Magnetic properties of natural pyrrhotite Part I: Behaviour of initial susceptibility and saturation-magnetization-related rock-magnetic parameters in a grain-size dependent framework

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The grain-size dependence of the initial susceptibility (X_{in}), saturation magnetization (J_s), saturation remanence (J_{rs}), coercive force (H_c), remanent coercive force (H_{cr}) and remanent acquisition coercive force ($H_{cr'}$), is reported for four natural pyrrhotites in a grain-size range from 250 μm down to $< 5 \mu\text{m}$. X_{in} decreases with decreasing grain size (range 7×10^{-5} – $1 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$); H_c , H_{cr} and $H_{cr'}$ all increase with decreasing grain size (ranges respectively 7–80, 8–85 and 14–80 kA m^{-1}). The magnitudes of J_s (8.9–16.7 $\text{A m}^2 \text{ kg}^{-1}$) and J_{rs} (2.0–6.0 $\text{A m}^2 \text{ kg}^{-1}$) correspond with the trend indicated by the microprobe analysis (47.8 down to 46.9 at.% equivalent Fe). J_{rs} shows a maximum in the pseudo-single domain region (range 2.0–6.0 $\text{A m}^2 \text{ kg}^{-1}$). J_s shows a marked decrease for the finest grain-size fractions. Typical for pyrrhotite are a large H_c/H_{cr} ratio and a J_{rs}/X_{in} ratio which is larger than H_{cr} . When the presence of pyrrhotite has been established in a sample, its grain size is preferable determined by the H_{cr} trend because pyrrhotite compositional differences hardly show up in this trend.

1. Introduction

The solid solution series of Fe–S compounds of composition Fe_{1-x}S , with x varying between 0 and 0.13, is usually referred to as pyrrhotite. Nearly stoichiometric FeS is known as troilite (an Fe-deficiency between 0.003 and 0.006 formula units is reported; cf., Ward, 1970). Though the pyrrhotite potential of carrying a remanent magnetization has been well established for a long time (e.g., Bertaut, 1953), pyrrhotite was for a long time regarded as a magnetic mineral of minor paleomagnetic importance, because it was believed to occur almost exclusively in association with sulphidic ores. However, the existence of pyrrhotite without spatial relation to these ores is increasingly reported. It is nowadays known from various types of igneous rocks (e.g., Soffel, 1977),

in metamorphic rocks (e.g., Carpenter, 1974; Rochette, 1987) and also in sediments (e.g., Kligfield and Channell, 1981; Freeman, 1986). This considerably increases the paleomagnetic significance of pyrrhotite.

The pyrrhotite crystal structure consists of alternating Fe and S layers, based on the NiAs crystal structure. The atoms in each Fe-layer are ferromagnetically coupled; antiferromagnetic coupling exists with each neighbouring Fe-layer. The crystallographic C-axis is the hard axis of magnetization; the easy directions are confined to the basal plane which shows a (strong) trigonal anisotropy (Bin and Pauthenet, 1963). The initial susceptibility is extremely anisotropic with magnetite-like figures in the basal plane and paramagnet-like figures along the hard axis (Schwarz, 1975). All Fe in pyrrhotite is Fe^{2+} and the valence

of S is < 2 (Ward, 1970). Pyrrhotite contains a certain amount of vacancies depending on its chemical composition. The most Fe-deficient pyrrhotite (Fe_7S_8) has a monoclinic crystal structure; the more Fe-rich pyrrhotites are hexagonal.

Since the vacancies show some tendency to concentrate in alternate Fe-layers (Goodenough, 1978), the vacancy distribution has direct consequences for the pyrrhotite magnetic properties. The vacancy distribution can be described by so-called superstructures. The more common integral superstructures are the 4C superstructure for the ferrimagnetic monoclinic Fe_7S_8 (Bertaut, 1953) and 5C, 11C and 6C superstructures for the antiferromagnetic hexagonal pyrrhotite (e.g., Fleet and MacRae, 1969; Morimoto et al., 1970, 1975a). Also, non-integral superstructures, previously thought to occur only at elevated temperatures, are reported at ambient temperatures (e.g., Morimoto et al., 1975a, 1975b).

Natural pyrrhotite usually consists of mixtures of superstructures of monoclinic and hexagonal pyrrhotite (e.g., Arnold, 1967), which results in an intermediate overall composition. Different superstructures can coexist within a single pyrrhotite crystal. This was detected with X-ray methods (e.g., Morimoto et al., 1975a, 1975b), with high-resolution electron microscopy (e.g., Morimoto et al., 1974; Pierce and Buseck, 1974) or made visible microscopically by applying etching techniques (e.g., Naldrett and Kullerud, 1967).

The 4C pyrrhotite saturation magnetization is reported to be $20 \text{ A m}^2 \text{ kg}^{-1}$ (e.g., Schwarz and Vaughan, 1972; Halgedahl and Fuller, 1981). Besnus and Meyer (1964) reported a saturation magnetization of $22.5 \text{ A m}^2 \text{ kg}^{-1}$ for an unspecified natural pyrrhotite crystal. The saturation magnetization of mixed pyrrhotite depends on the content of 4C pyrrhotite present. Domain observations (Soffel, 1977, 1981; Halgedahl and Fuller, 1981) showed that 180° domain walls prevail in the pyrrhotite domain structure. Grains of $\sim 100 \mu\text{m}$ size showed true multidomain (MD) behaviour; the range between 2–3 and $40 \mu\text{m}$ is regarded as a pseudo-single domain (PSD) region. The SD/PSD border is found between 1.5 and $2 \mu\text{m}$ (Soffel, 1977). Clark (1984) calculated $3 \mu\text{m}$ for the SD/PSD transition. The coercive force for a large

MD crystal is 9.0 kA m^{-1} (Halgedahl and Fuller, 1981) and for the PSD range 14.3 kA m^{-1} (Soffel, 1981). The ratio of the saturation remanence and saturation magnetization for the larger MD crystal is reported to be 0.14 (Halgedahl and Fuller, 1981). Clark (1984) described hysteresis properties of sized monophase monoclinic 4C pyrrhotite fractions in a grain-size range of $83 \mu\text{m}$ down to $< 3 \mu\text{m}$. He found a steadily increasing coercive force ($10.7\text{--}73.2 \text{ kA m}^{-1}$), remanent coercive force ($14.7\text{--}113.4 \text{ kA m}^{-1}$) and remanent acquisition coercive force ($21.5\text{--}106.6 \text{ kA m}^{-1}$) with decreasing grain size. The initial susceptibility decreases with decreasing grain size, whereas the saturation remanence increases with decreasing grain size down to $15 \mu\text{m}$ and subsequently decreases slightly with a further decrease in grain size.

Grain-size dependence of these and other rock-magnetic parameters for pyrrhotite is poorly documented at present: Clark's (1984) study is the only one which reports grain-size dependent trends in pyrrhotite. The present study reports the grain-size dependence of the saturation magnetization (J_s), saturation remanence (J_{rs}), the initial specific susceptibility (X_{im}), the coercive force (H_c) and remanent coercive force (H_{cr}) as well as the remanent acquisition coercive force ($H_{cr'}$) in a grain-size range from $250 \mu\text{m}$ down to $< 5 \mu\text{m}$. Therefore a series of artificial samples using the methodology of Dankers (1978, 1981) and Hartstra (1982a) was prepared containing homogeneously dispersed natural pyrrhotite of a well-defined grain-size range.

