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Magnetic Circular Dichroism of Sharp Optical Transitions in Antiferromagnetic FeF_2†

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Using magnetic circular dichroic (MCD) modulation techniques, we have reinvestigated the spectrum of antiferromagnetic FeF_2, concentrating on pure electronic transitions and their associated magnetic structure. We show in this paper that because vibronically induced bands do not exhibit circular dichroism, MCD spectra complement absorption spectra in aiding our understanding of magnetic effects. In particular, we present the results of studies of the magnetic field and temperature dependence of the MCD spectra in two absorption regions of FeF_2, i.e., the 21 500- and 25 900-cm^{-1} regions, and report the effective g factors of all excitations, simple and compounded, in these two regions. In the 21 500-cm^{-1} region we report the identification of a two-magnon sideband and its thermal and magnetic properties; in the other, we observe an additional purely electronic transition which is obscured by broad-band absorption and appears only through its MCD properties. Several observations are made on the additional information obtainable by consideration of the polarity of the MCD signal in antiferromagnets.

The spectra of antiferromagnetic insulators have been actively investigated in recent years and the major features of these spectra are generally understood.[1] In this paper, we wish to report measurements of the magnetic circular dichroism (MCD) properties of antiferromagnetic FeF_2 in order to emphasize that MCD can serve as a powerful complementary aid to our analysis of the absorption spectra in these materials. Hitherto, MCD and its associated Faraday rotation have been proved useful in the interpretation of the spectra of color centers, nonmagnetic insulators,[2] and ionic solutions.[3] The majority of the studies cited have involved broad-band spectra and only a few have utilized modulation techniques to detect small MCD signals.

In this paper, we present results of a high-resolution (~0.1 Å) study of the MCD of sharp optical transitions in the 21 000- and 25 800-cm^{-1} absorption bands of FeF_2. This type of a study is then shown to provide additional important information concerning the nature of excitations, the active light operator for the transitions, and their reaction to external perturbation. The MCD of the transitions, further, have allowed us to identify a previously unreported purely electronic magnetic-dipole transition in the 25 800-cm^{-1} band and an extremely weak two-magnon sideband in the 21 000-cm^{-1} region. MCD signals are observed for purely electronic magnetic-dipole (π-, σ-active) transitions and one- and two-magnon sidebands, but none have been observed for vibronically induced bands in any of the antiferromagnets we have investigated to date. It is this simplification of the MCD signal over the complex absorption spectrum that underscores the usefulness of these investigations.

Monochromatic light was polarization modulated at 50 KHz using techniques developed by Schnatterly.[4] The modulated light was passed along the *c* axis of the crystal which was oriented parallel to an external magnetic field of up to 60 kOe. The transmitted light provided an ac signal at 50 KHz proportional to the dichroism $(\alpha^+ - \alpha^-)/(\alpha^+ + \alpha^-)$ which was detected synchronously with a reference signal from the modulator. Dichroism of less than 0.01% could be detected, and in several cases a strong dichroism signal was observed for lines barely detectable in absorption owing to intrinsic weakness, thermal broadening, or being masked by a stronger nondichroic absorption.

The axial absorption and MCD of the 25 800-cm^{-1} region is shown in Fig. 1. The absorption spectrum for this spectral region in FeF_2 and associated Zeeman effects have been reported previously by McClure *et al.*[5] identifying purely electronic magnetic-dipole transitions at 25 857 cm^{-1}(π) and 25 894 cm^{-1}(σ). The dichroism of these magnetic-dipole lines can be seen to follow closely that expected for a simple two-sublattice antiferromagnet when the sublattice degeneracy of the transitions is removed by an external magnetic field. The σ transition, active on $M_\parallel$ shows no dichroism as expected, and there was no dichroism observed in the absence of an external field as was observed in MnF_2.[6]

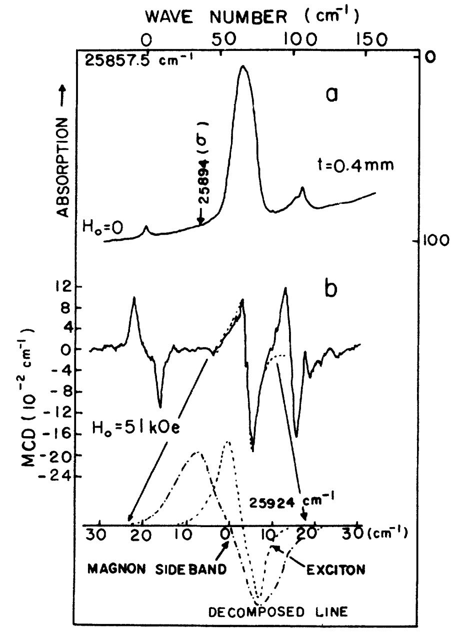

FIG. 1. (a) Axial absorption spectrum of FeF_2 in the 25 800-cm^{-1} region. *t* designates the thickness of the crystal. (b) MCD spectrum of FeF_2 in the 25 800-cm^{-1} region. Dotted line indicates the calculated MCD line shape by composing an exciton line (25 927 cm^{-1}) and a magnon sideband (25 924 cm^{-1}). Temperature is 4.2 °K.

