

NMR in magnetite below and around the Verwey transition

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(Received 29 April 1999)

NMR on ^{57}Fe nuclei was measured in two single crystals of magnetite between 4.2 and 135 K (temperature of the Verwey transition $T_V=121.5$ and 123.9 K). We were able to register all lines detected at 4.2 K also at higher temperatures up to T_V . The spectra are compatible with the space group Cc , which predicts 8 and 16 lines for iron on tetrahedral (A) and octahedral (B) sites, respectively. One of the $\text{Fe}(A)$ lines is doubly degenerate for all $T < T_V$, which restricts the possible models of the Fe^{2+} and Fe^{3+} ordering on the B sites. Above T_V no remnant of the low-temperature spectrum was detected. At 4.2 K the NMR spin-spin and spin-lattice relaxation times were determined.

I. INTRODUCTION

Magnetite Fe_3O_4 is a mixed valence compound with the tetrahedral (A) sublattice completely occupied by ferric ions, while in the octahedral (B) sublattice half of the sites are occupied by Fe^{2+} and half by Fe^{3+} ions. At high temperatures the crystal symmetry is cubic and both NMR and Mössbauer spectroscopy see no difference between Fe^{2+} and Fe^{3+} ions on the B sites, pointing to the delocalized character of the charge carriers. At the Verwey temperature T_V the crystal symmetry is lowered to monoclinic and the electric conductivity drops by more than two orders of magnitude. The NMR spectra of ^{57}Fe on the B sites at 4.2 K show that the charge carriers are localized or, at least, that their hopping time is much longer comparing to the characteristic time of NMR measurement (10^{-8} s). Despite considerable effort many questions concerning the physics of magnetite below the Verwey transition remain open. In particular there is no consensus concerning the ordering of Fe^{2+} and Fe^{3+} on the octahedral sites. By analyzing the angular dependence of NMR spectra Mizoguchi proposed an ordering pattern¹ which is in conflict with the symmetry group Cc found by x-ray,² neutron,³ and electron-diffraction⁴ experiments. Moreover, the measurements of the magnetoelectric effect (Ref. 5 and references therein) indicates that at low temperatures the symmetry may be triclinic rather than monoclinic.

Fe^{3+} ion has half-filled $3d$ electron shell and zero angular momentum in the ground state. On the other hand, the ground state of the free Fe^{2+} ion (electron configuration $3d^6$) is 5D and considerable orbital momentum remains even when the 5D term is split by the crystal field. As a consequence faster NMR relaxation is expected for the ferrous ion, which may help to establish the correspondence between NMR lines and the valency of iron. Yanai *et al.*⁹ measured the relaxation of several NMR lines, no such analysis was attempted, however.

The dynamics of the charge carriers for temperatures be-

low T_V is also unclear. From an early study of the nuclear magnetic relaxation in magnetite Mizoguchi and Inoue⁶ deduced that above 80 K the charge carriers move with the frequency higher compared to the NMR frequency. This conclusion was based on an indirect evidence, as they were unable to observe the spectra of iron on the B sites above 14 K and only the relaxation of Fe on A sites was studied in the whole temperature range.

The electric conductivity above T_V has been explained by Ihle and Lorenz⁷ as a superposition of small polaron band and hopping conductivities. These authors believe that due to a strong intersite Coulomb interaction a considerable short-range order of Fe^{2+} and Fe^{3+} persists above T_V .

In the present paper the temperature dependence of ^{57}Fe NMR in magnetite is studied by the spin-echo method between 4.2 and 135 K. There exist several earlier measurements of this dependence,^{8,9} but we succeeded in registering all lines detected at the liquid-He temperature also at higher temperatures up to T_V . At the liquid He temperature the nuclear spin-spin and spin-lattice relaxations were also determined. To ascertain whether a short-range order exists above T_V and whether below T_V some of the charge carriers give rise to the motionally narrowed spectrum, the NMR close to the Verwey temperature was measured.

