Demagnetization Energy and Internal Stress in Magnetite From Temperature-Dependent Hysteresis Measurements

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Abstract The magnetization state of magnetite controls acquisition and stability of remanent magnetization in Earth and planetary rocks. Although commonly interpreted in terms of grain size, also stress, grain shape, and magnetostatic interactions can substantially modify magnetic stability. Here, we show that scaled reversible work (SRW) in the approach-to-saturation (ATS) of hysteresis curves is temperature independent if anisotropy is due to demagnetizing energy. Stress anisotropy vanishes with increasing temperature. With a new measurement and evaluation procedure stress-induced anisotropy is separated from demagnetization effects. We calibrated the new method using theoretical ATS curves for different stress and demagnetization regimes. Experimental results for synthetic magnetite samples underpin the validity of the method and provide insight into the relationship between magnetostatic, magnetocrystalline, and stress energies. The SRW method provides a new tool to study the reliability of paleomagnetic recording mechanisms, and enables quantitative investigation of stresses due to tectonics, meteorite impacts, oxidation, exsolution, or quenching.

Plain Language Summary Magnetic particles in rocks store information about past magnetic fields and about the physical conditions during formation of the magnetic minerals. Magnetic measurements are sensitive which makes them useful for understanding magnetic minerals and their recording mechanisms. Magnetite is the most abundant natural magnetic mineral in Earth’s crust and understanding its magnetic recording properties is a central task of rock magnetism. Here, a temperature-dependent measurement technique is developed and tested that can determine internal stress in magnetite crystals that was generated during crystal growth or by later mechanical forces due, for example, to tectonics or meteorite impacts. Also, chemical or thermal gradients, produced by oxidation or rapid cooling can generate internal stresses. It was previously difficult to separate stress from other parameters that influence the properties of magnetite particles. Our new method makes it possible to study stresses in magnetite in relation to tectonic, paleomagnetic, and paleointensity studies in Earth and planetary magnetism.

1. Introduction

Thermoremanent magnetization (TRM) of magnetite is a primary source of natural remanence in igneous rocks. Its stability depends on the state of magnetite particles, and grain size is considered to control their properties (Dunlop, 2021). Comparative studies of temperature-dependent coercivity and magnetic susceptibility (Hoddy, 1982, 1986; Stacey & Wise, 1990) indicate that these quantities largely covary with magnetostriction. The TRM intensity of nickel is directly related to its state of internal stress (Shive, 1969). While these results emphasize the importance of stress, they provide no quantitative estimates because coercivity and initial susceptibility both depend also on grain size, shape, and magnetostatic interactions (Dunlop, 2021).

Internal stress in magnetite can have different physical origins (Xu & Merrill, 1989) it may arise from dislocations (Shive & Butler, 1969; Stacey & Wise, 1967) or misfit at phase boundaries, caused, for example, by exsolution, chemical gradients due to oxidation, or other diffusion fronts. Macrostress is due to external stress sources on a length scale larger than the magnetic particle. It can originate, for example, from burial, tectonic forces, or shock. The micromagnetic influence of microstress on domain wall controlled coercivity has been studied by Moskowitz (1993). Effects of stress due to newly formed dislocations through deformation, upon domain wall pinning and coercivity were observed by Lindquist et al. (2015). Oxidation induced stress has been directly observed in magnetite nanoparticles, where it was shown to originate from a topotactic transformation to off-stoichiometric magnetite and maghemite (Yuan et al., 2019).

For titanomagnetite with ulvöspinel content of about 60% (TM60), which is common in oceanic basalt, the magnetic anisotropy is controlled by magnetostriction (Appel & Soffel, 1984; Fabian, 2006). Magnetostatic...
interaction and shape anisotropy in TM60 can be neglected. This allows approximation of the amount of internal stress from the hysteresis work in the approach-to-saturation (ATS) region (Appel, 1987; Kersten, 1932). Explicit stress fields resulting from low temperature oxidation in spherical titanomagnetite particles have been calculated by Fabian and Shcherbakov (2020). Stress in magnetite can be quantified indirectly by comparing modeled hysteresis loops for exsolved and unexsolved individual magnetite particles to bulk measurements by assuming that the model without stress is representative of the bulk sample, and that the difference between model and measurement is due to intrinsic stress (ter Maat et al., 2020). This approach is technically challenging and is not applicable to larger sample numbers.