2. Sample description

Pyrrhotite, belonging to various geologic associations, was selected for investigation from four locations. It was sampled at Isola di Vocca (Ivrea Zone, Italy) from an orthomagmatic disseminated Fe–Ni–Cu ore in a noritic–gabbroitic complex (cf., Rivalenti, 1979; Natale and Zuchetti, 1979; Bigioggero et al., 1979; Ferrario et al., 1983); at Temperino (Tuscany, Italy) from a pyrometamorphic pyrrhotite–pyrite–chalcopyrite ore zone (cf., Bodechtel, 1965, 1968); and at Ortano and Ginevro (both on Elba, Italy) from reheated, originally volcano-sedimentary, pyrite–hematite

TABLE IA

Average pyrrhotite composition determined by microprobe analyses

	TTE			EOR			DIS			EGI		
	Av.	sd	Norm.	Av.	sd	Norm.	Av.	sd	Norm.	Av.	sd	Norm.
S	53.03	0.19	39.27	53.14	0.35	39.39	52.25	0.30	38.47	52.85	0.23	39.04
Fe	46.76	0.18	60.32	46.70	0.36	60.30	47.41	0.29	60.80	46.95	0.34	60.41
Mn	0.02	0.03	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.03	0.02
Ni	0.17	0.14	0.23	0.14	0.10	0.19	0.39	0.11	0.52	0.27	0.08	0.41
Cu	0.06	0.09	0.09	0.03	0.05	0.04	0.05	0.06	0.07	0.04	0.06	0.06
Zn	0.04	0.08	0.06	0.04	0.08	0.06	0.08	0.13	0.12	0.04	0.08	0.06
Total	100.08		99.99	100.06		99.99	100.19		99.99	100.18		100.00

Analyses were carried out with a TPD (Technisch Physische Dienst) microprobe fitted with a TRACOR Northern Energy Dispersive (ED) system. Operating conditions were 15 keV and 2–3 nA. ZAF matrix correction was applied. Av. is average atom percentage; sd is standard deviation; Norm. is normalized weight percentage. Most spots contained no detectable Mn, Cu and Zn. Ni is enhanced in the DIS pyrrhotite and slightly raised in EGI pyrrhotite; in the others its amount is insignificant. TTE 32 spot analyses; EOR 21 analyses; DIS 16 analyses; EGI 16 analyses. Fe₇S₈ contains 53.33 at.% S (4C superstructure); Fe₈S₉ 52.94 at.% S; Fe₉S₁₀ 52.63 at.% S (5C); Fe₁₀S₁₁ 52.38 at.% S (11C); and Fe₁₁S₁₂ 52.17 at.% S (6C).

ores (cf., Bodechtel, 1965; Dimanche, 1971; Waldeck, 1977). All samples contained well-crystalline pyrrhotite. A concise description of each pyrrhotite sample is given below; for a more detailed overview the reader is referred to Dekkers (1988). Chemical and X-ray diffraction data of the

pyrrhotites and the intergrowth amount of each final grain-size fraction are compiled in Tables I–III.

2.1. Isola di Vocca (abbreviation DIS)

The DIS pyrrhotite belongs to a pyrrhotite–pentlandite–chalcopyrite ore assemblage with minor mackinawite, magnetite, ilmenite and sphalerite. The host-rock mineralogy is dominated by olivine and pyroxenes. Magnetite occurs only accessory (< 2%) in the pyrrhotite concentrate; pentlandite and chalcopyrite are hardly observed. The grains in the final fractions are approximately equidimensional. The larger grain-size fractions (> 30 µm) consist of pyrrhotite intergrown with silicates.

2.2. Temperino (abbreviation TTE)

The TTE pyrrhotite is concentrated from a pyrite/pyrrhotite skarn from a complex Cu–Zn-bearing ore zone. Pyrrhotite and pyrite occur in a long prismatic habit in sheaf-like aggregates intergrown predominantly with ilvaite. The width of the sulphide parts is a few hundred micrometers. The pyrrhotite concentrates contain equidimensional grains. Intergrowths are rare; no magnetite is identified.

TABLE IB

Pyrrhotite trace element content (wet chemical) in ppm

	TTE	EOR	DIS ^a	EGI
Co	215	320	755	440
Pb	< dl	< dl	< dl	< dl
Ba	< dl	< dl	< dl	< dl
Mn	430	85	815	285
V	< dl	< dl	528	< dl
Zn	795	< dl	325	< dl
Cu	< dl	715	3220	835
Ni	85	130	2430	205
Cr	< dl	< dl	< dl	< dl

^a The DIS sample contains 37% non-pyrrhotite minerals (almost exclusively silicates, > 99%). Analyses were carried out by the Service Laboratory, Institute of Earth Sciences, State University of Utrecht. All elements were analysed with ICPES (Induction Coupled Plasma Emission Spectrometry); the detection limit (dl) for each element is ~10 ppm. Comparison of Tables 1A and 1B shows that the number of spots in the MP analyses is too low to obtain reasonable estimates for elements which are below 0.3 at.%.

TABLE II

Unit cell dimensions of the pyrrhotite samples

	TTE 4C	EOR 4C	DIS 4C	DIS 5C	DIS 6C	EGI 4C
<i>a</i> -Axis	11.840 ± 0.007	11.818 ± 0.007	11.847 ± 0.007	6.846 ± 0.003	6.852 ± 0.004	11.843 ± 0.007
<i>b</i> -Axis	6.845 ± 0.004	6.835 ± 0.004	6.849 ± 0.004	6.846 ± 0.003	6.852 ± 0.004	6.850 ± 0.004
<i>c</i> -Axis	22.706 ± 0.013	22.656 ± 0.013	22.669 ± 0.013	28.504 ± 0.014	34.131 ± 0.018	22.720 ± 0.013
Volume	1840 ± 1	1830 ± 1	1839 ± 1	1156 ± 1	1387 ± 1	1843 ± 1
α	90.00 ± 0.015	90.00 ± 0.014	90.00 ± 0.015	90.00 ± 0.000	90.00 ± 0.000	90.00 ± 0.015
β	90.410 ± 0.000	90.409 ± 0.000	90.369 ± 0.000	90.00 ± 0.000	90.00 ± 0.000	90.369 ± 0.000
γ	90.00 ± 0.000	90.00 ± 0.000	90.00 ± 0.000	120.00 ± 0.013	120.00 ± 0.014	90.00 ± 0.000
<i>NiAs cell</i>						
<i>a</i> -Axis	3.42	3.42	3.42	3.42	3.43	3.42
<i>c</i> -Axis	5.68	5.66	5.67	5.70	5.69	5.68

Cell dimensions are in Å; cell volumes in cubic Å. The indicated errors are standard deviations. 4C, 5C and 6C refer to the pyrrhotite superstructure. In hexagonal pyrrhotite the (408) and ($\bar{4}$ 08) reflections coincide and have a *d*-value of ~ 2.06 Å, depending on the pyrrhotite chemistry. In monoclinic 4C pyrrhotite the (408) and ($\bar{4}$ 08) reflections show up as a doublet at $d \sim 2.06$ Å and $d \sim 2.04$ Å. Both reflections of this doublet are of similar intensity in TTE, EOR and EGI pyrrhotite; the second (monoclinic) reflection is much more weakly developed in the DIS pyrrhotite sample. This indicates that there is least ferrimagnetic 4C phase in the last sample. A distinct lower susceptibility of the DIS pyrrhotite, observed during the magnetic separation step, is in agreement with the X-ray determination.

