From measurements of the photoresponse, as a function of wavelength, of a number of GaAs p-si-n diodes (3 different si crystals) in the range from $2.1\,\mu$ to $0.76\,\mu$, we conclude that the level E_R lies between 0.75 and 0.8 eV below the conduction band. This is near the level in si GaAs which has been attributed to oxygen and which plays a role in making GaAs semi-insulating.[2] Similar measurements on various Si units have given values for E_R near 0.55 eV and near 0.65 eV. The former level fits the known 0.54-eV Au acceptor level in Si; the latter is near an acceptor level thought to be due to Cu. From these measurements, and the initial assumption that Lampert's model fit our experimental results in GaAs and Si, we predicted the Ge unit of Fig. 3 and obtained double injection negative resistance by deliberately introducing Cu into Ge, and presumably the 0.33-eV double Cu acceptor level. The consistency of all of these results (300°K) with Lampert's model, plus the V^2 space-charge-limited-emission electron currents we observe at low currents in GaAs and Si, tends to confirm the general features of Lampert's work, as well as some of the broader ideas first advanced by Stafeev and

until now demonstrated only at low temperatures.

We should like to thank S. J. Lubowski and C. V. Bielan for photoresponse measurements, R. E. Morrison for assistance in crystal preparation, H. A. Jensen for preparation and assembly of the Ge units, and T. R. Selig and C. O. Hull for communicating to us confirming results in diffused Si diodes.

---

[1]R. N. Hall, Proc. Inst. Radio Engrs. 40, 1512 (1952).
[2]C. H. Gooch, C. Hilsum, and B. R. Holeman, J. Appl. Phys. 32, 2069 (1961).
[3]M. A. Lampert, Phys. Rev. 125, 126 (1962).
[4]V. I. Stafeev, Fiz. Tver. Tela. U.S.S.R. 1, 841 (1959) [translation: Soviet Phys. −Solid State 1, 763 (1959)].
[5]V. I. Stafeev, Fiz. Tver. Tela. U.S.S.R. 3, 2513 (1961) [translation: Soviet Phys. −Solid State 3, 1829 (1962)].
[6]I. Melngailis and R. H. Rediker, J. Appl. Phys. (to be published).

NUCLEAR MAGNETIC RESONANCE IN MnF$_2$ NEAR THE CRITICAL POINT*

P. Heller†

Gordon McKay Laboratory, Harvard University, Cambridge, Massachusetts

and

G. B. Benedek

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received May 8, 1962)

The F^{19} nuclear resonance in MnF$_2$, first observed by Shulman and Jaccarino,[1,2] has been studied in detail in the very interesting temperature region around the paramagnetic-antiferromagnetic critical temperature $T_N = 67.4°K$. Our experimental system permits temperature measurement and control to within one millidegree for as long as six hours, any temperature variation across the sample being much less than a millidegree. Temperatures were measured with a platinum resistance thermometer calibrated very carefully using the vapor pressure-temperature curve for nitrogen.[3] An inductive coupling arrangement used with a very high frequency spectrometer,[4] plus a standard Pound-Knight-Watkins spectrometer, made possible nuclear magnetic resonance obser-

vations at frequencies from 23 to 110 Mc/sec without making any changes inside the low-temperature apparatus. Nuclear resonances of width up to 3 Mc/sec could be detected with this system.

We have determined the temperature dependence of the F^{19} resonance frequency ν_{19} in zero applied field in the antiferromagnetic state between T_N and 52°K. Our data start at $T = T_N - 0.005K°$ at which temperature ν_{19} is about 8 Mc/sec. This frequency corresponds to a reduction of the sublattice magnetization to 5% of the magnetization at absolute zero. For the first few degrees below the Néel point, the data very accurately fit the expression