Magnetite is magnetically soft, so internal stress and magnetocrystalline anisotropies are smaller than demagnetizing energies arising from self-demagnetization fields and contribute to either shape anisotropy or magneto-static interparticle interaction (Hubert & Schäfer, 1998). Variations in grain shape, packing density, and texture easily dominate the influence of stress on the ATS, and direct stress estimates based on reversible magnetization work are hampered (Hodych, 1990). Determining the demagnetizing energy in magnetite is, thus, an important unsolved problem in rock magnetism that hinders progress in paleomagnetism, planetary magnetism, and paleointensity studies.

Here, we substantially modify the reversible work method of Appel (1987) by measuring ATS at elevated temperatures to separate the work required to overcome demagnetizing energies from those related to magnetostriction or magnetocrystalline anisotropy (Hodych, 1982, 1986, 1990). We experimentally verify our theoretical approach with measurements on stressed, oxidized, and unstressed synthetic magnetite, and develop a method to determine their temperature-dependent ATS behavior in terms of the corresponding scaled reversible work (SRW).

2. Materials and Methods
2.1. The Scaled Reversible Work Method

The ATS of a hysteresis loop is the high-field region where only reversible magnetization changes occur. The theory of ATS was the starting point for the development of micromagnetics (Brown, 1940) and has been studied extensively in the context of metals and material science (Aharoni, 1969; Brown, 1941; Grady, 1971; Iglesias & Rubio, 2002; Kronmüller & Seeger, 1961). We here analyze hysteresis curves, which are controlled by the temperature-dependent material constants of saturation magnetization ($M_s$), cubic magnetocrystalline anisotropy ($K_1$), and magnetostriction ($\lambda_{111}, \lambda_{100}$). We define the demagnetizing energy density

$$K_d = \frac{1}{2} \mu_0 M_s^2,$$

and measure temperature $T$ in terms of the scaled temperature

$$\tau = 1 - \frac{T}{T_C},$$

where $T_C$ is the Curie temperature.

In the ATS region it is commonly assumed that the magnetization of a magnetic particle is homogeneous in some direction $m = (m_1, m_2, m_3)$. If an external field $B$ is applied in the direction $v$, the micromagnetic energy density $E$ in case of magnetite is

$$E(m) = -M_s B v + K_1 (m_1^2 m_2^2 + m_1^2 m_3^2 + m_1^2 m_2^2) - \frac{3}{2} \sigma \lambda (m u)^2 + K_d m^2 N m.$$

Here, $u$ is the uniaxial stress direction, $\lambda$ the relevant magnetostriction constant, and $N$ is the geometric shape anisotropy tensor. In a prolate particle with elongation axis in direction $d$ and demagnetizing factors $0 < N_1 < N_2 < 1$ with $\Delta N = N_2 - N_1 > 0$, the last term can be simplified to $-K_d \Delta N (m d)^2$. After dividing by $K_d$ and introducing $b = B/\mu_0 M_s$, where $J_s = \mu_0 M_s$, the scaled energy density becomes

$$e(m) = -2 b v m + Q (m_1^2 m_2^2 + m_1^2 m_3^2 + m_2^2 m_3^2) - S (m u)^2 - \Delta N (m d)^2.$$

