MAGNON-MAGNON AND EXCITON-MAGNON INTERACTION EFFECTS ON ANTIFERROMAGNETIC SPECTRA

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Two-magnon absorption and Raman experiments create pairs of magnons in close proximity, and hence, the magnon-magnon interaction has an important effect on the spectral line shape. Green's-function methods have been used to calculate this effect and the results applied the example of cubic antiferromagnets like RbMnF$_3$. Similar techniques are used to find the effect of exciton-magnon interaction on the sidebands in RbMnF$_3$; corresponding experimental results are presented.

The interactions between magnons in magnetically ordered materials have been extensively studied. At low temperatures, where magnon theory holds, they lead to comparatively small changes in the magnon self-energy and in average thermodynamic properties.[1] It has been pointed out by Wortis and others[2] that in some circumstances the interaction can lead to the formation of bound pairs of magnons, but in ferromagnets they consider that there is no experimental evidence bearing on this prediction.

Recently, there has been great interest in the optical properties of antiferromagnets in which two magnons are simultaneously created by light absorption[3] or Raman scattering.[4] It is our purpose to point out that because of the local nature of the interaction between light and the magnetic system in these experiments, the measurements are made on pairs of magnons which are created close together in real space, and are therefore always in close interaction. In this situation, the effects of magnon interaction are much more striking than for those properties depending on magnons which are far apart on average. It is analogous to the ordinary exciton problem,[5] where the absorption-edge shape of a semiconductor or insulator is greatly modified by the Coulomb interaction of the electron and hole.

A similar effect arises in the explanation of magnon sidebands on exciton lines in the optical spectra of magnetic crystals.[3,6] Here again the exciton and the magnon are created in close proximity, and their interaction has an important effect on the magnon sideband shape.[7,8]

We have made a theory of two-magnon[9] and exciton-magnon[10] absorption, using Green's-function methods.[11] The equations are similar to those found in the treatment of magnons near defects,[12] since the change caused by the first magnon or exciton looks like an impurity to the second magnon. As an example of the general procedure which shows the essential features, we have applied the theory to simple cubic antiferromagnets like RbMnF$_3$, where nearest-neighbor interactions are dominant, and the perfect-lattice Green's functions are readily obtained from those published for the ferromagnetic case.[13] Unfortunately, since the Mn pairs have a center of symmetry, the two-magnon absorption in this material is weak,[14] but the Raman effect should be observable, and the observation of a magnon sideband is reported below. The extension of the calculations to MnF$_2$, where much experimental evidence is available,[3,4,6] is planned.

For two-magnon absorption, the interaction of the spin system with light having electric vector $\vec{E}$ can be written

$$\sum_{\vec{R}}\sum_{\vec{r}} \sum_{\alpha\beta\gamma} E_\alpha A_{\alpha\beta\gamma}(\vec{r}) S_{\vec{R}}^\beta S_{\vec{R}+\vec{r}}^\gamma , \tag{1}$$

while for a second-order Raman process giving outgoing light with field $\vec{E}'$ it has the form

$$\sum_{\vec{R}}\sum_{\vec{r}} \sum_{\alpha\beta\gamma\delta} E_\alpha E'_\delta B_{\alpha\delta\beta\gamma}(\vec{r}) S_{\vec{R}}^\beta S_{\vec{R}+\vec{r}}^\gamma . \tag{2}$$

Here $\vec{r}$ is normally summed over the nearest

neighbors, and the tensors A and B reflect the symmetry of the lattice. The sum over all spin sites $\vec{R}$ arises because the light has essentially zero wave vector and, thus, ensures that the composite excitation has zero total wave vector. For a cubic crystal, the expression multiplying E in (1) must transform[15] as $\Gamma_4{}^-$, while the expression multiplying EE' in (2) can transform as $\Gamma_1{}^+$, $\Gamma_3{}^+$, and $\Gamma_5{}^+$.

