Ge, but to be a definite and apparently monotonically increasing function of q in both directions for diamond.

In interpreting this result, we must remember that the original data are subject to considerable experimental uncertainty—about 12% for Ge and 9% for diamond are the maximum probable deviations estimated by the experimenters[8–10] themselves. The slight scatter about zero of the points for Ge in Fig. 1 is, therefore, physically not significant—we may conclude that trace-variable forces are absent in Ge within the limits of present-day experimental precision. By contrast, the deviation from zero of the points for diamond exceeds the experimental uncertainty by a considerable margin, and indicates that trace-variable forces are active in that crystal; their contribution to the trace seems roughly describable by a function $1-\cos\pi q$ in the [111] direction and by $2(1-\cos\pi q)$ in the [100] direction. The curve which has been drawn into Fig. 1 is the function const. $\times\ \psi_{\text{fcc}}^{(1)}$, which the points should follow if the only trace-variable force in the crystal were a central interaction between second neighbors; the fact to notice is that along [111] they do not do this, showing that central second-neighbor interaction cannot explain our results. The reader may verify, by plotting $\psi_{\text{fcc}}^{(2)}$, that fourth-neighbor central interaction would not work either. It seems likely, therefore, that a trace-variable force in diamond is a long-range, nonelectrostatic one, or a short-range one with a noncentral component.

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[10] In addition, we should quote Hardy and Smith's (reference 9) description of their own results as "somewhat tentative"—a necessary consequence of the rather involved analysis required to translate infrared absorption into phonon energies. Analysis of neutron scattering is comparatively straightforward.

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Temperature Dependence of Nuclear Magnetic Resonance of Fe^{57} in Magnetite

E. L. Boyd
Thomas J. Watson Research Center, International Business Machines Corporation,
Yorktown Heights, New York

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A report is made of an attempt to fit the temperature dependence of the observed nuclear magnetic resonance (NMR) frequencies for the two sublattices in magnetite to the measured temperature dependence of the magnetization. It is shown that when the microwave g_{eff} values as reported in the literature are used in this calculation, no fit between the NMR experiment and the moment measurement is obtained. If a $g_{\text{eff}}=2$ is assumed, however, the data may be brought into good agreement.

THE temperature dependence of the nuclear magnetic resonance (NMR) frequency for Fe^{3+} ions has been shown to be a good measure of the sublattice magnetization in many ferrimagnetic oxides (e.g., YIG[1–4] GdIG,[2–4] and $Li_{0.5}Fe_{2.5}O_4$ [5]). In this paper a report is made of the temperature variation of the sublattice magnetization in Fe_3O_4 where both Fe^{3+} and Fe^{2+} ions are present. Magnetite in the cubic phase, above 118°K, is an inverse spinel with all tetrahedral sites occupied by Fe^{3+} ions, and with Fe^{2+} and Fe^{3+} ions occurring in equal numbers in octahedral sites. Verwey[6] has proposed that there is a rapid interchange of electrons among the iron ions in octahedral symmetry to explain the high conductivity of cubic magnetite. The NMR data are analyzed in terms of this model and in terms of the published values for the electronic g factor as measured by microwave means. It is shown that the Verwey model holds for this analysis but that the microwave g factor does not indicate an unquenched orbital moment.

Some features of the nuclear resonance of Fe^{57} in magnetite have been published elsewhere and need only be briefly described.[7] The signals come from the bulk of the material rather than domain walls as in the case of the magnetic metals. The resonance from the Fe^{3+} ions in tetrahedral symmetry is a sharp single line. That from octahedral ions is a very broad distribution of resonances, the distribution being due prinicpally to a dipolar magnetic field acting on these ions due to the rest of the magnetic lattice. The shape of the resonance distribution from octahedral sites unambiguously shows that it is from octahedrally located ions and that these ions are in the bulk of the material. Figure 1 shows the observed frequencies of the tetrahedral resonance, the distribution of the octahedral resonance and the magnetic moment (as measured by a force balance) versus temperature. The NMR data were taken

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[3] S. Ogawa and S. Morimoto, J. Phys. Soc. Japan 17, 4 (1962).

