Magnetic properties of single and multi-domain magnetite under pressures from 0 to 6 GPa

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[1] Using novel experimental methods, we 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. We find that the saturation remanence of MD magnetite increases 2.8 times over initial, non-compressed values by 6 GPa, while its remanent coercivity remains relatively constant. For SD magnetite, remanent coercivity and saturation remanence vary little from 0 to 1 GPa, increase markedly from 1 to 3 GPa, then plateau above 3 GPa. These new findings suggest that by 3 GPa, SD magnetite either undergoes a magnetic phase transition, or that it reaches an optimal magnetic state where magnetostriction and/or magnetocrystalline energy constants attain some threshold state without reorganization of the pre-existing magnetic lattices. Similar behavior is not observed in MD magnetite, likely due to domain wall effects. INDEX TERMS: 1540 Geomagnetism and Paleomagnetism: Rock and mineral magnetism; 1594 Geomagnetism and Paleomagnetism: Instruments and techniques; 3924 Mineral Physics: Highpressure behavior; 3929 Mineral Physics: NMR, Mossbauer spectroscopy, and other magnetic techniques; 3994 Mineral Physics: Instruments and techniques. Citation: Gilder, S. A., M. LeGoff, J.-C. Chervin, and J. Peyronneau (2004), Magnetic properties of single and multi-domain magnetite under pressures from 0 to 6 GPa, Geophys. Res. Lett., 31, L10612, doi:10.1029/ 2004GL019844.

1. Introduction

[2] The spontaneous magnetic moment of magnetite (Fe₃O₄) arises from electron exchange between iron atoms, where the electrons pass between the iron atoms indirectly through an oxygen atom [see Dunlop and Özdemir, 1997, and references therein]. Electron exchange is organized into magnetic lattices, depending on the bond lengths and bond angles between iron and oxygen atoms, via magnetocrystalline and magnetostriction energies. When stress acts on a material, the bond lengths and angles change, which in turn modify the magnetocrystalline and magnetostriction constants. This is why the nature of the stress, be it uniaxial, hydrostatic, compressive or tensile, affect the magnetic properties of materials differently. An isotropic compression under purely hydrostatic stress will reduce bond lengths, yet bond angles will remain unchanged; uniaxial or shear stress can change bond angles as well as bond lengths.

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[3] How stress influences magnetic remanence also depends on the size and shape of the substance. The magnetizations of single domain (SD) and multi-domain (MD) magnetite grains react differently to imposed stresses. Stress may cause the net spontaneous moment in a SD grain to reorient to a new position depending on the angle between the stress and magnetic easy axis direction, the grain's shape, etc. [Hodych, 1977]. The individual domains in a multi-domain grain grow or shrink to compensate for the stress, which modify the grain's magnetic intensity and direction [Bogdanov and Vlasov, 1966]. In sum, two processes contribute to the piezo-remanence of magnetite: a "microscopic" effect that modifies the electron exchange couple, and a "macroscopic" effect where the magnetization becomes reoriented within a grain; the latter being analogous to how externally applied magnetic fields reorient a grain's magnetic vector.

[4] Measuring a material's full magnetic vector under high pressures is experimentally difficult, with most work being performed at non-hydrostatic stresses, at pressures less than 1 GPa, and using large, whole-rock samples. Unfortunately, the magnetic mineralogies, and the grain size distributions of those minerals, in whole-rock samples are rarely well known. Below, we introduce a new method that enables direct measurements of the full magnetic vector of well-characterized mineral separates under pressures exceeding 5 GPa.

2. Experimental Methods

[5] We constructed a pressure cell made entirely of BeCu except for moissanite pistons and a Bronze-Be gasket housing the sample. The cell is small enough that it can be introduced into the bore of a three-axis, superconducting (SQUID) magnetometer. The measurement procedure is the same as that for a paleomagnetic sample in which each SOUID participates in measuring the x, y and z magnetic components of the sample and the cell it is housed in. Four discrete measurements of the full magnetic vector are made, once each time the cell is rotated about its three orthogonal axes, then the average moment and its angular uncertainty are calculated after accounting for the baseline of the magnetometer (<2 \times 10^{-11} Am²) and the magnetization of the sample handler $(5 \times 10^{-11} \text{ Am}^2)$. When demagnetized, the empty cell has a magnetic moment $<5 \times 10^{-9}$ Am² with angular uncertainties >10°.

