# Comment on the magnetic circular dichroism spectrum of $MnF_2$†

W. C. Egbert and W. M. Yen
*Department of Physics, University of Wisconsin, Madison, Wisconsin 53706*
(Received 6 April 1976)

A recent article by Shatwell and McCaffery questioned the usefulness of magnetic-circular-dichroism (MCD) techniques applied to $MnF_2$. We show that the Zeeman splitting of the purely excitonic lines tests for sample to sample variations which would be reflected in the MCD spectrum. We present Zeeman and MCD data which show long-term reproducibility and suggest experimental variables which may have affected Shatwell and McCaffery's results.

## I. INTRODUCTION

Antiferromagnetic $MnF_2$ has been studied extensively in the past, both with standard optical techniques[1-5] and with magnetic circular dichroism[6-8] (MCD). Recently, Shatwell and McCaffery[9] reported their results from MCD and emission experiments, which were at variance with data of an earlier study,[7] leading them to suggest possibly uncontrollable experimental variables as the source of the disagreement. Noting that a critical parameter of their model is easily tested by measuring the excitonic $g$ factor, we chose to restudy the Zeeman splitting of the two $^4T_1(^4G)$ exciton lines. As a check on earlier experiments, we remeasured the MCD of the one-magnon sidebands. Results of these experiments are presented below, as well as our comments on the discrepancy between our results and those of Ref. 9 and a suggestion for further experiments.

## II. THEORETICAL MODEL

We will briefly review the model applied to the $^4T_1(^4G)$ region in the absorption spectrum of $MnF_2$. The $\sigma$ spectrum, shown in Fig. 1(a) is characterized by two magnetic dipole lines $E1$ and $E2$, identified as purely electronic (excitonic) transitions, and two electric dipole lines $\sigma 1$ and $\sigma 2$, identified as magnon sidebands of the excitons.[3,4] Our theoretical treatment will be directed toward developing an expression for the $g$ factors which characterize the Zeeman splitting of $E1$ and $E2$, illustrated in Fig. 1(b).

Clogston[10] derived expressions for the $^4T_1$ states as combinations of states describing the $3d^5$ free-ion configuration. Although we will not repeat Clogston's calculations, knowledge of the orbital and spin character of the $^4T_1$ states aids the interpretation of MCD and absorption spectra. Dietz *et al.*[11] applied stress to a $MnF_2$ crystal while observing the absorption spectrum and used the results of these experiments to conclude that the excitons $E1$ and $E2$ are linear combinations of just two of the $^4T_1$ states described by Clogston. Labeling the state vectors for $E1$ and $E2$ with the superscripts 1 and 2, respectively, and subscript 1 (2) for the sublattice parallel (antiparallel) to an axial magnetic field, we write

$$\begin{aligned} |e_1^1\rangle &= c_1\left|1,\tfrac{3}{2}\right\rangle + c_2\left|-1,\tfrac{3}{2}\right\rangle, \\ |e_1^2\rangle &= c_2\left|1,\tfrac{3}{2}\right\rangle - c_1\left|-1,\tfrac{3}{2}\right\rangle \end{aligned} \tag{1}$$

and

$$\begin{aligned} |e_2^1\rangle &= c_2\left|1,-\tfrac{3}{2}\right\rangle + c_1\left|-1,-\tfrac{3}{2}\right\rangle, \\ |e_2^2\rangle &= c_1\left|1,-\tfrac{3}{2}\right\rangle - c_1\left|-1,-\tfrac{3}{2}\right\rangle, \end{aligned} \tag{2}$$

with $c_1^2 + c_2^2 = 1$ preserving the orthonormality of the exciton states. In Eqs. (1) and (2), the state $|X, M_s\rangle$ corresponds to Clogston's $^4T_1(X, M_s)$.

