PHYSICAL REVIEW B VOLUME 8, NUMBER 11 1 DECEMBER 1973

Temperature Dependence of the Hyperfine Field and Hyperfine Coupling Constant of Iron

P. C. Riedi
Department of Physics, University of St. Andrews, St. Andrews, Fife, Scotland

(Received 26 February 1973)

The hyperfine field of ^{57}Fe in natural iron has been measured by continuous-wave NMR in the temperature range 4.2–400 °K. The measurements below 32 °K follow a $T^{3/2}$ law and are in good agreement with the magnetization data. A single extra term in $T^{5/2}$ is sufficient to fit the hyperfine-field measurements, reduced to zero spin-wave gap, between 32 and 400 °K. The hyperfine coupling constant is temperature dependent, despite the agreement in the $T^{3/2}$ term found by magnetization and hyperfine field measurements, with the form $A_T = 1 - 6.58 \times 10^{-9} T^{5/2} + 8.9 \times 10^{-12} T^{7/2}$.

I. INTRODUCTION

The hyperfine-coupling constant (A_T) of iron, defined by the equation

$$\nu_T / \nu_0 = A_T M_T / M_0 \ , \qquad (1)$$

where ν_T is the hyperfine field at temperature T and M_T is the magnetization, is known to be a weak function of temperature, whether evaluated at constant pressure[1] or constant volume.[2] Keffer[3] therefore concluded, after analysis of some early NMR measurements[4] of the hyperfine field at temperatures above 77 °K, that the NMR technique was unsuited to the precise measurement of the spin-wave parameters of the magnetization of iron.

In the present paper it is shown that, because of the very high accuracy obtainable by NMR, it is in fact possible to derive the $T^{3/2}$ coefficient of the magnetization from measurements at temperature below 30 °K, where the temperature dependence of the hyperfine-coupling constant is unimportant. A new expression for the temperature dependence of A_T has also been obtained which is valid up to 400 °K. The present results for pure iron are consistent with the recently reported measurements[5] of the temperature dependence of the distribution of hyperfine fields of iron alloys containing $\frac{1}{2}$ at.% of Co, Ni, or Sn.

The spin-wave theory and experimental results for the magnetization of iron are reviewed in Sec. II. The experimental technique and results are then discussed and finally the temperature dependence of the hyperfine-coupling constant is reviewed.

II. SPIN-WAVE THEORY

A full review of the spin-wave theory has been given by Keffer.[3] The following equations are therefore quoted simply to establish the notation and include only terms of experimental importance.

In the absence of a gap in the spin-wave spectrum the magnetization at temperature T is given by

$$(M_0 - M_T)/M_0 = BT^{3/2} + CT^{5/2} + \cdots \ , \qquad (2)$$

where B and C are related to the spin-wave stiffness coefficient D and may also be functions of temperature. In particular,

$$B = (2.361 g\mu_B / M_0)(k_B / 4\pi D)^{3/2} \ , \qquad (3)$$

where g is the Landé splitting factor, μ_B is the Bohr magneton, and k_B is Boltzmann's constant.

When an energy gap ϵ_g exists in the spin-wave spectrum due to the presence of magnetic fields, a gap temperature may be defined by

$$\epsilon_g = k_B T_g = g\mu_B (H_0 - H_D + H_L + H_A) \ , \qquad (4)$$

where H_0 is the external magnetic field, H_D is the demagnetizing field, H_L is the Lorentz field, and H_A is the anisotropy field. When T_g is much smaller than any experimental temperature the coefficient B in Eq. (2) becomes

$$B[1 - 1.355(T_g/T)^{1/2} + 0.559(T_g/T) - \cdots] \qquad (5a)$$

and the coefficient C,

$$C[1 - 1.95(T_g/T) + 1.76(T_g/T)^{3/2} - \cdots] \ . \qquad (5b)$$

The leading correction term due to the energy gap is therefore linear in T and proportional to the square root of the gap temperature.

