ELSEVIER

Earth and Planetary Science Letters 169 (1999) 51–58

EPSL

Low-temperature susceptibility and hysteresis of magnetite

A.R. Muxworthy *

Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR, UK

Received 1 December 1998; revised version received 15 March 1999; accepted 15 March 1999

Abstract

Measurement of susceptibility (χ) and hysteresis loops below room temperature for large multidomain hydrothermal magnetite and an acicular single domain magnetite are reported. Hydrothermal samples all display frequency dependent anomalies in χ across the Verwey transition (T_v). A second frequency dependent anomaly in χ is found at 50 K. In both cases the frequency dependency of χ is attributed to discontinuities in the hopping frequency of electrons at T_v and 50 K respectively. The coercive force (H_c) of the hydrothermal samples displays sharp discontinuous behavior at the magnetocrystalline anisotropy isotropic point (T_k). On plotting the hysteresis parameters on 'Day' plots, the hydrothermal grains move towards more pseudo-single domain-like regions on cooling through T_k. It is suggested that the difference in low-temperature anomalous behavior between 'high-field' parameters, e.g., H_c at T_k, and 'low-field' parameters, e.g., χ at T_v, is due to the partial destruction of the Vonsovskiĭ exchange interaction in the presence of high-fields, where according the magneto-electronic model of the Verwey transition, the Vonsovskiĭ exchange interaction is the mechanism by which electronic ordering occurs at T_v. The acicular single domain sample displays no anomalous behavior in either χ or hysteresis parameters near T_k or T_v.

Keywords: magnetite; magnetic hysteresis; magnetic susceptibility; magnetic domains

1. Introduction

Magnetic remanence which remains after low-temperature demagnetization (LTD) of multidomain (MD) magnetite is of high stability [1]. Understanding the origin of this stability will increase the paleomagnetists knowledge of stable MD natural remanent magnetization (NRM). To understand the mechanisms which control partial demagnetization of MD remanence during LTD, it is essential to know the low-temperature behavior of fundamental magnetic properties such as susceptibility (χ) and coercive force H_c [2].

On cooling from room temperature, χ and H_c of MD grains are strongly effected by the behavior of the controlling magnetic energies [3,4]. The first cubic magnetocrystalline anisotropy constant changes sign on passing through an isotropic point (T_k) at 130 K [5]. A few degrees below T_k the crystal structure changes from cubic to monoclinic at the Verwey transition, 120–124 K, T_v [6], and there are anomalies in most of the controlling magnetic energies, most notably in the magnetocrystalline anisotropy energy, where there is a very large increase in its magnitude and a reduction in its symmetry [7]. The large increase in the magnetocrystalline anisotropy is

* Present address: GeoForschungsZentrum, Sedimente und Beckenbildung, Telegrafenberg Haus C, 14473 Potsdam, Germany. E-mail: adrianm@earth.ox.ac.uk

0012-821X/99/$ – see front matter
PII: S0012-821X(99)00067-9

a result of a sharp reduction in the mobility of electrons from 3d shells which move or 'hop' between the Fe^{3+} and Fe^{2+} cations on the *B*-sublattice, on cooling through T_v [7,8].

Previous studies have found large discontinuities in χ [3] and H_c [4] in the vicinity of T_v and T_k. However these studies have concentrated on the low-temperature behavior of either small single domain (SD) and pseudo-single domain (PSD) magnetite samples or large natural multidomain (MD) crystals [2–4].

This paper reports the first low-temperature measurements of χ and hysteresis loops for large multidomain (MD) crystals produced by hydrothermal recrystallization [9]. Previous studies have cited both the importance of stress on the low-temperature magnetic behavior of MD magnetite, and the extremely low dislocation densities of hydrothermal magnetite samples [10]. Therefore examination of hydrothermal samples is useful in validating the importance of stress.

