High-Field Antiferromagnetic Resonance in MnF_2 Using Pulsed Fields and Millimeter Wavelengths*

SIMON FONER
Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, Massachusetts
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Preliminary observations of the high-field antiferromagnetic resonance mode in MnF_2 from 4.2°K up to T_N are presented. The experiments, which employ pulsed magnetic fields and relatively low frequencies (4 and 8 millimeter wavelengths), are briefly described. The absolute value and general temperature dependence of $(2H_EH_A)^{\frac{1}{2}}$ are in close agreement with estimates made earlier by Keffer and recent high-frequency measurements by Johnson and Nethercot near T_N. The results demonstrate the general validity of the molecular-field approximation of antiferromagnetic resonance. Qualitative features of the resonance absorption and upper bounds of line widths are also presented.

THE high-field antiferromagnetic resonance mode has been studied in single-crystal[1] MnF_2 from 4.2°K up to the Néel temperature ($T_N \cong 68$°K) using 4- and 8-mm waves and pulsed magnetic fields. When compared with the resonance results of Johnson and Nethercot,[2] the molecular-field antiferromagnetic resonance theory of Keffer and Kittel[3] and others,[4] the results lead to an unambigious verification of the theory.

The resonance equation[3] is

$$\omega/\gamma=[2H_EH_A+(\tfrac{1}{2}\alpha H_0)^2]^{\frac{1}{2}}\pm H_0(1-\tfrac{1}{2}\alpha), \qquad (1)$$

where ω is the applied angular frequency, γ the magnetomechanical ratio $ge/2mc$, H_E the Weiss exchange field ($H_E \gg H_A$), H_A the anisotropy field, H_0 the magnetic field at resonance applied parallel to the c axis ($H_0 \ll H_E$), and α the ratio of parallel to perpendicular susceptibility, $\chi_{\parallel}/\chi_{\perp}$. With sufficiently high frequencies, antiferromagnetic resonance can be observed at $H_0=0$, in which case $(2H_EH_A)^{\frac{1}{2}}$ can be obtained. When such high frequencies are not available, the high-field mode given by the minus sign in Eq. (1) may be observed.[5] Fields of several hundred kilogauss allow a wide range of materials to be investigated, and with independent measurements of $\chi_{\parallel}$ and $\chi_{\perp}$, the behavior of $(2H_EH_A)^{\frac{1}{2}}$ can be examined as a function of temperature.

For the experiments described here, a thin slab of MnF_2 (0.015 to 0.030 in thickness) was fixed on a shorting end wall of a long, thin-walled, silvered stainless steel wave guide. Resonant absorption was observed as a change in 35-kMc/sec or 70-kMc/sec radiation reflected from the end-wall assembly to a silicon crystal detector when a pulsed field was applied. The wave guide was placed into a liquid helium Dewar and inserted into the pulsed field coil, constructed as described earlier.[6] The single-crystal sample was centered in the coil with H_0 parallel to the c axis within 5°. Pulsed fields were produced in coils with i.d. of $\frac{5}{8}$ in., $\frac{3}{4}$ in., and 1 in.[7]

Resonance oscillograms of antiferromagnetic MnF_2 using 35 kMc/sec are shown in Fig. 1 with a corresponding magnetic-field trace. Curve A was obtained at 4.2°K, while curves B, C, and D were obtained at successively higher temperatures, demonstrating that initially H_0 increases with increasing temperature. The maximum observed H_0 is less than 100 kilogauss for 35 kMc/sec, and is thus considerably less than that estimated by Keffer.[8] If the peak field is adjusted so that the antiferromagnetic resonant absorption peak is obtained at $H_0=H_{\max}$, an accurate estimate of the line width can be made (see curve D). The full half-widths of the resonance at 35 kMc/sec for 4.2°K and 40°K are ≤ 1200 gauss and ≤ 2300 gauss, respectively. The latter value is in agreement with Johnson and Nethercot's data. The possibility of fine structure of the low-temperature resonance lines is being investigated.[9] The qualitative features of the resonance are: (1) the line width increases with increasing temperature and is sensitive to orientation; (2) the peak absorption decreases from about $10A_p$ at 4.2°K (where A_p is the peak amplitude of the paramagnetic resonance just above T_N) to $0.5A_p$ near 60°K; (3) the g value is constant within the experimental error (see Fig. 2 and reference 2).

