Low-temperature magnetic hysteresis properties of partially oxidized magnetite

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SUMMARY

Hysteresis loops have been measured as a function of temperature between 10 K and room temperature for two samples of pseudo-single-domain magnetite. One sample, with mean grain size of 2–3 μm, displays just surface oxidation, the bulk of the material remaining relatively stoichiometric with a Verwey transition temperature (T_V) of 112 K. In contrast, another sample, which contains much finer grains ($\sim$0.15 μm), having been exposed to air for about 20 yr, shows evidence of oxidation affecting the whole grain volume. This process has apparently formed two-phase grains in which the core is composed of non-stoichiometric magnetite with a T_V of 95 K, and a superficial layer of probably pure maghemite. In accordance with previous studies, for both samples hysteresis properties below the Verwey transition depend critically on the mode of cooling through the transition. The difference in sample stoichiometry affects the temperature dependence of the hysteresis properties over the whole temperature range studied. Below the Verwey transition, the (relatively) stoichiometric sample shows a behaviour fairly close to that reported previously for a sample of similarly sized magnetite with a T_V of 118 K. Common features include (1) a rapid decrease of the M_{rs}/M_s ratio with increasing temperature after cooling in a strong magnetic field (FC), compared with the near constancy of this parameter after zero-field cooling (ZFC); (2) equally rapid decrease of the coercive force with increasing temperature after ZFC; (3) a small but significant difference between the temperature dependences of the coercive force after ZFC for a demagnetized versus a magnetized starting magnetic state. In the non-stoichiometric sample some of these features are also observed; however, it also shows a distinctive behaviour of the M_{rs}/M_s ratio after ZFC, which reaches a maximum at 30–35 K. Above the Verwey transition, the stoichiometric sample shows the behaviour typical of magnetite, i.e. an increase in the M_{rs}/M_s ratio and the coercive force, which starts approximately 10 K above the T_V and extends up to 200–210 K. In contrast, in the non-stoichiometric sample both parameters just slowly decrease between 110 K and room temperature.

Key words: magnetic domains, magnetite, phase transitions.

INTRODUCTION

During the last decade there has been a considerable increase of studies of the magnetic properties of rocks and minerals at cryogenic temperatures. An obvious impetus of these studies is the need, in palaeomagnetism and environmental magnetism, to identify the magnetic minerals present in a rock sample without altering them by heating, which is required for the determination of the Curie points. Although low-temperature techniques will never totally replace conventional high-temperature ones, they offer a useful and often invaluable complementary tool. Fortunately, several important mag-

netic minerals, such as magnetite, haematite and pyrrhotite, undergo phase transitions below room temperature (Dunlop & Özdemir 1997). The low-temperature phase transition in magnetite, called the Verwey transition (Verwey 1939), is the transition from a cubic to, most probably, a monoclinic crystal structure. Such a profound change in crystal symmetry manifests itself in abrupt change of many physical properties of the material, e.g. electrical conductivity, heat capacity and magnetization. In nominally stoichiometric magnetite at atmospheric pressure, transition temperatures (T_V) in the 119–124 K range have been reported (Gmelin *et al.* 1983; Shepherd *et al.* 1985; Gridin *et al.* 1996). The transition temperature is decreased by virtue of vacancies and impurities (Miyahara 1972; Gmelin *et al.* 1983; Aragón *et al.* 1985; Brabers *et al.* 1998), and of elevated pressures (Samara 1968; Tamura 1990; Rosenberg

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et al. 1996). A review of physical properties of the low-temperature phase of magnetite from the point of view of rock magnetism has been given recently by Muxworthy & McClelland (2000).

For natural samples, only in a few cases were transition temperatures reported that approach the values typical of truly stoichiometric magnetite (Torii 1997), which apparently occurs rarely in nature. More commonly, the observed T_V range from 115 to below 100 K (Kletetschka & Banerjee 1995; Brachfeld & Banerjee 2000a,b; Smirnov & Tarduno 2000; Kosterov 2001b). The effect of oxidation on low-temperature magnetization of magnetite has been studied previously on submicron (Özdemir *et al.* 1993) and on large multidomain grains (Cui *et al.* 1994). Özdemir *et al.* (1993) have observed (1) an apparent suppression of the Verwey transition in oxidized magnetites of size 37–220 nm and (2) a rapid decrease of the SIRM imparted at 5 K on heating in the interval 5–50 K, resulting in the loss of 30–40 per cent of the initial remanence. The latter effect has been ascribed to the superficial maghemite layer resulting from oxidation, supposed to exhibit superparamagnetism. Strikingly, a similar behaviour has been observed by Cui *et al.* (1994) on a truly multidomain sample with grain size >250 μm. In this case the loss of remanence cannot be explained by superparamagnetism of a superficially oxidized layer, since it would require an unrealistically large volume of oxidized material. Neither can it be a result of the multidomain nature of the sample, since a relatively stoichiometric sample of a similar grain size does not show any of the above features.

Magnetic hysteresis properties of the low-temperature phase of magnetite are still insufficiently known. Previous studies have been largely focused on the behaviour at the transition and immediately below it, to 77 K (e.g. Morrish & Watt 1958; Muxworthy 1999; Özdemir 2000). In fact, the only reliably established result is that both the coercive force and the M_{rs}/M_s ratio increase quite sharply on cooling down through the transition. Below 77 K, Schmidbauer & Schembera (1987) have measured hysteresis at a few temperatures for magnetite grains of size 60–160 nm prepared by reducing α-Fe_2O_3 particles in a H_2/H_2O atmosphere at 400 °C. For the two finest grain sizes (61 and 85 nm, respectively) M_{rs}/M_s ratios showed broad maxima between 50 and 100 K, while the coercive force showed a relatively rapid decrease. In contrast, two samples with slightly larger grain size (127 and 162 nm) showed much less temperature variation in either the M_{rs}/M_s ratio or the coercive force. Schmidbauer & Keller (1996) have measured hysteresis after cooling in a zero and in a strong magnetic field, respectively, on 220 nm magnetite grains prepared according to the method of Schmidbauer & Schembera (1987). Below the Verwey temperature, both M_{rs}/M_s and H_c were higher after field-cooling, showing at the same time little thermal variation after either treatment. Studying the effect of stress on hysteresis parameters, Sahu (1997) also measured hysteresis at several temperatures below 77 K for magnetite grains of 5–7 μm in size produced with the glass-ceramic method, and for a large natural single crystal (>500 μm). For the glass-ceramic sample, the coercive force was found to decrease from the initial value of 15 mT by about 20 per cent between 20 and 80 K, followed by a fourfold drop associated with the Verwey transition. For the single crystal, the coercive force decreased from 0.7 to 0.4 mT between 40 and 100 K and dropped further down to 0.2 mT at 130 K. External uniaxial stresses up to 120 MPa increased absolute values of the coercive force in both samples but did not change the shape of its temperature dependence.