[6] We also designed an electromagnet whose pole pieces slide through the cell's housing to abut the moissanite pistons, approaching the sample as close as possible. This apparatus, which allows us to measure the acquisition of isothermal remanent magnetization (IRM), generates fields

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Figure 1. (a) IRM acquisition of SD magnetite. (b) AF demagnetization of same SD magnetite sample as in Figure 1a. (c) Direct field demagnetization curve of a SD sample initially saturated in a negative 170 mT field (different sample than in Figure 1a). (d) IRM acquisition of MD magnetite. (e) AF demagnetization of same MD magnetite sample as in Figure 1d. Inset shows a zoom of AF demagnetization curves made prior to compression and after decompression from 4.06 and 5.96 GPa. (f) SIRM moment (M_{170}) as a function of pressure for MD magnetite (data from Figure 1d).

up to 170 mT in the sample region while avoiding large fields being applied to the cell itself. Once the sample has been saturated, the cell can then be placed within a coil to perform alternating field (AF) demagnetization experiments up to maximum applied fields of 40 mT—again in the same manner that paleomagnetic samples undergo stepwise demagnetization.

[7] We studied the magnetism of well-characterized, single domain (SD) and multi-domain (MD) magnetite previously described in *Gilder et al.* [2002]. For each case, several 10's of magnetite grains together with a few ruby chips were loaded in silica gel in a hole in the gasket. Ruby served to measure the pressure in the cell before and after each experiment using the shift in the R1 fluorescence spectra [*Chervin et al.*, 2001]. Distinct R1 and R2 spectral peaks suggest pressure conditions were dominantly hydrostatic. Once a sample was loaded, IRM

acquisition was measured over twelve steps from 0 to 170 mT. After completing each IRM experiment, the sample underwent AF demagnetization over ten steps from 0 to 40 mT. Pressure was then increased, and the IRM acquisition-AF demagnetization experiments were repeated.

[8] The empty cell becomes magnetized during IRM acquisition, although it is much less than that of the sample and does not significantly influence the results (Figure 1a). For example, at zero pressure and H_{IRM} of 12 and 113 mT, the moment (M) of the empty cell is 3.5×10^{-9} and 3.1×10^{-8} Am²; whereas when the cell is loaded with SD magnetite at the same applied fields at zero pressure, M is 2.5×10^{-8} and 3.2×10^{-7} Am², respectively, or about an order of magnitude greater than the contribution from the cell alone. Once the empty cell acquires a moment of 1×10^{-8} Am², the magnetic moment as a function of applied

field $[M(H_{IRM})]$ is highly reproducible, and angular uncertainties are $<2^{\circ}$ with rare exception. Importantly, $M(H_{IRM})$ of the empty cell does not vary as a function of pressure. The same is true for AF demagnetization— $M(H_{AF})$ of the empty cell is independent of pressure. Thus, $M(H_{IRM})$ and $M(H_{AF})$ of the empty cell were determined following the same analytic procedures as when a sample was present, and the M(H) of the empty cell was subtracted from the M(H) of the sample+cell.

3. Results

[9] The shapes and amplitudes of the IRM acquisition curves for SD magnetite vary little below 1 GPa (Figure 1a), then increase above 1 GPa. Upon pressure release from 4.1 GPa, the moment at 170 mT (M_{170}) remains nearly 25% higher than initial, uncompressed conditions. Stepwise AF demagnetization of SD magnetite shows only slight differences below 1 GPa (Figure 1b). Above 1 GPa, the material becomes increasingly resistant to AF demagnetization, which explains the elevated moments at low applied fields in the IRM experiments (Figure 1a). Upon pressure release from 4.1 GPa, SD magnetite is harder to demagnetize than at initial, uncompressed conditions (Figure 1b). The resistance to AF demagnetization prompted us to perform a second experiment, with a new sample, to measure the direct field demagnetization curve and coercivity of remanence (Hcr) by first saturating the sample in a single step at 170 mT, then incrementally adding a magnetization in the opposite sense (Figure 1c). Again, important changes in M(H_{IRM}, P) commence above 0.5 GPa yet below 1.3 GPa.

