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IMPURITY CONCENTRATION DEPENDENCE OF RAMAN-SCATTERING BY MAGNONS IN Ni DOPED RbMnF₃ AND KMnF₃

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Résumé. — Les fréquences des pics de diffusion Raman par excitation de paires dans le continuum d'ondes de spin ainsi que de « double magnons » d'impureté sₜd, croissent avec la concentration en Ni dans RbMnF₃ : Ni et KMnF₃ : Ni. A concentration nulle, ces fréquences sont en bon accord avec les résultats d'un calcul de perturbation d'un modèle d'Ising par des termes d'échange non diagonaux, et ceux résultant d'un traitement des ondes de spin par les fonctions de Green. On discute des variations de fréquence avec la concentration pour les deux types de modes dans le cadre d'un modèle d'Ising.

Abstract. — Raman scattering from continuum magnon pair modes and impurity sₜd magnons in RbMnF₃ : Ni and KMnF₃ : Ni exhibit shifts to higher frequencies with increasing Ni doping. Zero concentration impurity mode frequencies agree well with perturbation of an Ising model by transverse exchange and with Green's function spin wave theory. Continuum and sₜd mode shifts with Ni concentration are discussed with respect to an Ising model.

The effects of low (< 2 %) nickel impurity concentrations on the impurity magnon spectra of KMnF₃ and RbMnF₃ were investigated for the following three reasons:

1) to obtain experimental frequencies for impurity pair magnons which, with information on sₒ and s₂ modes previously measured [1] in crystals with ~ 10⁻⁶ mol fraction nickel impurities, may be used to test impurity magnon calculations made for a single impurity ion;
2) to investigate the effective range of the impurity magnon wave function; and 3) because the interaction between impurity magnons constitutes an extremely simple model system for energy transfer between localized states.

Since, unfortunately, the s-like modes are not observable in the IR or by Raman scattering, concentration dependence of these simplest of impurity magnons cannot be investigated by optical techniques (Broadening of the exciton lines by crystal field effects renders fluorescence measurements inaccurate above impurity concentrations of 10⁻⁵.) Thus, in this paper we confine our attention to the concentration dependence of the sₒ d pair modes observed by Raman scattering. Aside from concentration effects which are much weaker in MnF₃ : Ni, the pair mode spectra and their analysis which follows, are very similar to those observed for that system [2, 3].

The concentration dependence of the continuum two-magnon scattering is shown for two nickel impurity concentrations in RbMnF₃ in figure 1, and compared with the scattering from pure RbMnF₃, which was first observed by Fleury [4]. The shift of the band with concentration is linear up to about 1 % with δ Ec/dc = 2.3 cm⁻¹ (% Ni)⁻¹. Similarly, a concentration shift of the sₒ d mode is shown in figure 2 for the same concentrations. As with the continuum modes, the bands shift linearly to higher frequencies for increasing Ni concentration with little increase in width up to 1 % Ni. For this mode
The concentration dependence of the Raman scattering from impurity modes in RbMnF$_3$. The relative intensities were normalized by assuming that the peak heights of the continuum modes were unchanged by nickel concentration. The zero-concentration impurity mode frequencies are listed in the tables and compared with values calculated by Thorpe [5] using a Green's function spin wave theory, and with values computed by us, using perturbation theory to second order in the transverse exchange. Thorpe's calculation considered only nearest neighbor exchange, while we considered nnn exchange as well. In each case the impurity exchanges were adjusted to fit the $s_0$ modes, while the host exchanges were obtained from neutron scattering data [6, 7]. Note that the perturbation calculations require a small ferromagnetic impurity $J'_2$ exchange.

The concentration dependence of this $J'_2$ contribution is surprising in view of the fact that the frequency of the $s_0$ d mode, 292.1 cm$^{-1}$ in RbMnF$_3$: Ni, is reasonably well described by the Ising pair state in which the Ni spin and a nearest Mn neighbor spin are deviated:

$$\omega_{nn} = -25J - 30J_1 - 60J'_2 = 300 \text{ cm}^{-1},$$

whence the deviation of a more distant Mn spin would lead to a value $\omega_{nn}$ larger by the Ising magnon interaction $5J \approx 12 \text{ cm}^{-1}$. However, the only Ising contribution to $\partial \omega_{nn}/\partial c$ comes from excited Ni-Mn pairs in which a second Ni ion occupies a second neighbor site to the first one. This contribution is an order of magnitude smaller than the observed $\partial \omega_{nn}/\partial c$, although it has the correct sign. In fact, despite the close agreement between experiment and $\omega_{nn}$, which suggests that the pair state is localized on the impurity and its first neighbors, when transverse exchange is taken into consideration either by perturbation or by the Green's function spin wave calculation, a substantial part of the wave function is found on more distant Mn ions, which qualitatively explains the inadequacy of the above treatment for $\partial \omega_{nn}/\partial c$. Unfortunately, neither of these two calculations have provided a quantitative description of the impurity wave function.

