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Coercive force of single crystals of magnetite at low temperatures

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SUMMARY

The temperature dependence of coercive force H_c was studied on well-characterized and stoichiometric millimetre-sized single crystals of magnetite at a series of 16 temperatures from 300 to 10 K using a SQUID magnetometer. H_c decreases gradually with cooling to the isotropic temperature, $T_i = 130$ K, where the first magnetocrystalline anisotropy constant K_1 becomes zero. H_c exhibits a sharp increase at the Verwey transition, $T_v = 120$ K, where the structure changes from cubic to monoclinic. In crossing the Verwey transition, H_c increases by more than two orders of magnitude, from 20 μT to 2.4 mT, and the shape of the hysteresis loops becomes wasp-waisted.

Observed coercivity between 300 K and 170 K varies with temperature as λ_s/M_s, where λ_s is the magnetostriction constant and M_s is the saturation magnetization, indicating that the coercivity in MD magnetite is controlled mainly by internal stress associated with dislocations or other crystal defects. It seems likely that the stable single-domain-like magnetic memory observed in large MD magnetite crystals is due to magnetoelastically pinned domain walls. The discontinuous change in H_c at the Verwey transition is controlled by abrupt changes in magnetocrystalline and magnetostriction constants due to crystal deformation from cubic to monoclinic structure.

Key words: coercive force, magnetic anisotropy, magnetic hysteresis, magnetite, Verwey transition.

INTRODUCTION

It has long been recognized that part of the remanence of multidomain (MD) magnetite mimics that of single-domain (SD) grains in its resistance to alternating field and thermal demagnetization (Ozima *et al.* 1964; Kobayashi & Fuller 1968). The most popular technique for isolating the SD-like remanence has been low-temperature demagnetization (LTD), in which magnetite is cooled through the isotropic point, $T_i = 130$ K, and the Verwey transition, $T_v = 120$ K, and then rewarmed to room temperature in zero field (Dunlop & Özdemir 1997). LTD removes a large part of the MD remanence due to the loosely pinned domain walls, which are most responsive to the internal demagnetizing field and which impart an MD response in hysteresis (Heider *et al.* 1992; Özdemir & Dunlop 1998). The surviving remanence or magnetic memory after LTD has SD-like properties, including high coercivities. The hardness of the low-temperature memory has been attributed to domain walls strongly pinned by crystal defects rather than to separate SD regions in the crystal (Hodych *et al.* 1998; Özdemir & Dunlop 1999).

A knowledge of the temperature dependence of coercive force, H_c, from measurements of hysteresis parameters offers much information about what controls the stability of the low-temperature memory and also about the mechanism of domain wall pinning in magnetite. One can deduce the contributions to coercivity arising from magnetocrystalline-controlled domain wall pinning or magnetoelastic-controlled pinning. Considering the usefulness of such measurements, it is surprising that few experimental studies have been reported. Morrish & Watt (1958) measured coercivity on magnetite powders between 77 and 300 K and concluded that the variation of H_c with temperature depends upon the variation of the magneto-crystalline anisotropy constant, K_1. Schmidbauer & Schembera (1987) and Schmidbauer & Keller (1996) studied the grain size dependence of hysteresis parameters for spherical magnetite particles in the range 60–250 nm.

These studies have been reported on submicron-sized magnetites in which magnetization reversal occurs by domain rotation, mainly by shape anisotropy. In multidomain (MD) magnetites, the magnetization process is controlled by domain wall displacement or domain nucleation. Hodych (1990) reported that the coercivity of rocks bearing multidomain magnetite is probably controlled through internal stresses impeding domain wall motion.

In the present study, hysteresis experiments were carried out on pure, stoichiometric and well-characterized millimetre-sized single crystals of magnetite as a function of temperature in both cooling–warming and warming–cooling cycles between 300 and 20 K. This is the first time such experiments have

been reported for grains near the upper size limit of naturally occurring MD magnetite. The purposes were: (1) to understand how the coercivity of the high-temperature (cubic) and low-temperature (monoclinic) phases of magnetite changes with temperature after crossing the isotropic and the Verwey transitions; and (2) to document what mechanisms are responsible for the strongly pinned walls that are the source of the stable magnetic memory.

