Electron-Nuclear Double Resonance of Fe^{57} in MgO

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The accuracy of the value of the nuclear magnetic moment of Fe^{57} has been increased by a factor of 10 by an electron-nuclear double resonance measurement in the Fe^{3+} state in MgO, where the paramagnetic shielding correction is less than 1 part in 10^3. The value found is $\mu_I(Fe^{57}) = +0.09024\pm0.00007$ nm. Ludwig and Woodbury's earlier determination, $+0.0903\pm0.0007$ nm, is in excellent agreement with this result, although approximately ten times less accurate. An additional term in the hyperfine interaction of the type S^3I was observed. The hyperfine field at the Fe^{57} nucleus is shown to differ by less than $\frac{1}{2}\%$ from the value found by Robert for Fe^{3+} in octahedral coordination in yttrium iron garnet (YIG). Thus, whatever zero-point spin deviation may be present in YIG is apparently less than anticipated theoretically.

I. INTRODUCTION

THE nuclear moment of Fe^{57} figures prominently in hyperfine field studies of Fe in varied environments via the Mössbauer effect. The magnetic moment of Fe^{57} was determined to an accuracy of 0.8% by Ludwig and Woodbury[1] from an ENDOR (electron-nuclear double resonance) experiment of neutral Fe in silicon. This accuracy of 0.8% was not experimental uncertainty but arose from the uncertainty of the paramagnetic shielding correction δ, where

$$H_{\text{ext}}^{\text{effective}} = H_{\text{ext}}^{\text{applied}}(1+\delta).$$

The origin of δ is in cross terms which appear in second-order perturbation of the type[2]

$$-\sum_{n\neq 0} \langle 0|\beta \mathbf{H}\cdot\mathbf{L}|n\rangle\langle n|P\mathbf{L}\cdot\mathbf{I}|0\rangle/(E_n-E_0), \quad (1)$$

where $P\mathbf{L}\cdot\mathbf{I}$ is the orbital hyperfine interaction and $P=2g_I\beta\beta_N\langle r^{-3}\rangle$. This gives an added term to the spin Hamiltonian of the form

$$-2\beta H_i I_j P \sum_n \frac{\langle 0|L_i|n\rangle\langle n|L_j|0\rangle}{E_n-E_0} = H_i I_j P \Lambda_{ij}. \quad (2)$$

As the electronic g shift, $\Delta g = -2\lambda\Lambda_{ij}$,[3] where λ is the spin-orbit coupling constant,

$$\delta = -(2\beta^2\Delta g/\lambda)\langle 1/r^3\rangle. \quad (3)$$

For neutral iron in silicon $(3d^8)$, Ludwig and Woodbury estimated δ to be 0.012 ± 0.006. They gave the value $\mu_I = +0.0903\pm0.0007$ nm.

In view of the widespread use made of the Fe^{57} moment, it was deemed worthwhile to have an independent check on the Fe^{57} moment from an ENDOR[4] experiment on Fe^{3+} $(3d^5)$ in an ionic crystal such as MgO rather than a semiconductor. As Δg is much closer to zero in this case $(3d^5)$, the paramagnetic shielding would be an order of magnitude smaller, allowing a more accurate determination of the Fe^{57} moment.

In the course of the ENDOR experiment on Fe^{3+} in MgO, the higher order hyperfine term S^3I was observed and is discussed in Sec. IV.

The ENDOR measurement also provides a very accurate value of the hyperfine (hf) field of Fe^{3+} in sixfold oxygen coordination. A comparison between this value of the hf field with that observed by NMR in yttrium iron garnet (YIG) and by the Mössbauer effect in α-Fe_2O_3 indicates no apparent zero-point spin deviation in these antiferromagnets as will be described in Sec. V.

