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Inelastic scattering of light by magnetic excitons in the pseudo Ising antiferromagnets K_2CoF_4 and Rb_2CoF_4

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Résumé. — Outre l'effet Raman dû aux phonons, antérieurement signalé, nous observons la diffusion inélastique de la lumière liée aux excitons magnétiques dans K_2CoF_4 et Rb_2CoF_4 ; les spectres polarisés ont été étudiés à basse température en présence d'un champ magnétique pouvant atteindre 5 teslas environ. Nous interprétons les résultats au moyen d'un modèle multi-excitonique déduit d'un Hamiltonien tenant compte du couplage spin-orbite, du champ cristallin de basse symétrie et d'une interaction d'échange de type *Heisenberg*, perturbant l'état fondamental $^4\Gamma_4^+(O_h)$ des ions Co^{2+} . De l'étude de l'exciton de plus basse énergie, nous déduisons la valeur du champ cristallin quadratique Δ (-425 cm^{-1} et -635 cm^{-1} , respectivement pour K_2CoF_4 et Rb_2CoF_4) ainsi que celle du paramètre d'échange isotrope J ($-11,55\text{ cm}^{-1}$ et $-9,65\text{ cm}^{-1}$, respectivement pour K_2CoF_4 et Rb_2CoF_4). Le reste du spectre, qui contient des contributions à la diffusion par un et par deux excitons, est partiellement interprété, grâce au modèle ci-dessus décrit, pour les valeurs ainsi déterminées des paramètres Δ et J , dont il dépend. Les valeurs de J sont voisines de celles qui ont été antérieurement trouvées pour $KCoF_3$ et $RbCoF_3$, comme prévu. Le comportement de type *Ising*, qui provient du champ cristallin de basse symétrie, apparaît moins marqué lorsqu'on l'évalue à partir de la courbe de dispersion des magnons que ne le laissaient prévoir d'anciennes mesures magnétiques, résultat confirmé par une récente étude de diffusion inélastique de neutrons dans Rb_2CoF_4 .

Abstract. — In addition to previously reported phonon Raman scattering, we have observed inelastic light scattering by magnetic excitons in K_2CoF_4 and Rb_2CoF_4 ; the polarized spectra have been studied at low temperatures under an applied magnetic field up to about 5 teslas. The results are interpreted on the basis of a multilevel propagating exciton model deduced from a Hamiltonian including the single ion spin-orbit coupling, the low symmetry crystal field and a nearest neighbours *Heisenberg* exchange interaction, acting in the $^4\Gamma_4^+(O_h)$ ground state of Co^{2+} . From the lowest exciton study we derive a value of the tetragonal crystal field Δ (-425 cm^{-1} and -635 cm^{-1} , respectively in K_2CoF_4 and Rb_2CoF_4) and of the isotropic exchange parameter J (-11.55 cm^{-1} and -9.65 cm^{-1} , respectively in K_2CoF_4 and Rb_2CoF_4). The remaining features of the spectra, which include one and two exciton scattering, are partly interpreted using the above model with these values. The derived J values are close to previous determinations in $KCoF_3$ and $RbCoF_3$, as expected. The *Ising* character, which is caused by the low symmetry crystal field, is found to be less marked when evaluated from the magnon dispersion results than it was indicated by previous magnetic measurements, and this has been confirmed by recent inelastic neutron scattering data in Rb_2CoF_4 .

1. Introduction. — The study of magnetic excitations in cobaltous antiferromagnets has given rise to an abundant but rather controversial literature [1, 11].

The unquenching of the orbital momentum in the $^4\Gamma_4^+$ ground state of Co^{2+} provides a number of magnetic excitons, the description of which depends

upon the spin-orbit coupling, the low symmetry crystal field and the exchange interaction. Due to the orbital degeneracy this last term is expected to show a complex behaviour : various authors [12, 13] have proposed rather general forms for the exchange interactions including orbital effects ; a lot of independent constants are necessary, which considerably complicates the calculation of the magnetic excitons and hinders any convincing fit to the experimental data. On the other hand, several authors claim that a rather simple Heisenberg or Ising model provides a good agreement with experimental data [1, 2, 8, 11], while others [3, 10] find that such a model is only applicable to the lowest energy exciton.

In order to help to resolve this controversy we have performed electronic Raman scattering on K_2CoF_4 and Rb_2CoF_4 . These crystals are generally regarded as good examples of two-dimensional Ising antiferromagnets : such an assumption is mainly supported by magnetic susceptibility measurements [14, 15], which are essentially sensitive to the behaviour of the lowest Kramers doublet and do not drastically depend upon the precise form of the exchange interaction within the $^4\Gamma_4^+$ sublevels manifold. On the other hand, a direct spectroscopic investigation of several magnetic excitons is a rather severe test of the previously proposed exchange models [14, 16] based on a simple anisotropic Heisenberg Hamiltonian within $^4\Gamma_4^+$.

In the next section we briefly discuss the polarization selection rules for Raman scattering, derived from symmetry arguments, and we present the self-consistent excitonic models used. To a large extent, the symmetries of the magnetic excitons are independent of the models, but useful compatibility relations can be made, which help to evaluate their degree of validity. In section 3 we present the experimental data, which are discussed and interpreted in section 4.