SAMPLES

The hysteresis measurements were carried out on museum-quality 1.7 mm (M-1) and 1.5 mm (M-2) octahedral crystals of magnetite from Richmond County, Quebec. The cell edge parameter, room temperature hysteresis and other magnetic properties of M-2 are described in Özdemir & Dunlop (1999). X-ray diffraction using a Debye Scherrer camera with Cu–Kα radiation and a silicon standard was carried out on a small chip of crystal M-1. The spinel unit cell edge was 8.398 ± 0.004 Å. The Curie temperature for M-1 was $T_c = 578\,^{\circ}C$, determined from the temperature dependence of weak-field susceptibility measured by a Kappabridge. The chemical compositions of the crystals were determined using a Cameco MX-50 electron microprobe. Chips of the crystals were probed for Fe, O and seven other elements. The analyses gave 72.36 ± 0.23 weight per cent Fe, close to the theoretical value of 73.6 per cent. The oxygen concentration was 27.5 ± 0.09 weight per cent. The crystals are almost pure magnetite with no major impurities.

LOW-TEMPERATURE SIRM

Low-temperature remanence measurements were made from 20 to 300 K with an MPMS-2 SQUID magnetometer. Crystal M-1 was given a saturation isothermal remanent magnetization (SIRM) in a field of 2.5 T, and then measured in approximately zero field at 10 K intervals up to 300 K (Fig. 1). The remanence was almost temperature-independent between 20 and 105 K. At the crystallographic phase transition $T_v = 120$ K, the remanence for M-1 decreased abruptly from 1.79 $Am^2\,kg^{-1}$ to 0.03 $Am^2\,kg^{-1}$, where it remained during warming to 300 K. The SIRM for crystal M-2 decreased at $T_v = 119$ K in the same way as that of M-1. Thus SIRM produced in monoclinic magnetite is completely demagnetized in the transition to the cubic phase. Almost no memory of the original SIRM is recovered in cooling through T_v.

LOW-TEMPERATURE HYSTERESIS

Hysteresis loops were measured in a field of 0.4 T at selected temperatures from 300 to 20 K and back to room temperature. The room temperature hysteresis parameters for both crystals

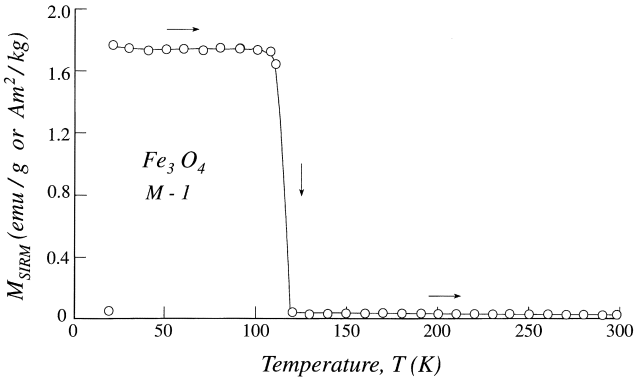

Figure 1. Zero field SIRM warming curve from 20 to 300 K for the crystal M-1. The sharp decrease in remanence around 120 K marking the Verwey transition is diagnostic for stoichiometric magnetite. The single point at 20 K is the memory after cooling.

are given in Table 1. The very low remanence ratios and very high coercivity ratios are hallmarks of ideal MD behaviour. The shapes of the hysteresis curves for both crystals between room temperature and 20 K show remarkably different features below and above the Verwey transition (Figs 2a and b). The curves between 300 and 120 K have a ramp-like shape and have the same slope. At the isotropic point, $T_i = 130$ K, H_c was almost zero. The hysteresis loop at 115 K was slightly wasp-waisted and the loop was not entirely closed. This observation shows that the crystallographic transformation in the vicinity of T_v was incomplete. The crystal, just below T_v, consists of coexisting monoclinic and cubic phases with vastly different coercivities. Below 114 K, where the structural transformation is complete, the hysteresis loops have an S-like shape with higher coercive force values, as shown in Fig. 2(b).