II. SAMPLES AND APPARATUS

The MgO crystals used to observe the Fe^{57} ENDOR were obtained from G. K. Wertheim. Enriched Fe^{57} in the form of Fe_2O_3 was diffused in air into the crystals at 1400°C overnight. The ratio of Fe^{57} to other Fe was approximately 1:1. The ratio of Fe to Mg was somewhere in the range of 10^{-3} to 10^{-4}. A CaO crystal used in a normal EPR experiment was obtained from Semi-Elements Inc., the Fe being present as an unintended impurity.

The experimental arrangement has been described by one of us in a previous article, with the exception of the provisions necessary for the extension to ENDOR.[5] Some of the features of the 24 kMc/sec EPR spectrometer described earlier are the use of a matched TE_{011} circular cavity, a balanced microwave bridge, and superheterodyne phase-sensitive detection at an intermediate frequency of 60 Mc/sec, enabling one to measure χ' as well as χ''. The crystal to be studied is placed in the center of the cavity, on top of a vertical polystyrene rod, which sticks out of the cavity through a hole in the center of its bottom plate.

ENDOR is made possible, using the same type of cavity, by mounting a small flat coil of four turns of insulated copper wire (e.g., A.W.G. No. 33) inside the

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[1] G. W. Ludwig and H. H. Woodbury, Phys. Rev. 117, 1286 (1960).
[2] J. N. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156 (1958).
[3] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).
[4] G. Feher, Phys. Rev. 103, 834 (1956).
[5] S. Geschwind, Phys. Rev. 121, 363 (1961).

cavity, on top of the polystyrene rod. The lead wires of the ENDOR coil are fed through a small axial hole in the center of the polystyrene rod and are connected outside the cavity to a coaxial cable which leads to outside the cryostat. The plane of the coil is vertical, and it is parallel to the microwave magnetic field near the crystal. The crystal is mounted inside the coil such that a major portion of it sticks out in a region where the microwave magnetic field can penetrate it. The rf signal applied to the coil (henceforth caller ENDOR signal) was obtained from a Hewlett–Packard generator, model 608A, and two wideband amplifiers, I.F.I. models 510 and 500A. This gave sufficient power for obtaining fields of the order of a few tenths of a gauss, without using matching devices. This magnitude could be estimated by setting the dc magnetic field H_0 parallel to the ENDOR field, which then acted as a field modulation which produced sidebands on the EPR signal.

When performing an ENDOR measurement, the direction of H_0 is perpendicular to the ENDOR field. Sensitive detection of ENDOR transitions was achieved by amplitude modulating the ENDOR signal at a rate of the order of 100 cps, and detecting the microwave χ'' signal of a partially-saturated EPR line phase-sensitively, at this frequency, with a P.A.R. model JB4 lock-in amplifier. Even then, the ENDOR lines of $(Fe^{57})^{3+}$ in MgO could only be observed when, after setting H_0 on top of an EPR line and adjusting the microwave power level properly, renewed balancing of the cavity was performed.

The ENDOR frequencies were measured with a Hewlett-Packard counter.

During the measurements, helium gas was kept inside the cavity. At high ENDOR power levels, spurious variations in the microwave χ'' signal were detected which had nothing to do with ENDOR, but perhaps with heating the crystal or with modulation of H_0. ENDOR lines could be distinguished easily from these unwanted effects by their strong dependence on the ENDOR frequency.

III. RESULTS OF ENDOR OF $(Fe^{57})^{3+}$ IN Mg)

The ENDOR of $(Fe^{57})^{3+}$ in MgO was performed with the dc field H_0 parallel to the [100] direction of the MgO crystal. For $Fe^{3+}(Fe^{57})$ $S=\frac{5}{2}$ and $I=\frac{1}{2}$, and the microwave absorption spectrum consists of five EPR fine-structure lines of which only the center one $(m_S=-\frac{1}{2} \leftrightarrow +\frac{1}{2})$ showed a resolved hyperfine structure (hfs). When looking at an ENDOR transition $(\Delta m_I=1; m_S=\text{constant})$, H_0 was set to the center of an EPR line and the microwave absorption coefficient χ'' was about one-half of its unsaturated value. Application of the ENDOR signal resulted in a very small increase of χ'' of the order of only 0.01%. This ENDOR signal strength (change in χ'') did not depend very much upon the position of H_0 within the EPR line,

TABLE I.