The Ising model is also very successful in estimating the mean continuum mode frequencies. In view of these successes, it is interesting to examine in what way the observed values of $\partial \omega_{nn}/\partial c$ arise from the concentration-dependent Ising energy. The Ising states of interest are those in which pairs of spin-deviations are excited on first neighbors, as these are the only states which contribute to the optical matrix element. The mean energy $E_M$ for the excitation of such a pair in a crystal containing $c$% impurities to first order in $c$ is:

$$100E_M = (100 - 2z_1)c(-2J[2z_1S - 1]) +$$
$$+ 2(z_1 - 1)c(-2J[2z_1S - 1 - 2J'_1S]) +$$
$$+ 2c(-2J[z_1 - 1]S - 2J'_1[z_1S + S' - 1] + 2J'_2z_2S).$$

(1)

Here the subscripts refer to first or second neighbors and primes to the impurity.

In the limit of $c = 0$, $E_M = E_c = 58J = 134.6 \text{ cm}^{-1}$ for the case of RbMnF$_3$, which is in good agreement with the experimental peak Raman scattering at 132.4 cm$^{-1}$. The concentration dependence of this energy is:

$$\partial E_M/\partial c = 116J - 80J'_1 +$$
$$+ 120J'_2 = 3.8 \text{ cm}^{-1} (\% \text{ Ni})^{-1}.$$  

(2)

In order to relate (2) to the observed parameters we must know the relative numbers of impurity bound modes $N_B$ and continuum modes $N_C$ where

$$N_B + N_C = 1.$$  

Thus:

$$E_M = N_B E_B + N_C E_C$$

and

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{Mode} & \textbf{Experiment (cm$^{-1}$)} & \textbf{Green's function (after Thorpe)} & \textbf{Perturbation Theory} \\
\hline
$s_0$ & 238.0 & 238.0 & 238.0 \\
$s_0^2$ & 486.9 & 489.1 & 486.9 \\
d & 73 (*) & 74 & 70.9 \\
sd & 292.1 & 293.2 & 294.9 \\
$J'_1$ & -8.18 & -7.40 & \\
$J'_2$ & +0.34 & & \\
\hline
\end{tabular}
\end{table}

\begin{tabular}{|c|c|c|}
\hline
\textbf{Mode} & \textbf{Impurity Magnons in KMnF$_3$ : Ni} & \\
\hline
$s_0$ & 255.9 & 255.9 \\
sd & 523.9 & 525.9 & 524.0 \\
sd & 315.5 & 315.0 & 315.5 \\
$J'_1$ & -8.82 & -8.11 & \\
$J'_2$ & +0.30 & & \\
\hline
\end{tabular}

(*) Osersoff (A.) et al., Phys. Rev., (1969), 188, 1046. Scattering from this mode, which is highly forbidden, is absent in our crystals.
Because of our lack of knowledge of the impurity mode scattering matrix element, we can obtain little experimental information on $N_B$ or $N_C$ or their derivatives. However, the other parameters are known. If we assume that the number of bound impurity modes is equal to the number of impurity-host pairs, a not unreasonable assumption at low concentrations, we find $100 N_C = 100 - 2c$ and $100 N_B = 2c$, which leads to an empirical expression for $\partial E_M/\partial c$ in the limit of zero concentration:

$$\partial E_M/\partial c = \partial E_C/\partial c + 2(E_B - E_C).$$

Inserting the experimental parameters on the r. h. s. of (4) we find that $\partial E_M/\partial c = 5.5$ cm$^{-1}$ (% Ni)$^{-1}$, in only fair agreement with the Ising value of 3.8 cm$^{-1}$ (% Ni)$^{-1}$, considering that the difference between these two numbers is a fair fraction of $\partial E_C/\partial c$. This discrepancy may arise either because we have overestimated $N_B$ ($2c/100$ is the maximum value), or because the transverse exchange is important in determining the first moments.

Throughout the above analysis we have assumed that

$$\partial J/\partial c = \partial J'/\partial c = 0.$$  

That this assumption is reasonable may be inferred from the susceptibility measurements of mixed KMnF$_3$-KNiF$_3$ crystals by Hashimoto [8], who found that $J'$ was independent of Ni concentration within a mean deviation of $\pm 0.4$ cm$^{-1}$ over a range of concentrations between 5 and 54 % Ni. Any constant $\partial J'/\partial c$ permitted within this error is more than an order of magnitude too small to explain the observed $\partial E/\partial c$'s.

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References