discrepancy to something in the neighborhood of the experimental error. The peaks numbered 3 on the three compounds are considered as a possible E_1 transition ($\Lambda_3 \rightarrow \Lambda_1$ or $L_{3'} \rightarrow L_1$ in the usual zincblende notation). They appear as leading peaks in the reflectivity spectra as it happens in group IV and group II-VI compounds. The similarity of the reflectance spectra of the diamond and zincblende structures has been extensively discussed in the literature. We are taking the suggestions of Lee[6] and Della Ricia[22] that the dominant features of the reflectance spectra should be determined by the shape of the Brillouin zone; this makes a comparison between the diamond and zincblende compounds and the present compounds a reasonable first step in interpreting these spectra.

Peaks numbered 4 are tentatively assigned to $E_1+\Delta_1$ transitions, i.e., the spin-orbit split component of the E_1 peak. This splitting Δ_1 corresponds to 0.13 eV for Mg_2Ge and thus agrees well with $\frac{2}{3}$ of Δ_0. The splitting Δ_1 equals 0.28 eV for Mg_2Sn, in agreement with the value predicted by the $\frac{2}{3}$ rule from the $\Delta_0=0.48$-eV splitting mentioned above.[21] Otherwise, this peak on the three compounds corresponds to peaks in ϵ_2 that agree with the character M_1 of Lee's[2] calculation.

With more uncertainty, we have attributed the structure numbered 9 to an E_1' transition because it appears in the same relative position in the reflectance spectrum as in the diamond and zincblende compounds. Peak 10, observed only in Mg_2Sn, could be the spin-orbit splitting 9, since it gives about the same value of 0.29 eV for Δ_1 as peaks 3 and 4. It appears as an M_2 transition in Lee's calculation and as a peak in ϵ_2 in Scouler's[16] results.

We shall refrain at this point from any more tentative assignments of the remaining structure shown in Figs. 2–4. This structure should easily be interpretable as soon as the next generation of band-structure calculations becomes available.

Note added in proof. A recent pseudopotential band-structure calculation by M. Y. Au-Yang and M. L. Cohen to be published in this journal supports the above assignments and further interprets the spectra. Unpublished OPW calculations by F. Herman also support our general conclusions.

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[22] J. Della Ricia, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 51.

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Magnon Corrections to the Effective Mass of an Electron in a Magnetic Semiconductor*

ROBERT M. WHITE AND ROY B. WOOLSEY†
Department of Physics, Stanford University, Stanford, California 94305
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We have computed the renormalization of the conduction-electron energy in a degenerate ferromagnetic semiconductor at zero temperature due to the virtual emission and reabsorption of spin waves. We find that as a result of the difference between the up- and down-spin Fermi momenta, this renormalization is quite small. However, in the case where the conduction electrons are antiferromagnetically coupled to the ionic moments, it is possible by doping to achieve a situation in which the effective mass of the down-spin electrons is increased by about 30%, while the up-spin electrons remain unaffected.

I. INTRODUCTION

MAGNETIC semiconductors have received a great deal of attention recently.[1] One reason for this is the possibility of extending the technological applications of semiconductors. Another reason is the hope that by doping these materials, one might gain some insight into the nature of band magnetism.

In the presence of such doping, one might ask how the conduction electrons affect the magnetic properties, or, alternatively, how the magnetic order affects the transport properties. The first type of question involves, for example, the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[2] The second type of question has

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† National Science Foundation Predoctoral Fellow.
[1] Symposium on Magnetic Semiconductors (invited talks), Bull. Am. Phys. Soc. **13**, 368 (1968).

[2] See, e.g., F. Holtzberg, T. McGuire, S. Methfessel, and J. Suits, Phys. Rev. Letters **13**, 18 (1964).

been largely directed toward understanding the conductivity of such materials.[3] To this end, various calculations have been made of the conduction-electron relaxation rate.[4] In this paper we investigate the complementary question of the electron effective mass. In particular, we consider how magnons—interacting with the electrons through a contact exchange interaction—renormalize the electron energy. Our results show that, in general, magnon corrections to the effective mass are small. However, under certain conditions, which will be discussed, these corrections can become important.