The results of several measurements are presented in Fig. 2 for MnF_2 as a function of temperature. The values of $(2H_EH_A)^{\frac{1}{2}}$ were calculated by using Eq. (1) and the resonance data. Because powder susceptibility data appear to be unreliable, values of α were chosen from only single-crystal susceptibility data. Values of $(\chi_{\parallel}-\chi_{\perp})$ as a function of T were obtained from Stout

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[1] We are indebted to Professor J. W. Stout of the University of Chicago for furnishing this single crystal of MnF_2.

[2] F. M. Johnson and A. H. Nethercot, Jr., Phys. Rev. **104**, 847 (1956).

[3] F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

[4] A comprehensive recent review of the subject is given by Nagamiya, Yosida, and Kubo, Advances in Phys. **4**, 1 (1955).

[5] C. Kittel, Phys. Rev. **82**, 565 (1952).

[6] S. Foner and H. H. Kolm, Rev. Sci. Instr. **27**, 547 (1956).

[7] Some characteristics of these coils were presented at the Conference on Magnetism, Boston, Massachusetts, October, 1956 (unpublished).

[8] F. Keffer, Phys. Rev. **87**, 608 (1952).

[9] Slight misorientation can result in a large angular tilt of the magnetization when H_0 is close to $(2H_EH_A)^{\frac{1}{2}}$. This effect as well as small cracks in the sample could lead to line broadening and fine structure.

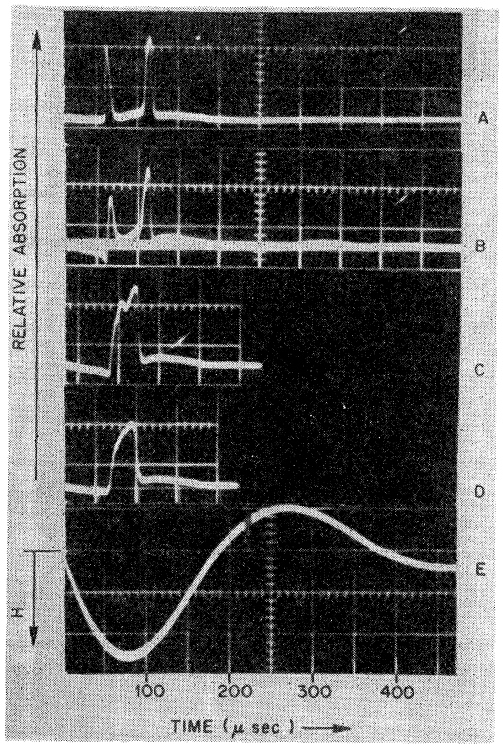

FIG. 1. Typical oscillograms of high-field antiferromagnetic resonance in MnF_2 at 35 kMc/sec. Resonant absorption *versus* time: *A*–4.2°K, *B*–15°K, *C*–33°K, *D*–40°K. Trace *E*—Corresponding H_0 *versus* time for traces *A* to *D*. The peak field (H_{max}) in each case was 91 kilogauss.

