Earth Planets Space, **61**, 125–131, 2009

Frequency and field dependent susceptibility of magnetite at low temperature

Özden Özdemir[1], David J. Dunlop[1], and Michael Jackson[2]

[1]*Geophysics, Department of Physics, University of Toronto, Toronto M5S 1A7, Canada*
[2]*Institute for Rock Magnetism, University of Minnesota, Minneapolis, MN 55455, USA*

(Received December 28, 2007; Revised April 3, 2008; Accepted May 17, 2008; Online published January 23, 2009)

We report the temperature dependence of in-phase and quadrature susceptibilities, k' and k'', between 20 K and 300 K for a stoichiometric natural single crystal of magnetite. Measurements were made for amplitudes of the AC driving field ranging from $H = 30$ A/m to 2 kA/m and frequencies ranging from $f = 40$ Hz to 4 kHz. In cubic magnetite above the Verwey transition, $T_V = 120$ K, k' is limited by self-demagnetization and does not vary greatly with T, H or f. As the crystal cools through T_V and transforms to monoclinic structure, k' decreases by about a factor 2, with a further more gradual decrease of 10–20% in cooling from 40 to 20 K. Saturation remanence also drops sharply at T_V but shows no further change in cooling below 40 K. Thus it appears that domain walls remain pinned throughout the 20–40 K range but small segments undergo reversible oscillations in an AC field, the amplitude of oscillation decreasing steadily with cooling below 40 K. In this same range, k'' reaches a peak, while the temperature at which k' decreases most rapidly changes with frequency. Both observations indicate that domain wall oscillations lag appreciably behind the driving field at very low temperature. Both k' and k'' increase markedly with increasing AC field amplitude below T_V. The field dependence is particularly strong below 40 K. Analysis of the $k'(f)$ data between 20 and 40 K based on an Arrhenius thermal activation equation gives a pre-exponential frequency factor $f_o \approx 2.5 \times 10^8$ s^{-1} and an activation energy $\Delta E = 0.035$ eV. The ΔE is appropriate for electron hopping but f_o suggests an indirect mechanism for wall mobility related to changes in electron ordering within walls.

Key words: Magnetite, susceptibility, low temperature, Verwey transition, frequency-dependent magnetization, field-dependent magnetization.

1. Introduction

Magnetic susceptibility, $k = M/H$, measures the response of a magnetic system to the application of a (usually weak) field H. M and H are both measured in A/m so that k is dimensionless. "SI unit" is often added as a reminder that k values are a factor 4π larger in SI than in cgs. If H is a steady field, for example the Earth's field, k is a simple number. Changing fields evoke a delayed response and k is complex: $k = k' - i\omega k''$, k' measuring the in-phase response of M to an oscillating field $He^{i\omega t}$ and k'' the 90° out-of-phase (or quadrature) response.

Response is delayed because single-domain (SD) magnetic moments and domain walls in multidomain (MD) grains have finite response times, ranging upward from $\sim 10^{-9}$ s, the minimum set by activation of a single atomic moment. Changes in magnetic remanence M_r require complete reversal of SD moments or large irreversible jumps of domain wall segments, whereas reversible changes of M in response to small-amplitude field changes involve only small excursions of SD moments or wall segments. For this reason, response times affecting susceptibility are generally much less than relaxation times for weak-field remanence changes. The quadrature susceptibility k'' is therefore typically 1–2 orders of magnitude smaller than the in-phase susceptibility k'. Only in very small quasi-superparamagnetic grains are k'' and the dependence of M on frequency $f = \omega/2\pi$ closely related to viscous changes in M_r with time t (Mullins and Tite, 1973).

The dependence of susceptibility on temperature T is useful in detecting variations in magnetic anisotropy and magnetostriction, both continuous and discontinuous. Examples of the latter are Hopkinson peaks in k near structural transitions like the Curie point and the Verwey transition ($T_V = 120$ K) where magnetite transforms from cubic to monoclinic symmetry (Clark and Schmidt, 1982).

In a study of titanomagnetites ranging in composition from magnetite (TM0) to TM60, Moskowitz *et al.* (1998) found that the changing distribution of Fe^{2+}, Fe^{3+} and Ti^{4+} on the magnetic sublattices profoundly affects $k(T)$ at low temperatures. Step-like increases in k' during heating of a synthetic magnetite crystal occurred at 40–50 K and 120–125 K. The latter step coincides with the Verwey transition, which is prominent also in SIRM heating curves. The lower-temperature step has no matching remanence transition. Unlike the 120–125 K step, it is frequency dependent, shifting from ≈40 K when $f = 40$ Hz to ≈50 K at 1 kHz, and is accompanied by a peak in k''.

Muxworthy (1999) found similar $k(T)$ variations for dispersed hydrothermal magnetite crystals with mean sizes of 76 and 108 μm. The increases in k' are less step-like than for Moskowitz *et al.*'s single crystal, perhaps because the angle between the monoclinic easy axis and H varies from

crystal to crystal. The k' increases from 118–126 K were slightly frequency dependent but the temperature shift was only ≈1 K for a 2-decade change in f (from 40 Hz to 4 kHz).

In the study by Kosterov (2003), only crushed 100–150 μm natural magnetites showed clear double step increases in k' at low T. In contrast to previous studies, the upper step, between 120 and 125 K, had an associated Hopkinson peak around 135 K, close to the isotropic temperature of cubic magnetite. The lower step, from 15–30 K, had no peak on the upper side, only a slightly descending plateau extending from 30 up to 120 K. The ∼50 K "peak" mentioned by Moskowitz *et al.* (1998) and Muxworthy (1999) is in neither case very marked, merely the upper termination of a rapid increase occurring at lower T (in Kosterov's data, 15–30 K). Kosterov (2003) also demonstrated frequency dependence of k' around 30 and 117 K, amounting to a 10–15% difference in k' for a change in f from 10 Hz to 1 kHz at fixed T.

