Low-temperature magnetic properties of magnetite

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Abstract. Although several studies have recommended removal of secondary components of magnetic remanence by zero-field cycling from room temperature to a temperature much lower than the low temperature transition for magnetite (about 120 K), the method has not become a standard routine technique. This is partly due to the poor understanding of the behavior of magnetite particles at the low-temperature transition zone. Previous experiments by other researchers have used magnetite powders. In such powders it is always possible to attribute any discrepancy between the results observed and theory to possible existence of magnetostatic interaction effects or existence of elongated particles in samples presumed to contain only equant particles. Such factors need to be eliminated in order to have a better understanding of the low temperature behavior of magnetite particles. Low-temperature magnetic properties of lithographically produced arrays of both interacting and noninteracting cubic magnetite particles as well as those from powder particles have been measured as part of this study. A gradual increase in the amount of saturation isothermal remanent magnetization (SIRM) lost at the Verwey transition T_v with increasing particle size in the pseudo-single-domain size range has been observed. This behavior is consistent with the vortex state domain structure. The grain size dependence of the amount of SIRM lost at T_v is most probably what previous researchers reported as a magnetic memory particle-size-dependent trend. Magnetic memory measured during the cooling and warming process is shown to be a stress-related phenomenon. Such measurements could be useful in assessing the nature of stress in a magnetite sample.

1. Introduction

In order to isolate the primary magnetic remanence (i.e., the more stable and hence more ancient remanence) in rocks from secondary components (less stable), two techniques are often employed. This practice is often referred to as "magnetic cleaning". One technique is the stepwise alternating field (af) demagnetization [e.g., *Creer*, 1959], and the other is thermal demagnetization [e.g., *Collinson*, 1983, p. 335]. Apart from these two techniques, magnetic cleaning of samples whose major remanent magnetization carrier is magnetite can be obtained by zero-field cycling from room temperature to a temperature much lower than about 120 K, the so-called Verwey transition [*Verwey*, 1939]. Although several studies [e.g., *Ozima et al.*, 1964; *Kobayashi and Fuller*, 1968; *Merrill*, 1970] have recommended this technique as an effective means of "magnetic cleaning", it has not become a standard routine technique. This is due to lack of a clear understanding of magnetic properties of magnetite particles at low temperatures.

Previous experiments by other researchers have used magnetite powders [e.g., *Morrish and Watt*, 1958; *Heider et al.*, 1992; *Özdemir et al.*, 1993]. In such powders, it is always possible to attribute any discrepancy between the results observed and theory to possible existence of magnetostatic interaction effects or existence of elongated particles in samples presumed to contain only equant particles. Such factors need to be eliminated in order to determine low-temperature behavior of magnetite particles.

In this paper the results of low-temperature magnetic properties of lithographically produced arrays of both interacting and noninteracting cubic magnetite particles are presented. Where appropriate, the results of the magnetic measurements of these samples are compared to those of thin magnetite films, artificially laboratory grown magnetite powder particles, and natural magnetite crystals. In addition, comparison is extended to include results from studies by other researchers.

The results show a gradual increase in the amount of saturation isothermal remanent magnetization (SIRM) lost at the Verwey transition with increasing particle size in the pseudo-single-domain size range. This observation is similar to that reported by *Özdemir et al.* [1993]. They ascribed it to partial oxidation of the particles. We interpret the observation to be a reflection of the vortex domain structure. The vortex domain state has been observed in several studies [e.g., *Williams and Dunlop*, 1989, 1995]. The grain size dependence of the amount of SIRM lost at T_v is most probably what has been reported by previous researchers

Table 1. Description of Samples Used in This Study

Sample Name	Particle size, μm	Interparticle Spacing, μm	Sample Preparation Method
JK0.2	cube edge, 0.2	0.8	lithography method 2
JK0.3	cube edge, 0.3	1.2	lithography method 2
JK0.5	cube edge, 0.5	2	lithography method 2
JK1	cube edge, 1	4	lithography method 2
JK0.25@0.05	cube edge, 0.25	0.05	lithography method 2
JK0.6@≈0.0	cube edge, 0.6	≈ 0.0	lithography method 2
JK1@0.25	cube edge, 1	0.25	lithography method 2
Thin film	continuous layer	N/A	lithography method 2
Gel0.2	average diameter, 0.2	N/A	gel aging
JH0.5	average diameter, 0.5	N/A	hydrothermal
JH1	average diameter, 1	N/A	hydrothermal
JH>16	average diameter > 16	N/A	Hydrothermal The grains remained on top of a 16 μm sieve.
JSC1	2 mm octahedral natural single crystal	N/A	N/A

N/A denotes not applicable.

[*Dunlop and Argyle*, 1991; *Heider et al.*, 1992; *Özdemir et al.*, 1993] as a magnetic memory particle-size-dependent trend. Magnetic memory measured during the cooling and warming process is shown to be a stress-related phenomenon. Such measurements could be useful in assessing the nature of stress in a magnetite sample.

2. Brief Description of Samples Used in This Study

Table 1 contains basic information on the samples used in this study. A brief description of the method of production is provided below. Where appropriate, a reference containing a detailed description of the method is provided for the interested reader.

