Magnetic Effects in the Near Infrared Spectrum of FeF_2†

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We have investigated the near infrared spin-allowed transitions in antiferromagnetic FeF_2. At low temperatures we have observed a sharp transition accompanied by magnetic dipole structure; from the behavior of this structure with respect to temperature and magnetic field changes, it is possible to conclude that magnetic dipole magnon-assisted sideband processes are present in the spectrum. Using general symmetry considerations, selection rules are developed for magnetic dipole sidebands, and it is shown that the exciton-magnon transitions couple only at the R point of the Brillouin zone. From phenomenological considerations, it is also possible to deduce that the magnon-exciton pair are in fact created in opposite sublattices. These conclusions are then used to predict and identify the sideband structure. The strength and the nature of the exciton-magnon coupling mechanism are discussed as well as the mechanism for temperature broadening of the central or no-magnon, no-phonon transition.

I. INTRODUCTION

MAGNETIC excitations have recently been shown to play an important part in the determination of the optical spectra of antiferromagnetic materials. Spin-wave sidebands accompanying sharp transitions in the visible spectrum of MnF_2 were identified by Greene and co-workers[1]; this identification has since been amply supported by studies of external perturbative effects.[2,3] Simultaneously, Halley and Silvera, and Allen *et al.*[4] have observed two magnon-absorption processes in the far infrared (IR) spectra of FeF_2 and MnF_2. Theoretical interpretations have also been advanced by Halley,[5] and Tanabe *et al.*[6] The various mechanisms proposed to couple the magnon and ion systems have their common origin in an earlier theory by Dexter[7] and arise from the interactions between the ions. Certain modifications are necessary in dealing with concentrated materials, i.e., the optical-excited states are exciton states, and much, in fact, can be learned by consideration of the symmetry properties of the interacting excitons and magnons.

We have conducted studies of the near IR spectrum of FeF_2 and the effects various perturbations have on this spectrum. Strong absorption bands are observed corresponding to the spin-allowed $^5T_2 \rightarrow {}^5E$ (both ^5D) transitions of Fe^{2+} (Fig. 1). Strong and sharp magnetic dipole transitions and structure are observed at the low-energy side of the bands at low temperature (Fig. 2). From the behavior of the sharp structure with respect to temperature change and to the application of magnetic fields, it is possible to identify pure electronic transitions and their associated spin-wave sidebands. These sidebands differ from those previously reported in two ways; first, they are associated with spin-allowed no-magnon, no-phonon electronic transitions and, second, the sidebands are magnetic dipole instead of electric dipole active.

In this paper, we modify the existing theory dealing with the magnon-exciton interactions and develop the appropriate selection rules for magnetic dipole spin-wave sidebands. From these rules it is possible to conclude that the magnon-exciton pair are created in opposite sublattices. This, in turn, makes it possible to predict sideband behavior with respect to temperature and magnetic perturbations and allows us to sort out and identify the appropriate magnon sidebands.

II. EXPERIMENTAL DETAILS AND RESULTS

The single crystal of FeF_2 used in these studies were grown and kindly provided by H. J. Guggenheim of Bell Laboratories. The crystals were oriented with the c axis parallel and perpendicular to the absorbing surface (to within a few degrees). The samples used were approximately 10 mils in thickness.

The Fe^{2+} near IR spectrum was investigated with a 1-m Jarrell-Ash Czerny-Turner spectrometer used in first order. A high-voltage tungsten-iodine projection lamp served as the near IR source. The appropriately filtered signal was mechanically chopped at 95 Hz. The absorption spectra were then detected by a Kodak Ektron detector cooled to dry-ice temperatures.

Low temperatures were attained by immersion of the sample in liquid helium. In the intermediate range of temperatures (i.e., 4.2 to 77°K), a controlled flow of liquid-helium boil-off past the sample was used. Stable temperatures were maintained using a feedback technique devised by Graifman.[8] Temperatures were meas-

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[1] R. L. Greene, D. D. Sell, W. M. Yen, A. L. Schawlow, and R. M. White, Phys. Rev. Letters **15**, 656 (1965).

[2] D. D. Sell, R. L. Greene, and R. M. White, Phys. Rev. **158**, 489 (1967).

[3] D. D. Sell, thesis, Stanford University (unpublished).

[4] J. W. Halley and I. Silvera, Phys. Rev. Letters **15**, 654 (1965); S. J. Allen, Jr., R. Loudon, and P. L. Richards, *ibid.* **16**, 463 (1966).

[5] J. W. Halley, Phys. Rev. **149**, 423 (1966).

[6] Y. Tanabe, T. Moriya, and S. Sugano, Phys. Rev. Letters **15**, 1023 (1965).

