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INTERACTIONS DES ONDES DE SPIN

TWO MAGNON PAIRING EFFECTS

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Résumé. — Les interactions entre spins dans les matériaux ferromagnétiques ou antiferromagnétiques sont en général telles que la rotation de deux spins de deux ions situés dans la zone d'interaction d'échange coûte moins d'énergie que la rotation de deux spins plus éloignés. Il peut en résulter une paire de magnons liés possédant des énergies hors de la gamme d'énergie des magnons libres — cet effet est en général plus probable pour les paires dont le vecteur K est voisin de la limite de zone. Des résonances peuvent se produire à l'intérieur de la bande des paires non liées. Ces effets ont été observés en détail par absorption à deux magnons et par le spectre Raman de composés antiferromagnétiques où le mécanisme d'interaction favorise la création de paire proche accentuant ainsi cet effet. Les calculs ont été effectués essentiellement à 0 °K mais les expériences montrent que l'effet existe jusqu'à \( T > T_c \). Les expériences optiques sont limitées aux paires dont \( K = 0 \); il est possible que des expériences de diffusion de neutrons permettent de démontrer l'existence de paires liées pour des grandes valeurs de \( K \). On passe en revue les récents travaux théoriques et expérimentaux.

Abstract. — The interaction between spins in ferromagnets and antiferromagnets is usually such that two spin deviations on ions within the range of the exchange interaction cost less energy to create than two spin deviations at a greater distance. This can result in bound pairs of magnons with energies outside the range of energies of unbound pairs — an effect which is usually more likely for pairs with a \( K \) value near the zone boundary. Resonances may occur within the band of unbound pairs. These effects have been observed in detail in the two magnon absorption and Raman spectra of antiferromagnets where the interaction mechanism favours the creation of close pairs and hence accentuates the effect. Theoretical calculations which have been mainly confined to \( T = 0 \)°K but show that the effect exists up to \( T > T_c \). The optical experiments are confined to pairs with \( K = 0 \); it is possible that neutron scattering experiments may be able to demonstrate the existence of bound pairs at large \( K \). Recent theoretical and experimental work is reviewed.

1. Introduction. — The interactions between spin waves (magnons) in ordered magnetic materials are of great importance in determining the temperature dependence of the magnetic properties. The interactions are normally of two kinds, one arising when two spin deviations occur within the range of the exchange interactions; the other when two or more spin deviations occur on the same atom. We shall be concerned mainly with insulators where the exchange and hence the magnon interactions are of short range. As \( T \) approaches \( T_c \) and the number of spin deviations is large the problem is similar to that of a dense gas and is very difficult so that no really satisfactory theory exists. But at low \( T \) where the number is small and the system is like a very dilute gas, the interactions are a small perturbation. In fact for most experiments they have only a very small effect which is usually seen as a small renormalisation and small damping of the magnon energies [1]. This is because on the average the magnons spread over the whole crystal and spend very little time within the range of each other's interaction.