2.1. Lithographically Produced Magnetite Samples Method 1

These samples were produced by the method of electron beam lithography and the annealing technique referred to as method 1 by *King et al.* [1996]. The method involves vacuum evaporation of Fe on a silicon substrate with a patterned resist. The resist is later dissolved, and Fe particles are converted to magnetite by annealing for about 12 hours in a low-pressure (about 10^{-4} mbar) oxygen environment at a constant temperature of $300°C$. Cooling of the sample from $300°C$ to room temperature is done rapidly to avoid oxidation to hematite or maghemite. Since the thermal conductivity of Fe_3O_4 is different from that of the silicon substrate, the rapid cooling results in stressed samples.

2.2. Lithographically Produced Magnetite Samples Method 2

Fe particles produced using electron beam lithography techniques were converted to magnetite by annealing in an environment of gas mix ratio of 100:6, CO_2:H_2. At an annealing temperature of $600°C$, Fe particles were fully converted to Fe_3O_4 in about 4 hours. Unlike in method 1, slow cooling to room temperature without oxidation to hematite or maghemite was possible [*King et al.*, 1996]. In this paper, unless otherwise stated, samples referred to as lithography (or lithographically produced), without specifying whether they were produced using method 1 or 2, are those produced using method 2.

2.3. Magnetite Thin Film Samples

These samples are composed of a continuous thin film layer of magnetite. They were produced by converting an Fe thin film to a Fe_3O_4 thin film using method 2 annealing technique [*King et al.*, 1996].

2.4. Hydrothermal Recrystallization Samples

These samples were produced by the method of hydrothermal recrystallization similar to the method of *Heider and Bryndzia* [1987]. NH_4Cl (or distilled water) was placed in a platinum capsule containing commercially obtained magnetite before sealing its top. The capsule was then placed in a vertically mounted vessel (the so-called bomb). The bomb was subjected to a constant elevated temperature and a constant pressure of 2 kbar for 7 days. The elevated temperature can be chosen to be any value between $400°C$ and $800°C$. The higher the temperature, the larger the grain size produced.

2.5. Gel-Aging-Produced Samples

These samples were produced by aging ferrous hydroxide gel at $95°C$ constant temperature. This method is similar to that described by *Sugimoto and Matijevic* [1980].

2.6. The 2 mm Single Crystal

This is a natural octahedral single crystal from Shetland greenschist.

3. Curie Point Characterization of Samples

The interest in high-temperature magnetic measurements in the present study was limited to its use as a way of characterizing the magnetite produced. When a magnetite sample is heated at a temperature of about $580°C$ (the Curie point for magnetite), it loses all its magnetization. This loss in spontaneous magnetization is due to thermal agitations overcoming the exchange energy. This high-temperature transitional change is used often in rock magnetism to determine if a rock contains the mineral magnetite. The major problem in using this method is the possibility of chemical alteration of the sample during the heating. Small, unprotected grains of magnetite convert to maghemite, which in turn converts to hematite on heating to above $300°C$.
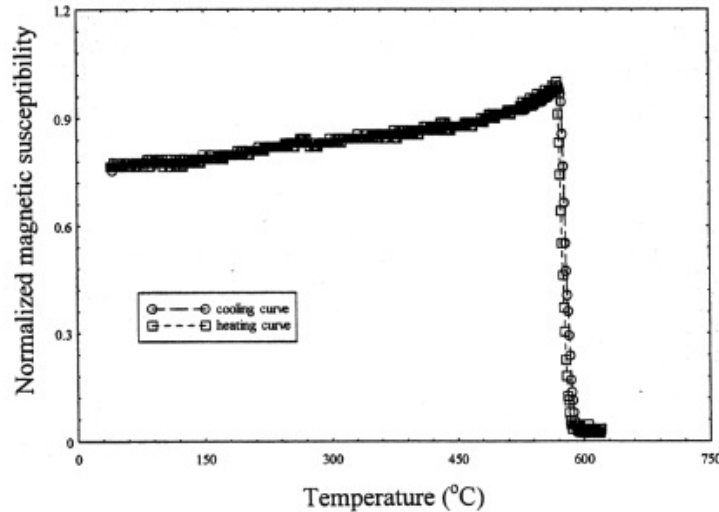
Figure 1. Normalized magnetic susceptibility as a function of temperature clearly showing a Curie-point of 580°C.

In this study the Curie point was determined using magnetite thin film samples. Owing to their weak total magnetic moment, lithographically produced arrays of magnetite particles were not used for the Curie point determination. It has been assumed that the Curie point for thin films of magnetite is the same as that for lithographically produced arrays of magnetite particles since annealing was done under the same conditions. A susceptibility meter model MS2 from Bartington connected to a heating system model MSWFP from the same company was found to be easier to use for the determination of the Curie point than using the Curie balance. It is easier to pass nitrogen gas over a sample during an experimental run in this instrument and hence avoid oxidation of the sample that could lead to chemical alteration than to house the whole Curie balance equipment in either a vacuum or an inert gas environment.

A typical plot of normalized susceptibility as a function of temperature using MS2 equipment is shown in Figure 1. The Curie temperature was found to be 580 +/- 12°C which is in good agreement with the literature value of 580°C for magnetite [Thompson and Oldfield, 1986].

