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Magnetic susceptibility of pyrrhotite: grain size, field and frequency dependence

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SUMMARY

The field and frequency dependences of the initial susceptibility of pyrrhotite have been analysed as a function of grain size, motivated by a strong field dependence recently observed for large (mm-sized) pyrrhotite crystals (Worm 1991) and smaller field dependences determined on smaller grain sizes by Clark (1984). In the present study, the frequency ranged from 30 Hz to 27 kHz. At 2 kHz, a field range from 0.05 to 1500 μT was investigated. Separate determinations of in-phase (k') and quadrature (k'') susceptibility components allow for the analysis of eddy current effects.

Up to 4 kHz the in-phase susceptibility of a pyrrhotite-ore specimen is practically independent of frequency whereafter it decreases while the quadrature component increases linearly with frequency to a value on the order of k' at 20 kHz for large grains. k'' is proportional to $d^2\mu\sigma f$ where d is grain diameter, μ the intrinsic permeability, σ the electrical conductivity and f the frequency. The frequency response of magnetite is essentially flat up to frequencies >20 kHz. Both frequency dependences agree well with calculations based on the theory by Wait (1951). The conductivity of the pyrrhotite ore has been determined to be $\sigma = 1.40$ $(\pm 0.05) \cdot 10^5\,\Omega^{-1}m^{-1}$.

The susceptibility of pyrrhotite and its field dependence increase strongly with grain size. While the susceptibility of grains smaller than 30 μm is field independent (up to 1.5 mT) it may increase as $k \propto H^{0.25}$ for mm-sized crystals in fields >10 μT. For most samples the Rayleigh law is inadequate to characterize induced magnetizations in weak alternating fields. When susceptibilities are measured for geomagnetic anomaly modelling, laboratory fields should be of similar intensity as the Earth's field and of frequency ≤1 kHz.

Key words: grain size, pyrrhotite, susceptibility.

1 INTRODUCTION

In geophysical applications, weak field (initial) magnetic susceptibilities (k_0) are measured on rocks to determine the in-field magnetization—induced by the geomagnetic field—for anomaly modelling. This is amongst others relevant for prospection of (sulfide) ores, which often contain magnetite and/or pyrrhotite in (fairly) large amounts. Hence, these ores potentially have a large magnetic expression making magnetic methods an attractive prospection tool. In palaeomagnetism, magnetic susceptibilities are used for Q-factor calculations, for example, and, in sedimentary rocks, for palaeoclimate studies. While the geomagnetic field can be regarded as a truly dc field varying in intensity with latitude between 30 and 60 μT (microTesla), in laboratory susceptibility measurements alternating fields of typically ≈1 kHz and peak intensities of up to 1 mT are often applied for sensitivity reasons. It is thus presumed that the susceptibility of rocks varies only insignificantly with frequency between 0 and 1 kHz and for field intensities up to several times the geomagnetic field strength.

For magnetite, the field dependence of initial susceptibility is indeed negligible (Dunlop 1986; Worm 1991). On the basis of Néel's (1950) theory of magnetic viscosity Vinzenz (1965) predicted that the susceptibility of magnetite should decrease with increasing frequency by 4 per cent per decade of frequency. However, an experimental study by Bhathal & Stacey (1969) on multidomain magnetite grains found their susceptibility to be independent of frequency over the frequency range 1–1060 Hz. On the other hand, Galt (1952) has shown that the *intrinsic* susceptibility of a picture-frame single crystal decreases severalfold with frequency above 1 kHz. At the low-grain-size end the susceptibility increases when the superparamagnetic threshold is reached (e.g. Stacey & Banerjee 1974). Since superparamagnetic properties are characterized by a short relaxation time τ, the apparent susceptibility of grains that are superparamagnetic at dc and low ac fields will decrease strongly at frequencies $f > 1/\tau$. This phenomenon is being used in environmental magnetism studies, for example, for magnetic granulometry analyses (e.g. Thompson & Oldfield 1986).

For pyrrhotite, however, a strong field dependence of susceptibility for fields between 0.01 and 1 mT has recently been observed on large (mm-sized) crystals (Worm 1991). The only previous study on susceptibility variations with field intensity for pyrrhotite gave a much smaller field dependence of susceptibility for grain sizes $<100\,\mu$m (Clark 1984). Susceptibility variations with frequency have not been studied yet for pyrrhotite.

In this paper we present results of grain-size effects on the field dependence of susceptibility of pyrrhotite measured on various ores and on sized and well defined samples from the collections of Clark (1984) and Dekkers (1988), respectively. We also show that the susceptibility of pyrrhotite changes significantly with increasing frequency in the kHz range.

The widespread occurrence of pyrrhotite in rocks has only recently been appreciated. So, if the presence of pyrrhotite in the rock can be demonstrated, the commonly applied calculation of the induced magnetization to an equivalent percentage of magnetite has little value. Moreover, the afore-mentioned presumptions regarding field and frequency independence of the susceptibility need to be verified for pyrrhotite.

2 THEORY

The general case of a conducting specimen with non-linear magnetic susceptibility subject to an alternating field is very complicated, especially if self-demagnetization is significant. The following effects come into play: (1) induced eddy currents, (2) magnetic viscosity, (3) non-linearity and hysteresis, and (4) self demagnetization.

2.1 Induced eddy currents

At high frequencies both the in-phase and quadrature components of the induced signal in the solenoid of a susceptibility bridge are functions of conductivity. More particularly, the controlling parameter for materials with negligible dielectric polarization (such as magnetite and pyrrhotite) is $\Theta = r(\mu\sigma\omega)^{1/2}$, where r is the radius of the specimen, μ the magnetic permeability $[=\mu_0(1+k_i)$, $\mu_0 = 4\pi \cdot 10^{-7}$ H/m, k_i: intrinsic susceptibility], σ the electrical conductivity and ω the angular frequency of the applied field. Wait (1951) calculated the complex magnetization of a spherical homogeneous and isotropic specimen for which the magnetization M depends linearly on field H (low field limit for ferro- and ferrimagnets). The complex apparent susceptibility is:

$$k' + ik'' = \frac{3\cdot\mu\cdot(\sinh\alpha - \alpha\cdot\cosh\alpha) + 3/2\cdot\mu_0\cdot(\sinh\alpha - \alpha\cdot\cosh\alpha + \alpha^2\cdot\sinh\alpha)}{\mu\cdot(\sinh\alpha - \alpha\cdot\cosh\alpha) - \mu_0\cdot(\sinh\alpha - \alpha\cdot\cosh\alpha + \alpha^2\cdot\sinh\alpha)} \quad (1)$$

with k' as in-phase component, k'' as quadrature component of the apparent susceptibility, $i=\sqrt{-1}$ and $\alpha = r(i\mu\sigma\omega)^{1/2}$. k' in the limit $\Theta \to 0$ is proportional to $k_i/(1+Nk_i)$, where N the demagnetizing factor of the sphere (=1/3). For $\Theta < 1.5$ this component is almost constant, but with increasing Θ it starts to decrease, eventually changing sign as eddy currents dominate the secondary field produced by the specimen.