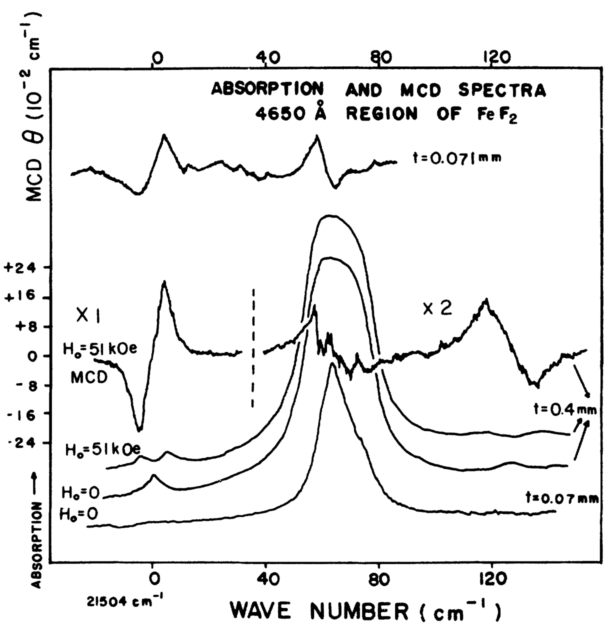

FIG. 2. Axial absorption spectra and associated MCD for the 21 000-cm^{-1} band (two different crystal thicknesses of $t = 0.071$ mm and $t = 0.4$ mm are used).

The strong dichroism signal centered at 25 926 cm^{-1} is a composite signal resulting from the 25 924-cm^{-1} magnon sideband splitting in the applied field and a weak-magnetic-dipole no-magnon no-phonon transition centered at 25 927 cm^{-1}. The signal may be decomposed as follows: The sideband dichroism arises from the lifting of the sublattice degeneracies in the applied field; this yields a line shape that depends on the amount of the splitting and the derivative of the absorption spectrum; since both these quantities are known, the expected line shape of the MCD from the sideband can be accurately determined[7]; the remainder then corresponds to a signal arising from a sharp Lorentzian transition. This procedure is illustrated in Fig. 1(b); as can be seen, the decomposition leaves little doubt of the existence of an additional transition. In a calculation by Kambara relevant to this region,[8] an additional π-active magnetic-dipole transition located at ~80 cm^{-1} above the 25 857-cm^{-1} line had been predicted. The position of the dichroism signal is in good agreement with this prediction (70 cm^{-1}). This exciton transition is completely masked in absorption by the strong electric-dipole sideband, appearing only as a minute shoulder in the absorption spectrum. Thus, the identification of this line in conventional absorption spectroscopy is difficult at best. Our identification of this transition as a purely electronic one is further supported by the observation of a magnon hot band 70 cm^{-1} lower in energy when the sample temperature is

TABLE I. $g_{\parallel}$ factors.

State	$g_{\parallel}$	Determination
Ground state	2.21	Ref. 15.
Exciton states		
21 504 cm^{-1}	2.20	MCD
25 857 cm^{-1}	0.32	MCD
25 894 cm^{-1}	0.52	Ref. 5
25 927 cm^{-1}	2.0	MCD
Magnon (eff)	2.3	Ref. 5 and MCD
One-magnon sidebands		
21 568 cm^{-1}	0.04	MCD
25 924 cm^{-1}	1.8	Ref. 5 and MCD
25 965 cm^{-1}	1.6	Ref. 5
Two-magnon sidebands		
21 631 cm^{-1}	2.5	MCD

elevated.[9]

The dichroism in the 25 964-cm^{-1} region [Fig. 1(b)] is due to the splitting of the magnon sideband of the 25 894-cm^{-1} σ transition. The shape of the dichroism again is of the differential form discussed above. All relevant g factors for transitions in this band are summarized in Table I.

The axial absorption spectra and associated MCD for the 21 000-cm^{-1} region are shown in Fig. 2. The magnetic-dipole transition at 21 504 cm^{-1} and the strong electric-dipole transition at 21 568 cm^{-1} were reported earlier,[5] but were reported to show no Zeeman splitting. Communication with the authors of Ref. 5 indicates that a crystal impurity band masked the splitting of the 21 504-cm^{-1} line in their crystal. The splitting of the sideband at 21 568 cm^{-1} is very small and is clearly observable only in the dichroism data. The g factors for the transitions of this band are also tabulated in Table I.