4. Verwey Transition and Stoichiometric Magnetite

Stoichiometric magnetite exhibits abrupt changes in magnetic properties near 120 K [Özdemir et al., 1993; Radhakrishnamurty et al., 1981; Hodych, 1986]. Associated with these magnetic changes is the change in crystal structure from cubic to monoclinic (upon cooling of the sample), as well as the isotropic point (i.e., the temperature near 130 K where the first magnetocrystalline anisotropy constant K_1 becomes zero). The Verwey transition is a signature for magnetite. Unlike in the Curie point determination, there is no risk of oxidation of a sample since it is not heated. Hence the process is more appropriate for use in lithographically produced magnetite particles in this study that easily oxidize

on heating unless protected than the Curie point determination. The Verwey transition temperature was obtained using a magnetic property measurement system (MPMS2) superconducting quantum interference device (SQUID), from the company Quantum Design. This instrument is more sensitive than the susceptometer used to determine the Curie point.

Scanning electron microscope (SEM) pictures of typical samples of lithographically produced noninteracting cubic magnetite particles used in this study are shown in Figure 2. These samples were cooled from 300 K through the Verwey transition in a zero magnetic field environment. The sample was then given a SIRM in a field of 1 Tesla (T) at a low temperature before warming it through the Verwey transition in zero field. While the majority of samples had their SIRM measured from 20 K to 170 K, some experiments were done in the temperature interval 1.8 K (or 5 K) to 300 K. This was done in order to check for the presence of superparamagnetic (SPM) particles. Moskowitz et al. [1993] observed that the presence of superparamagnetic magnetite particles in a sample led to a rapid decrease in SIRM in the temperature interval 5 to 40 K. This behavior was ascribed to the distribution of blocking temperatures due to different sizes of SPM particles. Starting from 1.8 K, we checked for the presence of even the smallest sized SPM particles. Since, to our knowledge, there are no reported SIRM measurements done below 4.2 K for magnetite in the literature, it was also interesting to check if the expected behavior of SIRM continues in this temperature range.

Figure 3 shows thermal demagnetization of SIRM intensity given in a field of 1 T for sample JK0.5. The sample was warmed from 1.8 K to 300 K and from 20 K to 170 K. It can be seen from this figure that when the sample was warmed from 20 K, a relatively larger SIRM intensity was lost while approaching the Verwey transition than when the sample was warmed from 1.8 K. There is not a big decrease in SIRM intensity below 40 K (reported to be about 30 - 40% by
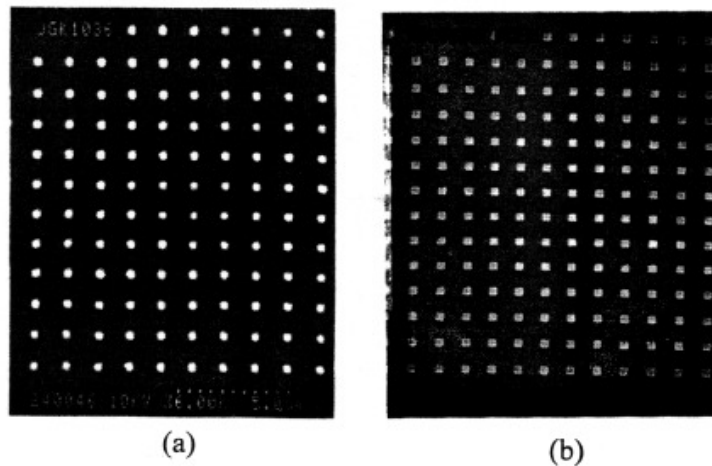
(a)   (b)

Figure 2. Scanning electron microscope (SEM) pictures of (a) 0.3 μm cubic magnetite particles at 1.2 μm spacing and (b) 1 μm cubic magnetite particles at 4 μm spacing.

Özdemir et al. [1993]) indicative of the presence of superparamagnetic-sized particles. This observation is in agreement with results of X-ray diffraction (XRD) data of coproduced magnetite thin films [King et al., 1996].

Figure 4 shows typical curves for magnetite samples JK0.1, JK0.2, JK0.5, and JK1 and a 0.5 μm thin film having Verwey transitions of 119 K, 120 K, 119 K, 120 K, and 119 K, respectively. According to Aragón et al. [1985], stoichiometric magnetite exhibits a Verwey transition of about 120 K; hence Verwey transitions for samples of this study are consistent with stoichiometric magnetite. This result is consistent with the results of XRD [King et al., 1996] and Curie point (Figure 1) obtained using magnetite thin films concurrently produced with these samples.
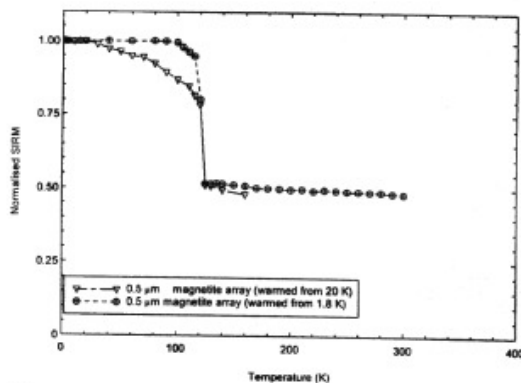
The amount of SIRM loss at the Verwey transition decreases with decreasing particle size. Powdered samples (Figure 5) also exhibit this trend, although the amount of loss of SIRM intensity is in general more than that for samples of arrays of magnetite (Figure 4). Özdemir et al. [1993] attributed this behavior to surface oxidation. According to this explanation, surface oxidation results in the formation of a maghemite shell with a smaller lattice parameter than the magnetite core. The resulting stretching due to the differences in lattice parameters produces cracks on the surface, creating ultrafine particles whose sizes are in the superparamagnetic range. It is the progressive unblocking of magnetization with temperature by these ultrafine particles which suppresses the Verwey transition. The smaller the particle, the larger the surface-to-body ratio, and hence the more the Verwey
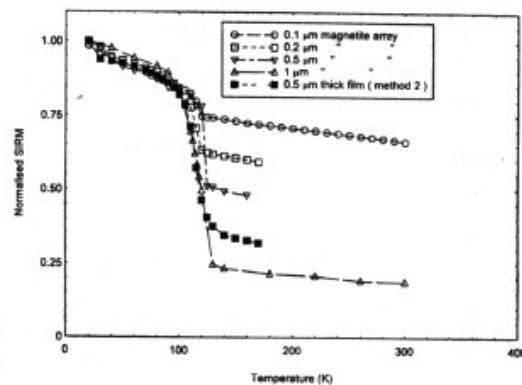

