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Study of the Low-Temperature Transition in Magnetite and the Internal Fields Acting on Iron Nuclei in Some Spinel Ferrites, Using Mössbauer Absorption*

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A study has been made of the internal fields acting on Fe^{57} nuclei in some spinel ferrites, with particular reference to the low-temperature order-disorder transition in magnetite, using the techniques of Mössbauer absorption. For the Fe^{3+} ions at both the octahedral and tetrahedral sites in nickel ferrite ($NiFe_2O_4$) at 300°K, γFe_2O_3 at 85° and 300°K, and magnetite (Fe_3O_4) at 85°K, the effective magnetic field at the Fe^{57} nuclei is the same and equal to about 5.1×10^5 oe. In magnetite, the value of H_{eff} in the Fe^{2+} ions is about 4.5×10^5 oe at 85°K. Measurements on Fe_3O_4 at room temperatures provide a microscopic confirmation of Verwey's hypothesis that above the transition temperature of magnetite there is a fast exchange between the ferrous and ferric ions in the octahedral sites.

INTRODUCTION

THE study of the Zeeman effect associated with the recoil-free resonance absorption (Mössbauer effect)[1] of the 14.4-kev gamma rays of Fe^{57m} in ferro- and ferrimagnetic materials containing iron has provided information on the nature of the internal fields acting on the iron nuclei in these materials.[2–5] In particular, values for the effective magnetic field, H_{eff}, acting on the nuclei have been obtained. This information has been most valuable for furthering our understanding of some of the basic aspects of ferri-, ferro-, and antiferromagnetism.

In the present work, these techniques have been used in order to investigate the internal fields acting on iron nuclei in some magnetic compounds belonging to an important class of ferrimagnetic materials—the ferrites having the spinel type structure (i.e., structure resembling that of the mineral spinel $MgAl_2O_4$). The compounds investigated were magnetite Fe_3O_4, ferrimagnetic γFe_2O_3, and nickel ferrite $NiFe_2O_4$. The study of magnetite is of particular interest since, as has been recently suggested,[6] the new techniques based on the Mössbauer effect are likely to throw some light on the unusual order-disorder transition taking place between 110° and 120°K. Magnetite is the simplest of the compounds $X^{2+}(Y^{3+})_2O_4$ crystallizing in the spinel structure, space group $Fd3m-O_h^7$. Verwey *et al.* have reached the conclusion that magnetite has an inverse spinel structure, the unit cell having eight ferric ions and eight ferrous ions at the octahedral sites (B sites) each with six O^{2-} nearest neighbors, and eight ferric ions at the tetrahedral sites (A sites) each with four O^{2-} nearest neighbors (this may be represented by the formula $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$).[7–9] Between 110° and 120°K magnetite displays marked changes in many physical properties. Thus there is a sudden change in magnetization, an anomalous peak in the specific heat curve, and a sharp drop in the electrical conductivity as the temperatue is lowered through the transition region. Verwey advanced the hypothesis that the transition is of an order-disorder type particularly in order to explain the behavior of the electrical conductivity. He suggested that above the transition region there is a dynamic disorder between the ferric and ferrous ions in the octahedral sites associated with a fast electron exchange between ferric and ferrous states, leading to an increased conductivity, whereas below the transition region, the ferric and ferrous ions in the octahedral sites are separately ordered. Verwey, in fact, proposed a particular ordering arrangement having orthorhombic symmetry (the disordered lattice has cubic symmetry), with the ferric and ferrous irons in mutually perpendicular rows.[8] The ordering scheme proposed by Verwey has been confirmed in some detail in recent years by neutron diffraction measurements on single crystals of magnetite carried out by Hamilton.[10]

A direct test that the order-disorder transition proposed by Verwey really manifests itself in the microscopic magnetic properties is in principle possible through a measurement of the effective magnetic fields (H_{eff}) at the iron nuclei at different temperatures. In the ordered state (assuming for the sake of simplicity conditions near magnetic saturation) it is to be expected that the values of H_{eff} at the iron nuclei in the octahedral sites, situated in ferrous and ferric ions, respectively, will be different in the two cases, since the