There are, however, some experiments which do not measure this average but strongly weight these states where the spin deviations are close together. For these experiments it is necessary to include the spin wave interaction in detail to obtain a correct theoretical interpretation. Indeed, Bethe [2] showed as long ago as 1931 that in the one-dimensional Heisenberg ferromagnet with spin \( S = \frac{1}{2} \), pairs of magnons form bound states, and Wortis [3] confirmed that this also occurred in three dimensions in more restricted conditions. However, these results remained of only theoretical interest until comparatively recently since there appeared to be no way of observing them, although Silberglied and Brooks and Harris [4] have proposed that the pairing might be seen through a resonance with the single magnon excitations. Recently there has been great interest in the optical properties of antiferromagnets in which two magnons are simultaneously created by optical absorption or Raman scattering. The earliest absorption experiments were performed by Halley and Silvera [5] and Allen et al. [6] and Raman scattering by Fleury et al. [7]. Since that time the spectra of several simple antiferromagnets of the fluorite structure \( \text{MnF}_2 \) [6, 7], \( \text{CoF}_2 \) [8], \( \text{FeF}_2 \) [9] and \( \text{NiF}_2 \) [10], the perovskites \( \text{K}_2\text{NiF}_4 \) [11], \( \text{RbMnF}_3 \) [12, 9] and the planar compound \( \text{K}_2\text{NiF}_4 \) [13] have been studied. In these experiments the interaction with the light is such that two spin deviations are created close together in the crystal where they interact strongly. The results cannot, therefore, be explained satisfactorily by a simple theory with non-interacting magnons, but are accounted for very well when the interaction is included. In a sense these results are analogous to excitons in a semiconductor where the optical absorption edge is dominated by the coulomb interaction between the electron and the hole which are created close together. No bound spin wave pairs have yet been observed in these materials but the interaction does give sharp resonances which dominate the observations. The detailed theory of this effect was first given by Elliott et al. [14], more recent work has applied a similar theory to \( \text{MnF}_2 \) [15] and planar compounds [16]. The selection rule for the main processes requires no total change in the component of spin angular momentum. This gives two spin wave processes in antiferromagnets but not in ferromagnets, though it should be possible to see similar effects in ferrimagnets. If there are strong mixing effects because of dipole-dipole interaction or anisotropic exchange this selection rule is relaxed as in \( \text{CoCl}_2 \text{H}_2\text{O} \) where Torrance and Tinkham [17] have seen bound clusters containing various numbers of spin deviations. They developed the \( \text{Ising} \) model for a linear chain in a way similar to the discussion of § 2.
The magnon side bands on exciton absorption lines in the optical spectra of magnetic crystals [18] are another phenomenon which has a similar explanation [19]. Since the magnon and the exciton are created close together their interaction again modifies the absorption.

All such optical experiments have a selection rule that the total \( K \) value of the excitations created is equal to that of the photons in the experiment and essentially zero. On the other hand, inelastic neutron scattering allows the observation of excitations of any \( K \) in the Brillouin zone. Two magnon processes are weak in this case but they may in principle be observed in antiferromagnets and have in fact been studied in MnF\(_2\) [20] and CoF\(_2\) [21]. Smith [22] has recently given a theory of this effect showing that bound states in antiferromagnets are more likely to occur near the zone boundary as Wortis found for ferromagnets. We shall draw extensively on this work in the following. Balcar and Lovesey [23] have also considered this effect in the one dimensional case.

In addition, experiments have been made of two magnon optical absorption and Raman scattering in antiferromagnetic crystals containing a low concentration of defects which produce localised spin waves. These also show the effect of spin wave interactions quite strongly [24].

2. Magnon Theory. — We consider a simple model of a crystal with nearest neighbour anisotropic exchange interactions and a single ion anisotropy with the same axis. Although it is somewhat inconsistent we shall take the space lattice as simple cubic. Interactions in such a system have recently been considered in detail by Silberglitt and Torrance [25]. The hamiltonian is written

\[
\mathcal{H} = -\frac{J}{2} \sum_{\mathbf{R}} \sum_{\delta} \left[ I S_{\mathbf{R},\delta}^x S_{\mathbf{R},\delta+\delta}^x + J (S_{\mathbf{R},\delta}^x S_{\mathbf{R},\delta+\delta}^z + S_{\mathbf{R},\delta}^z S_{\mathbf{R},\delta+\delta}^x) \right] - \sum_{\mathbf{R}} D S_{\mathbf{R}}^2 \tag{1}
\]

where the sum over \( \mathbf{R} \) is over all sites, that over \( \delta \) sums over the neighbours. For positive \( I, J, \) and \( D \) this is a uniaxial ferromagnet. The magnon energies are then

\[
\varepsilon(\mathbf{k}) = [I(0) - J(\mathbf{k})] S + (2 S - 1) D \tag{2}
\]

and \( \delta \) are the nearest neighbour distances. The spectrum is symmetric about the mid-point \( I(0) S + D(2 S - 1) \) and a width 12 \( SJ \) and has a gap at \( k = 0 \) which goes to zero in the isotropic case \( I = J, D = 0 \).

The states of the crystal with two magnons present and total wave vector \( \mathbf{k} \), can have different relative wave vector \( \mathbf{k} \). For pairs with \( \frac{1}{2} (\mathbf{k} + \mathbf{k}) \), \( \frac{1}{2} (\mathbf{k} - \mathbf{k}) \) the variation of \( \mathbf{k} \) gives a band at each \( \mathbf{k} \) again symmetric about the mid-point with a width

\[
4 S J (\cos \frac{1}{4} K_x \delta + \cos \frac{3}{4} K_y \delta + \cos \frac{1}{4} K_y \delta) \tag{4}
\]

Thus the width of the band of two magnon excitations decreases with increasing \( K \) and in this simple model goes to zero at the corner of the zone (see Fig. 1).