Figure 3. Thermal demagnetization of saturation isothermal remanent magnetization (SIRM) given at 1.8 K in a field of 1 T for sample JK0.5. There is no sharp decrease in SIRM below 40 K indicative of superparamagnetic (SPM) particles. The curve for this sample when it was given SIRM at 20 K shows more loss in SIRM as it approaches the Verwey transition temperature than the other curve.

Figure 4. Thermal demagnetization of SIRM intensity for lithographically produced noninteracting cubic magnetite particles of sizes 0.1 μm, 0.2 μm, 0.5 μm, and 1 μm (i.e., samples JK0.1, JK0.2, JK0.5, and JK1, respectively). Also shown is that for a thin film of 0.5 μm thickness. A sharp drop in the SIRM intensity lost at the Verwey transition is evident.
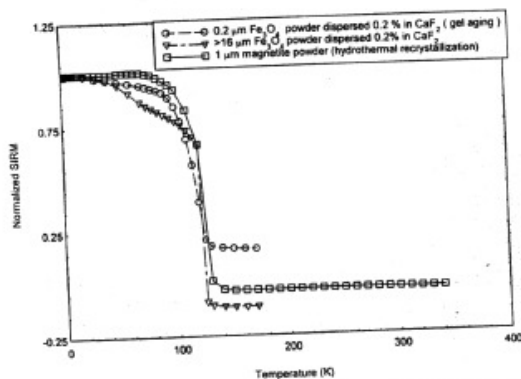
Figure 5. Thermal demagnetization of normalized SIRM for powdered samples whose particle sizes are 0.2 μm, 1 μm, and greater than 16 μm (i.e., samples Gel0.2, JH1, and JH>16, respectively), showing a decrease in the amount of SIRM lost at the Verwey transition with decreasing grain size.

transition suppression. *Levi and Merrill* [1976] attributed the source of the observed smaller decrease in SIRM with grain size of magnetite samples to shape anisotropy. This is unlikely in the present case since the arrays of cubic-shaped particles of this study have no significant shape anisotropy (their error in dimensions is less than 5%).

Although partial oxidation plays a role (Figure 6), it is not a convincing explanation for samples whose Verwey plots are shown in Figure 4 which were placed in ethanol (a nonoxidizing environment) immediately after annealing and taken for Verwey transition measurements. Further, XRD of co-annealed thin films of magnetite did not show any lines expected from oxidation. *Moskowitz et al.* [1993] observed a similar difference between the loss of SIRM at the Verwey transition between inorganic magnetite powders and intact magnetotactic bacteria magnetite.

5. Possible Explanation for the Observed Decrease in the SIRM Lost at the Verwey Transition

The magnetization of a grain is sensitive to its atomic arrangement. Testimony to this is the existence of magnetocrystalline anisotropy. It is reasonable to expect the distortion of atomic arrangement at a particle's surface to play a role in its magnetic behavior. At the boundary of grains, regular interatomic spacing is distorted [e.g., *Mercer*, 1990, p. 50].

Since the surface-area-to-body ratio of a particle increases with the decrease in particle size, this contribution could result in a similar trend to that exhibited by partially oxidized samples. Thus the observed decrease in SIRM intensity loss at the Verwey transition with particle size for unoxidized samples could be a surface-to-body ratio phenomenon that has nothing to do with oxidation of the sample.

An alternative explanation is to assume that the domain structure of particles in this size range is the vortex state [*Williams and Dunlop*, 1989]. These samples do not have all their atomic moments aligned in the (111) and (100) crystal

directions at temperatures above and below the Verwey transition temperature, respectively. Hence on cooling a sample through the Verwey transition, not all its atomic moments will align themselves from the (111) to the nearest (100) crystal axis, and hence a smaller decrease in the SIRM is expected.