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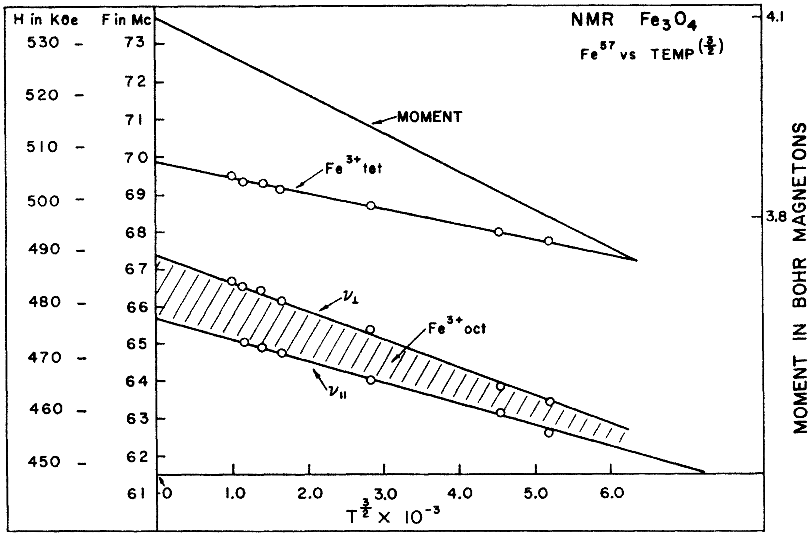

FIG. 1. Measured moment, resonance frequency from tetrahedral sites, and distribution of resonance frequencies from octahedral sites versus $T^{3/2}$ for Fe_3O_4.

from samples made from crushed single crystals and were from samples in which the Fe^{57} was in the natural abundance (2.5%) and enriched abundance (90%). The moment data were taken by Lilienthal[8] on a single-crystal specimen. All curves are reasonable fits to a $T^{3/2}$ law and continue through the phase transition, 118°K, in an unbroken manner. Nuclear resonance signals persist into the orthorhombic phase of magnetite to temperatures of about 90°K. The cell is distorted sufficiently at this temperature that even tetrahedral sites no longer are in cubic fields; and in addition, the electron jump time is probably near the NMR frequency, broadening of the lines should be expected at this point. Ogawa and Morimoto[3] report a single resonance in Fe_3O_4 at 77°K which is somewhat higher than the frequency obtained from the extrapolated curve of tetrahedral ions in Fig. 1. This could be due to the lattice distortion. No resonance has been obtained here at either nitrogen or at helium temperatures.

Solomon, Bauminger *et al.*, Ruby, Wertheim, and Ono *et al.*[9] have studied the hyperfine interaction in Fe_3O_4 by means of the Mössbauer effect and find, at room temperature, two interactions which correspond to the two sets of NMR frequencies. The octahedral sites produce twice as much absorption as the tetrahedral sites in the Mössbauer experiment, so we may be sure that all ions are contributing to the observed results.

For a free ion the hyperfine interaction may be written as the sum of two interactions, the Fermi contact interaction which in this case results in a field due to a net unbalance in spin density of *s* electrons which are polarized by *d* electrons, and what amounts to a dipolar field from electrons with unquenched orbital moments.[10] Thus we have

$$\mathcal{H}_{\mathrm{hf}} = \mathcal{H}_{\mathrm{Fermi}} + \mathcal{H}_L. \tag{1}$$

Usually this is written in terms of one "constant" A and the spin vectors for the nucleus and the electronic state of the ion;

$$\mathcal{H}_{\mathrm{hf}} = A\mathbf{I}\cdot\mathbf{S}. \tag{2}$$

In terms of frequency and for a magnetic sublattice, i, this becomes

$$h\nu_i = A_i\langle S_i\rangle, \tag{3}$$

where $\langle S_i\rangle$ is the time average of the electronic spin. $\langle S_i\rangle$ may be found from the expression for the lattice magnetization M_i,

$$M_i = N_i g_i \beta\langle S_i\rangle, \tag{4}$$

where N_i is the number of ions in the ith sublattice, and g_i is the electronic g factor of the ith sublattice.

