

THERMOREMANENT BEHAVIOR OF SMALL  
MULTIDOMAIN SYNTHETIC MAGNETITES

Vol. II

by

Gary D. Storrick

B.S.E., The University of Pittsburgh, 1977

M.S.E.E., The University of Pittsburgh, 1981

Submitted to the Graduate Faculty of  
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of the requirements for the degree of  
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# THERMOREMANENT BEHAVIOR OF SMALL MULTIDOMAIN SYNTHETIC MAGNETITES

Gary D. Storrick, Ph. D.

University of Pittsburgh, 1993

This study investigates the details of how Néel-type theories of multidomain TRM are violated for high quality synthetic magnetites produced by the glass-ceramic method of Worm and Markert [1987]. The glass-ceramic method provides a simple means of preparing nearly uniformly-sized, dispersed, almost chemically pure, and relatively unstressed magnetite crystals that are well-suited for this work.

Six samples were selected for detailed study. SEM observations showed well-formed magnetite crystals with diameters ranging from 0.8 to 5.8  $\mu\text{m}$ , well within the multidomain range yet small enough to display pseudo-single-domain behavior. The samples were heated to slightly above the magnetite Curie temperature, then allowed to cool in an applied magnetic field. Fourteen cases per sample were run using fields ranging from 10  $\mu\text{T}$  to 30 mT. The resulting TRM curves show the  $M_{\text{TRM}} \propto B^1$  dependency expected at low fields, with a smooth transition towards saturation in the higher fields. Saturation was not reached, even in the 30 mT cases. The distinct thermal-activation blocking ( $M_{\text{TRM}} \propto B^1$ ), Néel blocking ( $M_{\text{TRM}} \propto B^{1/2}$ ), and saturation regions discussed by Schmidt [1973, 1975] are not readily apparent.

In each case, the sample was sequentially demagnetized using alternating fields ranging from 5 mT to 140 mT. The demagnetization curves for most samples show a shift in the coercivity spectrum of the grains contributing to

the TRM, with an increase in the importance of the low-coercivity grains as the applied field is increased. This contradicts the behavior predicted when the Schmidt-Néel theory is applied to an assemblage of grains. The 5.8  $\mu\text{m}$  sample showed anomalous behavior, which is attributed to the relatively large variation in grain size within the sample.

Theory predicts a shift in blocking temperature to lower temperatures as the applied field is increased. This can be observed through the field-dependence of partial TRM (PTRM), provided the high-temperature isothermal-remanence (IRM) is taken into account as a correction. A series of PTRM and high-temperature IRM acquisition runs demonstrated that the predicted shifts occur, and that Thellier's Law of Additivity of PTRMs was satisfied.

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## TABLE OF CONTENTS

Acknowledgements.....	v
List of Figures.....	xi
List of Tables.....	xx
List of Symbols.....	xxviii
1.0 INTRODUCTION.....	1
2.0 STATEMENT OF PROBLEM.....	7
3.0 REVIEW OF ROCK MAGNETIC THEORIES.....	10
3.1 SD theories.....	10
3.1.1 The Néel SD model.....	10
3.1.2 Unblocking in the Néel domain-reversal mechanism.....	15
3.2 MD theories.....	15
3.2.1 The Néel-Schmidt MD model.....	15
3.2.2 Unblocking in the Néel wall-motion mechanism.....	19
3.2.3 Other MD theories.....	21
3.3 PSD theories.....	23
3.3.1 Barkhausen discreteness of domain wall movements.....	24
3.3.2 Surface domains.....	27
3.3.3. Domain wall moments.....	28