II. EXPERIMENTAL

In most of the experiments a synthetic Fe_3O_4 single crystal with $T_V=121.5$ K was used. Measurements at 4.2 K were repeated using a high-purity synthetic Fe_3O_4 single crystal with $T_V=123.9$ K, for which also NMR spin-lattice relaxation time T_1 was determined. Very pure crystal is prepared from iron oxide, which is obtained from the decomposition of pure iron oxalate. The crystals were grown by a floating-zone technique using a homebuilt mirror furnace.¹⁰ NMR spectra were measured by the spin-echo method using the phase-coherent spectrometer with an averaging technique

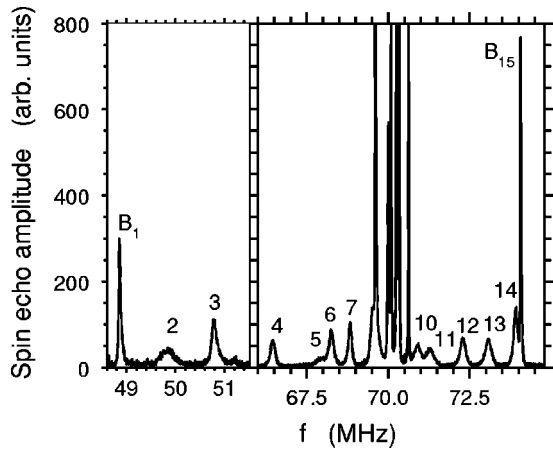


FIG. 1. NMR spectrum of ^{57}Fe in Fe_3O_4 single crystal obtained at 4.2 K.

and the complex Fourier transformation. The measurements were made at zero external magnetic field. The high rf power was used in order to excite only the signals from the domains. At 4.2 K the NMR spectra of both samples were very similar. We did not attempt to anneal the crystals in an external field, where the treatment is known to make the specimen untwinned and leads to narrowing of the NMR lines.^{1,9} The signal-to-noise ratio was significantly improved by using the Carr-Purcell pulse sequence.¹¹ Spin-spin relaxation time T_2 can be then determined from the decrease of the spin-echo amplitude in the echo series. This may be performed for every value of the excitation frequency. The spin-lattice relaxation time T_1 was determined from the dependence of the maximum of the amplitude of the line in question on the repetition time of the two-impulse spin echo. We found, however, that neither spin-spin nor spin-lattice relaxation are strictly exponential.

III. RESULTS

The spectrum measured at 4.2 K is shown in Fig. 1. In Fig. 2 the region of the intensive Fe(A) lines is presented. The resonance frequencies as well as the lineshapes are very close to the ones observed by Mizoguchi.¹ The spectrum at 121 K is shown in Fig. 3, while the region of Fe(A) lines at 118 K is displayed in Fig. 4. It is seen that at 4.2 K the line

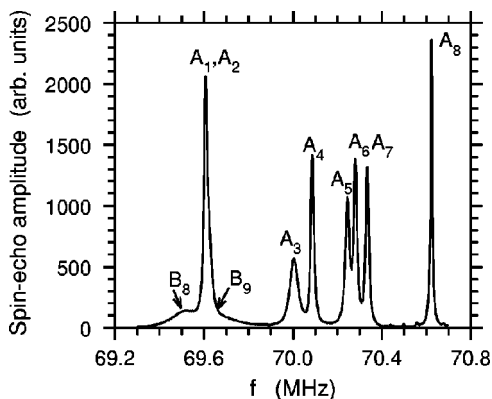


FIG. 2. Region of $\text{Fe}^{3+}(\text{A})$ lines at 4.2 K.

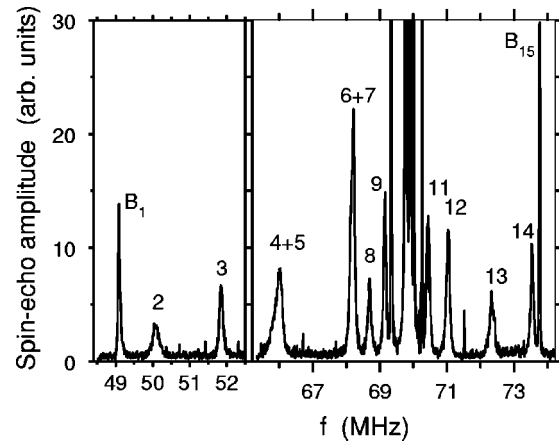


FIG. 3. NMR spectrum of ^{57}Fe obtained at 121 K.