The quadrature component arising from eddy currents is proportional to $\Theta^2 = r^2\mu\sigma\omega$ and is almost independent of susceptibility, apart from the weak dependence via μ, for $\Theta \leq 1.5$. This corresponds to the region for which the skin depth is much greater than the radius and hence the applied field permeates the specimen completely. Under these conditions, the quadrature signal is proportional to frequency ω and the power loss is proportional to ω^2 (see e.g. Chikazumi & Charap 1978, pp. 321–322). With increasing Θ the quadrature component peaks and then decreases gradually.

Using eq. 1 we have calculated in-phase and quadrature susceptibilities for model magnetite and pyrrhotite specimens, respectively, with a radius of $r = 1$ cm. As susceptibility parameters we took $k_i = 50$ for magnetite, and $k_i = 0.33$ for pyrrhotite. The conductivity of magnetite (depending on stoichiometry) is $\sigma \leq 2.5 \cdot 10^4\,\Omega^{-1}m^{-1}$ (Lefever 1980), while the conductivity of pyrrhotite may be an order of magnitude higher than that of magnetite although existing data scatter (Beblo 1982) with a highest literature value of $\sigma = 5 \cdot 10^5\,\Omega^{-1}m^{-1}$, which we used. Fig. 1 shows that frequency effects on the susceptibility of magnetite should be negligible up to about $f \approx 10$ kHz, while for pyrrhotite, k' and k'' change already noticably above 1 kHz. The onset of frequency effects will shift towards higher frequencies with decreasing grain sizes and conductivities.

2.2 Magnetic viscosity

The capability of a magnetic moment to follow a changing applied magnetic field (regardless of frequencies, ranging from 10^{-13} Hz for a reversing geomagnetic field to >1 kHz for susceptibility measurements) is customarily characterized by a time constant τ with the moment following the field for $\tau \ll 1/f$ and being unaffected by the field for $\tau \gg 1/f$. Thus, magnetization calculations using ac susceptibility measurements alone will possibly underestimate the magnetization component of rocks along the Earth's magnetic field. The difference can range from negligible to manyfold depending on the distribution of relaxation times. Magnetizations characterized by time constants larger than a second or so are commonly termed viscous magnetizations; however, magnetic viscosity may occur on still shorter time scales due to the presence of superparamagnetic grains ($\tau < 1$ s), for example.

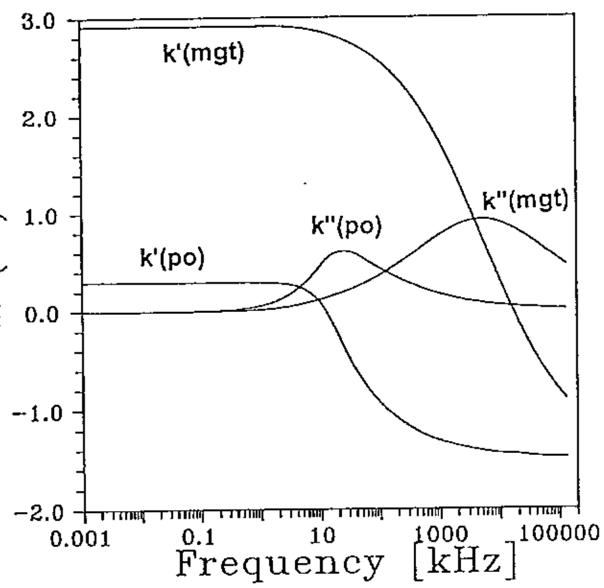

Figure 1. Theoretical frequency dependence of in-phase (k') and quadrature (k'') susceptibilities for model magnetite (mgt) and pyrrhotite (po) spheres of 1 cm radius, conductivities $\sigma(\text{mgt}) = 2.5 \cdot 10^4\,\Omega^{-1}m^{-1}$, $\sigma(\text{po}) = 5 \cdot 10^5\,\Omega^{-1}m^{-1}$, and intrinsic susceptibilities $k_i(\text{mgt}) = 50$, $k_i(\text{po}) = 0.33$. Calculations according to Wait (1951) (eq. 1).

When there is a broad distribution of time constants $\tau_{min} \ll 1/f \ll \tau_{max}$, experiment and a simple phenomenological theory give viscous decay of magnetization (M) proportional to $\log t$, constant decrease of total susceptibility k ($=M/H$) per decade of frequency and frequency-independent quadrature susceptibility (k'') (Dunlop 1973; Mullins & Tite 1973). In particular:

$$dk/d(\log \omega) \approx -2k''/\pi \approx (1/H)\, dM/d(\log t), \tag{2}$$

provided that $\tau_{min} \ll t \ll \tau_{max}$ and $1/\tau_{max} \ll \omega \ll 1/\tau_{min}$.

On the other hand, when there is a relaxation phenomenon with a single time constant τ, such as domain-wall resonance, the associated contributions to the in-phase and quadrature susceptibilities are, respectively:

$$k' = k(\omega = 0)/(1 + \omega^2\tau^2) \tag{3}$$

$$k'' = \omega\tau k(\omega = 0)/(1 + \omega^2\tau^2). \tag{4}$$

The in-phase susceptibility decreases monotonically with increasing frequency, whereas the quadrature component exhibits a resonance peak at $\omega = 1/\tau$. At resonance the two components are both equal to half the dc susceptibility.

2.3 Non-linearity and hysteresis

Provided a sample obeys the Rayleigh law (for $H \ll H_c$.H_c: coercivity), the initial magnetization curve is given by, respectively:

$$M = k_0H + \alpha H^2. \tag{5}$$

In an alternating field the hysteresis loop consists of a pair of parabolic arcs. The ascending and descending branches of the Rayleigh loop for $-H_0 \le H \le H_0$ are given by:

$$M = (k_0 + \alpha H_0)H \pm \tfrac{1}{2}\alpha(H_0^2 - H^2). \tag{6}$$

When $H = H_0 \sin \omega t$, the magnetization lags behind the field due to the hysteresis and odd harmonics are introduced by the non-linearity (Chikazumi & Charap 1978, pp. 296–297). The induced magnetization is:

$$M = (k_0 + \alpha H_0)H_0 \sin \omega t - (4\alpha H_0^2/3\pi) \cos \omega t + \text{odd harmonics}. \tag{7}$$

Thus the in-phase susceptibility for an applied field amplitude H is:

$$k' = k_0 + \alpha H, \tag{8}$$

and the quadrature susceptibility is:

$$k'' = 4\alpha H/3\pi. \tag{9}$$

If there is a cubic term in the M–H curve, reflecting a levelling off of the magnetization, even harmonics are also introduced into the signal.