The experimental values of the magnetization of iron, corrected for the gap given by Eq. (4), are found to be in good agreement with a $T^{3/2}$ law at low temperature,[6,7] but it is not possible to perform the measurements at higher temperatures with sufficient accuracy to determine the next term in the series uniquely. The most recent measurements[7] however strongly suggest a term in $T^{7/2}$, due to the temperature dependence of the spin-wave stiffness coefficient, rather than the $T^{5/2}$ term of Eq. (2).

The spin-wave stiffness coefficient D has been shown, by neutron scattering measurements,[8] to have the form $D = D_0 - D_1 T^2 - D_2 T^{5/2}$. Taking the simplified version $D = D_0 - D_1 T^2$ as sufficient for the magnetization, it was found[7] that $D_0 = 311 \pm 10$ meV Å^2 and $D_1 = (6.1 \pm 0.8) 10^{-4}$ meV Å^2 °K^{-2} in good agreement with the neutron measurements.

The temperature dependence of the magnetization of iron up to room temperature, corrected to zero spin-wave gap, may therefore be written

$$(M_0 - M_T)/M_0 = (3.01 \pm 0.15)\,10^{-6}T^{3/2} + (8.9 \pm 1.9)\,10^{-12}T^{7/2} . \qquad (6)$$

An examination of other recent measurements of the magnetization[9,10] supports the conclusion of Aldred and Froehle but suggests that the coefficient of $T^{7/2}$ may be nearer the lower limit of the value given in Eq. (6).

Since in a continuous-wave NMR experiment the hyperfine field is observed at atoms within domain walls and in the absence of an external field, the energy gap in the spin wave spectrum given by Eq. (4) is no longer well defined and will vary through the wall. A spin-wave theory of the magnetization within a domain wall has been given by Janak[11] for uniaxial anistropy. The magnetization at temperature T is found to be dependent upon the distance from the center of the wall, but at a given position a correction term linear in T and proportional to the square root of the anisotropy field is found. The effect is therefore equivalent to the introduction of a gap temperature in Eq. (4) which is related to the anisotropy field and a number of domain wall parameters which are not well known.

The domain walls of iron are however known to be extremely broad, of the order of hundreds of lattice spacings, due to the cubic structure and low anisotropy field, so there should be little distinction between the atoms in walls and those in the bulk of the domains. It was in fact concluded in a recent paper[9] (note added in proof) that at absolute zero the hyperfine field of iron at atoms in domain walls, measured by NMR, and in bulk domains as mentioned by the Mössbauer effect "coincided within the precision of the measurements" and by 400 °K the difference was estimated to be only $\simeq 20 \pm 20$ kHz.

III. EXPERIMENTAL

A sample of Johnson Matthey iron sponge (99.999% iron) was annealed under hydrogen and cooled slowly to room temperature. The powder was placed in a coil at the end of a short transmission line in a continuous-flow helium cryostat. The temperature could be varied between 4.2 °K and room temperature and stabilized to better than 0.1 °K. A fuller account of the cryostat is in preparation and will be published elsewhere. The temperature was measured using a germanium or platinum resistance thermometer. The measurements above room temperature were made with the sample in a small furnace. The temperature was measured using copper-constantan thermocouples.

The distribution of ^{57}Fe hyperfine fields was measured by continuous wave NMR using the technique of adiabatic fast passage and phase sensitive detection.[12] The marginal oscillator was frequency modulated to a depth of 3 kHz peak-to-peak at modulation frequencies between 20 and 300 Hz depending upon the temperature, and the center frequency slowly swept through the line. The peak in the distribution could be measured to better than 1 kHz in a given run but it was found that shifts of about 1 kHz occurred for different modulation frequencies. These shifts did not seem to be temperature dependent and may simply be related to the difficulty of finding the center of an asymmetric line. The results are shown in Table I.

The line shape at 4.2 °K is shown in Fig. 1. The line is asymmetric with a full width at half-height of 24 kHz. The general shape of the line was independent of temperature but the width decreased to 15 kHz by 100 °K and then to 13 kHz at room temperature. This behavior is not consistent with either of the present theories[13] of NMR linewidth in ferromagnetic materials and will be discussed elsewhere.