2.3. Ortano (abbreviation EOR)

Pyrrhotite, collected from the mine dumps at Ortano on the eastern coast of Elba, is intergrown with epidote, ilvaite and minor hedenbergite. The pyrrhotite is well developed in the skarn. The separated grain-size fractions consist of equi-

dimensional pyrrhotite grains. The intergrowth amount is subordinate; no magnetite is identified.

2.4. Ginevro (abbreviation EGI)

Pyrrhotite occurs as a minor mineral in a magnetite/hedenbergite skarn at Ginevro on the

TABLE III

Amount of intergrowths, pyrrhotite and magnetite contents of the pyrrhotite grain-size fractions determined by point-counting (reflected light microscopy)

	TTE			EOR			DIS			EGI		
Fraction	po	mg	int.	po	mg	int.	po	mg	int.	po	mg	int.
250–150	> 99	bd	bd	> 99	bd	bd	31	bd	100	78	22	bd
150–100	> 99	bd	bd	> 99	bd	bd	48	bd	90	78	22	bd
100–75	> 99	bd	bd	> 99	bd	bd	72	bd	50	80	20	bd
75–55	> 99	bd	bd	> 99	bd	bd	63	bd	50	81	19	bd
55–40	> 99	bd	bd	> 99	bd	bd	70	bd	30	81	19	bd
40–30	> 99	bd	bd	> 99	bd	bd	88	bd	10	86	14	bd
30–25	> 99	bd	bd	> 99	bd	bd	94	bd	< 5	86	14	bd
25–20	> 99	bd	bd	> 99	bd	bd	96	2	bd	84	16	bd
20–15	> 99	bd	bd	92	bd	bd	97	1	bd	92	8	bd
15–10	95	bd	bd	80	bd	bd	90	2	bd	83	9	bd
10–5	65	bd	bd	70	bd	bd	59	1	bd	78	6	bd
< 5	60	bd	bd	60	bd	bd	57	bd	bd	54	3	bd

Volume percentages; grain sizes in μm ; po is pyrrhotite; mg is magnetite; int. is intergrowth; all in percentages; bd is below detection limit ($< \sim 1\%$). The percentages refer to the total sample, in the fine grain-size fractions silicate minerals remain present. The intergrowth percentage refers to the amount of pyrrhotite grains which are intergrown with silicate minerals.

south-eastern coast of Elba. Pyrrhotite-rich parts of the skarn zone were sampled from the mine dumps. The final grain-size fractions consist of a mixture of equidimensional pyrrhotite and magnetite grains. They occur predominantly as separate monomineralic grains; the magnetite content decreases with decreasing grain size from 25 wt.% down to ~ 5 wt.%.

2.5. Preparation of the artificial specimens

The pyrrhotite grain-size fractions were obtained by subsequent crushing, sieving, magnetic separation and ultrasonic microprecision sieving. Crushing was performed in a Cu mortar. The first sieving step was performed to optimize the magnetic separation step. The ASTM sieving set was used; wet sieving was performed with acetone as the flushing fluid. The coarse grain-size fractions ($> 37 \mu\text{m}$) of the TTE, EOR and EGI samples were separated by moving a hand-magnet quickly back and forth over the sample at a few centimetres distance. The DIS fractions were separated magnetically with a Frantz-isodynamic separator adapted for separation in a liquid medium (ethanol was used). The fine grain-size fractions ($< 37 \mu\text{m}$) were all separated with the aid of the modified Frantz-isodynamic separator; an input of the grains in suspended form was created (Dekkers et al., in preparation). Microprecision sieving was carried out in an ultrasonic bath to remove fine, magnetically adhered pyrrhotite particles from coarse ones. Each separation step was carried out as much as possible in an inert atmosphere, because pyrrhotite tarnishes easily in moist air. This applies especially for the microprecision sieving step: when microsieving in contact with air pyrrhotite grains oxidize instantaneously. The grains disintegrate, colouring the acetone red-brown. When sieving was performed in an inert atmosphere, no red-brown colouring of the acetone occurs and the pyrrhotite grains retain their typical brassy colour. After the separation procedure, the grain-size fractions were stored in an Ar atmosphere.

The results of the magnetic separation were checked optically (transmitted and reflected light)

and with X-ray diffraction; the grain-size ranges were controlled optically (transmitted light). The grain-size fractions were homogeneously dispersed in an epoxy resin matrix (Araldite D-hardener HY 956, Ciba-Geigy) or in a quartz/bassanite matrix (CM Löt soldering investment used for dental metalwork). Susceptibility measurements were corrected for the diamagnetic matrix moment; no correction had to be made for the remanent magnetization of both matrices. Approximately 100 mg of pyrrhotite was put in standard-sized paleomagnetic specimens (0.2% by volume). Samples for high-field susceptibility measurements were sized down on a lathe from epoxy resin cylinders initially of 1 cm diameter and 1 cm height to cylinders of 4.5 mm diameter and 5 mm height. Each final cylinder contained some 5 mg pyrrhotite (2% by volume).

2.6. Instrumentation for the magnetic measurements

Initial susceptibility was measured with a Jelinek KLY-1 susceptibility bridge. Acquisition curves of the isothermal remanent magnetization (RA curves) in fields up to 1600 kA m^{-1} (2 T) were determined with a Förster fluxgate magnetometer type 1.107, which was calibrated with an astatic magnetometer. Hysteresis loops in a 240 kA m^{-1} field (0.3 T) were determined by measuring the imbalance of a pair of coils, one of which contained the specimen. Measurements were carried out using an ac field. The determinations mentioned so far were carried out at the Paleomagnetic Laboratory 'Fort Hoofddijk' (University of Utrecht, The Netherlands).

A field of only 240 kA m^{-1} is too small to obtain correct figures for the pyrrhotite saturation magnetization. Therefore magnetization curves were determined in fields up to 1200 kA m^{-1} (15 T). Measurements in fields up to 1040 kA m^{-1} (1.3 T) were done with a vibrating sample magnetometer (Foner type); in higher fields a ballistic magnetometer was employed. These high-field measurements were carried out at the High Field Magnet Laboratory at the Department of Physics, University of Nijmegen (The Netherlands).

3. Results

3.1. Susceptibility measurements

The susceptibility measurements were corrected for the diamagnetic moment of the matrix. Partial

hysteresis loops in 240 kA m^{-1} fields (Fig. 1A) reveal that only the coarse grain-size fractions (from the $75\text{--}55 \mu\text{m}$ fraction upwards) show a reversible magnetization behaviour in the highest field strengths reached by this low-field equipment. Finer grain-size fractions do not show such be-

Fig. 1. (A) Partial hysteresis loops in 160 kA m^{-1} (0.2 T) or 240 kA m^{-1} (0.3 T) fields. The coarse grain-size fractions already behave reversibly in these small fields. The numbers on the ordinates refer to the magnetization in $\text{A m}^2 \text{ kg}^{-1}$. (B) Magnetization curves in fields up to 1040 kA m^{-1} (1.3 T). The fine grain-size fractions show reversible hysteresis behaviour in fields above 800 kA m^{-1} (1 T). (C) Magnetization curve in fields up to 12000 kA m^{-1} (15 T). The coarse grain-size fractions tend to be saturated in this field, whereas the magnetization of the fine grain-size fractions still increases. The magnetizations are corrected for the diamagnetic matrix moment.

