

Nuclear-Magnetic-Resonance Studies of Fe⁵⁷ in Barium Ferrite

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The nuclear magnetic resonance of Fe⁵⁷ has been studied in single-crystal and polycrystalline samples of barium ferrite (BaFe₁₂O₁₉). The resonance spectrum has been obtained by plotting the amplitude of the Fe⁵⁷ spin-echo signals as a function of frequency. The zero-field spectrum has been studied at both 4.2 and 77°K. The spectrum at 4.2°K has also been studied with externally applied static fields of up to 8.8 kG, using oriented single-domain powders. Five hyperfine fields are resolved, corresponding to the five magnetically and crystallographically inequivalent lattice sites of BaFe₁₂O₁₉. Studies of the temperature dependence of the hyperfine fields are made up to 180°K, and the hyperfine fields are compared with those obtained from Mössbauer studies. Values of the hyperfine fields associated with the various crystallographic lattice sites are discussed.

I. INTRODUCTION

MANY studies have been made in recent years of the hyperfine fields in spinel ferrites and iron garnets using both the Mössbauer and nuclear-magnetic-resonance (NMR) techniques. Relatively few studies, however, have been made of the hexagonal ferrites. The author has recently begun a study of the hyperfine fields in hexagonal ferrites using the NMR technique, and in this paper the results of a study of the Fe⁵⁷ NMR in barium ferrite (BaFe₁₂O₁₉) are discussed. Preliminary results have been reported previously.¹

Barium ferrite is of particular interest because it has Fe³⁺ ions located on five magnetically and crystallographically inequivalent lattice sites.² A number of Mössbauer studies³⁻⁷ of this material have been made; however, not all lines corresponding to the various sites have been resolved and some points remain unclear. The author has obtained the nuclear resonance spectrum by plotting the amplitude of the Fe⁵⁷ spin-echo signals as a function of frequency across the inhomogeneously broadened resonance lines. The NMR spectrum is basically simpler than the Mössbauer spectrum and the resolution obtained with the NMR is considerably better. Hyperfine fields corresponding to two of the lattice sites are found to have nearly the same magnitude but are oppositely oriented with respect to the net magnetization. By application of an external static (dc) magnetic field, the author has been able to resolve hyperfine fields associated with all five crystallographically inequivalent Fe³⁺ ions in this material.

In Sec. II the experimental techniques are discussed briefly. In Sec. III the experimental results are pre-

sented. In Sec. IV the experimental results are interpreted and compared with the Mössbauer results. In Sec. V a discussion of the hyperfine fields in BaFe₁₂O₁₉ is given and comparisons with the hyperfine fields of spinel ferrites are made.

II. EXPERIMENTAL METHODS

A. Samples

Zero-field studies at 4.2°K were made using powdered single crystals of BaFe₁₂O₁₉ which were encapsulated in glass tubes. Preliminary studies in externally applied dc magnetic fields were made using the single-crystal powders and single-domain powders obtained from the Stackpole Carbon Co. Because of the strong anisotropy the single-domain or single-crystal powders readily aligned themselves in externally applied fields of a few kG (with their *c* axis along the field direction). However, in order to overcome any problem of different degree of alignment between runs, an oriented single-domain sample was prepared by mixing the powder in an Epoxy and allowing it to set several hours in a field of 10 kG. The oriented single-domain sample was in the form of a cylinder about 3 in. long and ½ in. in diam. The single-domain particles were oriented so that the easy magnetization direction was perpendicular to the axis of the cylinder.

Because of the limited availability of the single crystals some single-domain powder was also resintered to the size where domain walls were present. These samples were used in studies at higher temperatures where the strongly enhanced signals from nuclei in domain walls were needed to obtain the required signal strength.

B. Nuclear-Resonance Equipment

The nuclear-resonance spectrometer consisted of a pulsed rf oscillator and a superheterodyne receiver of conventional design. The sample coil was tuned by means of a parallel capacitance. Coupling loops at either end of the coil in series with small capacitors provided approximate impedance matches to 50-Ω transmission lines which connected to the receiver and oscillator.