IV. TEMPERATURE DEPENDENCE OF HYPERFINE FIELD

The measured values of the hyperfine field in the range 4.2–51 °K are shown as a function of $T^{3/2}$ in Fig. 2. The result of a least-squares fit to the measurements below 32 °K was

TABLE I. NMR measurements of the hyperfine field in iron at constant pressure. The NMR measurements have an accuracy of ± 1 kHz.

Temperature (°K)	Hyperfine field (MHz)
4.2	46.647
6.8	46.646
9.3	46.645
11.8	46.643
13.4	46.641
15.9	46.639
18.1	46.637
21.6	46.635
23.7	46.633
24.5	46.632
27.8	46.628
31.9	46.624
36.4	46.618
44.0	46.606
51.0	46.594
68.9	46.561
77.3	46.542
105.6	46.465
152.0	46.300
164.0	46.252
229.7	45.925
297.6	45.468
350.0	45.037
400.0	44.555

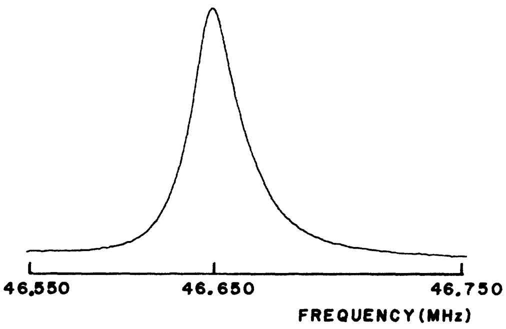

FIG. 1. Distribution of hyperfine fields at ^{57}Fe in natural iron at 4.2 °K as measured by continuous-wave NMR. The distribution is asymmetric, with a full width at half-height of 24 kHz.

$$(\nu_0-\nu_T)/\nu_0=(2.944\pm0.062)\,10^{-6}T^{3/2}\ ,\qquad \nu_0=46.648\ \text{MHz}\ . \tag{7}$$

The coefficient of $T^{3/2}$ is in good agreement with the value for the magnetization given in Eq. (6). The linear dependence upon $T^{3/2}$ seen in Fig. 2 also shows that the gap temperature must be much less than 4.2 °K. Since the effect of thermal expansion is negligible at such low temperatures, the value of the $T^{3/2}$ coefficient given in Eqs. (7) is essentially the result for constant volume.

At higher temperatures the hyperfine field decreased more rapidly than would be expected from Eqs. (7) and the deviation was found to be proportional to $T^{5/2}$ (Fig. 3). The temperature dependence of the spin-wave stiffness coefficient therefore does not appear in the hyperfine field. The result of a least-squares fit to the measurements between 150 and 400 °K was

$$(\nu_0-\nu_T)/\nu_0=2.978\times10^{-6}T^{3/2}+6.57\times10^{-9}T^{5/2}\ . \tag{8}$$

The excellent agreement with the coefficient of $T^{3/2}$ measured directly at low temperatures [Eqs. (7)] should be noted, suggesting that the $T^{3/2}$ term is insensitive to the volume change due to thermal expansion.

The measurements between 20 and 100 °K shown in Fig. 3, fall below the values given by Eq. (8) by more than the expected experimental error. This behavior is consistent with a small gap in the spin-wave spectrum, or equivalently to the term linear in T found by Janak for the magnetization within a domain wall. It is not possible to determine the value of the gap accurately from the present measurements since the effect is small and proportional to the square root of the gap. As an example of the order of magnitude of the gap however the upper points in Fig. 3 show the effect of a correction made using Eq. (5) assuming that the gap is due to the anisotropy field of 600 Oe. The gap temperature is then 0.084 °K at low temperatures, decreasing slightly with the anisotropy field at higher temperature.