Fig. 2. X_{in} versus grain size. $\square$, TTE pyrrhotite; $\circ$, EOR pyrrhotite; $\triangle$, EGI pyrrhotite; and ∇ , DIS pyrrhotite. The higher X_{in} of the EGI fractions is caused by their magnetite content.

haviour in fields up to 240 kA m^{-1} . The field strength above which reversible behaviour is observed increases with decreasing grain size. For the $< 5 \mu\text{m}$ fractions this field is some 800 kA m^{-1} (Fig. 1B). Hence, such fields are required for a proper determination of the coercive force.

In extremely small applied fields the movement of the spontaneous magnetization from one easy direction to a more favourably positioned one is fairly difficult, as is indicated by the onset of the magnetization curves (Fig. 1B) and the low initial susceptibility (Fig. 2, Table IV). Domain walls move relatively easily in pyrrhotite in somewhat larger applied fields, as is indicated by the steep rise of the magnetization curves. In high applied fields the spontaneous magnetization is pulled out of the basal plane. This is opposed by a strong magnetocrystalline anisotropy. Large fields are required to saturate a set of randomly distributed pyrrhotite grains (Fig. 1C).

Hysteresis loops of pyrrhotite are characterized by steeply rising branches in small fields and much less steep continuations in higher fields leading to a more or less rectangular curve (Fig. 1A). Pyrrhotite hysteresis loops are much more

rectangular than magnetite hysteresis loops: the branches of the hysteresis loop of the EGI 250–150 μm fraction containing 25 wt.% magnetite (as separate monomineralic grains) are much more gently increasing and decreasing with the external field than loops of samples without magnetite containing the same grain-size range (e.g., TTE 250–150 μm and EOR 250–150 μm).

The initial susceptibility (X_{in}) decreases with decreasing grain size (Fig. 2, Table IV). Similar grain-size fractions of the different pyrrhotite samples have initial susceptibilities of the same order. The much larger X_{in} of the EGI samples is due to their magnetite content. The much more pronounced decreasing X_{in} trend with grain size in the EGI pyrrhotite fractions is also caused by a decreasing magnetite content with smaller grain size (cf., Table III). Figures for the pyrrhotite initial susceptibility are somewhat lower than Clark's (1984) figures for pure ferrimagnetic 4C pyrrhotite. The more or less constant X_{in} in the DIS fraction for grain sizes $> 30 \mu\text{m}$ is due to the presence of ubiquitous silicate intergrowths in these coarse fractions limiting the size of the pyrrhotite parts in these grains to $\sim 30 \mu\text{m}$.

The susceptibility of the hard axis, derived from the high-field parts of the magnetization curves, is for EGI 34×10^{-8} , for TTE 38×10^{-8} , for EOR 38×10^{-8} and for DIS pyrrhotite 32×10^{-8} (all figures are in $\text{m}^3 \text{kg}^{-1}$). These figures are of the same order as those determined by Schwarz and Vaughan (1972).

The saturation magnetization (J_s) is approximately grain-size independent (Fig. 3, Table IV) with a tendency to decrease with decreasing grain size. In the finest grain-size fractions a clear J_s decrease is observed. A slightly decreasing J_s with decreasing grain size is reported for magnetite by Mauritsch et al. (1987).

TTE pyrrhotite has the highest average J_s ($\sim 16.7 \text{ A m}^2 \text{kg}^{-1}$), followed by EOR and EGI pyrrhotite (respectively 11.5 and $\sim 12.6 \text{ A m}^2 \text{kg}^{-1}$) and DIS pyrrhotite ($\sim 8.9 \text{ A m}^2 \text{kg}^{-1}$). The EGI figures have to be regarded as somewhat approximate because of the large influence of the magnetite present in these fractions (cf., Table III) on the pyrrhotite J_s determination (1% difference in magnetite weight percentage leads to a change

TABLE IV
Some rock-magnetic parameters for natural pyrrhotite

Grain-size fraction	X_{in} ($\text{m}^3 \text{ kg}^{-1} \times 10^{-5}$)	H_c (kA m^{-1})	H_{cr} (kA m^{-1})	H_{cr}' (kA m^{-1})	J_{rs} ($\text{A m}^2 \text{ kg}^{-1}$)	J_s ($\text{A m}^2 \text{ kg}^{-1}$)		
TTE 250–150	6.15	7.78	7.96	13.05	2.04	9.2		
TTE 150–100	6.75	8.49	9.55	14.80	3.40	14.2		
TTE 100–75	6.24	10.02	10.74	17.82	3.89	13.7		
TTE 75–55	5.93	12.41	12.34	21.96	4.46	17.0		
TTE 55–40	3.86	15.60	17.51	21.01	5.00	17.1		
TTE 40–30	4.43	20.21	22.68	29.92	5.70	16.2		
TTE 30–25	4.81	24.27	27.45	36.61	6.10	16.2		
TTE 25–20	4.45	23.08	31.04	40.58	6.47	17.9		
TTE 20–15	4.26	30.96	34.62	43.93	6.28	16.4		
TTE 15–10	3.49	38.68	41.78	50.45	6.54	16.0		
TTE 10–5	2.19	49.74	51.72	60.00	4.12	9.3		
TTE < 5	1.17	68.04	70.03	73.85	2.54	5.4		
EOR 250–150	5.76	7.77	8.75	14.08	2.58	13.6		
EOR 150–100	4.87	9.04	10.74	19.82	2.80	13.1		
EOR 100–75	3.92	10.28	13.53	21.41	3.15	12.5		
EOR 75–55	3.03	15.36	17.51	22.92	3.46	10.4		
EOR 55–40	2.25	20.13	21.88	29.28	3.81	10.1		
EOR 40–30	1.88	23.87	28.25	34.62	4.58	16.7		
EOR 30–25	1.17	32.71	33.02	41.38	5.25	12.1		
EOR 25–20	1.15	35.17	36.61	45.12	4.55	10.8		
EOR 20–15	1.11	36.05	37.40	44.17	4.86	10.8		
EOR 15–10	0.94	45.76	46.95	55.23	4.95	10.8		
EOR 10–5	0.99	57.69	60.08	66.53	4.64	10.4		
EOR < 5	0.57	77.35	83.16	67.88	1.51	3.5		
EGI 250–150	25.08	6.00	12.34	21.17	2.28	2.48	31.4	12.9
EGI 150–100	24.83	6.45	13.13	22.20	2.39	2.78	31.5	13.1
EGI 100–75	23.70	7.96	15.52	23.95	2.82	3.25	31.4	14.9
EGI 75–55	21.33	8.75	18.30	27.14	3.11	3.54	28.8	12.6
EGI 55–40	18.22	11.70	21.09	29.68	4.09	4.76	27.1	10.4
EGI 40–30	15.22	14.72	26.66	35.81	4.55	5.03	24.5	12.5
EGI 30–25	13.55	17.43	27.85	37.64	4.98	5.44	23.8	11.6
EGI 25–20	13.19	18.30	29.44	38.04	4.97	5.48	23.4	8.8
EGI 20–15	11.27	21.41	32.23	40.35	5.65	5.89	23.4	16.8
EGI 15–10	9.04	28.17	39.79	46.31	6.19	6.40	21.3	13.7
EGI 10–5	6.22	39.79	53.72	60.00	6.28	6.27	18.2	11.9
EGI < 5	3.10	54.27	74.01	80.77	3.89	3.43	10.5	5.9
DIS 250–150	3.45	21.04	31.43	33.26	2.49		7.9	
DIS 150–100	2.30	26.45	33.02	33.02	1.78		5.9	
DIS 100–75	2.40	23.00	33.02	37.64	1.60		6.6	
DIS 75–55	3.49	21.41	31.51	37.00	2.35		6.9	
DIS 55–40	3.85	20.37	30.80	38.83	2.36		9.0	
DIS 40–30	3.52	20.93	32.71	40.58	2.64		9.6	
DIS 30–25	4.25	21.88	31.83	39.63	3.76		11.8	
DIS 25–20	4.08	21.88	31.99	39.39	4.18		11.0	
DIS 20–15	3.09	28.17	35.41	47.75	3.86		11.4	
DIS 15–10	2.50	34.06	44.96	54.83	3.31		9.8	
DIS 10–5	1.54	43.13	58.89	67.32	2.53		7.3	
DIS < 5	1.04	57.46	75.60	72.42	1.81		4.9	