¹ R. L. Streever, *Phys. Letters* **27A**, 563 (1968).

² J. Smit and H. Wijn, *Ferrites* (John Wiley & Sons, Inc., New York, 1959).

³ W. Zinn *et al.*, *Z. Angew. Phys.* **17**, 147 (1964).

⁴ J. J. Van Loef and P. J. M. Franssen, *Phys. Letters* **7**, 225 (1963).

⁵ J. J. Van Loef and A. Broese Van Groenou, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), pp. 646-649.

⁶ J. S. Van Wieringen and J. G. Rensen, *Z. Angew. Phys.* **21**, 69 (1966).

⁷ J. S. Van Wieringen, *Phillips Tech. Rev.* **28**, 33 (1967).

The low-temperature studies were made with nitrogen and exposed-tip helium Dewars which fitted in to the sample coil. For studies above 77°K a gas-flow cryostat was used.

C. Measuring Techniques

The nuclear-resonance line shapes were obtained by plotting the spin-echo amplitudes as a function of frequency over the frequency range between about 55 and 80 MHz. The amplitude of the echo signal was sampled approximately every 0.25 MHz. Two rf pulses of equal width were used to excite the echo signal. For the single-crystal studies at 4.2°K in zero-field pulse widths of 20 μ sec were needed to obtain the necessary resolution. The applied rf fields and nuclear signals were strongly enhanced by domain-wall motion in the single crystals at this temperature, and it was necessary to attenuate the rf pulses by as much as 40 dB in order to minimize saturation effects (at the pulse width of 20 μ sec). At higher temperatures and in externally applied dc fields (where the domain walls were absent), smaller rf enhancements and weaker signal strengths required the use of narrower rf pulses and higher rf power levels. Pulse separations of about 30 μ sec were used.

At each frequency, the oscillator, rf coil, and receiver were tuned to a maximum echo signal and the signal was calibrated by means of an auxiliary signal generator. More details of the measuring techniques and calibration procedures have been given previously.^{8,9}

In the external field studies, the geometry was such that the cylindrical axis of the oriented single-domain sample was coaxial with that of the sample coil and perpendicular to the applied field direction. The sample was then allowed to rotate so that its easy magnetization direction was along the direction of the external magnetic field.

III. EXPERIMENTAL RESULTS

A. Zero-Field Studies

The experimental Fe⁵⁷ line shapes at 4.2°K for the single-crystal powders are shown in Fig. 1(a). Similar results were obtained with the resintered single-domain powder. The line shape at 77°K obtained with the resintered powder is shown in Fig. 1(b). No correction has been made in Fig. 1 for the frequency dependence of the resonance signal. One should divide the integrated intensities of the various lines by a factor ν^2 , where ν is the frequency of the line, to take into account the fact that the nuclear signal induced in the sample coil is proportional to the frequency and to account for the increased nuclear polarization at higher frequencies.

Above 77°K the signal-to-noise ratio was too poor to obtain a detailed point-by-point plot of the resonance spectrum but frequencies of the peaks of lines I, II, and

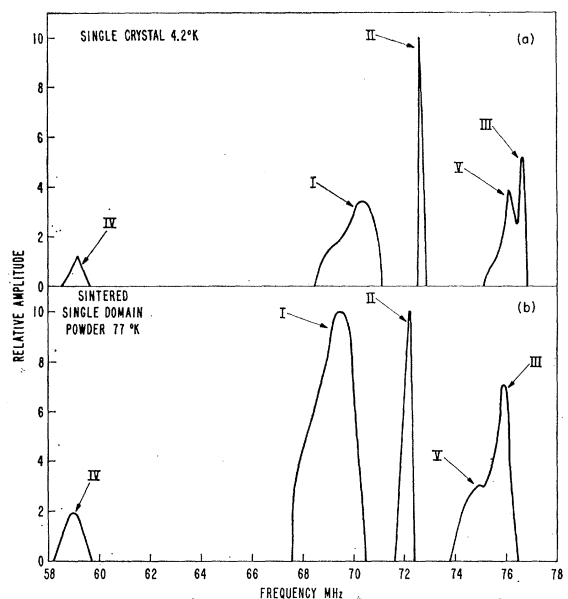


FIG. 1. (a) Zero-field Fe⁵⁷ line shapes at 4.2°K for the single-crystal powders. (b) Zero-field line shapes for the resintered single-domain powder at 77°K.

