ELECTRON-NUCLEAR DOUBLE RESONANCE OF Ni^{61} IN Al_2O_3 AND VARIATION OF hfs THROUGH AN INHOMOGENEOUS LINE DUE TO RANDOM CRYSTAL FIELDS

P. R. Locher* and S. Geschwind†
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 29 August 1963)

A recent nmr measurement of the nuclear moment of Ni^{61} in nickel metal was reported in this journal.[1] The value of 0.70 ± 0.04 nm was a factor of 2.3 times larger than an earlier determination of $\mu_I(Ni^{61})$ as estimated from the hfs in the electron spin resonance (ESR) spectrum of Ni^{2+} in MgO.[2] We have measured the ENDOR[3] (electron-nuclear double resonance) spectrum of Ni^{61} in Al_2O_3 and have determined the absolute value of the nickel moment to be 0.746 ± 0.007 nm. At the same time we can clearly explain the apparent inconsistency between the two earlier results. It will be shown that orbital hyperfine (hf) fields play a crucial role in nominally orbital singlet ground-state ions such as Ni^{2+}, and its earlier neglect in MgO led to the erroneous estimate of $\mu_I(Ni^{61})$ by a factor of 2.5. In addition, the significance of orbital hf fields will be illustrated in a striking new effect; a variation in hf field was observed through an inhomogeneously broadened line. This rose from a variation of orbital hf field in the different spin packets associated with slightly different axial crystal fields.

The Ni^{2+} concentration in the Al_2O_3 crystal studied was Ni:Al $\approx 1:10^4$ and the Ni was 75% enriched with Ni^{61} ($I = 3/2$).[4] The crystal was placed in the center of a cylindrical TE_{011} cavity, and the ENDOR signal was applied by means of a few turns of wire directly around the crystal. The ENDOR measurements were taken at several angles θ, but the main results were obtained with $\vec{H}_0$ parallel to the c axis ($\theta = 0$) at the $m_S = 0 \leftrightarrow +1$ ESR line, which has a full width at half-height of 180 gauss (see Fig. 1). The observation of a partly resolved Ni^{61} hfs in the much narrower, partially forbidden, $m_S = -1 \leftrightarrow +1$ line at angles θ of 3° to 10° was very helpful in bracketing the frequency range in which to search for the ENDOR transitions. At $\theta = 0$, three strong ENDOR lines were observed, corresponding to $m_S = +1$. At the same ESR line ($m_S = 0 \leftrightarrow +1$), three very weak ENDOR lines could be detected, corresponding to transitions between hyperfine levels in the $m_S = -1$ state (see Fig. 2). The full width at half-height of the ENDOR lines was only 23 kc/sec. All these data can be described, within a few kc/sec for the ENDOR frequencies, with the following spin Hamiltonian ($S = 1$ and $I = 3/2$):

$$\mathcal{H} = D[S_z^2 - \tfrac{1}{3}S(S+1)] + g_{\parallel}\beta H_0 S_z \cos\theta + \tfrac{1}{2}g_{\perp}\beta H_0 (S_+ + S_-)\sin\theta + A S_z I_z + \tfrac{1}{2}B(S_+ I_- + S_- I_+) - g_I(\mathrm{eff})\beta_N \vec{H}_0 \cdot \vec{I} + \{3e^2qQ/[4I(2I-1)]\}[I_z^2 - \tfrac{1}{3}I(I+1)], \quad (1)$$

with the constants given in Table I.

Note that the value of $|A|$ in Al_2O_3 as listed in Table I is 1.5 times larger than in MgO, and the significance of this fact will be made clear in relating our results to the earlier work. Orton,