2.4 Self demagnetization

The magnetic behaviour of a sample can be strongly affected by its shape due to self demagnetization. Demagnetizing fields are homogeneous only for bodies of uniform magnetization and bound by a second-degree surface (ellipsoids). Average demagnetization factors have been calculated for uniformly magnetized cylinders (Joseph 1966), rectangular prisms (Sharma 1968) and octahedra (Williams, Evans & Thorpe 1989) of varying elongations. It is mostly assumed that the demagnetization tensor has unit trace as for ellipsoids:

$$N_a + N_b + N_c = 1. \tag{10}$$

However, this relationship is not generally valid as has been shown experimentally (Åm & Stemland 1975) as well as theoretically (Eskola & Tervo 1980). Considering induced magnetization only, the trace of the demagnetization tensor for cubes and prisms decreases from $\Sigma N = 1$ for intrinsic susceptibilities $k_i < 0.1$ (SI) to $\Sigma N = 0.85$ for $k_i \to \infty$. Since the apparent (measured) susceptibility is

$$k = k_i/(1 + N \cdot k_i) \tag{11}$$

the intrinsic susceptibility can be calculated for massive samples of cubic shape utilizing the calculations of Eskola & Tervo (1980) (Fig. 2). Hence intrinsic susceptibilities to $k_i \approx 50$ can approximately be determined on samples of cubic and probably also of equidimensional cylindrical shape.

In the general case, the intrinsic susceptibility is complex and there is an interaction between the observed in-phase (real) and the quadrature (imaginary) susceptibilities via the self-demagnetizing field. This happens because the phase of the magnetization differs from that of the internal field, due to viscosity and hysteresis, which in turn differs from that of the applied field, because of the contribution of the self-demagnetizing field (which is in phase with the magnetization). In the linear region the apparent in-phase susceptibility is:

$$k' = \frac{k_i'(1 + Nk_i') + Nk_i''^2}{(1 + Nk_i')^2 + N^2k_i''^2}. \tag{12}$$

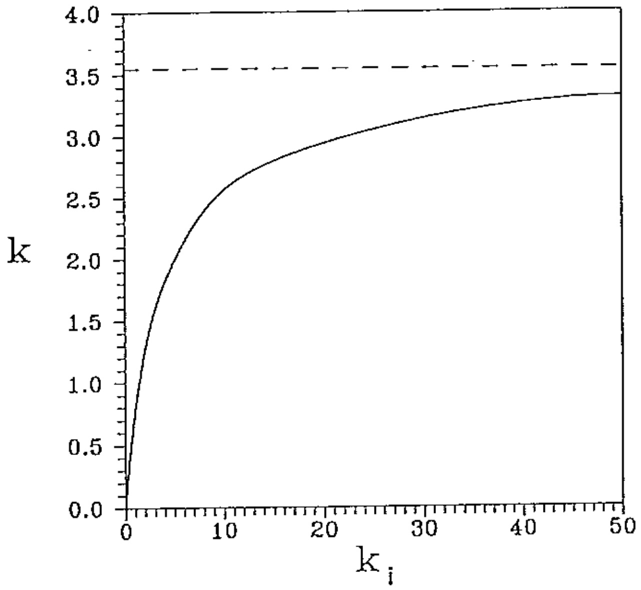

Figure 2. Apparent susceptibility k versus intrinsic susceptibility k_i for samples of cubic shape: $k = k_i/(1 + Nk_i)$. The demagnetization factor N decreases with increasing k_i (Eskola & Tervo 1980). Dashed line indicates limit for $k_i \to \infty$.

The apparent quadrature susceptibility is:

$$k'' = k_i''/[(1 + Nk_i')^2 + N^2 k_i''^2] + \text{eddy current component.} \quad (13)$$

Hence, the intrinsic quadrature susceptibility k_i'' becomes largely shielded from observation for specimens with only moderately large in-phase intrinsic susceptibilities and demagnetizing factors (e.g. magnetite). Note that the eddy-current contribution to the quadrature susceptibility already includes the effects of self demagnetization, because it is derived by solving the boundary value problem for a permeable conducting specimen in an alternating field.

When there is hysteresis as well, the situation becomes more complicated and the total effect is no longer simply the superposition of the contributions from each phenomenon.

3 EXPERIMENTS

Ac susceptibilities have been measured on a number of pyrrhotite samples and a magnetite specimen for comparison. Frequency-dependent measurements resolved for in-phase and quadrature components have been performed in the frequency range from 30 Hz to 27 kHz. The field dependence of susceptibility has been investigated for fields ranging from 0.05 to >1000 μT at 2 kHz.

3.1 Sample description

A variety of pyrrhotite samples has been collected for the field-dependent susceptibility studies. These comprise massive ores as well as crushed and sieved grain size fractions from different localities:

(1) two equidimensional polycrystalline agglomerates of monoclinic-pyrrhotite crystals (labeled SE09 and SE7) with roughly aligned *c*-axes from Santa Eulalia, Mexico; SE09 having larger (mm-sized) crystals than sample SE7.

(2) A cylinder-shaped (axial ratio: 0.85) massive pyrrhotite ore (labelled CERRO) from Cerro de Pasco, Peru. Its grain sizes range from 50 to 300 μm while the overall susceptibility anisotropy is fairly small with $k_{max}/k_{min} < 1.5$ (depending on applied field) (de Wall & Worm 1993).

(3) Three pyrrhotite ore samples from Australia. The Elura specimen originates from the Elura ore body in Cobar, N.S.W., Australia, and is a semi-massive to massive (70 per cent–80 per cent) sulfide mineralization containing ≈20 per cent pyrrhotite with pyrite, sphalerite, galena, minor chalcopyrite and arsenopyrite. The pyrrhotite consists of intergrowths of monoclinic and intermediate pyrrhotite with monoclinic dominating (Clark 1983). *Q54x* and *Q53c* are massive ores from Mount Bonnie, N.T., Australia, and contain only monoclinic 4*C* pyrrhotite.

(4) Three-sized fractions obtained by crushing and sieving monoclinic 4*C* pyrrhotite ore also from Mt Bonnie, and dispersing in epoxy, previously studied by Clark (1984). NRC3 consists of 83 ± 38 μm grains in a concentration of 0.43 vol. per cent, R8 has 20 ± 6 μm grains dispersed to 0.21 vol. per cent, and R14 has 15.5 ± 5.7 μm grains diluted to 0.51 vol. per cent.

(5) The TTE sample collection of Dekkers (1988) with the pyrrhotite originating from the abandoned Temperino mine, Tuscany, Italy;

(6) The EOR sample collection also of Dekkers (1988) from the abandoned Ortano mine on Elba Island, Italy. The metallogenesis for both locations is described by Bodechtel (1965, 1968) and Dekkers (1989). The collections consist of sieved grain-size fractions from 5 to 250 micrometers. The samples were crushed, upgraded by magnetic separation and micro-precision sieved as much as possible in an inert atmosphere. The equant TTE and EOR pyrrhotite grains are of high purity, only trace amounts of Ni were detected by microprobe analysis (Dekkers 1988, 1989). These samples have not been dispersed in a non-magnetic matrix in order to reduce magnetostatic interactions, because an initial check on the most strongly magnetic EOR250 material revealed an increase in susceptibility of only 8 per cent upon dilution to 0.9 Vol. per cent. The field dependence of k (the main focus of this study) is virtually indistinguishable for both specimens except for more noise distortion with the diluted specimen. Therefore, the field-dependent experiments have been performed with the non-dispersed TTE and EOR samples of typically ≈200 mg.

(6) A paragneiss sample from the pilot hole of the German Continental Deep Drilling Program (KTB) V559Flad (depth: 2325.33 m) containing pyrrhotite grains ranging from 30 to 300 μm in size.