III (see Fig. 1) were measured as a function of temperature up to about 180°K and are plotted in Fig. 2.

B. Results in External dc Fields

The Fe⁵⁷ line shapes for the oriented single-domain sample in fields of 2.3, 5.5, and 8.8 kG are shown in Fig. 3. Line IV is not shown; but in a separate measurement, it was observed to shift down in frequency with increasing external field. The frequency of the peaks of

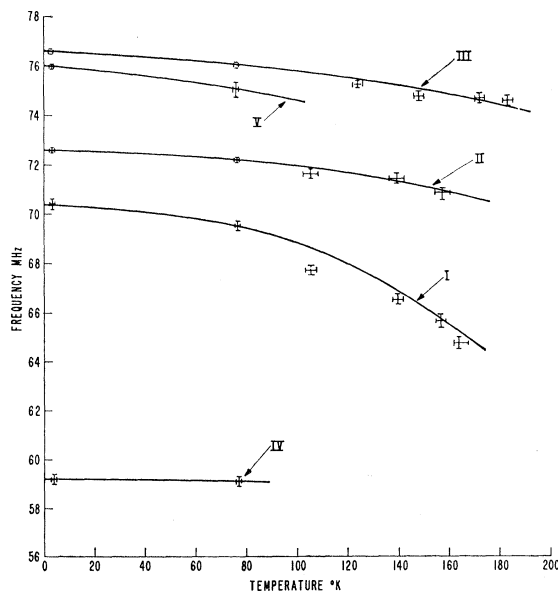


FIG. 2. Frequencies of the peaks of the various resonance lines shown in Fig. 1 as a function of temperature.

⁸ R. L. Streever and G. A. Uriano, Phys. Rev. **139**, A305 (1965).

⁹ R. L. Streever and G. A. Uriano, Phys. Rev. **139**, A135 (1965).

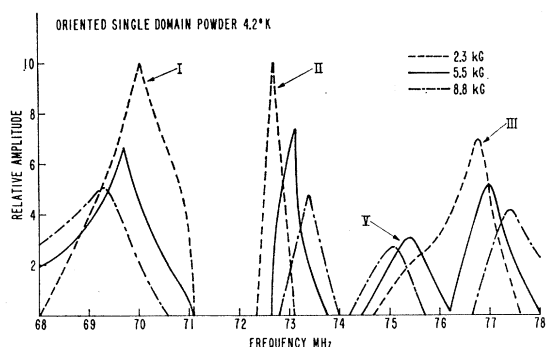


FIG. 3. The Fe^{57} line shapes at 4.2°K for the oriented single-domain sample in fields of 2.3, 5.5, and 8.8 kG for lines I, II, III, and V.

the various lines were also measured as a function of magnetic field and a typical plot is shown in Fig. 4 for line II.

C. Relaxation Times

T_2 was observed to be approximately the same for the various lines and was about 1.0 msec at 4.2°K and 0.3 msec at 77°K .

IV. INTERPRETATION OF RESULTS

A. Assignment of Lines to Sites

Barium ferrite has a crystal structure which can be built up from spinel blocks of two oxygen layers which are connected by a block R containing the barium ion.² In all five crystallographically inequivalent sites exist for the Fe^{+3} ions: three different octahedral sites, a tetrahedral site, and a site which is surrounded by five