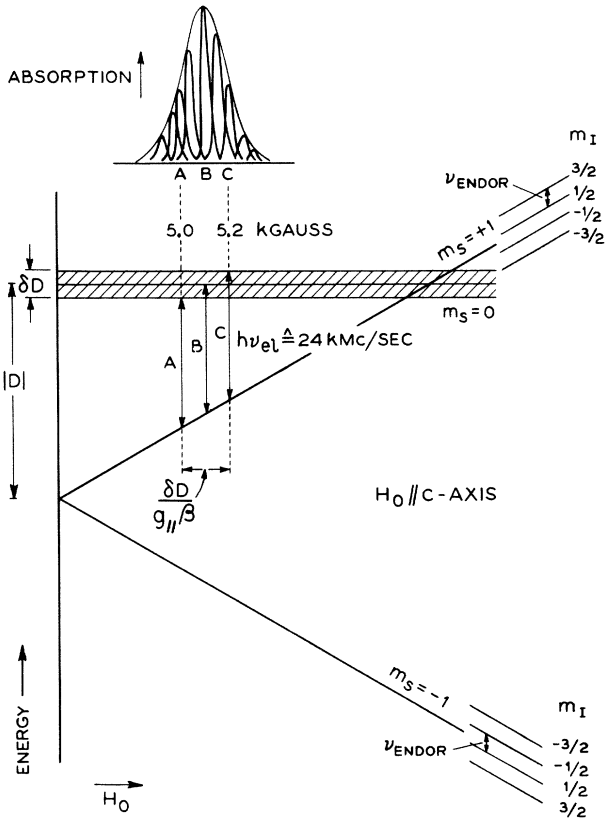

FIG. 1. Ground-state energy levels of a Ni^{2+} ion in Al_2O_3 for the external magnetic dc field $\vec{H}_0$ parallel to the c axis. The ESR absorption line at 24 kMc/sec is indicated. The spin packets (e.g., A, B, and C) correspond to different D values for these packets.

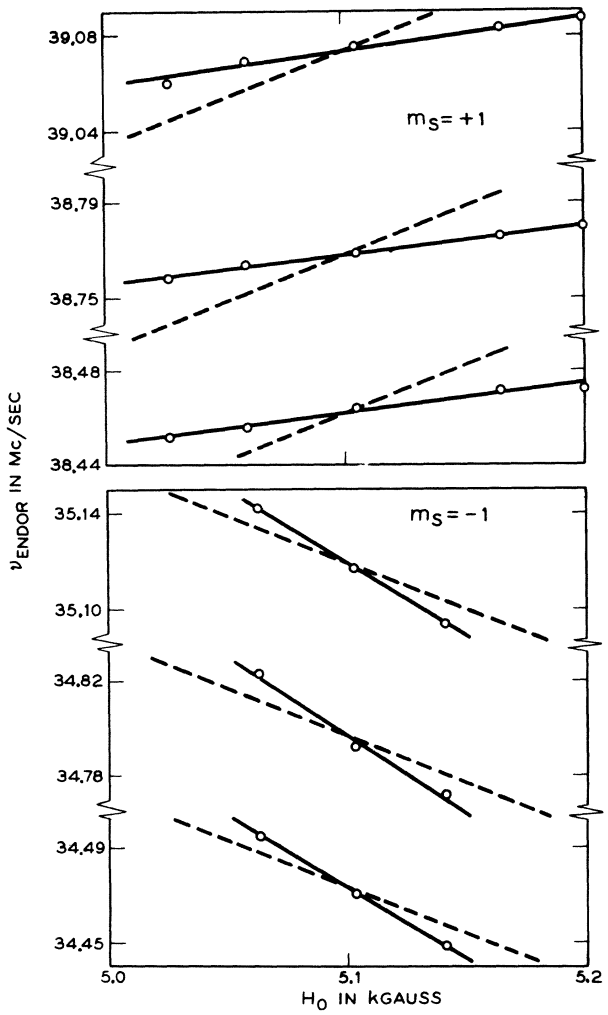

FIG. 2. The six ENDOR frequencies ν_{ENDOR} of Ni^{61} in Al_2O_3 for $\vec{H}_0 \| c$ axis at the $m_S = 0 \leftrightarrow +1$ ESR line. H_0 was varied within the broad ESR line, keeping the microwave frequency constant. The points and the solid lines give the experimental results whereas the dashed lines indicate what would be expected for a constant hfs parameter, A, throughout the inhomogeneous line.