Because of the high symmetry of RbMnF$_3$ only one term appears in (1),

$$A\sum_{\vec{R}}\sum_{\vec{r}}\vec{E}\cdot[(\vec{S}_{\vec{R}}\times\vec{S}_{\vec{R}+\vec{r}})\times\vec{n}], \qquad (3)$$

where $\vec{n}$ is a unit pseudovector in the direction $\vec{r}$, and A is expected to be small.[16] For lower symmetry crystals like MnF$_2$, larger terms proportional to $\vec{S}_R\cdot\vec{S}_{\vec{R}+\vec{r}}$ occur. Terms of this type occur for the second-order Raman effect in RbMnF$_3$ and are expected to be the most important. Equation (2) has the form

$$\sum_{\vec{R}}\sum_{\vec{r}}[B_3(\vec{E}\cdot\hat{r})(\vec{E}\cdot\hat{r})$$
$$+ (B_1 - \tfrac{1}{3}B_3)(\vec{E}\cdot\vec{E}')]\vec{S}_{\vec{R}}\cdot\vec{S}_{\vec{R}+\vec{r}}, \qquad (4)$$

B_1 and B_3 giving terms transforming as $\Gamma_1{}^+$ and $\Gamma_3{}^+$, respectively.

To calculate the two-magnon spectra, it is necessary to extract the parts of the spin operators which combine to create a pair of magnons. The largest contribution comes from $S_{\vec{R}}{}^+S_{\vec{R}+\vec{r}}{}^-$, where $\vec{R}$ is a down-spin site and $\vec{R}+\vec{r}$ is an up-spin site. Because of the nature of the antiferromagnetic ground state, there are other contributing terms, but their effect is small. The main intensity in the two-magnon spectrum thus results from the Green's function[17]

$$G_{\vec{r}\vec{r}'}{}^{(1)} = \langle\langle\sum_{\vec{R}}{}'S_{\vec{R}}{}^-S_{\vec{R}+\vec{r}}{}^+;$$
$$\sum_{\vec{R}'}{}'S_{\vec{R}'}{}^+S_{\vec{R}'+\vec{r}'}{}^-\rangle\rangle, \qquad (5)$$

where the primed summation is over the down-spin sites.

For the magnon-sideband-absorption process, the interaction of the exciton and the spin system with the light wave can be written

$$\sum_{\vec{R}}\sum_{\vec{r}}\sum_{\alpha\beta}E_\alpha C_{\alpha\beta}(\hat{r})c_{\vec{R}}{}^\dagger S_{\vec{R}+\vec{r}}{}^\beta, \qquad (6)$$

where $c_{\vec{R}}{}^\dagger$ is the creation operator for an exciton at site $\vec{R}$, and there is a corresponding destruction part, which we do not write down. The

coefficient C must have $\Gamma_4{}^-$ symmetry; its explicit form for RbMnF$_3$ is complicated and depends on the symmetry of the exciton under consideration.[10] If $\vec{R}$ refers to a down-spin site, then the largest contribution to the process where an exciton and a magnon are simultaneously created comes from the terms $c_{\vec{R}}{}^\dagger S_{\vec{R}+\vec{r}}{}^-$ and $c_{\vec{R}+\vec{r}}{}^\dagger S_{\vec{R}}{}^+$. The magnon sideband shape is then given by the imaginary part of the Green's function

$$K_{\vec{r}\vec{r}'}{}^{(1)} = \langle\langle\sum_{\vec{R}}{}'c_{\vec{R}}S_{\vec{R}+\vec{r}}{}^+;$$
$$\sum_{\vec{R}'}{}'c_{\vec{R}'}{}^\dagger S_{\vec{R}'+\vec{r}'}{}^-\rangle\rangle \qquad (7)$$

and the similar function involving sums over exciton operators on up-spin sites.