[7] D. L. Dexter, Phys. Rev. **126**, 1962 (1962).

[8] M. B. Graifman (private communication).

ured with a copper versus gold-cobalt thermocouple mounted in the vicinity of the sample.

FeF_2 has the rutile structure common to many of the antiferromagnetic fluorides. The spin ordering or Néel temperature occurs at 78.3°K. Figure 1 shows the Fe^{2+} spectrum in the 1.6- to 0.8-μ spectral region for FeF_2 near the ordering temperature (77°K). The spectrum in absorption consists of two extremely broad bands peaking at 1.42 and 0.92 μ, respectively. The bands may be assigned to transitions between components of the cubic $^5T_2$ ground state and ^5E excited state. Polarization studies indicate that these transitions are electric dipole active and that they are likely to be vibronic in nature.

At sufficiently low temperatures, a strong and sharp transition with associated structure is observed on the low-energy side of the 1.42-μ band. This region of the spectrum at a temperature of 4.2°K is illustrated in Fig. 2; it can be seen from the figure that the sharp line along with the majority of the diffuse structure appears in $\pi(\mathbf{E} \parallel c, \mathbf{H} \perp c)$ and $\alpha(\mathbf{E} \perp c, \mathbf{H} \perp c)$ polarizations. Thus, for all these transitions the magnetic vector of the light is the important perturbation, and they are magnetic dipole transitions.

The splittings of the structured peaks from the central 6381.8 cm^{-1} are also given in Fig. 2. The value of some of the splittings and the asymmetric shapes of the absorption, particularly those at 77.3 and 155 cm^{-1}, are suggestive of magnon-assisted transitions. Quantitative arguments could be made from the shapes of the sidebands; however, the magnon-exciton interactions in FeF_2 are not clearly understood at this time.

We have investigated the behavior of the central (no-phonon, no-magnon) line and its associated structure as a function of temperature and applied external magnetic field ($\mathbf{H}_0 \parallel c$). The entire spectrum broadens appreciably as the temperature is increased; temperature-dependent line shifts are observed as well. The temperature dependence of the width of the central line is given in Fig. 3. At temperatures higher than ~45°K, the 6382-cm^{-1} line and its adjacent structure

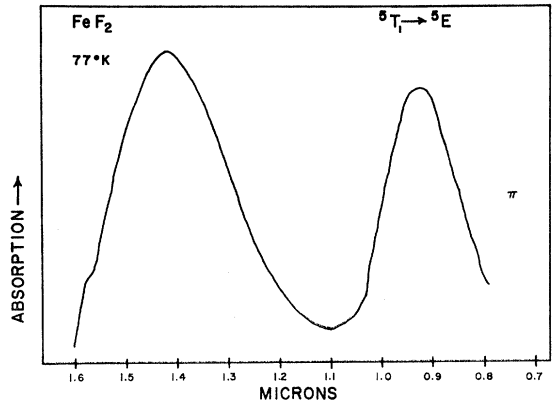

FIG. 1. FeF_2 spectrum in near IR region at 77°K.

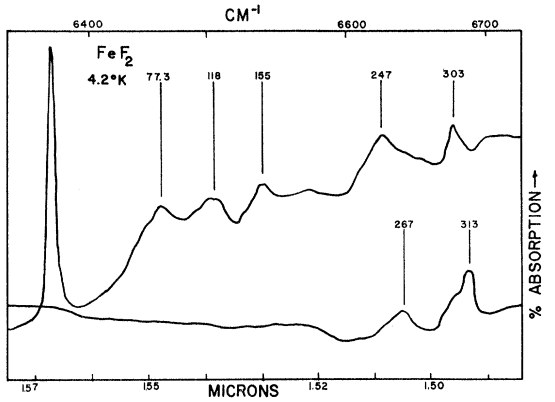

FIG. 2. FeF_2 spectrum at 4.2°K. Upper trace appears in π and α, lower trace in σ polarization.

are severely broadened and widths, positions, and splittings, particularly the latter two, are difficult to determine with any degree of accuracy.

The central transition is not split or shifted by the application of a 10-kOe magnetic field parallel to the c axis. Recently Sturge and Imbusch have applied fields up to 70 kOe and no splitting of the 6382 cm^{-1} is observed.[9]

Because of the broadness of the peak at 77 cm^{-1} higher energy from the 6382-cm^{-1} line, its position is difficult to determine to within better than 1.8 cm^{-1}. On the assumption that this is a one-magnon-assisted transition, a 10-kOe magnetic field parallel to the c axis should split the peak into two peaks $2g\mu_B H \sim 2$ cm^{-1} apart. No such splitting could be resolved within these broad transitions. Furthermore, because of the smallness of the splitting and uncertainty in position of the maxima, even a broadening of the line proved to difficult to detect.