B_9 , and partially also B_8 , are masked by intensive lines A_1 , A_2 . At elevated temperatures, due to the steeper temperature dependence of the resonance frequency, B_8 and B_9 lines come out of the Fe(A) spectrum, while B_{10} and B_{11} lines occur within it. The temperature dependence of the NMR frequencies is shown in Fig. 5. The resonance frequency, linewidth, and relaxation times of the NMR lines at the liquid He temperature are summarized in Table I. In order to compare the intensity of the NMR lines we performed a standard f^2 correction of the spectrum. Moreover, we also took into account the fact that T_2 is different for different lines and reconstructed the spectrum in the limit $\tau \rightarrow 0$, where τ is the time interval between the exciting and refocusing radio frequency pulses. In Table I the areas S under the lines of such reconstructed spectrum are given. T_1 , T_2 , and S for the line B_9 could not be reliably determined, hence these values are omitted. Because the f^2 correction is only a rough approximation to the frequency dependence of the spin-echo amplitude and because the relaxation is not strictly exponential the values of S should be taken with some caution. Nevertheless, we can conclude with some confidence that the line at 69.606 MHz is a double line. It retains the doubled intensity also at higher temperatures as clearly seen in Fig. 4. With possible exception of the line A_3 , relative intensities of the NMR lines are similar ($0.79 < S < 1.21$) indicating that the lines originate from the same number of ^{57}Fe nuclei.

Above T_V the spectrum is reduced to two lines as ex-

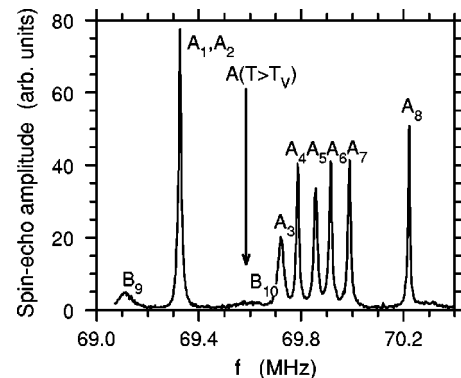


FIG. 4. Region of $\text{Fe}^{3+}(\text{A})$ lines at 118 K. The arrows indicate the frequency of eventual motionally narrowed spectrum.

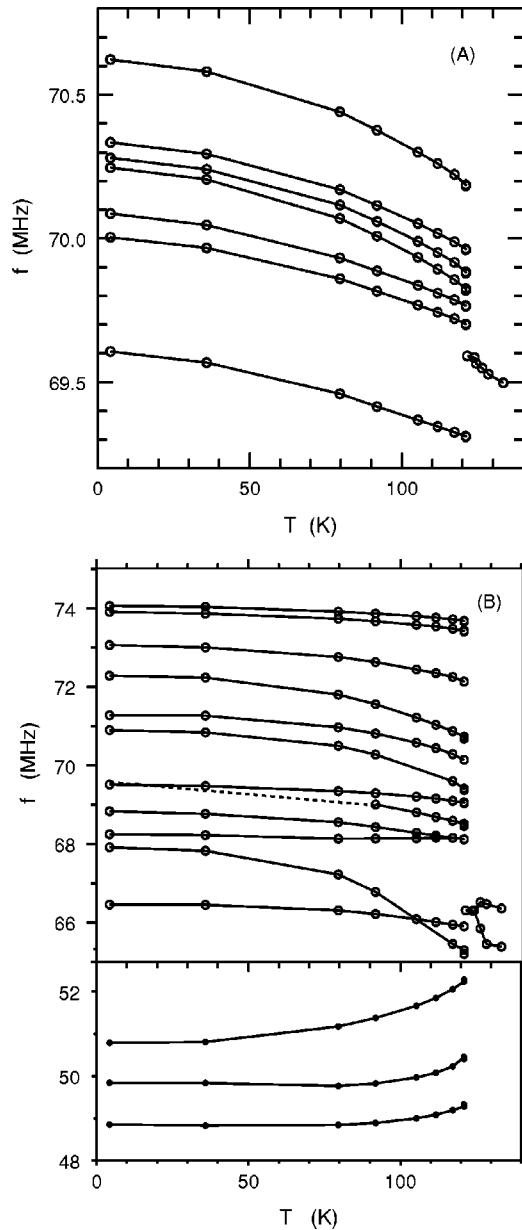


FIG. 5. Temperature dependence of the NMR frequency of lines corresponding to Fe on tetrahedral (A) and octahedral (B) sites.