2. Symmetries and excitonic models. — 2.1 SYMMETRIES AND SELECTION RULES. — In the paramagnetic state ($T > T_N$), K_2CoF_4 and Rb_2CoF_4 crystallize in the D_{4h} system. Below T_N (respectively 107 and 101 K in K_2CoF_4 and Rb_2CoF_4), they antiferromagnetically order with a sublattice magnetization parallel to Z (fig. 1), their crystal structure [15, 17, 18] being described by a $[D_{2h} + (\theta, t_0) D_{2h}]$ type IV Shubnikov space group : $C_A ccm$ (in the preceding notation, θ is the time inversion operator and t_0 a non primitive translation). Strictly speaking the fourfold symmetry around Z is destroyed ; however the crystal consists of very weakly magnetically coupled plane layers perpendicular to Z , which means that, practically, the fourfold symmetry does not disappear and that the crystals can be viewed as planar antiferromagnets described by a $[C_{4v} + (\theta, t_0) C_{4v}]$ type IV Shubnikov space group.

The Co^{2+} site unitary symmetry group changes

Fig. 1. — Magnetic unit cell of K_2CoF_4 and Rb_2CoF_4 .

from D_{4h} to C_{2h} when the crystals order antiferromagnetically but, in the above more realistic planar approximation, C_{2h} has to be replaced by C_4 . It is useful to introduce the C_{4h} site symmetry which would be involved in a mean field model (mean field parallel to Z) since our effectively used single ion Hamiltonian remains invariant under the C_{4h} symmetry operations (see below).

The $^4\Gamma_4^+$ ground state (in the cubic O_h symmetry approximation) is split into 6 Kramers doublets under the combined effect of the low symmetry tetragonal crystal field and spin-orbit coupling, in the paramagnetic phase where the Co^{2+} site symmetry is D_{4h} : the Kramers doublets belong to $[19] \Gamma_6^+(D_{4h})$ or $\Gamma_7^+(D_{4h})$. The mean field then splits each doublet into either $\Gamma_5^+(C_{4h})$ and $\Gamma_6^+(C_{4h})$ or $\Gamma_7^+(C_{4h})$ and $\Gamma_8^+(C_{4h})$ states. The lowering of the symmetry to C_{2h} or, more realistically, to C_4 allows a final classification of the single ion levels. The crystal magnetic excitons in D_{2h} or C_{4v} are then easily found using the Loudon method [20]. In the planar fourfold symmetry approximation each single ion transition induces a doubly degenerate exciton or a Davydov split pair, depending upon the representation of the

transition. The Raman polarization selection rules are ZX , XZ , ZY , YZ for the degenerate excitons while such polarizations are forbidden for Davydov pairs. The use of the exact in place of the approximate space group removes the equivalence of X and Y : the above mentioned degenerate excitons are split and the ZX and ZY polarizations are no longer equivalent. In the following we shall neglect this last effect which is probably very weak. On the other hand, we shall refer to the representations of D_{4h} rather than C_{4v} , in conformity with the effectively used Hamiltonian (see below) : the forms of the Raman tensors are not modified but, in the labelling of the exciton representations, the even parity is explicitly indicated.

2.2 EXCITONS. — The model uses a simple anisotropic Heisenberg Hamiltonian in order to describe the exchange interaction within $^4\Gamma_4^+$.

2.2.1 The mean field model. — The cubic crystal field splits the 4F free Co^{2+} ion ground state into three components $^4\Gamma_4^+$, $^4\Gamma_5^+$ and $^4\Gamma_2^+$, the lowest being $^4\Gamma_4^+$. The mean field substates are obtained by diagonalizing the following Hamiltonian within $^4\Gamma_4^+$:

$$\mathcal{H}_0 = \mathcal{H}_1 + \mathcal{H}_{MF} \quad (1)$$

where $\mathcal{H}_1$ is a single ion Hamiltonian describing the spin orbit coupling and the tetragonal crystal field :

$$\mathcal{H}_1 = \lambda \mathbf{L} \cdot \mathbf{S} + \Delta \left(L_z^2 - \frac{1}{3} L(L+1) \right) - \frac{15}{4} \frac{\lambda'^2}{U} [2(L_x^2 S_x^2 + L_y^2 S_y^2 + L_z^2 S_z^2) - (\mathbf{L} \cdot \mathbf{S})^2]. \quad (2)$$

Within $^4\Gamma_4^+$ the standard basis is defined by a set of twelve $|L, S, L_z, M_S\rangle$ functions where $S = 3/2$ and where the orbital part is generated by a pseudo $L=1$ angular momentum [21].

The first term in $\mathcal{H}_1$ is related to the first order spin-orbit coupling ; λ can be written as [21] :

$$\lambda = \alpha' \lambda' \quad (3)$$

where the α' coefficient takes into account the mixing of the 4F and 4P free ion states ; in the weak field limit (no mixing) it would be equal to -1.5 , while it is evaluated to be -1.42 from spectroscopic data in Co^{2+} complexes [21]. λ' is an effective spin-orbit coupling constant which is slightly smaller than the free ion value. $^4\Gamma_4^+$ interacts with $^4\Gamma_5^+$ through the spin-orbit coupling and the tetragonal crystal field. The resulting second order spin-orbit coupling has been shown by Kanamori [22] to take the effective form defined by the third term in $\mathcal{H}_1$ where U is the energy of $^4\Gamma_5^+$ above $^4\Gamma_4^+$ ($U = 8 D_q$ in the weak field limit). Finally the second term in $\mathcal{H}_1$ simultaneously takes into account the first order tetragonal crystal field effect and the remaining second order terms [23] (which act by renormalizing Δ).

$\mathcal{H}_{MF}$ is written as :

$$\mathcal{H}_{MF} = 2 z J_{\parallel} \langle S_z \rangle_0 S_z \quad (4)$$

where $2 J_{\parallel}$ is the (negative) Ising part of the exchange between two neighbouring antiferromagnetic ions in a plane layer and where $\langle S_z \rangle_0$ stands for the mean value of S_z in the ground state ; $z = 4$ is the number of antiferromagnetic neighbours.