II. HAMILTONIAN

Let us begin by considering a magnetic semiconductor which has been doped or alloyed to produce enough conduction electrons to provide a well-defined, yet small, Fermi sphere. We shall assume that the ionic moments experience a ferromagnetic exchange interaction only with their z nearest neighbors. The ionic Hamiltonian is then

$$\mathcal{H}_{\text{ionic}}=-g\mu_B H\sum_i S_i^z-\hbar J\sum_{i,\delta}\mathbf{S}_i\cdot(\mathbf{S}_{i+\delta})\,, \tag{1}$$

where g is the ionic g value, μ_B the Bohr magneton, and J the exchange constant. If we are well below the Curie temperature, we may express $\mathcal{H}_{\text{ionic}}$ in terms of magnon creation and annihilation operators $a_{\mathbf{q}}^\dagger$ and $a_{\mathbf{q}}$, in the usual[5] way. Thus,

$$\mathcal{H}_{\text{ionic}}=E_0+\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}a_{\mathbf{q}}^\dagger a_{\mathbf{q}}\,, \tag{2}$$

where

$$\hbar\omega_{\mathbf{q}}=g\mu_B H+2z\hbar JS(1-\gamma_{\mathbf{q}})$$

and

$$\gamma_{\mathbf{q}}=\frac{1}{z}\sum e^{i\mathbf{q}\cdot\boldsymbol{\delta}}\,.$$

If the magnetic field is not too strong, we may describe the conduction electrons by plane-wave states. The second-quantized electron Hamiltonian is then

$$\mathcal{H}_{\text{elec}}=\sum_{\mathbf{k},\sigma}\epsilon_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}\,, \tag{3}$$

where

$$\epsilon_{\mathbf{k}\sigma}=\hbar^2k^2/2m-\mu_B H\sigma\,.$$

Here $\sigma=+1$ for "up" moments and -1 for "down" moments. Throughout this paper we shall occasionally refer to these spin moments merely as "spins" which are not to be confused with the spin angular momenta which point in the opposite direction. Also, notice that we are taking the g value of the conduction electrons to be 2.

As the conduction electrons move about in the lattice, they will interact with the ionic electrons. If the conduction-electron wave function does not vary very much over an ionic dimension, the exchange part of this interaction may be represented by a spin-dependent contact potential. Thus,

$$\mathcal{H}_{\text{int}}=-\hbar IV\sum_{i,j}\mathbf{S}_i\cdot\mathbf{s}_j\delta(\mathbf{R}_i-\mathbf{r}_j)\,, \tag{4}$$

where the sum over i refers to the ions, and that over j to the conduction electrons. The crystal volume V has been included to compensate for the dimensions of the δ function. An interaction of this form has also been used by Rys, Helman, and Baltensperger[6] to investigate the temperature dependence of the band edge in magnetic semiconductors. Second-quantizing the electron part of this Hamiltonian, and expressing the ionic moments in terms of magnon operators gives

$$\begin{aligned}\mathcal{H}_{\text{int}}=&-\hbar INS\sum_{\mathbf{k},\sigma}\sigma c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}\\&+\hbar I\sum_{\mathbf{k},\sigma}\sum_{\mathbf{q},\mathbf{q}'}\sigma a_{\mathbf{q}}^\dagger a_{\mathbf{q}'}c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}+\mathbf{q}-\mathbf{q}',\sigma}\\&-\sqrt{(\tfrac{1}{2}NS)}\hbar I\sum_{\mathbf{k}}\sum_{\mathbf{q}}(c^\dagger_{\mathbf{k}+\mathbf{q},\downarrow}c_{\mathbf{k}\uparrow}a_{\mathbf{q}}+a_{\mathbf{q}}^\dagger c^\dagger_{\mathbf{k}-\mathbf{q},\uparrow}c_{\mathbf{k}\downarrow})\,.\end{aligned} \tag{5}$$