and Griffel's data,[10] and $\chi_\perp = 24.5 \times 10^{-3}$ per mole was taken to be a constant independent of T as observed by Bizette and Tsai.[11] Two complete warming curves obtained at 35 kMc/sec for two different samples (squares and circles) are shown. Two measurements at 70 kMc/sec and 4.2°K are also indicated. The two circles at 4.2°K indicate the change in $(2H_EH_A)^{\frac{1}{2}}$ for the same sample when it was tilted by a few degrees. The vertical line at 69°K, indicating the lowest temperature at which paramagnetic resonance has been observed in our experiments, is in agreement with unpublished results of Hutchison.[2] The temperature, measured with a thermocouple, is estimated to be accurate within ±2°K over most of the range. The absolute accuracy of the field measurements is ±5% calibrated by both the paramagnetic resonance line of MnF_2 ($g = 2.05$ was measured at *x* band with a dc H_0 parallel to the *c* axis) and integrated flux measurements. Changes of H_0 as small as 200 gauss could be observed by keeping H_{max} within 10% of H_0. Thus the general dependence of $(2H_EH_A)^{\frac{1}{2}}$ *versus* T is accurately given even though the position of the entire family of points may be in error by as much as 5 kilogauss. The solid curve is the modified Brillouin function for spin $\frac{5}{2}$ normalized at only two points—the saturation value at $T = 0$°K was chosen equal to $(2H_EH_A)^{\frac{1}{2}} = 96$ kilogauss and T_N was chosen equal to 67.7°K. The excellent fit with the experimental points confirms Keffer's[8] suggestion that $(2H_EH_A)^{\frac{1}{2}}$ varies as the magnetization of the sublattices involved[12] for MnF_2. The somewhat surprisingly good agreement of $(2H_EH_A)^{\frac{1}{2}}$ at $T = 4.2$°K with Keffer's estimate (100 kilogauss) may be fortuitous.[12] The four crosses, high-frequency ($H_0 = 0$) data obtained by Johnson and Nethercot, also fit the present data within the accuracy of the measurements. The conclusion reached from these data is that the simple molecular-field treatment for antiferromagnetic resonance in MnF_2 describes the phenomenon accurately.

Orientation and line-width experiments using resonant-cavity techniques are in progress. The pulsed-field technique has been applied to other materials[13] and a more detailed account will be presented later.

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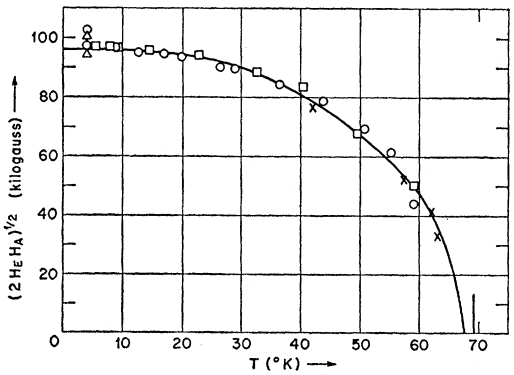

FIG. 2. Values of $(2H_EH_A)^{\frac{1}{2}}$ derived from resonance data for MnF_2 as a function of T. Circles and squares—two warming runs at 35 kMc/sec with different samples. Triangles—data at 4.2°K for two different samples and 70 kMc/sec. The lower triangle corresponds to the same sample as the circles. Two circles at 4.2°K—indicate effect of changing orientation of sample a few degrees. Crosses—data of Johnson and Nethercot[2] obtained at high frequencies and $H_0 = 0$. Solid curve—Brillouin function for spin $\frac{5}{2}$ and $H_0 = 0$ normalized at only $T = 0$ and $T_N = 67.7$°K.

[10] J. W. Stout and M. Griffel, J. Chem. Phys. **18**, 1455 (1950).
[11] H. Bizette and B. Tsai, Compt. rend. **238**, 1575 (1954).

[12] It is difficult to determine the accuracy of Keffer's estimate of H_A, however, the close agreement with susceptibility data and inclusion of some of this data in the theoretical estimates assures a fairly good value of H_A. Although the agreement at 4.2°K is somewhat better than expected, the very satisfactory agreement of the resonance data as a function of temperature (which also includes susceptibility data obtained earlier) demonstrates the general validity of the theory. It should be noted that the solid line in Fig. 2 should also be modified slightly to include H_0, which is close to 90 kilogauss for most of the resonance data, in the Brillouin function. This effect is small, except near T_N, and does not affect the present interpretation.