Room temperature saturation magnetization values for M-1 and M-2 were 92.8 and 93.6 $Am^2\,kg^{-1}$, respectively. These values are in good agreement with previously reported M_s values for pure stoichiometric magnetite. For both crystals, M_s increased with decreasing temperature between 300 K and T_v (Fig. 3). Just above the transition temperature, M_s reached 98.19 and 98.34 $Am^2\,kg^{-1}$ for M-1 and M-2, respectively. In cooling through the Verwey transition, M_s abruptly decreased by 6.7 and 7.5 per cent for M-1 and M-2, respectively. The 0.4 T field was not enough to saturate the magnetization of monoclinic magnetite. These results clearly show that the magnetocrystalline anisotropy of monoclinic magnetite below T_v is much greater than the anisotropy of cubic magnetite above T_v. Only along the [001] monoclinic *c*-axis, and in much higher fields (~ 2 T) that are sufficient to saturate the magnetization of a monoclinic crystal, does the $M_s(T)$ curve of the oriented crystal change continuously, with a discontinuity of only ≈ 0.1 per cent at T_v (Özdemir & Dunlop 1999).

Table 1. Various experimental properties for the natural single crystals.

Crystal	d (mm)	a (Å)	T_c (°C)	T_v (K)	T_i (K)	M_s ($Am^2\,kg^{-1}$)	H_c (mT)	M_{rs}/M_s	H_{cr}/H_c
M-1	1.7	8.399	578	120	—	92.8	0.18	0.002	41
M-2	1.5	8.402	575	119	130	93.6	0.11	0.003	47