The second columns of J_{rs} and J_s of the EGI fractions refer to the specific parameters corrected for the magnetite content of each fraction (cf., Table III). The J_s corrected figures in particular are prone to a rather large error (the scatter in the individual values for each fraction is rather large) due to the fact that a 1% error in the magnetite weight percentage determination leads to an increase (or decrease) of $\sim 1 \text{ A m}^2 \text{ kg}^{-1}$ in the ‘magnetic corrected’ pyrrhotite J_s figures. The magnetite impact on the correction of J_{rs} is considerably less, because the saturation remanence of magnetite and pyrrhotite per unit mass are of the same order.

Fig. 3. J_s versus grain size. For symbol meanings see Fig. 2. The magnetite correction in the EGI fractions is based on a saturation magnetization of $90 \text{ A m}^2 \text{ kg}^{-1}$ for magnetite. The magnetite corrected EGI figures are indicated by +. The corrected figures have to be regarded as somewhat approximate because 1% error in magnetite weight percentage leads to a change in pyrrhotite saturation magnetization of $\sim 1 \text{ A m}^2 \text{ kg}^{-1}$.

of $\sim 1 \text{ A m}^2 \text{ kg}^{-1}$ in the corresponding pyrrhotite J_s). Mark the impact of only 5.5 wt.% magnetite on the corrected pyrrhotite J_s figure for the smallest EGI fraction (Table IV).

The J_s trend corresponds well with the compositions indicated by the microprobe analysis (Table IA). The most Fe-deficient pyrrhotite has the highest saturation magnetization. Fluctuation in J_s values of the same pyrrhotite could be caused, apart from errors inherent in the J_s determination procedure (estimation of the magnetite amount in the EGI fractions, estimation of the pyrrhotite amount occurring intimately intergrown with silicates in the coarse DIS fractions), by minute compositional changes between fractions of the same pyrrhotite samples. The J_s decrease in the coarsest TTE fractions could be explained in this way. It should be realized that small differences in pyrrhotite chemical composition result in considerable differences in saturation magnetization.

It was tested whether the J_s decrease in the fine grain-size fractions could be related to a change in pyrrhotite composition. This was done with the TTE fractions because the J_s decrease is largest in the TTE pyrrhotite. The six finest fractions were heated in a vacuum (10^{-6} mm Hg) at 350°C and subsequently quenched to obtain monophasic hexagonal (high temperature) pyrrhotite. The exact position of the compositional dependent $d_{(102)}$ reflection (single hexagonal reflection at $2.06 \text{ \AA}$) was determined with Philips diffractometer system PW 1700 (Cu K_α rays) at room temperature with Si as internal standard (the $d = 1.9201 \text{ \AA}$ reflection was used). The position of the $d_{(102)}$ reflection was fitted with the Yund and Hall (1969) calibration curve. The resulting Fe atom percentages were 46.68, 46.54, 46.59, 46.65, 47.05 and 46.73 respectively for the 30–25, 25–20, 20–15, 15–10, 10–5 and $< 5 \mu\text{m}$ fractions (the standard deviation of the X-ray method is estimated at 0.06 at.% Fe by Yund and Hall, 1969). Slight compositional differences exist, and the decrease in J_s in the 10–5 μm grain-size fraction may be related to its more Fe-rich composition. The $< 5 \mu\text{m}$ fraction with an even lower J_s , however, has a composition approaching that determined in the coarser fractions with a much higher J_s . The low J_s of the $< 5 \mu\text{m}$ fraction can thus not be related to a change in chemical composition.

The coercive force (H_c) increases with decreasing grain size for all samples (Fig. 4; Table IV). No large differences are observed between the

Fig. 4. H_c versus grain size. For symbol meanings see Fig. 2.

different pyrrhotites. H_c figures derived in the present study concur with Clark's (1984) determinations and for MD grains with the determination of Halgedahl and Fuller (1981). The figures for the PSD range in the present study are somewhat higher than those for this range reported by Soffel (1981). H_c is roughly proportional to the logarithm of the grain size throughout the investigated grain-size range. $H_c \propto d^{-0.67}$ is obtained for the present pyrrhotites for grain-size fractions from 5 μm upwards, which is in reasonable agreement with Clark's (1984) determination of $H_c \propto d^{-0.79}$ for a similar grain-size range. The nearly constant H_c in the coarse fractions of DIS pyrrhotite is due to the silica intergrowths in these fractions. The H_c trend for the magnetite-bearing

Fig. 5. Examples of acquisition curves of the isothermal remanent magnetization (RA curves) for pyrrhotite normalized to their saturation remanence. Identical grain-size fractions of different pyrrhotite samples revealed identical shapes for their normalized RA curves with coarse grain-size fractions saturating in smaller fields than fine grain-size fractions. $\circ$, TTE 150–100 μm fraction, $\square$, DIS 10–5 μm fraction, and $\times$, EOR 30–25 μm fraction. The inset shows the same RA curves with a 4 $\times$ expanded abscissa to display more clearly the differences in grain-size behaviour in small applied fields.

Fig. 6. J_{rs} versus grain size. For symbol meanings see Fig. 2. The magnetite-corrected J_{rs} figures for the EGI pyrrhotite fractions are indicated by +. Hartstra's (1982b) magnetite J_{rs} values were employed because the present magnetite grains underwent similar treatment during the sample preparation procedure. The most Fe-deficient pyrrhotite (TTE) with consequently the highest J_s (Fig. 3) has also the highest J_{rs} . The compositional J_s and J_{rs} trends are equal.

EGI fractions is below the other curves, because the magnetite H_c is smaller than the pyrrhotite H_c (e.g., Dunlop, 1986; Worm and Markert, 1987; Heider et al., 1987; also for crushed grains, e.g., Day et al., 1977; Hartstra, 1982b).

3.2. Remanence measurements

Acquisition curves of the isothermal remanent magnetization (RA curves) are similar for identical grain-size fractions in all samples except for the magnitude of their saturation remanence (J_{rs}). The fine grain-size fractions are saturated in larger fields than coarse grain-size fractions (Fig. 5).

