

Theoretical model for the Raman scattering by localized and magnon modes in mixed transition-metal fluorides

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The low-energy magnetic excitations due to an impurity embedded in a magnetic structure are analyzed. We propose a model dealing separately with the Raman intensities scattered by the localized and the propagating modes. In fact the spin-orbit coupling is responsible for this inelastic interaction with the light but the real problem is the following: the magnon modes which are not observed in the pure crystal become largely activated when there is an impurity with spin-orbit coupling in the ground state. A complete description of the ground state of the Co^{2+} impurity in a rutile structure is given. The wave functions of the two types of excited states in the structure due to the impurity are also calculated. The Raman coupling takes place on the impurity sites and the intensities of each of the two processes are expressed and their ratio analyzed. The model uses a Green's-function formalism, the impurity concentration is assumed to be small, and the basic physical hypothesis is about the noninteraction between the impurities.

I. INTRODUCTION

The low-energy magnons perturbed by the presence of an impurity embedded in a magnetic structure are a very interesting problem illustrated in many experimental results by neutron scattering,¹⁻³ by NMR (Ref. 4), fluorescence,⁵ spectroscopy,^{6,7} and inelastic scattering of light.⁸⁻¹¹ They are also analyzed in theoretical results.^{12,13} Here, we are dealing, in detail, with the case of a transition-metal fluoride (an antiferromagnetic insulator MnF_2). We work out, by considering a typical impurity (Co^{2+} ion), a theoretical model for the description of the inelastic scattering of light. We are essentially interested in the formulation of the Raman intensities of two kinds of scattered modes: the localized ones, which are bound to the impurities; and the spin-wave ones, which are modified by the presence of the impurity in the structure. We have chosen an example ($\text{Mn}_{1-c}\text{F}_2\text{Co}_c$) in which the spin waves do not interact with light in the pure crystal MnF_2 , but which are so activated by Co^{2+} impurities that they give rise to a scattered intensity which can be of the same order of magnitude as the intensity scattered by the localized modes. It is reasonable to suppose that our model could be extended to other mixed crystals. Other previous calculations,¹⁴ some of them using the coherent potential approximation,^{15,16} are well adapted to a description of the case of large impurity concentration; they justify the enhancement of the magnon band and the position of the rays,¹⁷ but they do not permit a detailed description of local phenomena. So we make the opposite assumption of very small impurity concentration and we try to give an analytic description of the Raman scattering intensities.

In the first part we deal with the impurity Co^{2+} itself, as an isolated one in a nonmagnetic rutile crystal. We calculate its quantum structure, taking into account the fact that in this compound the chemical bonding has essentially a ionic character; the whole surrounding of the Co^{2+}

ion can be treated as a crystal field. To describe the electronic states in a simple model, we have made successively several assumptions. The first one is about the $3d^7$ configuration of the free ion. In fact, we have neglected the interaction between this configuration and the excited ones, the energies of which are about 10^5 cm^{-1} higher.¹⁸ In the same way, to take into account the influence of the 4P term on the ground 4F term, following previous authors,^{19,20} we describe it by a method of effective operator. Lastly we treat, as a small perturbation of the cubic crystal field, the small distortions of lower symmetry, as is shown in the energy diagram²¹ of Fig. 1. We finally build the electronic ground-state wave function and we calculate the different components of the Raman tensor in the dipolar electric approximation. For each transition we analyze their dependence on spin-orbit coupling and crystal field. We conclude by comparison with some experimental data.²²

In the second part, we are interested in the effect of an impurity on the spin waves of the magnetic matrix in which it is embedded. We have calculated in detail the effect of an impurity on the spin waves of a ferromagnetic matrix in which it is embedded. Actually the phenomena we are interested in has been observed in antiferromagnetic compounds. But to avoid the complexities due to the lack of knowledge of the ground antiferromagnetic state,²³ we did our calculations on a ferromagnetic model. It is reasonable to think that the comparison between the contribution to the Raman intensities of the localized and the nonlocalized modes is not affected much by the true nature of the ground state. There is no serious reason to suppose that the existence of the double degeneracy of the magnon bands in an antiferromagnetic should affect the essential features of our results concerning this comparison. At first, we calculate the excited wave functions of the crystal both for localized modes and the spin waves perturbed by the impurities. Secondly, we calculate separately the Raman intensities scattered by these two

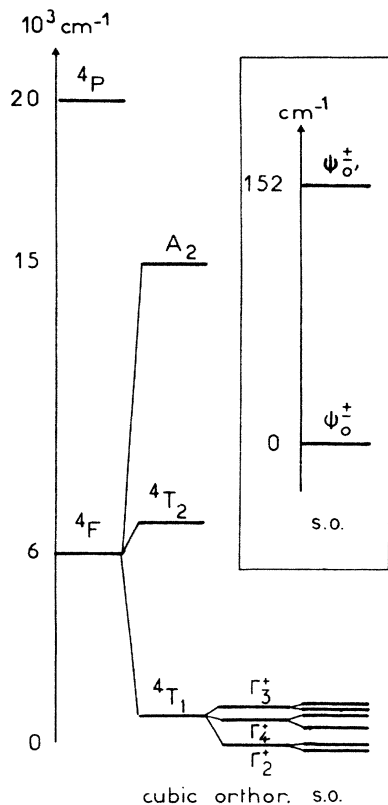


FIG. 1. Splitting of the 4F term by the cubic crystal field.

kinds of modes, in order to compare their magnitudes. When the impurity concentration is small, we can consider each one of the impurities as noninteracting with the others and the total intensity scattered by the localized modes is proportional to the concentration. On the other hand, the intensity scattered by the magnon modes, activated by the impurities, is proportional to the square of the concentration of impurities. When the energies of the localized modes are not too far from the edge of the energy band of the pure crystal, the intensities scattered by the two kinds of modes can be of the same order of magnitude. Thus our model explains why, in that case, one observes^{22,24} the Raman scattering of light by the spin waves of the matrix as well as by the localized modes.

II. RAMAN TENSOR

In the electric dipolar approximation the probability of a Raman transition between two electronic states, described by the wave functions Φ_i and Φ_f , is given by the well-known formula

$$T_{if} = \sum_{m \neq i, f} \left[\frac{\langle \Phi_f | \hat{\mathbf{e}}_2 \cdot \hat{\mathbf{P}} | \Phi_m \rangle \langle \Phi_m | \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{P}} | \Phi_i \rangle}{E_m - E_i - \hbar\omega_1} + \frac{\langle \Phi_f | \hat{\mathbf{e}}_1 \cdot \hat{\mathbf{P}} | \Phi_m \rangle \langle \Phi_m | \hat{\mathbf{e}}_2 \cdot \hat{\mathbf{P}} | \Phi_i \rangle}{E_m - E_i + \hbar\omega_2} \right], \quad (2.1)$$

where the summation runs over the complete set of intermediate electronic states Φ_m of the many-electron system. $\hat{\mathbf{P}} = \hat{\mathbf{P}}_j$, with $\hat{\mathbf{P}}_j$ the moment operator of the j th electron; $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are the unit vectors giving the polarization of the electromagnetic field (1 for incident, 2 for scattered). E_i , $E_f = E_i + \hbar(\omega_1 - \omega_2)$, and E_m are the energies associated with the Φ_i , Φ_f , and Φ_m states. When the transitions take place between two sublevels of the ground state, $\hbar(\omega_1 - \omega_2) \ll E_m - E_i$, we write $\omega_1 \simeq \omega_2 = \omega$, and T_{if} can be expressed as the sum of a symmetrical part S_{if} and an antisymmetrical one A_{if} : We have to calculate Φ_i and Φ_f and the matrix elements of the dipolar operator connecting them to the intermediate states Φ_m .