All pyrrhotite samples have been characterized by thermomagnetic curves measured in vacuum and a field of 0.55T (Fig. 3). There is an instrument-related temperature hysteresis, i.e. heating and cooling curve display an offset. Also, depending on grain size and material, some samples alter (oxidize) upon heating to 600 °C despite the applied vacuum. Nevertheless, three important informations can be gained from the heating curves: (1) strong field magnetization values M_s at room temperature range from about 6 $Am^2\,kg^{-1}$ (*Q53c*) to 18.7 $Am^2\,kg^{-1}$ (SE), (2) the kink at $T \approx 230$ °C in some M_s/T curves indicates the presence of

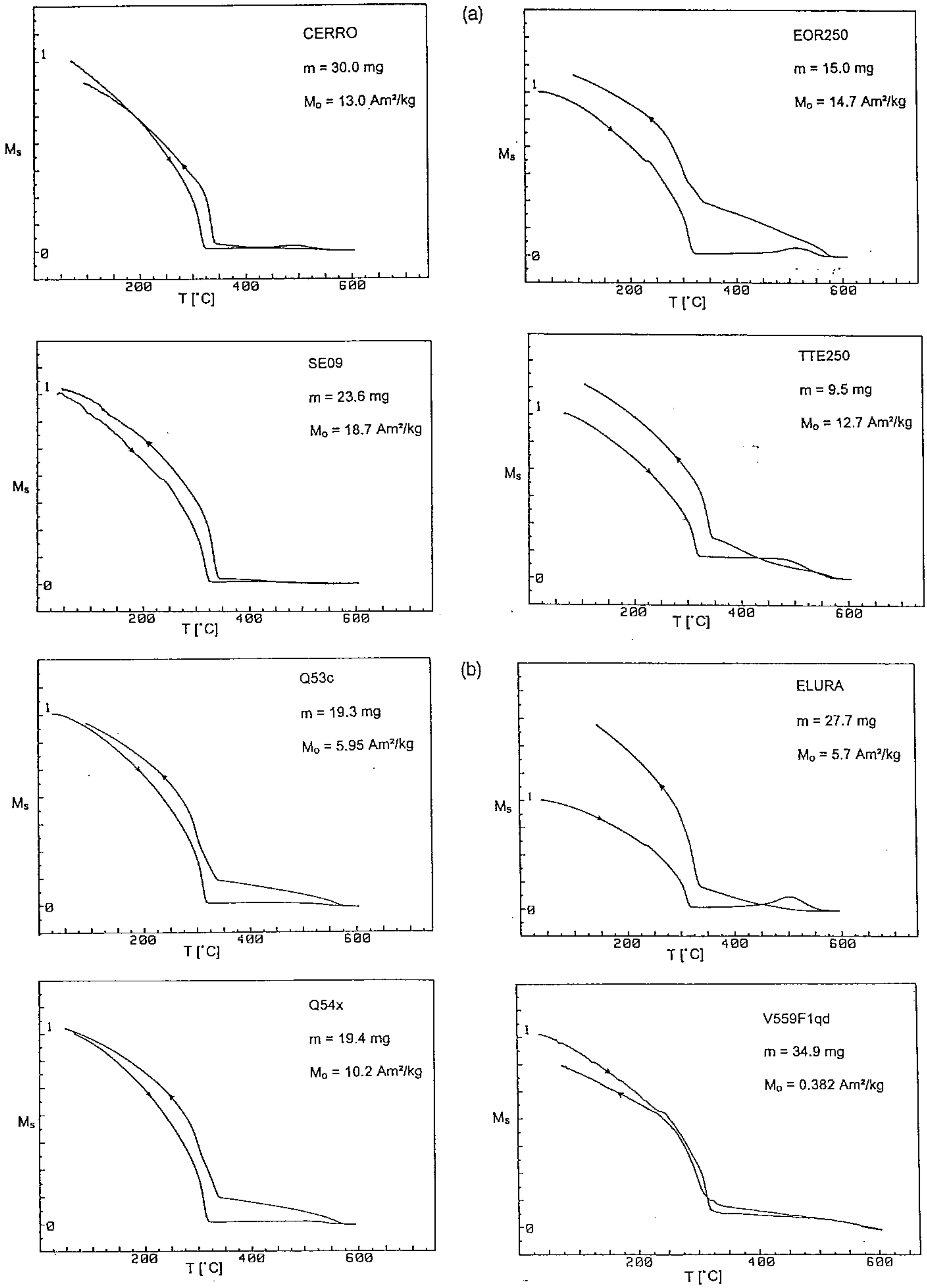

Figure 3. Thermomagnetic curves of various pyrrhotite samples: strong field (0.55 T) magnetization M_s versus temperature T measured in a vacuum ($\approx$10 Pa) with a heating rate of 20°/min. The observed temperature hysteresis (offset between heating and cooling curves) is instrument related.

hexagonal pyrrhotite, (3) all samples except for TTE250 have essentially zero magnetizations at 350°C upon heating, this means that only sample TTE250 is contaminated with magnetite ($T_c = 575$ °C). Here, the magnetite signal is $\approx 1.5\ Am^2\,kg^{-1}$ and with a saturation magnetization of magnetite $M_s(350\,°C) \approx 75\ Am^2\,kg^{-1}$ this amounts to a magnetite concentration of 2 per cent.

Hysteresis properties have been described previously for the sized sample collections by Clark (1984) and Dekkers (1988).

In addition to the various pyrrhotite samples a magnetite specimen and a paramagnetic oxide, Gd_2O_3, analytical grade (2.18g), have been measured as well mainly to verify the linearity of the ac-susceptibility bridge. The magnetite specimen has been synthesized by sintering in two steps at 1100 and 1400 °C, respectively, in an appropriate CO/CO_2 atmosphere. It was cylinder shaped with a diameter of 7 mm and an axial ratio of initially 1.28 (length/diameter); it was then cut to 5.5 mm in length to give approximately equal radial- and axial-susceptibility values.

3.2 Method of measurement

The ac-susceptibility apparatus in the laboratory Grubenhagen of the Niedersächsisches Landesamt für Bodenforschung, Germany, is of the mutual inductance bridge type (e.g. Brodbeck, Bukrey & Hocksema 1978) and consists of a long primary solenoid around which two identical, but well separated, secondaries are wound. The induced voltages in both coils differ when the inductance changes by inserting a specimen into one of the coils and is detected by a lock-in amplifier with a differential input. The amplifier also allows the separate determinations of in-phase and quadrature susceptibility components. The frequency can be varied between 30 Hz and 27 kHz while the field can have a maximum amplitude of 1.5 mT.

4 RESULTS

The main aim of this study was to establish the grain-size effects on the field dependence of susceptibility of pyrrhotite. Since the induced voltage in the used instrument—and therefore its sensitivity—increases proportionally to frequency, a high frequency is desirable. On the other hand, the in-phase susceptibility must decrease significantly above some frequency to be determined while the quadrature component increases, because the domain-wall motion cannot keep in phase with the rapidly changing field and because of losses owing to the high conductivity of pyrrhotite. Therefore, the frequency response of susceptibility has been determined first.