For a given set of the constants involved in the expression of $\mathcal{H}_0$, a self-consistent diagonalization has to be performed : it gives rise to twelve sublevels (labelled p , from 0 to 11), whose representations in C_{4h} are easily found.

A magnetic field along Z induces a perturbation which is approximately written as :

$$\mathcal{H}_H = (\alpha' r L_z + 2 S_z) \mu_B H \quad (5)$$

where r is an orbital reduction factor taking into account the admixture of the $2p$ and $2s$ fluorine ligand orbitals in the Co^{2+} d orbitals [21] : its measured value, from spin resonance experiments in $KMgF_3$: Co is 0.93 . Under $\mathcal{H}_H$ the two sublattices no longer remain equivalent and, as a result, a splitting δW_p of each sublevel, is easily calculated to first order in H :

$$\delta W_p = \left(K_{Sp} \frac{2 - 8 \alpha' r J_{\parallel} K_{LS}}{1 + 8 J_{\parallel} K_S} + \alpha' r K_{Lp} \right) \times 2 \mu_B H \quad (6)$$

with :

$$K_{Sp} = \langle p | S_z | p \rangle, \quad K_{Lp} = \langle p | L_z | p \rangle$$

$$K_S = -2 \sum_{1 \leq q \leq 11} \frac{|\langle q | S_z | 0 \rangle|^2}{E_q};$$

$$K_{LS} = -2 \sum_{1 \leq q \leq 11} \frac{\langle 0 | S_z | q \rangle \langle q | L_z | 0 \rangle}{E_q}$$

where E_q is the energy of the state $|q\rangle$ above the ground state $|0\rangle$, in the absence of H .

Expression (6) allows an effective $g_{\parallel p}$ factor to be defined for each $|0\rangle \rightarrow |p\rangle$ transition :

$$g_{\parallel p} = (\delta W_p - \delta W_0) / 2 \mu_B H. \quad (7)$$

Finally we have used a mean field model [9] to evaluate the pair-mode frequencies : such a calculation is known to provide a good approximation for the position of the maximum of the two-magnon band (which involves the lowest excited states of two neighbouring ions). Its energy ε is roughly given by :

$$\varepsilon = 2(W_1'' - W_0') \quad (8)$$

where W_0' and W_1'' are respectively the ground and the first excited state energies of :

$$\mathcal{H}'_0 = \mathcal{H}_1 + (2z - 1) J_{\parallel} \langle S_z \rangle_0 S_z \quad (9)$$

and

$$\mathcal{H}_0'' = \mathcal{H}_1 + J_{\parallel} [2(z-1) \langle S_z \rangle_0 + \langle S_z \rangle_1] S_z. \quad (10)$$

In (10), $\langle S_z \rangle_1$ is the mean value of S_z in the first excited state.

2.2.2 Propagating excitons. — Starting from the single ion mean field levels, the propagating excitons are found using the following Hamiltonian :

$$\mathcal{H}_T = \sum_i \mathcal{H}_{1i} + \sum_{\bar{i}} \mathcal{H}_{1\bar{i}} - \sum_{\substack{i, \bar{i} \\ \text{(next neighbours)}}} 2(J_{\parallel} S_{zi} S_{z\bar{i}} + J_{\perp} (S_{xi} S_{x\bar{i}} + S_{yi} S_{y\bar{i}})) \quad (11)$$

where i and $\bar{i}$ respectively run over up and down sublattices and where the last summation is restricted to antiferromagnetic nearest neighbours. Each mean field excited state $|p\rangle$ gives rise to a degenerate

exciton if $|p\rangle$ belongs to $\Gamma_6^+(C_{4h})$ or $\Gamma_8^+(C_{4h})$ and gives rise to a Davydov (eventually split) pair if $|p\rangle$ belongs to $\Gamma_5^+(C_{4h})$ or $\Gamma_7^+(C_{4h})$: the perturbation to the mean field model is only due to $J_{\perp}$ for the degenerate excitons and to $J_{\parallel}$ for the Davydov pairs. As previously noticed, some physical properties have been successfully interpreted using a Heisenberg exchange interaction (which is described by eq. (11) when $J_{\perp} = J_{\parallel}$, while a pure Ising exchange within $4\Gamma_4^+$ implies $J_{\perp} = 0$) : the Ising-like properties are explained by the large value of Δ which leads to a large gap and a rather small dispersion of the lowest excitonic branch, even supposing an isotropic exchange. The question then arises whether a Heisenberg exchange still can account for the new experimental data in K_2CoF_4 and Rb_2CoF_4 .

The excitonic states are obtained using the pseudo-boson operator method described by Walker [24] and previously used by Buyers *et al.* for the study of $KCoF_3$ [1] and CoF_2 [2]. Introducing the operators :

$$a_{pi}^+ = |pi\rangle \langle oi| \quad \text{and} \quad a_{pi} = |oi\rangle \langle pi| \quad 1 \leq p \leq 11 \quad (12)$$

$$a_{p\bar{i}}^+ = |p\bar{i}\rangle \langle o\bar{i}| \quad \text{and} \quad a_{p\bar{i}} = |o\bar{i}\rangle \langle p\bar{i}|$$

which act on the single ion mean field states and satisfy $[a_{pi}, a_{pi}^+] = [a_{p\bar{i}}, a_{p\bar{i}}^+] = 1$ (the other commutators being 0), the Hamiltonian can be written, neglecting the 3rd and 4th order terms, as :