The only attempt to develop a micromagnetic model describing the behaviour of fine grains of magnetite in the vicinity of the Verwey transition is that of Muxworthy & Williams (1999a,b). They have considered a simplified model where the magnetic state of a cubic grain had been found by minimizing the grain free energy, into which the magnetostatic, magnetocrystalline and Zeeman (energy in the external magnetic field) terms were included. An assumption is made implicitly that below T_V a grain is crystallographically uniform and possesses a unique easy magnetization axis. However, this model does not generally produce results compatible with available experimental observations. Predicted coercivities below the Verwey transition are higher than experimental values by at least a factor of 2, and do not show the observed grain size dependence (Schmidbauer & Schembera 1987; Schmidbauer & Keller 1996). Moreover, the model predicts that the SD upper limit in the low-temperature phase is about 0.14 μm (Muxworthy & Williams 1999b), while in the hysteresis cycle a SD-like state was found to occur in zero field even in grains as large as 0.3 μm (Muxworthy & Williams 1999a). At the same time, experimental values of the M_{rs}/M_s ratio do not reach the SD limit of 0.5 (for randomly oriented uniaxial grains) even in 60 nm grains (Schmidbauer & Schembera 1987).

Recently, Kosterov (2001a) has carried out a detailed experimental study of the magnetic hysteresis from 10 K to the Verwey temperature on a multidomain (size 100–150 μm) and a pseudo-single-domain (size 1–5 μm) sample of crushed natural magnetite. Both samples contained rather pure material, with Verwey temperatures of 115 and 118 K, respectively. However, hysteresis properties of the low-temperature phase were found to be strongly different owing to the contrasting grain size of the two samples. Of particular interest is the behaviour of the pseudo-single-domain sample, for which the temperature dependences of both M_{rs}/M_s ratio and the coercive force appear to depend critically on the mode of sample cooling prior to hysteresis measurements. The present work aims to extend the above study by using variably oxidized magnetite samples of comparable or smaller grain size.

SAMPLES AND EXPERIMENTAL PROCEDURE

Two samples of commercially produced magnetite were used in the present study, designated, respectively, as 3006 (Wright Company) and BK5099 (Pfizer Company). Sample 3006 with a nominal grain size of 2–3 μm was acquired in 1999 (Smirnov, personal communication, 1999), and sample BK5099 in 1981 (Özdemir, personal communication, 1999). For BK5099, room-temperature magnetic properties and grain size distribution have been measured by Özdemir & Banerjee (1982). Using transmission electron microscopy (TEM), they found the median grain size to be 0.12 μm, and minimum and maximum sizes of 0.05 and 0.6 μm, respectively. Grains were mostly of spherical and cubic shape. Both samples have been re-examined under a scanning electron microscope (Fig. 1). Grains in sample 3006 are of rather irregular shape and have a broad size distribution, from 0.5 to about 5 μm. For BK5099, SEM observations could only confirm very fine grain size, which apparently was not changed by about 20 yr of storage in air.

The Curie points of the two samples were determined from susceptibility versus temperature curves measured with a KLY-3 instrument in an argon atmosphere (Fig. 2). For both samples, heating curves show bumps at 300–400 °C, which might be an indication of partial conversion of maghemite to magnetite and of the annealing of some defects and/or internal stresses. The latter is also a likely reason for a 15–20 per cent increase of susceptibility after a thermomagnetic run, observed in both samples. Curie points, determined by averaging values obtained from heating and cooling curves, are
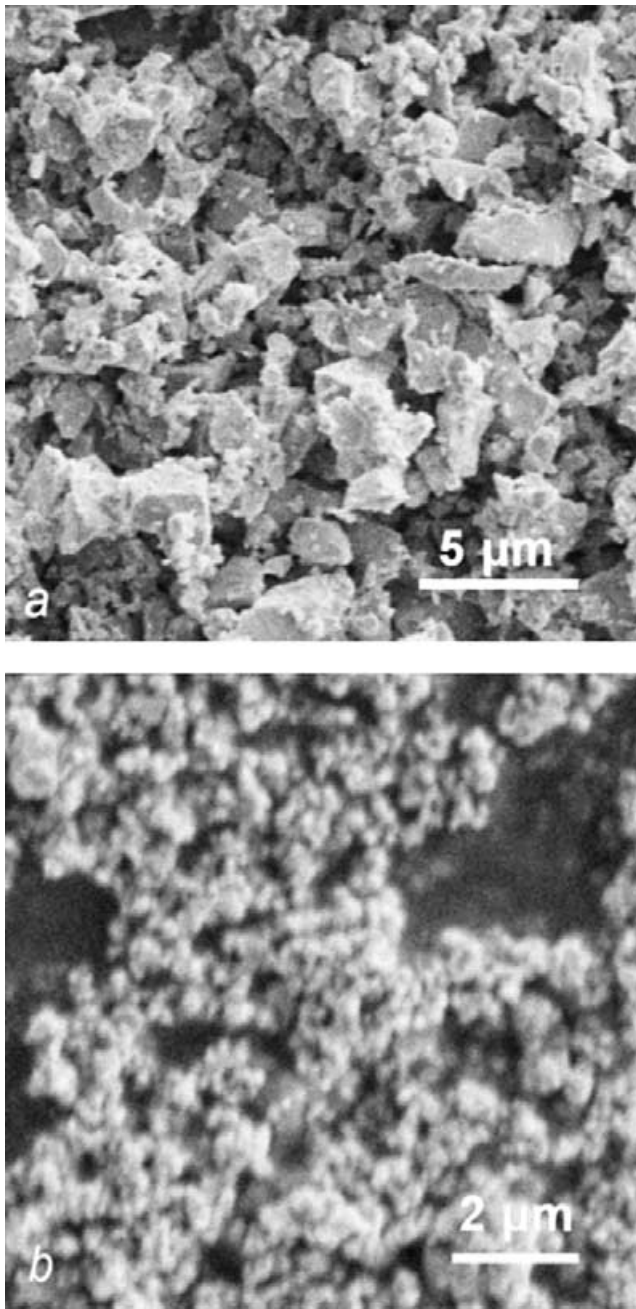
Figure 1. SEM images of sample (a) 3006 and (b) BK5099.

