IMPURITY MAGNONS ASSOCIATED WITH Co IONS IN RbMnF3

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Résumé. — $RbMnF_3$-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 J_{Mn-Co}, ce qui permet de calculer les fréquences des modes d'impureté. On trouve en particulier pour le mode s_0 une fréquence en bon accord avec celle que laisse prévoir la mesure correspondante par diffraction de neutrons dans $KMnF_3$-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 O_h de symétrie paramagnétique plutôt que dans celui du groupe exact de symétrie autour de l'impureté : $D_{4h}(C_{4h})$. Le mode s_0-d appartient alors à la représentation Γ_3^+ de O_h. Les règles de sélection sont les mêmes que pour $RbMnF_3$-Ni.

Abstract. — Raman scattering from impurity s_0-d pair modes is reported in $RbMnF_3$-Co near 263 cm^{-1}. An Ising Hamiltonian leads to a — 4.3 cm^{-1} J_{Mn-Co} value and allows to calculate the frequencies of impurity modes. The calculated frequency of the s_0 mode is in agreement with a value obtained by scaling the s_0 mode measured in Co doped $KMnF_3$ 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 O_h paramagnetic cubic symmetry rather than the $D_{4h}(C_{4h})$ rigorous magnetic symmetry around the impurity : the s_0-d mode then belongs to the Γ_3^+ representation in O_h. The selection rules are the same as in $RbMnF_3$-Ni.

The investigation of $RbMnF_3$-Co by Raman scattering was undertaken to compare the results with the extensively investigated but less simple MnF_2-Co [1, 2, 3], and to the nearly analogous $KMnF_3$-Co, where the s_0 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 $RbMnF_3$-Ni : whence, for sufficiently high Co concentration, the anisotropy field lies along one of the $< 1, 0, 0 >$ directions [5], which implies a $D_{4h}(C_{4h})$ 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 $D_{3d}(C_{3i})$ 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 Γ_3^+ Raman tensor in the O_h cubic symmetry (Table 1). The same conclusions, after similar investigations, were found for the 294 cm^{-1} line in $RbMnF_3$-Ni, a s_0-d mode [8, 9, 10], and, to a lesser extent, for the corresponding 314 cm^{-1} line in $KMnF_3$-Ni [8,10].

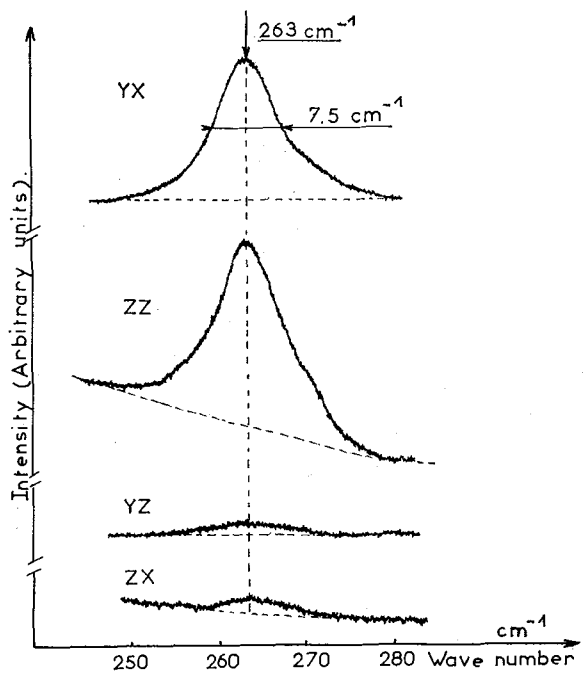

FIG. 1. — Raman spectrum of $RbMnF_3$-Co near 260 cm^{-1} for different polarizations. X, Y, Z lie respectively along $< 1, 1, 0 >$, $< 1, \bar{1}, 0 >$ and $< 0, 0, 1 >$ direction (see Table 1). $T = 2$ °K.

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 H_c (about 10^4 gauss) [5]. For fields

TABLE 1

Comparison of the relative intensities of different spectra for various sample orientations. Theoretical evaluation corresponds to a Γ_3^+ Raman tensor in O_h symmetry. X and Y respectively refer to incident and scattered direction of light propagation, Z is perpendicular to (X, Y) plane. The sample orientation is defined by indicating the crystal axes along X, Y, Z. The polarization direction of the incident light followed by that of the scattered light provides the indexation of each spectrum. The experimental intensities are in arbitrary units and not related to each other for the three different sets of data. The low residual intensities for polarizations forbidden by theory are due to small crystal misorientations and large optical aperture.

Sample orientation	ZX	ZZ	YX	YZ	
<1,0,0>	30	400	60		experimental
<0,1,0>					
<0,0,1>	0	4	0	0	theoretical.
<1,1,0>	210-240	80-120	40		experimental.
<0,0,1>					
<1,$\bar{1}$,0>	3	1	0	0	theoretical.
<1,1,0>	35	450-480	320	35	experimental.
<1,$\bar{1}$,0>					
<0,0,1>	0	4	3	0	theoretical.

smaller than H_c, with the geometrical arrangement used, one can show that the broadening expected from a pair mode g_{PM} factor around 1.5 [2] is too small to be measured.