3.3.4	Moments pinned by dislocation stress fields.....	28
3.3.5	Metastable SD-like states.....	29
3.3.6	Intrinsic SD-like properties of small MD grains.....	30
3.4	Micromagnetic models.....	30
4.0	GEOCHEMISTRY OF IRON-TITANIUM OXIDES.....	32
4.1	Titanomagnetite geochemistry.....	32
4.1.1	FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> phase diagram.....	32
4.1.2	Stability fields.....	41
4.2	Titanomagnetite crystallography.....	46
4.3	Effects of impurities.....	50
5.0	SAMPLE PREPARATION.....	51
5.1	Equipment.....	51
5.1.1	Furnace.....	51
5.1.2	Gas mixing apparatus.....	54
5.2	Glass-ceramic procedure.....	59
5.2.1	Ingredients and initial glass formation.....	59
5.2.2	Heat-treatment process.....	64
5.3	Discussion of procedure.....	68
6.0	NONMAGNETIC SAMPLE CHARACTERIZATION.....	70
6.1	SEM imaging.....	70
6.2	Electron microprobe.....	88
6.3	X-Ray diffraction.....	88



6.4 Optical microscopy.....	89
<b>7.0 MAGNETIC SAMPLE CHARACTERIZATION.....</b>	<b>90</b>
7.1 IRM properties.....	90
7.1.1 Initial characterization.....	90
7.1.2 High-temperature IRM acquisition.....	93
7.2 Hysteresis properties.....	118
7.2.1 Equipment and Procedure.....	118
7.2.2 Results.....	118
7.3 TRM field dependency.....	125
7.3.1 Equipment and procedure.....	125
7.3.2 Sources of magnetic noise and experimental error.....	130
7.3.3 Results.....	139
7.4 PTRM Spectra.....	167
7.4.1 Equipment and procedure.....	167
7.4.2 Sources of noise and experimental error.....	172
7.4.3 Results.....	175
<b>8.0 SUMMARY AND CONCLUSIONS.....</b>	<b>237</b>
8.1 Results of this study.....	237
8.2 Thoughts for future model development.....	239
8.3 Suggestions for future work.....	242
<b>APPENDIX A.....</b>	<b>245</b>
A.1 Sample preparation and initial characterization.....	246

A.2 TRM experiments.....	411
A.3 PTRM Experiments.....	432
A.4 IRM Experiments.....	467
A.5 Other experiments.....	498
A.6 Summary of Magnetometer errors.....	502
A.7 Hysteresis Experiments.....	505
A.8 Final Sample Characterization.....	537
APPENDIX B.....	556
B.1 Initial Glass Manufacture.....	557
B.2 Heat-treating to Crystallize and Grow (Titanio)Magnetite.....	560
B.3 Terminating a Glass-manufacture or Heat-treating Run.....	563
B.4 Operating the Gas-mixing Apparatus for Sample Preparation.....	565
B.5 Operating the Gas-mixing Apparatus With the TRM Furnace.....	567
B.6 Calibrating Gas-mixer Flow Orifices.....	569
B.7 Operating the TRM Furnace Temperature Controller.....	571
B.8 Deperming the TRM Furnace.....	576
B.9 Operating the TRM Furnace.....	577
B.10 Measuring IRM for Raw Samples.....	580
B.11 Thermal-cycling Encapsulated Samples.....	582
APPENDIX C.....	585
C.1 Gas Mixing Apparatus Orifice Calibration.....	586
C.2 Sample-preparation Furnace Temperatures.....	591

C.3 TRM Furnace Field Coil Calibration.....	594
APPENDIX D.....	596
D.1 Conversion Factors.....	597
APPENDIX E.....	599
E.1 Expected Measured Maximum Diameter for an Octahedron.....	600
E.2 Thermal Blocking Condition in the Schmidt-Néel Model.....	605
E.3 Thermal Time-constant for Encapsulated Samples.....	607
E.4 TRM data fit to the Schmidt-Neél Model.....	611
APPENDIX F.....	634
F.1 Abnormal Gas-Mixing Apparatus Behavior.....	635
F.2 Thermocouple Characteristics.....	636
F.3 Deltech furnace modifications.....	638
APPENDIX G.....	641
G.1 Micrographs.....	642
BIBLIOGRAPHY.....	656