Figure 2. Susceptibility versus temperature curves measured in an argon atmosphere for (a) 3006 and (b) BK5099.

Figure 3. Low-temperature SIRM demagnetization curves showing the Verwey transition for 3006 (solid symbols) and BK5099 (open symbols) magnetite samples. Solid lines show the derivative of the SIRM (T) curve for 3006; dashed line for BK5099. Transition temperatures are defined as the minima on the SIRM derivative curves.

592 °C for 3006 and 589 °C for BK5099, slightly higher than the nominal Curie temperature of stoichiometric magnetite.

Zero-field warming curves of the low-temperature SIRM were measured with an MPMS XL instrument. A decrease of magnetization associated with the Verwey transition was observed on both samples, yielding, however, rather different transition temperatures: 112 K for 3006, and 95 K for BK5099 (Fig. 3). Hysteresis parameters at room temperature were: $M_{rs}/M_s = 0.30$, $H_c = 24.5$ mT, $H_{cr} = 38.7$ mT for 3006 and $M_{rs}/M_s = 0.17$, $H_c = 11.3$ mT, $H_{cr} = 24.7$ mT for BK5099. Also worth noting is that the values for BK5099 are significantly lower than those measured on this sample soon after acquisition (Özdemir & Banerjee 1982), possibly indicating the presence of fine maghemite particles coating oxidized magnetite grains.
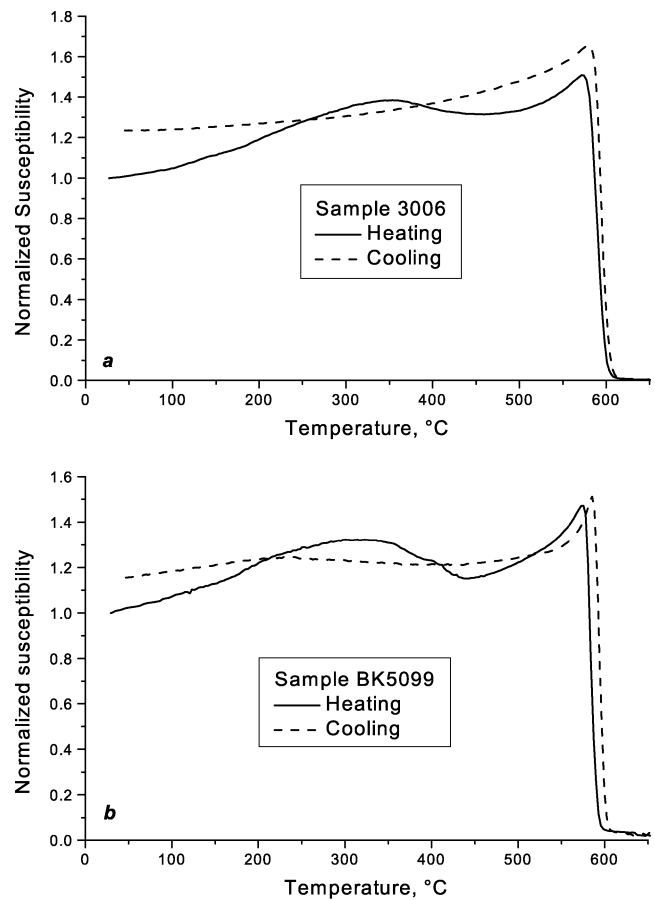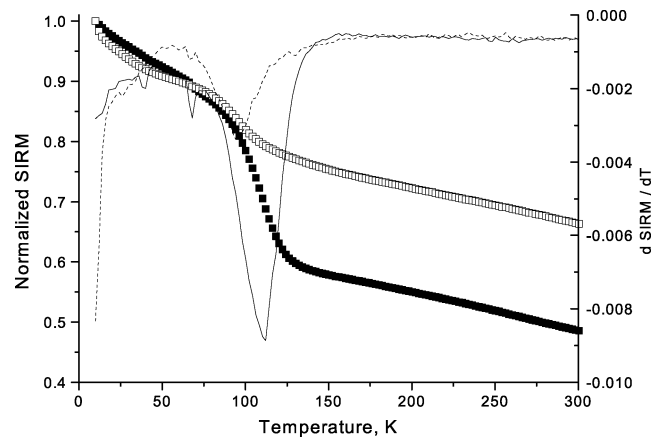
The set-up of the low-temperature hysteresis experiments closely followed that described previously (Kosterov 2001a). Measurements were performed using a Princeton Measurements vibrating sample magnetometer (VSM) equipped with a cryostat (Institute for Rock Magnetism, Minneapolis). About 1 mg of BK5099 and about 15 mg of 3006 powders have been placed into a gelcap and gently

pressed with the tip of a VSM sample holder. As previous trials to break clumps of magnetite grains present in both samples had proven unsuccessful, no attempt was taken to disperse magnetite in a non-magnetic matrix. This means that hysteresis data were certainly influenced by magnetic interactions, but, on the other hand, this allows one to avoid the problem of having to correct for matrix magnetization in strong fields. The maximal field of the hysteresis loop was 1.4 T; magnetic field increments of 5 mT were used. For both samples, hysteresis loops were measured on warming after initial cooling to 10 K in a 1.5 T field (field cooling, FC) and twice after cooling in zero magnetic field (ZFC). In the latter experiments, an initial magnetic state was either magnetized (hereafter termed ZFC$^+$), or DC-demagnetized (hereafter termed ZFC^0). In these experiments, hysteresis loops were measured in the direction of either a pre-cooling magnetization or a magnetic field applied during cooling. In another experiment, following either a FC or a ZFC$^+$ treatment, at 10 K a sample was turned by 90° in the horizontal plane, and hysteresis loops were measured in this new direction. Temperature increments were slightly different for the two samples. For 3006 they were 5° in the 10–100 K range, 2° in the 100–130 K range and 20° above 130 K. For BK5099 the temperature increments were 5° in the 10–80 K range, 2° in the 80–140 K range and 20° above 140 K in regular runs; 5° increments throughout the 10–140 K range were used in the experiments with the sample 90°-turn at 10 K. After reaching a target temperature, a sample was equilibrated for 15 s at a 2° temperature step, for 30 s at a 5° step, and for 2 min at a 20° step. During the ~3 min required to trace a complete loop the temperature could be kept to within 0.25 °C of a target temperature.