J_{rs} shows a maximum in the 10–30 μm range (Fig. 6; Table IV). Absolute figures are somewhat lower than in pure 4C pyrrhotite (Clark, 1984), especially in the fine grain-size range. The trend in J_{rs} between the samples is the same as the J_s trend: TTE pyrrhotite has the highest J_{rs} , followed in decreasing order by EGI and EOR and finally by DIS. Since J_{rs} of magnetite (e.g.,

Fig. 7. H_{cr} versus grain size. For symbol meanings see Fig. 2. Note that the differences between the pyrrhotite samples in H_{cr} are considerably less than in H_c (Fig. 4).

Hartstra, 1982b) and pyrrhotite are of the same order, the magnetite contribution to the J_{rs} does not greatly affect the pyrrhotite trend in the EGI fractions (cf., Fig. 6).

The reason for the J_{rs} decrease in the small grain-size fractions is not known (also observed by Clark (1984) in pure 4C pyrrhotite, albeit to a lesser extent). In the $< 5 \mu\text{m}$ fractions this could partially be due to the presence of superparamagnetic (SP) particles. However, if present, their amount will be subordinate. In the other fractions SP particles will be (virtually) absent, so the reason for the J_{rs} decline has to be sought elsewhere.

Fig. 8. $H_{cr'}$ versus grain size. For symbol meanings see Fig. 2. Chemical differences between the pyrrhotites also hardly show up to the $H_{cr'}$ values.

It could be that the domain walls occupy a relatively large part of the grain volume, reducing the effective mass of the grains.

The remanent coercive force (H_{cr}) and remanent acquisition coercive force ($H_{cr'}$) both increase with decreasing grain size (Figs. 7 and 8). H_{cr} obeys a $\propto d^{-0.66}$ relationship and $H_{cr'}$ is proportional to $d^{-0.47}$ for grain-size fractions upwards from the $< 5 \mu\text{m}$ fractions. The differences between the different pyrrhotite samples are much smaller than in the H_c plot (Fig. 4). The H_{cr} and $H_{cr'}$ figures derived by Clark (1984) are somewhat larger than those determined in the present study. This could be due to the presence of harder fine-grained particles in Clark's grain-size fractions. The presence of magnetite hardly shows up in the H_{cr} and $H_{cr'}$ trends of the EGI fractions. The constant H_{cr} and to a lesser extent $H_{cr'}$ in the coarse fractions of the DIS sample can be attributed to the presence of silicate intergrowths. The true SD region is not yet reached in the $< 5 \mu\text{m}$ fractions, since H_c and H_{cr} both still increase with respect to the $10\text{--}5 \mu\text{m}$ fractions, albeit slightly less than would follow from the $\propto d^{-n}$ relationships. This concurs with the determinations of

Fig. 9. J_{rs}/J_s versus grain size. For symbol meanings see Fig. 2.

TABLE V

Ratios of some pyrrhotite rock-magnetic parameters

	H_c/H_{cr}	H_{cr}/H_{cr}'	J_{rs}/J_s		J_{rs}/X_{in} (kA m ⁻¹)	$(J_{rs}/X_{in})/H_{cr}$
TTE 250–150	0.98	0.61	0.22		33.17	4.17
TTE 150–100	0.89	0.64	0.24		50.37	5.27
TTE 100–75	0.93	0.60	0.28		62.34	5.80
TTE 75–55	1.01	0.56	0.26		75.21	6.10
TTE 55–40	0.89	0.83	0.29		129.53	7.40
TTE 40–30	0.89	0.76	0.35		128.67	5.67
TTE 30–25	0.88	0.75	0.38		126.82	4.62
TTE 25–20	0.74	0.76	0.36		145.39	4.68
TTE 20–15	0.89	0.79	0.38		147.42	4.26
TTE 15–10	0.93	0.83	0.41		187.39	4.48
TTE 10–5	0.96	0.86	0.44		188.13	3.64
TTE < 5	0.97	0.95	0.47		217.09	3.10
EOR 250–150	0.89	0.62	0.19		44.79	5.12
EOR 150–100	0.84	0.54	0.21		57.50	5.35
EOR 100–75	0.76	0.63	0.25		80.36	5.94
EOR 75–55	0.88	0.76	0.33		114.19	6.52
EOR 55–40	0.92	0.75	0.38		169.33	7.74
EOR 40–30	0.84	0.82	0.27		243.62	8.62
EOR 30–25	0.99	0.80	0.43		448.72	13.59
EOR 25–20	0.96	0.81	0.42		395.65	10.81
EOR 20–15	0.96	0.85	0.45		437.84	11.71
EOR 15–10	0.98	0.85	0.46		526.60	11.22
EOR 10–5	0.96	0.90	0.44		468.69	7.80
EOR < 5	0.93	1.22	0.43		264.91	3.18
EGI 250–150	0.49	0.58	0.07	0.19	9.09	0.74
EGI 150–100	0.49	0.59	0.08	0.21	9.62	0.73
EGI 100–75	0.51	0.65	0.09	0.22	11.90	0.77
EGI 75–55	0.48	0.67	0.10	0.28	14.16	0.77
EGI 55–40	0.56	0.71	0.13	0.46	19.92	0.94
EGI 40–30	0.55	0.74	0.18	0.40	28.45	1.07
EGI 30–25	0.63	0.74	0.19	0.47	33.36	1.20
EGI 25–20	0.62	0.77	0.20	0.62	34.80	1.18
EGI 20–15	0.66	0.80	0.22	0.35	44.72	1.39
EGI 15–10	0.71	0.86	0.26	0.47	62.06	1.56
EGI 10–5	0.74	0.89	0.34	0.53	98.71	1.84
EGI < 5	0.73	0.92	0.33	0.58	111.94	1.51
DIS 250–150	0.67	0.94	0.32		72.17	2.30
DIS 150–100	0.80	1.00	0.30		77.39	2.34
DIS 100–75	0.70	0.88	0.24		66.67	2.02
DIS 75–55	0.68	0.85	0.34		67.34	2.14
DIS 55–40	0.66	0.79	0.26		61.30	1.99
DIS 40–30	0.64	0.81	0.28		75.00	2.29
DIS 30–25	0.69	0.80	0.32		88.47	2.78
DIS 25–20	0.68	0.81	0.38		102.56	3.20
DIS 20–15	0.80	0.74	0.34		124.92	3.53
DIS 15–10	0.76	0.82	0.34		132.40	2.94
DIS 10–5	0.73	0.88	0.35		164.29	2.79
DIS < 5	0.76	1.04	0.37		174.04	2.30

The second J_{rs}/J_s column for the EGI fractions refers to the magnetite-corrected saturation magnetization/saturation remanence ratio. Owing to uncertainties in the magnetite percentage leading to relatively large errors in the pyrrhotite J_s in particular, the 'magnetite corrected' J_{rs}/J_s ratios have to be regarded as somewhat approximate. The fluctuations in the ratio superposed upon an increasing trend with decreasing grain size are due to (small) errors in the magnetite weight percentage determination.

the pyrrhotite SD threshold size at 1.5–2.0 μm (Soffel, 1977) or at 3 μm (Clark, 1984).

4. Discussion

4.1. Ratios of some rock-magnetic parameters

The J_{rs}/J_s ratio is increasing with decreasing grain size from ~ 0.2 to close to 0.5 (Fig. 9; Table V). The magnetite influence in the EGI fractions shows up in their lower uncorrected J_{rs}/J_s ratio. The spreading in the ratios for the corrected EGI fractions is related to their J_s correction for magnetite which is very sensitive for small errors in the determination of the magnetite content. The nearly constant ratios for the coarse DIS fractions again are due to silicate intergrowths.