A. Electronic wave functions Φ_i and Φ_f for the Co^{2+} ion in a rutile diamagnetic matrix

As we have shown in a previous paper,²⁵ Φ_i and Φ_f are the sublevels of the 4F ground state of the $3d^7$ configuration of the free Co^{2+} ion, perturbed by the crystal field and the spin-orbit coupling. Figure 1 shows the splitting of the 4F term by the cubic crystal field into two orbital triplets (4T_1 and 4T_2) and one orbital singlet (4A_2). The orthorhombic distortion completely removes the orbital degeneracy of the ground triplet 4T_1 . To obtain a non-vanishing Raman tensor, we must take into account the effect of the spin-orbit coupling on these orbital singlets. We have listed them with Koster's notations. The expansion of the wave functions to second order in the spin-orbit coupling can be summarized here as²⁶

$$\Phi_i = \Phi_i^{(0)} + \Phi_i^{(1)} + \Phi_i^{(2)}. \quad (2.2)$$

$\Phi_i^{(0)}$ is one of the Ψ described in the previous paper;²⁵ that is to say,

$$\begin{cases} \Phi_2^{(0)} \\ \Phi_1^{(0)} \end{cases} = (1 + C^2)^{-1/2} |{}^4T_1, \Gamma_2^+\rangle (C | \pm \frac{3}{2} \rangle + | \mp \frac{1}{2} \rangle) = \begin{cases} \Phi_2 \\ \Phi_1 \end{cases}, \quad (2.3a)$$

$$\begin{cases} \Phi_4^{(0)} \\ \Phi_3^{(0)} \end{cases} = (1 + C^2)^{-1/2} |{}^4T_1, \Gamma_2^+\rangle (| \pm \frac{3}{2} \rangle - C | \mp \frac{1}{2} \rangle) = \begin{cases} \Phi_4 \\ \Phi_3 \end{cases}, \quad (2.3b)$$

with

$$C = \frac{1}{\sqrt{3}} \left[\frac{2D_0}{D_-} - 1 \right] + \left[\left(\frac{2D_0}{D_-} - 1 \right)^2 + 3 \right]^{1/2}, \quad (2.4a)$$

$$D_0 = E(^4T_1\Gamma_4^+) - E(^4T_1\Gamma_2^+), \quad D_- = E(^4T_1\Gamma_3^+) - E(^4T_1\Gamma_2^+). \quad (2.4b)$$

We note here that they are the two components of the Kramers doublet since the spin degeneracy is not completely quenched:

$$\Phi_1^{(1)} = \sum_{k \neq 2, M_S} |^4T_1, \Gamma_k^+ M_S\rangle \frac{\langle ^4T_2, \Gamma_k^+ M_S | \lambda LS | \Psi_1 \rangle}{E_{\Psi_1} - E_{^4T_1\Gamma_k^+}} + \sum_{\gamma \neq ^4T_1, \Gamma_k^+ M_S} |\gamma, \Gamma_k^+ M_S\rangle \frac{\langle \gamma, \Gamma_k^+ M_S | \lambda LS | \Psi_1 \rangle}{E_{\Psi_1} - E_{\gamma\Gamma_k^+}}, \quad (2.5)$$

$$\begin{aligned} \Phi_1^{(2)} &= \sum_{k \neq 2} \sum_{k'} \sum_{M_S, M_S'} |^4T_1\Gamma_k^+ M_S\rangle \frac{\langle ^4T_1\Gamma_k^+ M_S | \lambda LS | ^4T_1\Gamma_{k'}^+ M_S'\rangle}{E_{\Psi_1} - E_{^4T_1\Gamma_k^+}} \frac{\langle ^4T_1\Gamma_{k'}^+ M_S' | \lambda LS | \Psi_1 \rangle}{E_{\Psi_1} - E_{^4T_1\Gamma_{k'}^+}} \\ &\quad - \frac{1}{2} \sum_{k \neq 2} \sum_{M_S} |\Psi_1\rangle \frac{|\langle ^4T_1\Gamma_k^+ M_S | \lambda LS | \Psi_1 \rangle|^2}{(E_{\Psi_1} - E_{^4T_1\Gamma_k^+})^2}. \end{aligned} \quad (2.6)$$

In these formulas we have written, up to second order in spin-orbit coupling, all the terms which are of the same order of magnitude (see Fig. 1).

B. Raman-tensor components

We have specified the wave functions of the possible initial and excited states and we are able to obtain all the Raman tensors and the corresponding intensities. The full calculations have been previously detailed²⁷ and the final results for the components are in Table I.

Some of the results in Table I are quite different from those previously obtained.²⁵ The parameters f_L and g_L , which are interrelated, do not need any assumption about the magnitude of $\hbar\omega$ in front of $E_m - E_i$, so that we have

written f_L as

$$f_L^{(i)} = \sum_{N'} \frac{E_{N'L'} - E_i}{\hbar\omega} g_{N'L'}^{(i)}, \quad (2.7)$$

where

$$g_{N'L'}^{(i)} = \frac{\hbar\omega}{(E_{N'L'} - E_i)^2 - (\hbar\omega)^2} |\langle 3d^7 || P || N'L' \rangle|^2. \quad (2.8)$$

The summation

$$g_L^{(i)} = \sum_{N'} g_{N'L'}^{(i)} \quad (2.9)$$

is implicit.

We can outline the following comments: in every case

TABLE I. Raman tensor components.

$T_{13}^{xx} = T_{24}^{xx} = \frac{1}{\sqrt{7}} \left[\frac{9}{8} \frac{\Lambda^2}{D_0^2} \frac{C - (1 - C^2)}{1 + C^2} \not\ell_1 + \frac{9}{2} \frac{\Lambda^2}{D_-^2} \frac{C}{1 + C^2} \not\ell_2 \right]$
$T_{13}^{yy} = T_{24}^{yy} = \frac{1}{\sqrt{7}} \left[\frac{9}{8} \frac{\Lambda^2}{D_0^2} \frac{C - (1 - C^2)}{1 + C^2} \not\ell_1 + \frac{9}{2} \frac{\Lambda^2}{D_-^2} \frac{C}{1 + C^2} \not\ell_3 \right]$
$T_{13}^{zz} = T_{24}^{zz} = \frac{1}{\sqrt{7}} \left[\frac{9}{8} \frac{\Lambda^2}{D_0^2} \frac{C - (1 - C^2)}{1 + C^2} \not\ell_4 + \frac{9}{2} \frac{\Lambda^2}{D_-^2} \frac{C}{1 + C^2} \not\ell_1 \right]$
$S_{13}^{yx} = S_{24}^{yx} = i \left[\frac{5}{4} \right]^2 \left[\frac{3}{7} \right]^{1/2} \frac{C}{1 + C^2} \frac{\Lambda}{\Delta_0} \left[\frac{1}{\sqrt{5}} f_2 + \frac{\sqrt{7}}{4} f_3 + \frac{1}{4} f_4 \right]$
$A_{13}^{yx} = A_{24}^{yx} = i \left[\frac{5}{4} \right]^2 \left[\frac{3}{7} \right]^{1/2} \frac{C}{1 + C^2} \frac{\Lambda}{\Delta_0} \left[-\frac{13}{5\sqrt{5}} g_2 + \frac{\sqrt{7}}{4} g_3 + \frac{3}{4} g_4 \right]$
with $\not\ell_1 = \frac{f_2}{\sqrt{5}} - \frac{\sqrt{7}}{2} f_3 + \frac{5}{6} f_4$, $\not\ell_3 = \frac{f_2}{\sqrt{5}} + \frac{11\sqrt{7}}{16} f_3 + \frac{5}{6} f_4$
$\not\ell_2 = \frac{3\sqrt{5}}{4} f_2 + \frac{73}{48} f_4$, $\not\ell_4 = \frac{5}{6} f_2 + \frac{8}{3} f_4$
$S_{14}^{xz} = -S_{23}^{xz} = i S_{14}^{yz} = i S_{23}^{yz} = -\frac{9}{8} \left[\frac{3}{7} \right]^{1/2} \frac{1 + C\sqrt{3}}{1 + C^2} \frac{\Lambda^2}{D_0 D_-} \left[\frac{2}{\sqrt{5}} f_2 + \frac{\sqrt{7}}{8} f_3 - \frac{3}{8} f_4 \right]$
$A_{14}^{xz} = -A_{23}^{xz} = -i A_{14}^{yz} = -i A_{23}^{yz} = -\frac{9}{8} \left[\frac{3}{7} \right]^{1/2} \frac{1 + C\sqrt{3}}{1 + C^2} \frac{\Lambda^2}{D_0 D_-} \left[\frac{4}{\sqrt{5}} g_2 - \frac{\sqrt{7}}{8} g_3 - \frac{13}{8} g_4 \right]$