Here, $Q = \frac{1}{2} (K_1 + 3 \sigma \lambda)$, and $S = \frac{1}{2} (K_1 - \sigma \lambda)$.
Figure 1. (a) Scaled plot of the reversible approach-to-saturation (ATS) part of a hysteresis curve (blue line). Scaling of the magnetization to $m = M/M_s$ and of the field to $b = B/J_s$ leads to unit free quantities. The shaded area represents $w_{\text{rev}}$ in the scaled field interval $[b_1, b_2] = [0.45, 1.6]$, in this sketch $w_{\text{rev}} = 0.092$. (b) Theoretical behavior of $w_{\text{rev}}$ as a function of scaled temperature $\tau$. If scaled reversible work (SRW) is exclusively due to demagnetizing energy, $w_{\text{rev}}$ is independent of temperature (circles). Other anisotropies decay with increasing temperature (red dots), so only demagnetizing work remains when extrapolating to $\tau = 0.3$, 0.42, and 0.6.

To apply the SRW method to real hysteresis data requires several careful measurement and evaluation steps. Determining $w_{\text{rev}}(\tau)$ at different temperatures is based on constructing and evaluating the diagram in Figure 1a. Its correct scaling requires a robust method to determine $M(\tau)$ for a range of temperatures between room temperature (RT) and $T_C$. This is achieved by extrapolating the ATS law at each temperature (Fabian, 2006; Jackson & Solheid, 2010), and by fitting the individual magnetic saturation moments $\mu_s(\tau)$ to the theoretical power law

$$\mu_s(\tau) = M_{s,0} V \tau^\gamma,$$

where $M_{s,0}$, the magnetite volume $V$, and the power-law exponent $\gamma$ are determined from experimental data. For the spontaneous magnetization $M_{s,0}$ we used the literature value for magnetite. The difference between upper and

where $Q = K_j/K_g$ and $S = 3 \sigma / 2(2 K_g)$ are temperature-dependent unit-free parameters representing cubic magnetocrystalline stress induced anisotropies. For isotropic distributions of the unit vectors $\mathbf{v}, \mathbf{u}, \mathbf{d}$, this energy can be numerically minimized to obtain $m(b)$, which after numerical integration approximates an assemblage of particles with random orientations and shapes. This provides the SRW

$$w_{\text{rev}}(Q, S, \Delta N) = \int_{b_1}^{b_2} \left(1 - m(b) \mathbf{v} \right) \, db$$

in the scaled field interval $[b_1, b_2]$. The blue line in Figure 1a is an upper hysteresis branch measured in its ATS region. In this diagram, the scaled sample magnetization $m = M/M_s$ is plotted as a function of scaled field $b$, and the shaded area represents the SRW. If no cubic magnetocrystalline and no stress induced anisotropies are present, which implies $Q = S = 0$, the scaled energy density (Equation 4) only depends on geometric quantities and is independent of temperature. Thus, discrimination between anisotropy work and demagnetizing work can be achieved by measuring $w_{\text{rev}}$ for the same scaled field interval $[b_1, b_2]$ at different temperatures (Figure 1b). The demagnetizing and anisotropy work curves converge because for magnetite both $Q$ and $S$ vanish in the limit $\tau \to 0$, which allows the lower curve to be inferred by extrapolating the upper curve to $\tau = 0$.

Model calculations based on Equation 4 after averaging over isotropically distributed directions $\mathbf{u}, \mathbf{d},$ and $\mathbf{v}$, are shown in Figure 1c. They confirm that the temperature evolution of $w_{\text{rev}}$ quantitatively distinguishes work against stress anisotropy from work against demagnetization, and that horizontal stress-free curves can be retrieved reliably by extrapolating sloped curves for stressed material to $\tau = 0$.

