Neutron depolarization measurements of magnetite in chiton teeth

M Seifert$^{1,2}$, M Schulz$^{1,2}$, G Benka$^2$, C Pfleiderer$^2$, S Gilder$^3$

$^1$ Heinz Maier-Leibnitz Zentrum (MLZ), Technical University of Munich, D-85748 Garching, Germany
$^2$ Physics Department, Technical University of Munich, D-85748 Garching, Germany
$^3$ Department of Earth and Environmental Sciences, Ludwig-Maximilians-Universität München, D-80339 Munich, Germany

E-mail: marc.seifert@frm2.tum.de

Abstract. Magnetite constitutes one of the most abundant magnetic minerals in the Earth’s crust. In the single domain state, magnetite often carries the magnetic remanence in rocks due to its stable and strong magnetic remanence. Hence it is of keen interest to paleomagnetists who study the ancient magnetic field preserved in the rock record. The extremely small size range and vulnerability to oxidation of single domain magnetite makes synthetization and preservation virtually impossible. Consequently, most experimental work on magnetite under pressure is carried out on multidomain magnetite. The radula of the marine mollusc chiton (Polyplacophora) is one of the few natural sources of single domain magnetite. We have performed a comparative study on samples of chiton radula in a vibrating sample magnetometer (VSM) and with the newly evolving neutron depolarization imaging (NDI) technique. Despite a constant offset between the VSM and NDI data in the coercivity we find a good agreement between the two techniques.

1. Introduction

The spontaneous magnetization of magnetite ($\text{Fe}_3\text{O}_4$) is produced within an inverse spinel structure where superexchange coupling occurs between iron and oxygen ions in two magnetic sublattices. Magnetite’s magnetic properties are governed by interatomic distances and angles in each sublattice, which in turn dictate the magnetocrystalline, magnetostrictive, and magnetostatic energies, all of which are anisotropic and vary with temperature, pressure and external magnetic fields [1, 2]. Magnetite constitutes one of the most abundant magnetic minerals in the Earth’s crust. In the single domain state, magnetite often carries the magnetic remanence in rocks due to its stable and strong magnetic remanence, hence it is of keen interest to paleomagnetists who study the ancient magnetic field preserved the rock record.

Although the influence of temperature on magnetic remanence has long been a subject of research, much less is known about how pressure modifies the magnetic properties of magnetite. Understanding how and why magnetite’s remanent intensity and magnetization direction change under pressure, and upon decompression from high pressure, are important to properly interpret magnetic field anomalies, the role of shock in meteorite impact craters and the magnetic field strength in the solar system preserved in meteorites.

Although single domain magnetite carries a stable remanence over solar-system time scales,
most experimental work under pressure is carried out on multidomain magnetite because single
domain magnetite’s extremely small size range (ca. 30 nm to a few 100 nm depending on its
shape) and vulnerability to oxidation makes it virtually impossible to synthesize and preserve.
However, a few animals synthesize single domain magnetite, one being the marine mollusc,
chiton (Polyplacophora) whose radula consists of a conveyor-belt like array of teeth that consist
of three distinct mineral zones: a core of apatite (like what humans have for teeth) covered by a
thin band of lepidocrocite, then a thicker layer of magnetite [3, 4]. The magnetite is precipitated
in a way that restricts individual grain sizes to be within the single domain range [5].

Gilder et al. [6] measured the acquisition of isothermal remanent magnetization, direct field
demagnetization, and alternating field demagnetization of multi-domain (MD) and single domain
(SD) magnetite under hydrostatic pressures to 6 GPa. The single domain material came from
chiton teeth. They found significant differences in the pressure behavior of the magnetizations
of MD and SD magnetite calling for further investigations.

Another important aspect of the magnetic properties of magnetite concerns the first-order
Verwey transition, which is a metal-to-insulator transition due to a slight rhombohedral
distortion of the lattice. Carporzen and Gilder [7] studied the effects of stress on the Verwey
transition for stoichiometric, synthetic multidomain magnetite and for natural multidomain
magnetite having both relatively low and high degrees of oxidation. Low temperature
measurements of the magnetic moments were carried out after pressure release. Their results
unambiguously showed an increase in the Verwey transition temperature with increasing pressure
that ranged from 1 K/GPa for stoichiometric magnetite to 3 K/GPa for highly oxidized
magnetite for pressures up to about 5 GPa. These findings could make the Verwey transition
suitable for use as a geobarometer in cases where high pressures (> 1 GPa) are involved, such
as in meteorite impact craters. Until now, no one has carried out similar experiments on SD
magnetite.