[13] S. Foner, Bull. Am. Phys. Soc. Ser. II, **2**, 128 (1957).

Mr. E. P. Warekois for orienting all the samples by means of x-ray techniques, Mr. B. Feldman for his assistance with the experiments and Dr. J. W. Meyer for the use of and aid with his x-band paramagnetic spectrometer.

Note added in proof.—Evidence of an additional resonance occurring above H_c given by[4] $H_0=[(\omega/\gamma)^2+2H_EH_A]^{\frac{1}{2}}$ at $T=0$ has recently been observed at 35 kMc/sec in MnF. This resonance appears to be extremely sensitive to orientation of the c axis with respect to H_0 at this frequency.

Note added in proof.—Similar antiferromagnetic resonance observations have been made on a single crystal of Cr_2O_3 kindly furnished by Dr. E. J. Scott of the Naval Ordnance Laboratory. Resonance data at 35 kMc/sec have been obtained from 77°K up to 325°K ($T\cong 307$°K) to date. The results of these experiments will be presented in the near future.

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Effect of Bleaching on the Optical Band Width of the F Center in KCl

JOHN D. KONITZER AND JORDAN J. MARKHAM
Zenith Radio Corporation, Chicago, Illinois

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Measurements have been made of the absorption in the F region in KCl at 78°K. It has been found that the structure in this region is dependent on the presence of the M, N, R, and K bands. The broadening in the presence of small amounts of M absorption indicates that it is not simply due to the overlapping of R, M, and N bands but is caused by an additional structure. These measurements support the present interpretation of the work of Van Doorn and Haven; they can explain the difference in the measurements of Pick and Geiger as well as the difference in the half-width observed by Mollwo and more recent data.

VAN DOORN and Haven[1] investigated the dichroism of the F and M bands in additively colored KCl, and suggest that there is a band under the F band which arises from the same center which causes the M band. Petroff,[2] working with additively colored KCl, indirectly deduced the presence of a band under the F band (the B band). We assume that bleaching should affect the optical absorption structure of the F band, and therefore carried out the following experiments.

Absorption measurements were made on additively colored KCl containing varying concentrations of F and M bands.[3] All colorations and quenches were performed in the absence of light. The quenches in oil were made as rapidly as possible (15 sec) from coloration temperature (~730°C) to room temperature in order to obtain only F centers. All measurements were made at 78°K with a Beckman Model DU spectrophotometer between 1.0 ev and 3.5 ev.[4] M and R centers were induced by bleaching at room temperature with a tungsten lamp.

The F band may be characterized by four wavelengths: the peak, ϵ_M; the half-height to the red, ϵ_r; the half-height to the violet, ϵ_v; and the half-width, $\Delta\epsilon$, the difference between ϵ_v and ϵ_r. The ratios of the M band and the K band to the F band (M/F and K/F, respectively) are reported in terms of the maximum absorption at the peaks.

An element of uncertainty occurs due to selection of a base line. When only F bands are present, the flatness to the red of the F band determines the line and the peak absorption with little doubt. When M, R, and N bands are present, we selected for the base a straight line from the absorption value at 1.1 ev to the lowest value on the violet side of the F band. If there is some true absorption at either or both of these points, the half-widths reported here are too small. Our selection, therefore, indicates the minimum $\Delta\epsilon$ to be expected.

The facts are as follows: when a crystal exhibiting mainly an F band is bleached, the $\Delta\epsilon$ increases and M band arises. Upon further bleaching the N, R_1, and R_2 bands appear, the M band increases, while the F band drops, its peak shifts to the violet, and $\Delta\epsilon$ further increases. From Fig. 1 we see that the increase in $\Delta\epsilon$ is not due to overlap on the red side. Subtraction of the K band still leaves a half-width wider than the value for

TABLE I. Summary of data on the F center in KCl.