## LIST OF FIGURES

Figure 1 TRM versus grain size and applied field in Stacey's [1962] model of PSD behavior.....	26
Figure 2 The FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> ternary system.....	34
Figure 3 Alteration in the FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> ternary system.....	35
Figure 4 Effect of oxidation on titanomagnetite Curie temperature.....	36
Figure 5 Effect of oxidation on titanomagnetite saturation moment.....	37
Figure 6 Effect of ulvöspinel content on titanomagnetite Curie temperatures.....	39
Figure 7 Effect of ulvöspinel content on titanomagnetite saturation moment.....	40
Figure 8 Phase relations for the FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> system in air.....	42
Figure 9 T-fO <sub>2</sub> for coexisting magnetite-ilmenite solid solution pairs.....	43
Figure 10 Oxygen isobars in the FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> system.....	44
Figure 11 Oxygen isobars in the FeO - Fe <sub>2</sub> O <sub>3</sub> - TiO <sub>2</sub> system.....	45
Figure 12 One-eighth of the magnetite unit cell.....	47
Figure 13 Effect of ulvöspinel content on the magnetite cell lattice parameter.....	48
Figure 14 Variation in the magnetite lattice parameter with ulvöspinel content and oxidation.....	49

Figure 15	Sample preparation furnace.....	52
Figure 16	Gas-mixing apparatus.....	56
Figure 17	Flammability limits of H <sub>2</sub> - N <sub>2</sub> - O <sub>2</sub> mixtures.....	57
Figure 18	The system CaO-FeO-SiO <sub>2</sub> in equilibrium with metallic iron.....	62
Figure 19	The system CaO-FeO-SiO <sub>2</sub> in equilibrium with air.....	63
Figure 20	Theoretical effect of temperature on the rate of homogeneous nucleation and crystal growth in a viscous liquid.....	66
Figure 21	Ideal heat-treating profile.....	67
Figure 22	Sample 004 grain diameter distribution.....	76
Figure 23	Sample 004 grain volume distribution.....	77
Figure 24	Sample 006 grain diameter distribution.....	78
Figure 25	Sample 006 grain volume distribution.....	79
Figure 26	Sample 023 grain diameter distribution.....	80
Figure 27	Sample 023 grain volume distribution.....	81
Figure 28	Sample 001 grain diameter distribution.....	82
Figure 29	Sample 001 grain volume distribution.....	83
Figure 30	Sample 012 grain diameter distribution.....	84
Figure 31	Sample 012 grain volume distribution.....	85
Figure 32	Sample 018 grain diameter distribution.....	86
Figure 33	Sample 018 grain volume distribution.....	87
Figure 34	Sample IRM acquisition curves.....	92

Figure 35 High-temperature IRM acquisition, Sample 004.....	94
Figure 36 High-temperature IRM acquisition, Sample 006.....	95
Figure 37 High-temperature IRM acquisition, Sample 023.....	96
Figure 38 High-temperature IRM acquisition, Sample 001.....	97
Figure 39 High-temperature IRM acquisition, Sample 012.....	98
Figure 41 Sample 004 30 mT HT-IRM demagnetizations.....	100
Figure 42 Sample 004 3 mT HT-IRM demagnetizations.....	101
Figure 43 Sample 004 300 $\mu$ T HT-IRM demagnetizations.....	102
Figure 44 Sample 006 30 mT HT-IRM demagnetizations.....	103
Figure 45 Sample 006 3 mT HT-IRM demagnetizations.....	104
Figure 46 Sample 006 300 $\mu$ T HT-IRM demagnetizations.....	105
Figure 47 Sample 023 30 mT HT-IRM demagnetizations.....	106
Figure 48 Sample 023 3 mT HT-IRM demagnetizations.....	107
Figure 49 Sample 023 300 $\mu$ T HT-IRM demagnetizations.....	108
Figure 50 Sample 001 30 mT HT-IRM demagnetizations.....	109
Figure 51 Sample 001 3 mT HT-IRM demagnetizations.....	110
Figure 52 Sample 001 300 $\mu$ T HT-IRM demagnetizations.....	111
Figure 53 Sample 012 30 mT HT-IRM demagnetizations.....	112
Figure 54 Sample 012 3 mT HT-IRM demagnetizations.....	113
Figure 55 Sample 012 300 $\mu$ T HT-IRM demagnetizations.....	114
Figure 56 Sample 018 30 mT HT-IRM demagnetizations.....	115
Figure 57 Sample 018 3 mT HT-IRM demagnetizations.....	116

