

## Relation between the Hyperfine Magnetic Fields and Sublattice Magnetizations in $\text{Fe}_3\text{O}_4$ †

F. VAN DER WOUDE,\* G. A. SAWATZKY, AND A. H. MORRISH

*Department of Physics, University of Manitoba, Winnipeg, Canada*

(Received 24 August 1967)

The temperature dependences of the hyperfine magnetic fields at  $\text{Fe}^{57}$  nuclei in *A* and *B* sites of  $\text{Fe}_3\text{O}_4$  have been determined with the Mössbauer-effect technique. A comparison with neutron diffraction data shows that the  $H_{\text{hpf}}$ -versus-*T* curves follow the sublattice-magnetization-versus-temperature curves very closely. Over the temperature range 300–800°K, the hyperfine constants for *A* and *B* sites in  $\text{Fe}_3\text{O}_4$  change less than 1%.

### INTRODUCTION

THE Mössbauer-effect (ME) technique has frequently been used to determine the temperature dependence of the hyperfine magnetic field  $H_{\text{hpf}}$  at nuclei in ferro-, ferri-, or antiferromagnetic materials.<sup>1–7</sup> Very often such a curve was assumed to be identical with the magnetization or a sublattice-magnetization-versus-temperature curve.

A detailed study of the relationship between  $H_{\text{hpf}}(T)$  and  $M(T)$  has been made only for iron.<sup>8,9</sup> Except for approximate comparisons made by van Loef,<sup>10</sup> such studies have not been made for iron in ionic compounds. In view of the current interest in ferrimagnets and antiferromagnets, it is pertinent to make detailed investigations.

We have studied the inverse spinel  $\text{Fe}_3\text{O}_4$  with the Mössbauer-effect technique because accurate values of the sublattice magnetizations at temperatures between 298 and 860°K, obtained from neutron diffraction experiments by Riste and Tenzer (RT), are tabulated.<sup>11</sup> For  $\text{Fe}_3\text{O}_4$ , RT performed all the necessary corrections for extinctions and the Debye-Waller factor. The magnetization-versus-temperature curve derived from these neutron diffraction experiments agreed well with the magnetization data obtained by Pauthenet (Ref. 5 in Ref. 11). Our sample of  $\text{Fe}_3\text{O}_4$  as well as the material measured by RT is of natural origin and contained less

than 1% impurities.<sup>12</sup> Another advantage of  $\text{Fe}_3\text{O}_4$  is that all the cations can be observed with the ME technique, because the material contains only iron cations. In addition, the splittings in these spectra can be determined accurately because the first three lines of the six-line hyperfine pattern attributed to nuclei in tetrahedral (*A*) sites are well separated from those attributed to nuclei in octahedral (*B*) sites above room temperature.

### METHODS AND RESULTS

Mössbauer spectra were obtained by using a constant velocity drive<sup>13</sup> with about 50 channels per mm/sec. The source was 10 mCi of  $\text{Co}^{57}$  in a chromium matrix. The vacuum furnace was similar in design to that described by Sharon and Treves.<sup>14</sup> The single crystals of  $\text{Fe}_3\text{O}_4$  were crushed and mixed with graphite. This mixture was placed into a graphite dish and pressed firmly in order to ensure temperature uniformity. The graphite dish served as the absorber holder in the furnace. The temperature was measured with a thermocouple inserted into a small hole at the edge of the graphite dish. The temperature gradient was not measured directly. However, the Mössbauer lines were not appreciably broadened at high temperatures, indicating that the temperature gradient over the sample was probably less than 2°C. Temperature control was achieved with a second thermocouple electrically insulated from the first. The amplified emf of the thermocouple drove the continuously variable power supply feeding the heater. The temperature stability was about  $\pm 0.5^\circ\text{C}$  over the period required to obtain one Mössbauer spectrum. The ferrimagnetic Néel temperature  $T_{\text{FN}}$  was measured by observing the

† Supported by the National Research Council of Canada.  
\* Present address: Laboratory for Solid State Physics, University of Groningen, The Netherlands.