The required Green's functions (5) and (7) are determined from their equations of motion using decoupling techniques. For $G^{(1)}$ the Hamiltonian just includes the usual nearest-neighbor Heisenberg exchange term, since the anisotropy is negligible[18] for RbMnF$_3$. For $K^{(1)}$, the Hamiltonian is augmented to include a term which allows for the fact that an atom excited into the exciton state will generally have spin S' and, with its neighbors, exchange J' which are different from the ground-state values S and J. The term is

$$\sum_{\vec{R}}\sum_{\vec{r}}[J\vec{S}_{\vec{R}}{}'\cdot\vec{S}_{\vec{R}+\vec{r}} - J\vec{S}_{\vec{R}}\cdot\vec{S}_{\vec{R}+\vec{r}}]c_{\vec{R}}{}^\dagger c_{\vec{R}}. \qquad (8)$$

No dispersion is assumed for the excitons. This appears to be the case[8] in MnF$_2$, but there is no direct evidence for RbMnF$_3$.

The details of the decoupling procedures will be described elsewhere.[9,10] They involve fairly standard techniques like replacement of z components of spin operators by the average value $\pm S$ in the Néel state, after those operators pertaining to the same site have been suitably ordered. The resulting equations can be manipulated to eliminate all functions $G_{\vec{r}\vec{r}'}{}^{(1)}$ or $K_{\vec{r}\vec{r}'}{}^{(1)}$ except those where $\vec{r}$, $\vec{r}'$ refer to nearest neighbors. The resulting 7×7 matrices have cubic symmetry and can be diagonalized into separate functions which transform as $\Gamma_1{}^+$, $\Gamma_3{}^+$, and $\Gamma_4{}^-$.

The resulting Green's functions are similar to those in defect problems.[12] The results for the $\Gamma_4{}^-$ part of $G^{(1)}$ are shown in Fig. 1 for varying values of S. This is proportional to the predicted two-magnon absorption except for a smooth function roughly equal to E. At large S, the results tend to the line shape obtained with zero magnon-magnon interaction. For decreasing S, a resonance appears which moves to lower energies for
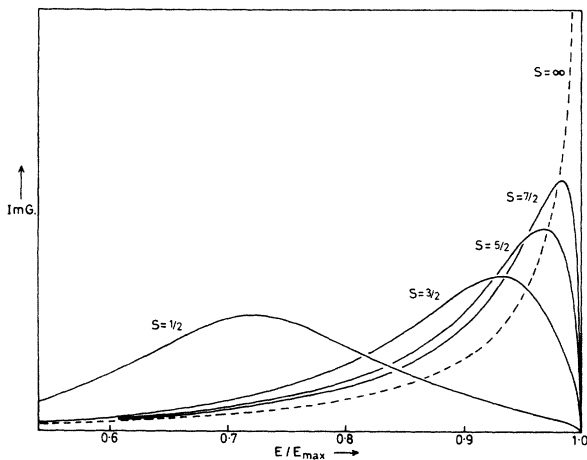
FIG. 1. The imaginary part of $G^{(1)}$ for $\Gamma_4{}^-$ symmetry, which will be proportional to the two-magnon absorption spectra predicted for cubic antiferromagnets for various values of S.

FIG. 2. Predicted forms of the two-magnon Raman spectra for RbMnF$_3$ for $\Gamma_1{}^+$ and $\Gamma_3{}^+$ scattering symmetries. The full and broken curves indicate the calculated spectra with and without inclusion of magnon-magnon interaction. (X is a critical point in the Brillouin zone.)

smaller S. This may be interpreted as follows: For an Ising interaction a single spin reversal costs an energy nJS, where n is the number of nearest neighbors, and two spin reversals costs twice this, unless they are on neighboring sites when it costs only $(2nS-1)J$. Although we have a Heisenberg interaction, the peak in the two-magnon density of states is still at $E_{max} = 2nSJ$. Thus, the magnons created in close association will respond mainly in a resonance at an energy J below this. The peak is broadened because of the Heisenberg interaction and shifted by symmetry effects, but this simple picture gives a good account of the general behavior. For a system with a narrow band because of anisotropy, this resonance could be a true bound state.