The present study was undertaken to study the dependence of k' and k'' on both frequency f (40 Hz to 4 kHz) and amplitude H (30 A/m to 2 kA/m) of the driving AC field. The role of field amplitude has only rarely been investigated in prior work (Jackson *et al.*, 1998; Balanda *et al.*, 2005). In an attempt to reconcile conflicting observations about rapid increases and peaks in k' and k'' at and below 50 K in MD magnetite, we chose to examine a stoichiometric natural single crystal of magnetite. Previous studies have used synthetic crystals (Walz *et al.*, 1982; Moskowitz *et al.*, 1998; Skumryev *et al.*, 1999; Balanda *et al.*, 2005; Janů *et al.*, 2007) or dispersions of crystals or crushed fragments of larger grains (Muxworthy, 1999; Kosterov, 2003). Our results are likely to be representative of natural MD magnetites. Cooling in zero field through T_V, as we did, does not suppress monoclinic twinning. However, dispersion of easy axes with respect to the subsequently applied field is considerably reduced compared to that of random grain assemblages.

2. Sample Characterization and Experiments

Our sample is a natural 1.7 mm octahedral magnetite single crystal (Özdemir, 2000), a sister crystal to the one studied by Özdemir and Dunlop (1999). The ⟨111⟩ crystal faces are flat and smooth with no indication of deformational twinning. The spinel unit cell edge determined by X-ray diffraction with Cu-Kα radiation is 8.399±0.002 Å, in close agreement with the standard value of 8.396 Å for pure magnetite. From the variation of k' at high T, measured with a Kappabridge in flowing argon gas, the Curie temperature was estimated to be 578°C. Element analyses using a Cameco SX-50 electron microprobe gave 72.36±0.23 weight% Fe, close to the theoretical 73.6%, and 27.5±0.01 weight% O. Al, Mn, Ti, Cr, Ni, Mg and Co concentrations ranged from 0.08 to 0.002 weight%.

The crystal is stoichiometric magnetite with no significant impurities. The crystal was given a saturation isothermal remanent magnetization (SIRM) in a 2.5 T field at 5 K, then warmed to 300 K in zero field while the magnetization was monitored using an MPMS2 SQUID magnetometer. A sharp decrease in remanence at 120 K marking the Verwey transition also indicates that the crystal is stoichiometric magnetite.

Hysteresis measured at 300 K with a Princeton Measurements MicroVSM yielded a value of 92.8 A m^2/kg for saturation magnetization M_s, identical to that of pure magnetite. The reduced SIRM M_{rs}/M_s was 0.002 and the ratio H_{cr}/H_c between remanent and induced coercive forces was 41. These values and the ramp-like shape of the hysteresis curve are characteristic of large MD structure with many easily mobilized domain walls. At 120 K, Özdemir (2000) measured a wasp-waisted hysteresis loop, indicating a mixture of soft cubic and hard monoclinic phases.

In the main sequence of experiments, AC susceptibility was measured at ≈10 K intervals from 20–300 K with a LakeShore 7130 cryogenic susceptometer. The field was not applied along a particular crystal axis. Heating/cooling between measurement temperatures was in zero field. At each T, k' and k'' were measured at frequencies of 40, 140, 400 and 1000 Hz for fields of 30, 100, 300, 1000 and 2000 A/m (0.4 to 25 Oe, approximately). Measurements were made at 4000 Hz for fields of 30 and 100 A/m only. In a sinusoidally varying field $H = Re\{He^{i\omega t}\}$, the magnetic response $M(t)$ is determined by factors that include the field dependence $k(H)$ as well as the time/frequency dependence of M. As explained earlier, the phase difference between M and H is usually described in terms of in-phase and quadrature components k' and k''. However, if $k(H)$ is not constant, i.e., $M(H)$ is nonlinear, $M(t)$ will not be a simple sine function but will contain higher harmonics. The lock-in amplifier of the Lakeshore susceptometer can be set to measure at the AC field frequency or higher multiples; all measurements in this study were made at the first harmonic ($f_{meas} = f_{AC} = f$).

3. Experimental Results

Figures 1–5 illustrate typical results selected from the 22 combinations of field amplitude H and frequency f examined. Figure 1 shows the temperature variation of k' measured at $f = 40$ and 400 Hz for five field amplitudes from 30 A/m to 2 kA/m. At either frequency, k' is almost independent of both T and H between 124 K and room temperature. As the crystal transforms from cubic to monoclinic across the Verwey transition (between 125 and 115 K for $f = 400$ Hz), k' drops by a factor of ≈2. Below T_V, k' levels out in a second plateau from 105 to 40 K, then drops a further 15–20% between 40 and 20 K. The 20–40 K step is not seen in SIRM data but is unmistakable in the susceptibility. There is a marked field dependence of k' below T_V, in both plateau and step regions. For fixed f and T, k' increases by about 15% for each decade increase in H. This is a weaker dependence than expected from the Rayleigh law, $M = aH + bH^2$, which predicts an increase $k' = a + bH$ in proportion to H, not log H.