6. Effect of Particle Interaction on the Verwey Transition

In order to determine the effects of magnetostatic interparticle interaction, lithographically produced interacting magnetite particles were used. Figure 7 shows SEM pictures for samples JK0.25@0.05, JK0.6@≈0.0 & JK1@0.25. The symbol @ in their name refers to interparticle spacing. For example, @0.05 means the interparticle spacing is 0.05 μm. A typical Verwey transition for interacting particles is shown in Figure 8. As can be seen from this figure, there is a larger drop in the SIRM lost at the Verwey transition for the sample with interacting particles than for that with noninteracting particles. Hence it is likely that the observed smaller drop in the SIRM at T_v for arrays of magnetite particles of this study (Figure 4) or those of arrays of intact magnetotactic bacteria [*Moskowitz et al.*, 1993] than magnetite powder samples [e.g., *Moskowitz et al.*, 1993; *Özdemir et al.*, 1993; this study, Figure 5] is due to particle clumping in the latter. The observed larger drop in SIRM at T_v for a magnetite thin film whose thickness is 0.5 μm than for an array of 0.5 μm noninteracting magnetite particles (Figure 4) is consistent with the deduction made above concerning particle clumping.

7. Effect of Stress on the Verwey Transition

Figure 9 shows SIRM as a function of temperature for an array of magnetite cubic particles after subjecting them to stress. Stress was induced in these samples by dropping the sample inside a sealed container from 600°C into water placed below the furnace. According to *Lowrie and Fuller* [1969], cooling magnetite at a high rate of greater than 30°C/s leads to structural defects. Hence the process of rapid quenching of samples described above insured that this rate
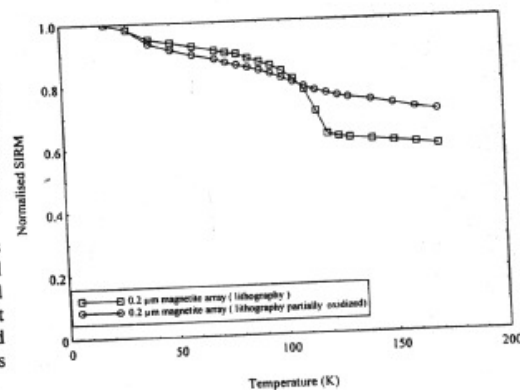

Figure 6. The Verwey transition for partially oxidized samples of lithographically produced arrays of 0.2 μm cubic magnetite particles compared to that of an unoxidized sample.
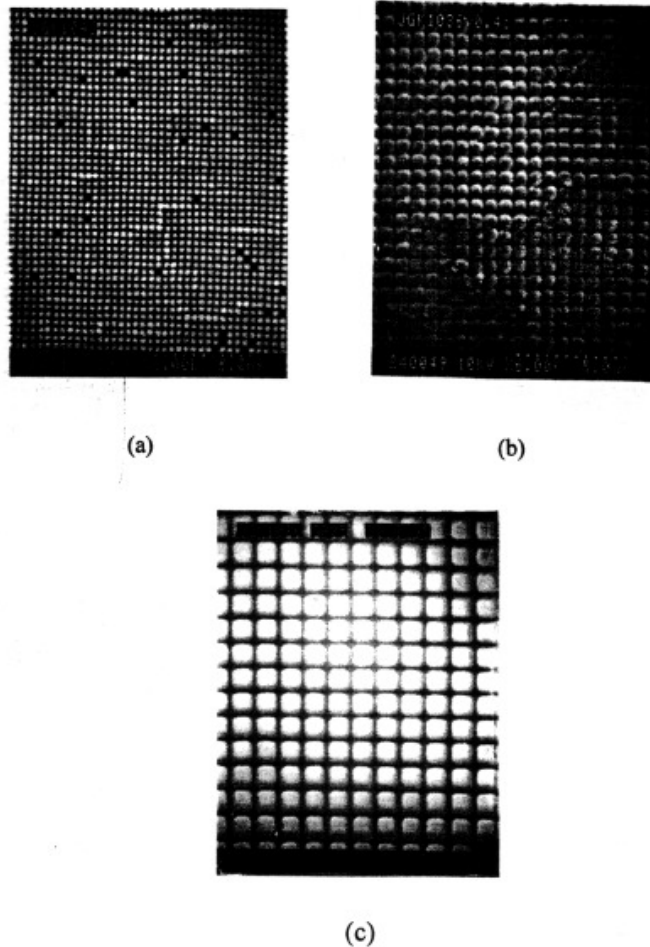
(a)   (b)

(c)

Figure 7. SEM pictures of interacting lithographically produced cubic magnetite particles of the following dimensions: (a) 0.25 μm cube edge and 0.05 μm interspacing (sample JK0.25@0.05), (b) 0.6 μm and about 0.0 μm interspacing (i.e. sample JK0.6@≈0.0) and (c) 1 μm and 0.25 μm interspacing (sample JK1@0.25).

was exceeded. Another way of subjecting the sample to stress was by applying physical pressure with a piston.

Figure 9 (curve marked with open circles) shows SIRM for a sample that was rapidly cooled by dropping from a temperature of 600°C into a water container at room temperature. A constant decrease in the amount of SIRM starting from a temperature of 70 K to 120 K is evident. The Verwey transition is still near 120 K. The curve marked with solid circles shows a typical example for an array of magnetite particles obtained using annealing method 1. Although the Verwey transition is centered near 120 K, the rate of decrease is almost constant and occurs over a large temperature interval. This is most likely due to the difference in the stress anisotropy. The stress anisotropy is expected to increase from the top of a particle to its center. Thus different regions in a magnetite particle behave as if they each have

their own magnetostriction anisotropy that is slightly different from the next region.