pected for the cubic symmetry and magnetization along the $\langle 100 \rangle$ direction. The very narrow line at 69.590 MHz corresponds to Fe^{3+} ions on the A sites, while $\text{Fe}(B)$ ions give rise to the line at 66.297 MHz. At ≈ 125 K the system undergoes a $\langle 100 \rangle \rightarrow \langle 111 \rangle$ spin reorientation transition, which leads to the splitting of the $\text{Fe}(B)$ line to two lines with ideal intensity ratio 1:3. The line at lower frequency corresponds to the B sites for which the local trigonal axis is parallel to the magnetization, while the remaining B sites give rise to the higher frequency line. The development of the NMR spectrum above T_V is shown in Fig. 6.

IV. DISCUSSION

First we discuss the spectra in the vicinity of the Verwey transition. The eventual presence of the short-range order

TABLE I. Resonance frequency f_{res} , linewidth Δ , spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 , and area S of NMR lines in magnetite at 4.2 K.

Line	f_{res} (MHz)	Δ (MHz)	T_1 (s)	T_2 (ms)	S (arb. units)
B1	48.856	0.044	6.6	59.2	1.19
B2	49.839	0.340	7.1	16.2	1.16
B3	50.783	0.125	5.4	7.4	1.05
B4	66.459	0.178	10.6	12.3	0.94
B5	67.900	0.310	10.9	14.9	0.90
B6	68.249	0.188	8.5	27.8	1.09
B7	68.840	0.124	10.3	7.3	0.83
B8	69.507	0.086	7.4	22.5	0.95
B9	69.630	≈ 0.2			
B10	70.900	0.225	8.2	7.8	0.94
B11	71.285	0.287	9.2	9.0	0.79
B12	72.292	0.188	8.2	11.7	0.88
B13	73.071	0.215	8.2	16.8	0.99
B14	73.908	0.065	7.8	97.4	1.11
B15	74.061	0.031	6.5	220.9	1.03
A1 + A2	69.606	0.019	7.9	197	2.42
A3	70.004	0.040	8.3	273	1.48
A4	70.087	0.015	7.9	240	1.20
A5	70.245	0.028	7.8	161	1.08
A6	70.280	0.017	7.8	201	1.13
A7	70.334	0.015	7.8	239	1.17
A8	70.622	0.009	7.6	446	1.12

above T_V is best demonstrated using the intensive and sharp spectra of the A sites. The inspection of Fig. 6 reveals only a single $\text{Fe}(A)$ line and no remnants of the low-temperature NMR spectrum. Consequently no static short-range order is present above T_V . However, there may be a short-range order which fluctuates with the frequency higher than the NMR frequency.

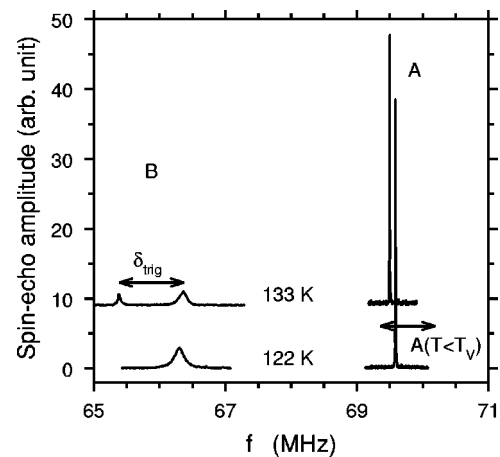


FIG. 6. NMR spectrum of ^{57}Fe in Fe_3O_4 single crystal above the Verwey temperature $T_V = 121.5$ K. At 122 K the magnetization is along $\langle 100 \rangle$ and the leftright arrow indicates the region of the $\text{Fe}(A)$ spectrum for T below T_V . At 133 K the magnetization is along $\langle 111 \rangle$ direction. δ_{trig} is the splitting caused by the trigonal anisotropy of the hyperfine field.