the antisymmetrical part appears to be smaller than the symmetrical one but not negligible. In fact,

$$\frac{A_{if}^{\alpha\beta}}{S_{if}^{\alpha\beta}} \sim \frac{\hbar\omega g_N^{(i)}}{f_N^{(i)}} \sim 2 \times 10^{-1}. \quad (2.10)$$

All these results contain even terms in Λ/Δ_0 , $(\Lambda/D_0)^2$, $(\Lambda/D_-)^2$, or Λ^2/D_0D_- which are of the same order of magnitude because the splitting Δ_0 by the cubic field is much larger than the splitting D_0, D_- of the orthorhombic distortion [$D_0 \sim 600 \text{ cm}^{-1}$, $D_- \sim 1250 \text{ cm}^{-1}$, $\Lambda = \lambda\mathcal{F}$, and \mathcal{F} is a constant which relates the ${}^4T_1\Gamma_2^+(L=3)$ to a ${}^4P(L=1)$ under the assumption of equivalent operators^{20,21}].

From these results we could deduce the existence of a strong anisotropy in the calculated Raman intensities. In fact, x and y must be exchanged when the impurity site is transferred from one sublattice to the other. Thus, if the two sublattices are equally occupied by the impurity, we should not observe any anisotropy in the Raman intensities. The anisotropy, which is experimentally observed, may indicate some correlation in the occupancy of the sites by the impurities.

C. The case of a Co^{2+} ion embedded as an isolated impurity in a magnetic structure

In the preceding sections we have described in detail the Raman scattering due to the Co^{2+} ion as an impurity, in a diamagnetic matrix with a rutile structure. By an analogous method, which also takes into account the exchange between the impurity and the host magnetic ions, we are able to analyze the case of a magnetic rutile structure. When the impurity mode is strongly localized, the magnetic excitation can hardly propagate from the impurity to its neighbors. In this case, a mean-field approximation is a roughly adequate description of the magnetic exchange interaction between Co^{2+} and the nearest magnetic neighbor ions. In this approximation the exchange can be described by an additional term:¹⁹

$$\mathcal{H}_{\text{exch}} = -\alpha S_z, \quad (2.11)$$

where the exchange constant α includes all the kinds of magnetic interactions in the magnetic structure (antiferromagnetic, ferromagnetic, etc.) and is proportional to the average spin component on the neighboring site in the ground state.

From experimental results^{28,29} and other theoretical studies,¹⁹ we can note that the exchange interaction, between different sites is of the same order of magnitude as the spin-orbit interaction which takes place inside each impurity ion. Then, as explained in the preceding sections, we treat simultaneously the exchange interaction and the spin-orbit coupling as a perturbation of the crystal

field:

$$V = \alpha S_z + \lambda LS. \quad (2.12)$$

We expand the eigenfunctions of the total Hamiltonian as previously with the help of the complete set of linear combinations of $|\gamma, \Gamma_k^+, M_S\rangle$. Keeping the same notation, $|\gamma, \Gamma_k^+\rangle$ are the eigenfunctions in the crystal field associated with the irreducible representation Γ_k^+ of the D_{2h} group and are defined as linear combinations of the spherical harmonics $|\gamma, L, M_L\rangle$. M_S is one of the possible values $\pm\frac{3}{2}, \pm\frac{1}{2}$ of the spin component. The exchange term αS_z has nonvanishing matrix elements inside the orbital singlet $|\gamma, \Gamma_k^+\rangle$. The eigenfunctions, denoted Ψ_i in the preceding sections, which diagonalize the perturbation V at the lowest order are linear combinations of the state vectors $|\gamma, \Gamma_k^+, M_S\rangle$ with coefficients $C_{T_1\Gamma_2^+M_S}^{(i)}$:

$$C_{T_1\Gamma_2^+ -3/2}^{(1) \text{ or } (3)} = \frac{2\sqrt{3}A}{I_{\pm}(\alpha)}, \quad (2.13a)$$

$$C_{T_1\Gamma_2^+ 1/2}^{(1) \text{ or } (3)} = \frac{\alpha + 2(A - 2B) \pm \sqrt{J(\alpha)}}{I_{\pm}(\alpha)}, \quad (2.13b)$$

$$C_{T_1\Gamma_2^+ 3/2}^{(2) \text{ or } (4)} = \frac{2\sqrt{3}A}{I_{\pm}(-\alpha)}, \quad (2.14a)$$

$$C_{T_1\Gamma_2^+ -1/2}^{(2) \text{ or } (4)} = \frac{\alpha - 2(A - 2B) \mp \sqrt{J(-\alpha)}}{I_{\pm}(-\alpha)}. \quad (2.14b)$$

Indices (1) and (4) are associated with the sign (+); indices (2) and (3) are associated with the sign (-), and

$$A = -\frac{9}{16} \frac{\Lambda^2}{D_0}, \quad (2.15a)$$

$$B = -\frac{9}{16} \frac{\Lambda^2}{D_-}, \quad (2.15b)$$

$$I_{\pm}(\alpha) = \{12A^2 + [\alpha + 2(A - 2B) \pm \sqrt{J(\alpha)}]^2\}^{1/2}, \quad (2.16)$$

$$J(\alpha) = [\alpha + 2(A - 2B)]^2 + 12A^2. \quad (2.17)$$

We can see that all the terms are of the same order of magnitude. Of course, for a nonvanishing value of the exchange constant α , the Kramers degeneracy has been removed. The Ψ_i which are not degenerate are the result of an expansion to zero order in perturbation V (the corresponding energies being calculated to the second order²⁶).

Thus as in the preceding section, to obtain a nonvanishing Raman tensor in the dipolar electric approximation, we must expand them to higher order, by the standard perturbation theory applied to the nondegenerate case, this time.