2. Sample description and experimental methods

Four samples are considered in this study; three MD synthetic samples (H(3.0 μm)–H(108 μm)) made by hydrothermal recrystallization [9], and a commercial acicular SD sample (SD(acic.)). The source material for the SD(acic.) sample had been previously investigated [11]. Grain size distributions and magnetic parameters of the samples are summarized in Table 1. XRD analysis and Mössbauer spectroscopy confirmed that the MD samples were pure magnetite. The chemical purity of the SD(acic.) sample was not examined using XRD or Mössbauer spectroscopy. The hydrothermal samples have slightly wider grain distributions than the hydrothermal crystals prepared by [9]. The hydrothermal samples have low values for H_c and low saturation remanence to (M_{rs}) to saturation magnetization (M_s) ratios suggesting that they have low-dislocation densities, in agreement with previous studies [10]. The values for H_c, H_{cr} and M_{rs}/M_s for the SD(acic.) sample, are typical for acicular SD magnetite [12], however they were slightly higher than those previously reported [11]. To explain this difference it might be suggested that the SD(acic.) sample had partially maghemitized (oxidation under ambient conditions), however, low-temperature thermomagnetic cooling curves of remanence induced in the SD(acic.) sample [13], displayed anomalous behavior at ≈120 K, i.e., the value of T_v for stoichiometric magnetite. This suggests that no or little maghemitization had occurred. The samples were loosely dispersed in KBr pellets.

Table 1
Summary of mean grain size, standard deviation σ, and hysteresis parameters H_c (coercive force), H_{cr} (remanent coercive force) and the ratio of the saturation remanence (M_{rs}) to the saturation magnetization (M_s) at room temperature, for the samples considered in this study

Sample name	Size (μm)	$\pm\sigma$ (μm)	H_c (mT)	H_{cr} (mT)	M_{rs}/M_s
H(3.0 μm)	3.0	2.4	2.4	26.5	0.018
H(76 μm)	76	25	0.96	19.9	0.006
H(108 μm)	108	31	0.94	18.2	0.005
SD(acic.)	0.05	–	65	88	0.470

H(3.0 μm)–H(108 μm) are MD hydrothermal samples, and SD(acic.) an acicular SD sample with aspect ratios up to 1 in 6.

For all four samples low-temperature χ was measured during warming from ≈20 K to room temperature at five frequencies (40, 140, 400, 1000 and 4000 Hz) using a Lakeshore Cryotronics Low-Temperature AC Susceptometer. Hysteresis loops were measured using a VSM, at various temperatures in the range 100–300 K. During the measurement of a hysteresis loop, the temperature was kept to within ±0.2 K of the required temperature.

3. Results

3.1. Susceptibility at low temperatures

Low-temperature χ curves at five frequencies (40, 140, 400, 1000 and 4000 Hz) for each of the four samples are shown in Fig. 1. The SD(acic.) sample increases gradually on warming to room temperature, and displays no discontinuous behavior in the vicinity of T_v and T_k, however, there is slight anomaly at 100 K (Fig. 1a). There is a degree of scatter between the different frequencies, giving a noisy signal. The hydrothermal crystals (H(3.0 μm), H(76 μm) and H(108 μm)) all display a sharp discontinuity across T_v (Fig. 1b–d). The increase of χ