EPR line	Observed ENDOR frequencies ν (m_S)
$m_S=-\frac{5}{2} \leftrightarrow -\frac{3}{2}$	$\nu\left(-\frac{5}{2}\right)$
$m_S=-\frac{3}{2} \leftrightarrow -\frac{1}{2}$	$\nu\left(-\frac{3}{2}\right)$ and $\nu\left(-\frac{1}{2}\right)$
$m_S=-\frac{1}{2} \leftrightarrow +\frac{1}{2}$	$\nu\left(-\frac{1}{2}\right)$ and $\nu\left(+\frac{1}{2}\right)$
$m_S=+\frac{1}{2} \leftrightarrow +\frac{3}{2}$	$\nu\left(+\frac{3}{2}\right)$
$m_S=+\frac{3}{2} \leftrightarrow +\frac{5}{2}$	$\nu\left(+\frac{5}{2}\right)$

even when this line showed a partly resolved hfs. Some of the EPR line broadening must have been inhomogeneous but no details of the ENDOR mechanisms were studied.

All six ENDOR lines $(m_S=-\frac{5}{2}, -\frac{3}{2}, \ldots, +\frac{5}{2})$ have been observed. The corresponding frequencies will be denoted by $\nu(m_S)$. These frequencies also depend upon H_0 as they contain the nuclear Zeeman term. Table I shows at which EPR lines the ENDOR frequencies could be measured. To a first approximation, the ENDOR frequencies are given by $h\nu(m_S) \approx |m_S A - g_I \beta_N H_0|$, but the final analysis of the experimental data has been done by solving the secular equation of the spin Hamiltonian to such an approximation as is required by the experimental accuracies. Doing so, the EPR and ENDOR results can be described, within 2 kc/sec for the ENDOR frequencies (the experimental limit of accuracy), by the following spin Hamiltonian with the parameters given in Table II:

$$H = g\beta H \cdot S$$
$$+\tfrac{1}{6}a[S_x{}^4+S_y{}^4+S_z{}^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]$$
$$+\{A-\tfrac{1}{5}U[3S(S+1)-1]\}S \cdot I - g_I\beta_N H \cdot I$$
$$+U(S_x{}^3 I_x + S_y{}^3 I_y + S_z{}^3 I_z). \quad (4)$$

The x, y, and z directions are along the cubic axes of the MgO crystal.

The necessity of introducing a $S^3 I$ term to describe the experimental data will be discussed in the following section. The actual angle between H_0 and the [100] direction of the MgO crystal was not more than about one degree; a study of the shift of the ENDOR frequen-

TABLE II. Results of EPR and ENDOR at liquid-helium temperatures.

g		2.0039	± 0.003
a/h	(Mc/sec)	$+634$	$\pm 1^{\text{a}}$
A/h	(Mc/sec)	-30.176	$\pm 0.002^{\text{b,c}}$
$g_I\beta_N/h$	[(Mc/sec)/10^4 G]	$+1.376$	$\pm 0.001^{\text{c}}$
U/h	(Mc/sec)	-0.0057	± 0.0003
$H^{hf} \equiv A/g_I\beta_N$	(kG)	-219.3	$\pm 0.2^{\text{c}}$
μ_I	(nm)	$+0.09024$	$\pm 0.00007^{\text{d}}$

[a] The values of g and a confirm those given by W. Low, Proc. Phys. Soc. (London) 69B, 1169 (1956); and by J. H. E. Griffiths and J. W. Orton, Proc. Phys. Soc. (London) 73, 948 (1959).
[b] A more accurate value of -30.1474 ± 0.0005 Mc/sec is obtained for $h^{-1}\{A-(1/5)U[3S(S+1)-1]\}$.
[c] The signs of A and g_I follow very clearly from the experimental data.
[d] Since we estimate that any paramagnetic or other shielding corrections are less than our experimental error, we call the moment μ_I rather than μ_I (effective).

cies upon rotating H_0 showed that this misorientation was not important.