Within the sensitivity of our measurement the NMR spectrum retains its character in the whole temperature interval $4.2 \text{ K} \leq T < T_V$, in particular there is no trace of the motionally narrowed Fe(A) spectrum close to T_V (Fig. 4). As the charge carriers are believed to be localized at low temperatures, we conclude that for all temperatures below T_V the charge carriers either remain localized, or at least they move with the characteristic time much longer compared to the characteristic time of the NMR measurement ($1.5 \times 10^{-8} \text{ s}$).

The NMR frequency f is connected with the effective magnetic field \vec{B} by

$$f = \gamma |\vec{B}| / 2\pi, \quad (1)$$

where γ is the gyromagnetic ratio. \vec{B} is the sum

$$\vec{B} = \hat{A} \vec{\mu} + \vec{B}_{\text{dip}}. \quad (2)$$

\hat{A} and $\vec{\mu}$ are the hyperfine coupling tensor and the electronic magnetic moment, respectively. The temperature dependence of f below the Verwey transition is connected with the change of both \hat{A} and $\vec{\mu}$. While $|\vec{\mu}|$ decreases monotonously with the increasing temperature, $\hat{A}(T)$ reflects the temperature dependence of the ordering parameter p and for inequivalent sites it may have different character. Above T_V $p=0$ and there is only one Fe(B) line at $f_B(T_V) = 66.297 \text{ MHz}$. It is therefore not surprising that for Fe(B) lines with $f < 53 \text{ MHz}$ $\hat{A}(T)$ dependence dominates and the frequency of these lines increases with increasing temperature. $f(T)$ of the line B5 (Fig. 5) is of interest. For $T \geq 100 \text{ K}$ its frequency is lower than $f_B(T_V)$, while it is higher at low temperatures. This behavior may be understood if we take into account that there are several different ordering parameters, one concerns the crystal structure, the other corresponds to the ordering of iron valencies (this is an oversimplification as more ordering parameters are involved¹²). NMR frequencies observed below T_V reflect only the change of the crystal structure¹³ and μ and they are not influenced by eventual decrease of the valency ordering. The static change of the valency ordering would result in broadening of the lines, while the dynamic change connected with the hopping would produce a distinct, motionally narrowed spectrum, which is not observed.

We now turn to the problem of the crystal symmetry and ordering of iron valencies below T_V . The monoclinic cell of Fe_3O_4 contains 32 formula units with 32 A and 64 B sites, which numbers are reduced by Cc symmetry to 8 A and 16 B crystallographically inequivalent sites. For magnetization along [001] (easy direction of magnetization at low temperatures) the presence of magnetization does not reduce the symmetry, so there are 8 and 16 magnetically inequivalent iron ions on A and B sites, respectively. As a consequence, using the symmetry only, 16 Fe(B) and 8 Fe(A) lines are predicted in the NMR spectrum below T_V . Indeed we observed eight lines corresponding to Fe^{3+} ions on the A sites, but one of the Fe(B) lines is missing. It might be, however, hidden in the intensive Fe(A) spectrum (cf. rather large intensity of line A3 in Table I). Though further effort to find

the missing B line is desirable, we can conclude that the NMR spectra observed below T_V are in accord with the Cc symmetry of magnetite. In this context the fact that we have observed the B9 line is important. Note that its existence could only be ascertained by careful measurement of the temperature dependence—this is the reason why only 14 B lines were found earlier.¹

As half of the B sites is occupied by $3+$ and other half by $2+$ iron, eight of the Fe(B) lines should correspond to Fe^{3+} and eight to Fe^{2+} ions. This contradicts Mizoguchi,¹ who ascribed only five of the B lines to the ferric ions, consequently his ordering scheme of iron valencies cannot be reconciled with the Cc symmetry. The main basis of the Mizoguchi ordering scheme comes from the measurement of the angular dependence of the five NMR lines ascribed to the $\text{Fe}^{3+}(B)$ ions. The magnitude of corresponding anisotropy of the resonance frequencies is larger than 2.5 MHz, at least for some of the lines. Above T_V we found that the anisotropy caused by the trigonal local distortion of the octahedral sites is 1.2 MHz (it is equal to 9/8 of the splitting δ_{trig} between Fe(B) lines in Fig. 6). Below T_V the magnetic moment increases by $\approx 1\%$ only and the increase of the trigonal anisotropy by more than a few percent would be surprising. The anisotropy connected with the trigonal distortion is thus only smaller part of the anisotropy found in Ref. 1. This contradicts one of the assumptions made by Mizoguchi when analyzing the angular dependence, explaining therefore why his proposal for the ordering may be incorrect.