To second order in V , we find the normalized wave functions (2.2):

$$\bullet |\Phi_i^0\rangle = |\Psi_i\rangle, \quad (2.18)$$

$$\bullet |\Phi_i^{(1)}\rangle = \sum_{j(\neq i)} |\Psi_j\rangle \frac{\langle \Psi_j | \alpha S_z | \Psi_i \rangle}{E_i - E_j} + \sum_{k \neq 2} \sum_{M_S} |{}^4T_1\Gamma_k^+ M_S\rangle \frac{\langle {}^4T_1\Gamma_k^+ M_S | \lambda LS | \Psi_i \rangle}{E_i - E_{{}^4T_1\Gamma_k^+}} \\ + \sum_{\gamma \neq {}^4T_1} \sum_k \sum_{M_S} |\gamma \Gamma_k^+ M_S\rangle \frac{\langle \gamma \Gamma_k^+ M_S | \lambda LS | \Psi_i \rangle}{E_i - E_{\gamma \Gamma_k^+}}, \quad (2.19)$$

$$\begin{aligned}
\bullet |\Phi_i^{(2)}\rangle = & \sum_{j(\neq i)} |\Psi_j\rangle \frac{\langle \Psi_j | \alpha S_z | \Psi_j \rangle \langle \Psi_j | \alpha S_z | \Psi_i \rangle}{(E_i - E_j)^2} \\
& + \sum_{k \neq 2} \sum_{M_s} |{}^4T_1 \Gamma_k^+ M_s\rangle \left[\sum_{k' \neq 2} \sum_{M_s'} \frac{\langle {}^4T_1 \Gamma_k^+ M_s | \lambda LS | {}^4T_1 \Gamma_{k'}^+ M_s' \rangle \langle {}^4T_1 \Gamma_{k'}^+ M_s' | \lambda LS | \Psi_i \rangle}{(E_i - E_{{}^4T_1 \Gamma_{k'}^+}) (E_i - E_{{}^4T_1 \Gamma_k^+})} \right. \\
& + \sum_{j \neq 1} \frac{\langle {}^4T_1 \Gamma_k^+ M_s | \lambda LS | \Psi_j \rangle \langle \Psi_j | \alpha S_z | \Psi_i \rangle}{(E_i - E_j) (E_i - E_{{}^4T_1 \Gamma_k^+})} \\
& \left. + \frac{\langle {}^4T_1 \Gamma_k^+ M_s | \alpha S_z | {}^4T_1 \Gamma_k^+ M_s \rangle \langle {}^4T_1 \Gamma_k^+ M_s | \lambda LS | \Psi_i \rangle}{(E_i - E_{{}^4T_1 \Gamma_k^+})^2} \right] \\
& - \frac{1}{2} |\Psi_i\rangle \left[\sum_{k \neq 2} \sum_{M_s} \frac{|\langle {}^4T_1 \Gamma_k^+ M_s | \lambda LS | \Psi_i \rangle|^2}{(E_i - E_{{}^4T_1 \Gamma_k^+})^2} + \sum_{j(\neq i)} \frac{|\langle \Psi_j | \alpha S_z | \Psi_i \rangle|^2}{(E_i - E_j)^2} \right]. \tag{2.20}
\end{aligned}$$

The time reversal operator transforms Φ_1 into Φ_3 and Φ_2 into Φ_4 (Kramers components). Now we are able to calculate explicitly the Raman components between two of these states, as shown in Table II.

We obtain two kinds of results. The first one concerns the components which are associated with transitions between two levels arising from two different Kramers doublets. These components were existing without exchange. They are noted in the table by an asterisk (*), but they are deeply modified by the terms $J(\alpha)$. The second one concerns the Raman components which are associated with transitions between two distinct levels arising from the same Kramers doublet. Some of them, such as S_{12}^{yz} (S_{34}^{yz}) and A_{12}^{yz} (A_{34}^{yz}), do not exist without exchange interaction

(when $\alpha=0$), and they are quadratic in perturbation. Strictly speaking, the other ones, A_{12}^{xz} and A_{34}^{xz} , would exist without exchange interaction. But it must be emphasized that if exchange were neglected, these transitions could not be considered as Raman transitions because they would take place between two states (the two partners of the same Kramers doublet) with the same energy. Thus, without exchange they would constitute a case of Rayleigh transition, so that the Raman nature of these transitions is directly connected to the presence of the exchange term. Their antisymmetrical character is a direct consequence of the effect of the time-reversal symmetry.

TABLE II. Raman components in the mean-field approximation.

$$\begin{aligned}
S_{12}^{yz} = S_{34}^{yz} &= \frac{3i}{4\sqrt{7}} \frac{1}{1+C^2} \left[\frac{\alpha}{\sqrt{J(\alpha)}} \frac{\Lambda^2}{D_0^2} + \frac{\alpha\Lambda}{D_0^2} C \right] \left[\frac{2}{\sqrt{5}} f_2 + \frac{\sqrt{7}}{8} f_3 - \frac{3}{8} f_4 \right] \\
A_{12}^{yz} = A_{34}^{yz} &= -\frac{3i}{4\sqrt{7}} \frac{1}{1+C^2} \left[\frac{\alpha}{\sqrt{J(\alpha)}} \frac{\Lambda^2}{D_0^2} + \frac{\alpha\Lambda}{D_0^2} C \right] \left[\frac{4}{\sqrt{5}} g_2 - \frac{\sqrt{7}}{8} g_3 - \frac{13}{8} g_4 \right] \\
A_{12}^{xz} = A_{34}^{xz} &= \frac{9}{8\sqrt{7}} \frac{1-C\sqrt{3}}{1+C^2} \frac{\Lambda^2}{D_0 D_-} \left[\frac{4}{\sqrt{5}} g_2 - \frac{\sqrt{7}}{8} g_3 - \frac{13}{8} g_4 \right] \\
T_{13}^{xx} = T_{13}^{xx*} &= -\frac{1}{2\sqrt{7}} \frac{C}{1+C^2} \frac{\alpha^2}{2J(\alpha)} \left[\frac{1}{\sqrt{5}} f_2 - \frac{11\sqrt{7}}{16} f_3 + \frac{5}{6} f_4 \right] \\
T_{13}^{yy} = T_{13}^{yy*} &= -\frac{1}{8\sqrt{7}} \frac{C}{1+C^2} \frac{\alpha^2}{2J(\alpha)} (3\sqrt{5} f_2 + \frac{73}{12} f_4), \\
T_{13}^{zz} = T_{13}^{zz*} &= -\frac{1}{2\sqrt{7}} \frac{C}{1+C^2} \frac{\alpha^2}{2J(\alpha)} \left[\frac{1}{\sqrt{5}} f_2 - \frac{\sqrt{7}}{2} f_3 + \frac{5}{6} f_4 \right] \\
S_{13}^{xy} = S_{13}^{xy*} &= +\frac{i}{8\sqrt{7}} \frac{3C}{1+C^2} \left[\frac{2\Lambda\sqrt{J(\alpha)-J(0)}}{D_-^2} + \frac{\alpha}{D_-} \frac{1-C^2}{1+C^2} \frac{3\alpha\Lambda}{2D_- \sqrt{J(\alpha)}} 1 - \frac{\alpha-10(A+B)}{2D_-} \right] \left[\frac{1}{\sqrt{5}} f_2 + \frac{\sqrt{7}}{4} f_3 + \frac{1}{4} f_4 \right] \\
A_{13}^{xy} = A_{13}^{xy*} &= +\frac{i}{8\sqrt{7}} \left[\frac{3C}{1+C^2} \frac{2\Lambda}{D_-} \left[\left[-\frac{\alpha-10(A+B)}{2D_-} \right] - \frac{\alpha}{2D_-} \right] + \frac{3\alpha\Lambda}{D_- \sqrt{J(\alpha)}} \frac{1-C^2}{1+C^2} \left[1 - \frac{(10A+B)}{2D_-} \right] \right] \left[\frac{7}{5} g_2 + \frac{1}{4} g_3 - \frac{\sqrt{7}}{4} g_4 \right]
\end{aligned}$$

III. RAMAN INTENSITIES DUE TO LOCALIZED AND SPIN-WAVE MODES

A. Physical introduction

Up to now we have not taken into account an essential phenomenon which is the transfer to the neighboring sites of the matrix due to the transverse terms in the spin Hamiltonian of the magnetic excitations produced by the scattering of light on the impurity sites through the spin-orbit coupling. The first effect is the following: the magnetic excitations which are bound to the impurity, in fact, extend some distance from the impurity; they are therefore more or less localized in the neighborhood of the impurities, according to the value of the strength of the coupling between the impurity and the ions of the matrix.³⁰ The second effect is that the impurity gives rise to a non-vanishing coupling of light with the spin waves which extend to infinity in the crystal and were not coupled to light by themselves in the pure matrix.¹⁰

As a result, we must consider that the light is scattered both by the localized modes and by the spin-wave modes through the spin-orbit coupling which is assumed to exist only on the impurity sites. Our purpose is to compare the intensities scattered by these two types of magnetic excitations, and to discuss their ratio according to the value of the relevant parameters. In spite of the fact that the genuine physical system is generally an antiferromagnetic one, we have built the theory assuming a ferromagnetic model, as we have explained in the general introduction.