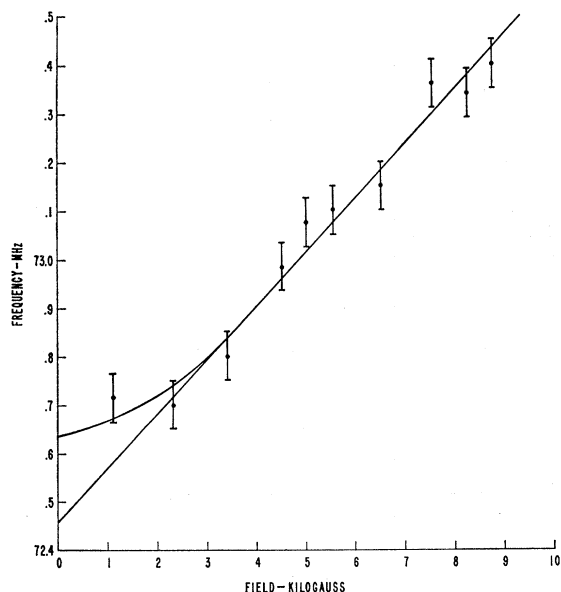


FIG. 4. The frequency of the peak of line II plotted as a function of external magnetic field at 4.2°K .

TABLE I. The type of site, number of ions per formula unit, moment direction, and magnitudes of dipolar fields (from Ref. 5) are given for the various sublattices of $\text{BaFe}_{12}\text{O}_{19}$. The assignments of the lines to the various sites and the hyperfine fields at 4.2°K are also given.

Sub-lattice	Site	No.	Direction	Magnitude of dipolar field ($H_{11}-H_{\perp}$) (kG)	Line	Magnitude of hyperfine field (4.2°K) (kG)
<i>a</i>	Octahedral	6	Up	-9	I	510
<i>b</i>	Octahedral	1	Up	+14	V	551
<i>c</i>	Tetrahedral	2	Down	-2	II	526
<i>d</i>	Octahedral	2	Down	+10	III	555
<i>e</i>	Trigonal-bipyramid	1	Up	+9	IV	429

oxygen ions which form a trigonal bipyramid. Iron ions on various sites which give rise to five magnetic sublattices are listed in Table I. The magnetic moment directions and the number of ions per formula unit are also given. Sites b and c , which are wholly within the spinel block of the structure, correspond to the B and A sites of spinels, respectively, and have the same number and type of metal-ion nearest neighbors as the corresponding sites in the spinel structure. Ions on sites a lie at the interface of the spinel block and R block, while ions on sites d and e are wholly within the R block. The quantities $H_{11}-H_{\perp}$, where H_{11} and H_{\perp} are the calculated^{5,10} magnitudes of the dipolar fields at the sites for the cases of the magnetization parallel and perpendicular to the c axis, are also given in Table I.

The major contribution to the hyperfine fields at the nuclei in these materials results from the polarization of the inner-core s electrons by the $3d$ moments of the parent ion.¹¹ Since this field is negative with respect to the moment of the parent ion, hyperfine fields associated with sites a , b , and e should decrease in absolute magnitude while hyperfine fields for sites c and d should increase.

On the basis of the relative intensities of the various lines and the direction in which they shift in external fields (see Fig. 3), we can assign line I to sublattice a , lines II and III to sublattices c and d , and lines IV and V to sublattices e and b .

The zero-field nuclear-resonance signals must be from nuclei in domain walls because of the strong rf enhancements. Consequently, we expect a broadening of the resonance lines by an amount which is qualitatively equal to the dipolar factors $H_{11}-H_{\perp}$ given in Table I. Because of the narrow width of line II, we must assign it to sublattice c while line III must be from sublattice d .

Because of the large axial quadrupole splitting of line IV observed in the Mössbauer experiments, line IV must be from site e while line V must be from site b .

¹⁰ H. B. G. Casimir *et al.*, *J. Phys. Radium* **20**, 360 (1959).

¹¹ R. E. Watson and A. J. Freeman, *Phys. Rev.* **123**, 2027 (1961).

These assignments together with the hyperfine fields at 4.2°K are given in Table I.

B. External-Field Studies and Effects of Dipolar Fields

The behavior of the nuclear-resonance signal in externally applied fields has been discussed in detail previously.¹² In a completely magnetized sample, with the external field along the easy direction of magnetization, the resonance frequency should be given by the following expression:

$$\nu = (\gamma/2\pi) |H_n(\parallel) + H_0 - H_d|. \quad (1)$$

Here $H_n(\parallel)$ is the hyperfine field for the magnetization parallel to the easy direction of magnetization, H_0 is the externally applied magnetic field, and H_d is the demagnetizing field.