<sup>1</sup> D. Treves, *J. Appl. Phys.* **36**, 1033 (1965).

<sup>2</sup> M. Eibschütz, S. Shtrikman, and D. Treves, *Phys. Rev.* **156**, 562 (1967).

<sup>3</sup> F. van der Woude and A. J. Dekker, *Phys. Status Solidi* **13**, 181 (1966).

<sup>4</sup> F. van der Woude, *Phys. Status Solidi* **17**, 471 (1966).

<sup>5</sup> J. J. van Loef, *Solid State Commun.* **4**, 625 (1966).

<sup>6</sup> G. K. Wertheim, H. J. Guggenheim, H. J. Williams, and D. N. A. Buchanan, *Phys. Rev.* **158**, 446 (1967).

<sup>7</sup> G. K. Wertheim, H. J. Guggenheim, and D. N. A. Buchanan, *Solid State Commun.* **5**, 537 (1967).

<sup>8</sup> D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, *Phys. Rev. Letters* **5**, 364 (1960).

<sup>9</sup> G. B. Benedek and J. Armstrong, *J. Appl. Phys.* **32**, 106S (1961).

<sup>10</sup> J. J. van Loef, *Physica* **32**, 2102 (1966).

<sup>11</sup> T. Riste and L. Tenzer, *J. Phys. Chem. Solids* **19**, 117 (1961).

<sup>12</sup> A spectographic analysis of our sample shows 1% Si and 0.1% Ca, but these elements are thought to be present in bits of schist (quartz and calcite) adhering to the surface. The presence of other elements was less than 0.01%. The deviation from stoichiometry ( $\text{FeO}/\text{Fe}_2\text{O}_3=1$ ) is less than 1% as reported by D. B. Bonstrom, Ph.D. thesis, University of Minnesota, 1959, p. 49. (unpublished).

<sup>13</sup> Manufactured by Elron Electronic Industries Ltd., Haifa, Israel.

<sup>14</sup> B. Sharon and D. Treves, *Rev. Sci. Instr.* **37**, 1252 (1966).