B. Hamiltonian model

We start the Heisenberg Hamiltonian of a pure ferromagnetic crystal

$$H_0 = - \sum_{i, \mathbf{R}} J_i [S_{\mathbf{R}}^z S_{\mathbf{R}+\Delta_i}^z + \frac{1}{2} (S_{\mathbf{R}}^+ S_{\mathbf{R}+\Delta_i}^- + S_{\mathbf{R}}^- S_{\mathbf{R}+\Delta_i}^+)] , \quad (3.1)$$

where \mathbf{R} are the sites of the Bravais lattice, Δ_i are the vectors which connect one site to each of its z nearest neighbors ($i=1$ to z), $S_{\mathbf{R}}^z$, $S_{\mathbf{R}}^+$, and $S_{\mathbf{R}}^-$ are the components of the spin operator of the site \mathbf{R} , and J_i describes the exchange interactions between the spin which occupy the \mathbf{R} and $\mathbf{R}+\Delta_i$ sites.

The ferromagnetic ground state of the pure system, in which the $S_{\mathbf{R}}^z$ component has the same eigenvalue, $-S$ on any site, can be described by the wave function

$$|\Phi_0\rangle = \prod_{\mathbf{R}} |S, -S\rangle_{\mathbf{R}} , \quad (3.2)$$

in which $\prod_{\mathbf{R}}$ is the product extended to all the sites of the system of the one-site eigenstate $|S, -S\rangle_{\mathbf{R}}$ of both the operators $S_{\mathbf{R}}^z$ and $S_{\mathbf{R}}^z$ with the eigenvalues $S(S+1)$ and $-S$, respectively. We shall use, as usual for small excitations, the mean-field approximation in order to simplify the first term of the Hamiltonian (3.1), which thus is reduced to

$$H_0 = - \sum_{i, \mathbf{R}} J_i [-SS_{\mathbf{R}}^z + \frac{1}{2} (S_{\mathbf{R}}^+ S_{\mathbf{R}+\Delta_i}^- + S_{\mathbf{R}}^- S_{\mathbf{R}+\Delta_i}^+)] . \quad (3.3)$$

Let us consider the spin excitation from the state $S_{\mathbf{R}}^z = -S$ to the state $S_{\mathbf{R}}^z = -S+1$ at the site \mathbf{R} . We shall introduce the notation $|\mathbf{R}\rangle$ for the wave functions describing the resulting excited state of the whole system, which can be written

$$|\mathbf{R}\rangle = |S, -S+1\rangle_{\mathbf{R}} \prod_{\mathbf{R}' (\neq \mathbf{R})} |S, -S\rangle_{\mathbf{R}'} , \quad (3.4)$$

that is to say,

$$|\mathbf{R}\rangle = (2S)^{-1/2} S_{\mathbf{R}}^+ |\Phi_0\rangle . \quad (3.5)$$

Two excitations localized on two different sites \mathbf{R} and \mathbf{R}' are orthogonal and we shall choose the states $|\mathbf{R}\rangle$ as an orthonormal set $\delta_{\mathbf{R}\mathbf{R}'} = \langle \mathbf{R} | \mathbf{R}' \rangle$.

In the Dirac formalism, the spin operators used in the Hamiltonian can be formulated as

$$S_{\mathbf{R}}^z = |\mathbf{R}\rangle (-S+1) \langle \mathbf{R} | , \quad (3.6)$$

$$S_{\mathbf{R}}^+ S_{\mathbf{R}+\Delta_i}^- = |\mathbf{R}\rangle (2S) \langle \mathbf{R}+\Delta_i | , \quad (3.7)$$

and

$$H_0 = -S \sum_{i, \mathbf{R}} J_i [(S-1) |\mathbf{R}\rangle \langle \mathbf{R} | + |\mathbf{R}\rangle \langle \mathbf{R}+\Delta_i | + |\mathbf{R}+\Delta_i\rangle \langle \mathbf{R} |] . \quad (3.8)$$

In an orthorhombic symmetry $\Delta_{-i} = -\Delta_i$ and we have three distinct exchange integrals $J_{|i|}$, with $i = \pm 1, \pm 2, \pm 3$. In the special case of a cubic symmetry, that we shall consider now, these three integrals have the same value J .

Let us now consider a substitutional impurity occupying the site \mathbf{R}_0 . In the preceding section we gave a detailed description of the quantum state of the impurity taking into account the crystal field, the spin-orbit excitation, and the exchange as a molecular field. The excitations of the quantum states of the impurity involve both orbital and spin variables. What we want to do now, is to describe the interaction between the impurity and the crystal; it will be convenient to keep a Heisenberg type of Hamiltonian.³¹ For this purpose we shall define a pseudospin operator $S_{\mathbf{R}}$ at the impurity site, with the special property that $S_{\mathbf{R}_0}^+$ is the operator which describes the excitation of the impurity from its ground state to its first excited state. The interaction between the impurity and the crystal will be described by an exchange integral, the value J_0 of which will differ from the value J between two sites of the pure crystal. In the presence of the impurity of spin S_0 , at the \mathbf{R}_0 site, the Heisenberg Hamiltonian becomes

$$H = -6S(S_0-1)J_0 |\mathbf{R}_0\rangle \langle \mathbf{R}_0 | - (S-1) \left[\sum_i S_0 J_0 + \sum_{j (\neq i)} S J \right] |\mathbf{R}_0+\Delta_i\rangle \langle \mathbf{R}_0+\Delta_i | - (2SS_0)^{-1/2} \sum_i J_0 (|\mathbf{R}_0\rangle \langle \mathbf{R}_0+\Delta_i | + |\mathbf{R}_0+\Delta_i\rangle \langle \mathbf{R}_0 |) + H' , \quad (3.9)$$

where H' represents all the other terms of the Hamiltonian which are unaffected by the impurity.

Writing $H = H_0 + V$ where V is the perturbation due to the impurity, we obtain

$$\begin{aligned} V = & 6S[J(S-1) - J_0(S_0-1)] |\mathbf{R}_0\rangle \langle \mathbf{R}_0| \\ & + [JS - J_0(S-1)] \sum_{i=1}^z |\mathbf{R}_0 + \Delta_i\rangle \langle \mathbf{R}_0 + \Delta_i| \\ & + \sqrt{S}(J\sqrt{S} - J_0\sqrt{S_0}) \sum_{i=1}^z (|\mathbf{R}_0 + \Delta_i\rangle \langle \mathbf{R}_0 | \Delta_i + \text{c.c.}) . \end{aligned} \quad (3.10)$$

The system actually contains several impurities occupying sites $\mathbf{R}_0^{(j)}$; in the diluted limit the impurity sites lie far from each other. The perturbation V will involve summation extended to all the impurity sites of terms similar to those appearing in (3.10).