The linear portions of the curves, such as those shown in Fig. 4, were found to have a slope of about 0.11 MHz/kG, which is somewhat less than the expected value of 0.138 MHz/kG for Fe⁵⁷. This may be due to an incomplete orientation of the single-domain sample. Extrapolating the linear portion of the curve for line II (Fig. 4) back to $H_0=0$ and correcting for the quantity H_d , we can obtain $H_n(\parallel)$. We have done this by assuming H_d is simply given by $\frac{4}{3}\pi M$, the demagnetizing field for a single spherical particle. For BaFe₁₂O₁₉ $\frac{4}{3}\pi M$ is about 2.2 kG corresponding to about 0.31 MHz. Adding this to the intercept of the linear portion of Fig. 4 gives a value for $H_n(\parallel)$ of 72.77 MHz, which is close to the zero-field value of about 72.6 MHz. Carrying out similar procedures for the other lines gave values of $H_n(\parallel)$ which were close to the peaks of the various zero-field lines. This indicates that the peaks of the zero-field resonance curves must be from nuclei near the ends of the domain walls which should have hyperfine fields close to the value $H_n(\parallel)$. The widths of the various lines are in qualitative agreement with the dipolar factors $H_{11}-H_{12}$ given in Table I, the spread in dipolar fields arising from the turning of the spins in going through the domain wall.

C. Comparison with Mössbauer Data and Discussion of Temperature Dependence

Mössbauer studies have been made on BaFe₁₂O₁₉ by Zinn *et al.*³ and by Van Loef and co-workers.^{4,5} More recently, Mössbauer studies have been made on SrFe₁₂O₁₉ and BaFe₁₂O₁₉ by Van Wieringen and Rensen⁶ and discussed in a review article by Van Wieringen.⁷ Van Wieringen^{6,7} resolves four separate hyperfine fields which he labels I, (II+V), III, and IV with strength ratios 6:2+1:2:1 (± 0.2), respectively. (We have followed this labeling, which is used in Ref. 7.) Van Loef and co-workers had previously assigned lines I, II, and III to sites *a*, *c*, and *d*, respectively, on the basis of relative intensities and the effects of an applied field. (Line II was identified with sublattice *c* on the basis of

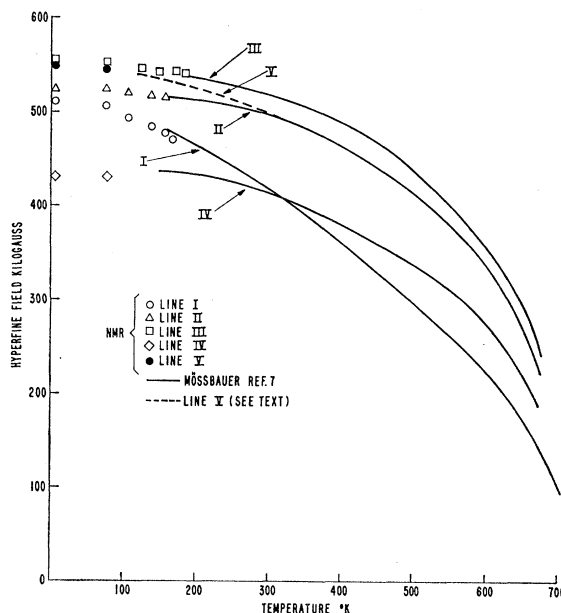


FIG. 5. Temperature dependences of the hyperfine fields obtained from Mössbauer and NMR experiments (Mössbauer data from Ref. 7).

its being least sensitive to the external field direction.) Van Wieringen assigns line IV to sublattice *e* on the basis of the large axial quadrupole splitting. Van Wieringen, therefore, assigns lines I, (II+V), III, and IV to sites *a*, *c+b*, *d*, and *e*, respectively.