The hyperfine coupling coefficients A_i may be found by extrapolating the NMR frequencies to 0°K and assuming a value for $\langle S_i\rangle$ knowing the ions involved. Since Fe_3O_4 is completely inverse, only Fe^{3+} ions of $\langle S_A\rangle = \frac{5}{2}$ are present on the tetrahedral, or A, lattice; thus A_A is 93.7×10^{-5} cm^{-1}. The octahedral, or B, lattice has the added dipolar field which must be removed by calculating a ν_B from the expression

$$\nu_B = \nu_\parallel + \tfrac{2}{3}(\nu_\perp - \nu_\parallel). \tag{5}$$

This ν_B versus temperature is then extrapolated to 0°K and an average spin of $\langle S_B\rangle = 4.5/2$ is assigned to each B ion; A_B is then 99.6×10^{-5} cm^{-1}. The spin 4.5/2 for $\langle S\rangle$ comes about since we are extrapolating the data from a region of temperature where the Verwey elec-

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[8] H. R. Lilienthal (unpublished).

[9] I. Solomon, Compt. Rend. **251**, 2675 (1960); R. Bauminger, S. G. Cohen, A. Marinov, S. Ofer, and E. Segal, Phys. Rev. **122**, 1447 (1961); S. Ruby (private communication); G. K. Wertheim (private communication); K. Ono, Y. Ishikawa, A. Ito, and E. Hirahara, Proc. Intern. Conf. on Magnetism, Kyoto, 1961.

[10] See, for example. A. J. Freeman and R. E. Watson, Watertown Ordnance Materials Research Office Report MRL-99 (unpublished).

tron exchange mechanism holds. Since this exchange of electrons is much more rapid than the nuclear procession the time average spin of a given ion will be the average spin of an Fe^{3+} at $\frac{5}{2}$ and an Fe^{2+} at 4/2.

Electronic g values for g_B and g_A must be found. Bickford[11] has measured the value g_{eff} by microwave techniques in the temperature region 120–300°K for Fe_3O_4 and Bonstrom[12] has measured g_{eff} for Fe_3O_4 between 4.2 and 77°K. Their values together with a set of values for g_B are plotted in Fig. 2. The values of g_B are discussed later. For the present it must be noted that there is an apparent break in g_{eff} value at the phase transition 118°K; this does not appear in the magnetization curve. Neither does the moment at 4.2°K, as measured, $4.1\mu_B$ compare well with the $4.4\mu_B$ one would calculate from the value $g_{\text{eff}}=2.2$ at this temperature.

Figure 3 is a plot of ν_A/ν_{A0} and ν_B/ν_{B0} versus temperature for Fe_3O_4, the data being taken from Fig. 1. These data were measured to 90°K which is 28° below the phase transition. The curves are very smooth through the transition.

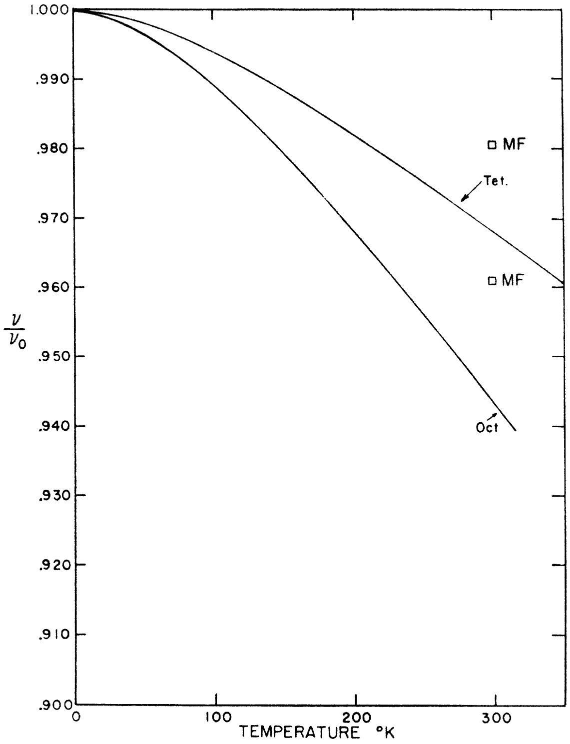

FIG. 3. Normalized frequency ν/ν_0 versus normalized temperature T/T_c for the octahedral and tetrahedral sites in Fe_3O_4. The two points labeled MF are from a molecular field calculation (reference 15).