A recalculation of the least-squares fit then gave

$$(\nu_0-\nu_T)/\nu_0=3.043\times10^{-6}T^{3/2}+6.58\times10^{-9}T^{5/2}\ . \tag{9}$$

The differences between the coefficients in Eqs. (8) and (9) are a measure of the uncertainty of the correct values for zero gap. A comparison with the errors of Eq. (6) for the magnetization shows the greater accuracy of the NMR technique. It is interesting to note[5] that in an alloy of iron the coefficient of $T^{5/2}$ appears to be unchanged for an iron atom with an impurity atom in its third-nearest-neighbor shell but the coefficient of $T^{3/2}$ may increase or decrease depending upon the particular impurity atom.

The low-temperature measurements shown in Fig. 2 are quite consistent with Eq. (9) and a gap temperature of 0.084 °K. The gap term and the $T^{5/2}$ contribution are not only small in the low-temperature region, but are also of opposite sign and cancel near 30 °K. The effect of these two terms is therefore to extend the temperature range over which a simple $T^{3/2}$ law appears to be followed.

V. HYPERFINE-COUPLING CONSTANT

It has been shown in earlier sections that the coefficient of $T^{3/2}$ of the magnetization is equal, to within the experimental accuracy, to that of the hyperfine field, and it is reasonable to assume exact equality since the $T^{3/2}$ term, unlike higher terms, is structure independent. The temperature dependence of the hyperfine-coupling constant is then found from Eqs. (6) and (8) to be

$$A_T=1-6.58\times10^{-9}T^{5/2}+8.9\times10^{-12}T^{7/2}\ . \tag{10}$$

The above result should apply at temperatures up to 400 °K, where there is little difference between

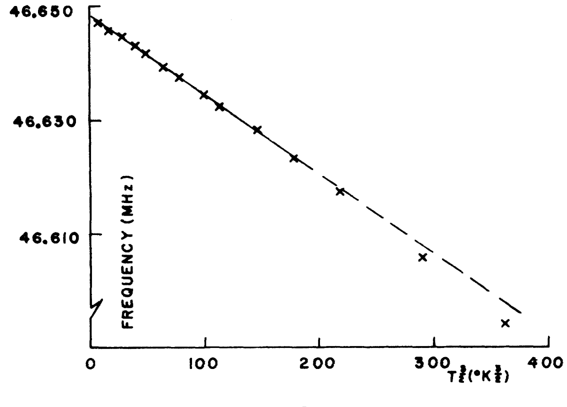

FIG. 2. Hyperfine field of ^{57}Fe in natural iron as a function of $T^{3/2}$.

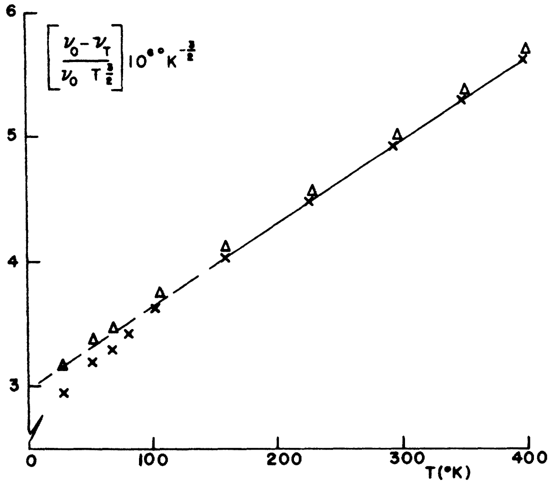

FIG. 3. $(\nu_0-\nu_T)/\nu_0 T^{3/2}$ as a function of temperature. The experimental points are shown by (×) and the effect of a correction for a gap in the spin-wave spectrum equal to the anistropy field by (Δ). The line is given by Eq. (8).

the hyperfine-coupling constant evaluated at constant pressure and at constant volume.[14] The temperature dependence of A_T given by Eq. (10) is almost identical up to 400 °K to the expression

$$A_T = 1 - 7.7\times10^{-8} T^2 \tag{11}$$

given by Benedek and Armstrong[2] for the constant volume case. The T^2 dependence of Eq. (11) therefore probably has no physical significance, and in particular cannot be used to support the theory that A_T is due to Stoner-like single-particle excitations. A similar conclusion has been drawn, on more general grounds, by Butler *et al.*[9] who suggest two alternative models for A_T which fit the experimental results equally well. Vincze[14] has also proposed a model, based on lattice vibration and expansion, but a rigorous theory of the hyperfine-coupling constant does not exist at present.