The dichroism observed at 127-cm^{-1} energy above the purely electronic transition at 21 504 cm^{-1} can be seen to be associated with a very weak absorption. Studies of the thermal behavior and the g factor measurement of this transition were not possible in absorption owing to its intrinsic weakness, but could be easily and accurately carried out using the dichroism of the band.

The thermal shifts of the transitions of this band were studied in the 4–50 °K temperature region to assist in the interpretation of the observed spectrum. The relative thermal shift of the one- and two-magnon sidebands to the purely electronic origin is in good agreement with the thermal shifts reported for Raman scattering by magnons in FeF_2 by Fleury *et al.*[10] The energy separation from the purely electronic transition and thermal behavior indicate that the 127-cm^{-1} band is a two-magnon sideband of the 21 504-cm^{-1} transition. The strong band 64 cm^{-1} above the origin has been confirmed as a one-magnon sideband of the same transition.[5] It is noted that the energy separations of the one- and two-magnon sidebands are somewhat less than the energy of one- or two-zone-edge magnons, 77 and 154 cm^{-1}, respectively.[10] This phenomenon has been commonly observed in the spectra of antiferromagnetic insulators and has been interpreted as due to exciton dispersion[10] or magnon-exciton interactions.[11]

Selection rules for one-magnon sideband activity have been reported for FeF_2.[12,13] The methods of Lax and Hopfield[14] may be easily extended to include three-center electric-dipole selection rules. In general, the latter are not very restrictive. The strong dichroic activity of the two-magnon sideband allows us to determine its magnetic splitting factor accurately; since the g factors of the various components of the excitation are known, we can determine that the two magnons are created on one sublattice and the zone-center exciton is created on the other. For the stated case, the calculated splitting factor is 2.4, whereas if the magnons are created on opposite sublattices a value determined by the exciton g factor of 2.2 would be expected. The experimentally determined value of 2.5 for this sideband strongly supports our assignment; the activity is related to the X, Z, M and R points of the Brillouin zone.[13] The energy separation from the assigned origin can then be used to further identify the magnons to be two M-point magnons.

Comparison of Figs. 1 and 2 reveal another interesting feature of MCD data for antiferromagnets. It can be seen that the polarity of the MCD of the purely electronic transitions is opposite for the two regions studied. In cases where M_s remains a good quantum number and for transitions involving the $^5T_2(\mathrm{Fe}^{2+})$ ground state and triplet excited states, a normal sublattice Zeeman splitting always moves the S^+ active transition to higher energies. This is observed in the 25 800-cm^{-1} region but is not the case for the 21 504-cm^{-1} transition. The 25 856-cm^{-1} absorption may be assigned to a $|^5T_2, B_1, \pm 2\rangle$ to $|^3T_1(4), B_1, \pm 1\rangle$ transition.[5,8] The 21 504-cm^{-1} line cannot be unambiguously assigned because an accidental degeneracy of a $^3E_1(1)$ and a $^3T_1(3)$ state of Fe^{2+} occurs in this energy region.[8] We believe that in view of the polarity results a calculation of the relevant g factors will now permit the designation of the transition, illustrating once more the power and usefulness of MCD techniques.

The polarity of the sidebands in relation to their exciton origin yields additional information as well. For a one-magnon sideband, the polarity of the MCD signal will be the reverse of that of the exciton if

$$\Delta_1 = g_{\mathrm{eff}}^{\mathrm{exc}} - g_{\mathrm{eff}}^{\mathrm{mag}} < 0 \;, \tag{1}$$

where $g_{\mathrm{eff}}^{\mathrm{mag}}$ and $g_{\mathrm{eff}}^{\mathrm{exc}}$ are the effective g factors for the magnon and exciton involved, respectively. These effective g factors are defined as

$$g_{\text{eff}} = \frac{\text{"observed" magnetic field splitting}}{2\mu_B H_0} \qquad (2)$$

and include the magnetic field dependence of various interactions between the excitations. Conversely, if $\Delta_1 > 0$ in one-magnon sidebands, its MCD signal will have the same polarity as the exciton.

In the case of the two-magnon sideband reported here, the signal polarity is reversed from that of the exciton and corresponds to the case where

$$\Delta_2 = g_{\text{eff}}^{\text{exc}} - 2g_{\text{eff}}^{\text{mag}} < 0 \ . \qquad (3)$$

In conclusion, we again wish to emphasize that MCD techniques serve us well as a complement to our interpretation of spectra of antiferromagnetic insulators. The determination of various magnetic properties of exciton transitions and one- and two-magnon sidebands illustrate our contention.

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