2.2. Measurement Evaluation

To apply the SRW method to real hysteresis data requires several careful measurement and evaluation steps. Determining $w_{\text{rev}}(\tau)$ at different temperatures is based on constructing and evaluating the diagram in Figure 1a. Its correct scaling requires a robust method to determine $M(\tau)$ for a range of temperatures between room temperature (RT) and $T_C$. This is achieved by extrapolating the ATS law at each temperature (Fabian, 2006; Jackson & Solheid, 2010), and by fitting the individual magnetic saturation moments $\mu_s(\tau)$ to the theoretical power law

$$\mu_s(\tau) = M_{s,0} V \tau^\gamma,$$

where $T_C$, the magnetite volume $V$, and the power-law exponent $\gamma$ are determined from experimental data. For the spontaneous magnetization $M_{s,0}$ we used the literature value for magnetite. The difference between upper and
lower hysteresis branches results from irreversible magnetization processes; beyond the loop closure fields \( B_c(T) \) the magnetization structure changes reversibly. To exclude irreversible processes, the scaled limit fields \( b_1 \) and \( b_2 \) for all \( T \) must obey the inequalities

\[
B_c(T)/J_s(T) < b_1 < b_2 < B_{\text{max}}/J_s(T).
\]

(7)

For our specimens, the closure field at and above RT is \(<260 \text{ mT}\), which limits \( b_1 \) to \( b_2 > 0.45 \). For our maximal available field of \( B_{\text{max}} = 1 \text{ T} \) one obtains at RT the minimal value of \( b_{\text{max}} = 1.66 \). For calculating \( \omega_{\text{rev}} \) it is therefore possible to use the interval \([b_1, b_2] = [0.45, 1.6]\) at all temperatures above RT, as depicted in Figure 1a, even if the measurement extends beyond this interval.

The reversible high-field branch at each temperature is fitted to the theoretical ATS law

\[
M_{\text{rev}}(B) = M_s + \chi B + a B^\beta.
\]

(8)

The corresponding scaled magnetization after removing the linear term \( \chi B \) and dividing by \( M_s \) is

\[
m_{\text{rev}}(b) = 1 + a \mu_0 J_s^{\beta-1} b^\beta.
\]

(9)

The SRW is then computed as

\[
\omega_{\text{rev}} = \int_{b_1}^{b_2} 1 - m_{\text{rev}}(b) \, db = \frac{a \mu_0 J_s^{\beta-1}}{\beta + 1} (b_1^{\beta+1} - b_2^{\beta+1}).
\]

(10)

The parameters in Equation 8 are strongly correlated (Jackson & Solheid, 2010) and uncertainties in \( \chi(T) \) are traded off for uncertainties in \( \alpha(T) \), \( \beta(T) \), and \( M_s(T) \), which finally generate uncertainties in \( \omega_{\text{rev}}(\tau) \). To minimize this progression of uncertainty the measurement procedure needs to be carefully designed to reduce noise.

### 2.3. High Temperature Hysteresis Measurements

Hysteresis measurements were performed using a Princeton Measurements Corporation MicroMag3000 VSM at NTNU, Trondheim, Norway. The specimens were heated and measured in a He gas flow. To minimize instrumental noise at high fields, the discrete sweep mode was used with a settling time of 250 ms and an averaging time of 600 ms per data point. At each temperature a full hysteresis curve, including the saturation initial curve, was measured at 10 mT field steps to maximum fields of \( \pm 1 \text{ T} \). The temperature was increased from RT in 25°C steps to 500°C, with a waiting time of 300 s after each increment. Higher temperatures have not been used to avoid the low signal-to-noise ratios close to \( T_C \).

#### 2.4. Magnetite Samples

Three sets of sized synthetic Wright magnetites were analyzed here (W4, W5, and W6) which have been characterized in previous studies (Fabian, 2003, 2006; Fabian & Leonhardt, 2010; Krása et al., 2003). To remove partial oxidation due to storage, most samples were reduced by heating in argon using an AGICO MKF1A Kappabridge system at NTNU. Each sample was repeatedly cycled from RT to 700°C until reversible magnetic susceptibility curves were obtained after two to three cycles. The Verwey transition of sample W4 was measured using the MKF1A before and after reducing (Table S1).