Hysteresis loops were processed as follows. First, the data were clipped at ±1.35 T field in order to avoid problems caused by electromagnet pole saturation. Since in the low-temperature phase of magnetite the approach to saturation depends strongly on the mode of cooling the sample through the Verwey transition, and fields above 2 T are required to reach complete saturation (Özdemir & Dunlop 1999), approximate M_s values were calculated by averaging magnetizations measured on the field absolute value ascent in the 1.25–1.35 T interval. In this interval, the magnetization varied by a maximum of 0.5 per cent, so these proxy M_s values underestimate the true ones by only few per cent. Finally, the saturation remanence and the coercive force were determined by second-degree polynomial interpolation of the $M(H)$ data measured in the vicinity of the $H = 0$ and $M = 0$ points, respectively.

RESULTS

Hysteresis of the low-temperature phase

The temperature dependence of the hysteresis loop parameters below the Verwey transition for sample 3006 are summarized in Fig. 4. The dependence of the hysteresis properties on the thermomagnetic history noted previously (Schmidbauer & Keller 1996; Kosterov 2001a) is observed for this sample as well. After the field cooling, the M_{rs}/M_s ratio is strongly anisotropic. It is higher but decreases rapidly with temperature between 10 and 90 K, if measured along the cooling field direction, while only a small temperature variation is observed when loops are measured at 90° to the latter. After zero-field coolings, M_{rs}/M_s ratios are intermediate between the FC(0°) and FC(90°) values, and are also almost temperature-independent below 90 K. In the same temperature range, the coercive force shows a somewhat opposite pattern: it decreases rapidly with increasing
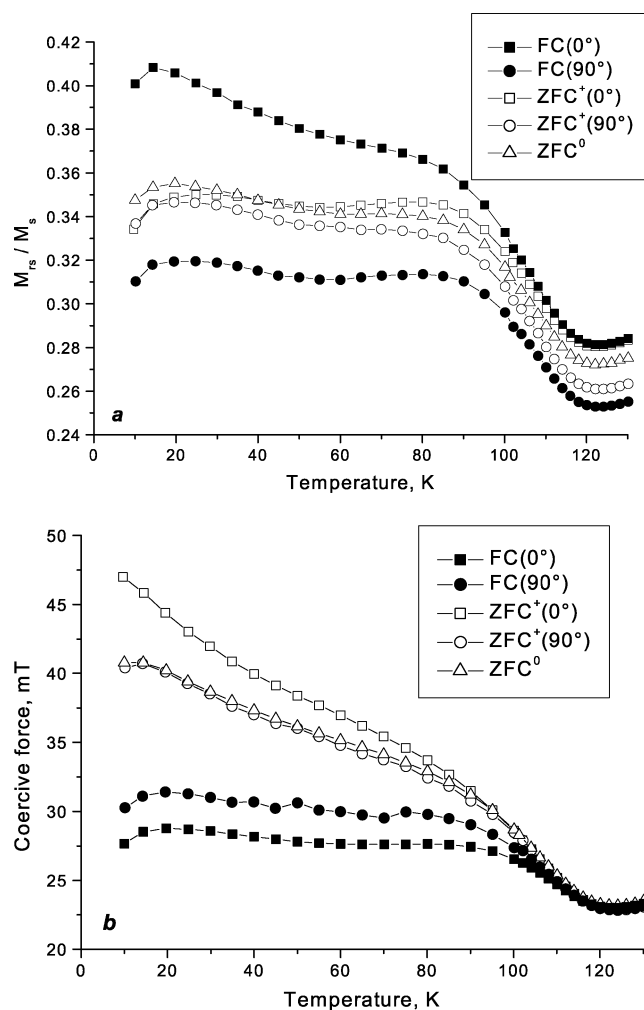
Figure 4. Temperature variation of (a) the M_{rs}/M_s ratio and (b) the coercive force for 3006. Hysteresis parameters derived from loops measured after FC are shown by solid symbols; those derived from loops measured after ZFC by open symbols. See the text for further notation.

temperature after ZFC, and is almost constant after FC. In common with the previous observation on a 1–5 μm sample of crushed magnetite (Kosterov 2001a), coercivity after ZFC depends on the pre-cooling magnetic state, being higher after the ZFC on the magnetized sample (Fig. 4b).