From the above mentioned observations concerning stressed samples of magnetite, it can be concluded that stressed magnetite grains can lead to an increase in the temperature interval where the Verwey transition occurs.

8. Effect of Oxidation on the Verwey Transition

Low-temperature oxidation of magnetite often results in the formation of a layer of maghemite on the surface. Owing to the difference in lattice constants between magnetite (3.96 Å) and maghemite (3.34 Å), stress as a result of lattice mismatch is expected in partially oxidized samples. It had already been shown in the above section that stress can lead to an increase in the temperature interval at which the Verwey
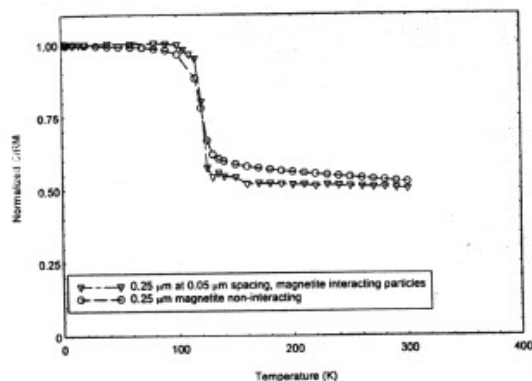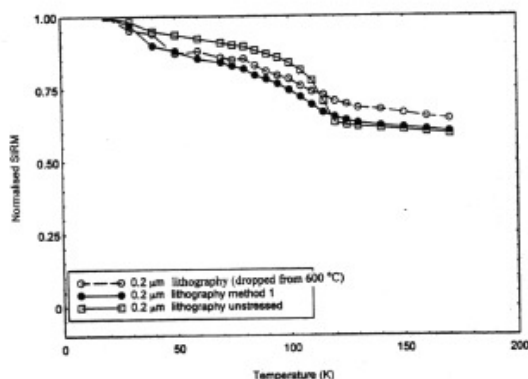
Figure 8. Thermal demagnetization of normalized SIRM given at 1.8 K in a field of 1 T for sample JK0.25@0.05 (interacting) compared to that for sample JK0.25 (noninteracting). A larger drop in SIRM at the Verwey transition for the interacting sample is evident.

transition occurs; hence one can expect partially oxidized particles to exhibit this behavior. This has been found to be the case (Figure 6). There is not the large decrease in SIRM intensity below 40 K that was observed by *Özdemir et al.* [1993], and which they ascribed to possible existence of small particles in the SPM size range. Such SPM particles are expected from the postulated cracking of a grain due to the lattice mismatch between the magnetite at the core and the maghemite at the surface. Using a high-resolution SEM, no cracked grains were observed in the samples of this study.

9. The Definition of Magnetic Memory

In this section it will be shown that two definitions of magnetic "memory" exist in the literature. The definition of *Haigh* [1957], which is the same as that of *Ozima et al.* [1964], *Creer and Like* [1967], *Kobayashi and Fuller* [1968]

Figure 9. Thermal demagnetization of normalized SIRM given at 20 K in a 1 T field, showing an increase in the temperature interval at the Verwey transition for stressed samples (i.e., lithography method 1 and lithography dropped from 600°C).
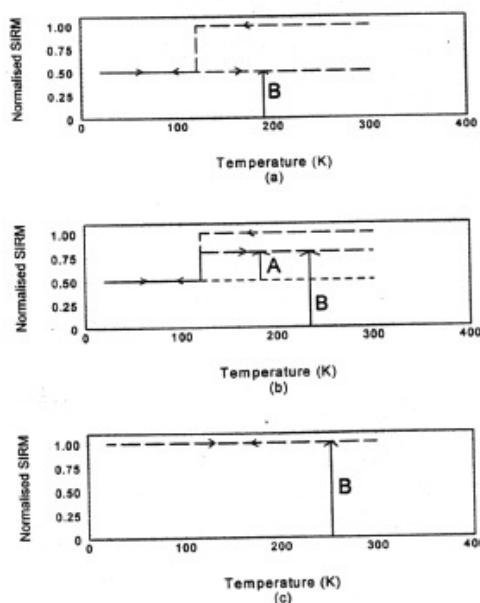
Figure 10. Hypothetical normalized SIRM for magnetite showing (a) no memory according to definition 1, but memory equal to B according to definition 2, (b) memory according to definitions 1 and 2 equal to A and B, respectively, and (c) no low-temperature transition, yet a memory according to definition 2 equal to B (a 100% memory).

and *Nagata et al.* [1964], is different from that of *Heider et al.* [1992]. The former definition will hereafter be referred to as definition 1, while the later is definition 2.

9.1. Definition 1

According to this definition, memory refers to the recovery of the original direction of remanent magnetization after cooling and warming through a low-temperature transition in zero field. In this definition, there has to be a recovery of the remanence in the same direction as the original remanence. The amount of recovered memory is indicated by the letter A in Figure 10b. This definition will also be referred to as the "true" memory.