If the 263 cm^{-1} line is related to the s_0-d mode, one roughly expects [7] the s_0 mode to lie at a frequency lowered by $-(z-1) \times S^z_{Mn} \times 2\,J_{Mn-Mn}$, or, using known values of J_{Mn-Mn} [11], about 205 cm^{-1}. A line is thought to have been observed at 211 cm^{-1} : but, due to its weakness compared to the diffuse background, its presence cannot be assigned with certitude ; its intensity does not exceed 1 or 2 % of the 263 cm^{-1} line.

II. Discussion. — 1. FREQUENCIES. — Although, rigorously speaking, the orbital degeneracy of the Co^{2+} ion ground state $^4\Gamma_4^+$ implies an anisotropic exchange [12] it has been shown both theoretically [13] and experimentally [14] that the anisotropic term does not exceed 5-10 %. Supposing a Heisenberg isotropic exchange consisting of one J_{Mn-Co} exchange integral between the impurity and its next Mn neighbours, the impurity modes frequencies were calculated in the Ising approximation [2, 7]. The desired energy levels are found by diagonalizing the Hamiltonian :

$$\mathcal{H} = \frac{J_0}{3}\mathbf{L}_{Co}.\mathbf{S}_{Co} - 2\,J_{Mn-Co} \times \left[S^z_{Mn} - \frac{25}{2}\right] S^z_{Co} - 25\,J_{Mn-Mn}\,S^z_{Mn}$$

on the set of functions $|\,\varphi_{iCo}> |\,S^z_{Mn}>$ where $|\,\varphi_{iCo}>$ is one of the 12 eigen functions which form a basis to describe the lower energy states derived from $^4\Gamma_4^+$, as studied by J. H. M. Thornley et al. [15].

J_{Mn-Co} was calculated assuming the pair mode to lie at 263 cm^{-1}. To evaluate J_{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 cm^{-1}), one finds

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

Moreover, a moderate variation of U does not drastically affect J_{Mn-Co} (it varies from -4.35 to -4.29 cm^{-1} when U increases from 300 to 400 cm^{-1}). The -4.31 cm^{-1} value leads to 208 cm^{-1} for the s_0 mode, which is closed to the hypothetically observed 211 cm^{-1} line (conversly this last value for s_0 gives $J_{Mn-Co} = -4.37$ cm^{-1} and a pair-mode frequency of 266.7 cm^{-1}). A 208 cm^{-1} frequency is slightly smaller than the 218 cm^{-1} one determined in $KMnF_3$-Co by neutron diffraction [4]. The same calcultion gives $J_{Mn-Co} = -4.54$ 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.

Notice that, using evaluations for $RbMnF_3$ [11] and $RbCoF_3$ [17] the semi-empirical law

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

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

Finally, although the model is rather poor for g calculations [2], it leads to $g_{s_0} = 3.73$ and $g_{PM} = 1.84$.

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_{4h} [20]. The different pair-modes are written $s_0 - s_1$, $s_0(p_x + ip_y)$, $s_0(p_x - ip_y)$, $s_0 - p_z$, $s_0 - d_{(3z^2-r^2)}$, $s_0 - d_{\sqrt{3}(x^2-y^2)}$ 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 Γ' to the permutation of the ions only (Γ' is immediately related to the notation of the modes). For the pair modes and for the ground state $\Gamma(S)$ is the same ($\Gamma(S) = \Gamma_8^+$). 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 Γ' only. The Raman active modes consist of $s_0 - s_1$, $s_0 - d_{(3z^2-r^2)}$, $s_0 - d_{\sqrt{3}(x^2-y^2)}$, but the $s_0 - s_1$ probably lies at lower frequencies [21] and is not observed. We are then left with $s_0 - d_{(3z^2-r^2)}$ and $s_0 - d_{\sqrt{3}(x^2-y^2)}$, which res-

pectively transform as Γ_1^+ and Γ_2^+ in C_{4h}. It follows from the low anisotropy that the symmetry is practically cubic. Hence $s_0 - d_{(3z^2-r^2)}$ and $s_0 - d_{\sqrt{3}(x^2-y^2)}$ are nearly degenerated in the representation Γ_3^+ of the cubic group O_h. The two corresponding components of the Raman tensors are [22] :

$$\begin{pmatrix} -b & 0 & 0 \\ 0 & -b & 0 \\ 0 & 0 & 2b \end{pmatrix} , \quad \begin{pmatrix} \sqrt{3}\,b & 0 & 0 \\ 0 & -\sqrt{3}\,b & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

Notice that the Γ_1^+ and Γ_2^+ Raman tensors in C_{4h} (if assumed symmetric) are respectively expressed as :

$$\begin{pmatrix} -b & 0 & 0 \\ 0 & -b & 0 \\ 0 & 0 & \alpha \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} \beta & \gamma & 0 \\ \gamma & -\beta & 0 \\ 0 & 0 & 0 \end{pmatrix} .$$

The conditions insuring the invariance of the sum of the intensities against the three possible domain orientation ares $\alpha = -b$, $\beta = \gamma = 0$ (Γ_1^+ in O_h) *or* $\alpha = 2b$, $\beta = \sqrt{3}\,b$, $\gamma = 0$ (Γ_3^+ in O_h). The experimental relative intensities impose the second one (a result which confirms that $s_0 - s_1$ is not observed !).

Finally we point out that similar arguments would work for $RbMnF_3$-Ni and $KMnF_3$-Ni which behave in the same way, although the direction of anisotropy is different.

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