Figure 57	Sample 018 300 $\mu$ T HT-IRM demagnetizations.....	117
Figure 59	Normalized saturation magnetization versus applied field.....	121
Figure 60	Normalized retentivity versus applied field.....	122
Figure 61	Coercivity versus applied field.....	123
Figure 62	Hysteresis data.....	124
Figure 63	TRM furnace construction.....	127
Figure 64	Sample capsule.....	128
Figure 65	Typical residual field in TRM furnace as a function of height.....	131
Figure 66a	Comparison of duplicate 30 mT TRM acquisition runs.....	135
Figure 67a	Comparison of duplicate 30 mT 550-525 $^{\circ}$ C PTRM acquisition runs.....	137
Figure 68	Sample 004 TRM acquisition versus applied field.....	143
Figure 69	Sample 004 AF demagnetization of TRMs.....	144
Figure 70	Sample 004 differential AF demagnetization of TRMs.....	145
Figure 71	Sample 006 TRM acquisition versus applied field.....	146
Figure 72	Sample 006 AF demagnetization of TRMs.....	147
Figure 73	Sample 006 differential AF demagnetization of TRMs.....	148
Figure 74	Sample 023 TRM acquisition versus applied field.....	149
Figure 75	Sample 023 AF demagnetization of TRMs.....	150
Figure 76	Sample 023 differential AF demagnetization of TRMs.....	151
Figure 77	Sample 001 TRM acquisition versus applied field.....	152
Figure 78	Sample 001 AF demagnetization of TRMs.....	153

Figure 79	Sample 001 differential AF demagnetization of TRMs.....	154
Figure 80	Sample 012 TRM acquisition versus applied field.....	155
Figure 81	Sample 012 AF demagnetization of TRMs.....	156
Figure 82	Sample 012 differential AF demagnetization of TRMs.....	157
Figure 83	Sample 018 TRM acquisition versus applied field.....	158
Figure 84	Sample 018 AF demagnetization of TRMs.....	159
Figure 85	Sample 018 differential AF demagnetization of TRMs.....	160
Figure 86	Sample 004 Schmidt-Néel model fit.....	161
Figure 87	Sample 006 Schmidt-Néel model fit.....	162
Figure 88	Sample 023 Schmidt-Néel model fit.....	163
Figure 89	Sample 001 Schmidt-Néel model fit.....	164
Figure 90	Sample 012 Schmidt-Néel model fit.....	165
Figure 91	Sample 018 Schmidt-Néel model fit.....	166
Figure 92	Zijderfeld plot of a valid PTRM run.....	169
Figure 93	Zijderfeld plot of an intermediate-quality PTRM run.....	170
Figure 94	Zijderfeld plot of an invalid PTRM run.....	171
Figure 95	Sample 004 additivity of partial TRMs.....	201
Figure 96	Sample 006 additivity of partial TRMs.....	202
Figure 97	Sample 023 additivity of partial TRMs.....	203
Figure 98	Sample 001 additivity of partial TRMs.....	204
Figure 99	Sample 012 additivity of partial TRMs.....	205
Figure 100	Sample 018 additivity of partial TRMs.....	206



Figure 101	Shift in blocking temperature with increase in applied field, Sample 004.....	207
Figure 102	Shift in blocking temperature with increase in applied field, Sample 006.....	208
Figure 103	Shift in blocking temperature with increase in applied field, Sample 023.....	209
Figure 104	Shift in blocking temperature with increase in applied field, Sample 001.....	210
Figure 105	Shift in blocking temperature with increase in applied field, Sample 012.....	211
Figure 106	Shift in blocking temperature with increase in applied field, Sample 018.....	212
Figure 107	Sample 004 30 mT PTRM demagnetizations.....	213
Figure 108	Sample 004 3 mT PTRM demagnetizations.....	214
Figure 109	Sample 004 300 $\mu$ T PTRM demagnetizations.....	215
Figure 110	Sample 004 30 $\mu$ T PTRM demagnetizations.....	216
Figure 111	Sample 006 30 mT PTRM demagnetizations.....	217
Figure 112	Sample 006 3 mT PTRM demagnetizations.....	218
Figure 113	Sample 006 300 $\mu$ T PTRM demagnetizations.....	219
Figure 114	Sample 006 30 $\mu$ T PTRM demagnetizations.....	220
Figure 115	Sample 023 30 mT PTRM demagnetizations.....	221
Figure 116	Sample 023 3 mT PTRM demagnetizations.....	222
Figure 117	Sample 023 300 $\mu$ T PTRM demagnetizations.....	223
Figure 118	Sample 023 30 $\mu$ T PTRM demagnetizations.....	224