In Fig. 1, the Verwey transition is expressed at slightly lower T when k' is measured at 40 Hz rather than 400 Hz. The 20–40 K step in k' is also frequency dependent. Plotting k' vs. T for a fixed field (30 A/m in Fig. 2) over the full range of f from 40 to 4000 Hz makes this easier to see. As f changes from 4 kHz to 40 Hz at $T = 30$ K, for example, k' increases in 4 steps averaging 15% per decade of f

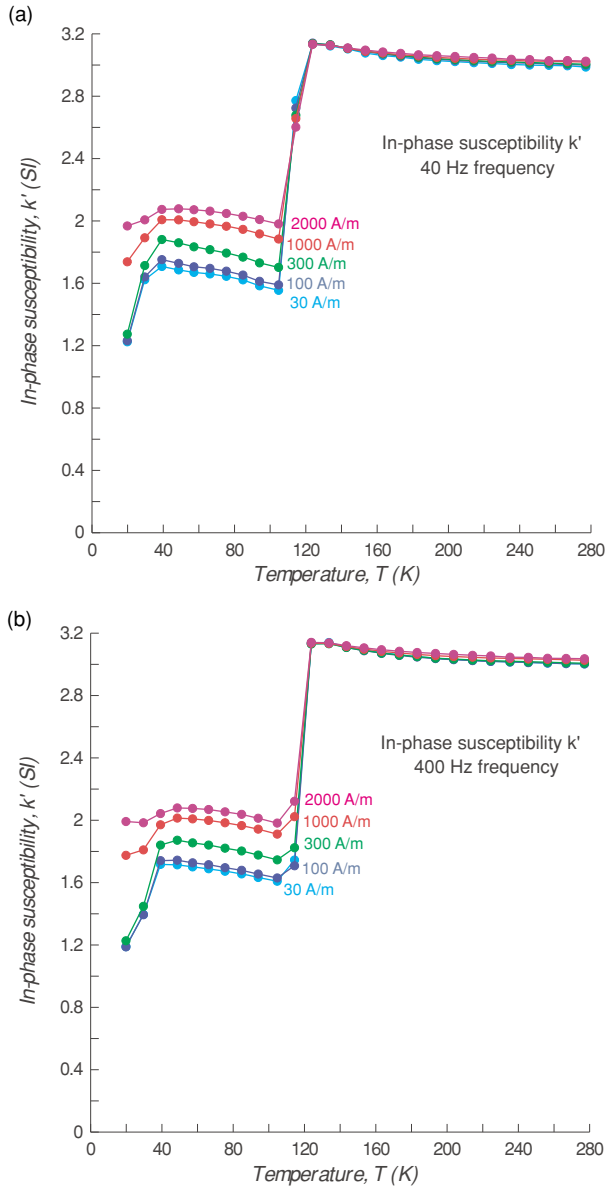

Fig. 1. Variation of in-phase susceptibility k' with temperature for fields from 30 A/m to 2 kA/m at frequencies of (a) 40 Hz and (b) 400 Hz. There is a noticeable dependence of k' on field at and below the Verwey transition T_V but k' is independent of the field used above T_V.

(Fig. 2(b)). The frequency dependence is much smaller in the plateau regions from 40 to 105 K and above T_V from 125 to 300 K (Fig. 2(a)), but is appreciable at the Verwey transition itself for the two lowest frequencies, 40 and 140 Hz (Fig. 2(c)). Because measurements are made at 10 K intervals, it is entirely possible that the entire change across the Verwey transition is confined to the interval 113–117 K for all frequencies, i.e., the frequency dependence of T_V may not be as marked as it appears to be in Fig. 2(c).

In Fig. 3 we plot the parameter $[k'(1\ \text{kA/m}) - k'(30\ \text{A/m})]\ /\ k'(30\ \text{A/m})$, a measure of the field dependence of k', vs. T for $f = 40$, 140, 400 and 1000 Hz. The field dependence is very nearly zero above T_V, increases to 15–20% in monoclinic magnetite below T_V, and again increases sharply below 40 K, reaching 40–50% at 20 K. The field dependence transitions and the regions of rapidly

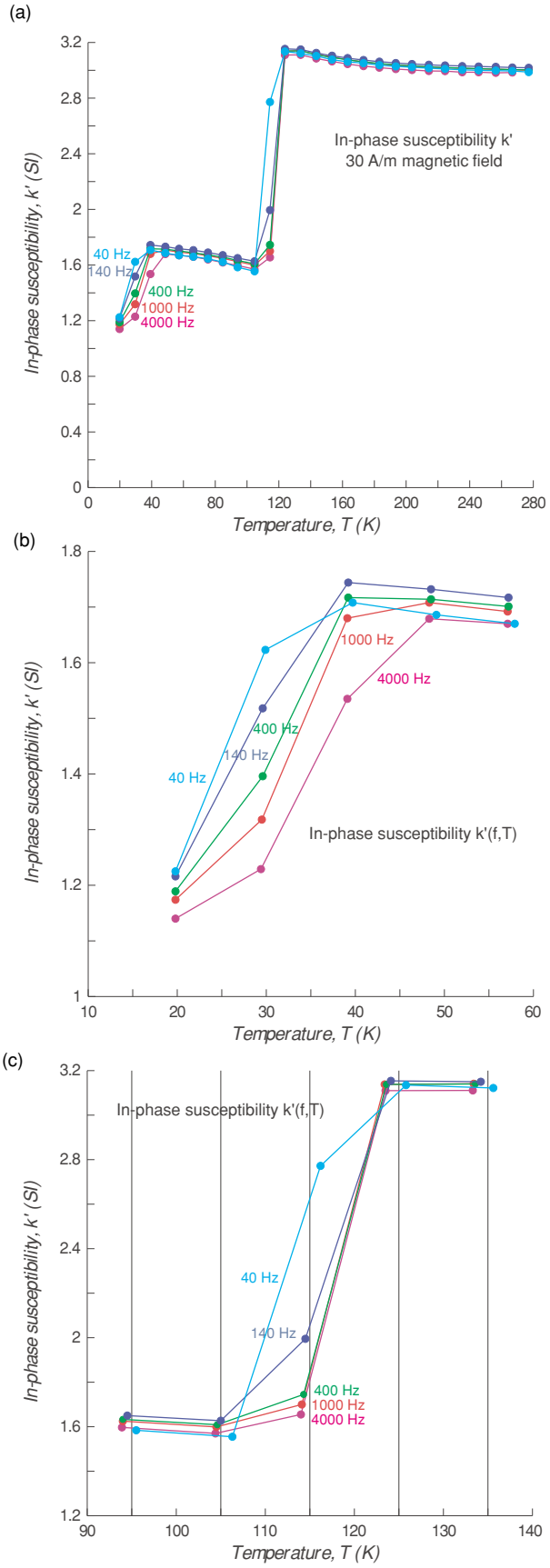

Fig. 2. Variation of in-phase susceptibility k' with temperature for frequencies from 40 Hz to 4 kHz and a field of 30 A/m. The dependence of k' on frequency at and below the Verwey transition is shown in expanded views (b) between 20 and 60 K and (c) between 95 and 135 K.