$$\begin{aligned} \mathcal{H}_T \simeq & \sum_{\substack{p \in \Gamma_7^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) \\ & + \sum_{\substack{p \in \Gamma_5^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) + 2J_{\parallel} \sum_{\substack{p, q \in \Gamma_5^+ \\ (i, \bar{i} : \text{next neighbours})}} S_Z^{op} S_Z^{oq} (a_{pi}^+ a_{q\bar{i}}^+ + a_{pi} a_{q\bar{i}} + a_{p\bar{i}}^+ a_{qi}^+ + a_{p\bar{i}} a_{qi}) \\ & + \sum_{\substack{p \in \Gamma_6^+ + \Gamma_8^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) - 2J_{\perp} \sum_{\substack{p, q \in \Gamma_6^+ + \Gamma_8^+ \\ (i, \bar{i} : \text{next neighbours})}} S_X^{op} S_X^{oq} [(1 + \varepsilon_p \varepsilon_q) (a_{pi}^+ a_{q\bar{i}}^+ + a_{pi} a_{q\bar{i}}) + (1 - \varepsilon_p \varepsilon_q) (a_{p\bar{i}}^+ a_{qi}^+ + a_{p\bar{i}} a_{qi})] \end{aligned} \quad (13)$$

where :

$$S_Z^{op} = \langle oi | S_z | pi \rangle,$$

$$S_X^{op} = \langle oi | S_x | pi \rangle$$

and $\varepsilon_p = \pm 1$ ($S_Y^{op} (= \langle oi | S_y | pi \rangle)$ and S_X^{op} have the same modulus but, depending upon the state $|p\rangle$, their arguments differ by $+\pi/2$ or $-\pi/2$, which leads to $\varepsilon_p = \pm 1$).

The Hamiltonian (13) is diagonalized with the help of a Fourier development followed by a linear transformation, as described in reference [1]. It is

easily seen from eq. (13) that the diagonalization can be performed separately for the degenerate excitons and for the Davydov pairs. Moreover the specific form of $\mathcal{H}_1$ does not induce any shift or splitting for the excitons related to the $p \in \Gamma_7^+$ mean field states : actually they have not to be regarded as forming a Davydov pair and they behave in the same way as mean field states.

For a further discussion it is of interest to compare the above model with the simplified one [5, 7] where the interaction between excited levels is neglected, i.e. :

$$\begin{aligned} \mathcal{H}_T \sim & \sum_{\substack{p \in \Gamma_7^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) \\ & + \sum_{\substack{p \in \Gamma_5^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) + 2J_{\parallel} \sum_{\substack{p \in \Gamma_5^+ \\ (i, \bar{i} : \text{next neighbours})}} S_Z^{p^2} (a_{pi}^+ a_{p\bar{i}}^+ + a_{pi} a_{p\bar{i}} + a_{p\bar{i}}^+ a_{pi} + a_{pi} a_{p\bar{i}}) \quad (14) \\ & + \sum_{\substack{p \in \Gamma_6^+ + \Gamma_8^+ \\ i, \bar{i}}} E_p (a_{pi}^+ a_{pi} + a_{p\bar{i}}^+ a_{p\bar{i}}) - 4J_{\perp} \sum_{\substack{p \in \Gamma_6^+ + \Gamma_8^+ \\ (i, \bar{i} : \text{next neighbours})}} S_X^{p^2} (a_{pi}^+ a_{p\bar{i}}^+ + a_{pi} a_{p\bar{i}}). \end{aligned}$$

The dispersion formula resulting from eq. (14) are given by :

$$E_p(\mathbf{k}) = E_p \quad \text{if} \quad |p\rangle \in \Gamma_7^+ \quad (15a)$$

$$E_p^\pm(\mathbf{k}) = E_p(1 \pm (4 z J_{\parallel} S_Z^{op^2} \gamma_{\mathbf{k}})/E_p)^{1/2} \quad \text{if} \quad |p\rangle \in \Gamma_5^+ \quad (15b)$$

$$E_p(\mathbf{k}) = E_p(1 - ((4 z J_{\perp} S_X^{op^2} \gamma_{\mathbf{k}})/E_p)^2)^{1/2} \quad \text{if} \quad |p\rangle \in \Gamma_6^+ \text{ or } \Gamma_8^+ \quad (15c)$$

with : $\gamma_{\mathbf{k}} = \cos(ak_X) \cos(ak_Y)$ (a : distance between 2 antiferromagnetic neighbours).

As shown in section 4, for the used values of the constants, expressions (15b) and (15c) do not much differ from the results that we obtained from an exact diagonalization of eq. (13). On the other hand, for these values, the lowest exciton is degenerate and an immediate comparison can be made between its dispersion given by eq. (15c) (for $p = 1$ in this case) and the corresponding expression using a spin 1/2 model : Breed *et al.* [15] interpret the magnetic properties of K_2CoF_4 and Rb_2CoF_4 using the following effective spin 1/2 Hamiltonian :

$$h = - \sum_{i,i'} (2 j_{\parallel} s_{Zi} s_{Zi'} + 2 j_{\perp} (s_{Xi} s_{Xi'} + s_{Yi} s_{Yi'})) \quad (16)$$

(next neighbours)

The spin-wave spectrum derived from (16) is given by :

$$e(\mathbf{k}) = - z j_{\parallel} \left(1 - \left(\frac{j_{\perp}}{j_{\parallel}} \gamma_{\mathbf{k}} \right)^2 \right)^{1/2} \quad (17)$$

