ODD-EXCITON MAGNON INTERACTION AND EXPLANATION OF ANOMALOUS FAR-INFRARED ABSORPTION IN ANTIFERROMAGNETIC FeF_2†

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We describe a previously unrecognized interaction by which the center of symmetry at an ion site in a magnetic material is removed by excitation of a short-wavelength spin wave. The interaction explains the existence of magnon sidebands in optical-absorption spectra which were anticipated by us on such a basis and which were very recently observed independently[1] in MnF_2. In addition, the interaction is essential to our explanation of a very unusual and previously anomalous line[2] observed in far-infrared absorption in the antiferromagnet FeF_2 at the wave number 154.4 cm^{-1}. In this Letter we describe the interaction and the analytical approach which is used in the theory. We then describe the experimental and theoretical results for the infrared-absorption experiment, showing that they are consistent and that the explanation of the line is unique. Finally, we describe the mechanism by which magnon sidebands in optical-absorption spectra can exist. The optical-absorption experiments which confirm its occurrence in MnF_2 are described in the accompanying Letter.[1]

To describe the interaction, we consider the magnetic analogy to the removal by a phonon of a center of symmetry at an ion site in a crystal[3] [Fig. 1(a)]. The magnetic analogy is indicated schematically in Fig. 1(b). When a spin wave with large k vector is excited, the center of symmetry at a site like that at j in the sketch is removed. In the phonon case, an electric field (or, equivalently, a crystal field with odd part) is produced at the ion site by the phonon. Similarly, in the magnetic case, an electric field is produced by the following indirect mechanism: On the neighbors $j+\vec{\delta}$ of a given ion site j, the spins interact with their electronic charge clouds via the spin-orbit interaction, giving these ions a spin-dependent quadrupole moment $Q_{j+\vec{\delta}}$. These quadrupole moments produce a field at the site j. Explicitly,

$$Q_{j+\vec{\delta}} = 2\lambda \sum_{m\neq 1} \langle\Gamma_1|Q^{(\mathrm{op})}|\Gamma_m\rangle \times\langle\Gamma_m|\vec{L}_{j+\vec{\delta}}|\Gamma_1\rangle\cdot\vec{S}_{j+\vec{\delta}}/(E_1-E_m), \qquad (1)$$

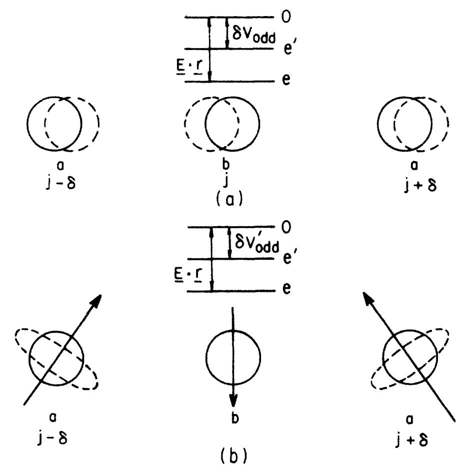

FIG. 1. Phonon- and magnon-assisted electronic transitions. (a) In the phonon case, the displacement of neighboring ions gives an odd part δV_{odd} to the crystal-field potential at j, which can induce even-even transitions in the ion at j. (b) In the magnon case, the spins of neighboring ions ($j\pm\vec{\delta}$) perturb the quadrupole moments at $j\pm\vec{\delta}$, thus giving an odd part $\delta V_{\mathrm{odd}}'$ to the crystal-field potential at j and inducing even-even transitions.

where $Q^{(\mathrm{op})}$ is the electron quadrupole-moment tensor operator for the ion at j; $|\Gamma_1\rangle$ is the electronic ground state, and $|\Gamma_m\rangle$ are electronic excited states; $\vec{L}_{j+\vec{\delta}}$ is the angular-momentum operator; and λ is the spin-orbit coupling constant. The potential at j, arising from these spin-dependent moments at $j+\vec{\delta}$, is

$$V_j = e\sum_{i=1}\sum_{\vec{\delta}}(\vec{x}_i-\vec{x}_{j+\vec{\delta}}^{(0)})\cdot Q_{j+\vec{\delta}}\cdot(\vec{x}_i-\vec{x}_{j+\vec{\delta}}^{(0)})/|\vec{x}_i-\vec{x}_{j+\vec{\delta}}^{(0)}|^5. \qquad (2)$$

Here $\vec{x}_{j+\vec{\delta}}^{(0)}$ is the position of the $(j+\vec{\delta})$th ion; the $\vec{x}_i$ are the coordinates of the n electrons of the jth ion. This potential has an odd part with respect to inversion about $\vec{x}_j^{(0)}$ when a spin wave with $\vec{k}\neq 0$ is excited.