In order to further explore the magnetic properties of magnetite from chiton radula, we
carried out a comparative study between “classic” magnetometry using a vibrating sample
magnetometer (VSM) with the newly developed neutron depolarization imaging (NDI) technique
at the instrument ANTARES at the Heinz Maier-Leibnitz Zentrum, Garching. Imaging with
polarized neutrons has proven to be sensitive to magnetic field distributions on the macroscopic
[8, 9, 10, 11] and the microscopic [12, 13, 14] scale. In this publication we show the potential
of this new technique which is intrinsically sensitive to different microscopic parameters than
standard magnetometry for applications to paleomagnetic materials.

2. Methods and Experimental setup
The neutron depolarization imaging (NDI) technique is based on the combination of a neutron
imaging beam line using a position sensitive detector with a neutron polarization analysis setup.
It enables the spatially resolved measurement of the influence of a sample on the neutron
polarization. A typical NDI setup is sketched in Fig. 1. The neutron beam first passes
a transmission polarizer in which magnetic neutron supermirrors reflect neutrons with spin
direction up out of the beam such that the beam is polarized in down direction. A Mezei spin
flipper allows to flip the spin direction from down to up if it is turned on. Guide fields with
magnetic fields of the order of B=1 mT have been installed to prevent depolarization of the
beam due to the earth’s magnetic field and stray fields from electrical components. A Helmholtz
magnet enables to apply fields up to 300 mT at the sample position. Both positive and negative
fields can be applied due to the installation of horizontal guide fields which allow for an adiabatic
coupling of the neutron spin to the field of the magnet. After the magnet an analyzer is located
which works the same way as the polarizer. The subsequent 2d neutron detector, which is not
shown in the figure, uses a 100 μm thick LiF/ZnS scintillator to convert the neutron beam
into visible light. A CCD camera with a pixel size of 6.5 μm and an objective set to 1:3.7
Figure 1. Sketch of a neutron depolarization imaging (NDI) setup. The neutron beam first passes a polarizer which polarizes the beam. A subsequent spin flipper allows the rotation of the polarization by $\pi$. Vertical and horizontal guide fields prevent a depolarization of the neutron beam due to the earth’s magnetic field. The sample is placed in a Helmholtz magnet. The installation of horizontal guide fields allows to apply positive and negative fields at the sample position. An analyzer which is identical to the polarizer is placed right before the 2d detector. Magnification detects the light which is proportional to the incoming neutron intensity.

A 18 mm pinhole close to the neutron source was used to adjust the beam divergence. The detector position from the pinhole is 9.0 m which gives a L/D of 500. The distance from the sample to the detector is approximately 0.8 m. As the polarizers operate only with cold neutrons a neutron velocity selector was used to set the neutron wavelength to $\lambda = 4.2 \text{ Å}$ with a resolution of $\Delta\lambda/\lambda = 10\%$.

The polarization $P$ of the neutron beam at the detector is determined by

$$P = P_0 \cdot \frac{I_\downarrow - I_\uparrow/f}{I_\downarrow + I_\uparrow/f}.$$  

($P_0$ is the instrument polarization, a normalization factor which accounts for the polarization efficiencies of the polarizers and possible depolarization along the flight path of the neutron. $I$ is the intensity at the detector where the indices depict the polarization direction after the spin flipper, i.e. whether the spin flipper is turned off ($\downarrow$) or on ($\uparrow$). As the flipping efficiency $f$ of the spin flipper for the given setup is very close to 1 [17] it can be omitted. This evaluation is done pixelwise and therefore gives the spatial distribution of the neutron beam polarization in the field of view of the detector. The measured polarization was around $P_0 = 0.80$ and not completely uniform over the field of view due to the beam divergence and the used polarizers. For each data point 5 spin-up and 5 spin-down images were taken with an exposure time of 45 s each to achieve good statistics. Artifacts in the images caused by gamma radiation (white spots) were removed by median filtering the stack of images.