$e(\mathbf{k})$ has the same form as $E_1(\mathbf{k})$ if one chooses :

$$j_{\parallel} = - E_1/z \quad (18a)$$

$$j_{\perp} = 4 J_{\perp} S_X^{012}. \quad (18b)$$

Moreover, we found that the exact dispersion law for the lowest degenerate exciton obtained by diagonalizing eq. (13) can be written in the form of eq. (17) but the derivation of $j_{\perp}$ is no longer given by eq. (18b). Finally the effect of a magnetic field applied along the Z axis can be calculated using the self-consistently modified mean field states which form a new basis where the two sublattices are no longer equivalent. The diagonalization is substantially simplified if one neglects the interaction between excited mean field levels of different p : to first order in H , it is easily shown that the degenerate excitons are split exactly in the way predicted by the mean field model (expressions (6) and (7)) ; indeed, this result is no longer true for the Davydov pairs which show a shift quadratic in H , at least when $\mu_B H$ is small compared to the $H = 0$ Davydov splitting. As discussed in the following sections, our experimental data in a magnetic field only concern the degenerate excitons ; as long as, for $H = 0$, the simplified excitonic model of eq. (14) and the more exact one of eq. (13) do not too markedly differ, we believe that the mean field $g_{\parallel}$ values provide a sufficiently good approximation,

and we used these values to fit our results. Notice that a more precise evaluation involving a complete diagonalization in presence of H is slightly tedious but not difficult, but due to the limited experimental precision we assumed, at least as a first step, that it was not necessary.

3. Experimental results. — 3.1 EXPERIMENTAL SET UP. — The crystals were grown by a modified Bridgman technique and were of good optical quality. The samples used were cut into rectangular parallelepipeds with one pair of faces perpendicular to the Z fourfold axis and the two others respectively perpendicular to the X and Y twofold axes. Table I summarizes the polarizations which were studied using two different settings, each with a right angle scattering geometry arrangement. As pointed out in the preceding section, the reference group for the corresponding symmetries of the observed excitations is D_{4h} , which is the most convenient and which nearly exactly describes the physical situation.

Most of the spectra were observed with samples immersed in superfluid Helium : the effective tempe-

Table I. — Observed polarization and symmetry representations in D_{4h} ($Z//C_4$; $X, Y//C_2$).

Spectrum	Symmetry	Spectrum	Symmetry
1st setting		2nd setting	
$X(ZX) Y$	Γ_5^+	$X(ZY) Z$	Γ_5^+
$X(YX) Y$	Γ_2^+, Γ_4^+	$X(YY) Z$	Γ_1^+, Γ_3^+
$X(YZ) Y$	Γ_5^+	$X(YX) Z$	Γ_2^+, Γ_4^+
$X(ZZ) Y$	Γ_1^+	$X(ZX) Z$	Γ_5^+

Raman tensors in D_{4h} , with the same reference axes as above :

$$\begin{array}{ccc}
 \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix} & \begin{bmatrix} 0 & c & 0 \\ -c & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} & \begin{bmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{bmatrix} \\
 \Gamma_1^+ & \Gamma_2^+ \text{ (antisymmetric)} & \Gamma_3^+ \\
 \\
 \begin{bmatrix} 0 & e & 0 \\ e & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 0 & f \\ 0 & 0 & 0 \\ g & 0 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & g & 0 \end{bmatrix} \\
 \Gamma_4^+ \text{ (symmetric)} & \underbrace{\hspace{10em}} & \Gamma_5^+
 \end{array}$$

Table II. — *Raman lines in K_2CoF_4 near liquid Helium temperature. H is the applied magnetic field, γ is the width at half-maximum (vw : very weak ; w : weak ; ms : medium strong ; s : strong ; vs : very strong. There are roughly three orders of magnitude between vw and vs).*

Position (cm^{-1})	Intensity, width : γ (cm^{-1})	Polarization	Observations	Symmetry
108	s, $\gamma = 3$	ZX, ZY	phonon	Γ_5^+
154	s, $\gamma = 3$	ZX, ZY	phonon	Γ_5^+
163.5	vw, $\gamma = 2$	ZX, ZY	split by H	Γ_5^+
184	s, $\gamma = 3$	ZZ	phonon	Γ_1^+
207	ms, $\gamma = 3$	ZX, ZY	split by H	Γ_5^+
314	vw	ZX, ZY		Γ_5^+
335	s, $\gamma = 3$	ZZ		Γ_1^+
355	shoulder			
374	vs	ZZ	phonon	Γ_1^+
407	broad band vs	major component ZZ		Γ_1^+
426				
445				
465	vw			
555				
565	w			
592	ms	ZZ		Γ_1^+
716	w	XY		
729	vs, $\gamma = 40$	ZZ		Γ_1^+
1180	w	ZZ		Γ_1

perature of the scattering volume was estimated to lie around a few K. Some studies of their temperature dependence were performed using an exchange gas cryostat in the 5-300 K temperature range. A magnetic field up to 4.8 teslas, parallel to the studied scattering direction, was available for the low temperature measurements.

Absorption is severe in the visible and useful spectra could be obtained principally with the 4 579 Å and 4 765 Å Argon laser lines (~ 500 mW) and the 6 471 Å Krypton laser line (~ 300 mW). For all the lines used the absorption is stronger when the polarization is perpendicular to Z : the experimental intensity is then significantly lower when the incident light is polarized along X and Y . A Coderg T800 monochromator with a photon counting detection was used to analyse the scattered light. For some lines the weak intensities prevented polarization selection rules to be studied.

3.2 RESULTS. — Besides the 4 known phonon lines [25], which are slightly shifted and sharpened, we observed new features at low temperatures. The complete results are listed in table II and table III, respectively for K_2CoF_4 and Rb_2CoF_4 .