III. INTERPRETATION AND DISCUSSION

A. Unassisted Transitions

In FeF_2, the Fe^{2+} ion has D_{2h} symmetry in the paramagentic phase. Magnetic ordering reduces this symmetry to C_{2h}. The $^5T_2$ cubic ground-state representations, originating from the ^5D free-ion states, become nondegenerate with the application of the orthorhombic field and L-S coupling in second order. Similar considerations are applicable to the ^5E excited state. The solution of the total Hamiltonian for the Fe^{2+} in the ordered phase, including the combined effect of spin orbit, and orthorhombic and exchange fields, is extremely complicated and not necessarily a tractable problem. It suffices here to identify the strong absorption at 6382 cm^{-1} (Fig. 2) as a pure electronic transition between components of the cubic $^5T_2$ and ^5E representations. Several other transitions are mag-

[9] M. D. Sturge and G. F. Imbusch (private communication).

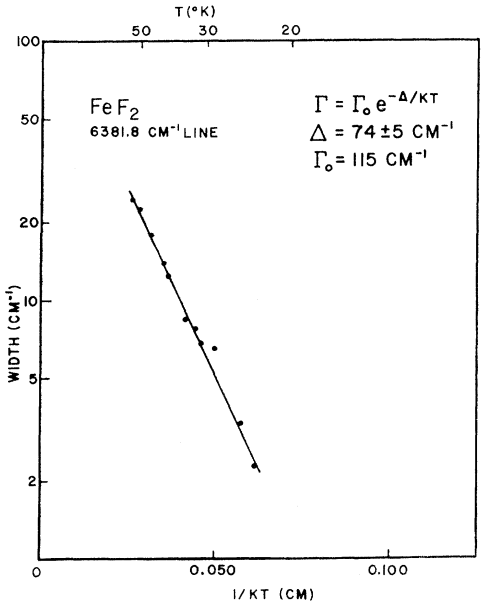

FIG. 3. Strain corrected half-width of 6382 cm^{-1} line versus temperature.

netic dipole allowed and some of the structure appearing in Fig. 2 must, in fact, correspond to such transitions.

It has been pointed out that when the symmetry is sufficiently low, as is the case of FeF_2 in the magnetic phase, the Jahn-Teller effect is not likely to occur and introduce further complications in distorting the proper quantization axis.[10] Consequently, in further discussion, we neglect the Jahn-Teller effect.

Application of an extenal magnetic field parallel to the crystalline c axis affects the Fe^{2+} ions in the two magnetic sublattices in a different way. For spin-allowed transitions, the optical transition should split according to[11]

$$\Delta\epsilon = 2\beta H_0 S[g - g'], \qquad (1)$$

where $\Delta\epsilon$ occurs symmetrically about the zero field position and g and g' are g-values of the ground and excited states, respectively. This is in contrast to previously reported cases where the effective spin change S contributes as well. The relative insensitivity of the 6382-cm^{-1} transition to applied external fields of up to 70 kOe allows us to place an upper limit of 0.01 in the $[g-g']$ difference of Eq. (1).

[10] G. D. Jones, Phys. Rev. **155**, 259 (1967).

[11] In this formula and in some of the following developments, we implicitly rely on the fact that only the L^+ part of the magnetic dipole operator $(L^+ + 2S^+)$ accomplished the optical transition for $\mathbf{H} \perp c$. The argument is as follows: Ignoring spin-orbit coupling and noncubic crystalline terms, we write the wave functions as direct products of spin and orbital parts. Because of the orthogonality of the orbitals of the T_2 and E states, we must conclude that L^+ is active or that $\Delta S = 2$ which is somewhat less likely. For orbital representations used, see J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, New York, 1964), p. 393.

In the molecular-field approximation, the temperature-dependent line shifts of the position of the 6382-cm^{-1} line scale roughly as the sublattice magnetization weighed by the difference in the value of the exchange constant J in the ground and excited states. The transition is observed to shift -0.8 cm^{-1} in going from 4.2 to 35°K, indicating that J_f of the excited state is somewhat smaller than J_i of the initial state In view of the lack of any data on thermal expansion which change the FeF_2 lattice parameters anisotropically and thus the line positions, no more quantitative estimates may be made at this time.[12]

The large anisotropy in FeF_2 restricts the available magnons to a band ranging from 53 to 79 cm^{-1}. The broadening of the central line (Fig. 3) may be understood in terms of magnon Raman scattering into this narrow magnon band. If one approximates the density of states by an Einstein distribution peaking at the zone boundary, the broadening is expected to vary as

$$\Gamma = \Gamma_0 \exp(-\Delta/kT), \qquad (2)$$

where Δ is approximately the boundary energy. Experimentally, the fitted function, shown in Fig. 3, yields a value $\Delta = 74 \pm 5$ cm^{-1} and $\Gamma_0 = 115$ cm^{-1}, which are in good agreement with previously reported results.[12]