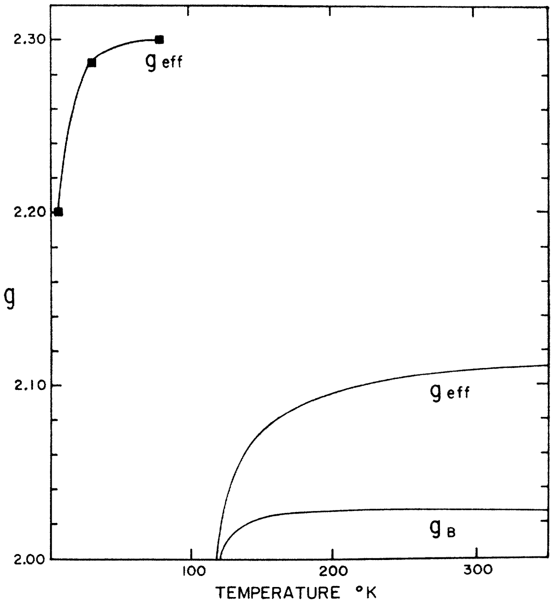

FIG. 2. Microwave g_{eff} values for Fe_3O_4 as reported by Bonstrom *et al.*, for temperatures below 77°K, and Bickford above 120°K versus temperature. Included is a plot of values for g_B calculated using the Wangsness equation.

Wangsness[13] gives a formula

$$g_{\text{eff}}=M\bigg/\left(\frac{M_B}{g_B}-\frac{M_A}{g_A}\right) \tag{6}$$

for the g_{eff} in the case of a two-sublattice magnetic material. If we combine Eqs. (3) and (4) we get

$$M_i=N_ig_i\beta(h\nu_i/A_i). \tag{7}$$

If this is inserted into Eq. (6) then

$$M=\frac{N\beta h}{3}g_{\text{eff}}\left(\frac{2\nu_B}{A_B}-\frac{\nu_A}{A_A}\right). \tag{8}$$

The magnetization may then be calculated from the NMR frequencies and the values of g_{eff}. Since g_{eff} has a strong temperature dependence this leads to a magnetization curve with dips and rises in it. In particular, if we take Bickford's values for g_{eff} and assume a g_{eff} of 2 between 100 and 118°K which his data seems to suggest, then the reduced magnetization versus temperature is as in curve A of Fig. 4. Curve M in this figure is the reduced magnetization $(M-M_0)/M_0$ as measured.

The values of g_B in Fig. 2 were obtained by assuming that g_A is 2.00 and is temperature independent since the A sublattice is made up entirely of Fe^{3+} ions. M_B and M_A are then calculated from assigned values of 9 and 5 at 0°K and the data for the normalized frequencies in Fig. 3. The magnetization is assigned a value of 4 at 0°K and calculated from the reduced moment curve at higher temperatures. The electronic g value of the octahedral sublattice was then calculated and appears in Fig. 2.

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[11] L. R. Bickford, Phys. Rev. **76**, 137 (1949).

[12] D. B. Bonstrom, A. H. Morrish, and L. A. K. Watt, J. Appl. Phys. **32**, 3 (1961).