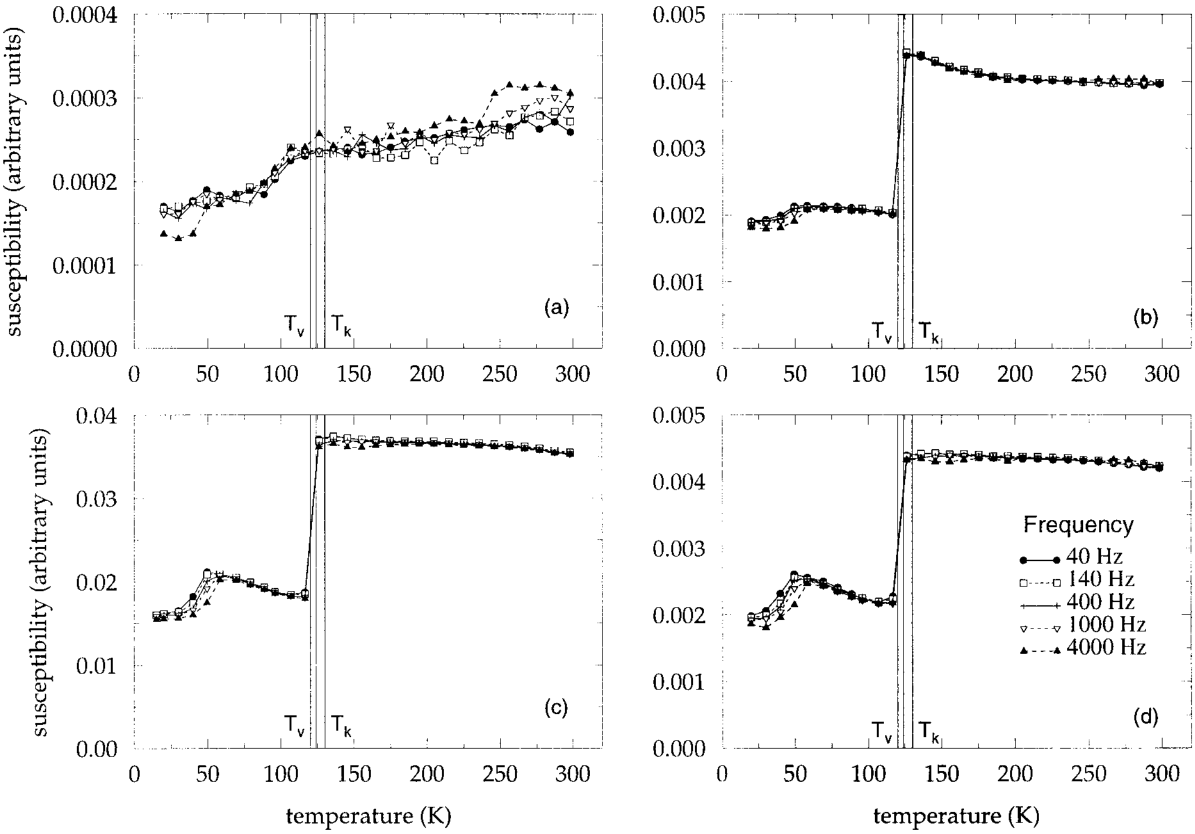

Fig. 1. Susceptibility vs. temperature at various frequencies for (a) SD(acic.), and hydrothermal samples (b) H(3.0 μm), (c) H(76 μm) and (d) H(108 μm). Susceptibility curves were measured on warming from ≈20 K. Both T_v and T_k are marked, T_v as a band because of the uncertainty in its value (120–124 K).

on heating through T_v and T_k for the three samples H(3.0 μm), H(76 μm) and H(108 μm) is ≈120%, ≈105% and ≈100% respectively (Fig. 1b–d). This large increase in χ in the range 120–130 K for MD grains is in agreement with previous studies [3,14]. On warming from T_v to room temperature χ decreases gradually for all three hydrothermal samples. The smallest sample H(3.0 μm) displays a 'peak' or maximum at ≈126 K, which is not observed in the larger hydrothermal samples H(76 μm) and H(108 μm) (Fig. 1c,d).

There is a small anomaly in χ at ≈50 K observed for H(3.0 μm), H(76 μm) and H(108 μm) (Fig. 1b–d). The anomaly has been reported before for single crystals of magnetite [3,14,15]. The relative size of the anomaly is greater for the two largest samples, i.e., H(76 μm) and H(108 μm), than the smallest sample H(3.0 μm). There is a frequency dependency of χ at this anomaly; the temperature of the anomaly increases with frequency (Fig. 1b–d).

Measurement of low-temperature χ for H(108 μm), was repeated with smaller temperature steps in the range in 110–130 K (Fig. 2). There was very good repeatability in χ in this temperature range (cf. Fig. 1d and Fig. 2). The anomaly associated with T_v occurs over the range of temperatures 118–126 K (Fig. 1). That the transition is over a temperature range rather than a discontinuous jump is in agreement with the magneto-electronic model of the Verwey transition [7,8]. The magneto-electronic model proposes that the reduction of electron hopping is due to a negative exchange interaction between the hopping electrons and the B-sublattice, which causes both a reduction in electron mobility and the magnetic moments of