The ground state of the system is described by the wave function

$$|\Phi_i\rangle = \prod_j | -S_0 \rangle_{\mathbf{R}_0^{(j)}} \prod_{\mathbf{R} (\neq \mathbf{R}_0^{(j)})} | -S \rangle_{\mathbf{R}} , \quad (3.11)$$

in which we note that only the $| -S_0 \rangle_{\mathbf{R}_0^{(j)}}$ which represent the states of impurities are able to interact with light.

$$|\Phi_f(\mathbf{k})\rangle = \frac{1}{\sqrt{N}} (2S_0) \left[\sum_j^{-1/2} \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k}) S_{\mathbf{R}_0^{(j)}}^+ + \sum_{\mathbf{R} (\neq \mathbf{R}_0^{(j)})} (2S)^{-1/2} \beta_{\mathbf{R}}(\mathbf{k}) S_{\mathbf{R}}^+ \right] |\Phi_i\rangle , \quad (3.14)$$

where \mathbf{k} is the wave vector.

The factor $N^{-1/2}$, where N is the (infinite) number of periodic sites of the lattice, has been introduced to normalize the wave function Φ_f to unity.

$\beta_{\mathbf{R}_0^{(j)}}(\mathbf{k})$ and $\beta_{\mathbf{R}}(\mathbf{k})$ are the amplitudes of the wave function on the impurity sites $\mathbf{R}_0^{(j)}$ and the matrix sites \mathbf{R} , respectively. There is no reason for the $\beta_{\mathbf{R}}(\mathbf{k})$ to be smaller on sites which are far from any impurity than on sites which are close to an impurity. In the limit of the pure crystal the $\beta_{\mathbf{R}}(\mathbf{k})$ are equal to the factor $\exp(-i\mathbf{k} \cdot \mathbf{R})$ of the Bloch functions.

D. Expressions of the Raman scattered impurities

According to the formula (2.1), the Raman tensor associated with a transition from the ground state Φ_0 to an excited one Φ_f involves matrix elements of the type $\langle \Phi_f | O_{\text{eff}} | \Phi_0 \rangle$, where the expression of the effective operator O_{eff} can easily be expressed for the symmetrical and antisymmetrical part of the tensor. The wave function Φ_0 of the ground state is given by (3.11). Φ_f is given by (3.12) if the excited state is localized in the neighborhood of the impurity occupying the site $\mathbf{R}_0^{(j)}$, and by (3.14), if the excited state is a propagating one of wave vector \mathbf{k} . Since a nonvanishing spin-orbit coupling takes place on the impurity sites $\mathbf{R}_0^{(j)}$ only, the state Φ_0 and Φ_f are connected by O_{eff} on these sites only, through the matrix elements

$$\beta_{\mathbf{R}_0^{(j)}} \langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0^{(j)}} . \quad (3.15)$$

In the case of a localized excited state associated with

C. Excited states

Let us consider a Raman transition from the initial ferromagnetic ground state described by the above equation (3.11) to the final magnetic excited state. This excited state can be either an excited state bound to the impurity or a spin wave extended to the whole crystal.^{16,32}

We first describe a magnetic excited state bound to the impurity occupying the $\mathbf{R}_0^{(j)}$ site by

$$|\Phi_f^{(j)}\rangle = \sum_{\mathbf{R}} \gamma_{\mathbf{R}-\mathbf{R}_0^{(j)}} S_{\mathbf{R}}^+ |\Phi_i\rangle ; \quad (3.12)$$

as this wave function describes a bound state, it can be normalized to unity by the condition

$$\sum_{\mathbf{R}} |\gamma_{\mathbf{R}-\mathbf{R}_0^{(j)}}|^2 = 1 . \quad (3.13)$$

The phase of the coefficient $\gamma_{\mathbf{R}-\mathbf{R}_0^{(j)}}$ does not depend on the site R , and its amplitude decreases to zero at large distance from the impurity more rapidly as the state becomes more bound to the impurity.

On the other hand, the spin waves are described by propagating wave functions which can be written as

the impurity site $\mathbf{R}_0^{(j)}$, we have

$$\langle \Phi_f^{(j)} | O_{\text{eff}} | \Phi_0 \rangle = \sum_{\mathbf{R}} \gamma_{\mathbf{R}} \langle \Phi_0 | S_{\mathbf{R}}^- O_{\text{eff}} | \Phi_0 \rangle , \quad (3.16)$$

which reduces to

$$\langle \Phi_f^{(j)} | O_{\text{eff}} | \Phi_0 \rangle = \gamma_{\mathbf{R}_0^{(j)}} \langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0^{(j)}} . \quad (3.17)$$

In the same way, in the case of a propagating excited state, we have

$$\begin{aligned} \langle \Phi_f(\mathbf{k}) | O_{\text{eff}} | \Phi_0 \rangle = & \frac{1}{\sqrt{N}} \sum_j (2S_0)^{-1/2} \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k}) \\ & \times \langle \Phi_0 | S_{\mathbf{R}_0^{(j)}}^- O_{\text{eff}} | \Phi_0 \rangle , \end{aligned} \quad (3.18)$$

which reduces to

$$\begin{aligned} \langle \Phi_f(\mathbf{k}) | O_{\text{eff}} | \Phi_0 \rangle = & \frac{1}{\sqrt{N}} \sum_j \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k}) \langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0^{(j)}} . \end{aligned} \quad (3.19)$$

Our main assumption is that, as long as the bound states do not extend too far from the impurities, they do not interfere with each other for small concentrations; as a consequence, the total intensity I_{loc} scattered by the localized excited states, is equal to the sum of the intensities $I_{\text{loc}}^{(j)}$ scattered by the different impurities; that is to say,

$$I_{\text{loc}} = \sum_j I_{\text{loc}}^{(j)} , \quad (3.20)$$

with

$$I_{\text{loc}}^{(j)} = K |\gamma_{\mathbf{R}_0^{(j)}}|^2 |\langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0^{(j)}}|^2, \quad (3.21)$$

where K is a constant of proportionality.

When all impurities are identical, (3.21) does not actually depend on the $\mathbf{R}_0^{(j)}$ and we obtain therefore the final expression

$$I_{\text{loc}} = cNK |\gamma_{\mathbf{R}_0}|^2 |\langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0}|^2. \quad (3.22)$$

\mathbf{R}_0 is any one of the impurity sites; c is the impurity concentration.

On the other hand, as the function $\Phi_f(\mathbf{k})$ of the spin wave extends to the whole crystal, the scattering of light coherently arises from all the impurities of the crystal. In that case, we must add the amplitudes scattered by the different impurities. Thus the total intensity $I_{\text{ext}}(\mathbf{k})$ scattered by the spin wave of \mathbf{k} vector is equal to

$$I_{\text{ext}}(\mathbf{k}) = \frac{1}{N} K |\langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0^{(j)}}|^2 \times \left| \sum_j \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k}) \right|^2. \quad (3.23)$$

If the impurities are randomly distributed in the crystal, the phases of the complex coefficients $\beta_{\mathbf{R}_0^{(j)}}(\mathbf{k})$ have all possible values for any \mathbf{k} not equal to zero, but all these phases vanish when the wave vector is $\mathbf{0}$, thus the expression $\sum_j \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k})$, extended to all the impurity sites, is

$$\sum_j \beta_{\mathbf{R}_0^{(j)}}(\mathbf{k}) = cN \beta_{\mathbf{R}_0}(\mathbf{k}) \delta_{\mathbf{k}, \mathbf{0}}. \quad (3.24)$$