4.1 Frequency dependence of susceptibility

For the massive pyrrhotite ore and for the sintered magnetite specimen, the two susceptibility components have been measured for frequencies between 30 Hz and 27 kHz in fields of 2 μT (rms). Fig. 4(a) reveals that for the pyrrhotite ore the in-phase susceptibility k' is practically constant up to frequencies of 4 kHz while the quadrature component k'' remains small. At higher frequencies, however, k'' contributes significantly and increases linearly with frequency to a value on the order of k' at 20 kHz. For comparison, k' of the magnetite specimen is frequency independent up to >20 kHz while k'' remains much smaller than k' (Fig. 4b).

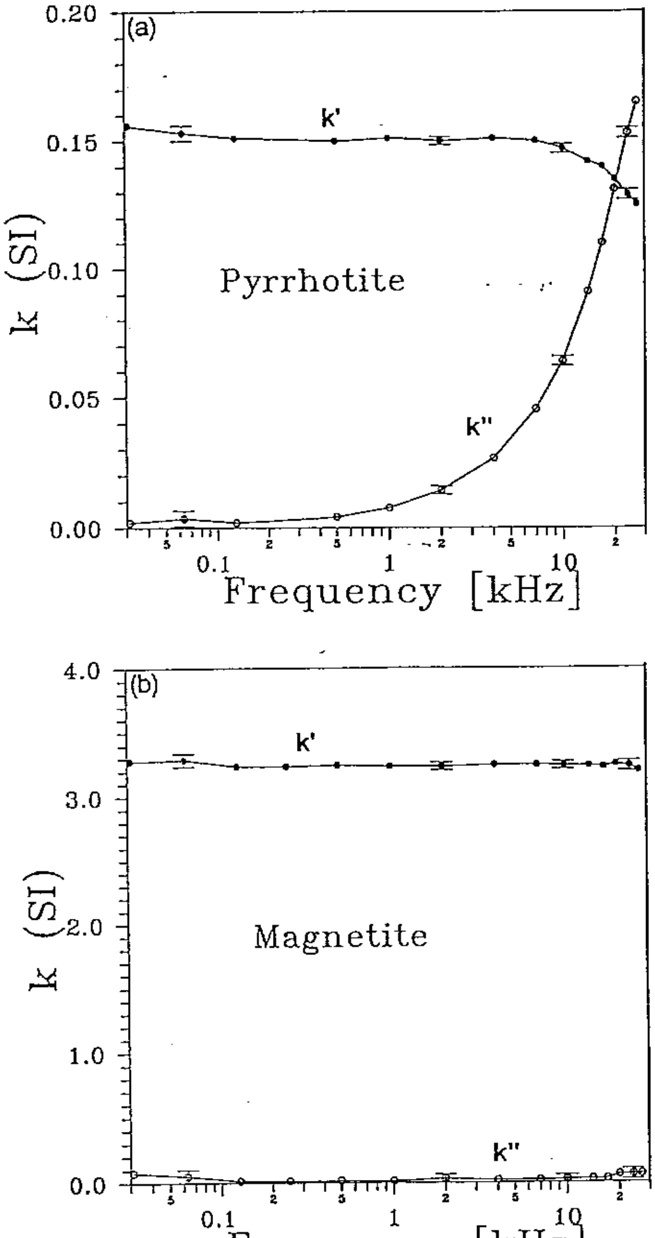

Figure 4. Frequency dependence of in-phase $k'(\bullet)$ and quadrature $k''(\circ)$ susceptibilities for cylinder-shaped (axial ratio: 0.8) pyrrhotite ore specimen Cerro de Pasco, Radius $r = 7$ mm, (a) and for the magnetite specimen, $r = 3.5$ mm, (b) applied field: $\mu_0 H = 2\,\mu$T (rms).

4.2 Field dependence of susceptibility

Based on the frequency-dependent measurements a constant frequency of $f = 2$ kHz has been chosen to conduct field dependent susceptibility studies in the field range 0.05 μT to 1.5 mT (0.5 *mOe* to 15 *Oe*). Besides pyrrhotite samples the measurements have also been performed on the magnetite cylinder and the paramagnetic oxide (Gd_2O_3), the latter in order verify linearity of the apparatus.

For magnetite and gadolinium oxide the susceptibilities vary by less than 1 and 3 per cent, respectively, over the field range, which is thought to represent the accuracy of the measurements. In absolute terms, the magnetite cylinder of length $l = 9$ mm and diameter $d = 7$ mm possessed an axial susceptibility of $k_{\|} = 4.33$ and radially $k_{\perp} = 2.87$; after shortening to 5.5 mm the susceptibilities became $k_{\|} = 3.24$ and $k_{\perp} = 3.30$. These values were confirmed and virtually identical when measured on two different Kappabridges KLY-2 and KLF-3, respectively, employing different field strengths of 375 and 50 μT, and frequencies of 720 Hz and 2 kHz.

Fig. 5 shows that for the Santa Eulalia samples the susceptibilities are constant up to fields of 2 μT (0.02 *Oe*) but k' increases strongly at larger fields. Fig. 6 displays the dependence of susceptibility on grain size and on the applied field for sized pyrrhotite grains from the source locations EOR and TTE. Susceptibilities of samples from Clark's collection are larger than for pyrrhotites of nominally similar grain sizes from EOR or TTE; their field dependence is small but comparable to EOR and TTE (Fig. 7). Finally, Fig. 8 demonstrates that for large pyrrhotite grains, massive and semi-massive ores, their normalized field dependences of susceptibility may vary significantly depending on origin.

4.3 Field independence of reversible susceptibility

In order to see whether the increase with field strength in (total) susceptibility is paralleled by a dc-field dependence of

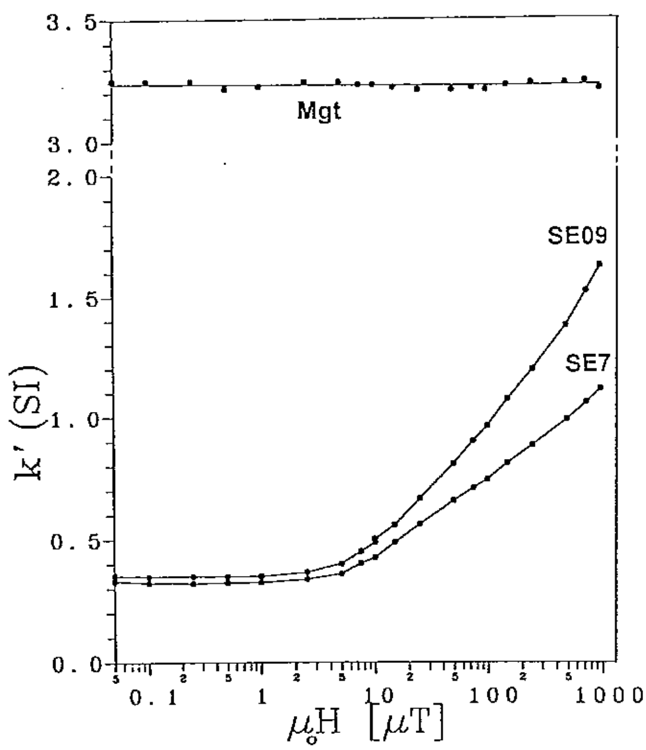

Figure 5. Field dependence of in-phase susceptibilities k' for pyrrhotite ores from Santa Eulalia, with SE09 having larger (mm-sized) crystals than SE7, and magnetite cylinder Mgt (axial ratio: 0.8); $f = 2$ kHz.