The first term corresponds to the polarization of the conduction electrons by the ionic magnetization. Applying the random-phase approximation to the second term amounts to taking $\mathbf{q}'=\mathbf{q}$ and replacing $a_{\mathbf{q}}^\dagger a_{\mathbf{q}}c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}$ by the symmetrical product $(\langle n_{\mathbf{q}}\rangle c_{\mathbf{k}\sigma}^\dagger c_{\mathbf{k}\sigma}+\langle n_{\mathbf{k}\sigma}\rangle a_{\mathbf{q}}^\dagger a_{\mathbf{q}})$. This leads to a shift in the magnon spectrum that is proportional to $(\langle n_\uparrow\rangle-\langle n_\downarrow\rangle)$, which is just the polarization of the conduction electrons. We shall add these contributions to $\hbar\omega_{\mathbf{q}}$ and $\epsilon_{\mathbf{k}\sigma}$, thereby defining the new energies $\hbar\tilde{\omega}_{\mathbf{q}}$ and $\tilde{\epsilon}_{\mathbf{k}\sigma}$:

$$\hbar\tilde{\omega}_{\mathbf{q}}=\hbar\omega_{\mathbf{q}}+\hbar I(\langle n_\uparrow\rangle-\langle n_\downarrow\rangle)\,,$$

$$\tilde{\epsilon}_{\mathbf{k}\sigma}=\epsilon_{\mathbf{k}\sigma}-\hbar NI\left(S-\frac{1}{N}\sum_{\mathbf{q}}\langle n_{\mathbf{q}}\rangle\right)\sigma\,.$$

At very low temperatures $(1/N)\sum\langle n_{\mathbf{q}}\rangle$ is very small and may be neglected.

The third term constitutes the electron-magnon interaction. In many magnetic semiconductors the band edge is observed[7] to shift by about 0.1 eV in going from the Curie temperature down to very low temperatures. It is thought[6] that this might be due to the interaction (4). If this is, in fact, the case, then this exchange interaction is very strong—about ten times stronger than the ion-ion exchange. This is reasonable, since it is essentially a screened intra-atomic exchange interaction. However, if the number of conduction electrons is small, this may not seriously affect our assumption that the ionic moments are ferromagnetically ordered. Equations

[3] See, e.g., H. W. Lehmann, Phys. Rev. **163**, 488 (1967).

[4] See, e.g., A. Yanase and T. Kasuya, J. Appl. Phys. **39**, 430 (1968).

[5] F. Keffer, in *Handbuch der Physik*, edited by H. Geiger and K. Scheel (Julius Springer, Berlin, 1966), Vol. 18, Part, 2, p. 1ff.

[6] F. Rys, J. Helman, and W. Baltensperger, Physik Kondensierten Materie **6**, 105 (1967).

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

(2), (3) and (5) constitute a coupled fermion-boson problem completely analogous to the electron-phonon problem. In Sec. III we shall use perturbation theory to compute the corrections to the electron energies produced by the 1-magnon terms in Eq. (5).

III. EFFECTIVE MASS

The total Hamiltonian for our coupled system is

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_1\,, \tag{6}$$

where

$$\mathcal{H}_0=\sum_{\mathbf{k},\sigma}\tilde{\epsilon}_{\mathbf{k}\sigma}c_{\mathbf{k}\sigma}{}^\dagger c_{\mathbf{k}\sigma}+\sum_{\mathbf{q}}\hbar\tilde{\omega}_{\mathbf{q}}a_{\mathbf{q}}{}^\dagger a_{\mathbf{q}} \tag{7}$$

and

$$\mathcal{H}_1=-\sqrt{(\tfrac{1}{2}NS)}\hbar I\sum_{\mathbf{k}}\sum_{\mathbf{q}}(c^\dagger{}_{\mathbf{k}+\mathbf{q},\downarrow}c_{\mathbf{k}\uparrow}a_{\mathbf{q}}+a_{\mathbf{q}}{}^\dagger c^\dagger{}_{\mathbf{k}-\mathbf{q},\uparrow}c_{\mathbf{k}\downarrow})\,. \tag{8}$$