When a neutron moves through a magnetic field not parallel to the spin direction of the neutron, the spin precesses around the magnetic field $B$ with the Larmor frequency $\omega_L = -\gamma B$ where $\gamma$ is the gyromagnetic ratio of the neutron $\gamma = 183 \text{ MHz/T}$. This effect is used in the neutron depolarization imaging method for the detection of ferromagnetism [15]. Ferromagnetic materials form ferromagnetic domains to decrease the energy of stray fields. On its path through such a domain configuration a neutron sees in each domain a magnetic field pointing in a different direction. Due to Larmor precession the neutron acquires a certain Larmor phase after passing the ferromagnetic sample. Each neutron has a slightly different path through the sample, sees a different domain configuration and therefore collects a different Larmor phase.
Figure 2. (a) Microscopic image of the chiton radula part that was investigated using neutron depolarization imaging. The black chiton teeth are arranged in two rows. (b) shows a magnification of one chiton tooth from the radula (indicated by the red frames).

Since the polarization is the average over the neutron spins at the detector in a certain area, a ferromagnetic sample leads to a decrease of neutron polarization. According to Ref. [16] the polarization for the case of small spin rotations per magnetic domain is given by

$$P = P_0 \exp \left( -\frac{1}{3} \gamma^2 B'^2 d \frac{\delta}{v^2} \right).$$

(2)

$B'$ is the average magnetic field per domain, $d$ is the sample thickness in beam direction, $\delta$ is the average domain size and $v$ is the neutron velocity. As $v$ and $d$ are known we can obtain the product $B'^2\delta$ from the polarization data. When determining $B'$ with magnetometer measurements the average domain size can be accessed.

Radulas were extracted from freshly deceased specimens of Acanthochitona fascicularis. We took a sample from two different radula (sample 1 and 2) and measured their hysteresis loops using a LakeShore MicroMag 3900 at 300 K, 140 K and 80 K, the latter two being above and below the Verwey transition. In order to measure the Verwey transition temperature, we cooled the radula in a low (Earth’s) field from 300 K to 80 K, briefly applied a 1 T field, and then warmed the sample to 140 K while measuring its magnetic remanence every 1 K.

The sample investigated using NDI is shown in Fig. 2a and is depicted as “NDI sample” in the following. It is the anterior part of a chiton radula which was stored in ethanol to prevent oxidation of the teeth’s magnetite. A magnification of a single chiton tooth is shown in Fig. 2b. The volume of the radula part is 1.7 mm $\times$ 0.8 mm $\times$ 1.0 mm. The chiton radula was mounted on an aluminium sample holder in a cryostat. Additionally, a neutron absorbing cadmium mask with a 2 mm circular hole was mounted before the sample. Magnetization hysteresis loops of the NDI sample were also acquired at 80 and 300 K using a Quantum Design Physical Property Measurement System (PPMS).

3. Results

Fig. 3a shows VSM data of sample 1 from a hysteresis loop at $T=80$ K. The applied field was ramped from $+0.5$ T to $-0.5$ T and then back to $+0.5$ T. To determine the coercivities $B_{c1}$ and
Figure 3. Comparison of VSM and neutron depolarization imaging data. (a) shows the magnetic moment of a whole chiton radula as a function of the applied magnetic field $B$ at a temperature of 80 K measured using a VSM. A hysteresis loop from +0.5 T to −0.5 T to +0.5 T was recorded. Lines (green) were fit to the VSM data close to the zero crossing of the x-axis. The intersection of these lines with the zero magnetic moment line gives the coercivities $B_{c1/2}$. (b) Neutron polarization as a function of the magnetic field $B$ at $T=80$ K is shown in (b). The applied fields range from $+0.25$ T to $-0.25$ T. The coercivities $B_{c1/2}$ were evaluated by fitting a Gaussian to the peaks close to $B=0$ (indicated as black lines).
Figure 4. Coercivities obtained from hysteresis loops as a function of temperature. Two whole chiton radula were measured using a VSM (sample 1 and 2). The corresponding data is indicated as orange and yellow triangles. Error bars for these data points are not shown since they are smaller than the symbols. Furthermore, coercivities obtained from NDI measurements are shown as green squares. A significant offset is visible. The black lines are a guide to the eye and are the same except for an offset. For a comparison, the coercivities of the sample from the NDI measurements were also determined using a PPMS (depicted as lilac rhombs).