For Mn^{++} antiferromagnets where $S = \frac{5}{2}$, the effect of magnon-magnon interactions is expected to be small. However, the shift in peak position calculated for RbMnF$_3$ is comparable with the discrepancy between experiment and zero-interaction theory in MnF$_2$, previously attributed to a long-range interaction.[19]

The same general remarks apply to the $\Gamma_1{}^+$ and $\Gamma_3{}^+$ parts of $G^{(1)}$. The results for $S = \frac{5}{2}$ and $S = \infty$ are shown in Fig. 2. Raman scattering on RbMnF$_3$ would be proportional to this and should show clearly the effect of magnon-magnon interactions, particularly in the $\Gamma_3{}^+$ component.

Finally, for the magnon sideband, we have made both calculations and measurements of the shape. Since there is only one $\Gamma_4{}^-$ component of $K^{(1)}$, the sidebands on exciton lines of all symme-
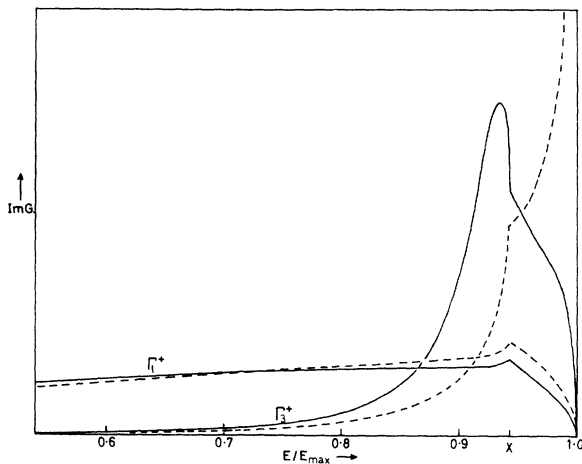
tries will be given by it. Figure 3 shows the experimentally observed magnon sideband on the $^6A_1 \rightarrow {}^4T_1$ exciton transitions in the absorption spectrum of RbMnF$_3$. The experimental details are as given in a previous report of other aspects of the exciton absorption.[20] A simple Ising theory gives a resonance in the sideband at roughly $JS-J'S'$ below the maximum magnon frequency of nJS. Two theoretical curves are included in Fig. 3. One of these is for zero exci-
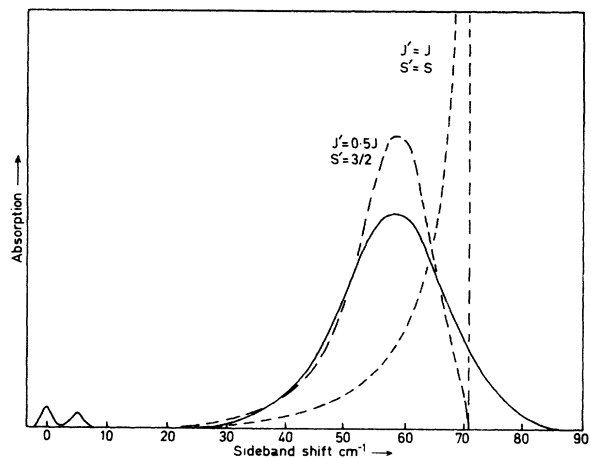

FIG. 3. The full curve shows the experimental absorption spectrum with two excitons (Ref. 20) and a magnon sideband. The dashed theoretical curves refer to the values of J' and S' indicated. The sideband has been assumed to belong to the lower frequency exciton (Ref. 10).

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ton-magnon interaction, $J' = J$ and $S' = S$. The other is a best fit to experiment, obtained by taking $S' = \frac{3}{2}$ and $J' = 0.5J$, and with the experimental and theoretical curves normalized to the same area (we have used[21] $J = 4.7$ cm^{-1}). It is seen that good agreement is obtained apart from a high-energy tail in the experimental curve, and that the exciton-magnon interaction has a striking effect on the spectrum. Unfortunately there is no reliable independent determination of J' for comparison. It is anticipated that inclusion of exciton-magnon interaction in the theory for MnF_2 may remove present discrepancies between theory and experiment.[6]

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