[10] The amplitudes of the IRM acquisition curves of MD magnetite increase gently from 0 to 1.2 GPa, then more steeply above 2 GPa, with M(H_{IRM}, P) at a given H gaining two to four times over initial conditions by 6 GPa (Figure 1d). MD magnetite is much less resistant to AF demagnetization than SD magnetite at any pressure (Figure 1e). Unlike the SD case, $M(H_{IRM}, P)$ for MD magnetite is even greater upon decompression than when under pressure (Figure 1f). At the maximum pressure of ~ 6 GPa, M₁₇₀, which is approximately the saturation remanence (or SIRM), is 2.8 times initial, uncompressed conditions. When decompressed from 6 GPa, M_{170} is 3.6 times that of initial conditions. Again, the cell itself cannot account for the entirely different response to M(H_{IRM}, P) and M(H_{AF}, P) between MD and SD magnetite: the origin comes from the material in the cell.

[11] We calculated the median demagnetization field (MDF), which is the applied field needed to demagnetize 50% of the initial magnetization and is proportional to the bulk coercive force (Hc) [*Dunlop and Özdemir*, 1997], as a function of pressure for SD magnetite (Figure 2a). MDF values at pressures >1.5 GPa were extrapolated because peak alternating fields of 40 mT could not remove 50% of the initial remanence. MDF changes little below 1 GPa, increases linearly from ~1.0 to 3.1 GPa, then flattens out above 3.1 GPa; upon pressure release, MDF is 66% higher (25 vs. 15 mT) than the original (zero-pressure) value. Very similar changes are observed for Hcr (Figure 2a). The MDF of MD magnetite also increases with pressure but much less than SD magnetite. The effect is most pro-



Figure 2. (a) Median destructive field (MDF), bulk coercivity (Hc), and coercivity of remanence (Hcr) of SD magnetite as a function of pressure from three separate samples. Note that Hc data in Table 1 of *Gilder et al.* [2002] are in Gauss and not milliTesla (mT); here they are in mT. (b) Comparison of saturation moment (M_{170}) between two different experiments (Figures 1a and 1c). The different scales result from unequal sample volumes. (c) Comparison of M_{170} (this study) and Mrs/Ms (from *Gilder et al.* [2002]), normalized relative to their maximum values, as a function of pressure.

nounced when pressure is released, where the MDF increases from 7.5 mT at 0 GPa to 10 mT after relaxation from 6 GPa (Figure 1e- inset).

4. Interpretation and Discussion

[12] Very few data concerning the magnetic properties of magnetite exist for pressures above 1 GPa-especially for magnetite whose domain and oxidation states are well characterized. Recently, Gilder et al. [2002] reported hysteresis parameters of pure SD and MD magnetite at hydrostatic pressures up to 6 GPa using a technique that measures reversible susceptibility in continuous fields from 0 to ± 1.2 T. They found that magnetite magnetic hysteresis parameters vary <15% below 1.0 GPa, while at higher pressures, significant increases occur in bulk coercivity (Hc) and the ratio of saturation remanent magnetization (Mrs) to saturation magnetization (Ms). They argued that the net effect of pressure is to displace magnetite toward a truer single domain state with both higher Mrs/Ms and Hc. An important limitation of their study, however, is that a hysteresis loop obtained using the reversible susceptibility method underestimates the full (differential) hysteresis loop and thus can only serve as a proxy for the true hysteresis parameters.

[13] Figure 2a compares the MDF and Hcr values of SD magnetite obtained here with the published bulk coercivity (Hc) values, where a rather good correlation exists. Figure 2b compares the SIRM (M_{170}) data from the two experiments of Figures 1a and 1c. Unequal volumes of SD magnetite account for the different absolute values of SIRM. However, the relative changes in SIRM are equivalent and occur over the same pressure interval as the changes in coercivity (Figure 2a). Figure 2c shows the Mrs/Ms values for SD magnetite obtained using the reversible susceptibility method (normalized to maximum values for comparison). Despite rather large uncertainties in both pressure and absolute value in the reversible susceptibility study, the tendency for Mrs/Ms to increase at ca. 1 GPa mimics the rise in the SIRM data.