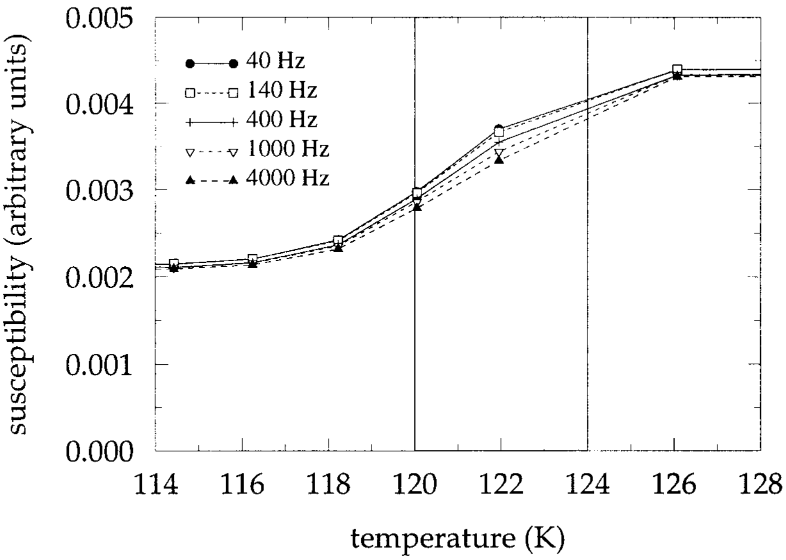

Fig. 2. Susceptibility as a function of temperature at various frequencies for hydrothermal crystals H(108 μm). The susceptibility was measured at smaller step intervals in the range 110–130 K than reported in Fig. 1. T_v is marked as a band because of the uncertainty of its value (120–124 K).

the hopping electrons to align in the opposite direction to the *B*-sublattice moment. This exchange interaction is called the Vonsovskiĭ interaction [16], and is broken by the application of strong magnetic fields or thermal energies, i.e., during hysteresis or heating above T_v respectively [8]. The magneto-electronic model and its implications for rock magnetism are discussed in [7]. The transition width of ≈8 K is wider than the 3 K reported for single crystals [14], however it is considerably narrower than the 17 K reported for powdered samples [14].

There is a slight frequency dependency for H(108 μm) across the transition, most noticeably at 122 K (Fig. 2). For most temperatures outside the range 118–126 K, the susceptibility measured at 40 Hz (χ_{40}), was almost identical to that measured at higher frequencies, however in the temperature range 118–126 K, χ is frequency dependent, i.e.: $\chi_{40} > \chi_{140} > \chi_{400} > \chi_{1000} > \chi_{4000}$. To the author's knowledge this has never been reported.

3.2. Low-temperature behavior of the hysteresis parameters

H_c is depicted as a function of temperature in Fig. 3 for the hydrothermal samples H(3.0 μm) and H(108 μm). On warming from ≈100 K, H_c decreases gradually to ≈128 K before dropping abruptly; H_c of H(3.0 μm) is reduced from ≈8.8 mT at 128 K to ≈2.1 mT at 132 K, and for H(76 μm) H_c drops from ≈4.0 mT at 127 K to ≈1.1 mT at 133 K (Fig. 3). In both cases H_c drops by a factor of approximately four.

For H(3.0 μm) there is a minimum in H_c at ≈135 K. On further warming H_c increases, levelling off towards room temperature (Fig. 3). This behavior has been observed previously for both natural samples [2] and synthetic crystals [4]. H(76 μm) displays similar behavior as H(3.0 μm) on heating, however the increase on warming is less pronounced suggesting a grain size dependency in agreement with results by [17]. SD(acic.) did not display any low-temperature anomaly in H_c at T_v or T_k.

It is common to summarize hysteresis parameters by plotting M_{rs}/M_s versus H_{cr}/H_c (i.e., a Day plot), because different domain states plot in different areas [18], e.g., SD grains have high M_{rs}/M_s ratios and low H_{cr}/H_c ratios (see inset in Fig. 4). Fig. 4 shows the Day plot for the two hydrothermal samples H(3.0 μm) and H(76 μm). H(3.0 μm) and H(76 μm) both plot in the multidomain region above T_k, and display a marked change on cooling through T_k. The smaller