The full width at half-height of the ENDOR lines was 10 to 15 kc/sec.

IV. THE S^3I TERM

If no S^3I term was present in the Hamiltonian, each pair $[\nu(-\tfrac{5}{2}),\ \nu(+\tfrac{5}{2})]$, $[\nu(-\tfrac{3}{2}),\ \nu(+\tfrac{3}{2})]$, or $[\nu(-\tfrac{1}{2}),\ \nu(+\tfrac{1}{2})]$ would have been sufficient to derive the values of A and g_I. This would have yielded A values of -30.183, -30.160, and -30.149 Mc/sec from the above pairs, respectively. These values diverge far

beyond the experimental inaccuracy and the ratio of 2:1 for $(30.183-30.160)/(30.160-30.149)$ strongly suggests that a term[6,7]

$$U\{S_x{}^3I_x+S_y{}^3I_y+S_z{}^3I_z-\tfrac{1}{5}[3S(S+1)-1](\mathbf{S}\cdot\mathbf{I})\}\quad(5)$$

should be added to the Hamiltonian.

That such a term should be present for an electron spin $S\geq\tfrac{3}{2}$ was pointed out by Bleaney[6] and Koster and Statz[7] and first seen for Co^{2+} in tetrahedral coordination.[8] This is the first report of its observation in Fe^{3+}. Such a term for $Fe^{3+}(3d^5)$ can have its origin in higher order perturbations of the type

$$\sum_{\substack{\alpha,\alpha'\\\alpha''}}\frac{\langle^6S\,|\,W_{s.o.}\,|\,_\alpha{}^4T_1\rangle\langle_\alpha{}^4T_1\,|\,P\sum_i\mathbf{l}_i\cdot\mathbf{I}\,|\,_{\alpha'}{}^4T_1\rangle\langle_{\alpha'}{}^4T_1\,|\,W_{s.o.}\,|\,_{\alpha''}{}^4T_1\rangle\langle_{\alpha''}{}^4T_1\,|\,W_{s.o.}\,|\,^6S\rangle}{(_\alpha{}^4T_1-{}^6S)(_{\alpha'}{}^4T_1-{}^6S)(_{\alpha''}{}^4T_1-{}^6S)}.\quad(6)$$

Here $P=2g_I\beta\beta_N\langle r^{-3}\rangle$ and $W_{s.o.}=\sum_i\zeta\mathbf{l}_i\cdot\mathbf{s}_i$, where ζ is the one-electron spin-orbit coupling parameter. The α's refer to the three cubic-field $^4T_1$ states in the d^5 configuration (each of which contains some free ion ^4P).

The positions of the excited quartets for Fe^{3+} are not known. We therefore attempt to make only the very roughest estimate of these terms. They will be of order $P\zeta^3/\Delta^3$ where Δ is an average separation to the excited states. For Fe^{57}, $P\approx100$ Mc/sec $\zeta\approx450$ cm^{-1} and $\Delta\approx1.5\times10^4$ cm^{-1}, so that $P\zeta^3/\Delta^3\approx3$ kc/sec which is of the right order of magnitude.

An S^3I term could also arise from higher order interactions involving the electron-nuclear dipolar interaction,

$$W_D=-P\mathbf{I}\cdot\sum_i\left\{\mathbf{s}_i-3\frac{\mathbf{r}_i(\mathbf{s}_i\cdot\mathbf{r}_i)}{r_i{}^2}\right\},$$

i.e.,

$$\sum_{\alpha\beta}\frac{\langle^6S\,|\,W_D\,|\,_\beta{}^4T_2\rangle\langle_\beta{}^4T_2\,|\,W_{s.o.}\,|\,_\alpha{}^4T_1\rangle\langle_\alpha{}^4T_1\,|\,W_{s.o.}\,|\,^6S\rangle}{(_\beta{}^4T_2-{}^6S)(_\alpha{}^4T_1-{}^6S)}\quad(7)$$