The reduced magnetite samples were mixed with Omega CC high temperature cement, a two part ceramic cement with a zirconium silicate filler and a sodium silicate liquid binder. From each mix several specimens were prepared for high temperature VSM measurements by adding the Omega liquid binder to the magnetite-filler-powder mix and directly placing it on HT-VSM specimen holders, these are further referred to as unstressed specimens. One specimen from the finest grain-size sample, \( W_4 = 5.7 \mu m \), was prepared without reducing the magnetite and is referred to as the oxidized specimen. Additional stressed synthetic specimens were prepared by crushing reduced magnetite grains in alcohol with a mortar and pestle before mixing with filler powder. Crushing induces mechanical stress within grains, and also changes average grain size, shape and inter-particle distance. The specimens have typical masses between 40 and 60 mg and contain 2–3 wt% magnetite, all sample sets and specimens
are listed in Table S1. For three stressed specimens, one for each Wright magnetite sample, the high-temperature sequence was repeated a second time, to identify if stress is annealed by heating.

3. Results

3.1. Hysteresis of Unstressed and Stressed Magnetite

Hysteresis parameters $M_s(T)$ and $B_s(T)$ were determined from the non-reversible part of the hysteresis loops. Both parameters decrease as a function of temperature (Figures 2a–2c). Lowest $M_s$ and $B_s$ values are observed for unstressed specimens (red curves, Figures 2a–2c), with W6 having the lowest values. $B_s$ decreases from ~2 mT at RT to 0.9 mT at 500°C, and $M_s$ decreases from ~9 to 4 kA/m over the same temperature range. For crushed W6 specimens (blue and orange), $B_s$ decreases from 5 to 1.8 mT and $M_s$ decreases from 22 to 7.5 kA/m from RT to 500°C. The annealed specimen (green) has a similar decreasing trend with temperature slightly lower values for $M_s$ and $B_s$. The scaled reversible work $w_{rev}$ versus normalized temperature $\tau$ is plotted for W4 (d), W5 (e), and W6 (f). For all reduced uncrushed specimens (red) $w_{rev}$ is essentially constant. Crushed specimens (orange or blue) have larger $w_{rev}$ also in the limit $\tau \to 0$. This is true also for oxidized specimen W4 (d: purple). Annealed repeat runs (green) have reduced $w_{rev}$ but the same limit $\tau \to 0$ as unannealed counterparts (orange and blue).

Figure 2. Plots of $M_s(T)$ versus $B_s(T)$ measured between 25°C and 500°C for W4 (a), W5 (b), and W6 (c). Specimen names include treatment options: R, reduced; CR, crushed reduced. Both $M_s$ and $B_s$ decrease with increasing temperature. Higher values are obtained for stressed (crushed: blue and orange; oxidized: purple) specimens compared to unstressed specimens (red). Repeated annealed runs (green) have similar linear trends with temperature slightly lower values for $M_s$ and $B_s$. The scaled reversible work $w_{rev}$ versus normalized temperature $\tau$ is plotted for W4 (d), W5 (e), and W6 (f). For all reduced uncrushed specimens (red) $w_{rev}$ is essentially constant. Crushed specimens (orange or blue) have larger $w_{rev}$ also in the limit $\tau \to 0$. This is true also for oxidized specimen W4 (d: purple). Annealed repeat runs (green) have reduced $w_{rev}$ but the same limit $\tau \to 0$ as unannealed counterparts (orange and blue).

Values of $M_s(T)$, $\chi(T)$, $\alpha(T)$, and $\beta(T)$ were obtained from reversible parts of each hysteresis loop with the robust bootstrap approach of Jackson and Solheid (2010). Values are plotted versus scaled temperature in Figures S1–S3.
Lowest $\beta$ values are obtained for unstressed specimens, with $\beta$ varying between $-2.20$ and $-1.75$. $\beta$ values for crushed counterparts are slightly higher, with values of $-1.90$ to $-1.60$. Both the oxidized W4 specimen and repeated measurements from all crushed specimens follow the $\beta(T)$ trend from the crushed specimens. An increasing trend with increasing temperature is observed for $\alpha$. For the unstressed specimens, RT $\alpha$ values are highest. At high temperatures, $\alpha$ values for stressed and unstressed specimens are similar. $M_s(T)$ curves for all specimens follow the power-law Equation 6 with decreasing $M_s$ for increasing temperature. $T_c$ varies between 570°C and 588°C for the reduced specimens, and the oxidized RW4-x specimen has a higher $T_c$ of 592°C. Specimen magnetic volumes vary between 0.20 and 0.24 mm$^3$. For $\gamma$, we find typical values of 0.36–0.39.