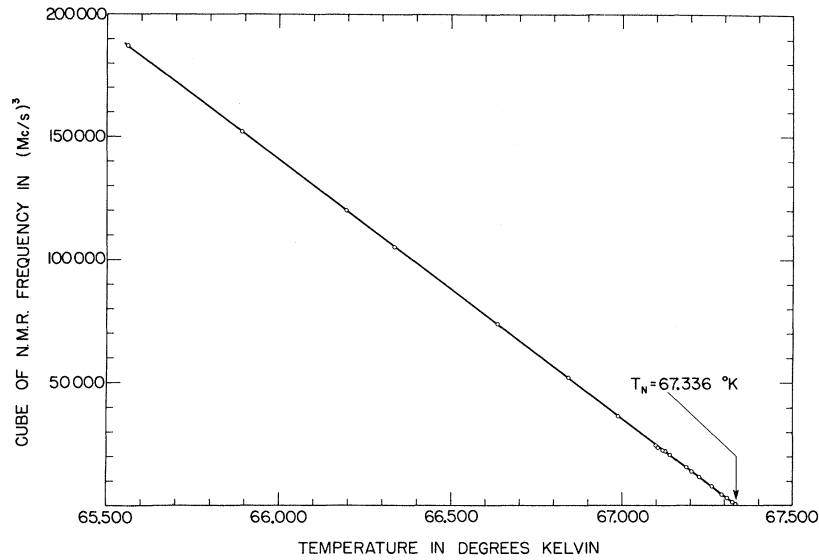$$\frac{M(T)}{M(0)} = \frac{\nu_{19}(T)}{\nu_{19}(0)} = A(T_N - T)^R, \tag{1}$$

FIG. 1. Temperature dependence of the cube of the F^{19} nuclear resonance frequency for the first 1.8 degrees below T_N. The points lie on the straight line shown to within the experimental uncertainty of about 5 millidegrees.

where $R = 0.335 \pm 0.01$, $A = (0.295 \pm 0.001)(\text{K}°)^{-R}$, and $\nu_{19}(0) = 159.978$ Mc/sec. The accuracy with which Eq. (1) fits the data can be seen in Fig. 1 which plots $\nu_{19}^3(T)$ versus the temperature for the first 1.8 degrees below T_N. Extrapolation over the last 5 millidegrees enables us to determine that

$$T_N = (67.336 \pm 0.003)°\text{K}. \tag{2}$$

Since Eq. (1) does not have the correct asymptotic behavior as $T \to 0$, it cannot be expected to hold far below T_N. The experimental results depart from the values given by Eq. (1) by $0.02\text{K}°$, $0.10\text{K}°$, and $0.5\text{K}°$ at $61°\text{K}$, $58.5°\text{K}$, and $53°\text{K}$, respectively. The experimental data for the range $52°\text{K} < T < T_N$ are plotted in Fig. 2. The cube root law that we observe shows that the sublattice magnetization rises much faster than the law $M \propto (T_N - T)^{1/2}$ predicted by the molecular field theory just below T_N. The molecular field theory prediction is shown together with our data for $\nu_{19}(T)$ in Fig. 2. The precision of the nuclear resonance measurements, as illustrated in Figs. 1 and 2 and Eq. (1), demonstrates the power of this method[5,6] in determining the sublattice magnetization in the theoretically difficult, but important, critical region.

By observing the shift of the nuclear resonances on applying a magnetic field H_0 along the C (antiferromagnetic) axis, we were able to determine the susceptibility $\chi_\parallel$ for each of the two Mn^{++}

sublattices separately near T_N. The susceptibilities of the up and down sublattices were found to be equal and their sum is in good agreement with the ordinary macroscopic susceptibility measurements.[7]

In the antiferromagnetic state the F^{19} linewidths are strongly anisotropic, depending on the direction of the vector sum $\vec{H}_{\text{nucl}}$ of the applied field and the field produced by the Mn^{++} spins at the F^{19} nucleus. The lines are broadest for $\vec{H}_{\text{nucl}}$ along C and narrowest for $\vec{H}_{\text{nucl}}$ along A. (See Fig. 3.) For $\vec{H}_{\text{nucl}}$ along C, the linewidth is given to within 20% by

$$\delta\nu_C = 490 \ [\text{kc/sec } (\text{K}°)^{1/2}](T_N - T)^{-1/2};$$

$$0.02\text{K}° < T_N - T < 15\text{K}°. \tag{3}$$

In this 15-degree temperature range the linewidth increases from 100 kc/sec to 3000 kc/sec. In the paramagnetic state the line shows an extraordinarily rapid broadening as T_N is approached. The broadening is anisotropic, being more marked at a given temperature with the applied field along C than along A. (See Fig. 4.) For $0.04\text{K}° < T - T_N < 10\text{K}°$ the linewidths are given to within 15% by

$$H_0 \text{ along } C: \ \delta\nu_C = 95 \text{ kc/sec } [1 + 0.33\text{K}°/(T - T_N)],$$