Bleaching[a]	Concentration of F[b]	ϵ_{max} (ev)	ϵ_v (ev)	ϵ_r (ev)	$\Delta\epsilon$[c] (ev)	% M/F	% K/F
None	3.67×10^{16}	2.303	2.409	2.216	0.193	1.2	4.0
None	4.41×10^{16}	2.304	2.410	2.215	0.195	1.7	3.2
None	4.62×10^{16}	2.300	2.410	2.215	0.195	0.7	3.8
None	4.18×10^{16}	2.304	2.411	2.215	0.196	1.4	3.6
None	3.92×10^{16}	2.304	2.411	2.215	0.196	1.6	4.1
None	4.16×10^{16}	2.308	2.410	2.214	0.196	5.8	4.8
None	4.57×10^{16}	2.308	2.415	2.218	0.197	1.1	3.8
10 min	4.15×10^{16}	2.308	2.413	2.214	0.199	7.8	4.9
5 min	2.78×10^{16}	2.300	2.415	2.210	0.205	29.4	8.1
5 min	3.18×10^{16}	2.304	2.431	2.213	0.218	20.4	8.8
15 min	2.08×10^{16}	2.308	2.439	2.206	0.233	29.2	15.1
30 min	1.87×10^{16}	2.302	2.445	2.210	0.235	23.0	18.4
30 min	2.20×10^{16}	2.310	2.442	2.206	0.236	21.6	16.5
1 hr	1.80×10^{16}	2.310	2.453	2.210	0.243	25.3	20.4
30 min	1.96×10^{16}	2.310	2.454	2.210	0.244	24.3	16.3
3 hr	1.50×10^{16}	2.312	2.457	2.205	0.252	38.6	25.1
X–300°K 3 hr	4.30×10^{16}[d]	2.304	2.410	2.218	0.192	2.2	4.7
X–78°K 3 hr	3.35×10^{16}[d]	2.304	2.409	2.214	0.195	0	4.6

[a] Optical bleaching (tungsten lamp) at room temperature.
[b] Calculated using Smakula's formula ($f=0.81$).
[c] Measured to ±0.001 ev.
[d] Average value. Filtered x-ray (140 kvp).

[1] C. Z. Van Doorn and Y. Haven, Phys. Rev. **100**, 753 (1955).
[2] St. Petroff, Z. Physik **127**, 443 (1950).
[3] G. A. Noble and L. Bronstein, Bull. Am. Phys. Soc. Ser. II, **1**, 33 (1956).
[4] H. N. Hersh, Phys. Rev. **105**, 1158 (1957).

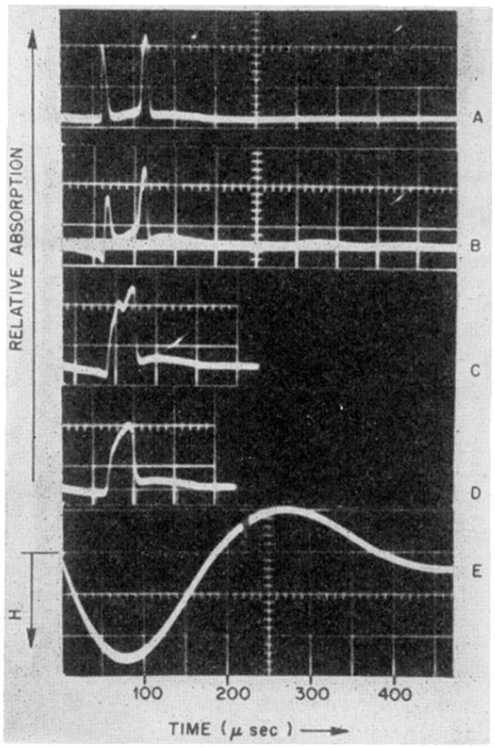

FIG. 1. Typical oscillograms of high-field antiferromagnetic resonance in MnF_2 at 35 kMc/sec. Resonant absorption *versus* time: *A*–4.2°K, *B*–15°K, *C*–33°K, *D*–40°K. Trace *E*—Corresponding H_0 *versus* time for traces *A* to *D*. The peak field (H_{max}) in each case was 91 kilogauss.