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IMPURITY MAGNONS ASSOCIATED WITH Co IONS IN RbMnF₃

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Résumé. — RbMnF₃-Co présente une raie de diffusion Raman vers 263 cm⁻¹. Un Hamiltonien d’Ising conduit à la valeur de — 4,3 cm⁻¹ pour Jₘₙ-Co, ce qui permet de calculer les fréquences des modes d’impureté. On trouve en particulier pour le mode s₀ une fréquence en bon accord avec celle que laisse prévoir la mesure correspondante par diffraction de neutrons dans KMnF₃-Co. Les règles de sélection sont étudiées avec et sans champ magnétique appliqué pour différentes orientations des cristaux. En raison de la faible anisotropie on montre expérimentalement et théoriquement qu’elles s’interprètent dans le formalisme du groupe O₈ de symétrie paramagnétique plutôt que dans celui du groupe exact de symétrie autour de l’impureté : D₄h(C₄h). Le mode s₀-d appartient alors à la représentation Γ₃⁺ de O₈. Les règles de sélection sont les mêmes que pour RbMnF₃-Ni.

Abstract. — Raman scattering from impurity s₀-d pair modes is reported in RbMnF₃-Co near 263 cm⁻¹. An Ising Hamiltonian leads to a — 4,3 cm⁻¹ Jₘₙ-Co value and allows to calculate the frequencies of impurity modes. The calculated frequency of the s₀ mode is in agreement with a value obtained by scaling the s₀ mode measured in Co doped KMnF₃ by neutron scattering. Selection rules are studied with and without an applied magnetic field for different samples orientations. Resulting from the low anisotropy it is shown both theoretically and experimentally that the selection rules have to be expressed with reference to the O₈ paramagnetic cubic symmetry rather than the D₄h(C₄h) rigorous magnetic symmetry around the impurity : the s₀-d mode then belongs to the Γ₃⁺ representation in O₈. The selection rules are the same as in RbMnF₃-Ni.

The investigation of RbMnF₃-Co by Raman scattering was undertaken to compare the results with the extensively investigated but less simple MnF₃-Co [1, 2, 3], and to the nearly analogous KMnF₃-Co, where the s₀ mode has been observed by neutron scattering [4]. Special attention was paid to selection rules which were compared to the observed ones in the case of RhMnF₃-Ni: whence, for sufficiently high Co concentration, the anisotropy field lies along one of the <1, 0, 0> directions [5], which implies a D₄h(C₄h) magnetic symmetry around the site of the impurity, in the case of Ni it probably lies along one of the <1, 1, 1> directions as in the pure crystal [6], which implies a D₃d(C₃h) symmetry.

I. Experiments. — Different samples with concentrations of 0.30 % and of 0.36 %, and various orientations were studied. The experimental technique has been described elsewhere [7]. Most of the experiments have been performed at 2 K. However a few spectra were also studied versus temperature, to confirm the magnetic origin of the spectrum. One observes a line centered at 263 cm⁻¹ (Fig. 1), with an experimental half-width of 7.5 cm⁻¹, which, when taking into account the instrumental resolution, leads to a 7 cm⁻¹ natural half-width. Careful examination of the spectra, after correction to take into account the diffuse background light, allows to show that, within the experimental accuracy, the spectrum is consistent with a Γ₃⁺ Raman tensor in the O₈ cubic symmetry (Table I). The same conclusions, after similar investigations, were found for the 294 cm⁻¹ line in RbMnF₃-Ni, a s₀-d mode [8, 9, 10], and, to a lesser extent, for the corresponding 314 cm⁻¹ line in KMnF₃-Ni [8, 10].

Fig. 1. — Raman spectrum of RbMnF₃-Co near 260 cm⁻¹ for different polarizations. X, Y, Z lie respectively along <1, 1, 0>, <1, 1, 1> and <0, 0, 1> direction (see Table I). T = 2 K.

In order to confirm the independence of the selection rules versus the domains orientation a magnetic field was applied along <1, 1, 0>. No intensity variation is observed when one crosses the spin-flop transition field Hₛ (about 10⁴ gauss) [5]. For fields...
TABLE 1

<table>
<thead>
<tr>
<th>Sample orientation</th>
<th>ZX</th>
<th>ZZ</th>
<th>YX</th>
<th>YZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;1,0,0&gt;$</td>
<td>30</td>
<td>400</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>$&lt;1,1,0&gt;$</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$&lt;1,0,0&gt;$</td>
<td>1</td>
<td>0</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>$&lt;1,0,0&gt;$</td>
<td>20-240</td>
<td>80-120</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>$&lt;1,1,0&gt;$</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;1,1,0&gt;$</td>
<td>35</td>
<td>450-800</td>
<td>320</td>
<td>35</td>
</tr>
<tr>
<td>$&lt;1,1,0&gt;$</td>
<td>0</td>
<td>4</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

Comparison of the relative intensities of different spectra for various sample orientations. Theoretical evaluation corresponds to a $s_0$ for the $s_0$ mode to lie at $263 \text{ cm}^{-1}$. To evaluate $J_{\text{Mn-Co}}$, one needs at least, the position of the first excited level in the paramagnetic phase. Assuming the same value as in KMgF$_3$-Co [16] ($U = 360 \text{ cm}^{-1}$), one finds

$$J_{\text{Mn-Co}} = -4.31 \text{ cm}^{-1}.$$ 

Moreover, a moderate variation of $U$ does not drastically affect $J_{\text{Mn-Co}}$ (it varies from $-4.35$ to $-4.29 \text{ cm}^{-1}$ when $U$ increases from $300$ to $400 \text{ cm}^{-1}$). The $-4.31 \text{ cm}^{-1}$ value leads to $208 \text{ cm}^{-1}$ for the $s_0$ mode, which is closed to the hypothetically observed $211 \text{ cm}^{-1}$ line (conversely this last value for $s_0$ gives $J_{\text{Mn-Co}} = -4.37 \text{ cm}^{-1}$ and a pair-mode frequency of $266.7 \text{ cm}^{-1}$). A $208 \text{ cm}^{-1}$ frequency is slightly smaller than the $218 \text{ cm}^{-1}$ one determined in KMnF$_3$-Co by neutron diffraction [4]. The same calculation gives $J_{\text{Mn-Co}} = -4.54 \text{ cm}^{-1}$ in KMnF$_3$-Co: as usual the exchange is smaller in Rb than in K fluoride. However, as observed in the case of Ni [10] we suspect the neutron diffraction data to be modified by concentration effects.


