cdot\vec{p}_i = -\frac{e}{mc\sqrt{V}}\sum_{\lambda}\sum_{\vec{k},\sigma}\{e^{i(\Delta E/\hbar-\omega)t}[\hat{\epsilon}_\lambda\cdot\vec{p}_{21}(\vec{k})]a_\lambda + e^{-i(\Delta E/\hbar-\omega)t}[\hat{\epsilon}_\lambda\cdot p_{21}(\vec{k})]a_\lambda{}^{\dagger}\}$$
$$\times c_{2,\vec{k},\sigma}{}^{\dagger}c_{1,\vec{k},\sigma}, \tag{2}$$

where $\alpha_\lambda{}^{\dagger}$ is the creation operator for a photon with polarization $\hat{\epsilon}_\lambda$, and $\vec{p}_{21}(\vec{k})$ is the interband momentum matrix element involving Bloch states having the same wave vectors.

There are various ways in which the indirect process may occur. Below the Curie point the $\vec{q}=0$ contribution from the first terms in $\mathcal{H}_2$ produces a spin splitting of the bands. In keeping with our earlier assumption concerning the magnitude of the conduction-band exchange interaction we shall assume that the splitting of the conduction band is larger than that of the valence band. Then, since the interband transition arising from $\mathcal{H}_1$ conserves the spin projection, the first parts of the indirect process are the interband transitions labeled 1 and 1′ in Fig. 1. These are then followed by the intraband transitions labeled 2 and 2′. Notice that the "primed" intraband processes involve spin-flip scattering while the "unprimed" processes do not.

The probability that a photon of energy $\hbar\omega$ is absorbed in such an indirect transition is

$$P = \frac{2\pi}{\hbar}\sum_{\vec{k},\sigma}\sum_{\vec{q},\sigma'}\left|\frac{\langle f|\mathcal{H}_2|i\rangle\langle i|\mathcal{H}_1|o\rangle}{(E_i-E_o)}\right|^2\delta(E_o-E_f), \tag{3}$$

where o refers to the original state, i to an intermediate state, and f to a final state. Here $\mathcal{H}_1$ is the coefficient of the time-dependent exponential in $\mathcal{H}_1(t)$.

Let us first consider the region below the Curie point. The main contribution to the absorption edge

will be the "unprimed" process in Fig. 1, for which

$$\langle i|\mathcal{H}_1|o\rangle = -(e/mc\sqrt{V})\sum_\lambda[\hat{\epsilon}_\lambda\cdot\vec{p}_{21}(\vec{k})]N_\lambda^{1/2}, \tag{4}$$

where N_λ is the number of photons of polarization $\hat{\epsilon}_\lambda$. The complementary matrix element of $\mathcal{H}_2$ is

$$\langle f|\mathcal{H}_2|i\rangle = -J_{\vec{k},\vec{k}+\vec{q}}\langle f|S_{\vec{q}z}|i\rangle. \tag{5}$$

This corresponds to elastic scattering from spatial fluctuations in the local-moment system, which is to be distinguished from spin-flip scattering which would involve magnons. Since the intermediate-state energy in Eq. (3) does not depend upon the local moment configuration, the sum over the intermediate states of the local moments may be removed by closure, leaving us with the thermal average of the square of $S_{\vec{q}z}$. Thus, the absorption coefficient is

$$\alpha = \frac{8\pi e^2}{m^2c^2\hbar V}\sum_{\vec{k}}\sum_{\vec{q}}\frac{J_{\vec{k},\vec{k}+\vec{q}}^2 p_{21}(\vec{k}_\perp)^2\langle|S_{\vec{q}z}|^2\rangle}{(\epsilon_{2,\vec{k},\uparrow}-\epsilon_{1,\vec{k},\uparrow}-\hbar\omega)^2}\,\delta(\epsilon_{1,\vec{k},\uparrow}+\hbar\omega-\epsilon_{2,\vec{k}+\vec{q},\uparrow}). \tag{6}$$

Notice that this absorption coefficient includes intermediate transitions to all the conduction-band states. In practice, however, one usually assumes that the intermediate states are those in the vicinity of that wave vector $\vec{k}_0$ at which the valence-band maximum occurs. Similarly, the final states are assumed to lie in the vicinity of the conduction-band minimum which, we shall assume, occurs at a wave vector $\vec{k}_0+\vec{Q}$. This enables us to approximate the absorption coefficient by

$$\alpha = \alpha_0[J_{\vec{k}_0,\vec{k}_0+\vec{Q}}^2 p_{21}(\vec{k}_{0\perp})^2\langle|S_{\vec{Q}z}|^2\rangle(\hbar\omega-E_g)^3]/(\Delta E-\hbar\omega)^2, \tag{7}$$

where $\Delta E = \epsilon_{2,\vec{k}_0,\uparrow}-\epsilon_{1,\vec{k}_0,\uparrow}$ and α_0 contains various numerical factors involving, among other things, the valence- and conduction-band masses.

There are two important features of this result. The first is its functional dependence on the photon energy. Since $\Delta E \gg \hbar\omega$ this dependence arises primarily from the density-of-states factor $(\hbar\omega-E_g)^3$. The second feature is its temperature dependence. If we neglect, for the moment, any temperature dependence of E_g, the remaining dependence resides in the correlation function $\langle|S_{\vec{Q}z}|^2\rangle$. At very low temperatures where spin-wave theory is applicable $S_{\vec{Q}z}$ may be expressed in terms of magnon operators as $S_{\vec{Q}z}=\sum_{\vec{k}}a_{\vec{k}+\vec{Q}}^\dagger \times a_{\vec{k}}$. This leads to the result that $\langle|S_{\vec{Q}z}|^2\rangle$ vanishes as $T^{3/2}$, reflecting the "freezing out" of the fluctuations. Closer to the Curie point this temperature dependence is much stronger. Figure 2 shows the resulting absorption coefficient for the conservative case in which the correlation function decreases as $T^{3/2}$ below the Curie point.