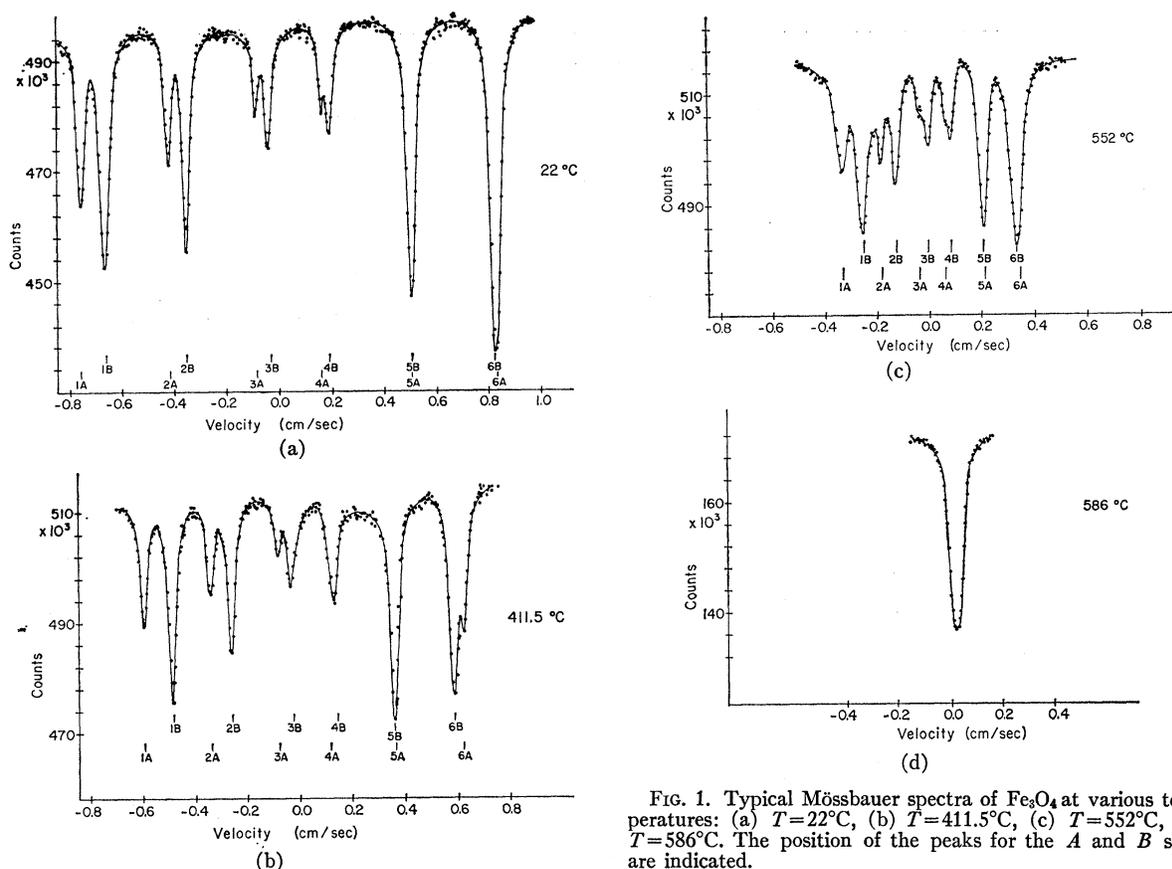


FIG. 1. Typical Mössbauer spectra of  $\text{Fe}_3\text{O}_4$  at various temperatures: (a)  $T=22^\circ\text{C}$ , (b)  $T=411.5^\circ\text{C}$ , (c)  $T=552^\circ\text{C}$ , (d)  $T=586^\circ\text{C}$ . The position of the peaks for the *A* and *B* sites are indicated.

temperature dependence of the absorption at a velocity corresponding to the peak position of the spectrum just above  $T_{\text{FN}}$ . This technique permitted  $T_{\text{FN}}$  to be determined to within a relative accuracy of about  $\pm 0.5^\circ\text{C}$ .

Typical Mössbauer spectra taken at temperatures ranging from room temperature to above the Néel point are shown in Fig. 1. A least-squares fit, assuming Lorentzian line shapes, was made to all spectra with the University of Manitoba's IBM system 360, model 65 computer. From the least-squares analysis, the relative error in the hyperfine field was less than 0.5% up to  $0.9T_{\text{FN}}$  and about 1% at  $0.97T_{\text{FN}}$ .

The temperature dependences of the hyperfine magnetic fields experienced by  $\text{Fe}^{57}$  nuclei in *A* and *B* sites, respectively, as determined from Mössbauer spectra, are plotted in Fig. 2. The magnetizations as a function of the temperature for the *A* and *B* sublattices, as obtained by RT, are also plotted in the same figure. RT normalized the  $M(T)$  data to the values 0.982 and 0.962 for  $M(298^\circ\text{K})$  of *A* and *B* sites, respectively. For comparison we have chosen the same normalization values for  $H_{\text{hpf}}(T)$  at room temperature. Since RT did not measure  $T_{\text{FN}}$  we estimated it by extrapolating the sublattice magnetization curves to zero. This left a large uncertainty in the value of  $T_{\text{FN}}$  ( $\sim 2^\circ\text{C}$ ) used for the RT data. As can be seen from Fig. 2 there is a