9.2. Definition 2

Here memory refers to the surviving remanent magnetization after cooling and warming through a low temperature transition in zero field. In this definition the lost remanence at the low temperature (if any) need not be recovered. Figure 10 shows such a memory indicated by the letter B. For example, a sample that does not exhibit a low-temperature transition, such as maghemite, will have 0% and 100% memory according to definitions 1 and 2, respectively (Figure 10c). Since there has to be recovery of the lost SIRM at the low-temperature transition of magnetite according to definition 1, its value should be measured at least once below the low-transition temperature for magnetite. Note that the particles size dependence of SIRM lost at the Verwey
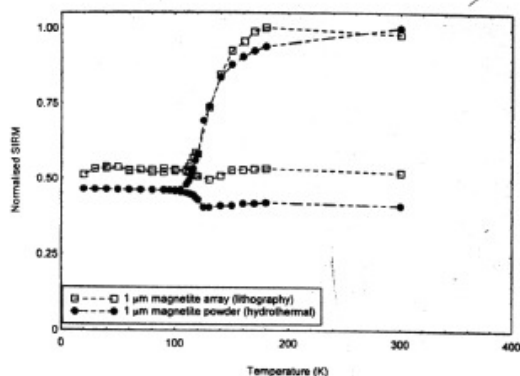
Figure 11. Magnetic memory for unstressed magnetite samples JK1 (lithography) and JH1 (powder), showing no memory according to definition 1, but memory according to definition 2.

transition (e.g., Figure 4) could be interpreted as memory according to definition 2. This is clearly not "true" memory.

10. Magnetic Memory for Unstressed Samples

SIRM was given in a field of 1 T at 300 K before cooling the sample in zero field to 20 K and then warming it back to 300 K. A second SIRM was then given to the same sample in a field of 1 T at 180 K and measured at 10 K temperature intervals during a cooling-warming cycle in zero field, from 180 K to 20 K, and back to 180 K. Figure 11 shows a plot of normalized SIRM for the thermal process described above. Sample JK1 is a lithographically produced sample of arrays of 1 μm magnetite particles, and sample JH1 is a magnetite powder of 1 μm average grain size. Both samples exhibit magnetic memory according to definition 2, but not according to definition 1.

11. Effect of Stress on Magnetic Memory

It has long been suspected that stress is the source of the observed magnetic memory [e.g. *Ozima et al.,* 1964; *Kobayashi and Fuller,* 1968; *Heider et al.,* 1992]. Lithographically produced magnetite particles of well-defined parameters including interparticle spacing are used in this study to investigating the effect of stress on magnetic memory for samples in the pseudo-single-domain size range. Unlike magnetite powders, these samples are not susceptible to particle clumping. The results are compared to those for magnetite powders and multidomain single crystals. From Figure 12 it can be seen that stressed samples exhibit "true" memory since there is a recovery of part of the SIRM loss at the Verwey transition.

The magnetic properties of a 2 mm natural crystal (sample JSC1) from Shetland greenschist were measured. The Curie temperature was found to be 550°C, while the Verwey transition temperature was 107 K. The lower than 120 K observed Verwey transition is most likely an indication of nonstoichiometry [*Aragón et al.,* 1985]. The magnetic memory of this sample was found to be very high (Figure 13). It can be concluded that this magnetite crystal is stressed. Greenschist facies in contractional deformation [*Yardley,* 1989] could induce stress in magnetite crystals. Stress may also have been induced in this sample during the crystal extraction process or during the process of Curie point determination by heating and cooling rapidly.

12. Saturation Magnetization as a Function of Low Temperature

According to theoretical predictions [e.g., *O'Reilly,* 1984], the saturation magnetization of magnetite should decrease with increasing temperature, until the Curie point. There should not be any other transitions. However, as can be seen from Figure 14, on warming the sample from 5 K, in a 1 T applied field, an increase in saturation magnetization is observed near 120 K.
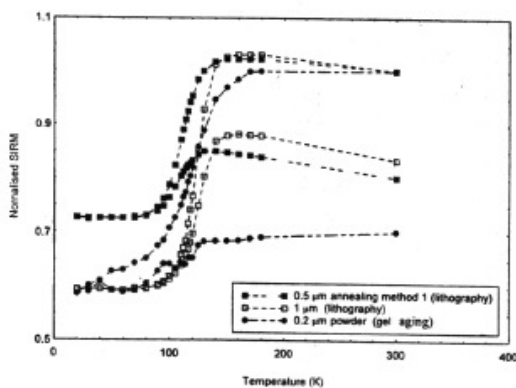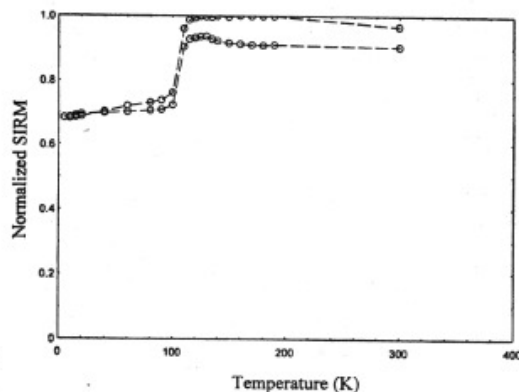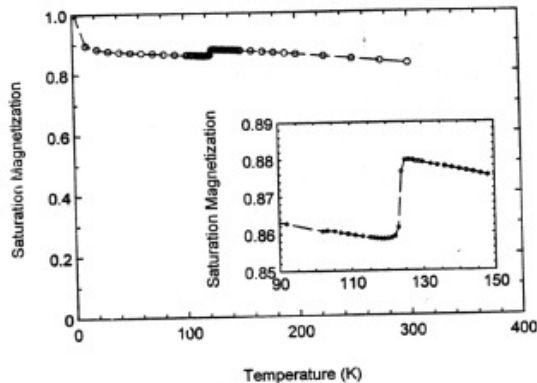

Figure 12. Magnetic memory for stressed magnetite samples Gel0.2, JK1 and JK0.5. All these samples exhibit "true" memory (i.e., the recovery of lost SIRM at Verwey transition).