The J_{rs}/J_s ratio of 0.14 determined by Halgedahl and Fuller (1981) for large polycrystalline pyrrhotite crystals concurs with the trend indicated by the present pyrrhotites. Clark's (1984) J_{rs}/J_s ratios for the coarse grain-size fractions are in good agreement with the present determinations; his figures for the fine grain-size fractions are slightly larger. The increase in J_{rs}/J_s ratio tends to slow down from some 25 μm downwards for EOR and DIS pyrrhotite. The ratios obtained for the $< 5 \mu\text{m}$ fractions are distinctly lower than the model ratio of 0.75 for SD grains (Dunlop, 1971). This is also observed by Clark (1984). Apparently, one of the easy axes is dominating, resulting in a uniaxial behaviour. The observation of Bin and Pauthenet (1963), who found six easy directions in the basal plane with one axis dominating, points also in this direction.

The H_c/H_{cr} ratio is remarkably close to unity for the TTE and EOR grain-size fractions; it displays no grain-size dependent trend (Fig. 10; Table V). For the DIS fractions the ratio is smaller (~ 0.7). The magnetite-bearing EGI fractions have lower H_c/H_{cr} ratios.

The $H_{cr}/H_{cr'}$ ratio increases with decreasing grain size from ~ 0.6 up to 1.0 (Fig. 11; Table V), an indication that self-demagnetization of MD grains could play an important role. This $H_{cr}/H_{cr'}$ ratio is similar for all pyrrhotite samples, since the magnetite content does not emerge in the H_{cr} and $H_{cr'}$ trends.

Fig. 10. H_c/H_{cr} versus grain size. For symbol meanings see Fig. 2. The large figures, which are uniform throughout the investigated grain-size range, make this ratio discriminative between pyrrhotite and magnetite (the EGI ratios are smaller than the others).

The J_{rs}/X_{in} ratio increases with decreasing grain size (Fig. 12; Table V); only EOR fractions display high ratios in the intermediate grain-size

Fig. 11. $H_{cr}/H_{cr'}$ versus grain size. For symbol meanings see Fig. 2. Its increase with decreasing grain size might be related to self-demagnetization effects which are more pronounced in MD grains.

Fig. 12. J_{rs}/X_{in} versus grain size. For symbol meanings see Fig. 2. The ratio is larger than H_{cr} throughout the investigated grain-size interval.

range. The J_{rs}/X_{in} ratios are typically larger than H_{cr} figures for pyrrhotite. (J_{rs}/X_{in})/ H_{cr} values are larger in 4C-rich pyrrhotite (TTE, EOR) than in more Fe-rich pyrrhotite (DIS, Table V).

4.2. Comparison of pyrrhotite room-temperature hysteresis parameters with those of magnetite

The following comparison between pyrrhotite and magnetite rock-magnetic parameters is made using the magnetite data of O'Reilly (1984), Dunlop (1986), Worm and Markert (1987) and Heider et al. (1987). The pyrrhotite saturation magnetization is smaller than that of magnetite whereas the saturation remanence is of the same order (except in the small grain-size fractions, where the magnetite saturation remanence is considerably larger). Pyrrhotite has thus typically higher J_{rs}/J_s ratios than magnetite, as is demonstrated by the low uncorrected EGI figures (Table V). The pyrrhotite initial susceptibility is considerably smaller than that of magnetite in similar grain-size ranges. Its coercive force is larger than the magnetite coercive force.

For comparison of pyrrhotite remanent coercive force and remanent acquisition coercive force

with the same parameters for magnetite, only magnetite data referring to crushed grains are available (e.g., Day et al., 1977; Hartstra, 1982b). The hysteresis properties of such crushed magnetite grains are influenced by stress (e.g., Dunlop, 1986; Heider et al., 1987). No data on H_{cr} and H_{cr}' for large non-crushed magnetite grains have yet been published. H_{cr} as well as H_{cr}' for pyrrhotite are larger than the respective parameters for magnetite in the fine grain-size fractions and smaller in the coarse grain-size fractions. H_{cr} and H_{cr}' are more or less equal for both minerals in the 75–55 μm range. Since crushing enlarges the magnetite coercive forces, it is reasonable to expect that the parameters for non-crushed magnetite grains will be smaller than those for pyrrhotite throughout the whole investigated grain-size range. Pyrrhotite is thus magnetically 'harder' than magnetite. Titanomagnetite shows, compared with pure magnetite, an increasing hardness with rising Fe^{2+} content owing to the anisotropic character of the Fe^{2+} ion. The hardness of pyrrhotite could possibly be explained similarly, because all Fe in pyrrhotite is considered to be in the divalent state.

The H_{cr}/H_{cr}' ratio is similar for pyrrhotite and magnetite in the coarse grain-size range, but this ratio increases with decreasing grain size in pyrrhotite whereas it is approximately grain-size independent in magnetite. Typical for pyrrhotite is its high H_c/H_{cr} ratio, which is approximately uniform throughout the investigated grain-size interval. Another discriminative parameter between pyrrhotite and magnetite is the J_{rs}/X_{in} ratio which is considerably larger in pyrrhotite. This ratio is larger than H_{cr} for pyrrhotite and smaller than H_{cr} for magnetite.

The presence of pyrrhotite in a sample can thus be established by a high H_c/H_{cr} ratio or by a J_{rs}/X_{in} ratio which is larger than H_{cr} when it is decided to leave heat treatment of the sample to avoid possible chemical alterations. The pyrrhotite grain-size interval can subsequently be determined by the observed coercive force or, preferably, by the remanent coercive force, because compositional differences in pyrrhotite appear to have only minor influence on its remanent coercive force.

4.3. Evaluation of the origin of anisotropy in pyrrhotite

The area between the ordinate, the descending branch of the hysteresis loop and the extrapolated line for the determination of the saturation magnetization minus the energy of the demagnetizing field ($0.5N \times J_s^2$) represents the reversible magnetization work (e.g., Appel, 1987).

$$W_{\text{rev}} = \int H \, dJ - 0.5N \times J_s^2$$

$\int H \, dJ$ can be planimetrically determined. For the present pyrrhotites it appeared that $0.5N \times J_s^2$ (N was set at 0.33) constitutes at most a few per cent of $\int H \, dJ$ (owing to a relatively low J_s). Therefore uncertainties regarding the actual value of the demagnetization factor led to negligible error in the W_{rev} determination.

Anisotropy can have its cause in shape, stress or magnetocrystalline anisotropy. The observed anisotropy can be a mixture of these three contributions. Usually one type of anisotropy is dominating. Neglecting shape anisotropy, it is first assumed that stress anisotropy is dominating. W_{rev} is then related to the average stress anisotropy energy (E_{sa}) by

$$W_{\text{rev}} = E_{\text{sa}} = 0.75\lambda\sigma_i$$

where λ denotes the magnetostriction constant and σ_i the average internal stress. Soffel (1977) determined a maximum value for the magnetostriction constant of 7×10^{-6} for pyrrhotite (the high Fe^{2+} amount in pyrrhotite apparently does not lead to high magnetostriction constants as in titanomagnetite). Calculation of average internal stress from the present pyrrhotite data yields values between 3500 and 7000 MPa, which are unreasonably large. This is demonstrated by the range of 27–63 MPa for average internal stress in titanomagnetites calculated by Appel (1987) and by a stress of some 200 MPa which is considered reasonable for ceramic materials (cf., O'Reilly, 1984). One may thus conclude that stress is not dominating.