Auzins, and Wertz[2] saw only the outside pair ($m_I = -\frac{3}{2}, +\frac{3}{2}$) of the hfs pattern of Ni^{61} in natural abundance in MgO. They then assumed that the hf fields in Ni^{2+} and Co^+ were essentially the same and from a comparison of the hfs splitting constant A for Ni^{2+} and Co^+ in MgO, using the known nuclear moment of Co^{59}, deduced a value of $\mu_I(Ni^{61}) = 0.3$ nm. Bennett and Streever[5] accepted the point of view of the essential equality of the two hf fields in Co^+ and Ni^{2+}, allowing, however, a variation of perhaps 20% between the two ions, and suggested that the hfs lines had been misidentified: that what had been seen were the $m_I = -\frac{1}{2}, +\frac{1}{2}$ lines and the $m_I = -\frac{3}{2}, +\frac{3}{2}$ lines were missed. We have rechecked the hfs coupling of Ni^{2+} in MgO, using 90% enriched Ni^{61}, and corroborated the measurement of $|A| = 24$ Mc/sec by Orton, Auzins, and Wertz.[2] However, what Orton, Auzins, and Wertz, and Bennett and Streever neglected was the large positive orbital hf field present which cancels a major portion of the negative core polarization field[6] so that, in fact, the total hf field for Ni^{2+} is 2.5 times smaller than for Co^+.[7] As the electronic g shift Δg measures the orbital angular momentum mixed into the $^3A_2$ ground state by spin-orbit coupling, the orbital hf field per unit unpaired spin can be related to the electronic g shift Δg, by the expression given by Abragam and Pryce[8]:

$$H_{orb}^{hf} = 2\beta\Delta g\langle 1/r^3\rangle = 125\Delta g\langle 1/r^3\rangle_{a.u.} \text{ kG}, \quad (2)$$

where $\langle 1/r^3\rangle_{a.u.}$ is in atomic units. In Table II, the orbital hf fields computed, using Eq. (2), are given for the isoelectronic sequence Co^+, Ni^{2+}, and Cu^{3+}. The significance of the cancellation between the positive orbital and negative core polarization fields is here clearly seen.

In addition, there is a not entirely negligible electron-nuclear dipolar hyperfine interaction for these ions.[8] In the case of cubic symmetry this dipolar hf field will be of the order of $\beta\langle 1/r^3\rangle \times \lambda^2/\Delta^2$, where λ is the spin-orbit coupling constant (≈ -300 cm^{-1}) and Δ is a cubic crystal field splitting ($\approx 10^4$ cm^{-1}), so that it is of the order of 0.2 kG and therefore negligible. However, for trigonal symmetry the dipolar hf field will be of the order of $\beta\langle 1/r^3\rangle v_{trig}/\Delta$ which is about 10 kG for $v_{trig} \approx 10^3$ cm^{-1}. A detailed calculation to be published later gives the values of H_{dip}^{hf} listed in Table II, assuming $v' = (\sqrt{3}/2)v$ and $v \approx +10^3$ cm^{-1}, where v and v' are the trigonal field parameters defined by Pryce and Runciman.[9]

Note that, while the orbital and observed hf fields are widely different, the core polarization hf field in the isoelectronic sequence comes out to be essentially constant.

The influence of orbital fields appeared in a dramatic new effect mentioned briefly at the beginning of the Letter and is best described by reference to Figs. 1 and 2. The variation in an ENDOR frequency observed as the external magnetic field was varied within the inhomogeneously broadened line (i.e., from A to C in Fig. 1), keeping the microwave frequency constant, is plotted in Fig. 2 for all six ENDOR lines. One expects a shift in ENDOR frequencies to reflect

Table I. ESR and ENDOR results, at liquid helium temperatures for the center of the inhomogeneously broadened line.

$g_{\parallel}$		2.1948 ±0.0010[a]
$g_{\perp}$		2.1853 ±0.0010[a]
D/h	(Mc/sec)	- 39800 ±20[a]
A/h	(Mc/sec)	(+)36.767 ±0.002 [b]
B/h	(Mc/sec)	(+)32.55 ±0.04 [b]
$g_I(\text{eff})\beta_N/h$	[(Mc/sec)/10^4 gauss][c]	(-) 3.884 ±0.003 [b]
$g_I\beta_N/h$	[(Mc/sec)/10^4 gauss][c]	(-) 3.787 ±0.034 [b]
μ_I	(nm)	(-) 0.746 ±0.007 [b]
$A/g_I\beta_N$	(kG)	- 97.0 ±0.8
$B/g_I\beta_N$	(kG)	- 85.9 ±0.7
$3e^2qQ/\{h[4I(2I-1)]\}$	(Mc/sec)	- 0.170 ±0.002

[a]The ESR results are in agreement with those given by S. A. Marshall, T. T. Kikuchi, and A. R. Reinberg, Phys. Rev. 125, 453 (1962).