It is convenient to describe the effects of this crystal field by means of a second-quantized formalism in which the electronic states of the ions are Fourier-analyzed in space and treated as excitons. In such a formalism, the potential (2) leads to an interaction between magnons and excitons which are phased linear combinations of those excited electronic states of the ions which have odd parity with respect to inversion about the ion site (odd excitons). The formalism is fully described in a forthcoming publication.[4]

The experimentally observed properties of the infrared-absorption line in FeF_2 are the following: The absorption intensity peaks at

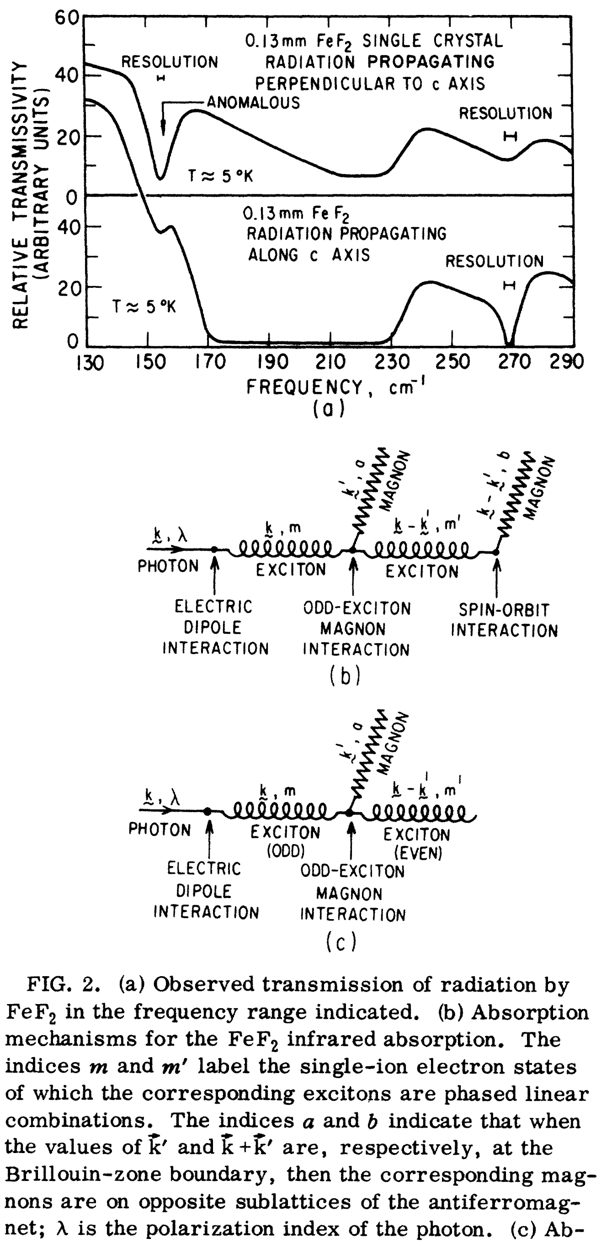

FIG. 2. (a) Observed transmission of radiation by FeF_2 in the frequency range indicated. (b) Absorption mechanisms for the FeF_2 infrared absorption. The indices m and m' label the single-ion electron states of which the corresponding excitons are phased linear combinations. The indices a and b indicate that when the values of $\vec{k}'$ and $\vec{k}+\vec{k}'$ are, respectively, at the Brillouin-zone boundary, then the corresponding magnons are on opposite sublattices of the antiferromagnet; λ is the polarization index of the photon. (c) Absorption mechanisms for magnon sidebands in optical absorption.

154.4 ± 1 cm^{-1}, has width ~6 cm^{-1}, and disappears above the Néel temperature of $T_N = 78°$K. The intensity is of the same order as that of the antiferromagnetic resonance (AFMR) at 52.7 cm^{-1}. The absorption for $E \parallel c$ axis is $\gtrsim 7$ times that when $E \perp c$ axis [Fig. 2(a)]. The line is unchanged in a dc magnetic field of 26 kG. The frequency was measured as a function of temperature and fell more slowly than the AFMR frequency as T approached T_N. These properties were puzzling because, though the polarization properties and magnetic field independence indicate that the line is due to an electric dipole transition, the temperature dependence indicates that the ordered spins are involved. No explanation for this line or for a similar one observed by Richards[5] in CoF_2 has previously been proposed.