$$H_0 \text{ along } A: \ \delta\nu_A = 85 \text{ kc/sec } [1 + 0.12\text{K}°/(T - T_N)]. \tag{4}$$
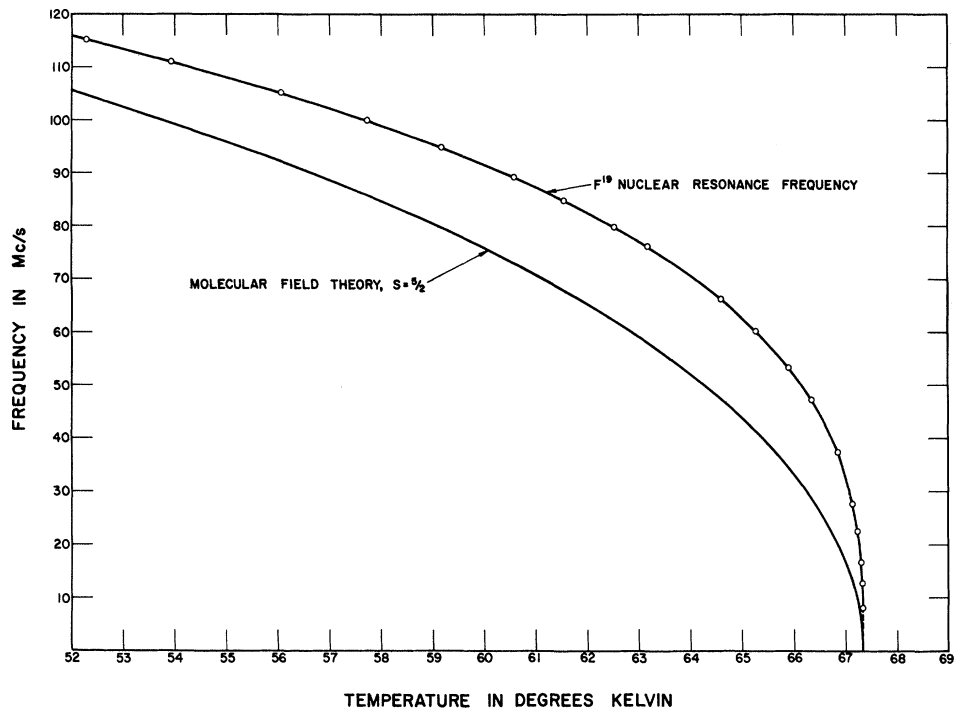
FIG. 2. Temperature dependence of the F^{19} resonance frequency in the range $52°K$ $< T < T_N$. The circles greatly exaggerate the size of the experimental uncertainties. The lower curve is computed using the molecular field theory.
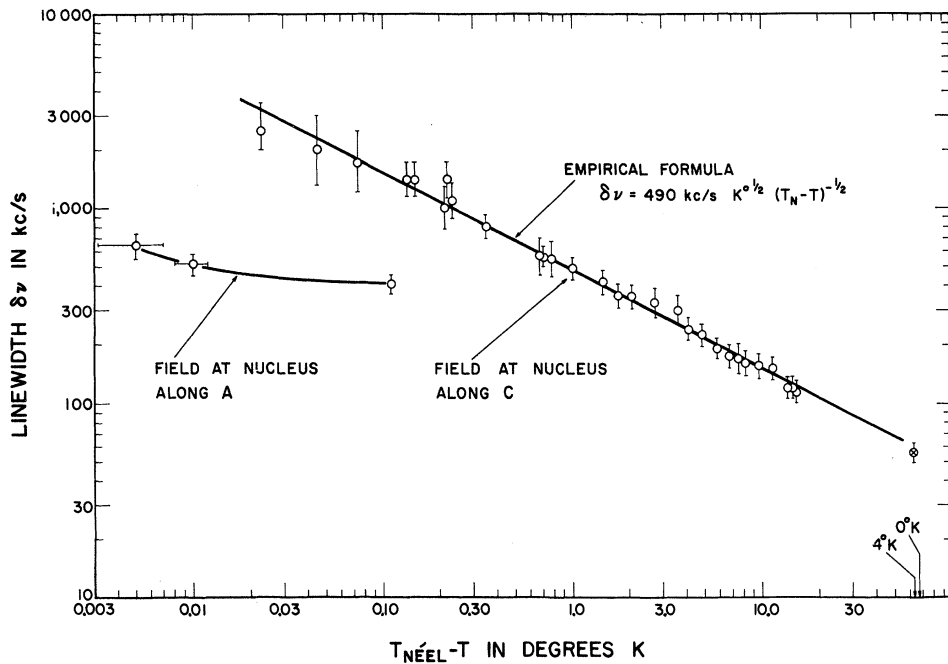