Because $E1$ and $E2$ are close in energy, an external magnetic field could mix the states. Considering the Zeeman interaction $V = \mu H_z(L_z + 2S_z)$

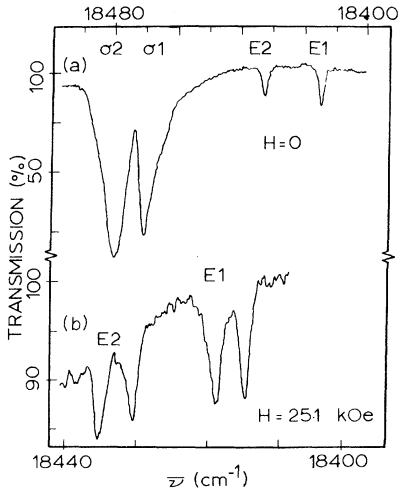


FIG. 1. $\sigma$ absorption spectrum of the $^4T_{1g}(^4G)$ region of $MnF_2$. (a) Zero applied field. (b) Zeeman splitting of $E1$ and $E2$ in a field of 25.1 kOe.

as a perturbation, we write the observed energy shift of $E1$ on sublattice 1 as the difference between the energy shift of the excited and ground states which carry spins $S'$ and $S$, respectively,

$$\delta\nu(|e_1^1\rangle) = \mu H(\langle e_1^1|L_z+2S_z|e_1^1\rangle - \langle g_1|L_z+2S_z|g_1\rangle)$$
$$= \mu H[(c_1^2-c_2^2)M+2(S'-S)], \quad (3)$$

with

$$M = \langle 1,\tfrac{3}{2}|L_z|1,\tfrac{3}{2}\rangle = -\langle -1,\tfrac{3}{2}|L_z|-1,\tfrac{3}{2}\rangle . \quad (4)$$

A similar calculation for sublattice 2 yields

$$\delta\nu(|e_2^1\rangle) = \mu H[(c_2^2-c_1^2)M-2(S'-S)] = -\delta\nu(|e_1^1\rangle), \quad (5)$$

giving the total splitting of $E1$ as

$$\Delta(E1) = 2\mu H[(c_2^2-c_1^2)M-2(S'-S)] = 2g^{\text{eff}}\mu H . \quad (6)$$

The $g$ factor for $E1$ is therefore

$$g(E1) = (c_2^2-c_1^2)M-2(S'-S), \quad (7)$$

and similarly for $E2$,

$$g(E2) = (c_1^2-c_2^2)M-2(S'-S) . \quad (8)$$

The difference $\Delta g$ between the $g$ factors is seen to be a measure of the coefficients $c_1$ and $c_2$:

$$\Delta g \equiv g(E2)-g(E1) = 2(c_1^2-c_2^2)M . \quad (9)$$

The matrix element $M$, determined by crystal-field terms which are large compared to the Zeeman terms[12] ($Dq/B \sim 1.125$, $Dq \sim 900$ cm$^{-1}$) ought to be insensitive to small changes in the stresses applied to the crystal. On the other hand, Shatwell and McCaffery note that $(c_1^2-c_2^2)$ is a sensitive function of the crystalline strain fields. Therefore $\Delta g$ measures the sample-to-sample variations in the mixing of the $^4T_1$ states which would be reflected in the MCD spectrum.[13]

In Ref. 9, the matrix elements $M$ are left in terms of a reduced matrix element of $L_z$ between the $^4T_1$ states forming the excitons. However, Clogston's expressions for the $^4T_1$ wave functions in terms of the free ion orbitals allows us to find a parametric value for $M$, and numerical values for the mixing coefficients $N$, $\alpha_P$, and $\alpha_F$ cited by Sell *et al.*[3] give an estimate for the size of $M$. Substituting for $^4T_1$ in Eq. (4), $M$ becomes

$$M = N^2(\tfrac{1}{2}+\alpha_P^2-\tfrac{3}{2}\alpha_F^2) = 0.639 . \quad (10)$$

### III. EXPERIMENTAL METHODS AND RESULTS

The experimental apparatus used to generate the MCD and absorption spectra is described elsewhere in detail.[14] For MCD measurements the output from a tunable dye laser pumped by a cavity-dumped argon laser is synchronized to a photoelastic modulator. The photoelastic modulator produces alternate pulses of right and left circularly polarized light which pass axially through the sample. Gated electronics detect the sum and difference in absorption of right and left circularly polarized light; plotting the difference signal versus wavelength gives an MCD spectrum. To generate absorption spectra, the linearly polarized dye laser output bypasses the photoelastic modulator. In addition, small right-angle prisms affixed to the sample allow the $\sigma$ absorption spectrum to be taken while the sample sits in the bore of the 70-kOe superconducting solenoid, the tightly focused laser beam being easily steered from $\alpha$ to $\sigma$ polarization.