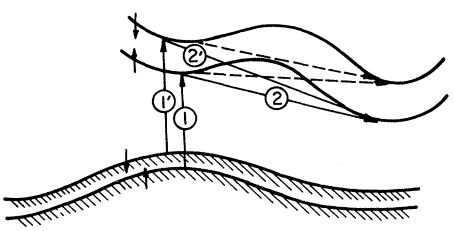

FIG. 1. Schematic diagram of local-moment fluctuation and magnon-assisted indirect transitions.

Notice that if for some reason, such as a large background absorption, the edge can only be measured at a high absorption level, the edge may appear to shift towards the blue with decreasing temperature. In fact, as Fig. 2 shows, this apparent shift can be quite large, of the order of the gap itself.

Of course, phonon-assisted indirect transitions will compete with these magnetically induced

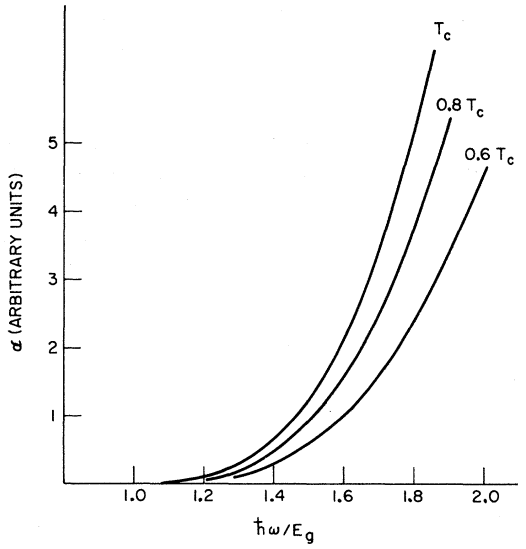

FIG. 2. Form of the absorption edge in a magnetic semiconductor due to indirect transitions arising from local-moment-fluctuation scattering.

transitions. If the electron-phonon interaction is small in comparison with the exchange interaction of Eq. (1) we might expect the magnetic mechanism to dominate in the vicinity of the Curie point. However, since this mechanism "freezes out" at lower temperatures, the phonon mechanism will take over in this region with the result that the absorption coefficient will be less temperature dependent.

Figure 2 does not tell the complete story, however, for the gap itself is also temperature dependent. This temperature dependence may arise from lattice dilatation and vibration as well as from the exchange splitting of the spin degeneracy. For the situation shown in Fig. 1 the exchange splitting will lead to a red shift of the edge with decreasing temperature. In fact, if the optical absorption is due to a direct transition, this exchange splitting will provide the dominant temperature dependence. This leads to a red shift as is observed in most magnetic semiconductors,[2,3] e.g., $CdCr_2Se_4$. For an indirect transition, however, the temperature dependence of the absorption coefficient may dominate giving a net apparent blue shift. The only known semiconductor with a blue shift below the Curie point is[3] $CdCr_2S_4$. This would seem to indicate that indirect transitions are the exception, not the rule. The reason for this is the fact that the valence band in most magnetic semiconductors is believed[4] to be very narrow. Thus, there is no well-defined maximum from which transitions are most likely to originate, but they can occur from any point in the zone. If the absorption edge in $CdCr_2S_4$ is, in fact, due to an indirect transition, it would be of interest to identify the direct transition at some higher photon energy and determine whether it does exhibit a red shift.

Above the Curie point the degeneracy of the spin states means that all the processes shown in Fig. 1 will contribute. The resulting absorption coefficient is then proportional to $\langle \vec{S}_{\vec{Q}} \cdot \vec{S}_{-\vec{Q}} \rangle$. It can be shown[5] from the fluctuation-dissipation theorem that this is proportional to $T\chi(\vec{Q})$, where $\chi(\vec{Q})$ is the generalized susceptibility. In the random-phase approximation this is given by

$$\chi(\vec{Q}) = \frac{C/T_C}{(T-T_C)/T_C + 1 - J(\vec{Q})/J(0)}, \tag{8}$$

where $T_C = J(0)CV/g^2\mu_B{}^2$, C being the Curie constant and $J(\vec{q})$ the $\vec{q}$th Fourier component of the local-moment exchange coefficient. If the wave vector $\vec{Q}$ does not lie near the center of the Brillouin zone, then $J(\vec{Q}) \ll J(0)$ and $\chi(\vec{Q})$ varies as T^{-1}, which means that $\langle \vec{S}_{\vec{Q}} \cdot \vec{S}_{-\vec{Q}} \rangle$ will be independent of temperature. Therefore, the only remaining temperature dependence in the absorption coefficient is that associated with the energy gap itself arising from lattice dilatation and vibration. This generally leads to a decreasing gap with increasing temperature.

In summary, we have shown that the absorption coefficient associated with a magnetically induced indirect transition increases with increasing temperature up to the Curie point, giving rise to an apparent narrowing of the gap. Above the Curie point the temperature dependence is that associated with the energy gap itself.

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[1]For a review of phonon-assisted indirect transitions see, for example, H. Y. Fan, Rept. Progr. Phys. 19, 107 (1956).

[2]G. Busch, P. Junod, and P. Wachter, Phys. Letters 12, 11 (1964).

[3]G. Harbeke and H. Pinch, Phys. Rev. Letters 17, 1090 (1966).

[4]See, for example, S. J. Cho, Phys. Rev. 157, 632 (1967).

[5]R. M. White, "Quantum Theory of Magnetism" (McGraw-Hill Book Company, New York, to be published).