Sample BK5099 exhibits a somewhat more complex behaviour below the Verwey transition (Fig. 5). Two characteristic temperature ranges can be recognized, in which the hysteresis parameters vary in a different way: 10–50 and 50–80 K. Below 50 K, the M_{rs}/M_s ratio decreases rapidly in the FC(0°) run, while in the four other runs a maximum of M_{rs}/M_s is observed at 30–35 K. In contrast, the coercive force decreases rapidly and with nearly constant rate after ZFC, while after FC it decreases rather slowly below 35 K and then much faster between 35 and 50 K. Between 50 and 80 K, M_{rs}/M_s shows a relatively slow decrease in the FC(90°) and in all ZFC runs, and a somewhat faster decrease in the FC(0°) run. The coercive force decreases rather slowly in this temperature range, with the rate being almost independent of the thermomagnetic history of the sample. Examination of hysteresis loops measured at 10 K (Fig. 6a) reveals yet another interesting feature: the loop measured after ZFC$^+$ is quite strongly asymmetric, the coercive force measured at the descending branch being larger by about 2.5 mT. This is far beyond the usual
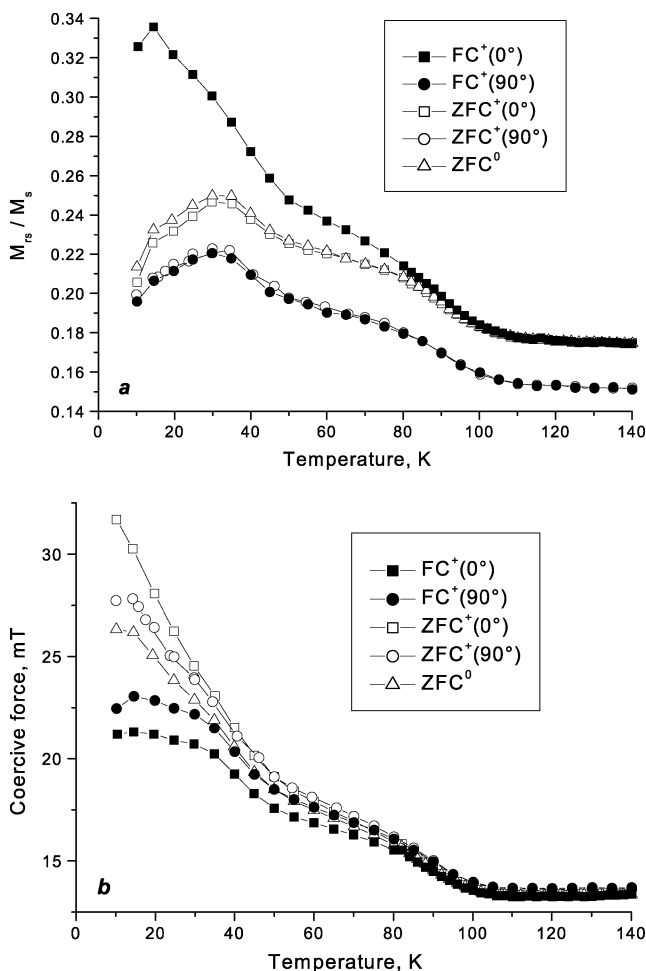
Figure 5. Temperature variation of (a) the M_{rs}/M_s ratio and (b) the coercive force for BK5099. Symbol conventions are as in Fig. 4.

Figure 6. (a) Hysteresis loops and (b) switching field distributions of sample BK5099 measured at 10 K after ZFC^+, ZFC^0 and FC treatments. The measuring field was applied parallel to the remanence of the sample in the case of ZFC^+ and parallel to the biasing field in the case of FC.

experimental discrepancy of 100–300 µT. No other thermal treatment results in such asymmetric loops. However, this asymmetry is not very stable and has disappeared already by 30 K. Loops after ZFC also have a considerably broader switching field distribution (Fig. 6b).

To confirm that the behaviour of the BK5099 sample at very low temperatures is not an artefact caused by, for example, incomplete saturation, this sample was re-examined using an MPMS XL instrument. Hysteresis loops have been measured after ZFC^+ from 5 to 130 K. A maximal field of 3 T was used to measure loops at temperatures from 5 to 35 K, and 1.5 T above 35 K. Also, two hysteresis loops at 10 and 40 K were measured after cooling in a 3 T field. Results of MPMS measurements are summarized in Fig. 7. All essential features observed in VSM experiments, including the M_{rs}/M_s maximum and the asymmetry of loops measured after ZFC^+, are confirmed with the MPMS data.

The Verwey transition

In both samples, the Verwey transition manifests itself in a decrease of the M_{rs}/M_s ratio and the coercive force. However, this decrease is not as large as reported in many previous studies (e.g. Morrish & Watt 1958; Hodych 1982; Schmidbauer & Schembera 1987;
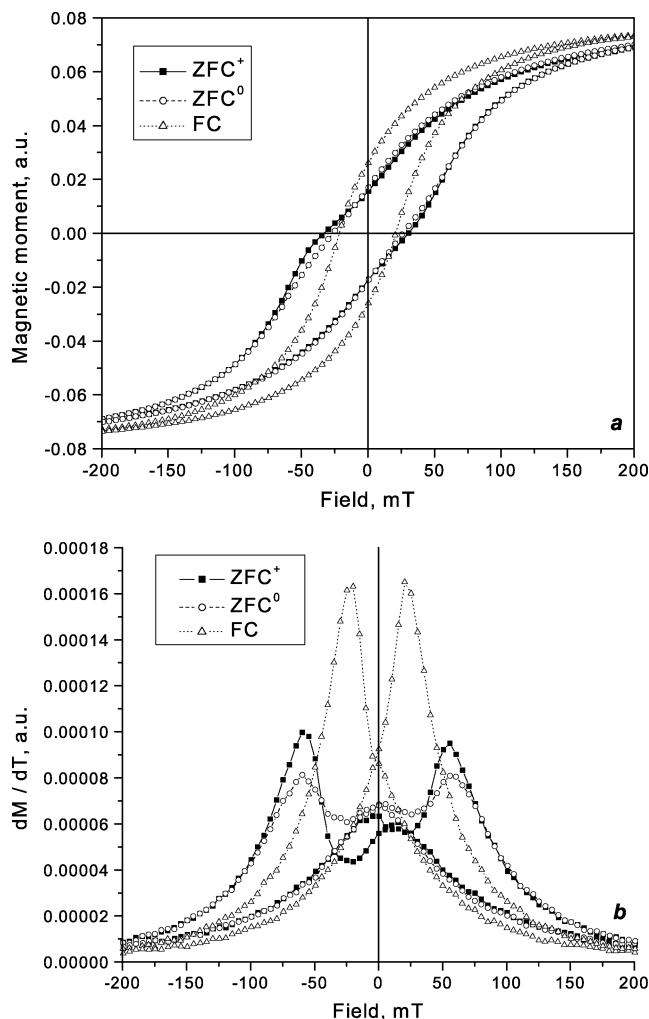
Schmidbauer & Keller 1996; Muxworthy 1999; King & Williams 2000), and far smaller than predicted by the micromagnetic model of Muxworthy & Williams (1999a). The temperature ranges associated with the transition are rather broad: 90–125 K for 3006 and 80–110 K for BK5099. For 3006, the coercive force drops from 27 to 31 mT at 90 K to about 22.5 mT at 122–124 K where it has a minimum; M_{rs}/M_s decreases from 0.31 to 0.35 at 90 K to 0.25–0.28 at 122–124 K. For BK5099, the decrease is somewhat smaller: H_c drops from 16 mT at 80 K to about 13 mT at 110 K, and M_{rs}/M_s from 0.18–0.21 to 0.15–0.17.