very close agreement between the  $H_{\text{hpf}}(T)$ -versus- $T$  and the  $M(T)$ -versus- $T$  curves for *A* sites as well as for *B* sites. Above  $0.9T_{\text{FN}}$  the values for  $M(T)$  drop below the  $H_{\text{hpf}}(T)$  values. However, this may be due to the uncertainty in  $T_{\text{FN}}$  for the neutron diffraction data. The errors in  $M(T)$  are not given by RT, but regarding the corrections that have to be made, we estimate this error to be about 1% for  $T < 0.9T_{\text{FN}}$ . The differences between the normalized  $H_{\text{hpf}}(T)$  and  $M(T)$  values are less than 1% up to  $0.9T_{\text{FN}}$ . In view of the combined experimental error this difference cannot be called significant. Therefore we conclude that within the experimental error of 1% the hyperfine magnetic field at the  $\text{Fe}^{57}$  nuclei in *A* and *B* sites of  $\text{Fe}_3\text{O}_4$  have the same temperature dependences as the respective sublattice magnetizations.

## DISCUSSION

In a recent survey article,<sup>10</sup> van Loef has tabulated, for ferrimagnets, the relative hyperfine magnetic field  $H_{\text{hpf}}(T)/H_{\text{hpf}}(0)$  obtained from ME or NMR measurements and the relative sublattice magnetization  $M(T)/M(0) = \bar{m}_s(T)$  as deduced from neutron diffraction data. It turns out that for a number of ferrimagnetic spinels and a garnet these two quantities differ by about 5% at  $0.5T_{\text{FN}}$  and even more at  $0.75T_{\text{FN}}$ .

van Loef suggests that time fluctuations of the ionic spin may be responsible for this difference. This influence can be discussed on the basis of the following relation between  $H_{\text{hpf}}$  and the magnetic quantum number of the ionic spin  $m_s$ :

$$H_{\text{hpf}}(t, T) = A(T)m_s(t, T). \quad (1)$$

Here,  $t$  refers to time and  $T$  to temperature.  $A(T)$  is the hyperfine coupling constant. The quantization direction has been chosen along the magnetization. Relaxation phenomena in the Mössbauer effect have been discussed by several authors.<sup>15-20</sup> The discussion has mainly been directed towards paramagnetic materials. However, one conclusion will also hold for magnetically ordered materials; viz., if the fluctuation of the ionic spin is rapid compared to the Larmor precession frequency  $\nu_L$  of the nucleus, the time average  $\bar{H}_{\text{hpf}}(T)$  will be proportional to  $\bar{m}_s(T)$ . In  $\text{Fe}_3\text{O}_4$  as well as in the spinels and the garnet tabulated in Ref. 10, this fluctuation frequency will be of the order of  $10^{13}$  cps, which is much larger than  $\nu_L = 10^8$  cps in a field of 500 kOe in the case of  $\text{Fe}^{57}$ . So, for these materials we may write (1) as

$$\bar{H}_{\text{hpf}}(T) = A(T)\bar{m}_s(T). \quad (2)$$

It may be noticed that a similar expression is in common usage in nuclear magnetic resonance.

A second factor that may impede a close connection between  $H_{\text{hpf}}$  and  $M$  is the temperature dependence of the hyperfine constant  $A$ . Only for metallic iron<sup>9</sup> and  $(\text{Mn}^{55})^{2+}$  in oxides<sup>21,22</sup> and in halides,<sup>23,24</sup> has  $A(T)$  been investigated experimentally and theoretically. Here the relation between  $A$  and the temperature can be represented empirically as

$$A(T) = A(0)[1 - cT^n], \quad (3)$$

where  $A(0)$  refers to  $A$  at  $0^\circ\text{K}$ , and  $c$  and  $n$  are constants depending on the materials in question. In the above-mentioned materials the difference between  $A(0^\circ\text{K})$  and  $A(1000^\circ\text{K})$  may vary from almost 0–10%. In the spinels and the garnet tabulated in Ref. 10, the different temperature behavior of  $H_{\text{hpf}}$  and  $M$  must be due to  $A(T)$ , assuming that the experimental results are suitable for such a comparison.

<sup>15</sup> A. M. Afanasev and Yu. Kagan, Zh. Eksperim. i Teor. Fiz. **45**, 1660 (1964) [English transl.: Soviet Phys.—JETP **18**, 1139 (1964)].