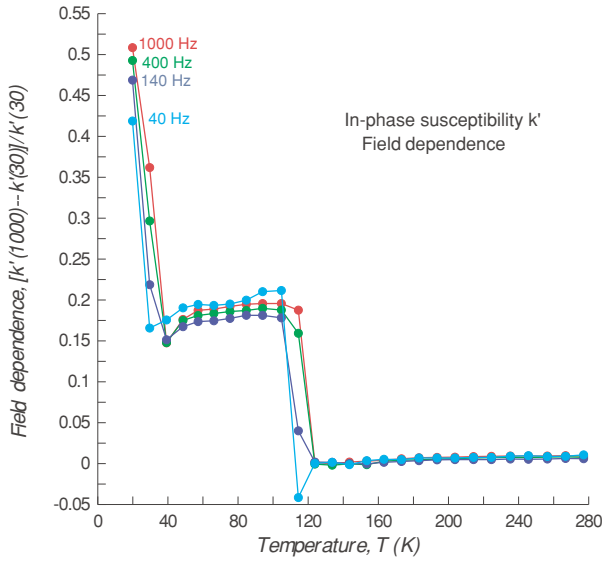

Fig. 3. The field dependence of k' as represented by the parameter $[k'(1000\ \text{A/m}) - k'(30\ \text{A/m})]/\ k'(30\ \text{A/m})$ as a function of temperature for frequencies of 40 Hz to 1 kHz. The field dependence below T_V is strong, particularly below 40 K.

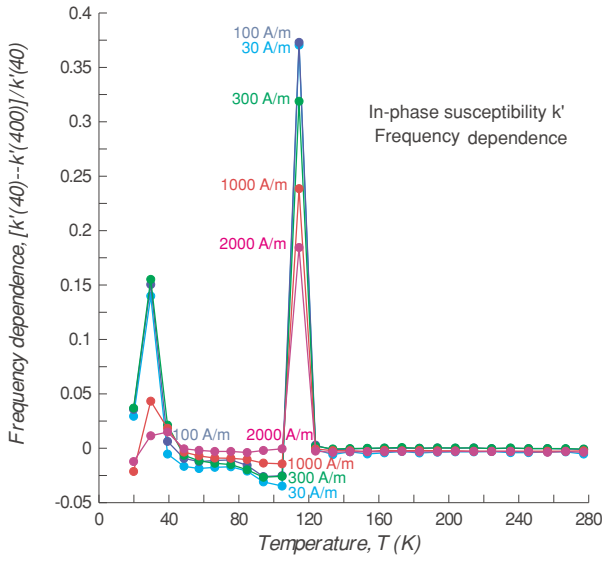

Fig. 4. The frequency dependence of k' as represented by the parameter $[k'(40\ \text{Hz}) - k'(400\ \text{Hz})]/\ k'(40\ \text{Hz})$ as a function of temperature for fields of 30 A/m to 2 kA/m. The frequency dependence peaks sharply between 25 and 35 K and at the Verwey transition but is near zero for all other temperature ranges.