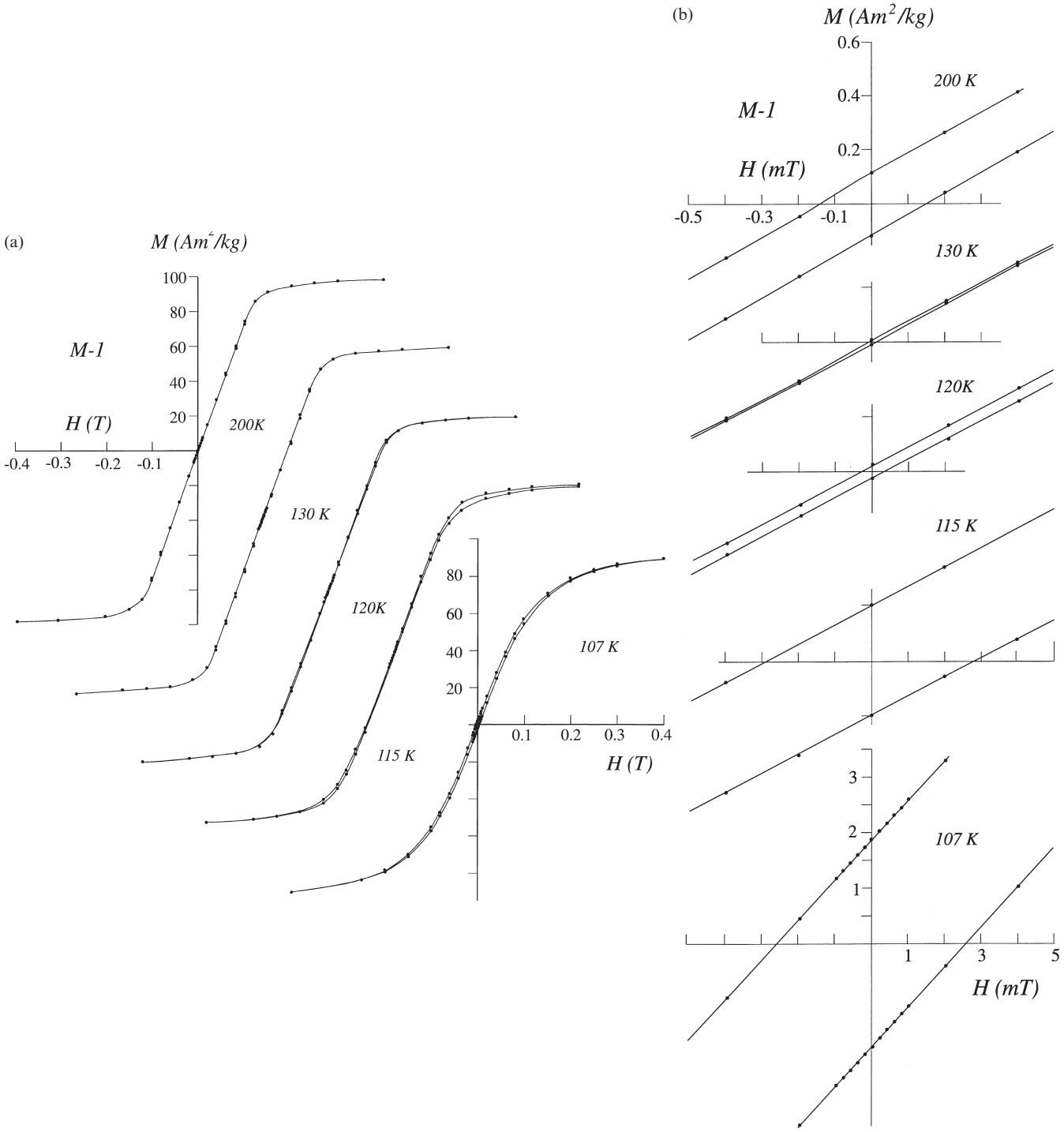

Figure 2. (a) Hysteresis loops measured at various temperatures. The loops have ramp-like shapes above the Verwey transition. At T_v, the hysteresis loop is wasp-waisted due to a mixture of cubic and monoclinic phases in the crystal. (b) Expanded view of the same hysteresis loops.

COERCIVE FORCE

The coercive force for crystal M-1 decreased with cooling to the isotropic temperature $T_i = 130$ K (Fig. 4). At T_i, H_c was nearly zero. In crossing the Verwey transition, the coercive force increased more than two orders of magnitude, from 20 μT to 2.4 mT, which is more than an order of magnitude higher than H_c at 300 K. A sharp increase in H_c in the vicinity of the Verwey transition has been reported for magnetite by Morrish & Watt (1958), Schmidbauer & Schembera (1987) and Muxworthy (1999). In further cooling below T_v, the coercivity decreased by about 7.6 per cent. As the crystal was warmed from 20 K, the coercivity retraced the cooling curve, decreasing dramatically to 20 μT in crossing the Verwey transition. Thus the process or processes affecting H_c of the monoclinic and cubic magnetite are perfectly reversible. The coercive force of crystal M-2 changed in the same way as that of M-1. Cooling through the Verwey transition resulted in a

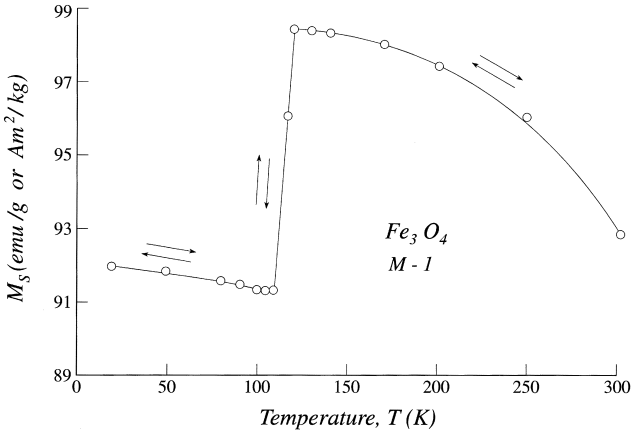

Figure 3. The temperature dependence of saturation magnetization for cubic magnetite (300 K $-$ T_v) and induced magnetization for monoclinic magnetite ($T_v - 20$ K). Note the abrupt change in M_s at the Verwey transition. The field of 4 KOe was not enough to saturate the monoclinic magnetite. See Fig. 2 of Özdemir & Dunlop (1999).

sudden increase in coercivity, reaching 1.1 mT, which is 56 per cent lower than H_c of M-1. The cooling and reheating curves below T_v were also similar to those of M-1.