FIG. 3. Temperature dependence of the F^{19} linewidths in the antiferromagnetic state. The single point at $4°K$ is from reference 2.
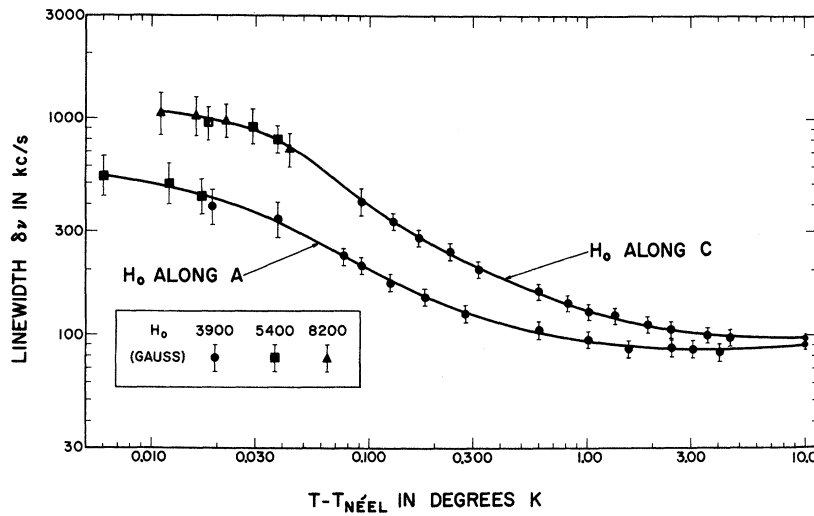
FIG. 4. Temperature dependence of the F^{19} linewidths in the paramagnetic state just above the Néel point.

Note that in the last degree above T_N the line broadens by about a factor of ten. It has been proposed[1,8] that the linewidth of the F^{19} resonance is determined by exchange narrowing of the hyperfine interaction between the F^{19} nucleus and the nearest neighbor Mn^{++} spins. If this is the case, the present measurements provide rather direct experimental information on the temperature dependence of the time-space correlation function for the manganese spins in the critical region.

The rapid fade-out of the line which accompanies this broadening provides an extremely sensitive method for measuring changes in the Néel temperature. In particular we have measured the depression of the Néel temperature due to an applied field. In Table I we list the results obtained, together with the predicted Néel point shifts on the molecular field model. We have also measured the effect of hydrostatic pressure on T_N. Our result,

$$dT_N/dP = 303 \pm 3 \text{ millidegrees per } 1000 \text{ kg/cm}^2,$$

$$(5)$$

Table I. Effect on T_N of raising applied field H_0 from 5.4 kG to 8.25 kG.

Field direction	ΔT_N in millidegrees	
	Expt.	Mol. field theory
A axis	-2.8 ±1	-0.87
C axis	-7.5 ±1	-2.6

agrees well with the estimate of Benedek and Kushida[4] obtained by a quite different method. The pressure dependence of T_N shows that the Néel point is itself a function of the temperature because of the effect of thermal expansion. Using our pressure data and the thermal expansion measurements of Gibbons,[9] we have estimated the importance of this effect in fitting the $\nu_{19}(T)$ data to Eq. (1) with $T_N = T_N(T)$. Our estimate shows that, with this correction, the coefficient A in (1) should be about one percent less than stated above. The effect on the exponent R is negligible.

Just below T_N we observe, to our surprise, lines corresponding to nuclei in both the antiferromagnetic and paramagnetic phases, the line at the paramagnetic location fading rapidly with decreasing temperature and disappearing entirely at about 25 millidegrees below T_N. At 5 millidegrees below T_N the areas under the two lines are roughly equal. We do not understand this effect. One obvious possibility is that it is due to an inhomogeneity in the sample's Néel temperature caused, perhaps, by internal strains. Such a mechanism would broaden the line below T_N. However, the actual linewidths for $\vec{H}_{nucl}$ along A are several times larger than possible for such a mechanism. Furthermore, the linewidths for $\vec{H}_{nucl}$ along C fall off more slowly as the temperature is reduced than can be predicted on this basis.