Figure 119	Sample 001 30 mT PTRM demagnetizations.....	225
Figure 120	Sample 001 3 mT PTRM demagnetizations.....	226
Figure 121	Sample 001 300 $\mu$ T PTRM demagnetizations.....	227
Figure 122	Sample 001 30 $\mu$ T PTRM demagnetizations.....	228
Figure 123	Sample 012 30 mT PTRM demagnetizations.....	229
Figure 124	Sample 012 3 mT PTRM demagnetizations.....	230
Figure 125	Sample 012 300 $\mu$ T PTRM demagnetizations.....	231
Figure 126	Sample 012 30 $\mu$ T PTRM demagnetizations.....	232
Figure 127	Sample 018 30 mT PTRM demagnetizations.....	233
Figure 128	Sample 018 3 mT PTRM demagnetizations.....	234
Figure 129	Sample 018 300 $\mu$ T PTRM demagnetizations.....	235
Figure 130	Sample 018 30 $\mu$ T PTRM demagnetizations.....	236
Figure 131	Thermal demagnetization of a partial TRM.....	244
Figure A.1	Sample 004, 50 mT hysteresis loop.....	507
Figure A.2	Sample 004, 100 mT hysteresis loop.....	508
Figure A.3	Sample 004, 150 mT hysteresis loop.....	509
Figure A.4	Sample 004, 200 mT hysteresis loop.....	510
Figure A.5	Sample 004, 250 mT hysteresis loop.....	511
Figure A.6	Sample 004, 500 mT hysteresis loop.....	512
Figure A.7	Sample 006, 50 mT hysteresis loop.....	513
Figure A.8	Sample 006, 100 mT hysteresis loop.....	514
Figure A.9	Sample 006, 150 mT hysteresis loop.....	515

Figure A.10	Sample 006, 200 mT hysteresis loop.....	516
Figure A.11	Sample 006, 250 mT hysteresis loop.....	517
Figure A.12	Sample 006, 500 mT hysteresis loop.....	518
Figure A.13	Sample 023, 50 mT hysteresis loop.....	519
Figure A.14	Sample 023, 100 mT hysteresis loop.....	520
Figure A.15	Sample 023, 150 mT hysteresis loop.....	521
Figure A.16	Sample 023, 200 mT hysteresis loop.....	522
Figure A.17	Sample 023, 250 mT hysteresis loop.....	523
Figure A.18	Sample 023, 500 mT hysteresis loop.....	524
Figure A.19	Sample 012, 50 mT hysteresis loop.....	525
Figure A.20	Sample 012, 100 mT hysteresis loop.....	526
Figure A.21	Sample 012, 150 mT hysteresis loop.....	527
Figure A.22	Sample 012, 200 mT hysteresis loop.....	528
Figure A.23	Sample 012, 250 mT hysteresis loop.....	529
Figure A.24	Sample 012, 500 mT hysteresis loop.....	530
Figure A.25	Sample 018, 50 mT hysteresis loop.....	531
Figure A.26	Sample 018, 100 mT hysteresis loop.....	532
Figure A.27	Sample 018, 150 mT hysteresis loop.....	533
Figure A.28	Sample 018, 200 mT hysteresis loop.....	534
Figure A.29	Sample 018, 250 mT hysteresis loop.....	535
Figure A.30	Sample 018, 500 mT hysteresis loop.....	536
Figure E1.1	Standard orientation for an octahedral grain.....	603