[14] The results from repeat experiments and from independent experimental methods suggest that the magnetic properties of SD magnetite undergo significant changes between 1 and 3 GPa, including a five-fold increase in Hcr, Hc and MDF, a large jump in SIRM and a three-fold increase in Mrs/Ms. Because the Verwey transition is also marked by abrupt variations in coercivity and magnetic remanence, the hypothesis that SD magnetite undergoes a magnetic phase transition should be taken seriously. If true, then one would expect Mössbauer resonance experiments to have recognized it. To our knowledge, only Halasa et al. [1974] has carried out a room temperature Mössbauer resonance study on magnetite in the pressure range considered here. They found that the octahedral lattices underwent significant isomer shifts in the first 5 GPa of compression before stabilizing at higher pressures, which leaves open the possibility of a transition. On the other hand, if a phase transition is indeed the cause, one might then expect the electrical resistivity of magnetite to undergo important variations from 1 to 3 GPa, which is not observed-electrical resistivity decreases linearly from 0 to 10 GPa [Morris and Williams, 1997]. Moreover, the Curie point of magnetite increases linearly in the 0 to 5 GPa range [Schult, 1970], which also argues against a phase transition.

[15] X-ray diffraction data suggest magnetite undergoes a linear volume decrease in the pressure range considered here. Much less clear, however, is the pressure dependence on Fe^{IV}—O and Fe^{VI}—O bond length [Finger et al., 1986], which leaves open the possibility of anisotropic compressibility and its potential influence on the magnetic lattice network via changes in magnetostriction and magnetocrystalline constants. Hydrostatic pressures to 0.2 GPa raise magnetostriction constants by 15%/0.1 GPa and decrease magnetocrystalline constants by 5%/0.1 GPa [Nagata and Kinoshita, 1967]. Although the pressure dependencies above 0.2 GPa are unknown, the change in magnitude of magnetic coercivity and remanence we observe clearly reflects an evolution toward a more perfect single domainlike state and can be accounted for by changes in magnetostriction and/or magnetocrystalline energies.

[16] Explaining the SD magnetite results via changes in magnetostriction and/or magnetocrystalline constants is also consistent with the results from MD magnetite, where enhanced SIRM can be attributed to restructuring the domain pattern and an increase in crystal defects [*Bogdanov and Vlasov*, 1966]. Further domain wall nucleation coupled

with an even greater increase in crystal defects that accompany tension likely explains why SIRM becomes even greater after decompression. The slight rise in coercivity could signal that some MD grains are broken into SD-sized grains.

[17] Although the grain size distribution and the presence of a marked Hopkinson peak suggest a single domain state for chiton teeth magnetite, the measured Mrs/Ms of 0.28 at ambient pressure on this material is lower than the ideal value of 0.5 for a volume of randomly oriented single domain magnetite grains. The departure is normally attributed to magnetic interaction; however, heightened magnetic interaction cannot explain our data because SD grain interactions will act to lower the coercivity spectrum [Cisowski, 1981], which is the opposite of what is observed. Because magnetic interaction varies with Ms, and because our earlier findings, as well as those by Nagata and Kinoshita [1964] on titanomagnetite, suggest that Ms decreases with pressure, magnetic interaction should also diminish with pressure. If magnetostriction energy increases with pressure, so too would Mrs/Ms and Hc. An alternative, yet less likely, explanation could be that the domain structure of chiton teeth at ambient pressure exists in a vortex or flower state, rather than a purely uniaxial SD state. It is possible that heightened magnetostriction energy due to stress induces a transformation from the vortex to flower and/or uniaxial SD states, which would raise both Mrs/Ms and Hc, as predicted by micromagnetic modeling [Tauxe et al., 2002]. Differentiating between the possibilities can be tested with further work on other SD magnetites.

[18] The implications of the results are that SD magnetite could potentially be developed as a pressure calibration tool and as a thermobarometer. Magnetite crystals that grow in the Earth's magnetic field during serpentinization in a subduction zone, where the Curie point isotherm is depressed, will have greater magnetic intensities than an equal volume of like grains that form near the surface. This could explain why magnetic anomalies are associated with certain subduction zones [*Clark et al.*, 1985].

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