DISCUSSION

In multidomain magnetite, the crystal defects play a major role in hysteresis and coercivity by hindering the motion of domain walls. The kinds of defects that can pin walls include volume defects such as voids and non-magnetic inclusions, and line and planar defects such as dislocations and stacking faults (Özdemir & Dunlop 1997). The MD hysteresis is also affected by wall nucleation, which usually occurs at sharp corners where the demagnetizing field is locally enhanced, either on an internal boundary such as a void or crack or at the crystal surface. The temperature dependence as well as the magnitude of coercivity is different for nucleation and various types of defect pinning. Magnetocrystalline-controlled domain wall pinning (Kersten 1943) or domain nucleation (Goodenough 1954) leads to a coercivity

$$H_c(T) \propto K_1(T)/M_s(T). \quad (1)$$

Wall pinning due to stress fields of dislocations or planar defects (Träuble 1969; Xu & Merrill 1990) gives

$$H_c(T) \propto \lambda_{111}(T)/M_s(T), \quad (2)$$

where λ_{111} is the magnetostriction constant along the $\langle 111 \rangle$ direction of cubic magnetite. For multidomain crystals similar to those used in the present study, the experimental $H_c(T)$ data between room temperature and Curie temperature vary approximately as $\lambda_{111}(T)/M_s(T)$, indicating that the high-temperature coercivity in large MD crystals is mainly magnetoelastic (Özdemir & Dunlop 1998). Using (1) and (2) with values of published $K_1(T)$ and $\lambda_{111}(T)$ for magnetite, the low-temperature coercive force between 300 K and T_i for crystal M-1 was predicted (Fig. 5).

H_c above T_v

The temperature variation represented by (1) was fitted empirically to the experimental data. The data of Abe *et al.* (1976) were used for $K_1(T)$. The hump in the model curve