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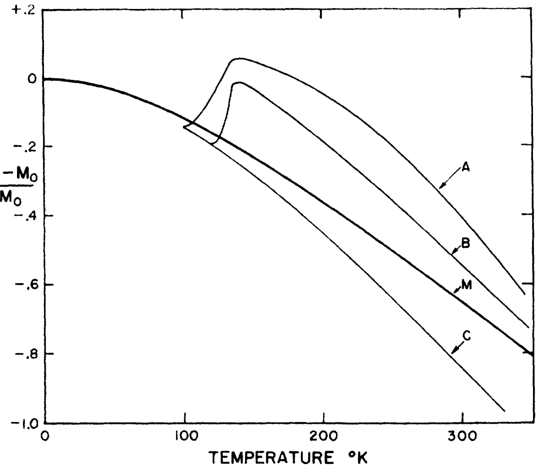

FIG. 4. Curve M is the reduced magnetization $(M-M_0)/M_0$ versus temperature for magnetite. Curves A, B, and C are reduced magnetization versus temperature as calculated for magnetite using the NMR data.

The magnetization can now be calculated from the formula

$$M=\frac{N\beta h}{3}\left(2g_B\frac{\nu_B}{A_B}-g_A\frac{\nu_A}{A_A}\right), \tag{9}$$

taking the values of g_B from Fig. 2 and taking g_A equal to 2.00. This is curve B in Fig. 4. It still does not agree with curve M.

The curve labeled C in Fig. 4 was obtained when the electronic g gactor was ignored to the extent that it was assumed to be 2 in all cases and at all temperatures. This curve, C, is a reasonable fit of M since no accounting for the thermal expansion of the lattice was made.[14]

In all the above, the hyperfine coupling constants A_i were assumed constant with temperature. The Fermi contact interaction is essentially a volume effect and is thus temperature dependent. More important is the possibility of an unquenched orbital moment producing a dipolar field. The values of the microwave g_{eff} ratio are known to be temperature dependent as is shown in Fig. 2 so the A should be also temperature dependent if the g_{eff} value results from an unquenched orbital moment. Following Eq. (1) we will redefine the hyperfine interaction in terms of a term which is temperature independent and comes from the core of the ion (thus is related to the Fermi term), and a term which depends on the orbital moment

$$h\nu_i=\frac{M_i}{N_i\beta}\left(\frac{A_0}{2.00}+A_1\frac{\Delta g_i}{g_i}\right), \tag{10}$$

where Δg_i is g_i-2. For the A sublattice this reduces to terms involving only A_0 and need not be considered. For the B sublattice this leads to a value of A_1 which is temperature dependent. Table I shows values of A_1 calculated from the moment data and the g value data where g_B is taken to be g_{eff}. (This may be done since we are in essence assuming that the B ions are divalent iron and thus contribute all the observed g values.) A_1 has what is presumably the correct sign for a field due to unquenched orbital momentum but the temperature dependence is too great to attribute to error.

TABLE I. A tabulation of values of the hyperfine interaction due to an orbital moment in Fe^{2+} as calculated using the NMR and magnetization data for Fe_3O_4.

Temp. (°K)	g_{eff}	A_1 (cm^{-1})
125	2.035	$+74\times10^{-5}$
140	2.065	$+60\times10^{-5}$
200	2.096	$+58\times10^{-5}$
273	2.105	$+49\times10^{-5}$
300	2.110	$+51\times10^{-5}$

In view of the excellent fit obtained when the NMR data were compared with the moment data by ignoring the temperature-dependent g values it would seem that these g values are not indicative of unquenched orbital momenta but indicate some other effect.

There is always the possibility of a pulling of the ferromagnetic resonance line because the material is lossy. This could lead to errors in the g values. The ferromagnetic resonance lines are broad in Fe_3O_4 and may lead to errors in g value due to uncertainties in locating the centers of these lines.

The quenching of the orbital moment of the Fe^{2+} ions in the cubic phase of magnetite which this work suggests is a point of interest which is not discussed here.

To shift the point of view a bit, Fig. 3, the plot of normalized frequency versus temperature, contains two points which were calculated using molecular field theory and were tabulated by Riste and Tenzer.[15] It is seen that these magnetizations are higher than the observed magnetizations. This effect has been shown true in the case of the garnets and of lithium ferrite and seems to show an overestimation of the magnetization which is inherent in the molecular field theory.

The author wishes to thank Dr. M. W. Shafer and Gordon Evans for the preparation of the material used in this study, and Dr. J. C. Slonczewski and Dr. J. S. Smart for many discussions of the handling of the data.

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