The perturbation $\mathcal{H}_1$ leads to an effective electron-electron interaction. The usual procedure for obtaining this effective interaction is to apply a canonical transformation to $\mathcal{H}$ which removes the off-diagonal magnon terms to lowest order. The result is

$$\mathcal{H}'=\mathcal{H}_0-\tfrac{1}{4}NS\hbar^2I^2\sum_{\mathbf{k},\mathbf{k}'}\sum_{\mathbf{q}}[(\tilde{\epsilon}_{\mathbf{k}\downarrow}-\tilde{\epsilon}_{\mathbf{k}-\mathbf{q},\uparrow}-\hbar\tilde{\omega}_{\mathbf{q}})^{-1}$$
$$-(\tilde{\epsilon}_{\mathbf{k}'\uparrow}-\tilde{\epsilon}_{\mathbf{k}'+\mathbf{q},\downarrow}+\hbar\tilde{\omega}_{\mathbf{q}})^{-1}]c^\dagger{}_{\mathbf{k}'+\mathbf{q},\downarrow}c_{\mathbf{k}'\uparrow}c^\dagger{}_{\mathbf{k}-\mathbf{q},\uparrow}c_{\mathbf{k}\downarrow}\,. \tag{9}$$

This effective electron-electron interaction is represented graphically in Fig. 1(a).

In the phonon case the $\mathbf{k}'$ dependence of the interaction coefficient may be removed by certain wave-vector translations. This results in a form which clearly shows that the interaction is attractive between electrons whose energies lie within a Debye energy of the Fermi surface and whose momenta are equal and opposite. This, of course, may lead to a superconducting ground state.

In the magnon case this transformation is not possible because of the spin dependence imposed by the magnon. However, if one neglects this spin dependence in the electron energies and writes $\tilde{\epsilon}_{k\uparrow}=\tilde{\epsilon}_{\downarrow k}$, then the coefficient in the interaction between electrons of equal and opposite momenta becomes

$$-\tfrac{1}{2}NS\hbar^2I^2\frac{\hbar\omega_{\mathbf{q}}}{(\epsilon_{\mathbf{k}}-\epsilon_{\mathbf{k}-\mathbf{q}})^2-(\hbar\omega_{\mathbf{q}})^2}\,.$$

This has the same form as the phonon-mediated interaction except that it has the opposite sign. For this reason one says that the electron-magnon interaction leads to the destruction of Cooper pairs.[8] However, there are regions in which this interaction is attractive, and, as Cohen *et al.*[9] have shown, the presence of such a potential may actually enhance the superconducting transition. Thus, it may be that superconductivity and ferromagnetism can be made to coexist in a ferromagnetic semiconductor. Let us, however, return to the subject of this paper, namely, the magnon renormalization of the electron energy.

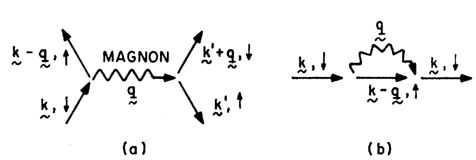

FIG. 1. (a) Diagrammatic representation of the magnon mediated electron-electron interaction; (b) diagrammatic representation of the renormalization process considered in this paper.

The correction to the electron energy due to the magnon process illustrated in Fig. 1(b) is obtained from Eq. (9) by setting $\mathbf{k}'=\mathbf{k}-\mathbf{q}$. The result is

$$\mathcal{E}_{\mathbf{k}\downarrow}=\tilde{\epsilon}_{\mathbf{k}\downarrow}-\tfrac{1}{2}NS\hbar^2I^2\sum_{\mathbf{q}}(\tilde{\epsilon}_{\mathbf{k}\downarrow}-\tilde{\epsilon}_{\mathbf{k}-\mathbf{q},\uparrow}-\hbar\omega_{\mathbf{q}})^{-1}\,, \tag{10}$$

where $\mathcal{E}_{\mathbf{k}\downarrow}$ is the renormalized electron energy. The corresponding process for down-spins involves a diagram similar to Fig. 1(b) but with the vertices reversed in time. That is, the down-spin absorbs a magnon which has already been produced along with an electron-hole pair. However, at zero temperature this process is frozen out. Therefore, at very low temperatures in a degenerate semiconductor, we expect down-spins to have different mobilities. This raises the intriguing possibility of spatially separating the different spin polarizations.