Measurements of the Zeeman splitting of $E1$ and $E2$ are shown in Fig. 2, with least-squares fits to the data indicated by solid lines. Values for $g(E1)$ and $g(E2)$ are given in Table I along with results from earlier experiments on several different samples.[15] Uncertainty in the measurement of the magnetic field accounts for the slight variation in the absolute value of the $g$ factors of Table I. However, in light of Eq. (9), the more germane quantity is $\Delta g$, which is a measure of the repeatability of MCD and Zeeman experiments. As noted in Table I, it is fairly constant.

In Figs. 3(a)–(c) we illustrate MCD spectra of three different crystals, taken with two different experimental methods. The lack of marked differences in MCD line shape reflects again the relative stability of $(c_1^2-c_2^2)$ from crystal to crystal.

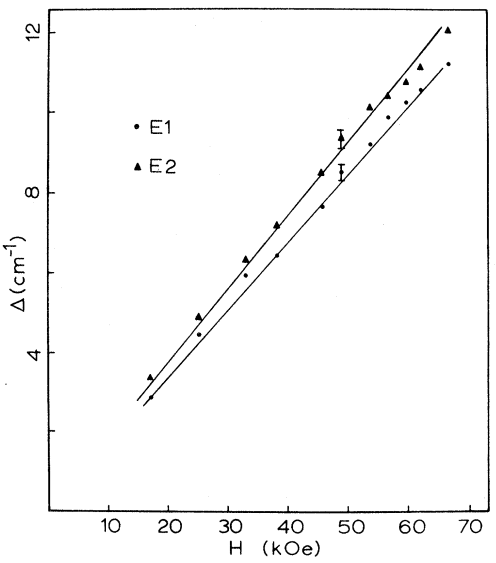


FIG. 2. Zeeman splitting of the lines $E1$ and $E2$ as a function of applied field. Straight lines indicate a least-squares fit to the data. The bars on the data at 40 kOe indicate the estimated uncertainty in the measurement of the Zeeman splitting.

TABLE I. $g$ factors for $^4T_{1g}(^4G)$ excitons in $MnF_2$.

| $g(E1)$ | $g(E2)$ | $\Delta g$ |
|---|---|---|
| 1.79 | 1.90 | 0.11 [a] |
| 1.85 | 1.97 | 0.12 [b] |
| 1.83 | 1.94 | 0.11 [c] |

[a] Reference 7.
[b] Reference 6.
[c] This study.

Although we agree that MCD spectra would not be useful if they varied greatly from sample to sample, we have seen no experimental evidence for such variation.

## IV. CONCLUSIONS AND COMMENTS

We conclude from the small deviations in $\Delta g$ that sample-dependent effects are not as crucial as the authors of Ref. 9 predicted. The constancy of MCD line shape over time and with different samples and experimental techniques is further evidence that MCD spectra are reproducible and can offer new insight into the behavior of these antiferromagnetic systems. The discrepancy between our work and that of Shatwell and McCaffery probably can be traced to the sensitivity and resolution of their apparatus. The MCD data of Ref. 7, represented in Fig. 3(a), were taken with an instrumental resolution of 1.5 $cm^{-1}$; the more recent data, Figs. 3(b) and 3(c), were taken with the dye laser giving a resolution of 2 $cm^{-1}$, as shown in the inset of Fig. 3. Though Shatwell and McCaffery do not specify the resolution of their MCD apparatus, comparison of Figs. 3(a)–(c) to Fig. 4 suggests that they did not have resolution sufficient to see some of the details of the MCD spectrum. Specifically, the feature to the low-energy side of the one-magnon sidebands, identified as $E3$,[7] is visible in Figs. 3(a)–(c) but is not apparent in Fig. 4. In addition, Fig. 3(c) shows far more structure than Fig. 4, even though these spectra were taken in approximately the same magnetic field. This apparent lack of detail in their primary data leads us to question the efficacy of their moments analysis.

The feature which appears at 18 535 $cm^{-1}$ in the MCD spectrum, identified as a two-magnon sideband of $E2$,[7] was not studied in our most recent experiments. However, Selzer *et al.*[6] found that the temperature dependence of the observed Zeeman splitting fit Saslow's renormalization theory for magnons.[16] A phonon at the $X$ point of the Brillouin zone has been observed recently by Rotter[17]; although considerations of its energy, symmetry, and linewidth cannot distinguish it from two $X$-point magnons, we feel that the renormalization data noted above indicate that this feature is in fact a two-magnon sideband. Such three-center excitations are not as improbable as Shatwell and McCaffery seem to feel; in the MCD spectrum of $FeF_2$, a similar feature appears at 21631 $cm^{-1}$.[18] Because the zero-magnon line exhibits MCD (unlike $E2$ in $MnF_2$), the reversal of phase of the MCD signal is direct evidence that this sideband in $FeF_2$ cannot be a phonon sideband. In addition, Riederer[19] has recently observed multimagnon lines in $KMnF_3$.