In Fig. 5, we compare the temperature dependences of the hyperfine fields obtained from the Mössbauer and NMR results, where the Mössbauer data are taken from Ref. 7. We have cut the Mössbauer data off at about 150°C in Fig. 5, since the curves below this point appear to be extrapolations (see Ref. 6). We see that only for sublattice *b* (line V) does there appear to be an appreciable discrepancy between the NMR and Mössbauer results. According to the Mössbauer data, sites *c* and *b* have approximately the same hyperfine field (at least at the higher temperatures where the Mössbauer experiments were done), while our data at 4.2°K shows site *b* to have nearly the same hyperfine field as site *d*. Note, however, that the hyperfine-field-versus-temperature curve for line V appears from the data at 77°K to be decreasing more rapidly with temperature than that for line III. In Fig. 5, we have dashed in the curve for line V so that it joins with the Mössbauer curve for line II at about room temperature. This would largely eliminate the discrepancy between the Mössbauer and NMR data for this line and, as will be discussed in the following section, gives a reasonable reduced magnetization curve for sublattice *b*.

D. Exchange Interactions

By assuming the hyperfine fields to be proportional to the sublattice magnetizations one can obtain the

¹² R. L. Streever, Phys. Rev. Letters **10**, 232 (1963).

TABLE II. The interactions between sublattices of BaFe₁₂O₁₉ in units of J_{ac} .

Sub-lattice	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
<i>a</i>	0	0	3	$2W_{ad}$	$-W_{ae}$
<i>b</i>	0	0	$6W_{bc}$	0	0
<i>c</i>	9	$3W_{bc}$	0	0	0
<i>d</i>	$6W_{ad}$	0	0	$-W_{dd}$	$3W_{de}$
<i>e</i>	$-6W_{ae}$	0	0	$6W_{de}$	0

reduced sublattice magnetizations from the curves of Fig. 5 as a function of reduced temperatures as has been done by Van Loef and Van Groenou.⁵ The curves for sublattices *c*, *d*, and *e* all have nearly the same decrease at low temperatures. The curve for sublattice *a* decrease more rapidly at low temperatures than those for sublattices *c*, *d*, and *e*. The dashed curve for sublattice *b* decreases more rapidly than that for sublattices *c*, *d*, and *e* at low temperature but less rapidly than that for sublattice *a*.

Van Loef and Van Groenou have used a Weiss field model and have estimated exchange interactions which give agreement between the calculated and experimental sublattice magnetizations. The important exchange interactions which exist between sublattices are shown in Table II, which is taken from Ref. 5. The entries in the table are the quantities $Z_{ij}W_{ij}$, where Z_{ij} is the number of neighbors of spin *i* on sublattice *j* and W_{ij} is the exchange constant between spins on sublattices *i* and *j* relative to the exchange constant J_{ac} ($J_{ij}=W_{ij}J_{ac}$). Van Loef and Van Groenou take $W_{bc}=1$, $W_{ad}=1$, $W_{ae}=W_{da}=0$, and $W_{de}=1.5$.

Their calculated magnetization curves using these values (see Fig. 1 of Ref. 5) are in approximate agreement with the experimental reduced magnetizations from Fig. 5 with the exception of curve V, for which the calculated curve decreases more rapidly than the experimental (dashed) curve at low temperatures. Note, however, that the magnetization of sublattice *b* depends only on the value of W_{bc} and the magnetization of sublattice *c*. By taking $W_{bc}=1.2$ rather than 1.0 and using the experimental reduced sublattice magnetization for sublattice *c*, we have obtained a calculated magnetization curve for sublattice *b* which is in approximate agreement with experiment. Also, using this value of W_{bc} does not effect any of the other calculated magnetization curves except that of sublattice *c*, and then only to a small extent. This is, moreover, a reasonable value of W_{bc} in that it makes J_{bc} closer to the corresponding octahedral-tetrahedral interaction in spinels where $J_{AB}=1.5J_{ac}$.⁵

The lower value of J_{ac} relative to J_{bc} may be a result of a distortion of the oxygen environment around the *a*-site ion.¹³ The distortion is such as to make the *a*-site oxygen distances (to those oxygen's which connect with *c* sites) longer by about 5% than the corresponding *b*-

site oxygen distances. This would have the effect of reducing J_{ac} relative to J_{bc} .