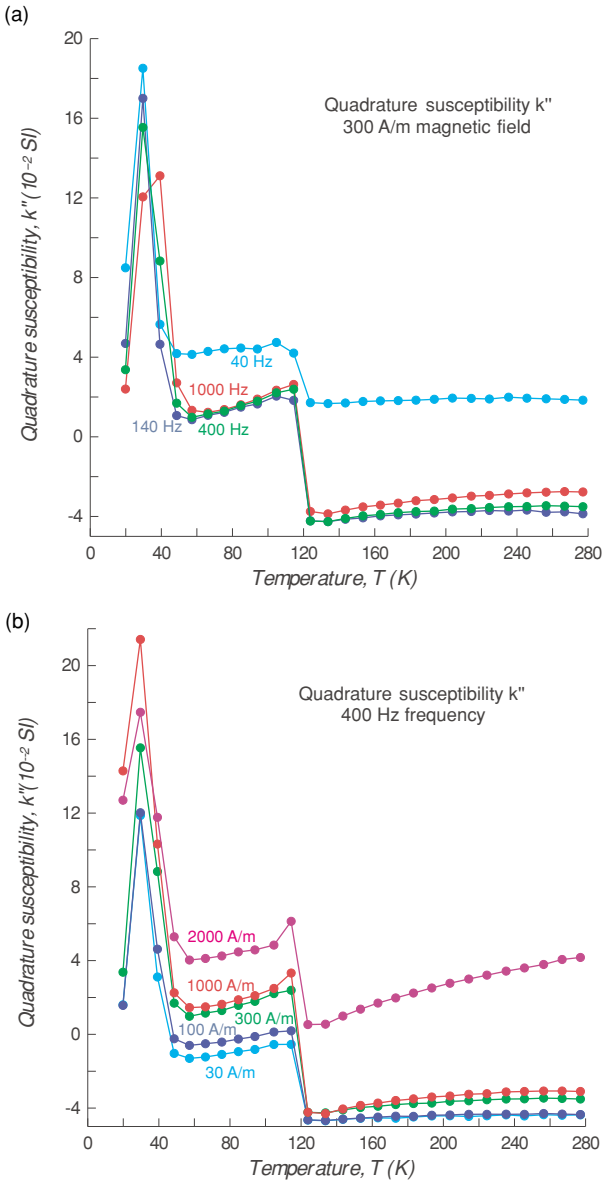

Fig. 5. Quadrature susceptibility k'' as a function of temperature. (a) Dependence of k'' on frequency from 40 Hz to 1 kHz at a field of 300 A/m. (b) Dependence of k'' on field from 30 A/m to 2 kA/m at a frequency of 400 Hz. In both diagrams, k'' peaks sharply around 30 K, has near-zero values between 50 and 110 K, and changes abruptly across the Verwey transition. The k'' peak is in the same temperature range where k' is strongly frequency dependent; the minor k'' peak at T_V also corresponds to a region of strong k' frequency dependence (Fig. 4).

changing k' precisely coincide.

The parameter $[k'(40\ \text{Hz}) - k'(400\ \text{Hz})]/\ k'(40\ \text{Hz})$ is a measure of the frequency dependence of k'. It peaks at 30 K and 120 K (Fig. 4), exactly the temperatures where k' undergoes step-like changes. The 120 K peak is more than twice the height of the 30 K peak, exaggerated by the sharpness of the Verwey transition and the choice of 40 Hz as the lower frequency. As pointed out above, the displacement of the 40 Hz $k'(T)$ data downward by ≈5 K compared to all other frequencies (Fig. 2(c)) may be an artifact of the relatively coarse measurement interval. The 20–40 K step in k' is more broadly distributed in both T and f. In the plateau region between 40 and 105 K, the frequency dependence parameter is zero for the strongest field used (2 kA/m or ≈25 Oe) and decreases with decreasing H. However, a best fit over all frequencies would result in positive values of the frequency-dependence parameter over this T interval (cf. Fig. 2(a)).

Quadrature susceptibility k'' is almost two orders of magnitude weaker than k' except near 30 K, where it has a pronounced peak for all fields and frequencies (Figs. 5(a), (b)). Ignoring the 40 Hz data, which diverge from those for other f, the frequency dependence of k'' is subdued, apart from a positive dependence in and on the flanks of the 30 K peak (Fig. 5(a)). Negative values of k'' above T_V, which would

imply that M leads H rather than lagging it, may be an instrumental artifact.

Like k', k'' has a pronounced field dependence (Fig. 5(b)). Even discounting the 2 kA/m data, which are discordant with other results, k'' clearly increases with increasing H, above as well as below T_V. During its increase in the 50–105 K range, k'' changes from negative for $H = 30$ and 100 A/m to positive for 300 and 1000 A/m.

4. Discussion

Between 125 and 300 K, k' and k'' are almost independent of T and f; k'' increases somewhat with increasing H but k' does not. This region has been found to be featureless for MD magnetite in previous studies of $k'(T)$, the relaxation of k' in the $t = 1$–18 s range (Walz *et al.*, 1982), and viscous changes in M in the 50–2500 s range (Muxworthy and Williams, 2006). The flat response means that k' has reached the limit $1/N$, where N is the temperature-independent demagnetizing factor. Using a long cylindrical sample to reduce N and raise the self-demagnetization limit $k' = 1/N$, Skumryev *et al.* (1999) measured a classic Hopkinson rise in k' as T approaches the Verwey transition. The k' peak was at the isotropic point (130 K) where $K_1 \rightarrow 0$ and walls unpin en masse. Kosterov (2003) also observed a Hopkinson peak; the irregular fragments of crushed magnetite in his 100–150 μm sample have lower N values than our octahedral crystal, for which $N = 1/3$.

At the Verwey transition, centred on 115–120 K, k' decreases sharply and k'' increases. There is a slight dependence of the step temperature on f but little or none on H. The reason for the drop in k' is the massive increase in anisotropy as magnetite transforms to monoclinic structure (Abe *et al.*, 1976). Domains rotate or renucleate in new directions, and their walls are afterward much less mobile. Another factor is the similar size of magnetic domains and structural twin domains in the monoclinic phase, which inhibits free movement of domain walls (Balanda *et al.*, 2005). The crystallographic transition is sharp (Walz and Kronmüller, 1991). The temperature at which k' changes depends on f (Fig. 2(c); Muxworthy, 1999) because of the delay time for walls to react to a changing field: when excited at higher f, the walls take longer to respond. The positive values of k'' just below T_V, showing that M lags H by a (small) phase angle $\varphi = \tan^{-1}(k''/k')$, support this idea.

Between 40 and 105 K there is a quasi-plateau in k' and k'': k' descends slightly with increasing T while k'' rises gently (to a minor peak at 115 K for 400 and 1000 Hz). Balanda *et al.* (2005) report a similar plateau between 60 and 120 K. Both k' and k'' are field dependent in this range but frequency independent. Magnetic relaxation or $k'(t)$ spectra (Walz *et al.*, 1982) are also flat in this range, although magnetic viscosity rises to a substantial peak just below T_V (Muxworthy and Williams, 2006).

The marked dependence of k' on H in this T interval implies that the region of linear field behavior is more limited in monoclinic magnetite than in cubic magnetite above T_V. The limit is reached when $k' = a + bH$ becomes noticeably larger than the field-independent initial susceptibility a. A generous estimate would be $H = a/b$, for which $k' = 2a$, but whatever fraction is deemed reasonable for the second Rayleigh term, the limit field is $\sim a/b$. Now a/b is akin to an inverse Koenigsberger ratio, $1/Q$, because larger b corresponds to larger remanence (in the weak-field region, $1/2\,bH^2$). The effective magnetic grain size of magnetite decreases in cooling through T_V (Muxworthy, 1999; Dunlop, 2002; Özdemir *et al.*, 2002), i.e., grains which are MD in the cubic phase become more SD-like in the low-T monoclinic phase. Thus Q should increase below T_V, and the field a/b above which k' grows with increasing H should decrease, as we observe. (The Rayleigh law predicts that $\Delta k' = k'(H_2) - k'(H_1) = b(H_2 - H_1)$, proportional to H, not log H as measured (Fig. 1). However, the Rayleigh law concerns differential susceptibility, dM/dH; $k' = M/H$ as measured by the susceptometer varies more slowly with H.)