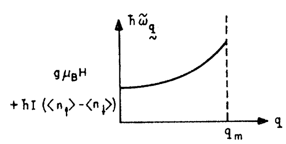

FIG. 2. Magnon spectrum in the presence of polarized conduction electrons.

Before evaluating Eq. (10), let us consider the nature of the intermediate state appearing in the denominator. This denominator becomes

$$\tilde{\epsilon}_{\mathbf{k}\downarrow}-\tilde{\epsilon}_{\mathbf{k}-\mathbf{q},\uparrow}-\hbar\omega_{\mathbf{q}}=\frac{\hbar^2k^2}{2m}-\frac{\hbar^2(\mathbf{k}-\mathbf{q})^2}{2m}+(2-g)\mu_BH+\hbar I$$
$$\times[2NS-(\langle n_\uparrow\rangle-\langle n_\downarrow\rangle)]-2z\hbar JS(1-\gamma_{\mathbf{q}})\,. \tag{11}$$

We shall approximate our ferromagnetic magnon spectrum by a quadratic dispersion relation with a wave-vector cutoff q_m as shown in Fig. 2. This approximation is not very critical, as we find that our final result is insensitive to the actual value of q_m. For a simple cubic spin array, Eq. (11) then becomes

$$\epsilon_{\mathbf{k}\downarrow}-\epsilon_{\mathbf{k}-\mathbf{q},\uparrow}-\hbar\omega_{\mathbf{q}}=\frac{\hbar^2k^2}{2m}-\frac{\hbar^2(\mathbf{k}-\mathbf{q})^2}{2m}-2\hbar JSa^2q^2+\Delta\,, \tag{12}$$

where a is the lattice parameter and

$$\Delta=(2-g)\mu_BH+\hbar I[2NS-(\langle n_\uparrow\rangle-\langle n_\downarrow\rangle)]\,. \tag{13}$$

[8] S. V. Vonsovskii and Yu. A. Izyumov, Usp. Fiz. Nauk. **78**, 3 (1962) [English transl.: Soviet Physics—Usp. **5**, 723 (1963)].

[9] M. L. Cohen, C. S. Koonce, and M. Y. Au-Yang, Phys. Letters **24A**, 582 (1967).

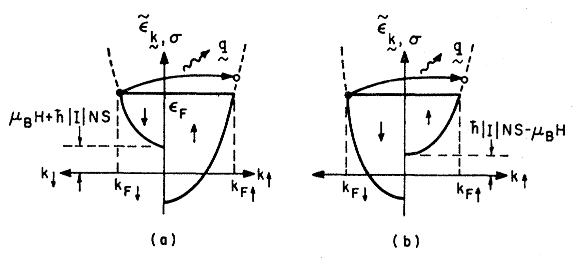

FIG. 3. Electron energies in the molecular-field approximation for (a) ferromagnetic coupling and (b) antiferromagnetic coupling.

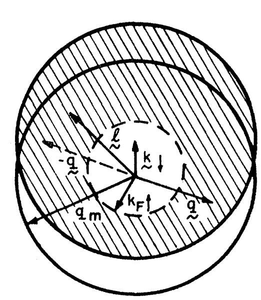

FIG. 4. Region of integration used in the evaluation of Eq. (14).

The energetics of this process may be understood with the help of Fig. 3. When an electron on the down-spin Fermi surface jumps to some point outside the up-spin Fermi surface, its kinetic energy is increased while its Zeeman-exchange energy is decreased. Since $\tilde{\epsilon}_{F\uparrow}=\tilde{\epsilon}_{F\downarrow}$, the processes indicated in Fig. 3 always lead to states of higher energy. Therefore, the denominator in Eq. (10) is always negative. The fact that there are no poles justifies our use of perturbation theory. The sum over $\mathbf{q}$ is evaluated by converting to an integral.