3.2. Scaled Reversible Work

SRW versus normalized temperature $\tau$ is plotted in Figures 2d and 2e. For unstressed specimens (red curves: RW4-A, RW5-8, and RW6-x), $w_{\text{rev}}(\tau)$ values are relatively constant (±5%). For these specimens, $w_{\text{rev},0}$ values of 0.0194, 0.0190, and 0.0187 are obtained from a best-fit to the region between $\tau = 0.2$ and 0.5 and extrapolating this to $\tau \to 0$. The $w_{\text{rev}}(\tau)$ values for stressed specimens (blue, orange, and purple) decrease markedly (20%–50%) as $\tau \to 0$. In the region from RT ($\tau \approx 0.7$) to $\tau = 0.5$, $w_{\text{rev}}$ values increase for the W4 and W5 specimens, whereas for W6 this increase is less profound. Values for $w_{\text{rev},0}$ are approximately: 0.0223, 0.0215, and 0.0254, for CRW4, CRW5, and CRW6, for the same best-fit line interval. A $w_{\text{rev},0}$ of 0.0218 is obtained for the oxidized W4 specimen. Repeated annealed measurements for crushed specimens (green) also have decreasing $w_{\text{rev}}$ for $\tau \to 0$, RT $w_{\text{rev}}$ is lower than for the non-annealed measurement (orange), and $w_{\text{rev}}$ does not increase from RT but stays approximately constant until $\tau \approx 0.5$. Extrapolation of $\tau \to 0$ results in similar $w_{\text{rev},0}$ for these specimens.

4. Discussion

4.1. High Temperature Hysteresis Data and Their Stress Dependence

The classical hysteresis parameters $M_s(T)$ and $B_s(T)$ in Figures 2a–2c are both larger for stressed specimens than for unstressed specimens, but they do not only reflect stress because they are also grain-size dependent. Repeated measurements indicate lower $M_s(T)$ and $B_s(T)$ because heating increases thermal motion of lattice atoms that leads to diffusion and healing of dislocations. This annealing effect reduces the amount of microstress and stress-induced coercivity (Dankers & Sugiura, 1981), but does not change the effects of fragmentation. For natural samples, when grain size is unknown or varies over a larger range, the distinction between stress and grain-size influences upon these plots of $M_s(T)$ and $B_s(T)$ is ambiguous and non-quantitative.

In contrast, the temperature evolution of the SRW theoretically distinguishes perfectly between demagnetizing work and work against stress anisotropy. This is experimentally confirmed, as we observe distinctly different $w_{\text{rev}}(\tau)$ curves for stressed and unstressed specimens from our synthetic sample set in Figures 2d and 2e. In all stressed specimens SRW is larger than in unstressed specimens, and decreases linearly for $\tau < 0.45$. Stressed specimens from the coarsest grained sample, W6 = 12.3 μm, have the highest SRW and annealing from repeated measurements is the least of all specimens. SRW of the oxidized W4 specimen is even larger than for the crushed specimen, and $w_{\text{rev}}(\tau)$ also has a steeper decrease with increasing temperature. This indicates that different stress mechanisms may be distinguished based on the SRW if they reflect different combinations of the magnetostriiction constants, although both decay with temperature as expected from theory. In the limit $\tau \to 0$, all crushed specimens have higher $w_{\text{rev},0}$ values compared to uncrushed specimens, also the crushed W4 specimens has a higher $w_{\text{rev},0}$ values than the uncrushed oxidized specimen. To better understand this $w_{\text{rev},0}$ shift and to find a quantitative estimate for stress from $W_{\text{rev}}(\tau)$ we extend the theory with an empirical approximation.