A conspicuous feature of the spectra observed is the doubling of the lowest frequency Fe(A) line. As this line is not broadened when the temperature is increased, we can conclude with some confidence that two formally inequivalent Fe^{3+} ions, which give rise to this line, have nearly the same oxygen environment and also their effective exchange fields H_{exch} are equal. Analysis of the line shape shows that the difference of H_{exch} larger than 2% would already lead to detectable splitting of the line. Equality of H_{exch} means that also the cation environment of the two sites in question must be very similar, requiring the same number of nearest $\text{Fe}^{3+}(B)$ and $\text{Fe}^{2+}(B)$ neighbors and very close geometry of the Fe(B)- O^{2-} - $\text{Fe}^{3+}(A)$ triads. This provides a stringent condition for the arrangement of iron valencies on the B sublattice. Until now all models of this arrangement make use of the Anderson condition for the short-range ordering,¹⁴ which states that in every tetrahedron formed by nearest-neighbor B sites there are two Fe^{3+} and two Fe^{2+} ions. As showed by Zuo *et al.*⁴ there are only nine models (leaving out the original proposal of Verwey) which possess the Cc symmetry and comply with the Anderson condition. We made an analysis of the geometry of $\text{Fe}^{3+}(A)$ environment using the positional parameters given by Iizumi *et al.*³ Only one of the nine models—model 6 in the notation of Ref. 4—satisfies the requirement that relative positions of the oxygen ligands and the nearest B neighbors of two of $\text{Fe}^{3+}(A)$ ions is the same (model 2 is preferred by Zuo *et al.*,⁴ on the basis of the electron-diffraction study). We have to note, however, that unfortunately in order to facilitate the structural analysis Iizumi *et al.*³ assumed orthorhombic $Pmc2_1$ symmetry group and it is difficult to estimate the effect of this approximation on the calculation of the exact geometry.

Inspection of Table I reveals that the spin-lattice relaxation time T_1 is almost the same for all resonance lines and, with the exception of three lines, also T_2 of the B lines has the same order of magnitude. This does not correspond to the usual situation, when Fe^{2+} relaxation is much faster, and it indicates that there may be a strong mixing of $3d^5$ electron configuration of $\text{Fe}^{3+}(B)$ with the $3d^6$ configuration of $\text{Fe}^{2+}(B)$. Such strong mixing is further supported by a bond-length analysis, which we performed using the structure data of Ref. 3. For the nine models of the valency ordering, which satisfy both the Anderson condition and the Cc symmetry, the ionic radii of $\text{Fe}^{2+}(B)$ and $\text{Fe}^{3+}(B)$ were calculated. The result is surprising—within all models the difference of these radii ΔR_{ion} is very small (maximal $\Delta R_{\text{ion}}=0.01 \text{ \AA}$), contrasting with $\Delta R_{\text{ion}}=0.135 \text{ \AA}$ calculated using the conventional ionic radii of $\text{Fe}^{2+}(B)$ and $\text{Fe}^{3+}(B)$ as given in Ref. 15.

V. CONCLUSIONS

The analysis of the NMR spectra below and around the Verwey transition brought several significant results. Above T_V the spectra reveal that if the short-range order exists for $T > T_V$ it must fluctuate rapidly. Below T_V we showed that the NMR spectra are in accord with the Cc symmetry and the reason was given why the earlier analysis¹ of these spectra may be incorrect. Finally, and perhaps most importantly, the NMR relaxation results and also the bond length analysis indicate that below T_V the states of iron ions on the B sublattice are mixed so strongly that the notion of 2+ and 3+ valency may lose its meaning.

ACKNOWLEDGMENTS

This work was supported by Grants No. 202/97/1018 and 202/97/P070 of the Grant Agency of the Czech Republic and by Grant No. GAUK 25/97/B-FYZ/MFF.

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