The field dependence of k'' for 50 K $\leq T \leq$ 105 K is perplexing (Fig. 5(b)). Larger fields not only result in very substantial increases in k'' but also cause k'' to change sign for most frequencies. The phase angle φ is positive for stronger fields (300, 1000 and 2000 A/m) but negative for weaker fields (30 and 100 A/m: 0.4 and 1.25 Oe, approximately). Physically, $\varphi < 0$, or M leading H, makes no apparent sense; there is no equivalent of a capacitor in the response of a domain wall to a changing field.

Finally, between 20 and 40 K there is a second step in k', not as large or sharp as at T_V but with a strong dependence on both f and H. In the same range, k'' peaks sharply around 30 K for all H and all f except 1 kHz. This k' step and k'' peak were first reported by Iwauchi *et al.* (1976). Their peak shifted from $\approx$35 K for $f = 100$ kHz to $\approx$45 K at 1 MHz. The activation energy for the magnetic relaxation was 0.057 eV, similar to that for electrical conductivity (0.04 eV). They attributed both processes to electron hopping between Fe^{2+} and Fe^{3+} ions on octahedral sites, although no mechanism coupling this to magnetic changes was suggested.

There is some disagreement in the literature about the temperature range over which the k' step and k'' peak occur. Although Iwauchi *et al.* (1976) find approximately the same range we observe, their frequencies were three orders of magnitude higher than ours, which according to Fig. 2(b) should push the k' step to higher temperatures. Janů *et al.* (2007) report exactly the same range as ours, 30–40 K, but their frequencies are much lower, 1–25 Hz approximately. Skumryev *et al.* (1999) find broader k' steps and k'' peaks in the 30–50 K interval for a frequency range similar to ours (10–1000 Hz). Finally, Balanda *et al.* (2005) report, for a stoichiometric synthetic magnetite crystal, frequency-independent step decreases in k' and minor peaks in k'' at 28 K which are not seen in the other studies. They do observe frequency-dependent step increases in k' and major peaks in k'', for a frequency range of 15–1000 Hz similar to ours, but these occur between 50 and 60 K. Furthermore, only for their lowest field (1 Oe or 80 A/m) were these steps and peaks clear. At higher fields, they were subdued and above 10 Oe (800 A/m) unresolvable. Our 30–40 K k' steps and k'' peaks, on the other hand, have similar resolution for weak and stronger fields alike (30–2000 A/m; cf. Figs. 1(a), (b), 3, 4, 5(b)). Similar instrumentation was used in almost

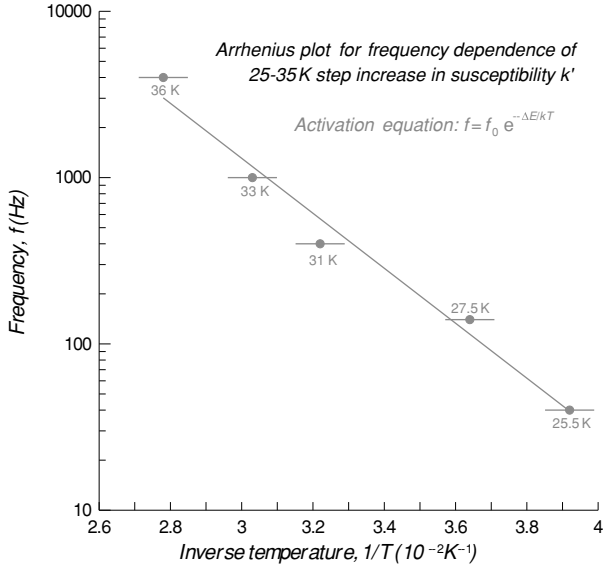

Fig. 6. An Arrhenius plot of the frequency/time dependence of the temperature at which the rate of increase in k' at very low temperatures is maximum (see Fig. 2(b)). The best-fitting regression line between log f and $1/T$ yields both the pre-exponential factor f_0 and the activation energy ΔE.

all these studies. The differences must have their source in the samples used. Magnetite's behaviour at very low temperatures seems to depend strongly on subtle differences in composition and purity, and on the method of preparation in the case of synthetic material.

We calculated an activation energy from the frequency dependence of the ~30 K step in our k' data. Assuming thermally activated increases in domain wall response with a characteristic non-thermal response time τ_o, the relaxation time τ obeys an Arrhenius law

$$\tau = \tau_o e^{\Delta E/kT} \quad \text{or} \quad f = f_o e^{-\Delta E/kT}, \qquad (1)$$

where $f_o = 1/\tau_o$. There is a distribution of activation energies ΔE, leading to distributed rather than sharp increases in k' at each f. We therefore took the midpoint temperature of each k' step in Fig. 2(b) in fitting to Eq. (1). The result is an approximately linear plot of ln f vs. $1/T$ (Fig. 6) from whose slope and intercept we find $\Delta E = 0.035 \pm 0.005$ eV and $\tau_o = 4.0 \times 10^{-9}$ s (range: 4.8×10^{-10} s to 1.8×10^{-8} s). From analysis of the temperature of the k'' peak over the 10–1000 Hz range, Skumryev *et al.* (1999) find comparable values, $\Delta E = 0.04$ eV and $\tau_o = 6 \times 10^{-9}$ s.