In the case of ferromagnetic coupling [Fig. 3(a)] the magnitude of the magnon wave vector must exceed a certain value depending upon its direction. Since the effect is isotropic, let us consider $\mathbf{k}_\downarrow=k_\downarrow\hat{z}$. Defining the variable $\mathbf{l}=\mathbf{k}_\downarrow-\mathbf{q}$, the integral is

$$-\frac{2\pi V}{(2\pi)^3}\int_{-1}^{1} du \int_{k_{F\uparrow}}^{l_m(u)} \frac{l^2 dl}{(\hbar^2/2m+2\hbar JSa^2)l^2-4\hbar JSa^2 k_\downarrow ul-[(\hbar^2/2m-2\hbar JSa^2)k_\downarrow^2+\Delta]}, \tag{14}$$

where

$$l_m(u)=k_\downarrow u+[q_m^2-(1-u^2)k_\downarrow^2]^{1/2}, \tag{15}$$

and $u=\cos\theta$, θ being the angle between $\mathbf{l}$ and $\hat{z}$. The region of integration is indicated by the shaded region in Fig. 4. In evaluating this integral we have assumed that $k_\downarrow$ is small in comparison with q_m. This enables us to expand in powers of $k_\downarrow/q_m$. The integration of Eq. (14) is rather tedious and the result rather lengthy. In the case of ferromagnetic coupling we find that there is very little correction to the mass of the electron.

In the case of antiferromagnetic coupling, however, the situation is somewhat different. As we see from Fig. 3(b), the down-spin Fermi momentum may be larger than the up-spin Fermi momentum. It then becomes possible for the constant term in the denominator of the integrand of Eq. (14) to become very small. In particular, this vanishes for $k_\downarrow$ such that

$$2\mu_B H-2\hbar|I|NS+\hbar^2k_\downarrow^2/2m =g\mu_B H+\hbar|I|(\langle n_\downarrow\rangle-\langle n_\uparrow\rangle)+2\hbar JSa^2k_\downarrow^2. \tag{16}$$

For values of $k_\downarrow$ around this value, there is a significant correction to the effective mass of the electron. To evaluate this correction we use the parameters listed in Table I. These values have been chosen to make $k_{F\downarrow}$ correspond to the value of $k_\downarrow$ at which Eq. (16) is satisfied so that the most striking correction will occur at the Fermi surface. We obtain the energy correction shown in Fig. 5. Using the relation

$$m^*=\frac{\hbar^2}{\partial^2\mathcal{E}_k/\partial k^2}, \tag{17}$$

we find that $m^*=1.28\ m$ at the Fermi surface. Thus, under this condition the magnon contribution to the effective mass will be comparable to the phonon contribution.

TABLE I. Numerical values used in the evaluation of the effective mass.

$\hbar J=0.01$ eV $\quad S=1$
$k_{F\uparrow}=0.0528$ Å^{-1} $\quad k_{F\downarrow}=0.236$ Å^{-1}
$\hbar N\|I\|=0.1$ eV $\quad a=\pi$ Å
$n=1/(6\pi^2)(k_{F\downarrow}^3+k_{F\uparrow}^3)=2.25\times10^{20}$ (conduction electrons)/cm^3

A calculation of the magnon contribution to the electronic specific heat of a rare-earth metal using an $s-f$ interaction has recently been made by Cole and Turner.[10] Since $\Delta C_V/\gamma T\sim m^*/m$, their large result implies a large effective mass. The reason for this large correction arises from the fact that in a metal, one is dealing with a Fermi energy that is much larger than the $s-f$ exchange energy. This has the effect of greatly increasing the phase space entering the integral (14).

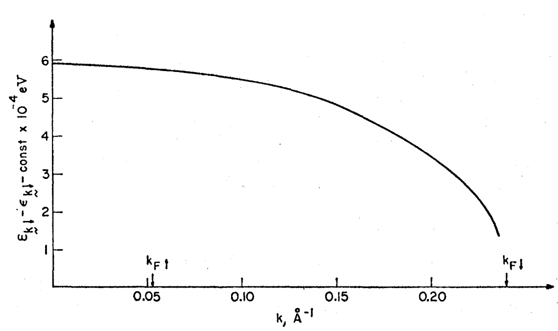

FIG. 5. Magnon-induced energy shift as a function of wave vector.

[10] H. S. D. Cole and R. E. Turner, Phys. Rev. Letters **19**, 501 (1967).