Figure E1.2 Top view of an octahedral grain.....	604
Figure F.2-1 Furnace top cap construction.....	640
Figure G.1 Sample 004 before magnetic experiments.....	644
Figure G.2 Sample 004 after magnetic experiments.....	645
Figure G.3 Sample 006 before magnetic experiments.....	646
Figure G.4 Sample 006 after magnetic experiments.....	647
Figure G.5 Sample 023 before magnetic experiments.....	648
Figure G.6 Sample 023 after magnetic experiments.....	649
Figure G.7 Sample 001 before magnetic experiments.....	650
Figure G.8 Sample 001 after magnetic experiments.....	651
Figure G.9 Sample 012 before magnetic experiments.....	652
Figure G.10 Sample 012 after magnetic experiments.....	653
Figure G.11 Sample 018 before magnetic experiments.....	654
Figure G.12 Sample 018 after magnetic experiments.....	655

## LIST OF TABLES

Table 1	Mean grain sizes before and after experiments.....	75
Table 2	Hysteresis data.....	120
Table 3	Temperature Reproducibility Estimated From the 3 mT, 550-525 °C PTRM Replicate Runs.....	174
Table 4	Temperature Reproducibility Estimated From the 2 mT, 560-555 °C PTRM Replicate Runs.....	174
Table 5	Sample 004 additivity of PTRMs, 30 mT case.....	177
Table 6	Sample 004 additivity of PTRMs, 3 mT case.....	178
Table 7	Sample 004 additivity of PTRMs, 300 $\mu$ T case.....	179
Table 8	Sample 004 additivity of PTRMs, 30 $\mu$ T case.....	180
Table 9	Sample 006 additivity of PTRMs, 30 mT case.....	181
Table 10	Sample 006 additivity of PTRMs, 3 mT case.....	182
Table 11	Sample 006 additivity of PTRMs, 300 $\mu$ T case.....	183
Table 12	Sample 006 additivity of PTRMs, 30 $\mu$ T case.....	184
Table 13	Sample 023 additivity of PTRMs, 30 mT case.....	185
Table 14	Sample 023 additivity of PTRMs, 3 mT case.....	186
Table 15	Sample 023 additivity of PTRMs, 300 $\mu$ T case.....	187
Table 16	Sample 023 additivity of PTRMs, 30 $\mu$ T case.....	188

Table 17	Sample 001 additivity of PTRMs, 30 mT case.....	189
Table 18	Sample 001 additivity of PTRMs, 3 mT case.....	190
Table 19	Sample 001 additivity of PTRMs, 300 $\mu$ T case.....	191
Table 20	Sample 001 additivity of PTRMs, 30 $\mu$ T case.....	192
Table 21	Sample 012 additivity of PTRMs, 30 mT case.....	193
Table 22	Sample 012 additivity of PTRMs, 3 mT case.....	194
Table 23	Sample 012 additivity of PTRMs, 300 $\mu$ T case.....	195
Table 24	Sample 012 additivity of PTRMs, 30 $\mu$ T case.....	196
Table 25	Sample 018 additivity of PTRMs, 30 mT case.....	197
Table 26	Sample 018 additivity of PTRMs, 3 mT case.....	198
Table 27	Sample 018 additivity of PTRMs, 300 $\mu$ T case.....	199
Table 28	Sample 018 additivity of PTRMs, 30 $\mu$ T case.....	200
Table A.1	Sample 001 preparation and characterization.....	248
Table A.2	Sample 002 preparation and characterization.....	256
Table A.3	Sample 003 preparation and characterization.....	267
Table A.4	Sample 004 preparation and characterization.....	272
Table A.5	Sample 005 preparation and characterization.....	280
Table A.6	Sample 006 preparation and characterization.....	291
Table A.7	Sample 007 preparation and characterization.....	302
Table A.8	Sample 008 preparation and characterization.....	310
Table A.9	Sample 009 preparation and characterization.....	312
Table A.10	Sample 010 preparation and characterization.....	317