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electronic configurations are different (the magnetic moments per free ion are indeed different—4.2 and 5 Bohr magnetons, respectively). If, on the other hand, there is a fast interchange between the ferrous and ferric ions above the transition temperature, and this interchange is rapid compared to the Larmor precession frequency of an iron nucleus in the hyperfine field ($\sim 10^8$/sec), then a unique value of H_{eff} will be observed pertaining to *all* the octahedral sites. The situation in magnetite is of course complicated by the presence of ferric ions in the tetrahedral sites, which, *a priori*, may have associated with them a value of H_{eff} differing from the value of H_{eff} in the ferric ions in an ordered state at the octahedral sites. In fact, recent work on the iron garnets by the authors have shown that for these materials the two different Fe^{3+} sites have associated with them appreciably different values of H_{eff} even at conditions approaching saturation.[5] Nevertheless, it turns out that the values of H_{eff} in the Fe^{3+} ions, corresponding to the tetrahedral and octahedral sites in magnetite, cannot be experimentally distinguished. In fact, the same value of H_{eff} was also found for the ferric ions in the other compounds of the spinel type investigated, γFe_2O_3 and $NiFe_2O_4$. Measurements of H_{eff} in γFe_2O_3 and $NiFe_2O_4$ are of interest in themselves and also as complementary studies to that of magnetite because of the structural resemblances and differences. γFe_2O_3 is crystallographically isomorphous with Fe_3O_4, except that it has only ferric ions, these being distributed between the octahedral and tetrahedral sites, which are however not fully occupied. Thus it has been suggested that the formula may be written $(Fe_{21.33}{}^{3+})\square_{2.67}(O^{2-})_{32}$, where $\square_{2.67}$ indicates 2.67 cation vacancies. Recent work indicates that the iron vacancies are predominantly at the octahedral sites.[11] Nickel spinel is another example of a material with an inverse spinel structure; the Ni^{2+} ions are situated at the octahedral sites and the Fe^{3+} ions at the octahedral and tetrahedral sites; thus it may be represented by the formula

$$Fe^{3+}[Ni^{2+}Fe^{3+}]O_4.$$

EXPERIMENTAL DETAILS

The experimental technique used in this work is identical with that described in an earlier investigation on the iron garnets.[5] The absorption of the 14.4-kev gamma ray of Fe^{57m} embedded in stainless steel was measured in the various absorbers as a function of the relative velocity between source and absorber. The source, giving an unsplit Mössbauer line, was made by diffusing Co^{57} into stainless steel and annealing at 800°C. The source was mounted on a loudspeaker membrane and vibrated sinusoidally at 65 cps and the counting rate as a function of relative velocity recorded automatically on a multichannel pulse-height analyzer as already described.[5] A scale of velocities was established by using as a frequent calibration the absorption spectrum of antiferromagnetic αFe_2O_3 which has been previously investigated by Kistner and Sunyar,[4] and by the authors.[5] The radiation was detected by a large proportional counter. The absorbers consisted of the polycrystalline ferrite samples, in the form of powder, spread out to a thickness of about 25 mg/cm^2 and held rigidly between thin Lucite disks. Measurements were carried out with the absorbers at room temperatures and at liquid air temperatures. The measurements at low temperatures were carried out with the absorbers immersed in liquid air contained in a Styrofoam container.

EXPERIMENTAL RESULTS AND DISCUSSION

Figures 1(a), 1(b), and 1(c) show the experimentally observed spectra for γFe_2O_3 at 85°K, Fe_3O_4 at 300°K, and Fe_3O_4 at 85°K, respectively. Spectra were also observed for γFe_2O_3 and $NiFe_2O_4$ at 300°K, but these latter spectra are not shown since they were almost identical with the spectrum shown in Fig. 1(a) for γFe_2O_3 at 85°K, consisting of a pattern of only six lines, which is characteristic of a Zeeman splitting of the nuclear levels in Fe^{57} produced by a *single* magnetic field at the iron nucleus. Now, in these materials, γFe_2O_3 and $NiFe_2O_4$, the Fe^{3+} ions are situated in both types of lattice sites (octahedral and tetrahedral). The results therefore show that in these materials the values of the magnetic field at the iron nuclei of the Fe^{3+} ions are the same in the two sites. As in previous work,[4,5] the Zeeman spectra were analyzed in terms of four parameters: g_0 and g_1, the magnetic splitting parameters for the $\frac{1}{2}$ and $\frac{3}{2}$ nuclear levels, respectively (from which the value H_{eff} at the iron nucleus can be obtained); ΔE, the shift between the center of gravity of the absorption lines and the emission lines of Fe^{57} in stainless steel (chemical shift); and ϵ the effective quadrupole interaction parameter, shifting only the substates belonging to the upper $\frac{3}{2}$ level. The values for the parameters obtained in this way for γFe_2O_3 and $NiFe_2O_4$ are shown in Table I. It is seen that for γFe_2O_3 at both temperatures and for $NiFe_2O_4$ at room temperature, the parameters are the same within the experimental errors. H_{eff} for the three cases is about 5.1×10^5 oe. ΔE is about 0.04 cm/sec (3.5×10^{-8} ev) and $|\epsilon|$ is smaller than 0.01 cm/sec. It is interesting to note that these values are very close to the value of H_{eff} obtained for antiferromagnetic αFe_2O_3 at room temperature,[4] which again contains only Fe^{3+} ions at a single site.