It has previously been assumed[9,14] that the hyperfine field arises from a local (core) term, proportional to the magnetization, and a conduction-electron term. The temperature dependence of the hyperfine-coupling constant is then due to the different contributions of these two terms as a function of temperature. An alternative way to view the present measurements is to note that, since terms beyond $T^{3/2}$ in Eq. (2) depend upon the *range* of the exchange interaction,[3] the temperature dependence of the hyperfine-coupling constant would arise automatically if the hyperfine field and magnetization saw a different effective range for the exchange interaction. The mean-square range of the exchange interaction $\langle r^2\rangle$ is given[3] in terms of Eq. (2) by

$$\langle r^2\rangle = 10.4 CD/Bk_B\ . \tag{12}$$

Using the values given in Eq. (9) for the hyperfine field, we find $\langle r^2\rangle = 13a^2$, where a is the nearest-neighbor distance. The magnetization measurements[6] show that C, and therefore $\langle r^2\rangle$ is roughly six times smaller than the value found for the hyperfine field. The large value for $\langle r^2\rangle$ found from Eq. (9) is however consistent with NMR measurements[5,15] on iron alloys which show the hyperfine field perturbed out to about six-nearest-neighbor shells from an impurity.

VI. CONCLUSION

The reduction in the magnitude of the hyperfine field of ^{57}Fe in iron at temperature T has been shown to be proportional to $T^{3/2}$ between 4.2 and 32 °K. The coefficient of $T^{3/2}$ is in good agreement with that found from magnetization measurements. At temperatures between 32 and 400 °K an extra term in $T^{5/2}$ is sufficient to fit the hyperfine-field measurements but the correction to the magnetization is proportional to $T^{7/2}$. The temperature dependence of the hyperfine-coupling constant is due to this difference in the terms beyond $T^{3/2}$.

---

[1] C. Robert and J. M. Winter, C.R. Acad. Sci. B **250**, 3831 (1960).

[2] G. B. Benedek and J. Armstrong, J. Appl. Phys. **32**, 106S (1961).

[3] F. Keffer, in *Handbuch der Physik* (Springer-Verlag, Berlin, 1966), Vol. 18.

[4] J. I. Budnick, L. J. Bruner, R. J. Blume, and E. L. Boyd, J. Appl. Phys. **32**, 120S (1961).

[5] P. C. Riedi, Phys. Lett. A **33**, 273 (1970); J. Phys. F **3**, 206 (1973).

[6] B. E. Argyle, S. H. Charap, and E. W. Pugh, Phys. Rev. **132**, 2051 (1963).

[7] A. T. Aldred and P. H. Froehle, Int. J. Magn. **2**, 195 (1972).

[8] M. W. Stringfellow, J. Phys. C **1**, 950 (1968).

[9] M. A. Butler, G. K. Wertheim, and D. N. E. Buchanan, Phys. Rev. B **5**, 990 (1972).

[10] J. Crangle and G. M. Goodman, Proc. R. Soc. A 321, 477 (1971).

[11] J. F. Janak, Phys. Rev. **134**, A411 (1964).

[12] D. L. Cowan and L. W. Anderson, Phys. Rev. **135**, A1046 (1964); A. M. Portis, Phys. Rev. **100**, 1219 (1955).

[13] H. Suhl, Bull. Am. Phys. Soc. **5**, 175 (1960); J. Friedel and P. G. de Gennes, C.R. Acad. Sci. B **251**, 1283 (1961).

[14] I. Vincze and J. Kollár, Phys. Rev. B **6**, 1066 (1972).

[15] J. I. Budnick, T. J. Burch, S. Skalski, and K. Raj, Phys. Rev. Lett. **24**, 511 (1970).