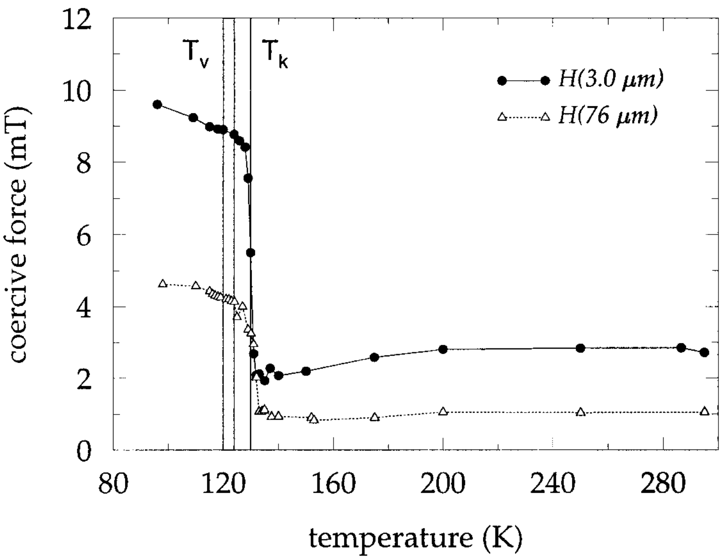

Fig. 3. Coercive force as a function of temperature for hydrothermal crystals H(3.0 μm) and H(76 μm). The coercive force was determined from hysteresis loops measured at a variety of temperatures.

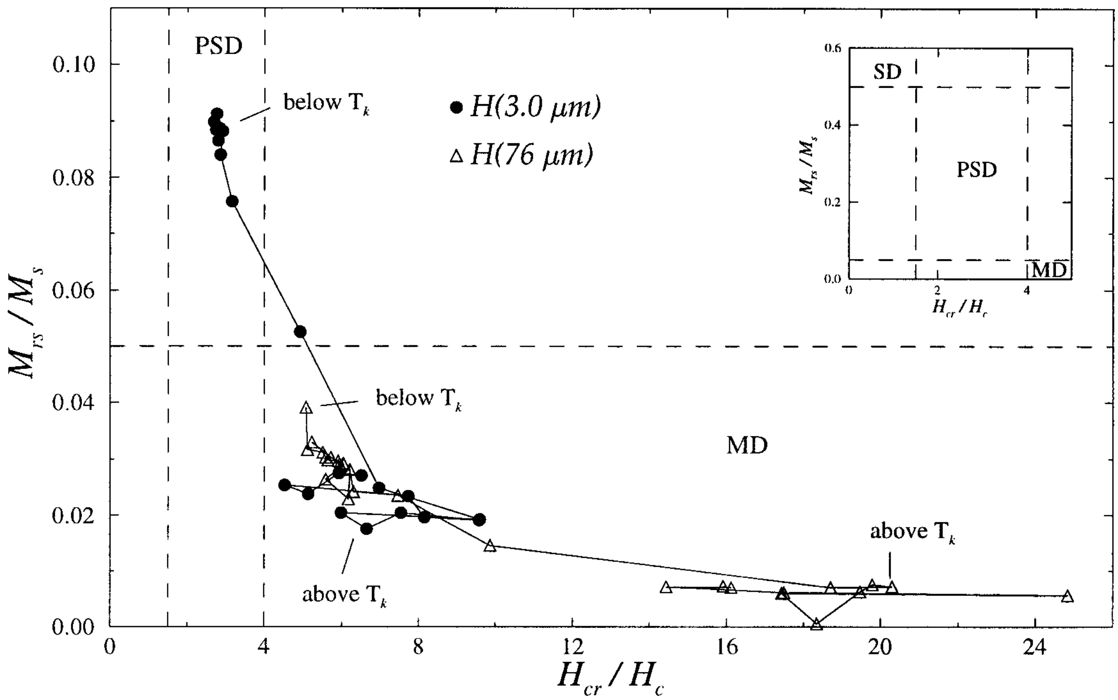

Fig. 4. M_{rs}/M_s vs. H_{cr}/H_c (Day plot) for the two hydrothermal samples H(3.0 μm) and H(76 μm).

sample H(3.0 μm) shifts from the MD region to the PSD region, and the larger sample H(76 μm) although still in the MD region shifts towards the harder more PSD-like region of the MD area on cooling through T_k. Sample SD(acic.) plots in the single domain region and does not vary in behavior with temperature.