Turning now to the spectra obtained with magnetite absorbers shown in Figs. 1(b) and 1(c), we see that at both 85° and 300°K, more complicated spectra are obtained which cannot be described by a single set of parameters characterizing a single magnetic field at the iron nuclei. As in previous work on the iron garnets,[5]

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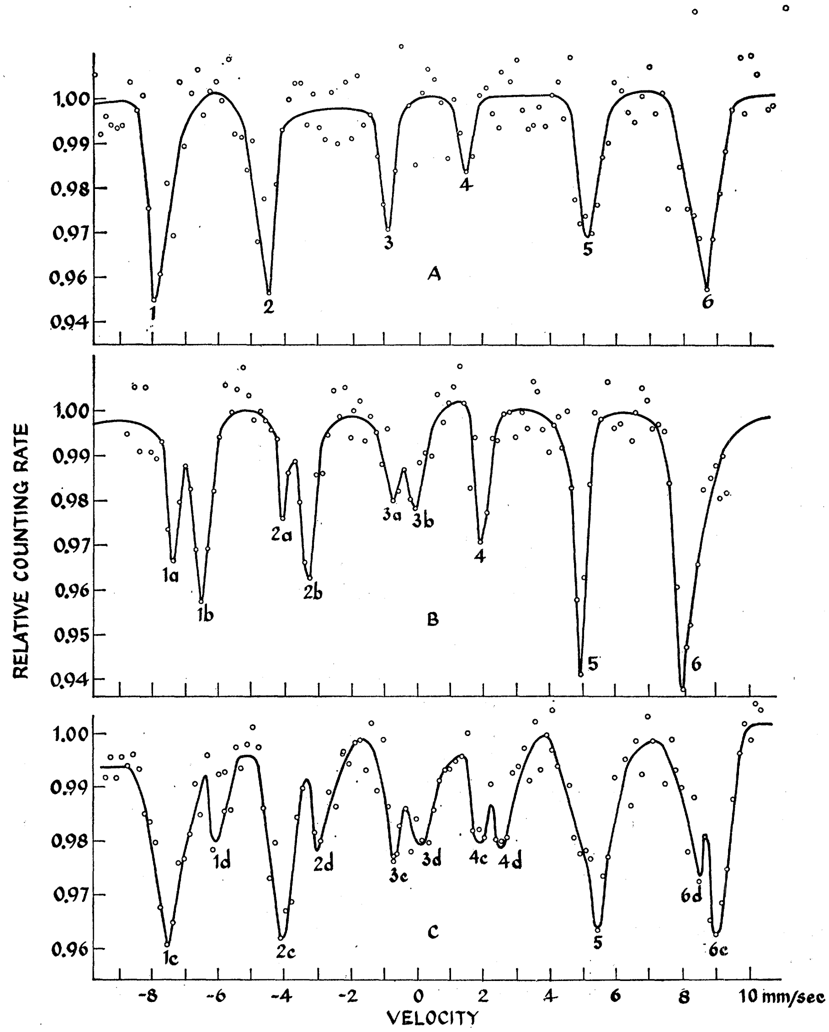

FIG. 1. The absorption of the 14.4-kev gamma ray emitted in the decay of Fe^{57m} embedded in stainless steel as a function of relative velocity between source and absorber. A. Absorption at 85°K by γFe_2O_3. B. Absorption at 300°K by Fe_3O_4. C. Absorption at 85°K by Fe_3O_4.

these spectra have been interpreted as being due to the superposition of two Zeeman patterns, each characterized by a different set of parameters. A simple analysis shows that for Fig. 1(b) one Zeeman pattern consists of 6 lines at 1a, 2a, 3a, and 4, 5, and 6, and the second Zeeman pattern of greater intensity consists of six lines at 1b, 2b, 3b, 4, 5, and 6; the doublets at 4, 5, and 6 are unresolved. Similarly in Fig. 1(c), the stronger Zeeman pattern is made up of six lines at 1c, 2c, 3c, 4c, 5, and 6c, and a relatively weaker pattern is made up of the lines at 1d, 2d, 3d, 4d, 5, and 6d; in this case only the doublet at 5 is unresolved. The splitting parameters and values of H_{eff} were calculated for each of these component Zeeman spectra, and the results are given in the bottom part of Table I.

It is seen from these results that the value of H_{eff} (5.1×10^5 oe) associated with the relatively stronger Zeeman pattern obtained with magnetite at 85°K is,

TABLE I. Results of analysis of measurement on γFe_2O_3, $NiFe_2O_4$, and Fe_3O_4.