Our ΔE and τ_o estimates and those of Skumryev *et al.* (1999) match closely the activation energies of conduction by electron hopping at these temperatures ($\Delta E = 0.055$ eV, $\tau_o = 4 \times 10^{-9}$ s: Lenge and Kronmüller, 1984), supporting the idea advanced by previous authors (Iwauchi *et al.*, 1976; Walz *et al.*, 1982; Moskowitz *et al.*, 1998; Muxworthy, 1999) that electron mobility/valence changes within domain walls are at the root of time/frequency dependent variations in susceptibility around 30–40 K. What is not clear is the mechanism. Iwauchi *et al.* speculate that the ion sites contributing to relaxation (magnetic and also FMR, dielectric and acoustic) are those with cation vacancies. Stoichiometric magnetites show the largest 30–40 K magnetic after-effect, however. Likewise, the 28 K and 50–60 K anomalies in k' and k'' observed by Balanda *et al.* (2005) disappeared in Zn-substituted and even slightly cation-deficient magnetites. The peak in isochronal magnetic after-effect spectra (inverse $k'(t)$ differenced at two instants t) is suppressed in vacancy-doped and non-stoichiometric magnetites (Kronmüller and Walz, 1980; Walz *et al.*, 1982). After electron radiation, which introduces massive numbers of point defects, annealing eventually restores the 30 K peak (Walz and Kronmüller, 1994; Walz *et al.*, 1997). Thus point lattice defects, a typical source of wall pinning, do not seem to be directly involved.

The connection with electron hopping must be indirect because $\tau_o = 4$–6×10^{-9} s as found by Skumryev *et al.* (1999) and by us is much larger than $\tau_o \sim 10^{-12}$–10^{-11} s for the hopping process below 50 K (Muxworthy, 1999). It is more comparable to the atomic reorganization time $\tau_o \sim 10^{-10}$–10^{-9} s between independent thermal excitations of SD grains and small segments of domain walls (Dunlop and Özdemir, 1997). Kronmüller and Walz (1980) report for their 30 K magnetic relaxation maxima $\Delta E = 0.075$ eV and $\tau_o = 10^{-12}$ s, which are more consistent with a direct electron-hopping mechanism, although the activation energy is about double that found by Skumryev *et al.* (1999) and us, or the ΔE associated with conduction by electron hopping. Low-Ti titanomagnetites (TM16 and TM35) exhibit similar frequency-dependent behavior between about 50 and 100 K, for which Carter-Stiglitz *et al.* (2006) calculated a somewhat higher activation energy of ~0.1 eV. In contrast to monoclinic magnetite, these titanomagnetites experience major loss of remanence on warming through this temperature interval.

Kronmüller and Walz's proposed mechanism is rearrangement of extra electrons from Fe^{2+}, which is the main source of single-ion anisotropy in ferrites, away from the wall centre, lowering the energy and making the wall more readily moved. Mizoguchi (1985) also inferred a change in electron ordering structure in domain walls from abrupt changes in NMR line shape beginning around 26 K during heating. The anisotropy constants of monoclinic magnetite hardly change with T between 4.2 and 40 K (Abe *et al.*, 1976), so that the distribution of Fe^{2+} in the lattice generally must remain unchanged.

It remains puzzling that the displaced walls responsible for SIRM give no indication of the changes in the 20–40 K range that are so clearly expressed in susceptibility and its relaxation. Large wall displacements in SIRM require pinning by major lattice defects acting in concert, such as pile-ups of dislocations. Seemingly while average wall positions remain fixed, perhaps near monoclinic twin boundaries (Balanda *et al.*, 2005), segments of the wall oscillate more readily or with larger amplitudes as T increases from 20 to 40 K. Clearly the origin of the ~30 K step in k' is entirely different from that of the larger and sharper step at T_V, where SIRM plummets irreversibly. From a practical point of view, it is also clear that k' measurements are not a good way of distinguishing between magnetite and pyrrhotite. SIRM or M_s measurements will pinpoint pyrrhotite's 30–34 K phase transition, however (Rochette *et al.*, 1990).

5. Conclusions

We find that in cubic magnetite above the Verwey transition, k' is limited by self-demagnetization and varies rather little with T, H or f. In cooling through T_V, the crystal transforms to monoclinic structure and k' decreases by about a factor 2. There is a further more gradual decrease of 10–20% in cooling from 40 to 20 K. The fact that saturation remanence drops sharply at T_V but does not change in cooling below 40 K implies that domain walls remain pinned. Small wall segments apparently oscillate reversibly in an AC field, with the amplitude of oscillation decreasing steadily during cooling below 40 K. In this same range, k'' peaks and the temperature at which k' decreases most rapidly changes with frequency. Evidently wall oscillations lag appreciably behind the driving field at these very low temperatures, the lag being more noticeable at higher frequencies. Both k' and k'' increase markedly with increasing AC field amplitude H below T_V. The H dependence is particularly strong below 40 K. Analysis of the $k'(f)$ data between 20 and 40 K based on an Arrhenius thermal activation equation gives a pre-exponential frequency factor $f_o \approx 2.5 \times 10^8$ s^{-1} and an activation energy $\Delta E = 0.035$ eV. The ΔE is appropriate for electron hopping but f_o favors an indirect mechanism (Kronmüller and Walz, 1980), the freedom with which wall segments oscillate depending on electron ordering within the walls.

Acknowledgments. We thank the referees, Andrei Kosterov and Eduard Petrovsky, for useful comments and the staff of the Institute for Rock Magnetism (IRM) for their help. The IRM is supported by the National Science Foundation's Earth Sciences Division, the Keck Foundation, and the University of Minnesota. This is IRM contribution number 0801. The research was supported by the Natural Sciences and Engineering Research Council of Canada through grant A7709 to DJD.