4. Discussion

4.1. Frequency dependency of susceptibility at low-temperatures

The susceptibility of sample SD(acic.) is unaffected by the transitions T_v and T_k (Fig. 1a). This is because χ of randomly orientated acicular SD grains is controlled by the shape anisotropy; $\chi \propto 1/N$, where N is the self-demagnetizing factor [12]. Spherical or near spherical SD grains are partially controlled by the magnetocrystalline anisotropy [4]. The susceptibility of MD hydrothermal crystals H(3.0 μm), H(76 μm) and H(108 μm) is governed by the behavior of domain walls which are dependent on the exchange, magnetocrystalline anisotropy and magnetostrictive anisotropy energies. Of these three energies, the magnetocrystalline anisotropy displays by far the greatest anomaly at T_v [7]. The sharp increase in χ on heating through T_v reflects this behavior of the magnetocrystalline anisotropy (Fig. 1b–d). The anomaly is spread over a small temperature range (118–126 K) for sample H(108 μm) (Fig. 2). It is uncertain why the range of the transition is larger than the value for the single crystal, i.e., 3 K [14]. It is not due to temperature inhomogeneity across the sample, because the sample was given sufficient time to thermally equilibrate (10–20 minutes within 2 K of measurement temperature). [14] attribute the large transition width for their powdered sample (18 K) to a range of internal stresses induced during milling, i.e., some grains are more stressed than others. Note, stress is known to decrease the Verwey transition temperature, whether it is induced by applying hydrostatic pressure [19] or uniaxial pressure [17]. Applying this theory to the H(108 μm) sample, implies that there was a distribution of stresses within the samples, however hysteresis parameters for H(108 μm) suggest that it was relatively stress free (Table 1). The difference in transition width be cannot attributed to grain interactions, because crystals in the H(108 μm) sample were too large to be significant (pers. comm. W. Williams, 1996).

A possible explanation for the large transition width of the H(108 μm) sample, is that the anomaly in χ is associated with domain structure. The domain structure of each grain within a sample will have a slightly different degree of stability. In response to the AC field and changes in the magnetic energies in the vicinity of T_v, the domain structure will 'break' at some temperature, giving rise to the increase in χ. By measuring only one crystal, with one domain structure, then the transition width will be relatively narrow [14], however by measuring a number of grains then the width of the transition will be larger (Fig. 2). It should be noted that different single crystals very rarely give the same temperature for the Verwey transition. Differences are normally attributed to small variations in the stoichiometry or stress, however even for 'perfect' magnetite there are a range of claimed temperatures for T_v, e.g., 125 K [15], ≈121 K [19] and 122–125 K [20].

It is postulated in this paper, that the small frequency dependency of χ across T_v (Fig. 2) is due to the mobility of hopping electrons across the Verwey transition. Above the transition the electrons hop with an 'attempt frequency', τ_0^{-1}, of $\approx 10^{14}$ s^{-1}, however below the transition $\tau_0^{-1} \approx 10^{12}$ s^{-1} [15]. The reduction in electron mobility is due to the domination of the Vonsovskiĭ interaction as the thermal energy decreases [7,8]. Across the transition itself, there will be a temperature where the hopping rate is very susceptible to external changes, i.e., a small external field may be able to break the influence of the Vonsovskiĭ interaction effectively pushing the electron mobility from the slower to the faster hopping rate. For MD grains, χ is inversely related to the magnitude of the magnetocrystalline anisotropy [12], which in turn is heavily influenced by mobility of Fe^{2+} ions [21], i.e., electron mobility. The localization of electrons below T_v causes large increases in the magnetocrystalline anisotropy [7], with a corresponding decrease in χ. At lower AC frequencies there is relatively more time for the Vonsovskiĭ interaction to be broken, increasing the hopping rate and increasing χ. As the AC frequency increases there is less time to respond, making the effective magnetocrystalline anisotropy higher, which in turn decreases χ. The temperature where the frequency dependency is greatest i.e., 122 K for H(108 μm) (Fig. 2), is probably a good indicator for T_v.