4.2. Demagnetizing Work in Magnetite

By measuring magnetizations relative to $M_s(T)$, and fields $B$ relative to $J_s(T)$, the SRW method compares all anisotropy energies to the demagnetizing energy $K_s(T)$. In Equation 4 demagnetizing effects are, therefore, represented by a temperature-independent number $\Delta N$ that is intended to reflect particle shape (Figure S5). In measurements $\Delta N$ subsumes also other demagnetizing effects. By linearizing Equation 4 near $v$ for the limit $\tau \to 0$, where $S = Q = 0$, the reversible work $w_{\text{rev},0} \approx c \Delta N^2$. We fitted this relation to exact numerical calculations for the interval $[b_1, b_2]$ (Figure S4) and, thus, obtain the approximation:
\[ \Delta N \approx 2.82 \sqrt{w_{\text{rev},0}}. \]  

(11)

With this relation, \( \Delta N \) values for our uncrushed specimens are all close to 0.4 and for corresponding crushed specimens it increases only slightly by up to 15%. For pure shape anisotropy, \( \Delta N \approx 0.4 \) corresponds to prolate particles with elongations of 4. When crushing particles with an initial elongation of 4, it is expected to obtain fewer elongated pieces, so the observed \( w_{\text{rev},0} \) increase after crushing is more likely explained by increased particle interactions, due to closely packed clusters of fragments.

For unstressed specimens, only small temperature variations are expected for \( w_{\text{rev}} \) due to the relatively weak cubic anisotropy of magnetite with rapidly decaying \( K(T) \). Indeed only small changes in \( w_{\text{rev}} \) are observed, but the remaining slopes often are negative. A negative slope could originate from an increasing reversible alignment of the internal magnetization structure with the field direction (magnetization stretching) which occurs in each individual particle even beyond the closure field. The SRW due to magnetization stretching depends not only on demagnetizing energy, but also on other material constants like \( A(T) \) and \( K(T) \); and, therefore, may have a small variation with temperature which can be negative if the temperature-dependent terms support the field-alignment.

4.3. Stress Determination in Magnetite

Model calculations like those in Figure 1c indicate that the slope \( \partial w_{\text{rev},0}/\partial \tau \) of \( w_{\text{rev}} \) near \( \tau = 0 \) is independent of \( \Delta N \) to first order and depends only on the internal stress \( S \) because \( Q \) decays more rapidly with temperature than \( S \). A similar linearization as in the previous paragraph for \( S \gg Q \) suggests the empirical approximation

\[ S \approx 1.5 \sqrt{\partial w_{\text{rev},0}/\partial \tau}. \]  

(12)

From \( S \), we estimate the internal stress \( \sigma \) based on the magnetostriction constant \( \lambda_{111} \) which is often dominant for internal stress sources (Klapel & Shive, 1974) and provides a lower stress estimate because for magnetite above RT \( \lambda_{111} > \lambda_{100} \). Fitting model slopes for \( \Delta N = 0.4 \) yields the estimate

\[ \sigma = \frac{2 K_1}{3 \lambda_{111}} S = 1.54 \text{ GPa} \approx 2.3 \text{ GPa} \sqrt{\partial w_{\text{rev},0}/\partial \tau}. \]  

(13)

Stresses estimated in this way provide a measure relative to the theoretical model used and depend not only on the validity of the magnetostriction constants of Klapel and Shive (1974), but also on details of stress variability in the magnetite particles, and corresponding magnetization structure changes. Relative to these uncertainties, the dependence on \( \Delta N \) is negligible.