Figure 2 displays a representative spectrum, for a wide wave-number range scan in K_2CoF_4 . The major new features are three sharp and rather intense lines at 163.5 cm^{-1} (Γ_5^+ i.e. : ZX, ZY, XZ, YZ), 207 cm^{-1} (Γ_5^+) and 335 cm^{-1} (Γ_1^+ : ZZ) and two broad bands around 460 and $1\,180\text{ cm}^{-1}$; in addition

Table III. — *Raman lines observed in Rb_2CoF_4 near liquid Helium temperature. H is the applied magnetic field.*

Positions (cm^{-1})	Observations	Symmetry
80	phonon ZX, ZY	Γ_5^+
124	phonon ZZ	Γ_1^+
155	ZX, ZY split by H	Γ_5^+
171	phonon ZX, ZY	Γ_5^+
178	ZX, ZY split by H	Γ_5^+
209	complex shape split by H	Γ_5^+
213		
332	ZZ	Γ_1^+
360	phonon ZZ	Γ_1^+
450	Broad band	
920		
1067		

we observed two sharp Γ_1^+ lines in the high frequency range (716 cm^{-1} , $1\,417\text{ cm}^{-1}$) and a weak XY line at 729 cm^{-1} . A magnetic field H parallel to Z linear-

Fig. 2. — A typical scan of the Raman spectrum of K_2CoF_4 on a wide wave-number range ($T \sim 2$ K).

ly splits the 163.5 and 207 cm^{-1} peaks, allowing an effective $g_{\parallel}$ factor to be defined (table IV), while it does not affect the remaining spectrum in a measurable way. Figure 3 shows the splitting of the 207 cm^{-1} line by H . As expected from the high anisotropy along Z , which predicts very small quadratic shifts when H is perpendicular to Z , we observed that H has no effect in this case.

Table IV. — Experimental $g_{\parallel}$ values for the lines split by a magnetic field.

Crystal	ω (cm^{-1})	$g_{\parallel} = \delta\omega/2\mu_B H$
K_2CoF_4	163.5	3.9
	207	3.7
Rb_2CoF_4	155	5
	179	1.4
	209	4.45
	213

Fig. 3. — Splitting of the 207 cm^{-1} Γ_s^+ line in K_2CoF_4 in a magnetic field parallel to Z .

In Rb_2CoF_4 the low frequency spectrum shows four new lines, three of them (155 , 178 , 213 cm^{-1}) being linearly split by a magnetic field parallel to Z and showing Γ_s^+ symmetry, while the fourth (322 cm^{-1}) is unsplit and has a Γ_1^+ behaviour. Here again a high frequency broad spectrum also exists.

The 213 cm^{-1} line presents a complex shape, with a shoulder at 209 cm^{-1} , which may indicate the existence of two neighbouring peaks ; however this shape is apparently unmodified under the magnetic field splitting (fig. 4) and, due to this apparent rigidity, we analyzed it as consisting of a single line. In contrast with the case of K_2CoF_4 , the precision for the $g_{\parallel}$ factors is poor in Rb_2CoF_4 (table IV) : the 155 and 178 cm^{-1} peaks lie very near to an intense phonon line, and precise position measurements cannot be made ; the complex shape of the 213 cm^{-1} also prevents precise evaluations being made.

Fig. 4. — Splitting of the 213 cm^{-1} Γ_s^+ line in Rb_2CoF_4 in a magnetic field parallel to Z . Notice the complex shape with a shoulder at 209 cm^{-1} .

When increasing the temperature up to around T_N , the low frequency spectrum (below about 350 cm^{-1}) broadens and disappears in both compounds, which proves that it is related to the magnetic ordering. In the high frequency range some broad band scattering persists, but it is difficult to analyse quantitatively.

4. Interpretation. — Due to their general properties it is clear that most of the new reported features are related to electronic Raman scattering by magnetic excitons. An attempt to give a very precise quantitative account of the high frequency spectrum (500 cm^{-1} and above) is known to be unrealistic in Co fluorides [7, 9, 10] partly because most of the lines are rather broad, which prevents precise measurements, especially when neighbouring features overlap, partly because it is difficult to separate the pair-excitation contributions (two-phonon and two-magnon spectra) from the single excitation ones. On the other hand, in the upper levels the frequencies are mainly monitored

by the spin-orbit and the low symmetry crystal field constants and an attempt to derive a reasonably precise determination of the exchange from their study would then be hopeless. We found it more efficient to focus on the low frequency spectrum, which is generally better understood, and to derive adequate constants in order to incorporate them in the Hamiltonian of the system ; in a further step it would be of interest to compare our high frequency spectrum with the predictions resulting from the diagonalization of this Hamiltonian.

At first glance, the 163.5 and 207 cm⁻¹ lines in K₂CoF₄ would have to be identified with the two lowest Γ_5^+ degenerate excitons : however it is not possible to find any reasonable set of values for Δ , A , $J_{\parallel}$, $J_{\perp}$... which provides good or even approximative fits to our experimental frequency and $g_{\parallel}$ values. The situation is worse in Rb₂CoF₄ where, in the same spirit, one could be tempted to attribute the three lowest lines (155, 178 and 213 cm⁻¹) to the three lowest Γ_5^+ degenerate excitons. From previously published data concerning magnetic properties [14, 15], we expected that, in both crystals, the lowest Γ_5^+ branch lies around 200 cm⁻¹, rather well below the other excitons. On the other hand, in K₂CoF₄ the 207 cm⁻¹ line shows an intensity stronger than that at 163.5 cm⁻¹, and in Rb₂CoF₄ the 213 cm⁻¹ line is the most intense among the three Γ_5^+ peaks : we then assumed that the 207 cm⁻¹ and 213 cm⁻¹ lines correspond to the lowest $\mathbf{k} = \mathbf{0}$ Γ_5^+ exciton respectively in K₂CoF₄ and Rb₂CoF₄. We were definitely convinced of the adequacy of this choice by the recently published inelastic neutron scattering measurements in Rb₂CoF₄ [4] which provide for the $\mathbf{k} = \mathbf{0}$ lowest exciton frequency a 206 ± 6 cm⁻¹ value, which is near our 213 cm⁻¹ measured value. Notice that, due to the better precision of optical spectroscopy measurements (± 0.3 cm⁻¹), the 213 cm⁻¹ determination appears to be the best one ; however, as mentioned above, the complex shape of the line, does not enable the exact value of the frequency to be established : in any case it is not lower than 209 cm⁻¹ ; such a 4 cm⁻¹ shift would not significantly change the following conclusions.