$B_{c2}$, lines were fitted to the data close to the points where the magnetic moment is zero. The intersections of the lines with the x-axis gives the coercivities.

Fig. 3b shows the neutron polarization of the NDI sample as a function of the applied field. Since the chiton radula is too small to be resolved in detail at the detector the polarization was averaged over the entire pinhole area, therefore, no spatial information is available. As the size of the sample was much smaller than the pinhole, only a small fraction of the beam is depolarized which results in small changes in polarization of only a few per cent.

The field was ramped from +0.25 T to -0.25 T and then back to +0.25 T. The up and down measurements are indicated in orange and green, respectively. Both data sets show peaks which are shifted from B=0 due to hysteresis. In zero field the polarization is comparably high. Small applied fields increase the average domain size in field direction at the expense of antiparallel domains and therefore decrease the polarization. Higher fields turn more and more domains into the direction of the applied field. This leads to smaller acquired Larmor phases which weakens the depolarization effect. Therefore, the polarization increases for higher fields again. The coercivities were determined as the centers of two Gaussians which were fitted to both peaks in the polarization signal.

Such magnetic field loops were measured using the VSM, the PPMS and the NDI method at the temperatures 80, 140 and 300 K. The coercivities from these measurements determined by the methods described above are shown in Fig. 4 as a function of temperature. All data sets show a decrease of the coercivity with increasing temperature. The VSM measurements are depicted as orange (sample 1) and yellow (sample 2) triangles. No error bars are shown for these data points as they are smaller than the symbols. The black line connecting the VSM data points is a guide to the eye. The corresponding coercivities obtained from NDI data are plotted
**Figure 5.** (a) shows VSM data from sample 1 as a function of temperature. The measurements were taken after applying a field of 1 T at 80 K during heating in zero field (zfh). The sharp kink at 118 K is caused by the Verwey transition. In (b) the neutron polarization is shown as a function of temperature. The sample was cooled in zero field (zfc), then a field of 50 mT was applied. The measurement was performed during heating with applied field (fh). Three lines (black) were fit to the data points in the temperature ranges $<80$ K, $80$-$120$ K and $>120$ K. A kink is visible at approximately 118 K.

as green squares. The error bars were obtained from the error values of the corresponding fits. Again, a black line is shown as a guide to the eye. The NDI data shows the same behavior as the VSM data except for an offset of about 7 mT. For a better comparison the radula used for the NDI measurements was also investigated using a PPMS at 80 and 300 K. The corresponding data points are depicted as lilac rhombs.

Furthermore, temperature sweeps using the VSM and NDI are shown in Fig. 5a and b, respectively. For the VSM measurement sample 1 was cooled down in zero field. At T=80 K a field of 1 T was applied to saturate the sample. The data was then acquired during heating...
in zero field up to 140 K. For the NDI measurement (see Fig. 5b) the sample was cooled down in zero field and measured during heating with a magnetic field of B=50 mT. The NDI data are noisier than the magnetic field sweep from Fig. 3 as only 3 up and down images per data point with 30 s exposure time were taken. The errors were determined from the standard deviation of the data points in the near-constant region above 120 K. Three lines were fitted to the polarization data in the temperature regions <80 K, 80-120 K and >120 K. A kink in the signal is visible approximately at the same temperature as in the VSM measurement.

4. Discussion
The coercivities obtained from conventional magnetometers (VSM and PPMS) and NDI measurements shown in Fig. 4 indicate good qualitative agreement except for an offset of about 7 mT. Although biological samples as the investigated chiton radula are susceptible to natural variation, this can be discarded as an explanation for the offset. The coercivities obtained by PPMS measurements of the NDI sample confirm the SD magnetite coercivities of sample 1 and 2. A possible influence of remanence due to the iron yoke of the used magnet is smaller than 1 mT. However, NDI is sensitive to other microscopic parameters compared to the VSM and PPMS methods. One possible explanation could be a magnetic screening of domains within a MD grain proposed by Xu and Merrill [18].