Table A.11	Sample 011 preparation and characterization.....	322
Table A.12	Sample 012 preparation and characterization.....	327
Table A.13	Sample 013 preparation and characterization.....	336
Table A.14	Sample 014 preparation and characterization.....	341
Table A.15	Sample 015 preparation and characterization.....	346
Table A.16	Sample 016 preparation and characterization.....	351
Table A.17	Sample 017 preparation and characterization.....	356
Table A.18	Sample 018 preparation and characterization.....	361
Table A.19	Sample 019 preparation and characterization.....	369
Table A.20	Sample 020 preparation and characterization.....	375
Table A.21	Sample 021 preparation and characterization.....	386
Table A.22	Sample 022 preparation and characterization.....	397
Table A.23	Sample 023 preparation and characterization.....	398
Table A.24	Sample 024 preparation and characterization.....	406
Table A.25	Total TRM, applied field = 0 T.....	412
Table A.26	Total TRM, applied field = 10 $\mu$ T.....	413
Table A.27	Total TRM, applied field = 20 $\mu$ T.....	414
Table A.28	Total TRM, applied field = 30 $\mu$ T.....	415
Table A.29	Total TRM, applied field = 40 $\mu$ T.....	416
Table A.30	Total TRM, applied field = 65 $\mu$ T.....	417
Table A.31	Total TRM, applied field = 100 $\mu$ T.....	418
Table A.32	Total TRM, applied field = 200 $\mu$ T.....	419

Table A.33 Total TRM, applied field = 300 $\mu$ T.....	420
Table A.34 Total TRM, applied field = 400 $\mu$ T.....	421
Table A.35 Total TRM, applied field = 650 $\mu$ T.....	422
Table A.36 Total TRM, applied field = 1 mT.....	423
Table A.37 Total TRM, applied field = 2 mT.....	424
Table A.38 Total TRM, applied field = 3 mT.....	425
Table A.39 Total TRM, applied field = 4 mT.....	426
Table A.40 Total TRM, applied field = 6.5 mT.....	427
Table A.41 Total TRM, applied field = 10 mT.....	428
Table A.42 Total TRM, applied field = 20 mT.....	429
Table A.43 Total TRM, applied field = 30 mT.....	430
Table A.44 Total TRM, applied field = 30 mT (Replicate).....	431
Table A.45 Partial TRM, 590-570 $^{\circ}$ C, applied field = 30 $\mu$ T.....	434
Table A.46 Partial TRM, 570-550 $^{\circ}$ C, applied field = 30 $\mu$ T.....	435
Table A.47 Partial TRM, 550-525 $^{\circ}$ C, applied field = 30 $\mu$ T.....	436
Table A.48 Partial TRM, 525-500 $^{\circ}$ C, applied field = 30 $\mu$ T.....	437
Table A.49 Partial TRM, 500-450 $^{\circ}$ C, applied field = 30 $\mu$ T.....	438
Table A.50 Partial TRM, 450-350 $^{\circ}$ C, applied field = 30 $\mu$ T.....	439
Table A.51 Partial TRM, 350-200 $^{\circ}$ C, applied field = 30 $\mu$ T.....	440
Table A.52 Partial TRM, 200-25 $^{\circ}$ C, applied field = 30 $\mu$ T.....	441
Table A.53 Partial TRM, 590-570 $^{\circ}$ C, applied field = 300 $\mu$ T.....	442
Table A.54 Partial TRM, 570-550 $^{\circ}$ C, applied field = 300 $\mu$ T.....	443