The game to play is now to find the parameters which provide a 207 cm⁻¹ frequency with a $g_{\parallel} = 3.7$ value in K₂CoF₄ and a 213 cm⁻¹ frequency with a $g_{\parallel} = 4.45$ value in Rb₂CoF₄ for the lowest $\mathbf{k} = \mathbf{0}$ Γ_5^+ exciton. The A , α' and U constants appearing in eqs. (2), (3) and (5) show nearly identical values in different cobaltous compounds, provided that the Co²⁺ environment is a pseudo-cubic fluorine octahedron : following Thornley [21], Buyers [1] and others, we then took : $A = 228$ cm⁻¹, $\alpha' = -1.42$ (and $\lambda' = -160$ cm⁻¹), $r = 0.93$, $U = 7500$ cm⁻¹. Since an Heisenberg interaction is often expected to provide a good approximate description of the exchange, we chose a fit with $J_{\perp} = J_{\parallel} = J$.

For each compound we are then left with two parameters Δ (or, most conveniently, for further comparisons, Δ/A) and J in order to fit two experimental results : the frequency and the $g_{\parallel}$ value of the $\mathbf{k} = \mathbf{0}$ lowest exciton. This was done using the model developed in section 2.

The method is shown on figure 5 in the case of K₂CoF₄. Fixing the lowest exciton frequency at 207 cm⁻¹ induces a relation between J and Δ : we have then reported graphically J as a function of Δ/A . Due to this relation between J and Δ/A , $g_{\parallel}$ can now be evaluated as a function of Δ/A only : the value of Δ/A corresponds to $g_{\parallel} = 3.7$. From figure 5, one immediately derives J and Δ/A . We have also reported on figure 5 the dispersion δ of the exciton, defined as the ratio of the difference between the Brillouin zone boundary and the $\mathbf{k} = \mathbf{0}$ frequencies to the Brillouin zone boundary frequency (which, in our model, is identified with the mean field value).

The results are reported in table V and are compared with other determinations. For K₂CoF₄ we find

$$\Delta/A = -1.86 \quad \text{and} \quad J = -11.55 \text{ cm}^{-1},$$

which lead to $\delta = 0.175$. In Rb₂CoF₄ we obtain :

$$\Delta/A = -2.78 \quad \text{and} \quad J = -9.65 \text{ cm}^{-1},$$

which give $\delta = 0.105$. In the case of Rb₂CoF₄ our calculated δ value allows a direct comparison to be made with the inelastic neutron scattering measurements of Ikeda and Hutchings [4] : we predict a 239 cm⁻¹ zone boundary frequency in good agreement with their 250 ± 8 cm⁻¹ direct experimental determination. Using eq. (17) we find that the $j_{\parallel}$ and $j_{\perp}$ parameters adequate for a spin 1/2 description are :

$$j_{\parallel} = -E_1(\mathbf{0})/4(1 - \delta) \quad (19a)$$

$$j_{\perp} = -\frac{\sqrt{\delta(2 - \delta)}}{4(1 - \delta)} E_1(\mathbf{0}) \quad (19b)$$

Fig. 5. — Variations of J , $g_{\parallel}$ and δ , as functions of Δ/A when assuming a 207 cm⁻¹ value for the lowest $\mathbf{k} = \mathbf{0}$ exciton frequency. From $g_{\parallel} = 3.7$ one immediately graphically derives Δ/A , J and δ .

Table V. — Comparative table of relevant quantities in K_2CoF_4 and Rb_2CoF_4 .

	Λ (cm^{-1})	Δ/Λ	J (cm^{-1})	$j_{ }$	$j_{\perp}$	$j_{\perp}/j_{ }$	$E_1(k=0)$ (cm^{-1}) meas. calc.	δ % meas. calc.	$g_{ }$ meas. calc.
Folen (14) et al K_2CoF_4	-243	-2.04	-12.5	-69.2 *			230 *	17 *	3.7 *
Breed (15) K_2CoF_4 et al Rb_2CoF_4			-13.4	-67.4	-20.6	0.31		3 *	
			-10.5	-63.2	-14.5	0.23			
Ikeda (4) Rb_2CoF_4 and Hutchings				-62.1	-34.2	0.55	205.6	17	
Present K_2CoF_4 work Rb_2CoF_4	-228	-1.86	-11.55	-62.8	-35.5	0.57	207	17,5	3.7
	-228	-2.78	-9.65	-59.6	-26.6	0.45	213	10,5	4.45

* from our calculations

where $E_1(0)$ is the exciton frequency at $\mathbf{k} = 0$ (respectively 207 and 213 cm^{-1} for K_2CoF_4 and Rb_2CoF_4). Our $j_{||}$ determination agrees rather well with the Breed *et al.* value [15], based on susceptibility measurements but our $j_{\perp}$ determination is significantly higher, which means that the Ising behaviour is less marked for the excitation spectrum than for the susceptibility measurements or for the magnetic transition temperature. It is to be noticed that eq. (13) does not take into account the Oguchi's quantum corrections [26], which appear in the normal ordering of the neglected four operator interactions : generally their main effect is to renormalize the exchange interaction by about 5 %. So, we do not think that neglecting these corrections could have major effects upon the Ising character. Anyway our predictions concerning the dispersion agree well with the inelastic scattering measurements in the case of Rb_2CoF_4 , which is a sufficient experimental justification.