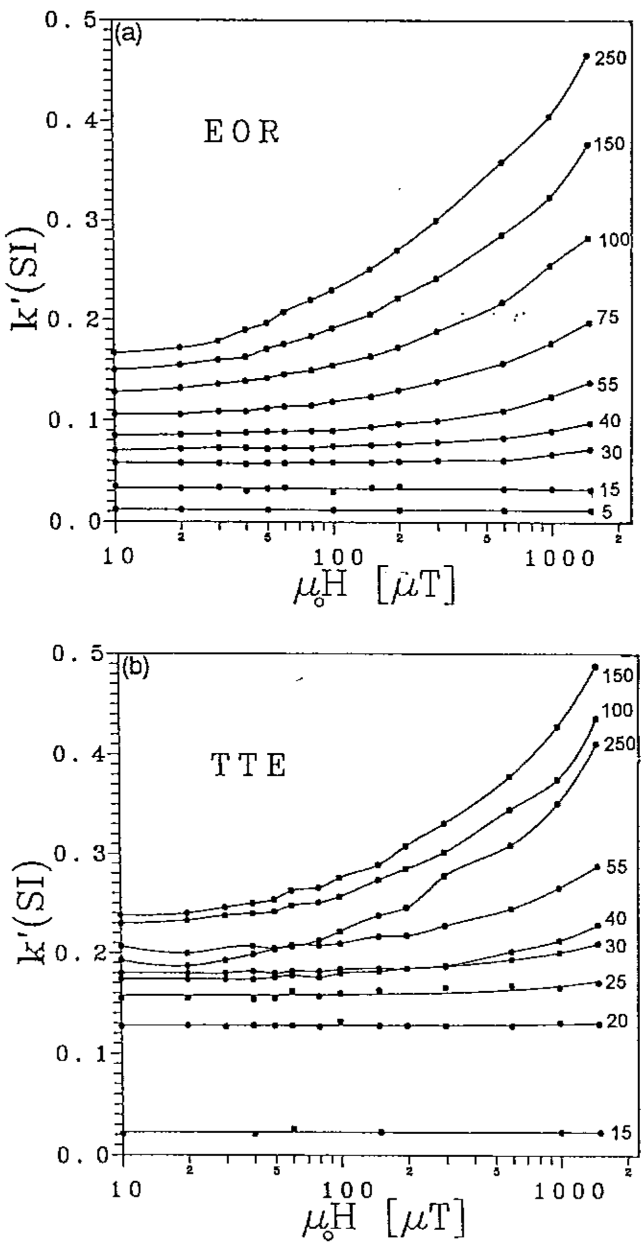

Figure 6. Field dependence of in-phase susceptibility k' for different grain-size fractions (in microns) of pyrrhotite from locations EOR (a) and TTE (b), respectively; $f = 2$ kHz. The numbers refer to the upper grain-size limit of each fraction in micrometers, so 250 refers to 250–150 μm, 150 to 150–100 μm, 100 to 100–75 μm, 75 to 75–55 μm, 55 to 55–40 μm, 40 to 40–30 μm, 30 to 30–25 μm, 25 to 25–20 μm, 20 to 20–15 μm, 15 to 15–10 μm, 10 to 10–5 μm, and 5 to <5 μm.

reversible susceptibility k_{rev}, a small (2 μT) alternating field (2 kHz) was used to measure k_{rev} while dc fields were superimposed, ranging from 0 to 5 mT. Even for the sample with the strongest field dependence (SE09) of k (Fig. 5) there is virtually no discernible change (<1 per cent) in k_{rev} with applied direct field.

4.4 Theoretical in-phase and quadrature susceptibilities

The theoretical grain size and frequency dependences of susceptibility have been calculated according to eq. 1. For

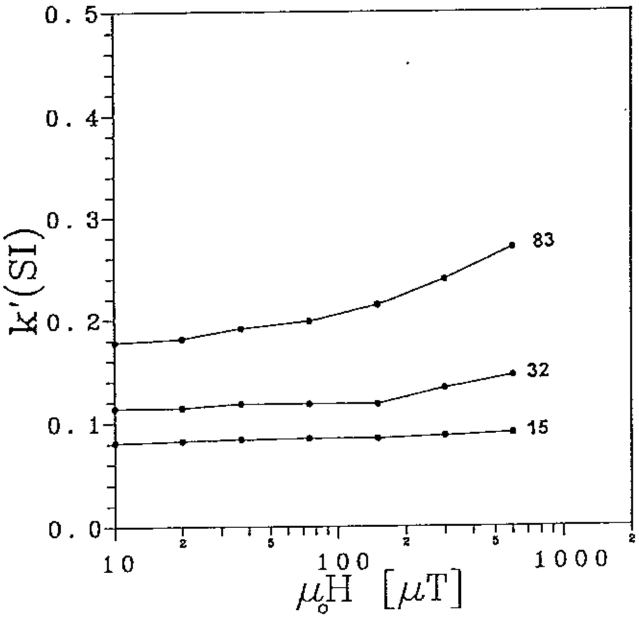

Figure 7. Field dependence of in-phase susceptibility k' for different grain-size fractions of pyrrhotite from the sample collection of Clark. Numbers refer to mean grain size (in microns). Frequency $f = 2$ kHz.

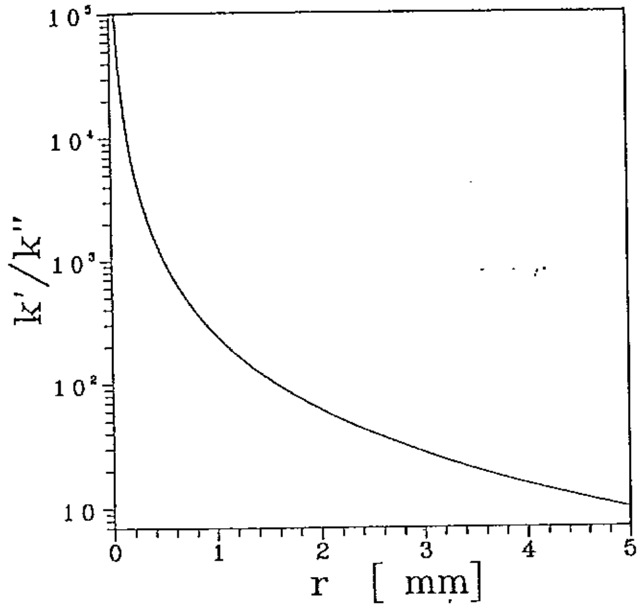

Figure 9. Theoretical ratio of in-phase to quadrature susceptibilities k'/k'' versus grain radius for a frequency of $f = 2$ kHz and an electrical conductivity $\sigma(\text{po}) = 5 \cdot 10^5\,\Omega^{-1}m^{-1}$. Calculations according to eq. 1.