V. HYPERFINE FIELDS

A. Hyperfine Fields in Ferrites

Hyperfine fields in ferromagnetic materials have been discussed in Ref. 11 and in review articles by Watson and Freeman.^{14,15} Hyperfine fields in ferrites have been discussed by Van Loef.¹⁶ Although the hyperfine fields at the nuclei of $3d^5$ ions arise primarily from the core polarization induced by the spin of the parent ion, one must consider, in addition, the effects of the covalent bonding of the metal ion with the neighboring oxygen ions and the effects of the supertransferred hyperfine fields induced by neighboring metal ions through the oxygen ions. Experimentally the effect of increasing covalency is to reduce the absolute magnitude of the hyperfine field at the nucleus of a $3d^5$ ion. This appears to be due to the covalent mixing of ligand electrons into the $4s$ orbitals of the metal ion.¹⁷ Also, the decrease in the $3d$ spin density arising from the covalency¹⁵ and the effect of a change in *g* value from its "spin-only" value must be considered as well.¹⁴ The supertransferred hyperfine fields have been discussed by Huang *et al.*¹⁸ In the case of 180° superexchange interactions between cations the effect of the supertransferred fields are to increase the absolute magnitude of the hyperfine field at the nucleus of the central metal ion.

B. Hyperfine Fields in Spinel Ferrites

In the spinel structure metal ions on octahedral *B* sites have strong superexchange interactions with six neighboring metal ions on tetrahedral *A* sites while ions on the *A* sites are coupled strongly with 12 neighboring metal ions on the *B* sites. The hyperfine field in Ni ferrite at *B* sites is about 557 kG¹⁹ and has approximately the same value in other inverse spinels.¹⁶ In view of the preceding discussion, this is evidently due to the approximate constancy of the octahedral ion-oxygen ion distance (~ 2.0 Å in spinels) as well as to the fact that in the completely inverse spinels metal ions on *B* sites have only Fe⁺³ neighbors on *A* sites. In spinels like Zn-substituted NiFe₂O₄^{19,20} and CuFe₂O₄,²¹ however, where some of the iron ions on tetrahedral sites are replaced by nonmagnetic ions, one finds a reduction in the *B* site

¹⁴ A. J. Freeman and R. E. Watson, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. II A.

¹⁵ R. E. Watson and A. J. Freeman in *Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

¹⁶ J. J. Van Loef, *Physica* **32**, 2102 (1966).

¹⁷ J. C. M. Henning, *Phys. Letters* **24A**, 40 (1967).

¹⁸ N. L. Huang *et al.*, *Phys. Rev.* **156**, 383 (1967), and references therein.

¹⁹ H. Abe *et al.*, *J. Phys. Soc. Japan* **18**, 1400 (1963).

²⁰ V. I. Gol'danskii *et al.*, *Zh. Eksperim. i Teor. Fiz.* **49**, 1681 (1966) [English transl.: *Soviet Phys.—JETP* **22**, 1149 (1966)].

²¹ B. J. Evans and S. S. Hafner, *J. Phys. Chem. Solids* **29**, 1573 (1968).

¹³ W. D. Townes *et al.*, *Z. Krist.* **125**, 437 (1967).

hyperfine field. In Zn-substituted NiFe_2O_4 at 77°K , a decrease in B -site hyperfine field of 14 kG per A -site neighbor is found¹⁹ on replacing an Fe neighbor by Zn. Although the supertransferred hyperfine field appears to be of the right order of magnitude to account for the effect, one must also take into account the possible reduction in the value of $\langle S_z \rangle$ for metal ions with large numbers of nonmagnetic neighbors.

The hyperfine fields at the tetrahedral sites in the spinel ferrites are found to be about 510 kG and roughly constant. The A -site field in NiFe_2O_4 is 511 kG¹⁹ and in CuFe_2O_4 (which is mainly inverse) about 508 kG.²¹ Since in the inverse spinels half of the B sites are occupied on the average by the divalent metal ion, the relative constancy of the A -site hyperfine field implies, as suggested by Evans and Hafner,²¹ a small supertransferred hyperfine field at the A sites from the neighboring B sites. Evans and Hafner suggest, moreover, that the larger A - to B -site transferred field may be due to the large covalency of the A site.