Material and temperature	g_0 (cm/sec)	g_1 (cm/sec)	ΔE (cm/sec)	ϵ (cm/sec)	H_{eff} (oe)
γFe_2O_3 at 300°K	0.595±0.020	0.340±0.015	(0.05 ±0.005)	−0.01 ±0.01	$(5.05\pm0.20)\times10^5$
γFe_2O_3 at 85°K	0.605±0.020	0.355±0.015	0.04 ±0.01	0.01 ±0.01	$(5.15\pm0.20)\times10^5$
$NiFe_2O_4$ at 300°K	0.605±0.015	0.345±0.010	0.035±0.01	0.01 ±0.01	$(5.1\ \pm0.20)\times10^5$
Fe_3O_4 at 85°K, *c* lines	0.605±0.020	0.345±0.015	0.065±0.010	0.000±0.010	$(5.1\ \pm0.2\ )\times10^5$
Fe_3O_4 at 85°K, *d* lines	0.54 ±0.025	0.300±0.015	0.115±0.015	0.000+0.010	$(4.5\ \pm0.2\ )\times10^5$
Fe_3O_4 at 300°K, *a* lines	0.590±0.020	0.335±0.015	0.045±0.010	0.00 ±0.01	$(5.0\ \pm0.2\ )\times10^5$
Fe_3O_4 at 300°K, *b* lines	0.53 ±0.02	0.31 ±0.01	0.07 ±0.01	0.00 ±0.01	$(4.5\ \pm0.2\ )\times10^5$

within the experimental accuracy, the same as the values of H_{eff} characteristic of the Fe^{3+} ions in the crystallographically similar materials γFe_2O_3 and $NiFe_2O_4$. Hence, the *c* lines in Fig. 1(c) must be ascribed to the ferric ions situated at *both* the octahedral and tetrahedral sites. On the other hand, the value of H_{eff} pertaining to the relatively weaker *d* lines is about 4.5×10^5 oe, which is appreciably smaller than that associated with the *c* lines. The magnetic moment of the free Fe^{2+} ions is less than the magnetic moment of the free Fe^{3+} ions ($4.2\ \mu_B$ as compared to $5.0\ \mu_B$) and one might expect the Fe^{2+} ions to give rise to a smaller value of H_{eff}. This, together with the fact that the ratio of the intensity of the *c* lines to that of the *d* lines is approximately equal to the ratio of the number of Fe^{3+} ions to Fe^{2+} ions in Fe_3O_4, indicates that the weaker spectra in 1(c) must be ascribed to the Fe^{2+} ions in the octahedral sites.[12] Thus we conclude that at 85°K, below the transition temperature, the ferric and ferrous ions in the octahedral sites of magnetite produce *distinct* and uniquely defined effective magnetic fields at the iron nuclei.

We will now discuss the interpretation of the spectrum obtained with magnetite at 300°K [Fig. 1(b)]. Table I shows that H_{eff} for the relatively weaker *a* lines is about 5×10^5 oe, again the value characteristic of ferric ions in a spinel structure. The value of H_{eff} pertaining to the relatively stronger *b* lines is about 4.5×10^5 oe. A comparison of the intensities of the *b* and *a* lines indicates that only about half the ferric ions in Fe_3O_4 can contribute to the higher value of H_{eff} at 5×10^5 oe and that the ferrous ions and the remaining ferric ions *both* contribute to the lower value of H_{eff} at 4.5×10^5 oe, which is uniquely defined within the accuracy of the measurements. It follows that there is indeed a fast exchange between the ferric and ferrous ions contributing to the lower value of H_{eff}, the exchange frequency being much greater than the Larmor frequency characteristic of the hyperfine interactions. It is clear that such an exchange can only occur in the octahedral sites, in which both ferric and ferrous ions are located. Thus, we conclude that the *a* lines correspond to the Fe^{3+} ions at the tetrahedral sites, and the *b* lines correspond to Fe ions in the octahedral sites which exhibit a fast exchange of the type $Fe^{2+} \leftrightarrows Fe^{3+}$.

These results, therefore, constitute a microscopic confirmation of the original hypothesis of Verwey concerning the nature of the low-temperature transition in magnetite.[8]

It is interesting to note the significant variations between the values of the chemical shifts ΔE obtained for the various cases, and the particularly large value of ΔE of 0.115 cm/sec for the Fe^{2+} ions at the octahedral sites at 85°K, relative to the other cases.

As indicated previously,[5] a reliable value for the quadrupole interaction cannot be obtained from measurements on polycrystalline materials because the shift in the magnetic sublevels due to the quadrupole interactions depends on the angle between the magnetic field and the direction of the electric field gradient, which are well defined with respect to the crystallographic axis. Thus, although Table I shows no evidence of an appreciable quadrupole shift in any of the cases investigated, it is impossible from these results to give a reliable upper limit for the quadrupole interaction at the iron nucleus.

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[12] In principle, the ratio of intensities of the Zeeman spectra produced at different sites could be affected by a possible difference in the binding of the atoms at the different sites, which may influence the Mössbauer efficiencies for recoil-free absorption. The fact that the ratio of the intensities between the *c* and *d* lines is about 2:1 shows that this effect cannot be large in this case.