where the β's refer to the different $^4T_2$ excited states each of which contains some free ion ^4D. If we assume matrix elements W_D/P of order unity (experience shows they are typically less than unity), we find that this interaction contributes approximately 90 kc/sec. While this estimate of 90 kc/sec is an order of magnitude larger than the observed value of ≈6 kc/sec, more exact evaluation of the appropriate matrix elements and possible cancellation of terms could bring this more in line with the observed value. It must be stressed that the estimates (6) and (7) are very rough indeed and are only intended to show that such terms might reasonably contribute to an S^3I term. A more exact calculation involving a summation over all the excited states and evaluation of the appropriate matrix elements does not seem warranted at this time in view of the uncertainty regarding the position of the excited states.

V. ZERO-POINT SPIN DEVIATION OF Fe^{3+} ANTIFERROMAGNETS

It is well known that the ground state of an antiferromagnet cannot be a perfectly aligned state, i.e., $\langle S_z\rangle\neq S$. Various estimates using spin-wave theory predict a spin deviation somewhere between 2 and 3%.[9-11] One attempts to observe this deviation experimentally by comparing the hyperfine interaction in the concentrated ordered material at sufficiently low temperatures (such that $\langle S_z\rangle$ has its maximum value) with the hyperfine interaction for the same ion in isomorphic surroundings in a dilute paramagnet in the $S_z=S$ state.

One might raise the objection that this procedure neglects the change of hyperfine field which could result from the change in lattice spacing between the dilute and concentrated salt. This objection is answered in Table III which shows that the hyperfine field is the same within $\tfrac{1}{2}\%$ for the same sixfold oxygen coordination even though the lattice spacing may change as much as 20%. As a matter of fact a detailed analysis of the core polarization hyperfine field (cphf) for the $3d$ transition-metal ions shows that for a given ion in the same ligand coordination (same ligand type and number), the cphf (at low temperatures where vibrational effects are minimized) is constant to within a few percent at low temperature.[12] More specifically for the $3d^5$ ions like Mn^{2+}, Fe^{3+} and Cr^+ and $3d^3$ ions like

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[6] B. Bleaney, Proc. Phys. Soc. (London) 73, 939 (1959).

[7] G. F. Koster and H. Statz, Phys. Rev. 113, 445 (1959).

[8] F. S. Ham, G. W. Ludwig, G. D. Watkins, and H. H. Woodbury, Phys. Rev. Letters 5, 468 (1960); G. F. Koster and H. Statz, Phys. Rev. 113, 445 (1959); B. Bleaney, Proc. Phys. Soc. (London) A73, 939 (1959).

[9] P. W. Anderson, Phys. Rev. 86, 694 (1952).

[10] T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. 4, 1 (1955).

[11] L. R. Walker, J. Appl. Phys. Suppl. 32, 264S (1961). This magnitude of deviation for both octahedral and tetrahedral sites of the ferrimagnet, yttrium iron garnet is implicit in this reference.

[12] M. Blume and S. Geschwind (to be published).

TABLE III. $|A|/h$ for Fe^{3+} in sixfold oxygen coordination in dilute crystals.

Crystal	$Fe^{3+}-O^{2-}$ distance	Temp. (°K)	$|A|/h$ (Mc/sec)
MgO[a]	2.10	4.2	30.176±0.002
CaO[b]	2.40	4.2	30.16 ±0.14
Al_2O_3[c]	1.98	4.2	30.27 ±0.15
	1.85		

[a] This paper. This value agrees with an earlier measurement by E. S. Rosenvasser and G. Feher, Bull. Am. Phys. Soc. 6, 117 (1961), but is far more accurate due to use of ENDOR.
[b] This paper. Also measured by W. Low and R. S. Rubins, *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1962), p. 79. This latter measurements was not done at 4.2°K and is less accurate.
[c] G. K. Wertheim and J. P. Remeika, Phys. Letters 10, 14 (1964). Hyperfine interaction was measured by Mössbauer effect.