We are greatly indebted to Dr. V. Jaccarino and Dr. H. Guggenheim of the Bell Telephone Laboratories for providing us with oriented sin-

gle crystals of MnF_2. It is a pleasure to thank
Dr. D. Gill, Dr. J. Jeener, and Dr. G. Seidel for
many helpful discussions.

[1] R. G. Shulman and V. Jaccarino, Phys. Rev. 108,
1219 (1957).

[2] V. Jaccarino and R. G. Shulman, Phys. Rev. 107,
1196 (1957).

[3] G. T. Armstrong, J. Research Natl. Bur. Standards
53, 263 (1954).

[4] G. B. Benedek and T. Kushida, Phys. Rev. 118, 46
(1960).

[5] N. J. Poulis and G. E. G. Hardeman, Physica 18,
391 (1952).

[6] V. Jaccarino and L. R. Walker, J. phys. radium
20, 341 (1959).

[7] J. W. Stout and M. Griffel, J. Chem. Phys. 18,
1455 (1950).

[8] T. Moriya, Progr. Theoret. Phys. (Kyoto) 16, 641
(1956).

[9] D. F. Gibbons, Phys. Rev. 115, 1194 (1959).

MICROWAVE GENERATION IN RUBY DUE TO POPULATION INVERSION PRODUCED BY OPTICAL ABSORPTION*

D. P. Devor, I. J. D'Haenens, and C. K. Asawa
Hughes Research Laboratories, Malibu, California
(Received April 30, 1962)

Microwave amplification and generation by the
stimulated emission of radiation (maser) were
observed in ruby as a result of population inver-
sion produced in the ground state of Cr^{3+} by the
absorption of the coherent optical emission from
a second ruby (optical maser). The maser crys-
tal was oriented in a magnetic field of about 6700

Oe to obtain a transition between a ground $^4A_2$
Zeeman sublevel and an excited $\bar{E}(^2E)$ Zeeman
sublevel which would match a spectral compo-
nent of the output of the optical maser. The ar-
rangement of the experimental apparatus is shown
schematically in Fig. 1.
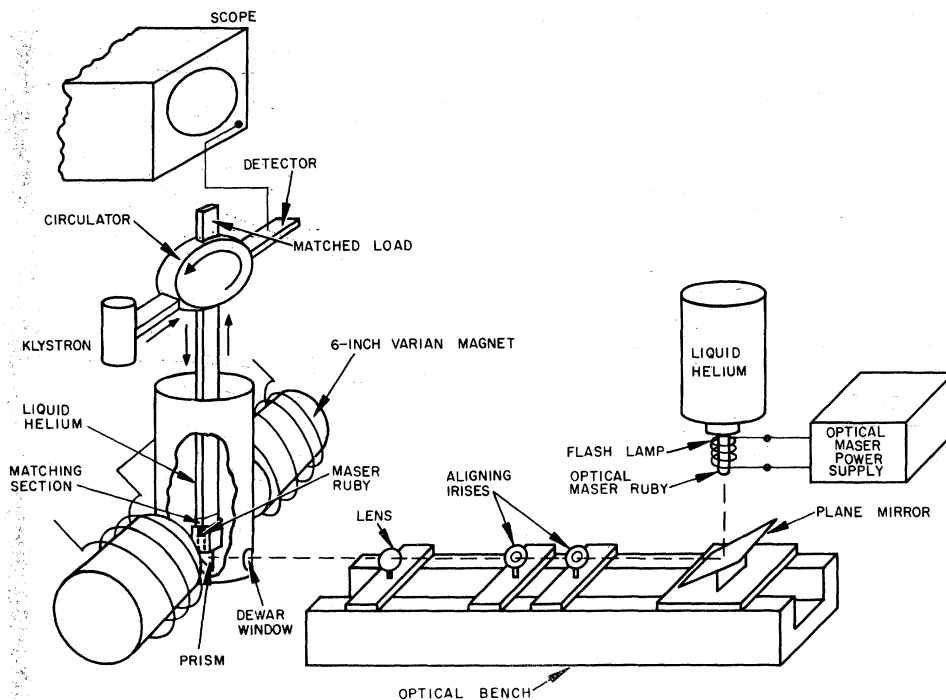
Detection of the interaction of optical and para-

FIG. 1. Arrangement of experimental apparatus.