B. Magnon-Assisted Transitions

The expected oscillator strength for the central unassisted transition has recently been calculated by Stout *et al.*[13] on the basis of the correlation between the measured value of the parallel susceptibility and the IR spectra of FeF_2. Their results indicate that the transition strength estimated in this manner is about five times larger than the empirically observed value. Imbusch has pointed out from general arguments that, for a magnetic dipole transition which is allowed, any magnetic dipole sideband process obtains its strength at the expense of the central transition.[14] The observed integrated intensity of the magnetic dipole structure adjacent to our central transition is in fact several times that of the central transition itself, supporting our belief that the structure results from sideband processes.

The position and asymmetric shape of the transition at 77 cm^{-1} from the 6382-cm^{-1} line along with its behavior suggests that it is a magnon-assisted transition. Failure to see another sideband on the low-energy side of the unassisted transitions as temperature is increased, a so-called hot band, can be explained on the basis of the small thermal population of magnon states because

[12] W. M. Yen, G. F. Imbusch, and D. L. Huber, *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Interscience Publishers, Inc., New York, 1967), p. 301.

[13] J. W. Stout, M. I. Steinfeld, and M. Yuzuri, in *Proceedings of the International Congress on Magnetism, Boston*, 1967 (to be published).

[14] G. F. Imbusch, thesis, Stanford University (unpublished).

of the large anisotropy gap (about 55 cm^{-1}). Phonon effects would obscure the appearance of this line at any temperature at which such a population might become appreciable.

The shape of the sideband scales roughly as the density of magnon states. The exciton-dispersion and exciton-magnon interactions change the shape considerably with the asymmetric shape somewhat preserved. Inspection of the shape of the sideband shows that these effects are non-negligible.

The sideband splitting from the central line is expected to change with temperature; the temperature dependence scales with certain corrections as the sublattice magnetization. Because of the large gap, this temperature-dependent change has been shown to be almost an order of magnitude down from those observed in MnF_2 by Jaccarino[15]; again, the broadness of the peak and the magnitude of the expected shifts made it difficult to ascertain whether this splitting change occurred.

Since previously reported spin-wave sidebands have been electric dipole in character, the magnetic dipole nature of the observed structure motivates us to consider selection rules and transition moments of even-parity magnon-assisted processes.

From the site symmetry, and as we have already mentioned, the Fe^{2+} ion in FeF_2 in the magnetic state has only one-dimensional representations. The combination of these site-group representations to obtain the space-group representations may be accomplished by methods recently reviewed by McClure.[16] This has been done by Loudon[17] for the center point Γ of the Brillouin zone of the space group P_{nnm} of D_{2h}^{12} appropriate to FeF_2. Using the compatibility tables of Dimmock and Wheeler,[18] representations of other sites in the zone compatible with the center point Γ have been found by Loudon.[17] Since the photon has negligible $\mathbf{k}$ vector compared to any magnon, the representation of a pseudovector is considered at the Γ site where it is found to transform as $\Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+$. For $\mathbf{H} \perp c$ (π, α polarizations), Γ_3^+, Γ_4^+ are the relevant representations of the transition operator. The states connected by this operator are unlike exciton states, and the representations to be considered in the rest of the Brillouin zone are shown in Fig. 4. Loudon has pointed out as well that the Γ_3^+ and Γ_4^+ representations become degenerate in the full space group when time reversal symmetry is also considered; it follows that no Davydov splitting is to be expected in the no-magnon line. This is experimentally confirmed.

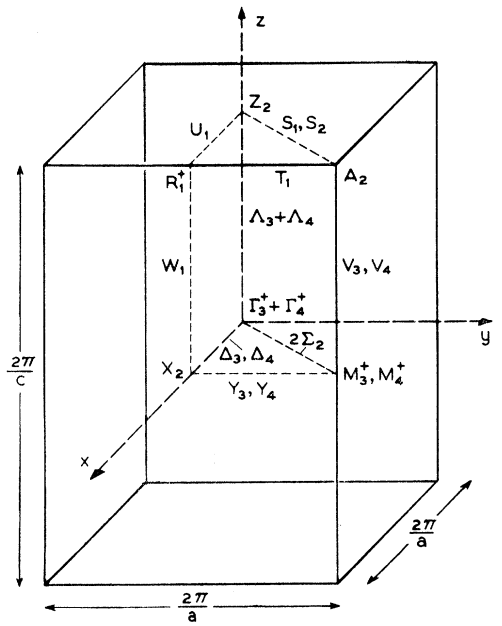

FIG. 4. Representations for unlike exciton states in the Brillouin zone of rutile structure [after Loudon (Ref. 17)].