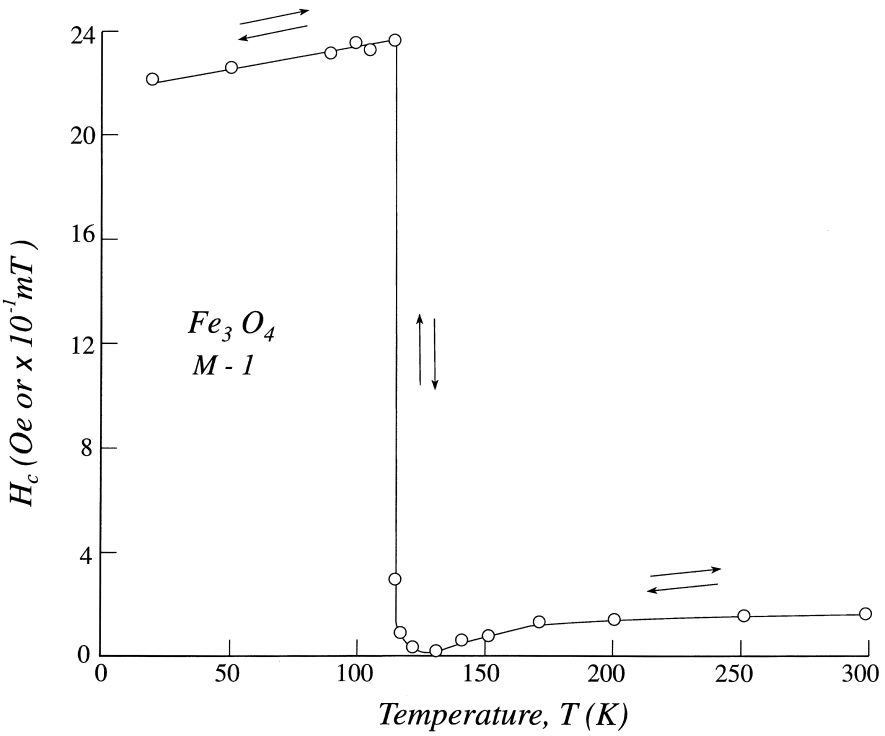

Figure 4. The temperature dependence of coercive force during cooling from 300 to 20 K and back to 300 K. The discontinuous increase at the Verwey transition is due to the abrupt changes in magnetocrystalline and magnetostriction constants when the crystal transforms from cubic to monoclinic.

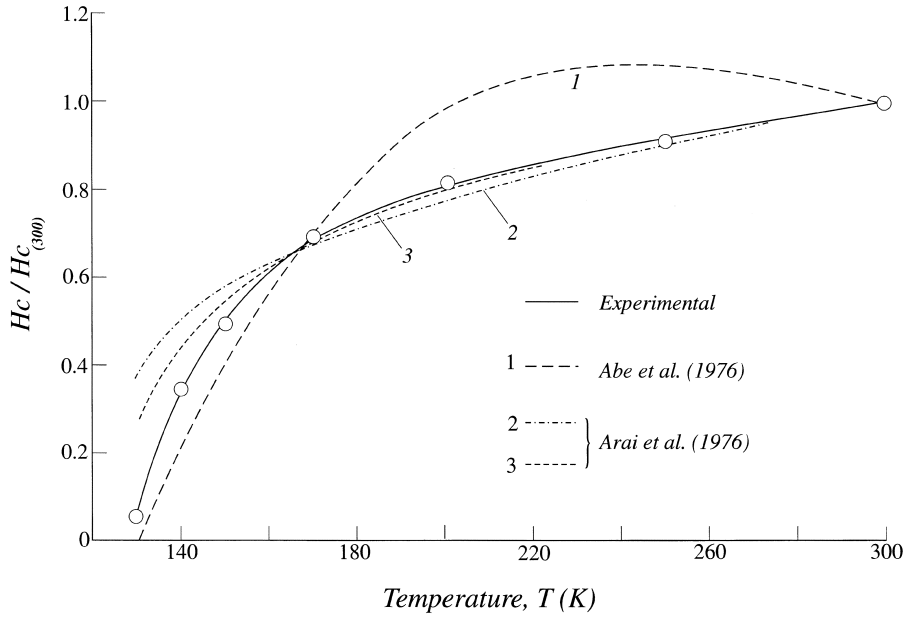

Figure 5. Comparison of experimental $H_c(T)$ data with the model curves arising from magnetocrystalline and magnetostrictively controlled coercivity. Curves 1, 2 and 3 represent calculated $H_c(T)$ variations proportional to K_1/M_s, λ_{111}/M_s and λ_s/M_s, respectively.

around 240 K correlates with the position of the $|K_1|$ maximum. The data do not follow a K_1/M_s temperature dependence between 300 and 170 K, indicating that magnetocrystalline anisotropy is not the dominant factor controlling the bulk coercive force. However, the magnetocrystalline model provides a better fit at the lower temperatures, between 170 and 130 K, where K_1 decreases with temperature very rapidly.

Curve 2 in Fig. 5 is the temperature variation of λ_{111}/M_s. The data of Arai *et al.* (1976) were used for $\lambda_{111}(T)$ variations. The experimental data vary approximately as $\lambda_{111}(T)/M_s(T)$ between 300 and 170 K, but the model curve does not fit observed data between 170 K and $T_i = 130$ K. Because the present crystal was not oriented along a principal axis, the actual λ is not λ_{111}, but some combination of λ_{111} and λ_{100}. Therefore, $\lambda_s(T)/M_s(T)$ for random orientation is also plotted for comparison (curve 3 in Fig. 5), where $\lambda_s = 2/5\lambda_{100}(T) + 3/5\lambda_{111}(T)$ is the isotropic magnetostriction and λ_{100} is the magnetostriction constant along the $\langle 100 \rangle$ direction of cubic magnetite. Curve 3 provides a somewhat closer fit to the data than that of the $\lambda_{111}(T)/M_s(T)$ curve but the difference between curves 2 and 3 is not great.