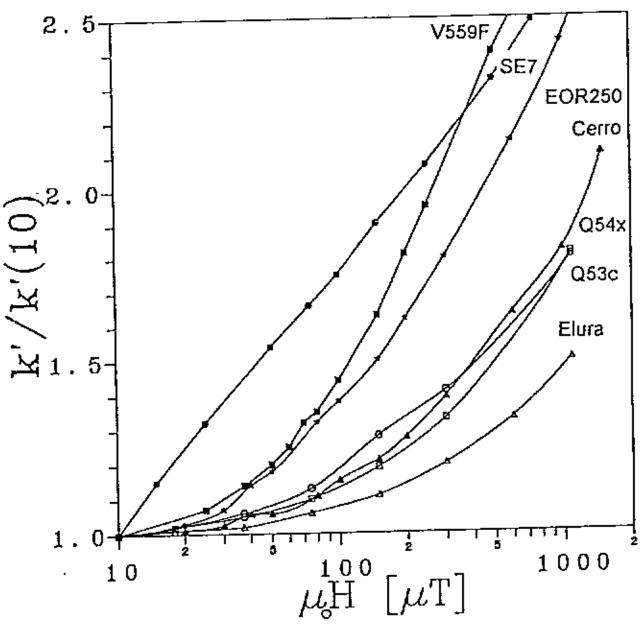

Figure 8. Normalized field dependence of in-phase susceptibility k' for various pyrrhotite samples; $f = 2$ kHz.

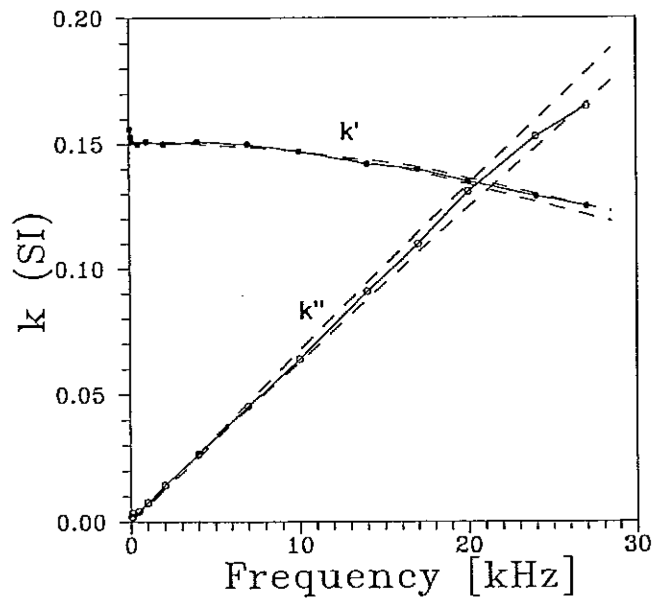

Figure 10. In-phase k' and quadrature susceptibilities k'' versus frequency of pyrrhotite specimen Cerro (data as in Fig. 4) and theoretical curves (dashed lines) according to eq. 1 with $r = 7$ mm, $k_i = 0.16$, $\sigma = 1.35 \cdot 10^5\,\Omega^{-1}m^{-1}$ and $\sigma = 1.45 \cdot 10^5\,\Omega^{-1}m^{-1}$, respectively.

pyrrhotite the ratio k'/k'' has been calculated as a function of grain size for 2 kHz using $k_i = 0.33$ and $\sigma = 5 \cdot 10^5\,\Omega^{-1}m^{-1}$ (Fig. 9). The k' and k'' frequency dependences of the pyrrhotite ore specimen (Fig. 4a) have been modelled with $k_i = 0.16$, $r = 7$ mm and the conductivity σ as a variable chosen to $\sigma = 1.35$ and $1.45 \cdot 10^5\,\Omega^{-1}m^{-1}$, respectively (Fig. 10).

For magnetite with the parameters $k_i = 40$, $\sigma = 2.5 \cdot 10^4\,\Omega^{-1}m^{-1}$ and radius $r = 3.5$ mm the calculations predict only a slight decrease for k' with frequency to k' (27 kHz) $= 0.995$ k' (0 Hz) and a linear increase of k''/k' with frequency to k''/k' (27 kHz) $= 0.02$.

5 DISCUSSION

The susceptibility of pyrrhotite shows strong variations depending on grain size, field strength and frequency.

Separate determinations of in-phase and quadrature susceptibilities may disclose informations on conductivity, hysteresis and magnetic viscosity. For magnetite, on the other hand, most of the intrinsic properties are 'shielded' from cognizance by self-demagnetization effects. This work establishes frequency and field ranges—and related errors—for laboratory susceptibility measurements to infer magnetizations induced in the Earth's magnetic field.

5.1 Susceptibility of multidomain magnetite

The susceptibility response (at 2 kHz) of the magnetite specimen to an increase in field strength over more than four orders of magnitude from 0.05 μT to 1 mT is virtually flat. This is a consequence of the $1/N$ self-demagnetization limit and not a truly invariable intrinsic susceptibility. The determination of a Rayleigh parameter, or other coefficients to describe a possible field dependence of intrinsic susceptibility k_i, is therefore practically impossible for specimens with high k_i and a significant demagnetizing factor. Nonetheless, an order of magnitude estimate of the intrinsic susceptibility can be obtained from the apparent—measured—susceptibility values k'. With $k' = 1/N$ and the measured susceptibilities for the magnetite cylinders we obtain $1/k'_{\|} + 2/k'_{\perp} = \Sigma N = 0.928$ for the 9×7 cylinder and very similarly $\Sigma N = 0.920$ for the 5.5×7 cylinder. With these values we calculate an equivalent isotropic susceptibility value of $3/\Sigma N = 3.23$ to 3.26 in order to use the model calculations by Eskola & Tervo (1980) for cubic specimens. According to Fig. 2 a measured susceptibility of 3.25 translates into an intrinsic susceptibility $k'_i \approx 40$. Single crystals of magnetite may have much larger k_i values (Galt 1952) while fine-grained magnetite powders obtained by grinding are likely to possess lower intrinsic susceptibilities due to increased defect densities and stress.

The frequency response of k' is certainly flat up to at least 20 kHz (Fig. 4b). The small decrease of k' above 20 kHz is in agreement with theory but also within the experimental error at these frequencies.

Since the apparent quadrature susceptibility is $k'' \approx k''_i/(1 + Nk'_i)^2$ (eq. 13) at low frequencies and $k''_i \ll k'_i$ at low fields, any variation of k''_i is hard to resolve. Noise dominates the k'' signal up to frequencies >10 kHz. There is, however, a small but noticeable increase of k'' above 15 kHz (Fig. 4b). This increase can be attributed to eddy current effects because it raises the k''/k' ratio to the calculated value of k''/k' (27 kHz) = 0.02 (Section 4.4).

The frequency independence of k' over a wide frequency range agrees with the experimental results of Bhatal & Stacey (1969) but disproofs the predicted decrease of k' with frequency by Vincenz (1965). Vincenz, however, assumes an unrealistically low intrinsic susceptibility of $k_i = 1.5$ so that 'shielding' of intrinsic properties by self-demagnetization effects would be much smaller than here inferred.