To determine the selection rules for a one-mangon sideband, we note that the perpendicular component of the magnetic dipole operator transforms as Γ_3^+ and Γ_4^+. The active excitons must transform as Γ_3^+ and Γ_4^+ since the ground-state belongs to the fully symmetric Γ_1^+ representation. For other points in the zone, the exciton and magnons transforms as X_2, M_3^+, M_4^+, Z_2, R_1^+, and A_2. We restrict ourselves to the zone boundaries since the density of states is expected to be greatest there. The method of Lax and Hopfield[19] may now be used to relate representations in the direct product site symmetry group other than Γ to the representations appropriate to Γ; we obtain

$$M_3^+ \times M_3^{+*} = \Gamma_1^+,$$
$$M_4^+ \times M_3^{+*} = M_3^+ \times M_4^{+*} = \Gamma_2^+,$$
$$M_4^+ \times M_4^{+*} = \Gamma_1^+,$$
$$Z_2 \times Z_2 = \Gamma_1^+ + \Gamma_2^+ + \Gamma_1^- + \Gamma_2^- = A_2 \times A_2,$$
$$X_2 \cdot X_2 = \Gamma_1^+ + \Gamma_2^+ + \Gamma_3^- + \Gamma_4^-,$$
$$R_1^+ \times R_1^+ = \Gamma_1^+ + \Gamma_2^+ + \Gamma_3^+ + \Gamma_4^+. \quad (3)$$

The necessary Γ_3^+, Γ_4^+ representations are found only in the $R_1^+ \times R_1^+$ product, indicating that only the R point can contribute to the sideband. Furthermore, the excitons fail to have their degeneracy removed at this point since they have a single representation, and no Davydov splitting is expected in any of the spin-wave sidebands present in our case.

[15] V. Jaccarino, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1959), Vol. III, p. 1.
[16] D. S. McClure, in *Advances in Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. VIII, p. 1.
[17] R. Loudon (to be published).
[18] J. O. Dimmock and R. G. Wheeler, Phys. Rev. **127**, 391 (1962).
[19] M. Lax and J. J. Hopfield, Phys. Rev. **124**, 115 (1961).

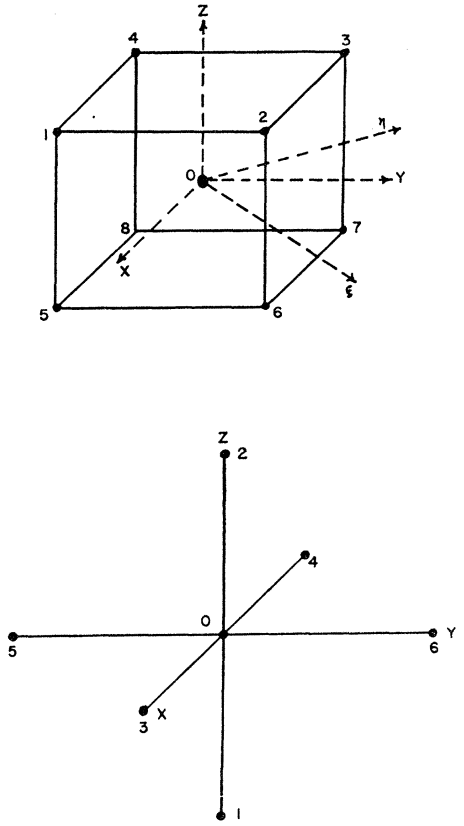

FIG. 5. (a) Numbering convention for first and third near neighbors on same sublattice of a rutile structure. $\hat{\xi}=(1/\sqrt{2})(\hat{x}+\hat{y})$ and $\hat{\eta}=(1/\sqrt{2})(\hat{y}-\hat{x})$. (b) Numbering convention for nearest neighbors on opposite sublattice of rutile structure [after Sell (Ref. 3)].