Thus, only the spin wave at $\mathbf{k}=\mathbf{0}$ gives a nonvanishing scattering of light, with the intensity

$$I_{\text{ext}}(\mathbf{0}) = c^2 NK |\beta_{\mathbf{R}_0}(\mathbf{0})|^2 |\langle -S_0 + 1 | O_{\text{eff}} | -S_0 \rangle_{\mathbf{R}_0}|^2. \quad (3.25)$$

As a first conclusion, the intensity scattered by the localized excited state is linear in the impurity concentration, but the one scattered by the spin wave is quadratic. This conclusion is in agreement with some experimental results.³³ The explicit calculations of each one of the two previous intensities would require a detailed knowledge of the electronic structure of the impurity in order to calculate the matrix element (3.15). Such a calculation has been made in the preceding section. The result is "model dependent" and rather complex. However, we obtain another interesting result by calculating the ratio of the intensities scattered by the localized and extended excited states, respectively. In fact, the matrix element (3.15) which depends on the model used to describe the electronic structure of the impurity is eliminated. The ratio leads to

$$\rho = \frac{I_{\text{ext}}(\mathbf{0})}{I_{\text{loc}}} = c \frac{|\beta_{\mathbf{R}_0}(\mathbf{0})|^2}{|\gamma_{\mathbf{R}_0}|^2}. \quad (3.26)$$

This result is valid within the limits where the concentration is small enough for the interaction between impurities to be neglected. The most interesting conclusion is

the following: as ρ depends on the $\beta_{\mathbf{R}_0}(\mathbf{0})$ and $\gamma_{\mathbf{R}_0}$ on the impurity sites, respectively, of the extended and localized wave function of the excited states, its order of magnitude will not be the same in the case of deep or shallow impurity states. As a matter of fact, for a shallow impurity state bound to an impurity at the $\mathbf{R}_0^{(j)}$ site, the wave function $\Phi_f^{(j)}$ extends relatively far (but, as said previously, not far enough for the states localized on two different impurities to interact) from $\mathbf{R}_0^{(j)}$ and thus, its amplitude $\gamma_{\mathbf{R}_0^{(j)}}$ at the impurity site itself is small. Furthermore, one gets a shallow impurity state when the impurity has physical properties which do not differ too much from those of the host ions, so that the spin waves are not very much perturbed by the presence of an impurity, and therefore their amplitude $|\beta_{\mathbf{R}_0}(\mathbf{0})|$, at the impurity site, does not differ very much from its value $\beta_{\mathbf{R}}(\mathbf{0})$ far from the impurity site. As a conclusion, the smallness of the concentration c can be compensated by the large value of the ratio $|\beta_{\mathbf{R}_0}(\mathbf{0})\gamma_{\mathbf{R}_0}^{-1}|^2$. In that case, the intensity scattered by the spin waves of vanishing wave vector \mathbf{k} can have the same order of magnitude as the one scattered by the localized modes.

On the other hand, in the case of a deep impurity level, the wave function $\Phi_f^{(j)}$ is well localized on the impurity site, and the amplitude $\gamma_{\mathbf{R}_0^{(j)}}$ is of the order of unity. Also, the orthogonality of the wave functions of the spin wave to that of the localized state leads to a small value of its amplitude $\beta_{\mathbf{R}_0^{(j)}}(\mathbf{0})$ at the impurity site. Thus, in that case, the ratio ρ is much smaller than unity. As a physical conclusion, the intensity of light scattered by a spin wave is much smaller than that scattered by a localized state for a deep impurity level, but it can be of the same order of magnitude in the case of a shallow impurity state. In order to give a more precise analysis of this phenomenon, we shall now describe a detailed calculation of $\beta_{\mathbf{R}_0}(\mathbf{0})$ and $\gamma_{\mathbf{R}_0}$ in terms of the physical parameters.

E. Calculation of $\gamma_{\mathbf{R}_0}$

To determine the state bound to a single impurity at the site $\mathbf{R}_0^{(j)}$, it will be convenient to choose that site as the origin $\mathbf{R}_0^{(j)}=\mathbf{0}$ of real space. The wave function (3.12) of this bound state $|\Phi_f\rangle$ must be a solution of the homogeneous equation

$$[1 - G_0(E)V]|\Phi_f\rangle = 0, \quad (3.27)$$

where we have introduced the Green's function $G_0(E) = (E - H_0)^{-1}$ of the pure crystal and where the perturbation V , due to the impurity, is given by Eq. (3.10).

By projection of the (3.27) equation on the one-site excited state (3.5), we can obtain the following linear and homogeneous system of equations for the unknown coefficients $\gamma_{\mathbf{R}}$:

$$\sum_{\mathbf{R}} \langle \Phi_0 | S_{\mathbf{R}}^- [1 - G_0(E)V] S_{\mathbf{R}}^+ | \Phi_0 \rangle \gamma_{\mathbf{R}} = 0. \quad (3.28)$$

The energies E of the bound states are defined by the condition on the determinant:

$$\| |1 - G_0(E)V| | = 0. \quad (3.29)$$

This determinant can be expressed on the basis of the infinite set of the states $| \mathbf{R} \rangle$ defined by (3.5) as

$$\| | \delta_{\mathbf{R}\mathbf{R}'} - \sum_{\mathbf{R}''} \langle \mathbf{R} | G_0(E) | \mathbf{R}'' \rangle \langle \mathbf{R}'' | V | \mathbf{R}' \rangle | | = 0, \quad (3.30)$$

where the matrix elements of the Green's function can be expressed as

$$\langle \mathbf{R}' | G_0(E) | \mathbf{R} \rangle = \frac{v}{(2\pi)^3} \int \int \int_{\mathcal{D}} \frac{e^{i\mathbf{k} \cdot (\mathbf{R} - \mathbf{R}')}}{E - E_{\mathbf{k}}} d^3\mathbf{k}, \quad (3.31)$$

with $E_{\mathbf{k}}$ the eigenvalues of the energy of the spin wave of wave vector \mathbf{k} of the pure crystal, v the volume of the unit cell, and the integral is extended over the first Brillouin zone.

According to (3.10) with $\mathbf{R}_0 = 0$ the perturbation V can be written as

$$| 0 \rangle A_0 \langle 0 | + \sum_{i \neq 0} | i \rangle A \langle i | + B (| 0 \rangle \langle i | + | i \rangle \langle 0 |). \quad (3.32)$$

Here we have introduced the simplified notations $| i \rangle = | \mathbf{R}_0 \rangle = | 0 \rangle$ and $| i \rangle = | \Delta_i \rangle$ for $i = \pm 1, \pm 2, \pm 3$, and we have

$$A_0 = 6S[J(S-1) - J_0(S_0-1)], \quad (3.33a)$$

$$A = (S-1)(SJ - S_0J_0), \quad (3.33b)$$

$$B = \sqrt{S}[J\sqrt{S} - J_0(S_0)^{1/2}]. \quad (3.33c)$$

With the previous notations the infinite system (3.28) splits into a subsystem of seven linear and homogeneous equations which is written as

$$\sum_i \left[\delta_{ii'} - \sum_{i''} \langle i | G_0(E) | i'' \rangle \langle i'' | V | i' \rangle \right] \gamma_i = 0 \quad (3.34)$$

and an infinite set of separated equations

$$\gamma_{\mathbf{R}} = \sum_{i, i''} \langle \mathbf{R} | G_0(E) | i'' \rangle \langle i'' | V | i \rangle \gamma_i \quad (3.35)$$

for each $\mathbf{R} \neq 0$ or Δ_i .