Previous studies (Umemura & Iida 1976; Aragón 1992; Özdemir & Dunlop 1999; King & Williams 2000) have shown that in magnetite close enough to ideal stoichiometry, a small increase in saturation magnetization is observed at the Verwey transition. Whereas it is still uncertain whether this feature reflects the true increase of the spontaneous magnetization, or is just an artefact arising from incomplete saturation of the low-temperature phase, it is still a useful method for determining the transition temperature. For example, Kosterov (2001a) has shown that, although the effect of the incomplete saturation of the low-temperature phase was evident, the transition range as defined from M_s variation appears somewhat
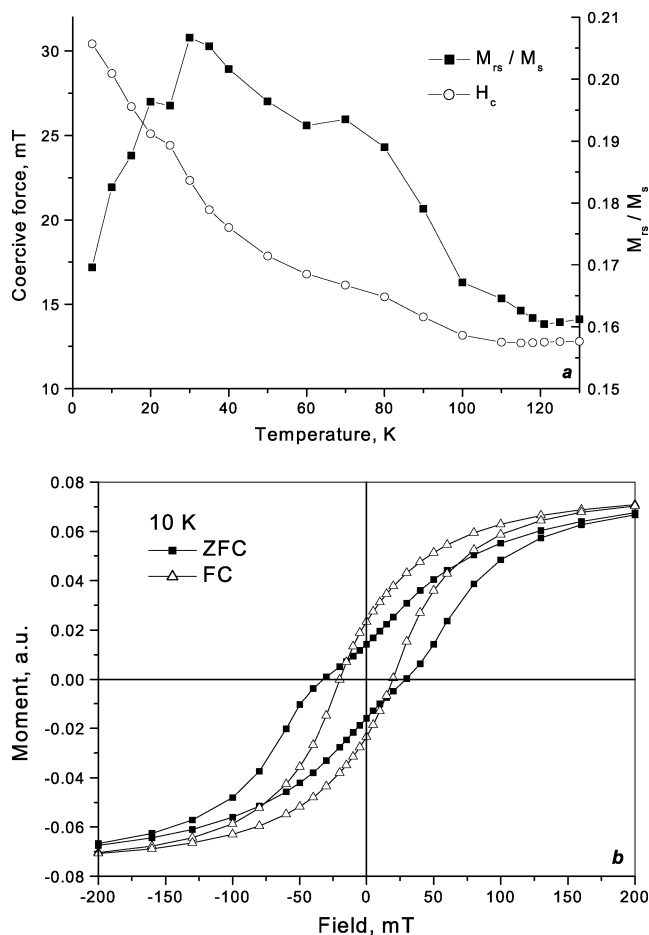
Figure 7. Hysteresis properties of BK5099 measured with an MPMS XL instrument. (a) Temperature variation of the M_{rs}/M_s ratio and the coercive force after ZFC$^+$; (b) comparison of hysteresis loops measured at 10 K after ZFC$^+$ and FC, respectively.
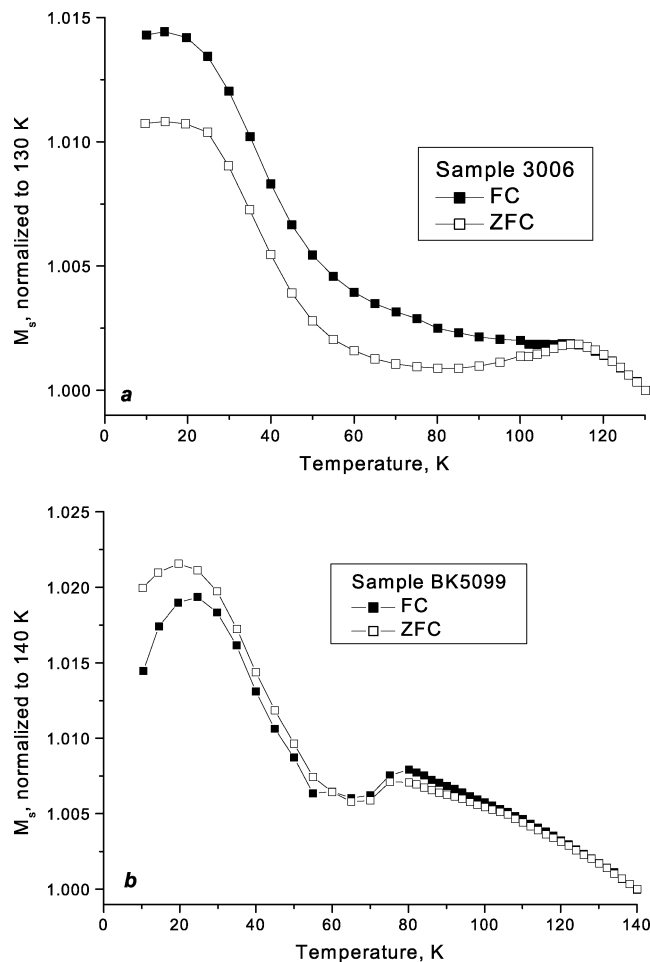

Figure 8. 'Saturation' magnetization versus temperature curves for (a) 3006 and (b) BK5099.

Behaviour above the Verwey transition

The temperature dependences of hysteresis parameters of the two samples above the Verwey transition are summarized in Fig. 9. Sample 3006 shows the behaviour typical for magnetite grains of submicron to micron size (Morrish & Watt 1958; Schmidbauer &
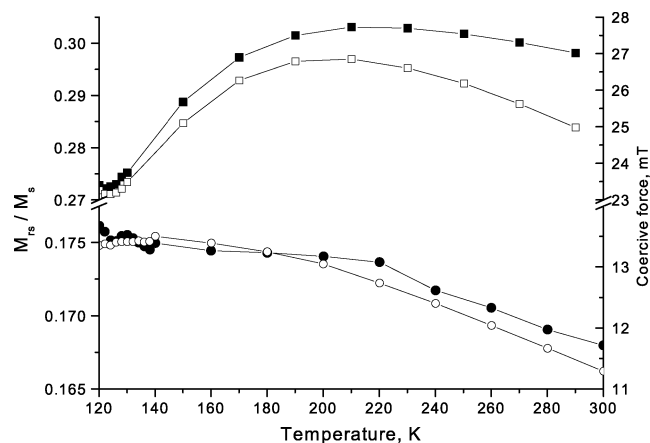
narrower than that obtained from the SIRM(T) decay. However, for the samples used in the present study the M_s(T) curves (Fig. 8) are more complex. In both samples, saturation has not been reached at low temperatures. For 3006, a small increase of M_s, derived from loops measured after ZFC, is observed between 100 and 114 K, yielding a tentative transition temperature of 108 K. This transition temperature is more or less compatible with the value obtained from the SIRM(T) curve (112 K). However, the M_s(T) curve obtained from loops measured after FC only shows a plateau in the same temperature range. In contrast, in BK5099 an increase of M_s is observed between 70 and 80 K, i.e. at much lower temperatures than the transition temperature of 95 K obtained from the SIRM(T) curve. This temperature, however, corresponds closely to the midpoint of the interval (80 to ~110 K), where M_{rs}/M_s and the coercivity decrease relatively rapidly, independent of the previous thermomagnetic treatment. These arguments lead us to consider 95 K as the transition temperature for this sample. At the same time, no anomaly in the M_s(T) curves is observed at this temperature. Note that the study of the influence of magnetite stoichiometry on the magnetization of the low-temperature phase (Aragón 1992) also did not reveal an anomaly at the transition temperature (95 K) for a sample of non-stoichiometric magnetite with composition $\delta = 0.006$ in the formula $Fe_{3(1-\delta)}O_4$, which corresponds to an oxidation parameter (z) of 0.054.