$$J_{\text{Mn-Co}} = \left( J_{\text{Mn-Mn}} \times J_{\text{Co-Co}} \right)^{1/2}$$

would lead to $J_{\text{Mn-Co}} = -4.21 \text{ cm}^{-1}$, very close to our $-4.31 \text{ cm}^{-1}$ determination.

Finally, although the model is rather poor for $g$ calculations [2], it leads to $g_{\text{Mn}} = 3.73$ and $g_{\text{Co}} = 1.84$.

2. SELECTION RULES. — The extreme weakness of the $s_0$ mode is a surprising feature of the Raman spectrum: since one magnon scattering needs spin-orbit coupling [18, 19], the situation seems ideal for Co impurity where the spin-orbit coupling is a zero-order perturbation within the ground state, in contrast with other impurities where it arises from excited energy levels. It explains the high intensity of the $s_0$ mode in MnF$_2$-Co [2], compared to the Nickel-doped crystals for instance, but the RbMnF$_3$-Co remains a puzzle. One has also to notice that, for MnF$_2$-Co, the $s_0$ mode shows a rather strong magnetic dipole absorption in the infrared [2], a process which does not necessarily need spin-orbit coupling.

For the pair modes, the selection rules are well understood. Strictly speaking, one has to classify the modes using the irreducible corepresentations of the $D_{4h}(C_{4h})$ group, which in this particular case coincide with the irreducible representations of $C_{4d}$ [20]. The different pair-modes are written $s_0 - s_1$, $s_0(p_x + i p_y)$, $s_0(p_x - i p_y)$, $s_0 - P_r$, $s_0 - d_{2z^2 - r^2}$, $s_0 - d_{\sqrt{3}(x^2 + y^2)}$ with self-evident notations. The representation of each mode has to be considered as a product $\Gamma(S) \times \Gamma'$ where $\Gamma(S)$ refers to the spin transformation properties only and $\Gamma'$ to the permutation of the ions only ($\Gamma'$ is immediately related to the notation of the modes). For the pair modes and for the ground state $\Gamma(S)$ is the same ($\Gamma(S) = \Gamma_S$). It results that, as long as we limit our study to the excitation of pair modes, we are allowed to ignore the spin variables and to work with $\Gamma'$ only. The Raman active modes consist of $s_0 - s_1$, $s_0 - d_{2z^2 - r^2}$, $s_0 - d_{\sqrt{3}(x^2 + y^2)}$, but the $s_0 - s_1$ probably lies at lower frequencies [21] and is not observed. We are then left with $s_0 - d_{2z^2 - r^2}$ and $s_0 - d_{\sqrt{3}(x^2 - y^2)}$, which res-
pectively transform as \( r: \) and \( Tzf \) in \( Chh \). It follows from the low anisotropy that the symmetry is practically cubic. Hence \( s_0 = d_{(3z^2-y^2)} \) and \( s_0 = d_{3(3x^2-y^2)} \) are nearly degenerated in the representation \( \Gamma_3^+ \) of the cubic group \( O_h \). The two corresponding components of the Raman tensors in \( C_{4h} \) (if assumed symmetric) are respectively expressed as

\[
\begin{pmatrix}
-b & 0 & 0 \\
0 & b & 0 \\
0 & 0 & 2b
\end{pmatrix},
\begin{pmatrix}
\sqrt{3}b & 0 & 0 \\
0 & -\sqrt{3}b & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]

Notice that the \( \Gamma_1^+ \) and \( \Gamma_2^+ \) Raman tensors in \( C_{4h} \) (if assumed symmetric) are respectively expressed as:

\[
\begin{pmatrix}
-b & 0 & 0 \\
0 & -b & 0 \\
0 & 0 & a
\end{pmatrix} \quad \text{and} \quad \begin{pmatrix}
\beta & \gamma & 0 \\
\gamma & -\beta & 0 \\
0 & 0 & 0
\end{pmatrix}.
\]

The conditions insuring the invariance of the sum of the intensities against the three possible domain orientations are \( a = -b \), \( \beta = \gamma = 0 \) \( (\Gamma_1^+ \text{ in } O_h) \) or \( a = 2b \), \( \beta = \sqrt{3}b \), \( \gamma = 0 \) \( (\Gamma_2^+ \text{ in } O_h) \). The experimental relative intensities impose the second one (a result which confirms that \( s_0 = 0 \) is not observed).

Finally, we point out that similar arguments would work for \( \text{RhMnF}_4\text{Ni} \) and \( \text{K MnF}_3\text{Ni} \) which behave in the same way, although the direction of anisotropy is different.

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References

[14] Buyers (W. J. L.), Cowley (R. A.), Holden (J. M.), Svensson (E. C.), Hutchings (M. T.), Hukin (D.) and Stevenson (R. W. H.), Proc. 11th Int. Conf. on Low Temperature Physics, edited by Allen (J. F.), Finlayson (D. M.) and McCand (D. M.), St Andrews, Scotland, p. 1330.