Using the formalism of Sell *et al.*,[2] we can define an effective magnetic dipole moment pair operator $\mu_{01,n2}{}^{\text{eff}}$ such that the total dipole moment is the sum of pair moments

$$M=\langle E^1,\mathbf{k};M^2,-\mathbf{k}\mid H^{\text{eff}}\mid G\rangle$$
$$=\sum_{n=1}^{N}\exp(i\mathbf{k}\cdot\boldsymbol{\delta}_{01,n2})\mathbf{H}\cdot\langle e_{01},m_{n2}\mid \boldsymbol{\mu}_{01,n2}{}^{\text{eff}}\mid Pg_{01}g_{n2}\rangle. \tag{4}$$

Consideration of nearest-neighbor interactions on the opposite sublattice only reduces this to the following form:

$$M_1{}^j(\mathbf{k})=\exp(ik_zc/2)\{\mu_1{}^j\exp[i(k_x-k_y)a/2]$$
$$+\mu_2{}^j\exp[i(k_x+k_y)a/2]+\mu_3{}^j\exp[i(-k_x+k_y)a/2]$$
$$+\mu_4{}^j\exp[i(-k_x-k_y)a/2]\}+\exp(-ik_zc/2)$$
$$\times\{\mu_5{}^j\exp[i(k_x-k_y)a/2]+\mu_6{}^j\exp[i(k_x+k_y)a/2]$$
$$\times\mu_7{}^j\exp[i(-k_x+k_y)a/2]+\mu_8{}^j\exp[i(-k_x-k_y)a/2]\}, \tag{5}$$

where the numbering convention is that of Ref. 3 and repeated in Fig. 5(a). For the situation at hand, $\mathbf{H}\perp c$; and so the relevant components are $j=\xi,\ \eta$. Using the results tabulated in Ref. 3, with the necessary modifications that $\boldsymbol{\mu}$ is a pseudovector and hence invariant under inversion, and the fact that the excitons transform as the magnons, we can deduce

$$\mu_1{}^{\xi,\eta}=-\mu_3{}^{\xi,\eta}=\mu_7{}^{\xi,\eta}=-\mu_5{}^{\xi,\eta},$$
$$\mu_2{}^{\xi,\eta}=-\mu_4{}^{\xi,\eta}=\mu_8{}^{\xi,\eta}=-\mu_6{}^{\xi,\eta},$$

and hence

$$M_1{}^{\xi,\eta}(\mathbf{k})=-4\sin(k_zc/2)[\mu_1{}^{\xi,\eta}\sin(k_x-k_y)a/2$$
$$+\mu_2{}^{\xi,\eta}\sin(k_x+k_y)a/2] \tag{6}$$

for the exciton on one sublattice and the magnon on the opposite sublattice. An analogous expression is obtained for the interchange of sublattice roles.

Consistent with the previous results of this section, we observe that only the R point with $\mathbf{k}=(k_x,k_y,k_z)=(\pi/a,0,\pi/c)$ gives a nonvanishing result:

$$M_1{}^{\xi,\eta}(\mathbf{k})=-4[\mu_1{}^{\xi,\eta}+\mu_2{}^{\xi,\eta}]. \tag{7}$$

If we consider the magnon and exciton on the same sublattice, we write

$$M_3{}^{\xi,\eta}=\mu_1{}^{\xi,\eta}\exp(-ik_zc)+\mu_2{}^{\xi,\eta}\exp(ik_zc)$$
$$+\mu_3{}^{\xi,\eta}\exp(ik_xa)+\mu_4{}^{\xi,\eta}\exp(-ik_xa)$$
$$+\mu_5{}^{\xi,\eta}\exp(-ik_ya)+\mu_6{}^{\xi,\eta}(ik_ya). \tag{8}$$

However, using the transformation properties under space-group operations $(C_2{}^Z\mid 0)$ and $(I\mid 0)$, we can conclude that all pair elements must vanish, i.e., $\mu_i{}^{\xi,\eta}=0$; $i=1,\cdots,6$. Thus $M_3{}^{\xi,\eta}=0$ indicates that the magnon and exciton are necessarily on opposite sublattices. This is a nonrigorous result in the sense that we include only interactions with first and third near neighbors. However, we expect these to be much more dominant if exciton-magnon interactions on the same sublattice were to exist. With this in mind we point out that a 10-kOe magnetic field parallel to the c axis should split the sideband peaks by $2g\mu_BH\sim 2\ \text{cm}^{-1}$, assuming $g=g'$, as argued previously, but that magnon dispersion is likely to obscure this.

We can treat the $\mu_{1,2}{}^{\xi,\eta}$ as phenomenological parameters whose value is obtained empirically. We can relate the absorption coefficient to the dipole moment by

$$\alpha_j(\nu)=[(2\pi)^3\nu/hcVn]\sum_{k=1}^{N}\sum_i\mid M_i{}^j(\mathbf{k})\mid{}^2\Delta(\nu-\nu_k{}^e-\nu_k{}^m), \tag{9}$$

where the summation over i takes into account all contributing processes; n is the index of refraction.