<sup>16</sup> F. van der Woude and A. J. Dekker, Phys. Status Solidi **9**, 775 (1965).

<sup>17</sup> H. Wegener, Z. Physik **186**, 498 (1965).

<sup>18</sup> H. H. Wickman and G. K. Wertheim, Phys. Rev. **148**, 211 (1966).

<sup>19</sup> E. Bradford and W. Marshall, Proc. Phys. Soc. (London) **87**, 731 (1966).

<sup>20</sup> H. H. Wickman, *Mössbauer Effect Methodology* (Plenum Press Inc., New York, 1966), Vol. 2, p. 39.

<sup>21</sup> W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965).

<sup>22</sup> R. Orbach and E. Simánek, Phys. Rev. **158**, 310 (1967).

<sup>23</sup> J. S. van Wieringen and J. G. Rensen, Philips Res. Rept. **20**, 659 (1965).

<sup>24</sup> Chao-Yuan Huang, Phys. Rev. **158**, 280 (1967).

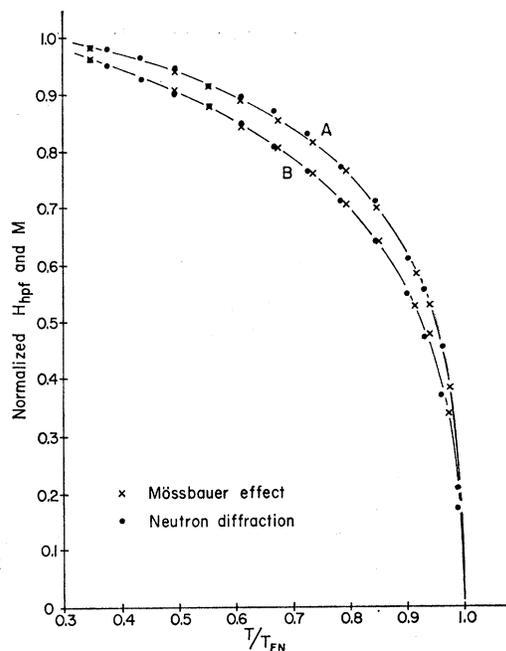


FIG. 2. Normalized hyperfine magnetic fields at  $\text{Fe}^{57}$  nuclei and sublattice magnetizations of  $A$  and  $B$  sites in  $\text{Fe}_3\text{O}_4$  as a function of the reduced temperature  $T/T_{\text{FN}}$ . The hyperfine magnetic fields have been determined from Mössbauer spectra and the sublattice magnetizations have been taken from Ref. 11.

Since magnetite is a completely inverse spinel, only ferric ions occupy the  $A$  sites. It is reasonable to expect that other inverse spinels of the type  $\text{MFe}_2\text{O}_4$  would exhibit a similar behavior for  $A$ -site ions. Of course, the temperature independence found for the hyperfine coupling constant may be a consequence of all the  $A$ -site ions being in  $S$  states.

Of the inverse spinels, magnetite is unusual in that the  $B$  sites are occupied by equal numbers of ferric and ferrous ions. Above room temperature, however, the ferrous and ferric ions are indistinguishable because fast electron exchange occurs. Therefore, the temperature independence of the hyperfine coupling constant observed for the  $B$ -site ions of magnetite may not be a general property for all spinels.

For the spinels and the garnet discussed by van Loef,<sup>10</sup> there appeared to be a decrease in the hyperfine coupling constant  $A(T)$  of at least 5% for the ions in both  $A$  and  $B$  sites. However, some of these data were obtained on nonstoichiometric samples, and were not corrected for all contributing factors. In view of our results on magnetite, it would appear to be worthwhile to conduct a more careful study of  $A(T)$  in ferrimagnets.

#### ACKNOWLEDGMENTS

We are indebted to A. W. Gibb for his assistance with the measurements. One of us (F.vdW.) would like to thank Dr. R. M. Housley for discussions on this matter.