Figure 13. SIRM measured in zero field as a function of temperature for a natural 2 mm magnetite single crystal (sample JSC1). The sample exhibits a very high memory, a sign of stress.
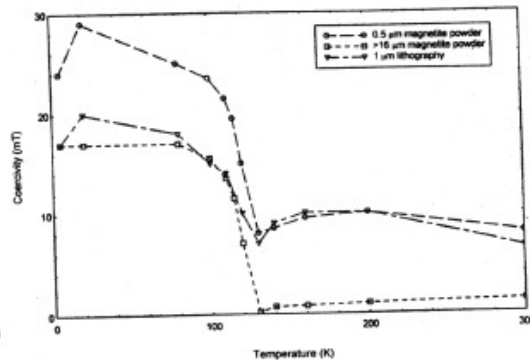
Figure 14. Normalized saturation magnetization obtained in a field of 1 T. The sample was warmed from 5 K to 300 K. An increase in magnetization is evident near 120 K. The transition is easily visible from the inset plot.

Figure 15. Coercivity as a function of temperature. The smaller magnetite particles (JK0.5 and JK1) show a smaller increase followed by a decrease in coercivity on either side of 130 K, but this is not evident for JH>16, the comparatively larger sized sample.

This observation is not entirely explicable in terms of the Verwey model of a "structural-electronic" transition in which some observed transition parameters are explained in terms of electron hopping between the iron cations in the B site of the magnetite crystal structure [O'Reilly, 1984]. A possible model that can explain the observed increase in saturation magnetization (M_s) near 120 K is the so-called "magnetic-electronic" model [Belov, 1993]. According to this model, some conducting electrons are trapped by the field of iron cations in B sites. Such trapped electrons have their magnetic moment in a direction that is antiparallel to that of cations in the B sites, hence the reduction of magnetization. It is not the intention of the present study to vindicate this theory, hence the interested reader is referred to the review article by Belov [1993]. However, the intention here is to draw attention to a possible high-field, low-temperature method of identifying magnetite. This could be done by measuring M_s as a function of low temperature and observing if there is an increase near 120 K. This method would not require the sample to be in an essentially field-free environment, which is necessary when observing SIRM changes.

13. Coercivity as a Function of Low Temperature

An attempt was made to measure hysteresis loops of lithographically produced particles as a function of low temperature using the MPMS2 SQUID. However most of the lithographically produced magnetite arrays had too weak a moment to produce loops with clearly resolvable coercivities. Only one lithographically produced sample, namely, sample JK1 (an array of 1 μm cubic particles of magnetite), had large enough total moments for the coercivity to be resolved by the MPMS2 SQUID.

Figure 15 shows coercivities (Hc) plotted as a function of temperature for samples JK1, JH0.5, and JH>16. The curves for samples JK1 and JH0.5 show a gradual increase in coercivity with decreasing temperature before a comparatively sharp decrease to a minimum around the Verwey transition temperature. The coercivity then increases drastically with decreasing temperature, before reaching a maximum and then gradually decreasing again. On the other hand, the curve for JH>16 shows no such increase and decrease with temperature above the Verwey transition.

From the above observations it seems reasonable to deduce that the existence of a small maximum in the observed coercivity, as a function of temperature above the Verwey transition, could be typical of pseudo-single-domain particles. Upon checking available data in the literature [e.g. Hodych, 1986, 1990; Schmidbauer and Schembera, 1987; Morrish and Watt, 1958], the same behavioral difference was observed.

14. Conclusions

Using samples of arrays of magnetite particles of well-defined dimensions, including particle interspacing, the following results were obtained. The larger drop in SIRM at the Verwey transition observed in this study, and other studies, compared to samples of magnetite powders, was shown to be consistent with the effects of interparticle magnetostatic interactions in the latter. The particle size dependence of the drop in SIRM at the Verwey transition displayed by magnetite particles in the pseudo-single-domain range is explicable in terms of the vortex domain structures obtained from three-dimensional micromagnetic calculations or surface-area-to-body ratio (independent of particle surface oxidation). The particle size dependent memory reported by other researchers is most likely a reflection of the amount of the SIRM lost at the Verwey transition instead of being the "true" magnetic memory. Magnetic memory has been shown to be a stress-related phenomenon. This observation might be useful in assessing the nature of stress in rocks. A possible method of identifying rocks containing magnetite by measuring saturation magnetization as a function of low temperature has been identified. Such a method does not require the sample to be in an essentially field-free space as is necessary when SIRM is measured.

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