References

Abe, K., Y. Miyamoto, and S. Chikazumi, Magnetocrystalline anisotropy of low temperature phase of magnetite, *J. Phys. Soc. Jpn.*, **41**, 1894–1902, 1976.

Balanda, M., A. Wiecheć, D. Kim, Z. Kąkol, A. Kozlowski, P. Niedziela, J. Sabol, Z. Tarnawski, and J. M. Honig, Magnetic AC susceptibility of stoichiometric and low zinc doped magnetite single crystals, *Eur. Phys. J.*, **B43**, 201–212, 2005.

Carter-Stiglitz, B., B. Moskowitz, P. Solheid, T. S. Berquó, M. Jackson, and A. Kosterov, Low-temperature magnetic behavior of multidomain titanomagnetites: TM0, TM16, and TM35, *J. Geophys. Res.*, **111**, B12S05, doi:10.1029/2006JB004561, 2006.

Clark, D. A. and P. W. Schmidt, Theoretical analysis of thermomagnetic properties, low-temperature hysteresis and domain structure of titanomagnetites, *Phys. Earth Planet. Inter.*, **30**, 300–316, 1982.

Dunlop, D. J., Theory and application of the Day plot (M_{rs}/M_s versus H_{cr}/H_c), 2. Application to data for rocks, sediments, and soils, *J. Geophys. Res.*, **107**, 2057, doi: 10.1029/2001JB000487, 2002.

Dunlop, D. J. and Ö. Özdemir, *Rock Magnetism: Fundamentals and Frontiers*, 573 pp., Cambridge Univ. Press, Cambridge and New York, 1997.

Iwauchi, K., N. Koizumi, M. Kiyama, and Y. Bando, Magnetic relaxation in Fe_3O_4 and ferrites, *Bull. Inst. Chem. Res. Kyoto Univ.*, **54**, 255–262, 1976.

Jackson, M., B. Moskowitz, J. Rosenbaum, and C. Kissel, Field dependence of AC susceptibility in titanomagnetites, *Earth Planet. Sci. Lett.*, **157**, 129–139, 1998.

Janů, Z., J. Hadač, and Z. Švindrych, Glass-like and Verwey transitions in magnetite in details, *J. Magn. Magn. Mat.*, **310**, e203–e205, 2007.

Kosterov, A., Low-temperature magnetization and AC susceptibility of magnetite: effect of thermomagnetic history, *Geophys. J. Int.*, **154**, 58–71, 2003.

Kronmüller, H. and F. Walz, Magnetic after-effects in Fe_3O_4 and vacancy-doped magnetite, *Phil. Mag.*, **B42**, 433–452, 1980.

Lenge, N. and H. Kronmüller, Electrical conductivity and magnetic after-effect in the ordered phase of magnetite, *Adv. Ceramics*, **15**, 331–339, 1984.

Mizoguchi, M., Abrupt change of NMR line shape in the low temperature phase of Fe_3O_4, *J. Phys. Soc. Jpn.*, **54**, 4295–4299, 1985.

Moskowitz, B. M., M. Jackson, and C. Kissel, Low-temperature magnetic behavior of titanomagnetites, *Earth Planet. Sci. Lett.*, **157**, 141–149, 1998.

Mullins, C. E. and M. S. Tite, Magnetic viscosity, quadrature susceptibility, and frequency dependence of susceptibility in single-domain assemblages of magnetite and maghemite, *J. Geophys. Res.*, **78**, 804–809, 1973.

Muxworthy, A. R., Low-temperature susceptibility and hysteresis of magnetite, *Earth Planet. Sci. Lett.*, **169**, 51–58, 1999.

Muxworthy, A. R. and W. Williams, Low-temperature viscous magnetization of multidomain magnetite: Evidence for disaccommodation contribution, *J. Magn. Magn. Mat.*, **307**, 113–119, 2006.

Özdemir, Ö., Coercive force of single crystals of magnetite at low temperatures, *Geophys. J. Int.*, **141**, 351–356, 2000.

Özdemir, Ö. and D. J. Dunlop, Low-temperature properties of a single crystal of magnetite oriented along principal magnetic axes, *Earth Planet. Sci. Lett.*, **165**, 229–239, 1999.

Özdemir, Ö., D. J. Dunlop, and B. M. Moskowitz, Changes in remanence, coercivity and domain state at low temperature in magnetite, *Earth Planet. Sci. Lett.*, **194**, 343–358, 2002.

Rochette, P., G. Fillion, J.-L. Mattéi, and M. J. Dekkers, Magnetic transition at 30–34 Kelvin in pyrrhotite: insight into a widespread occurrence of this mineral in rocks, *Earth Planet. Sci. Lett.*, **98**, 319–328, 1990.

Skumryev, V., H. J. Blythe, J. Cullen, and J. M. D. Coey, AC susceptibility of a magnetite crystal, *J. Magn. Magn. Mat.*, **196–197**, 515–517, 1999.

Walz, F. and H. Kronmüller, Evidence for a single-stage Verwey transition in perfect magnetite, *Phil. Mag.*, **B64**, 623–628, 1991.

Walz, F. and H. Kronmüller, Analysis of magnetic point-defect relaxations in electron-irradiated magnetite, *Phys. Stat. Sol.*, **B181**, 485–498, 1994.

Walz, F., V. A. M. Brabers, S. Chikazumi, H. Kronmüller, and M. O. Rigo, Magnetic after-effects in single- and poly-crystalline magnetite, *Phys. Stat. Sol.*, **B110**, 471–478, 1982.

Walz, F., V. A. M. Brabers, and H. Kronmüller, Analysis of magnetite and related ferrites by means of magnetic after-effect-spectra, *J. Phys. IV France*, **7 suppl. C1**, 569–572, 1997.

Ö. Özdemir, D. J. Dunlop (e-mail: dunlop@physics.utoronto.ca), and M. Jackson