Fig. 13. The stippled area represents W_{rev} ; the hatched area represents the minimum work done against the hard axis anisotropy.

The magnetocrystalline anisotropy for pyrrhotite is given by Bin and Pauthenet (1963) as

$$E_{\text{an}} = K_1 \sin^2\theta \sin^2\phi + K_2 \sin^4\theta \sin^4\phi + K_3 \cos^2\phi + K_4 \cos^4\theta + K_5 \sin^2\cos^2\theta \sin^2\phi + \dots$$

θ is the angle between the magnetization direction and the easy axis. ϕ is the angle in the basal plane between an easy axis and the projection of direction of magnetization onto the basal plane. They neglect terms of K_5 and above. At room temperature K_1 is $0.35 \times 10^5 \text{ J m}^{-3}$, $K_2 \sim 0$, K_3 $1.18 \times 10^5 \text{ J m}^{-3}$ and K_4 $32.2 \times 10^5 \text{ J m}^{-3}$. The large K_3 and K_4 are related to the pyrrhotite hard axis of magnetization (measured with applied field parallel to C -axis) and K_1 and K_2 to basal plane anisotropy. Bin and Pauthenet (1963) note during their measurements six easy directions of magnetization in the basal plane with one axis dominating. They ascribe this to twinning in their pyrrhotite crystal.

Since the reversible work determined for the present pyrrhotites is referring to the energy necessary to overcome basal plane anisotropy (the hard axis behaviour is excluded by the extrapolation to J_s) and J_{rs}/J_s ratios of close to 0.5 were found in the smallest pyrrhotite fractions, we treat

the anisotropy as uniaxial for approximation. W_{rev} is related to the anisotropy energy (E_k) as

$$W_{\text{rev}} = E_k = 0.66K_{\text{an}}$$

where K_{an} is the magnetocrystalline anisotropy constant. Calculation yields anisotropy constants in the range of 0.35 up to $0.70 \times 10^5 \text{ J m}^{-3}$ for all pyrrhotites, in fair agreement with the $0.35 \times 10^5 \text{ J m}^{-3}$ determination of K_1 by Bin and Pauthenet (1963). The minimum work done against the anisotropy of the hard axis is given by the hatched triangle in Fig. 13. Assuming uniaxial anisotropy for the hard axis, as in Besnus et al. (1968), calculation yields an anisotropy constant range of $5\text{--}8 \times 10^5 \text{ J m}^{-3}$ for the hard axis. The range obtained is similar to the anisotropy used by Besnus et al. (1968).

4.4. Trends in coercive and remanent coercive force

The present pyrrhotites consist of various intergrown superstructures. Three of the samples (TTE, EOR and EGI) have compositions close 'ideal 4C pyrrhotite' so that the 4C superstructure is dominating. The fourth (DIS) is a more Fe-rich pyrrhotite which consists apart from the 4C superstructure of antiferromagnetic NC superstructures. All pyrrhotites show smooth grain-size dependent trends in H_c , H_{cr} and $H_{\text{cr}'}$ (Figs. 4, 7, 8), so apparently the presence of the antiferromagnetic parts does not show up in these trends. It could be that the 'antiferromagnetic' parts carry a kind of defect magnetization (non-integral superstructures) and as such cannot be regarded as non-magnetic intergrowths. Nakazawa and Morimoto (1971) mention that the 5C, 6C, etc., superstructures are (slightly) ferrimagnetic and not perfectly antiferromagnetic. Soffel (1981) reported the presence of 'pseudo domain walls' which were immobile under the application of an external magnetic field, contrary to normal domain walls which moved due to the same field. He related the presence of pseudo domain walls to minute differences in pyrrhotite superstructure (which he could not make visible by etching).

5. Conclusions

The pyrrhotite rock-magnetic parameters, determined in the present study, show smooth grain-size dependent trends. The initial susceptibility is considerably smaller than that of magnetite and decreases with decreasing grain size (7×10^{-5} – $1 \times 10^{-5} \text{ m}^3 \text{ kg}^{-1}$). The susceptibility of the hard axis is $\sim 30\text{--}40 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}$ for all pyrrhotites. The coercive force, remanent coercive force and remanent acquisition coercive force all increase with decreasing grain size; respectively, 7–80 for H_c , 8–85 for H_{cr} and 14–80 for $H_{\text{cr}'}$ (all in the kA m^{-1}). The coercive forces all obey $d \sim n$ relationships with grain size above $5 \mu\text{m}$ with $n = 0.67$ for H_c , $n = 0.66$ for H_{cr} and $n = 0.47$ for $H_{\text{cr}'}$. The pyrrhotite coercive force is larger than the magnetite coercive force; the remanent coercive force and remanent acquisition coercive force are smaller for pyrrhotite than for magnetite in the coarse grain-size fractions whereas the reverse is true in the fine grain-size fractions. The saturation remanence increases with decreasing grain size down to $\sim 30 \mu\text{m}$ and decreases with a further grain-size decrease (increase from 2.0 to $6.0 \text{ A m}^2 \text{ kg}^{-1}$; decrease down to $\sim 2.0 \text{ A m}^2 \text{ kg}^{-1}$). Its decrease in the fine grain-size range might be related to a relatively large grain volume of domain walls. The saturation magnetization is approximately grain-size independent with a marked decrease for the finest fractions. The reason for this decrease is not known. It varies from $\sim 16.7 \text{ A m}^2 \text{ kg}^{-1}$ for TTE via 12.6 for EGI and 11.5 for EOR down to $8.9 \text{ A m}^2 \text{ kg}^{-1}$ for DIS pyrrhotite. The trends indicated by figures for the saturation magnetization and saturation remanence correspond with the equivalent Fe trend indicated by the microprobe analysis.

Typical for pyrrhotite are its larger J_{rs}/J_s ratio (0.20 to close to 0.50) and its large H_c/H_{cr} ratio, which is uniform throughout the investigated grain-size interval (~ 0.9 for relatively Fe-poor pyrrhotite and 0.8 for Fe-richer pyrrhotite). The $H_{\text{cr}}/H_{\text{cr}'}$ ratio increases with decreasing grain size, indicative for self-demagnetization of MD grains. The $J_{\text{rs}}/X_{\text{in}}$ ratio is larger than H_{cr} for pyrrhotite; it increases with decreasing grain size. Calculation of the average internal stress from the reversible

work given by the reversible part of hysteresis curves yields unreasonably large figures in a range of 3500–7000 MPa, so the anisotropy is not dominated by stress anisotropy. Assuming a dominating uniaxial magnetocrystalline anisotropy yields a range of $0.35\text{--}0.70 \times 10^5 \text{ J m}^{-3}$ for the anisotropy constant, in fair agreement with the determination of $0.35 \times 10^5 \text{ J m}^{-3}$ of Bin and Pauthenet (1963).

Pyrrhotite and magnetite can be discriminated by the large J_{rs}/J_s and H_c/H_{cr} ratios for pyrrhotite and a J_{rs}/X_{in} ratio which is larger than H_{cr} for pyrrhotite. The presence of pyrrhotite in a sample can be established by the H_c/H_{cr} or the J_{rs}/X_{in} ratio; the pyrrhotite grain size can subsequently be derived by the H_{cr} trend, because pyrrhotite compositional differences appear to have only minor influence on H_{cr} versus grain-size trend.

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