Although one must take the supertransferred interactions into account, it appears that the lower hyperfine fields at the tetrahedral sites are largely due to the greater covalency of these sites, the tetrahedral metal ion-oxygen distance being about 1.9 Å in the spinel ferrites.

C. Hyperfine Fields in Barium Ferrite

Consider first the hyperfine fields at the b and c sites which will be wholly within the spinel part of the structure. The hyperfine field at the b site is about 550 kG, in agreement with that found at the octahedral site of spinels and in agreement with what one would expect from the preceding discussion. The hyperfine field at the c site of $\text{BaFe}_{12}\text{O}_{19}$ is 526 kG compared to tetrahedral site fields of 511 kG in NiFe_2O_4 and 508 kG in CuFe_2O_4 (at 4.2°K). By comparing the hyperfine field at the tetrahedral site of $\text{BaFe}_{12}\text{O}_{19}$, where the 12 neighboring metal ions are Fe^{3+} , with that in CuFe_2O_4 , where approximately half of the neighboring metal ions are Cu, we can obtain a value of about 3 kG/iron neighbor for the transferred hyperfine field at the tetrahedral site. This supports the suggestion by Evans *et al.* that the supertransferred hyperfine field at A sites due to neighboring B sites is indeed small.

The hyperfine field for octahedral ions on site a is seen to be reduced relative to that for ions on octahedral sites b and d . As already mentioned, the octahedron of oxygen ions about the a site is distorted,¹³ so that two of the oxygen ions are at a distance of only 1.93 Å (compared to an average distance of about 1.99 Å for the b site and 2.02 Å for the d site). The average oxygen distance for the a site is about 2.02 Å, however, so that it seems doubtful that the covalency could be entirely responsible for the low hyperfine field of this site.

The low value of the hyperfine field at the a site may rather be a result of the low molecular field and corre-

spondingly low value of supertransferred hyperfine field at this site. From the preceding discussion, the transferred hyperfine fields at octahedral sites from neighboring tetrahedral sites should be the most important. We see from Table II that site a has only three tetrahedral bonds compared to six for site b . Using a value of 14 kG per superexchange linkage from the Zn substituted NiFe_2O_4 results would give a 42 kG lower hyperfine field at the a site, about the right magnitude to explain the difference. The hyperfine field at site d , which has strong superexchange interactions with iron ions on site e , would be expected to be large, however.

The Fe ion on site e has nominally trigonal bipyramidal symmetry. There is evidence from recent crystal-structure data¹³ that the Fe ion may not be at the center of the trigonal bipyramid formed by the five oxygen neighbors but may be either oscillating along the c axis or statistically distributed on two sites displaced 0.156 Å from the central position. If the Fe ion is assumed to lie at the central position, however, the coordination is that of a trigonal bipyramid with an equatorial Fe-O distance of 1.893 Å and an apical Fe-O distance of 2.316 Å. The close proximity of the planar oxygen ions suggests that the site may be strongly covalent. The observed hyperfine field for site e of 429 kG is considerably lower than that for the tetrahedral site of YIG (478 kG), where the oxygen distance is 1.88 Å and where the low value of hyperfine field is believed due to the covalency.

VI. CONCLUSION

Studies of the hyperfine fields in $\text{BaFe}_{12}\text{O}_{19}$ provide one with a way of obtaining rather detailed information about the magnetic sublattices and their interaction. Because of the good resolution obtained with the NMR, it is particularly useful when studying a system with many different hyperfine fields.

By using iron enriched in the Fe^{57} isotope, one should be able to extend the temperature dependence of the hyperfine fields to higher temperatures and examine more closely the temperature dependence of sublattice b . Also, studies with external fields using large single crystals of $\text{BaFe}_{12}\text{O}_{19}$ would be useful in order to obtain more detailed information about the anisotropy in the material.

NMR studies in spinel ferrites and other hexagonal ferrites would be useful in order to sort out the various contributions to the hyperfine fields of these materials. Studies on hexagonal ferrites with other crystal structures are in progress.

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