The calculated $H_c(T)$ values agree well with experimental results between 170 and 300 K, indicating that the coercivity in the present MD crystal is mainly magnetoelastic, that is, due to pinning of magnetization by internal stresses, over this temperature range. However, below 170 K, there is a difference between the experimental data and curves 2 and 3, which could arise in the following way. The magnetocrystalline anisotropy constant decreases much more rapidly with temperature than does λ_{111} between 180 and 130 K (Fig. 12 of Abe *et al.* 1976), resulting in a considerable broadening of the domain walls because wall width is proportional to $K_1^{-0.5}$. Wall pinning by stress concentrations localized near lattice defects such as dislocations will become less effective and the walls will eventually escape (Xu & Merrill 1990; Moskowitz 1993). Although, K_1 becomes zero at T_i, the observed coercive force of 20 μT at 130 K shows that some domain walls are likely to resist the unpinning and remain at their pinning sites. This could be the source of stable magnetic memory observed in large MD magnetite (Özdemir & Dunlop 1998). The observed H_c(T) variation between 170 K and the Verwey transition reflects the competing influences of magnetocrystalline and stress-controlled anisotropies.

H_c in the vicinity of T_v (120–110 K)

The crystallographic phase transition has a significant effect on the temperature dependence of coercive force for the present crystals (Fig. 4). In crossing T_v, H_c abruptly increased by more than two orders of magnitude and the shape of the hysteresis loops became wasp-waisted. In the vicinity of T_v, where the crystallographic transformation is incomplete, the single crystal consists of cubic and monoclinic phases with distinct coercivities, which results in wasp-waistedness (Roberts *et al.* 1995; Tauxe *et al.* 1996). This observation is consistent with high-resolution electron microscopy studies on the low-temperature phase of magnetite, which show the coexistence of low- and high-temperature phases (Otsuka & Sato 1986). It seems unlikely that the cubic → monoclinic phase transition occurs as one sharp discontinuous change.

H_c below T_v

The increase in coercive force with cooling below 120 K is associated with the discontinuous changes in magnetic anisotropy and magnetostriction constants due to the switching of the easy axes at T_v. Below the transition, the crystal is much easier to magnetize along the *c*-axis and more difficult to magnetize to saturation along the *a*- and *b*-axes (Özdemir & Dunlop 1999). The magnetic anisotropy constants of monoclinic magnetite are all temperature-dependent and show abrupt changes at T_v (Abe *et al.* 1976). The temperature dependences of the magnetostriction constants λ_s, λ_{111} and λ_{100} also show discontinuous changes at the Verwey transition

(Tsuya *et al.* 1977). According to eqs (1) and (2), any increases in magnetocrystalline and magnetostriction constants below T_v will result in an increase in coercive force.

CONCLUSIONS

(1) The temperature dependence of the coercive force is approximately as λ_s/M_s between 300 and 170 K, indicating that the coercivity in the present multidomain crystal is mainly magnetoelastic over this temperature range. Wall pinning by crystal defects could be the source of stable magnetic memory observed in large MD magnetite. Below 170 K, $H_c(T)$ variation for cubic magnetite is controlled by magnetostrictive and magnetocrystalline anisotropies.

(2) The observed wasp-waisted hysteresis loops in the vicinity of T_v (120–110 K) are diagnostic of coexisting low- and high-temperature phases of magnetite.

(3) The sharp increase in coercive force at the Verwey transition is associated with rapid changes in magnetostriction and magnetocrystalline anisotropy constants as the crystal deforms from cubic to monoclinic structure.

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