Fig. 1. — Density of states for two magnons in a s.c. crystal : A. Ferromagnet \( K = 0, K = \pi/2a (0, 0, 1) \), \( K = -\pi/2a (1, 1, 1) \). B. Antiferromagnet \( K = 0, K = \pi/2a (1, 1, 1) \).

In the antiferromagnet \( I \) and \( J \) have the opposite sign and the spin wave frequencies are

\[
\varepsilon(\mathbf{k})^2 = [I(0) S + D(2 S - 1)]^2 - [J(\mathbf{k}) S]^2 \tag{5}
\]

There is a double degeneracy in this simple model over a zone which is half the size of the cubic zone in the ferromagnetic case. The spectrum band reaches up to \( I(0) S + D(2 S - 1) \) and has an infinity in the density of states at this frequency. There is a gap at \( K = 0 \) except in the isotropic case. The two spin wave states form a band for all \( K \). In each case the maximum is at \( 2[I(0) S + D(2 S - 1)] \) and there is an infinity in the density of states there. The band narrows as \( K \) increases but does not become very narrow as in the ferromagnetic case (cf. Fig. 1).

These pair states will be excited with different probabilities in various processes and it will be necessary to examine the nature of the interaction of the spin system with the exciting particles to predict experimental observations. We shall return to this point in \( \S \) 4. First we wish to examine the effect of the magnon interaction between the spin deviations on the two magnon states described above. To do this we consider a simple approximation.

3. Effect of Interactions on the Nearly Ising Model. — If \( J = 0 \) in (1) so that it represents the Ising model with single ion anisotropy, the proper eigenstates of the system can be described in terms of spin deviations on particular sites. There is no transfer of deviations across the crystal and no dispersion. The ground state has complete alignment of the spins in the ferro or antiferromagnetic order depending on the sign of \( I \). A description in terms of spin deviations applies to both systems.

The energy to create one spin deviation is

\[
I(0) S + D(2 S - 1) \tag{6}
\]

The energy to create two deviations outside the range of the interaction is just twice this. However, if the deviations are on neighbouring sites the energy is

\[
2[I(0) S + D(2 S - 1)] - I \tag{7}
\]

lower by an amount \( I \). For two spin deviations on the same site it is

\[
2[I(0) S + D(2 S - 1)] - 2 D \tag{8}
\]

lower by \( 2 D \). This state is not allowed if \( S = \frac{1}{2} \).
This suggests that the magnon interaction creates two new types of state, one where the deviations are confined to neighbours, and one where the deviations are on the same site, although the latter only occurs with single ion anisotropy.

The effect of $J$ may be considered in perturbation theory when $J$ is small. The results are rather different for the ferro and antiferromagnetic cases. In the former there is a dispersion of the single magnon branch which is proportional to $J$ given by (2). The two deviation states are broadened into a band with a width given by (4). In first order the bound pair states with energies (7) and (8) are not connected with other states of the same energy. When $2SJ/2K \approx 1$ the band spreads to cover the nearest neighbour pair energies and bound states of this type will no longer exist. They will, however, always remain near the zone boundary where the band of unbound pairs stays narrow. When the pair energy lies in the band there will be a resonant state which will be broadened as the nearest neighbour pairs decay into unbound pairs. This width increases as the density of states increases.

The state with energy (8) will persist until

$$2SJ/2K \approx 2D$$

and will be an important feature when $D$ is large. To first order in $J$ it is coupled to the nearest neighbour pairs, and to the unbound pairs only in second order. Thus even when it lies in the band we expect a fairly sharp resonance.