In agreement with [3] the anomaly in χ in the hydrothermal samples at ≈50 K is attributed to magnetic after-effect/relaxation processes [15]. At 50 K there is a reduction in the attempt frequency of electron hopping from $\tau_0^{-1} \approx 10^{12}$ s^{-1} above

50 K to $\tau_0^{-1} \approx 10^{11}$ s^{-1} below [15]. Changes in electron mobility effect χ in a similar manner as at T_v. It is suggested here that the mechanism of frequency dependency of χ at the anomaly at ≈50 K is analogous to the frequency dependency at T_v, i.e., the small AC field is sufficient to increase the hopping of electrons to the higher rate at lower frequencies increasing χ. H(76 μm) and H(108 μm) display larger anomalies than H(3.0 μm) because they are truly MD rather than PSD.

There are reports in literature of peaks in χ at T_k, [8,22], however the only sample to display a peak near T_k was the small H(3.0 μm) sample (Fig. 1b). It is suggested that the peak could be an indicator of grain size.

4.2. Hysteresis parameters at low-temperatures

On heating from below T_v, H_c sharply decreases at T_k for both H(3.0 μm) and H(76 μm), before reaching a minimum at ≈132 K (Fig. 3). The decrease in H_c occurs at T_k rather than T_v, because at T_v there is a discontinuous jump in the magnetocrystalline anisotropy energy (E_k), i.e., $E_k > 0$ at all times across T_v, however at T_k, $E_k \rightarrow 0$.

Below T_v, H(3.0 μm) and H(76 μm) are more PSD-like than they are above it, having both higher M_{rs}/M_s and lower H_{cr}/H_c ratios (Fig. 4). This is due to anomalies in a number of controlling energies, especially the increase in the magnetocrystalline anisotropy energy.

4.3. Comparison of χ and hysteresis parameters

For the hydrothermal MD grains, anomalous behavior of χ occurred across T_v (Fig. 1) and H_c displayed anomalous behavior at T_k (Fig. 3). It appears that 'high-field' measurements, e.g., hysteresis loops, are strongly effected by T_k, whilst 'low-field' measurements, e.g., χ, and 'zero-field' measurements, e.g., cooling of remanence [2], display anomalous behavior at T_v. This reflects a difference in MD magnetite's response to high and low external magnetic fields at low-temperatures. It is suggested here, that this difference between high and low-field measurements, may be due to the destruction of the Vonsovskiĭ interaction in the presence of high-fields, which in turn reduces the dominance of the Verwey transition. It may be concluded that it is incorrect to directly infer behavior of remanence from high-field measurements.

5. Conclusions

(1) MD hydrothermal magnetite samples display similar low-temperature χ behavior to natural samples considered in previous studies [2]. The SD(acic.) sample displays no anomalous in χ at T_v and T_k.

(2) The sharp anomaly in χ is associated with T_v not T_k.

(3) The width of the anomaly in χ at T_v (Fig. 2) reflects a range of stable domain structures within the assemblage of MD grains.

(4) The frequency dependency of χ across T_v is associated to variations in the hopping rate of electrons above and below T_v.

(5) The anomaly in χ at 50 K is attributed to a reduction in electron hopping at this temperature [15]. The frequency dependency of χ at 50 K is analogous to the frequency dependency of χ across T_v.

(6) H_c drops by a factor of four on cooling through T_v and T_k for MD hydrothermal samples, SD(acic.) displays no anomaly in H_c at T_v or T_k.

(7) H_c displays a minimum at 132 K ≈ T_k for the MD hydrothermal samples.

(8) Both hydrothermal samples H(3.0 μm) and H(76 μm) shift towards more PSD-like regions of a Day plot on cooling through T_k and T_v (Fig. 4).

(9) Depending on whether a high-field or a low-field magnetic characteristic is measured, e.g., H_c or χ respectively, the magnetic property displays anomalous behavior at either T_v or T_k respectively. It is suggested that this difference is due to the partial destruction of the Vonsovskiĭ interaction in high fields. It maybe erroneous to directly infer behavior of remanence properties from high-field measurements.

Acknowledgements

The author would like to thank E. McClelland for useful discussions, and helpful comments from J. King and two anonymous reviewers. The measurements were carried out at the Institute for Rock Magnetism, University of Minnesota, which is funded by the University of Minnesota and the Keck Foundation. ***[VD]***

References

[1] E. McClelland, V. Shcherbakov, Metastability of domain state in MD magnetite: consequences for remanence acquisition, J. Geophys. Res. 100 (B3) (1995) 3841–3857.