Figure 9. Temperature variation of the M_{rs}/M_s ratio (solid symbols) and the coercive force (open symbols) for the two samples between 120 K and room temperature. Squares denote sample 3006, circles BK5099.

Schembera 1987; Argyle & Dunlop 1990; Schmidbauer & Keller 1996) and for magnetite-bearing rocks (Hodych 1982, 1986, 1990, 1996): an initial increase of the M_{rs}/M_s ratio and the coercive force on warming from the transition, with both parameters reaching a maximum around 210 K, followed by a slow decrease. A relatively small variation of both parameters between T_V and room temperature in this sample is compatible with its grain size. In contrast, BK5099 shows no increase of M_{rs}/M_s and H_c above the transition. Rather, both parameters remain virtually constant over a wide temperature range, up to 220 K for M_{rs}/M_s and up to 160 K for the coercive force, and then start to decrease slowly.

DISCUSSION

Effect of field cooling on the magnetic hysteresis of the low-temperature phase

Li (1932) was the first to investigate experimentally the effect of a magnetic field applied during cooling through the low-temperature transition upon the magnetic properties of magnetite. His and later studies on natural and synthetic single crystals, including magnetic resonance, torque and magnetization measurements (Bickford 1950; Domenicali 1950), have led to a model accounting for most of the observed features (Bickford 1950; Williams *et al.* 1953). Essentially, cooling in a strong magnetic field sets an easy magnetization axis of the low-temperature phase approximately along the [001] direction of the cubic phase closest to the magnetic field. Cooling through the transition in zero field would set an easy axis along a randomly chosen [001] direction. At the same time, easy axis switching in the low-temperature phase by applying a magnetic field at a large angle to an initial easy axis has been observed (Bickford 1950; Calhoun 1954; Abe *et al.* 1976). Also, Hamilton (1958) and more recently Medrano *et al.* (1999) have provided evidence that the magnetic field applied during cooling through the Verwey transition controls, to a large extent, the formation of the crystallographic monoclinic and possibly triclinic (Medrano *et al.* 1999) twins.

The above model has been shown recently (Kosterov 2001a) to account, at least qualitatively, for the hysteresis properties of the low-temperature phase of multidomain magnetite. In a sample of magnetite ($T_V = 115$ K) containing 100–150 μm grains, both the M_{rs}/M_s ratio and the coercive force of the low-temperature phase were about twice as high after ZFC compared with FC, demonstrating that any change in magnetization was indeed much easier in the direction of the magnetic field applied during cooling. The near constancy of both M_{rs}/M_s and H_c was observed in FC(0°), ZFC$^+$(0°) and ZFC^0 experiments, which is compatible with the behaviour of the magnetocrystalline anisotropy below T_V (Palmer 1963; Abe *et al.* 1976; Kakol & Honig 1989) and direct domain observations on the monoclinic phase (Moloni *et al.* 1996). Progressive switching of the easy axis into a new direction starting above 60 K was also evident when hysteresis loops had been measured at right angles to the field direction applied during cooling.

However, in the same study a considerably more complex behaviour has been observed for a pseudo-single-domain (grain size 1–5 μm) magnetite sample of comparable stoichiometry ($T_V = 118$ K). This sample and the two samples used in the present work show several similar features: (1) after FC(0°), the M_{rs}/M_s ratio decreases rapidly with increasing temperature, while the coercive force remains nearly constant or (in BK5099) decreases at a slower rate than after ZFC, until the drop associated with the Verwey transition begins; (2) after ZFC, the coercive force decreases rapidly with

increasing temperature, while M_{rs}/M_s remains nearly constant, or (in BK5099) shows a maximum; and (3) a small but discernible difference exists between the $H_c(T)$ curves measured after ZFC$^+$ and ZFC^0 treatments, respectively. Taking into account a considerable difference in both stoichiometry and grain size between these three samples, these properties can be viewed as being characteristic of the pseudo-single-domain magnetite.

Since the magnetic hysteresis properties of PSD magnetite grains below T_V appear to be so different from those of large multidomain grains, the above simple model has to be modified. However, it seems likely that its two postulates, namely, (1) setting of the easy magnetization axis along the [001] direction closest to the magnetic field applied during cooling and (2) the possibility of the easy axis switching into the direction of the magnetic field applied below T_V at a large angle to the initial easy axis, would hold independent of the grain size. On the other hand, this model does not specify whether a new easy axis is set uniquely over the whole volume of a single crystal, or whether a crystal can be divided into several domains with easy axes following different allowed directions. Experimental data on large crystals (Moloni *et al.* 1996) indicate that the latter is possible after a zero-field cooling, while the results of Medrano *et al.* (1999) show that the monoclinic twin structure is very much simpler after FC, implying that an easy magnetization axis is set uniquely in this case. In millimetre-size crystals crystallographic twins are much larger than magnetic domains, and therefore would have a relatively little effect on the magnetic hysteresis. In contrast, in micron-size and smaller grains twins would be of same size or just slightly larger than magnetic domains, and so a much greater influence on the magnetic hysteresis may be expected. On the other hand, the formation of the crystallographic twins themselves would be influenced by the domain structure existing at the Verwey transition. Difference in the properties of ZFC$^+$ and ZFC^0 states observed previously (Kosterov 2001a) and in the present study, and the peculiar effects of a non-saturating field applied during cooling through T_V upon the hysteresis properties of the low-temperature phase, observed recently by Smirnov & Tarduno (2002), probably originate in this way. A rapid decrease of the coercive force with increasing temperature would then indicate that a twin distribution formed after ZFC is not particularly thermally stable.