A final point deserves mention. Equation (9) indicates that $\Delta g$ is proportional to $(c_1^2 - c_2^2)$ and the matrix element $M$. Using the estimate of $M$ which is given in Eq. (10), we calculate $c_1 = 0.737$ and $c_2 = 0.676$. These values do not agree with those of Ref. 9, where a moments analysis gave $c_1 = 0.807$ and $c_2 = 0.591$ at 36.8 kOe. A better estimate of $M$ would allow us to say whether these differences are significant.

An experiment which would measure the Zeeman splitting and MCD while simultaneously stressing

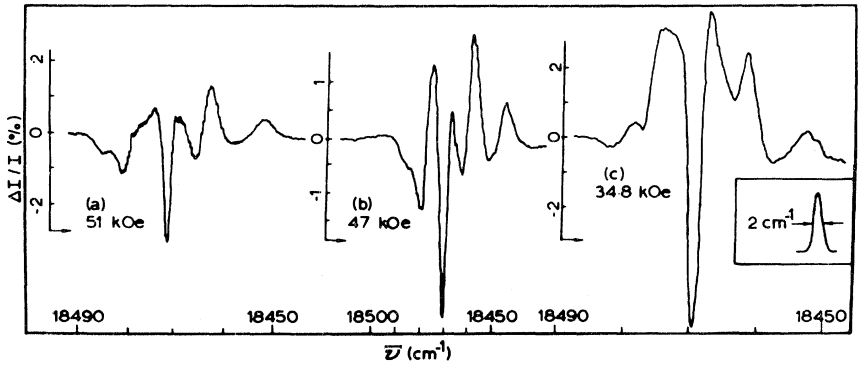


FIG 3. MCD of the one magnon sidebands in the $^4T_{1g}$ region of $MnF_2$. (a) From Fig. 1 of Ref. 7. (b) From Fig. 4 of Ref. 14. (c) Results from this study. Note in each case the similarity of the MCD line shapes. The inset indicates the spectral width of the dye laser used to generate traces *b* and *c*.

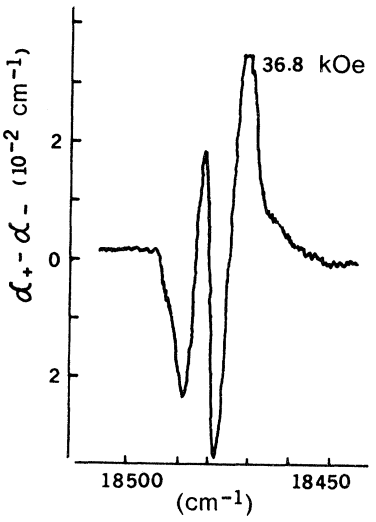


FIG. 4. Sample of the MCD spectra presented by Shatwell and McCaffery in Ref. 9, Fig. 4. Structure appearing near 18467 cm$^{-1}$ in Figs. 3(a)–(c) is not apparent in this spectrum.

the crystal in its basal plane and applying an axial magnetic field could provide useful information. The stress experiments of Dietz *et al.*[11] clearly indicate that $c_1$ and $c_2$ are modified by basal plane stress, and Eq. (9) shows that $\Delta g$ would measure the change in $c_1$ and $c_2$ as the crystal is stressed. Experiments carried out in this laboratory[7,20] showed that stresses on the order of 10 kg/cm$^2$ could change the MCD line shape drastically. Therefore, if Eqs. (35) and (36) of Ref. 9 accurately describe the MCD spectrum, one could isolate the $B$ term contribution to the MCD by stressing the crystal until $\Delta g = 0$ and, knowing that, work back to find the $A$ term contribution in the stress-free state.

## ACKNOWLEDGMENTS

The authors thank Professor C. A. Rotter for sending his unpublished data on the phonon spectrum of $MnF_2$. We also gratefully acknowledge many helpful discussions with Professor D. L. Huber, P. M. Selzer, and D. H. Berman.

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†Work supported in part by the NSF under Grant Nos. GH-40222 and DMR-73-02477.

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