The energies E of the bound state are the roots of the 7×7 determinant of the system (3.34). For each one of the solutions obtained for E the same system leads to the relative values of the seven coefficients γ_i , and Eq. (3.35) finally gives the complete set of $\gamma_{\mathbf{R}}$ in relative value. Taking into account the normalization written in (3.13), the $\gamma_{\mathbf{R}}$ coefficients are calculated in absolute values and espe-

$$\beta_{\mathbf{R}_0}(\mathbf{k}) = \frac{1}{2S_0\sqrt{N}} e^{i\mathbf{k} \cdot \mathbf{R}_0} \langle \Phi_i | S_{\mathbf{R}_0}^- (1 - G_0 V)^{-1} S_{\mathbf{R}_0}^+ | \Phi_i \rangle + \frac{1}{2(NS_0S)^{1/2}} \sum_{\mathbf{R} (\neq \mathbf{R}_0)} e^{i\mathbf{k} \cdot \mathbf{R}} \langle \Phi_i | S_{\mathbf{R}_0}^- (1 - G_0 V)^{-1} S_{\mathbf{R}_0}^+ | \Phi_i \rangle. \quad (3.40)$$

As the perturbation V has a nonvanishing matrix element only inside the subspace of the impurity site $\mathbf{R} = \mathbf{R}_0$ (noted 0) and its six nearest neighbors $\mathbf{R} = \mathbf{R}_0 + \Delta_i$ in which $i = \pm 1, \pm 2, \pm 3$, Eq. (3.40) is reduced to

$$\beta_{\mathbf{R}_0}(\mathbf{k}) = e^{i\mathbf{k} \cdot \mathbf{R}_0} \sum_i \langle 0 | (1 - G_0 V)^{-1} | i \rangle e^{i\mathbf{k} \cdot \Delta_i}. \quad (3.41)$$

cially the needful $\gamma_0 = \gamma_{\mathbf{R}}$. (All the details of these calculations can be found in Ref. 27.)

Equation (3.30) leads to several solutions for E , but in our model, only the bound states with a nonvanishing amplitude γ_0 at the impurity site are able to interact with the light. Therefore, we only have to retain the solutions which have the s symmetry for which $\gamma_0 \neq 0$ and γ_i do not depend on i for $i \neq 0$. Following all these previous steps for the calculations we have

$$|\gamma_0|^2 = (2\pi)^3 \left[\frac{JS}{3J_0(S_0 - S)} \right]^2 \frac{E - 6JS^2}{2JS}. \quad (3.36)$$

Our result relates the value of γ_0 to the value of the energy E of the s corresponding bound states; the value of E itself could be calculated numerically and is model dependent; according to the value of the A, A_0, B parameters we may have zero, one, or two solutions for E . However, we shall use our result in a very simple way to determine the value of γ_0 from that of E when this one is known from the experiments.

F. Explicit calculations of the amplitude $\beta_{\mathbf{R}_0}(\mathbf{0})$ of the perturbed spin wave function of wave vector $\mathbf{k} = 0$

For any value of \mathbf{k} the spin wave function $\Phi_{\mathbf{k}}^{\pm}$ scattered by the impurity at the site $\mathbf{R} = \mathbf{R}_0$ [the sign $+$ ($-$) is associated with the out- (in-) going wave, respectively], must be a solution of the Lippmann-Schwinger equation³⁴

$$\Phi_{\mathbf{k}}^{\pm} = [1 + G^{\pm}(E_{\mathbf{k}})V] \Psi_{\mathbf{k}}, \quad (3.37)$$

where $E_{\mathbf{k}}$ and $\Psi_{\mathbf{k}}$ are, respectively, the energy and the wave function of the unperturbed spin wave associated with the same vector \mathbf{k} ; $G^{\pm}(E)$ is the perturbed Green's operator which is defined by the equation³¹

$$G^{\pm}(E) = \frac{1}{E - H \pm i\epsilon} \quad \text{with } \epsilon \rightarrow 0^+. \quad (3.38)$$

Relating the perturbed $G(E)$ to the unperturbed $G_0(E)$ by the Dyson equation, we obtain a simple equation between $\Phi_{\mathbf{k}}$ and $\Psi_{\mathbf{k}}$

$$\Phi_{\mathbf{k}}^{\pm} = (1 - G_0^{\pm} V)^{-1} \Psi_{\mathbf{k}}. \quad (3.39)$$

The wave functions are developed in terms of the complete set on the \mathbf{R} sites as in (3.14). The coefficients $\beta_{\mathbf{R}}(\mathbf{k})$ can be expressed in detail by projecting (3.39) on the wave function (3.5) in which the \mathbf{R} site is excited so that we can write the $\beta_{\mathbf{R}_0}(\mathbf{k})$, when $\mathbf{R} = \mathbf{R}_0$, as

From (3.41), taking into account some physical properties of the matrix $(1 - G_0 V)^{-1}$, we obtain $\beta_{\mathbf{R}_0}(\mathbf{0})$ as

$$\beta_{\mathbf{R}_0}(\mathbf{0}) = \frac{1}{1 - G_{00}(E_{\mathbf{k}=0})(A_0 + 6A - 12B)}. \quad (3.42)$$

Let us call \mathbf{k}_0 the value of \mathbf{k} for which the spin-wave

energy is maximum. When the bound state is close to the band edge, Eq. (3.30), which determines the value of E , can be expanded in the form

$$A_0 + 6A - 12B = \frac{1}{G_0(E_{k_0})} - 4(A - B) \frac{E - 6JS^2}{2JS} \quad (3.43)$$

and (3.42) can be written as

$$\beta_{R_0}(0) = \frac{1}{4G_0(E_{k_0})(A - B)} \frac{2JS}{E - 6JS^2}. \quad (3.44)$$

The $G_0(E_{k=0})$ has the same limiting value²⁷ as this

$$\frac{I_{\text{ext}}(0)}{I_{\text{loc}}} = c \left(\frac{3^4}{\pi} \right)^{1/3} \frac{1}{8} \frac{J_0(S_0 - S)}{(S - 1)(S_0 J_0 - SJ) - \sqrt{S} [(S_0)^{1/2} J_0 - \sqrt{S} J]} \left[\frac{2JS}{E - 6JS^2} \right]. \quad (3.46)$$

This expression for the ratio is very useful, using only simple and accessible physical parameters J, J_0, S_0, S, c and E the energy of the bound states. We note firstly that the scattering of light can be produced as much by the perturbed spin-wave modes by the localized modes.

In the case of small impurity concentration c , this model confirms the experimental results, that is to say, that the ratio of the two intensities is linear in c . It is also interesting to note that this model predicts that the two intensities can be of the same order of magnitude up to a distance between the energy E of the bound state and the energy E_{k_0} of the edge of the energy band of about 25% of the extension of the band.

This is the case of a Co^{2+} impurity embedded in a

one calculated in the case of a bound state near the edge of the band, so that we can use for the matrix element of the Green's operator $G_0(\mathbf{k}=\mathbf{k}_0)$ the following approximate expression:

$$G_0(E_{k_0}) = - \left(\frac{3}{4\pi^4} \right)^{1/3} \frac{1}{2JS}. \quad (3.45)$$

And finally, with the help of (3.36), (3.44), and (3.45) the expression for the ratio of the intensities scattered by the two types of modes can be formulated as

MnF_2 crystal, for example. We can compare our results with those obtained by Gosso and Moch³³ and for concentration c about 0.07 with the use of dispersion curves for the MnF_2 in which the ratio is larger than 0.1. Thus, our physical conclusion is that the cobalt impurity can make the nonlocalized magnon mode as active as the localized one. The antiferromagnetic nature of the real system is probably not an essential factor in that problem.

We can also conclude that the expression (3.46) can be used to predict experimental results with several types of impurities embedded in a magnetic crystal for which J and S are known. For these impurities there is a spin-orbit coupling and J_0, S_0 are determined.

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