Although frequency variations up to >20 kHz appear to have little effect on susceptibility determinations for multidomain magnetite this does not imply that frequency effects are also negligible for AF demagnetization behaviour, for example, where larger field amplitudes force domain walls to move faster than in low fields. In fact, Maksimochkin & Valeev (1981) have reported a substantial decrease in efficiency with increasing frequency (up to 20 kHz) in removing remanent magnetization through AF demagnetization.

The field-independence of susceptibility of multidomain magnetite discerned in this study down to very low fields is in contrast to an earlier investigation by Smith & Banerjee (1987) where an increase in dc susceptibility below 10 μT to values as high as $k = 7$ (SI) had been measured. Their anomalously high susceptibilities (>$1/N$) of equidimensional particles suggest that their dc susceptibility measurements may be affected by short-lived remanence components or by uncompensated non-orthogonal acquisition of remanence, which may be significant when dealing with very low induced magnetizations.

5.2 Susceptibility of pyrrhotite

The intrinsic susceptibility in pyrrhotite is much lower than the self-demagnetization limit $1/N$. Therefore, and unlike for magnetite, intrinsic susceptibility properties have directly been observed as functions of frequency, field strength and grain size.

5.2.1 *Frequency effects*

At frequencies below 4 kHz the in-phase susceptibility k' of the pyrrhotite specimen Cerro is practically constant (Fig. 4a). The small increase of k' below 100 Hz is within the experimental error at these low frequencies and fields. The quadrature component becomes significant in the kHz frequency range. In susceptibility bridges that do not allow the separate determination of k' this may lead to erroneous susceptibility values at higher frequencies. On the other hand, the controlling parameter Θ (Section 2.1) depends on the square of the diameter of the specimen—or particle—so that for non-massive rocks containing smaller pyrrhotite grains, frequency effects will be negligible for the determination of induced magnetization.

However, it should be kept in mind for anomaly modelling, for example, that magnetizations parallel to the geomagnetic field may be much larger than 'instantly' induced magnetizations because of viscous magnetization components that are associated with much larger time constants than a few seconds. There is presently no reliable theory or experimental determination—other than a very long-term viscous acquisition experiment—to predict the magnitude of a viscous magnetization acquired over the Bruhnes epoch, for example (Worm *et al.* 1991).

The modelled frequency dependence of k' and k'' for the polycrystalline ore specimen matches the experimental results extremely well (Fig. 10) giving a conductivity value of $\sigma = (1.40 \pm 0.05) \cdot 10^5\,\Omega^{-1} m^{-1}$. No differences between experiment and theory owing to cylindrical instead of spherical specimen shape or anisotropies in magnetic and electrical properties can be detected.

5.2.3 *Field and grain size effects*

The initial susceptibility of large pyrrhotite grains is really constant only in fields below 1 μT (2 per cent of the geomagnetic field) (Fig. 5). For fields >5 μT the in-phase susceptibility k' rapidly increases in a way that is better described by a power law H^x rather than a Rayleigh law or other polynominal function. Even for samples from the same source locality (Santa Eulalia) the field dependence of k' is quite different with the exponent being as large as 0.25 (Fig. 5). Grain size is obviously the predominant parameter controlling susceptibility of pyrrhotite as the measurements on the sized sample collections demonstrate. The susceptibility and its field dependence generally increase with increasing grain size (Figs 6 and 7). The TTE samples have higher initial susceptibilities than the EOR grains of the same size. This may relate to the presence of magnetite in the TTE grains as shown by thermomagnetic measurements (Fig. 3). About 10 per cent of the strong field magnetization is carried by magnetite, enhancing the susceptibility and weakening its field dependence because the susceptibility of magnetite is not, or is only weakly, field dependent. Probably as an artefact TTE250 possesses lower k' values than the smaller grain-size fractions TTE150 and TTE100, possibly due to the presence of pyrite.

The comparison of normalized susceptibilities of the ores and large pyrrhotite grains (Fig. 8) demonstrates that there are no generally valid analytical descriptions for k that allow corrections to susceptibility measurements made in fields larger than the Earth's field, when induced magnetizations have to be calculated for anomaly modelling.

The calculated ratios of in-phase to quadrature susceptibilities k'/k'' (for 2 kHz) increase strongly with decreasing grain size (Fig. 9). Because very small quadrature susceptibilities ($k'' < k'/100$) cannot safely be resolved with the current experimental setup, measurements on pyrrhotite grains smaller than $\approx$1 mm will not facilitate the determination of conductivity, for example.

6 CONCLUSIONS

The apparatus employed here is capable of studying a number of effects, including field dependence of susceptibility, low field hysteresis, magnetic viscosity (associated with time constants <0.1 s), and eddy currents in conductive specimens. These effects can be distinguished by judicious choices of frequency and field strengths. Eddy current effects are important for conductive specimens at high frequencies, allowing specimen conductivity to be estimated from the theoretical relationship between quadrature susceptibility, conductivity and frequency. Inductively measured conductivities of ore samples and other conductive rocks have application to interpretation of EM surveys, and are more appropriate for this purpose than galvanically determined conductivities, which are greatly affected by specimen connectivity and grain-boundary effects.

The effects of self demagnetization on dc susceptibilities of strongly magnetic specimens are well known. It can be shown that in-phase and quadrature susceptibilities measured in alternating fields are both affected by, and interact via, the self-demagnetizing field, complicating interpretation of field and frequency-dependent susceptibility measurements in specimens containing strongly magnetic minerals. Self demagnetization strongly suppresses any intrinsic variations in susceptibility of magnetite grains with magnitude or frequency of applied field, whereas pronounced susceptibility variations are observable for pyrrhotite because of its much lower susceptibility.

The results certainly show the importance of measuring susceptibilities on pyrrhotite in field intensities similar to the geomagnetic field and at frequencies ≤1 kHz. Only when the in-phase susceptibility can be determined separately—which most commercial instruments do not—or for samples with dispersed pyrrhotite grains smaller than 1 mm, will measurements up to several kHz give results that are equivalent to dc susceptibilities.

For most samples the initial magnetization can only poorly or in a very limited field range be characterized by a Rayleigh 'law' (i.e. $k = k_0 + \alpha H$).

The experimental results demonstrate that for pyrrhotite the predominant parameter controlling susceptibility and its field dependence is grain size. Since all samples consist out of multidomain grains their magnetization variations in low fields result from the movement of domain walls. Hence, susceptibility measurements may lend clues about micromagnetic properties. Based on domain observations on pyrrhotite bearing rocks, Halgedahl & Fuller (1983) suggest three mechanisms in the response of domain walls to varying (strong) applied fields: (1) nucleation of walls, (2) pinning of walls on grain surfaces, and (3) bulk pinning. Similarly, Menyeh & O'Reilly (1991) discuss their experimental results on grain-size dependence of coercivity and susceptibility for pyrrhotite in terms of domain rotation, wall nucleation and wall pinning. The nucleation of new walls is highly unlikely in the relatively low fields of this study. The observed strong grain-size dependence favours surface pinning of walls (2) over bulk pinning (3) because in the latter case wall resistance should be proportional to wall area and thus the susceptibility should not be grain-size dependent. Other mechanisms controlling susceptibility may include inhomogeneous defect distributions.

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