[b]We were not able to determine the sign of μ_I. The sign of the five entries in the brackets are predicated on a negative μ_I, which is predicted from the nuclear shell model with configurational mixing; see H. Noya, A. Arima, and H. Horie, Progr. Theoret. Phys. (Kyoto), Suppl. 8, 33 (1958). In either case a positive μ_I would not change the values and the signs of $A/g_I\beta_N$ and $B/g_I\beta_N$.

[c]g_I and μ_I are the values corrected for the pseudofield effect; see J. N. Baker and B. Bleaney, Proc. Roy. Soc. (London) A245, 156 (1958); W. E. Blumberg, J. Eisinger, and S. Geschwind, Phys. Rev. 130, 900 (1963). $|g_I|$ is taken (2.5 ±0.8)% smaller than $|g_I(\text{eff})|$.

Table II. Hyperfine fields for $3d^8$ ions.

					hf fields $A/g_I\beta_N$ and $B/g_I\beta_N$ (kG)		
$3d^8$ ion	Compound	$\vec{H}_0 \parallel$ or $\perp$ to c axis of Al_2O_3	$\Delta g = g - g_e$	$\langle 1/r^3\rangle_{\text{a.u.}}$[a]	Observed $H^{\text{hf}}_{\text{total}}$	$H^{\text{hf}}_{\text{orb}}$	$H^{\text{hf}}_{\text{dip}}$	Left for $H^{\text{hf}}_{\text{core pol.}}$
Ni^{2+}[b]	MgO		0.2122	7.09	(-) 63 ±3	+188	≈0	-251
Ni^{2+}	Al_2O_3	$\parallel$	0.1925	7.09	- 96.8	+171	-12	-256
Ni^{2+}	Al_2O_3	$\perp$	0.1830	7.09	- 85.7	+162	+ 6	-254
Co^{+}[b]	MgO		0.1705	5.35	(-)160 ±1	+114	≈0	-274
Cu^{3+}[c]	Al_2O_3	$\parallel$	0.0765	9.02	-171.0	+ 86	- 8	-249
Cu^{3+}[c]	Al_2O_3	$\perp$	0.0749	9.02	-159.6	+ 84	+ 4	-248

[a]These are the free-ion values, computed by A. J. Freeman and R. E. Watson (to be published).

[b]See reference 2 and J. W. Orton et al., Proc. Phys. Soc. (London) 78, 554 (1961). In $H^{\text{hf}}_{\text{total}}$ the (-) sign indicates that the sign has not been measured, but we assume it to be negative.

[c]W. E. Blumberg, J. Eisinger, and S. Geschwind, Phys. Rev. 130, 900 (1963).

the change in nuclear Zeeman energy corresponding to the change in the external magnetic field, i.e., $\partial\nu_{\text{ENDOR}}/\partial H_0 = \pm g_I(\text{eff})\beta_N/h = \pm 0.39$ kc/G-sec. This expected variation is shown by the dashed lines in Fig. 2. Instead, one observes slopes $\pm g_I(\text{eff})\beta_N/h + \partial|A|/\partial H_0$, implying a change in hf field from point A to C in the ESR line given by $\partial|A|/\partial H_0 = -0.26$ kc/G-sec. This implies a decrease in the absolute value of the hf field of approximately 130 gauss from point A to C, a distance in H_0 of 200 gauss. The broadening of the ESR line is due to random axial crystal fields seen by individual Ni^{2+} ions, so that spin packet A corresponds to a smaller $|D|$ value than spin

packet C as shown in Fig. 1. But this variation in D carries with it slightly different g values for packet A as compared to C, and therefore different orbital hf fields, given by the following correspondence:

$$D \approx (\lambda/2)(g_{\parallel} - g_{\perp}) \rightarrow \delta D \approx (\lambda/2)(\delta g_{\parallel} - \delta g_{\perp}),$$

which, with $\delta g_{\perp} \approx -\frac{1}{2}\delta g_{\parallel}$, gives $\delta g_{\parallel} \approx (4/3\lambda)\delta D$, and from Eq. (2)

$$\delta H_{\text{orb}}^{\text{hf}} = 1.25\times 10^{5}(4/3\lambda)\delta D\langle 1/r^{3}\rangle_{\text{a.u.}} \text{ gauss}.$$