In both the VSM and NDI measurements shown in Fig. 5a kink at approximately 118 K is visible. This abrupt change in the slope of both signals is caused by the Verwey transition, a reconfiguration of the atomic lattice which also affects the magnetic behavior.

5. Conclusion and outlook
In conclusion, the NDI method reproduces the magnetometer measurements except for an offset of the obtained coercivities. As NDI measurements are not directly depending on the magnetization but also on microscopic parameters as the average domain size δ, additional or complementary results compared to the magnetometer measurements are expected. The origin of the offset may be explained by macroscopically screened domains and is subject of further investigations.

Since the chiton teeth are a comparably small sample for NDI we plan to use focussing neutron guides to achieve higher counting rates and therefore higher statistics. First measurements with the neutron guides report a gain in neutron intensity of a factor of 20. It is also planned to increase the density of magnetite in the sample volume by removing the biological material of the radula which should result in a larger depolarization signal. Of particular interest is also the pressure dependence of the Verwey transition. A new pressure cell has been developed for our NDI setup enabling to apply pressures up to 20 GPa.

6. Acknowledgments
The authors wish to thank the staff at MLZ for their help in conducting the experiments. Financial support from the German Science Foundation (DFG) in the research unit “Quantum phase transitions” (FOR960), and the Augsburg-Munich transregional collaborative research network “From electronic correlations to functionality” (TRR80) is gratefully acknowledged.

References
[1] Hodych J 1977 Can. J. Earth Sci. 14 2047-61
[2] Dunlop D J and Özdemir Ö 1997 Rock Magnetism (Cambridge: Cambridge Univ. Press)
[3] Wealthall R J, Brooker L R, Macey D J and Griffin B J 2005 J. Morphology 265 165-71
[4] Shaw J A, Macey D J, Brooker L R, Stockdale E J, Saunders M and Clode P L 2009 J. Morphology 270 588-600
[5] Kirschvink J and Lowenstam H A 1979 Earth Planet. Sci. Lett. 44 193-204
[6] Gilder S, Le Goff M, Chervin J C and Peyronneau J 2004 Geophys. Res. Lett. 31 L10612
[7] Carporzen L and Gilder S A 2010 J. Geophys. Res. 115 B05103
[8] Kardjilov N, Manke I, Strobl M, Hilger, Treimer W, Meissner M, Krist T and Banhart J 2008 Nat. Phys. 4 399-403
[9] Piegsa F, van den Brandt B, Hautle P, Kohlbrecher J and Konter J 2009 Phys. Rev. Lett. 102 145501
[10] Treimer W, Ebrahimi O and Karakas N 2012 Appl. Phys. Lett. 101 162603
[11] Treimer W, Ebrahimi O, Karakas N and Prozorov R 2012 Phys. Rev. B 85 184522
[12] Schulz M 2010 Radiography with polarized neutrons Ph.D. thesis, Technical University of Munich
[13] Schulz M, Neubauer A, Masalovich S, Mühlbauer M, Calzada E, Schillinger B, Pfleiderer C and Böni P 2010 J. Phys.: Conf. Ser. 211 012025
[14] Schulz M, Schmakat P, Franz C, Neubauer A, Calzada E, Schillinger B, Böni P and Pfleiderer C 2011 Physica B: Cond. Matter 406 2412-14
[15] Halpern O and Holstein T 1942 Phys. Rev. 59 960-81
[16] Mitsuda S, Yoshizawa H and Endoh Y 1992 Phys. Rev. B 45 9788
[17] Schmakat P 2016 Neutron Depolarisation Measurements of Ferromagnetic Quantum Phase Transitions, Wavelength-Frame Multiplication Chopper System for the Imaging Instrument ODIN at the ESS http://mediatum.ub.tum.de/node?id=1278491
[18] Xu S and Merrill R T 1990 J. Geomag. Geoelectr. 42 637-52