Independent of these empirical relations measurement results for \( w_{\text{rev},0} \) and \( \partial w_{\text{rev},0}/\partial \tau \) are plotted with their respective uncertainties into a nomogram based on model calculations for isotropic particle ensembles (Figure 3). Values of \( \Delta N \) and \( \sigma \) can be visually estimated from data of bulk measurements. Both internal stress and \( \Delta N \) agree well with the above empirical formulae. Data for uncrushed specimens plot close to the theoretical stress-free 0 MPa line; for W4 and W6 slightly negative slopes were obtained from \( w_{\text{rev}}(\tau) \) curves, while for W5 a slightly positive slope was obtained, which leads to internal stress estimates \( < 150 \text{ MPa} \). Data for crushed specimens have higher slopes, leading to higher internal stress estimates of \( \approx 270 \pm 10 \text{ MPa} \) for W4, \( 340 \pm 20 \text{ MPa} \) for W5, and \( 340 \pm 30 \text{ MPa} \) for W6. Repeated annealing measurements indicate a \( \approx 100 \text{ MPa} \) decrease for W4 and W5, whereas for W6 it is only \( \approx 30 \text{ MPa} \). The oxidized W4 specimen has an internal stress estimate of \( \approx 360 \text{ MPa} \).
4.4. Applications and Outlook

Our new SRW method enables quantification of the demagnetizing energy in magnetite-bearing samples and, thus, enables separate determination of internal stress that can originate from different sources. Stress at magnetite-ilmenite interfaces has long been theoretically estimated (Price, 1980), and its potential importance has been pointed out (Moskowitz, 1993; Shive, 1969; Stacey & Wise, 1967) but quantitative experimental verification is still missing. Through its stabilizing effect on remanent magnetization, internal stress is an essential factor that influences paleointensity determination and magnetic anomaly interpretation and it remains largely unknown how stress evolution, for example, by low temperature exsolution or oxidation, directly modifies TRM acquisition. Also, later stress overprints through tectonic processes or impact shock can create point defects, dislocations, and other crystallographic defects in magnetite. Shock-induced magnetic hardening refers to an increased magnetic coercivity observed after impact shock (Cisowski & Fuller, 1978; Pohl et al., 1975), but also shock-induced bulk coercivity decreases have been reported (Bezaeva et al., 2010). Improving the quantification of stress in such observations by the SRW method promises substantial progress (Bezaeva et al., 2016; Gattacceca et al., 2007; Kontny et al., 2018; Sato et al., 2021).

Challenges to the SRW method in natural samples will be related to magnetic mineralogical inhomogeneity and to cation reordering (Jackson & Bowles, 2018) or alteration at elevated temperatures. Possible precautions and improvements could include use of mineral separates and optimized measurement techniques. Ideal instrumentation would provide higher applied fields up to 3 T, and increased magnetization measurement accuracy at high fields.

5. Conclusions

Temperature-dependent SRW $w_{rev}$ from hysteresis curves allows separation and quantification of demagnetizing and stress effects in magnetite. This new method requires high-quality temperature-dependent hysteresis measurements at sufficiently high magnetic fields. The validity of the method is demonstrated for a suite of synthetic magnetite samples under different stress conditions. Our results indicate that demagnetization energy $w_{rev,0}$ is significant in magnetite and reflects not only shape anisotropy, but also magnetostatic particle interaction and changes of the internal magnetization structure. Oxidation induced stresses, dislocation stress fields, or external stresses vanish close to $T_c$. The temperature dependence of $w_{rev}$ thus, provides a new rock magnetic tool for studying stress in rocks, meteorites, or impact structures, and the origin and stability of magnetic remanence in magnetic anomalies, paleomagnetism, and paleointensity in Earth and planetary magnetism.

Data Availability Statement

All high temperature hysteresis data can be found in the Zenodo repository under the https://doi.org/10.5281/zenodo.5734996 at https://zenodo.org/record/5734996#.YaTqNNDML-g (Béguin & Fabian, 2021).

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