From A to C in Fig. 1 one has $\delta D = -\delta|D| = -200$ gauss, which together with the value of $\lambda \approx -280$ cm^{-1} leads to $\delta g_{\parallel} \approx +1.0\times 10^{-4}$ and $\delta H_{\text{orb}}^{\text{hf}} \approx +90$ gauss or $\delta H_{\text{total}}^{\text{hf}} = -90$ gauss, as compared to the observed value of -130 gauss. The agreement is quite satisfactory as other small effects may be present such as small variations in core polarization. Note that in going from A to C the increase of 130 gauss in the orbital hf field is out of a total orbital field of 170 000 gauss. One can anticipate the appearance of this phenomenon in other inhomogeneously broadened lines and correspondingly the probing of small changes in hf field with applied external electric field or axial pressure.

We wish to thank J. P. Remeika for preparing the crystals, G. E. Devlin for his experimental assistance and suggestions, and M. Blume, V. Jaccarino, L. R. Walker, R. E. Watson, and Y. Yafet for helpful discussions.

*On leave from the Kamerlingh Onnes Laboratory, Leiden, The Netherlands.

†Summer guest at Brookhaven National Laboratory, Upton, New York.

[1]R. L. Streever, Jr., Phys. Rev. Letters 10, 232 (1963).

[2]J. W. Orton, P. Auzins, and J. E. Wertz, Phys. Rev. 119, 1691 (1960).

[3]G. Feher, Phys. Rev. 103, 834 (1956).

[4]H. H. Woodbury and G. W. Ludwig, Phys. Rev. Letters 1, 16 (1958).

[5]L. H. Bennett and R. L. Streever, Jr., Phys. Rev. 126, 2141 (1962).

[6]For references to the subject of core polarization see reference 13 of R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961).

[7]T. T. P. Hall and W. Hayes, J. Chem. Phys. 32, 1871 (1960), also discuss a case where orbital hf field is important in an orbital singlet ground state; they treat Co^{2+} in tetrahedral coordination.

[8]A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) A205, 135 (1951).

[9]M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. 26, 34 (1958).

BOUND STATES IN THE HEISENBERG FERROMAGNET*†

Jean Hanus‡
Physics Department, Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received 17 July 1963)

This note reports the existence and some consequences of bound states in a Heisenberg ferromagnet.[1] In this work[2] the interactions of spin waves has been studied, following a method developed by Van Kranendonk.[3] A complete solution to the problem of two reverse spins in a crystal lattice of otherwise parallel atomic spins ($S = \frac{1}{2}$) has been found. A hard-core interaction has been introduced in the Hamiltonian to prevent these reversed spins from being localized on the same atomic site. As in the linear chain, it is found that for some eigenstates of this system, the two reversed spins are bound together in a stable complex, which travels through the crystal.

The Heisenberg Hamiltonian is

$$H = -2J\sum_{i<j}\vec{\mathbf{S}}_i\cdot\vec{\mathbf{S}}_j + \mu\sum S_i^{z} + \tfrac{1}{4}NcJ,$$

where the sum over i and j runs over all pairs of nearest neighbors in a simple cubic lattice, the spin vector $\vec{\mathbf{S}}_i$ being localized at the site $\vec{\mathbf{R}}_i$; $\mu = g\mu_B B$, where g is the g factor of the magnetic moment, μ_B the Bohr magneton, and B the externally applied magnetic field.

The space spanned by H can be divided into N orthogonal subspaces in which the total z component of the spin angular momentum is a constant. Each subspace is labeled by n, the number of reversed spins in the system.

The $n = 0$ subspace is the single ferromagnetic ground state; $n = 1$ has eigenfunctions which are the spin waves[4]; the $n = 2$ subspace was solved exactly and the results are described in this note. We consider spin deviation states $|i,j\rangle$ with two flipped spins at $\vec{\mathbf{R}}_i$ and $\vec{\mathbf{R}}_j$ and express the eigen-