For π polarization

$$\int \alpha_\pi(\nu)\,d\nu=\pi_R \sum_{\mathbf{k}} \sin^2(k_z c/2) \times[\sin^2(k_x a/2)\cos^2(k_y a/2) +\cos^2(k_x a/2)\sin^2(k_y a/2)] \times\{[(2\pi)^3(\nu_k{}^e+\nu_k{}^m)]/hcnV\}, \quad (10)$$

where

$$\pi_R=64[\,|\,\mu_1{}^\xi\,|^2+|\,\mu_2{}^\xi\,|^2]$$

assuming

$$|\,\mu_i{}^\xi\,|^2=|\,\mu_i{}^\eta\,|^2; \qquad i=1, 2.$$

If we replace the sum over $\mathbf{k}$ by an integral, this becomes

$$\int \alpha_\pi(\nu)\,d\nu=(64\pi^3\nu_0/hcvn)[\,|\,\mu_1{}^\xi\,|^2+|\,\mu_2{}^\xi\,|^2] =(5.9\times10^{44}\ \mathrm{erg^{-1}\ cm^{-5}})[\,|\,\mu_1{}^\xi\,|^2+|\,\mu_2{}^\xi\,|^2], \quad (11)$$

where v is the volume of a unit cell $=a^2c$.

Experimentally $[\int\alpha d\bar{\nu}]=2.7\times10^2\ \mathrm{cm^{-2}}$. Hence

$$[\,|\,\mu_1{}^\xi\,|^2+|\,\mu_2{}^\xi\,|^2]^{1/2}=6.8\times10^{-22}\ \mathrm{erg/G} =0.07\mu_B$$

in FeF_2.

A rough estimate of the strength of the coupling mechanism which affects the sideband can be made comparing the integrated absorption coefficient of the sideband to that of the main line. Without specifying any details as yet about the detailed nature of the coupling mechanism, we suppose that suitable approximations can be made to enable us to factor out the matrix elements connecting states for the unassisted line from those involved in the coupling mechanism so that the intensity can be expressed as

$$I_{\mathrm{SB}}=I_0\int\left|\frac{\langle f\,|\,h\,|\,i\rangle}{\hbar\omega}\right|^2\rho(\omega)\,d\omega, \quad (12)$$

where I_0 is the intensity of the main line and h is the interaction accomplishing the coupling. In the case of FeF_2, the relative intensity of the sideband is

$$I_{\mathrm{SB}}/I_0=\left|\frac{\langle f\,|\,h\,|\,i\rangle}{\hbar\omega_0}\right|^2=0.62, \quad (13)$$

so that $|\,\langle f\,|\,g\,|\,i\rangle\,|=60\ \mathrm{cm^{-1}}$.

C. Nature of the Interaction

Dexter[7] was the first to explain electric dipole absorption by pairs of ions. His theory has obvious modifications for magnetic dipole absorption. The transition magnetic dipole moment for the exciton-magnon pair is given as

$$M\sim\sum_q\langle e^A m^B\,|\,V\,|\,g^A q^B\rangle\langle q^B g^A\,|\,\mathfrak{y}\,|\,g^B g^A\rangle/(\Delta E-h c\nu) +(\text{term obtained by interchanging } V \text{ and } \mathfrak{y}) +(\text{two terms obtained by interchanging } A \text{ and } B \text{ in previous two terms}), \quad (14)$$

where A and B refer to the two sublattices and e, m, and q are, respectively, exciton magnon, and intermediate states.

The interaction operator V is the two-electron Coulomb operator e/r_{12}. The matrix elements $\langle e^A m^B\,|\,V\,|\,g^A g^B\rangle$ may be either the exchange type,

$$\int d\tau_1 d\tau_2\, e^{A*}(1)\,m^{B*}(2)\,V q^A(2)\,g^B(1),$$

or the direct type,

$$\int d\tau_1 d\tau_2\, e^{A*}(2)\,m^{B*}(1)\,V q^A(2)\,g^B(1).$$

Tanabe, Moriya, and Sugano (TMS)[6] have pursued consequences of the exchange terms; whereas, Halley[5] has considered effects of the direct terms for electric dipole processes. TMS have then reexpressed their moment operator in terms of spin-operator equivalents $\mathbf{S}_a\cdot\mathbf{S}_b$ and Halley has considered terms arising from a multipole expansion of the Coulomb interaction and invoked spin-orbit coupling in order to introduce the spin systems of the ion pairs.