The situation is quite different in the case of cooling in a strong field. Easy magnetization axes produced by FC are distributed uniformly within a cone with conical angle 54.73°, favouring magnetization in the direction of the field applied during cooling. Crystallographic twins may also be expected to form in an ordered way, offering less resistance to domain wall displacement than in the case of ZFC. This naturally results in a considerably smaller coercivity. In turn, the weak, if any, temperature dependence of the latter means that the pinning strength of twin boundaries does not depend on temperature either. However, the location of pinning centres (twin boundaries) does appear to be temperature dependent, as indicated by a decrease of the M_{rs}/M_s ratio in the FC(0°) experiment. At the same time, in the FC(90°) experiment the M_{rs}/M_s ratio is nearly temperature independent. These two observations can be reconciled assuming that twin boundaries formed by FC are, in fact, displaced by the measuring field (the field used to trace a hysteresis loop), which can only act in this way if it is close enough to the direction of the field applied during cooling.

Effect of variable oxidation

Apparently, in the two samples used in the present work the oxidation process has developed in a different way. In sample 3006,

the Verwey transition occurs around 110 K, the magnetic hysteresis properties of the low-temperature phase are very similar to those of a more stoichiometric sample HM4S (Kosterov 2001a), and the hysteresis properties above the transition are close to those observed for magnetite (e.g. Morrish & Watt 1958; Hodych 1982, 1986, 1990; Schmidbauer & Schembera 1987; Schmidbauer & Keller 1996). This evidence suggests that the material under study contains a relatively pure magnetite, despite over 1 year having elapsed between acquisition of the sample and magnetic measurements. On the other hand, Smirnov & Tarduno (2002) have been able to reduce this sample by annealing it at 400 °C in a CO/CO_2 atmosphere. This implies the presence of a certain amount of maghemite, which is also supported by the susceptibility versus temperature curves (Fig. 1). However, it is worth emphasizing that the hysteresis properties both below and above the Verwey transition are dominated by the 'magnetite' phase, which therefore far outweighs the maghemite phase by volume. A natural conclusion is that in magnetite grains that are several microns in size the oxidation process only affects a superficial layer, leaving the core of the grain relatively intact. Previously, Knowles (1981) suggested a similar model to explain the variation of the room-temperature magnetic hysteresis properties of partially oxidized magnetites. Housden & O'Reilly (1990) and van Velzen & Zijderveld (1995) observed a widespread surface oxidation of (titano)magnetite in submarine basalts and marine marls, respectively.

In contrast, in BK5099, which contains much finer grains, the oxidation affected the whole grain volume, forming the core composed of the non-stoichiometric magnetite. The superficial maghemite layer in this case probably has a volume comparable to that of the core. Taken together with the fine grain size, this explains readily why the M_{rs}/M_s ratio and the coercive force of this sample show a decrease rather than an increase above the Verwey transition. Since maghemite generally shows only a small variation in the magnetic properties in the 77–300 K range and probably below (Morrish & Watt 1958; Senanayake & McElhinny 1981; Özdemir *et al.* 1993; de Boer & Dekkers 1996), the peculiar features of the low-temperature phase of BK5099 such as the peak of M_{rs}/M_s at 30–35 K in the ZFC and FC(90°) experiments are caused by the strong non-stoichiometry of the magnetite cores of the grains. However, data on material properties of non-stoichiometric magnetite below the Verwey transition are rather limited, and so only a qualitative explanation of the observed hysteresis properties could be inferred. Magnetization experiments in the 4.2–77 K temperature range on magnetite single crystals ($Fe_{3(1-\delta)}O_4$) with the degree of non-stoichiometry δ varying from 0 to 0.0093, corresponding to an oxidation parameter z from 0 to 0.08, have revealed that easy axis switching occurs at progressively lower temperatures in highly non-stoichiometric samples (Kakol & Honig 1989). In the same study, magnetocrystalline anisotropy of the monoclinic phase of non-stoichiometric magnetite was found to decrease rapidly with increasing non-stoichiometry. The transition temperature of 95 K corresponds to δ values of about 0.006 ($z = 0.054$) (Aragón *et al.* 1985; Aragón 1992). In a material with a similar composition the magnetocrystalline anisotropy at 4.2 K was only about 60 per cent that in the stoichiometric magnetite, and the onset of axis switching was observed between 30 and 40 K (Kakol & Honig 1989), which corresponds fairly well to the maximum of the M_{rs}/M_s ratio in the BK5099 sample. Smaller magnetocrystalline anisotropy could be a reason for its relatively low coercivity. The increase of M_{rs}/M_s and the rapid decrease of the coercive force below 30 K is then explained by a switching of a progressively greater fraction of easy axes into the direction of the magnetic field applied during hysteresis measurements. However, this process is not as effective as the initial setting of easy axes by field cooling through the Verwey transition, and therefore the M_{rs}/M_s ratio is highest and the coercive force lowest after FC.

CONCLUSION

Magnetic hysteresis measurements between 10 K and room temperature have been carried out on two samples of variably oxidized grains of magnetite of pseudo-single domain size, particular emphasis being made on the behaviour below the Verwey transition temperature. Magnetic hysteresis properties of the PSD magnetite in the low-temperature phase appear to be controlled by the following factors: (1) easy magnetization axes distribution formed during cooling through the Verwey transition; (2) switching of easy axes by the measuring field (the field applied to trace a hysteresis loop); and (3) interaction between the magnetic domain structure and the crystallographic twins formed in the low-temperature phase. The above three mechanisms act in a similar way in both stoichiometric and non-stoichiometric magnetite. However, in the latter hysteresis in the low-temperature phase shows some peculiar features such as a rather low, with respect to the grain size, M_{rs}/M_s ratio and coercive force, and also a maximum of M_{rs}/M_s observed after ZFC. These features are probably explained by smaller magnetocrystalline anisotropy and easier switching of easy magnetization axes by a magnetic field applied below the Verwey temperature.

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