In the antiferromagnet all the energies are affected in second order $0(J^2/I)$ as may be seen by expanding (5). In fact the perturbation expansion gives a result which differs from (5) by terms of order $1/S$. This represents a shortcoming of the spin wave approximation in this limit where the interactions are important. The nearest neighbour pair states are split by the interaction into combinations of appropriate symmetry. For example, with $K = 0$ the combinations of pairs neighbouring a particular site have $I_1^+$, $I_2^-$ and $I_3^+$ symmetry types. Away from $K = 0$ there is dispersion and some of these degeneracies are split. The energy bands of these bound pair states for the $(111)$ direction of $K$ are shown in figure 2 (following Smith [22]) in units of $J^2/I$. The usual symmetry classification of space groups is used. The unbound pair states broaden into a band which will spread down and eventually cover the bound pair states as $J$ increases. This broadening is largest for small $K$. The dotted curves in figure show the bottom of this band for various values of $(J/I)^2$. Although perturbation theory should not be accurate up to such large values of the parameter the results do indicate that the bound pairs are likely to persist at the zone boundary when there is a sizeable amount of anisotropy and a large gap in the spin wave spectrum. This is confirmed by more precise calculations.

4. Interactions. — The experimental results depend on the nature of the matrix elements as well as the density of final states. The two magnon optical processes arise from terms quadratic in the spin operators. Both the electric dipole moment of the system and the Raman polarisability are affected by the exchange interaction to give terms of this form [7, 13, 26]. The general form of such interaction hamiltonians may be determined by group theory — in spin only system like Mn$^{3+}$ they will be dominantly of the isotropic form $S_a$ $S_{-a}$ with coefficients depending on the direction of the electric field vectors. Since the exchange is short range this interaction will also be short range. The important terms are $S_a$ $S_{-a}$ which create two spin deviations of opposite sign on nearest neighbour pairs. Combinations of these operators with appropriate symmetry will occur; for the case considered in § 3, $I_3^+$ states may be infra-red active, $I_1^+$ and $I_3^+$ states Raman active.

For the simple Ising model of § 2 the interaction would only create the bound pairs and there would be no matrix elements to the band of unbound pairs. As $J$ increases this simple selection rule is relaxed but we expect the strongest effect from that region of the spectrum where the pair states make the biggest contribution, i.e., to any bound pair or a resonance associated with one.

Inelastic neutron scattering arises from magnetic dipole-dipole interaction between the neutron and the crystal. It is therefore linear on the spin operators and the main processes involve $S_a$ and $S_{-a}$ which create single spin waves.
However, the matrix element of
\[ \sum_R S_R^2 e^{iK \cdot R} \] (9)
may give two magnon processes. For the simple Ising model it gives only elastic Bragg scattering but as \( J \) increases it is found that in the antiferromagnet there are matrix elements to the symmetric \((T^1_A, A_1, \text{etc.})\) pair states to order \((J/\hbar)^2\) but none to the unbound states until next order \((J/\hbar)^4\). This is in a sense due to the zero point motion in the antiferromagnet where the true ground state is different from that given by the Ising model. If the value of \(< S^z >\) of a single spin in this ground state is \( \pm (S - A) \) we expect the inelastic neutron scattering cross-section to be of order \( A\). This is largest in the isotropic case and increases as \( S \) decreases. There is no zero point motion in the ferromagnet described by Hamiltonian (1) and hence this process will be forbidden in that case. It might possibly be observed in a ferromagnet with a more complex Hamiltonian which did not have a completely saturated ground state.

Another possible way of observing magnon pairs may be through the interaction with phonons. The atomic vibration will modulate the exchange interaction by varying the interatomic distance. The interaction Hamiltonian has the form [27]

\[ \sum_{\mathbf{R}, \delta} [u(\mathbf{R}) - u(\mathbf{R} + \delta)] \delta \left( \frac{1}{\hbar} \frac{\partial J}{\partial \delta} \right) \mathbf{S}_\mathbf{R} \cdot \mathbf{S}_{\mathbf{R} + \delta} \] (10)
in the case of isotropic exchange. Here \( u \) is the atomic displacement which is linear in the phonon creation and destruction operators. Again the effect is large only for spins on neighbouring sites. This would give a strong repulsion between a phonon and a bound magnon pair branch of the same symmetry type at a cross over and possibly an observable effect near a resonance. It would be most easily investigated by a neutron scattering experiment.

5. General Theory and Comparison with Experiment.

The most complete theories of these effects use the method of double-time Green's functions which are directly related to the experimental observations. The energy states themselves are not calculated but the appropriate weighted average for the required response function is obtained directly. No details of this type of calculation will be given here but may be followed in the original papers [14]. Only the results will be summarised.