Failure of the unassisted line to split in a magnetic field parallel to the c axis leads us to conclude that the S_z components of the initial and final states of the ion undergoing an orbital transition are the same and also that it is possible to consider the ground states as "pure spin states" in some effective-Hamiltonian formalism. Also the dipole operator $\perp c$ axis is the active component here so that if we use spin-operator equivalents in Eq. (14) we expect terms of the form

$$M\sim\langle-2^B1^A\,|\,S_B{}^-S_A{}^-\,|\,-1^B2^A\rangle\langle-1^B2^A\,|\,S_B{}^+\,|\,-2^B2^A\rangle+\langle-2^B1^A\,|\,S_B{}^-\,|\,-1^A1^B\rangle \times\langle-1^B1^A\,|\,S_B{}^+S_A{}^-\,|\,-2^B2^A\rangle+\langle-1^B2^A\,|\,S_B{}^+S_A{}^+\,|\,-2^B1^A\rangle \times\langle-2^B1^A\,|\,S_B{}^-\,|\,-2^B2^A\rangle+\langle-1^B2^A\,|\,S_A{}^+\,|\,-1^B1^A\rangle\langle-1^B1^A\,|\,S_B{}^+S_A{}^-\,|\,-2^B2^A\rangle, \quad (15)$$

where the integers represent the values of S_z components on their respective sublattices. The diagonal exchange term $S_B^+S_A^-$ would give a larger contribution than the off diagonal terms $S_B^+S_A^+$, $S_B^-S_A^-$ since the latter must accomplish $|\Delta S_z|=2$ which is somewhat less probable than $|\Delta S_z|=0$ for diagonal terms.

However, a simple "Heisenberg" form of the exchange interaction $M_{ab}\mathbf{S}_a\cdot\mathbf{S}_b$ is not adequate here to describe our exciton-magnon coupling interaction because, when it is expanded in terms of second quantized operators and summation over near neighbors on the opposite sublattice is affected, all directions in the Brillouin zone will be weighted equally. This will conflict with our previous rigorous group-theoretical result that only the R point of the Brillouin zone contributes. Hence, off-diagonal terms in a more general exchange interaction $\sum_n m_{0n}\mathbf{S}_0\cdot\mathbf{S}_n$ must be invoked.

Pursuing the alternative approach, i.e., multipole moment expansion in the direct terms, we invoke parity considerations. Since the magnetic dipole is an even-parity operator, we should be able to couple exclusively to even-parity states throughout. The lowest-order even-even term in the expansion is the quadrupole-quadrupole term. Although this term is reduced in magnitude from a dipole-quadrupole term by a factor of the order

$$a/\rho=(\hbar^2/me^2)\,(\tfrac{1}{2}\text{ lattice diagonal})^{-1},$$

it need only be invoked once to couple to even excited states of somewhat lower energies than higher-energy odd excited states. The spin systems then enter the picture via spin-orbit coupling.

As a final remark, we might note that there might be a temptation to consider the dipolar coupling of the spin systems directly

$$H=\sum_i (g^2\mu_B^2/r_{i0}^3)\{\mathbf{S}_i\cdot\mathbf{S}_0-[3(\mathbf{S}_i\cdot\mathbf{r}_{i0})(\mathbf{S}_0\cdot\mathbf{r}_{i0})/r_{i0}^2]\},\tag{16}$$

where the sum is over near neighbors on the opposite sublattice, particularly since this contains terms of the correct symmetry even in the more general exchange interaction $\sum_n m_{0n}\mathbf{S}_n\cdot\mathbf{S}_0$. However, $(g^2\mu_B^2/r^3)\sim 0.02$ cm^{-1}, which is several orders of magnitude too weak.

IV. CONCLUSIONS

Symmetry arguments and group theory alone show that the magnetic dipole magnon sideband appearing with $\mathbf{H}\perp c$ can have only the R point of the Brillouin zone boundary contributing to the magnon sideband. A slightly less rigorous result (including only up to third-nearest-neighbor interactions) shows that the magnon and exciton reside on opposite sublattices if a pair interaction is involved. These conclusions assume no detailed knowledge of the coupling mechanism responsible for the sidebands.

If an exchange process accomplishes the coupling between the excited ion and spin system on the opposite sublattice, then off-diagonal terms in a general exchange interaction $\sum_n m_{n0}\mathbf{S}_n\cdot\mathbf{S}_0$ having a symmetry which does not conflict with our rigorous group-theoretic results must be responsible. On the other hand, if a direct process is considered, then one must go to a quadrupole-quadrupole term in the multipole expansion of the Coulomb interaction to satisfy parity conservation. In this latter case, spin-orbit coupling plays a crucial part in coupling to the spin systems. This an increase in spin-orbit coupling might enhance the sideband effects and hence favor the direct process. Our preliminary studies on Co^{2+} indicate very roughly that this may be the case.

For spin-allowed transitions, electric dipole spin-wave sidebands are allowed as well, but larger energy denominators in perturbation terms introduced in coupling to the higher-lying odd states seem to favor magnetic dipole processes to the exclusion of the former in FeF_2.

Direct dipolar coupling of neighboring spins does not seem to enter the picture as it is too weak to accomplish what is experimentally observed.

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