V^{2+}, Cr^{3+}, and Mn^{4+} in octahedral coordination this constancy holds to about 1%. One may therefore safely rule out any objection to this comparison of the cphf in the dilute and concentrated systems based upon change in lattice constants.

Boutron and Robert[13] have measured $|A|/h$ at 4.2 °K for both sites in YIG and found for the octahedral site $|A|/h=30.25\pm0.01$ Mc/sec. If we compare this value with those listed in Table III, we see that there is no apparent zero-point spin deviation in the octahedral site. Walsh and Rupp[14] have measured the Fe^{57} hf interaction in ZnO and by comparing their result with that of Boutron and Robert for the tetrahedral site in YIG one concludes that any spin deviation was less than 2% (the accuracy of their hf measurement).

Recently, Forrester[15] has measured the field at the Fe^{57} nucleus in α-Fe_2O_3 (at low temperature) using the Mössbauer effect. He finds a value of 548±6 kG. However, from the value +1.15 $\cos^2\theta$ cm^{-1} per ion at absolute zero for the dipolar anisotropy in Fe_2O_3 calculated by Tachiki and Nagamiya[16] we see that there is a dipolar field of +5 kG which *adds* to the hf field. The hyperfine field should therefore be

taken as 543±6 kG, or $|A|/h=29.9\pm0.3$ Mc/sec. Again here there is no apparent zero-point spin deviation any larger than about 1%.

Along similar lines, an upper limit of one half percent was placed on any spin deviation of Mn^{2+} in MnF_2 by Jones and Jefferts[17] and in $KMnF_3$ by Montgomery, Teaney, and Walsh[18] and Witt and Portis.[19]

It therefore still remains a puzzle as to why the theoretically expected spin deviation of 2 to 3% for $S=\frac{5}{2}$ is not observed.[20]

V. Jaccarino[21] has raised the question as to whether the comparison between the diamagnetic crystal and the ordered concentrated material is a valid one in that the presence of magnetic next-nearest neighbors as compared to diamagnetic neighbors might change the hf interaction through some different bonding effects. A more meaningful check might be had by measuring the hf interaction in the paramagnetic and ordered state in the same concentrated crystal, taking due account of any temperature variation which may be present in A. Keeping this possibility in mind it is none the less remarkable that no spin deviation greater than 1% seems to have been uncovered for Mn^{2+} and Fe^{3+} in several different types of environment based upon the paramagnetic measurement in a dilute crystal.

ACKNOWLEDGMENTS

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[14] W. M. Walsh, Jr. and L. W. Rupp, Jr., Phys. Rev. 126, 952 (1962).
[15] Forrester, D. W., Oak Ridge National Laboratory Report No. ORNL 3705, 1965 (unpublished).
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[17] E. D. Jones and K. B. Jefferts, Phys. Rev. 135, A1277 (1964).
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[20] Recently, M. Rubinstein, G. H. Stauss, and J. J. Krebs, Phys. Letters 12, 302 (1964), have measured the NMR frequency of Cr^{53} in Cr_2O_3 and found it to be approximately 3% less than that of Cr^{53} in Al_2O_3. They suggested that this discrepancy might partly be due to zero-point spin deviation. For $S=\frac{3}{2}$ one expects a spin deviation of more like 5 or 6% (see Ref. 10). E. D. Jones, Bull. Am. Phys. Soc. 10, 33 (1965), has recently measured the NMR frequency of Mn^{55} in MnO and has found it to be a few percent *higher* than Mn in MgO. Temperature variation of the hf interaction in dilute crystals as reviewed by W. M. Walsh, Jr. (to be published) indicate the presence of vibrational effects which are not understood. Perhaps an understanding of these effects coupled with further experimental and theoretical work will help explain the fact that the zero-point spin deviation is not observed.
[21] V. Jaccarino (private communication).