The mechanism to which we ascribe the line is indicated in Fig. 2(b). (The diagrams are given precise definitions in reference 4.) The mechanism can be described this way: An exciton consisting of odd-parity electronic states is mixed into the two-magnon state via the combined action of the ordinary spin-orbit interaction and the symmetry-breaking interaction we have described. The odd exciton can then couple to the electromagnetic field via the electric dipole interaction.

The evidence that this is the correct explanation for the line is the following: (1) From the observed AFMR wave number[6] of 53 cm^{-1} and the ratio $\omega_A/\omega_e = 0.371$ of anisotropy to exchange frequencies deduced from observed g values in the directions parallel and normal to the c axis, we deduce that the wave number of two Brillouin-zone magnons is 154 cm^{-1}, compared to our experimental wave number of 154.4 cm^{-1}.

(2) The calculated intensity is 1 to 10 times that of the AFMR absorption by use of known spin-orbit and crystal-field energies, compared to the experimental result of 1 to 5.

(3) By a point-ion calculation we predict that the polarization ratio is

$$10 < \left(\frac{\text{absorption with } E \parallel c \text{ axis}}{\text{absorption with } E \perp c \text{ axis}}\right) < 14,$$

compared with the experimental result of $\gtrsim 7$ for this number.

(4) The linewidth is $\gtrsim 3$ cm^{-1} from a simple approximation for the line shape, compared with the experimental result ~6 cm^{-1}. When the data shown in Fig. 1(a) are analyzed to ac-

count for background absorption and the conversion of transmission into absorption intensity, then the observed line is found to have the expected, asymmetric shape.

(5) From the fact that the two magnons are on opposite sublattices, we expect that the frequency should be magnetic-field independent, as observed.

(6) A molecular-field calculation shows that the frequency will fall with temperature more slowly that the AFMR frequency.

(7) The line is expected to disappear for $T > T_N$ as observed.

(8) A search of all processes through fourth order in perturbation theory in a model including excitons, magnons, and phonons, and their interactions shows that no other process in the model can explain the line.

The process by which magnon-assisted optical absorption is expected to take place is shown in Fig. 2(c). Experimental evidence for the existence of lines due to this process in MnF_2 is described in the accompanying Letter.

The work is described in more detail in a series of forthcoming papers. The authors are indebted to their research advisors, Professor M. Tinkham and Professor C. Kittel, for suggesting some of the studies reported here and for advice, encouragement, and helpful suggestions. We are also grateful to R. L. Greene et al. for showing us the results of the optical-absorption experiments described in the accompanying Letter prior to publication.

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OBSERVATION OF A SPIN-WAVE SIDEBAND IN THE OPTICAL SPECTRUM OF MnF_2†

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We have found evidence for a spin-wave sideband in the absorption spectrum of antiferromagnetic MnF_2 (Néel temperature 67.7°K. To our knowledge this is the first observation of a spin-wave sideband and provides a new method for investigating the spin-wave spectrum.

A familiar feature of optical spectra in crystals is the presence of vibronic or phonon sidebands which accompany pure electronic transitions (no-phonon lines).[1] In many cases these sidebands are stronger than the pure electronic transitions because of certain selection rules. For example, if the ground and excited states have the same parity, then electric dipole transitions are forbidden and only the weaker magnetic dipole transitions can occur. An odd vibration can destroy the inversion symmetry and permit electric dipole transitions to occur. It seems plausible then that other collective excitations such as spin waves (magnons) could have similar effects.

The sharp-line absorption spectra at 2.2°K for the transition ${}^6A_{1g}({}^6S)$ to ${}^4T_{1g}({}^4G)$ of the manganese ion in MnF_2 is shown in Fig 1(a). The position, shape, and temperature dependence of the electric dipole transition at 18 477.1 cm^{-1} indicate that this line is a spin-wave, or magnonic, sideband of the 18 419.6-cm^{-1} magnetic dipole line. The two lower energy lines shown in Fig 1(a) are magnetic dipole transitions. These are the first pure electronic transitions observed in MnF_2; all the other features of the spectrum are vibronic in nature. In this paper we will restrict ourselves to a discussion of the spin-wave sideband and its associated no-magnon line.