Our calculations shows that in order to relate $j_{||}$ and $j_{\perp}$ to J and Δ/Λ it is important to exactly diagonalize eq. (13) : the use of the simplified model of eq. (14) would lead to significantly different determinations for $j_{||}$ and $j_{\perp}$. In the J and Δ/Λ studied range the excited levels interaction, included in eq. (13), reduces the effective Ising character (as measured by $j_{\perp}/j_{||}$).

Coming back to our determination of J we find values which do not much differ from the observed ones in $KCoF_3$ [1, 9] and $RbCoF_3$ [8] (respectively $-10.6 cm^{-1}$ and $-8.9 cm^{-1}$) : since the super-exchange is mediated in the same way through a 180° fluorine bridge, the J values are expected to be about the same.

In table VI we have listed all the excitonic levels, as calculated from the model using the above discussed parameters ; the useful representations as well

as the polarization selection rules are indicated. The dispersion of the excitons against $\gamma(\mathbf{k})$ is drawn : indeed, the frequencies for $\gamma(\mathbf{k}) = 1$ are those of the mean field model. We have also reported the single ion energy levels resulting from $\mathcal{H}_1(D_{4h})$. As usual [1, 2], only the low frequency excitons show a non negligible dispersion and the mean field model can be used without loss of precision for the high energy excitons.

An attempt to account for the experimental high frequency spectrum using our model is only moderately satisfactory : in K_2CoF_4 the four components broad band around 460 cm^{-1} (table II) is related to the excitons arising from the $p = 2, 3$ and 4 mean field levels (table VI), while the 1180 cm^{-1} wide band is probably connected with the $p = 8$ and 9 mean field levels. In addition, the two-magnon peak maximum is predicted from eq. (8) to lie at 432 cm^{-1} , while its cut-off frequency is 500 cm^{-1} : the 460 cm^{-1} band, which, in fact, extends from 405 to 500 cm^{-1} , then certainly contains a two-magnon contribution, which is always present in such antiferromagnets [7, 9, 11]. While on the basis of frequency considerations the 716 and 1417 cm^{-1} lines could be attributed respectively to $p = 6$ and $p = 11$, we do not retain such an assignment since it would disagree with the observed polarization selection rules. In Rb_2CoF_4 , due to the poor quality of the high frequency observed spectra, we prefer to delay any attribution.

The above general analysis would finally be considered as successful if it completely explains the low frequency spectrum. Unfortunately in K_2CoF_4 our model is unable to give account of the Γ_5^+ 163.5 line and of the Γ_1^+ 335 cm^{-1} one ; in Rb_2CoF_4 , the 155 cm^{-1} and 178 cm^{-1} Γ_5^+ lines remain to be interpreted as well as the rather intense 332 cm^{-1} Γ_1^+ peak. The attribution of the Γ_1^+ lines to two-

Table VI. — *Kramers doublets, single ion mean field levels and excitons in K_2CoF_4 and Rb_2CoF_4 ($\Delta/A = -1.86$ and -2.78 respectively; $J = -11.55 \text{ cm}^{-1}$ and -9.65 cm^{-1} respectively). Level energies are in cm^{-1} ; (s) : symmetric; (a) : antisymmetric; BZB : Brillouin Zone Boundary.*

magnon scattering has probably to be rejected, due to the sharpness of the corresponding peaks which would not occur in a two-magnon process; on the other hand, an approximate evaluation of the two-magnon peak maximum position provides a value of 432 cm^{-1} and of 403 cm^{-1} , respectively for K_2CoF_4 and Rb_2CoF_4 , which is too high for such an attribution. The unexplained low frequency lines, could also derive from the doubling of the nuclear cell below the magnetic ordering temperature: strictly speaking, the nuclear Brillouin zone boundary phonons along $\mathbf{k} = \langle 1, 1, 0 \rangle$ are $\mathbf{k} = \mathbf{0}$ phonons when using the magnetic unit cell, and they could eventually give rise to Raman features. Such processes have been observed especially in Co compounds [1, 27]. However the intensity is non negligible only in the case of a strong exciton-phonon coupling, which supposes that the exciton and the phonon frequencies lie near to each other. Even if we do not disregard such an hypothesis, we would be surprised if it occurred for two or even three different phonon branches. Especially, the spectacular *electronic* character of the Γ_5^+ lines, attested by their large $g_{\parallel}$ values, implies a coupling to excitons much more efficient than the previously observed ones, in CoF_2 [7, 28] for instance.

The most probable hypothesis is that the unex-

plained lines are related to impurity modes: it is clear that such a vague attribution needs further analysis but we are not surprised of such occurrences and we have some experiment of impurity modes showing a unusually (and unexplained) high intensity in $RbMnF_3$ and $KMnF_3$.

In view of the remaining difficulties a pessimistic attitude would lead to reject completely the model, taking argument of the occurrence of complex exchange, which is expected in the difficult case of an unquenched orbital momentum [12, 13] in the $^4\Gamma_4^+$ ground state of Co^{2+} . We disagree with such an extreme position: our determinations on the basis of one exchange constant within $^4\Gamma_4^+$ are well consistent with all the other data available for the observed crystals. It has been shown for many other cobaltous compounds that, at least if one does not try to give account of the high energy excitons very precisely, such a model provides a good description of the magnetic properties. Finally our J determinations are consistent with the values reported for crystals where the exchange is expected to show approximately the same value.

NOTE ADDED IN PROOF. — In a recent letter [29], F. Macco *et al.* reported new Raman data in K_2CoF_4 .

Except for a few minor features, we agree with their results and with their assignment of the 206.5 cm^{-1} line as the one-magnon peak. We think that our experimental study, which deals also with Rb_2CoF_4 and which includes the dependence on magnetic

field, as well as our analysis, confirms and supplements these preliminary measurements.

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