[2] J. Hodych, R. Mackay, G. English, Low-temperature demagnetization of saturation remanence in magnetite-bearing dolerites of high coercivity, Geophys. J. Int. 132 (2) (1998) 401–411.

[3] B. Moskowitz, M. Jackson, C. Kissel, Low-temperature magnetic behavior of titanomagnetites, Earth Planet. Sci. Lett. 157 (34) (1998) 141–149.

[4] E. Schmidbauer, R. Keller, Magnetic properties and rotational hysteresis of Fe_3O_4 and γ-Fe_2O_3 particles $\sim$250 nm in diameter, J. Magn. Magn. Mater. 152 (1996) 99–108.

[5] L. Bickford Jr., J. Brownlow, F.R. Penoyer, Magnetocrystalline anisotropy in cobalt-substituted magnetic single crystals, Proc. I.E.E. B 104 (1957) 238–244.

[6] E. Verwey, Electronic conduction of magnetite (Fe_3O_4) and its transition point at low-temperature, Nature 44 (1939) 327–328.

[7] A. Muxworthy, E. McClelland, Review of the low-temperature magnetic properties of magnetite from a rock magnetic perspective, Geophys. J. Inter. (1999) in press.

[8] K. Belov, Electronic processes in magnetite (or ‘enigmas in magnetite’), Physics-Uspekhi 36 (5) (1993) 380–391.

[9] F. Heider, L. Bryndzia, Hydrothermal growth of magnetite crystals (1 μm to 1 mm), J. Cryst. Growth 84 (1987) 50–56.

[10] F. Heider, D. Dunlop, N. Sugiura, Magnetic properties of hydrothermally recrystallized magnetite crystals, Science 236 (1988) 1287–1290.

[11] L.G. Parry, Magnetization of immobilized particle dispersions with two distinct particle sizes, Phys. Earth Planet. Inter. 28 (1982) 230–241.

[12] D. Dunlop, Ö. Özdemir, Rock Magnetism: Fundamentals and Frontiers, Cambridge University Press, 1997, 573 pp.

[13] A.R. Muxworthy, Stability of magnetic remanence in multidomain magnetite, D.Phil. thesis, University of Oxford, 1998.

[14] F. Walz, H. Kronmüller, Evidence for a single-stage Verwey transition in perfect magnetite, Philos. Mag. B 64 (5) (1991) 623–628.

[15] F. Walz, H. Kronmüller, Analysis of magnetic point-defect relaxations in electron-irradiated magnetite, Phys. Stat. Sol. (B) 181 (1994) 485–498.

[16] S. Vonsovskiĭ, On the exchange interaction of the valence and inner electrons in ferromagnetic (transition) metals, J. Phys. 10 (1946) 468–475.

[17] J. King, Magnetic properties of arrays of magnetite particles produced by the method of electron beam lithography (EBL), Ph.D. thesis, University of Edinburgh, 1996.

[18] M. Dekkers, Environmental magnetism: an introduction, Geol. Mijnb. 76 (1997) 163–182.

[19] G. Rozenberg, G. Hearne, P. Pasternak, P. Metcalf, J. Honig, Nature of the Verwey transition in magnetite (Fe_3O_4) to pressures of 16 GPa, Phys. Rev. B 53 (10) (1996) 6482–6487.

[20] R. Aragón, D.J. Buttrey, J.P. Shepherd, J.M. Honig, Influence of non-stoichiometry on the Verwey transition, Phys. Rev. B 31 (1) (1985) 430–436.

[21] E.J. Fletcher, W. O’Reilly, Contribution of Fe^{2+} ions to the magnetocrystalline anisotropy constant K_1 of $Fe_{3-x}Ti_xO_4$ ($0 < x < 0.1$), J. Phys. C., Solid State Phys. 7 (1974) 171–178.

[22] J. Hodych, Evidence for magnetostrictive control of intrinsic susceptibility and coercive force of multidomain magnetite in rocks, Phys. Earth Planet. Inter. 42 (1986) 184–194.