For an isotropic Hamiltonian \( I = J \) the Green's function proportional to the optical absorption \((T^1_A \text{ symmetry})\) is shown in figure 3. The absorption peaks not at the density of states maximum but at a lower frequency appropriate to the resonance arising from the nearest neighbour pair states. The relative binding of this pair increases as \( S \) decreases and approximates well to the energy expected from (7) except for \( S = \frac{1}{2} \). For Raman scattering the appropriate Green's function has \( T^3_A \text{ symmetry} \) and for \( S = \frac{1}{2} \) may be compared directly with Fleury's experimental results [12] on RbMnF₃ (Fig. 3). Again the main peak occurs at a lower frequency than that predicted by the theory of non-interacting spin waves and the agreement with experiment when interactions are included is remarkably good. Similar satisfactory agreement is found for all the optical spectra measured at low \( T \).

Smith has recently extended this theory to \( K \neq 0 \) and calculated the Green's function proportional to the neutron cross-sections. The results shown in figure 5 are for an isotropic interaction in the body

\[ \sum_{\mathbf{R}, \delta} [u(\mathbf{R}) - u(\mathbf{R} + \delta)] \delta \left( \frac{1}{\hbar} \frac{\partial J}{\partial \delta} \right) \mathbf{S}_\mathbf{R} \cdot \mathbf{S}_{\mathbf{R} + \delta} \] (10)
centred structure and $S = \frac{1}{2}$ at $K = 0$ and at the zone boundary in the $(1, 0, 0)$ direction. The interaction between the spin waves has a relatively small effect which is somewhat more marked at large $K$. For $S = \frac{3}{2}$ when this calculation would be appropriate for MnF$_2$ the effect of the interaction was almost negligible. In fact no evidence of spin wave interactions was found in the two spin wave scattering of MnF$_2$ [20].

![Diagram](image)

**Fig. 6.** — Imaginary part of $\gamma^2$ Green's function related to neutron scattering for a model of CoF$_2$ at $K = 0$ and $K = n\pi/a$ ($0, 1$). Full line — interacting case, dotted line — non-interacting case. The bound state $\delta$-function contains an intensity comparable to the band.

In CoF$_2$ the lowest spin wave band may be approximately regarded as $S = \frac{1}{2}$ and $(J/I) \sim 0.8$ although orbital effects are important. The Green’s function theory does predict a very weakly bound state at the zone boundary in this case but because of the approximations this prediction is unreliable. In fact, no evidence of a bound state is seen in the experiment [21] although the resolution was poor. The spectra do show some evidence of spin wave interactions.

On the whole the theory of interacting magnons is essential to explain experiments where two magnons are created in close proximity even at $T = 0^\circ K$. As $T$ increases and more magnons are thermally excited the magnon interactions give rise to a self energy which alters the spin wave energies. No satisfactory theory of this effect exists. The recent experiments of Fleury [9, 13] showing the $T$ dependence of the two magnon optical effects present a new challenge and underline the need for such a theory.

6. Single Ion Anisotropy Effects. — In addition to the magnon interaction via the exchange we saw in § 2 that single ion anisotropy terms like $DSz^z$ lead to a magnon interaction giving bound states with two spin deviations on the same site. In general, such single ion terms are part of the crystal field, and may lead to splittings much larger than the exchange. In that case it is customary to regard them as excitons and quite separate from the magnons. There is a well defined branch for each excitation at about the crystal field energy with dispersion arising from the exchange. If the $D$ like terms are small they give only small effects. When the single ion and exchange terms are comparable in size rather complex spectra can result. Such small crystal field splittings may occur in salts with Co$^{2+}$ and Fe$^{2+}$ ions with distorted octahedral environments since the ground state then has orbital degeneracy, or in rare earth compounds like the pnictides, or transuranic materials like UO$_2$. There are several theories [28] of this type of excitation but all of them restrict attention to single magnons, or excitons corresponding to bound states on single ions. All of them neglect the possible interaction between such excitations and pairs (or large clusters) of excitations on adjacent sites. These will be important when such pair bands occur at comparable energies to the single excitations.

References

[26] Silberglitt (R.) and Torrance (J. B.), Phys. Rev. (to be published).