Table A.55	Partial TRM, 550-525 °C, applied field = 300 μT.....	444
Table A.56	Partial TRM, 525-500 °C, applied field = 300 μT.....	445
Table A.57	Partial TRM, 500-450 °C, applied field = 300 μT.....	446
Table A.58	Partial TRM, 450-350 °C, applied field = 300 μT.....	447
Table A.59	Partial TRM, 350-200 °C, applied field = 300 μT.....	448
Table A.60	Partial TRM, 200-25 °C, applied field = 300 μT.....	449
Table A.61	Partial TRM, 590-570 °C, applied field = 3 mT.....	450
Table A.62	Partial TRM, 570-550 °C, applied field = 3 mT.....	451
Table A.63	Partial TRM, 550-525 °C, applied field = 3 mT.....	452
Table A.64	Partial TRM, 525-500 °C, applied field = 3 mT.....	453
Table A.65	Partial TRM, 500-450 °C, applied field = 3 mT.....	454
Table A.66	Partial TRM, 450-350 °C, applied field = 3 mT.....	455
Table A.67	Partial TRM, 350-200 °C, applied field = 3 mT.....	456
Table A.68	Partial TRM, 200-25 °C, applied field = 3 mT.....	457
Table A.69	Partial TRM, 590-570 °C, applied field = 30 mT.....	458
Table A.70	Partial TRM, 570-550 °C, applied field = 30 mT.....	459
Table A.71	Partial TRM, 550-525 °C, applied field = 30 mT.....	460
Table A.72	Partial TRM, 550-525 °C, applied field = 30 mT (replicate).....	461
Table A.73	Partial TRM, 525-500 °C, applied field = 30 mT.....	462
Table A.74	Partial TRM, 500-450 °C, applied field = 30 mT.....	463
Table A.75	Partial TRM, 450-350 °C, applied field = 30 mT.....	464
Table A.76	Partial TRM, 350-200 °C, applied field = 30 mT.....	465

Table A.77	Partial TRM, 200-25 °C, applied field = 30 mT.....	466
Table A.78	Saturation IRM, 25 °C, applied field = 1 T.....	469
Table A.79	High-temperature IRM, 590 °C, applied field = 300 μT.....	471
Table A.80	High-temperature IRM, 570 °C, applied field = 300 μT.....	472
Table A.81	High-temperature IRM, 550 °C, applied field = 300 μT.....	473
Table A.82	High-temperature IRM, 525 °C, applied field = 300 μT.....	474
Table A.83	High-temperature IRM, 500 °C, applied field = 300 μT.....	475
Table A.84	High-temperature IRM, 450 °C, applied field = 300 μT.....	476
Table A.85	High-temperature IRM, 350 °C, applied field = 300 μT.....	477
Table A.86	High-temperature IRM, 200 °C, applied field = 300 μT.....	478
Table A.87	High-temperature IRM, 605 °C, applied field = 3 mT.....	479
Table A.88	High-temperature IRM, 590 °C, applied field = 3 mT.....	480
Table A.89	High-temperature IRM, 570 °C, applied field = 3 mT.....	481
Table A.90	High-temperature IRM, 550 °C, applied field = 3 mT.....	482
Table A.91	High-temperature IRM, 525 °C, applied field = 3 mT.....	483
Table A.92	High-temperature IRM, 500 °C, applied field = 3 mT.....	484
Table A.93	High-temperature IRM, 450 °C, applied field = 3 mT.....	485
Table A.94	High-temperature IRM, 350 °C, applied field = 3 mT.....	486
Table A.95	High-temperature IRM, 200 °C, applied field = 3 mT.....	487
Table A.96	Room-temperature IRM, 25 °C, applied field = 3 mT.....	488
Table A.97	High-temperature IRM, 590 °C, applied field = 30 mT.....	489
Table A.98	High-temperature IRM, 570 °C, applied field = 30 mT.....	490

Table A.99 High-temperature IRM, 550 °C, applied field = 30 mT.....	491
Table A.100 High-temperature IRM, 525 °C, applied field = 30 mT.....	492
Table A.101 High-temperature IRM, 500 °C, applied field = 30 mT.....	493
Table A.102 High-temperature IRM, 450 °C, applied field = 30 mT.....	494
Table A.103 High-temperature IRM, 350 °C, applied field = 30 mT.....	495
Table A.104 High-temperature IRM, 200 °C, applied field = 30 mT.....	496
Table A.105 Room-temperature IRM, 25 °C, applied field = 30 mT.....	497
Table A.106 Partial TRM, 560-555 °C applied field = 2 mT.....	500
Table A.107 Partial TRM, 560-555 °C applied field = 2 mT.....	501
Table A.108 Possible Magnetometer Errors.....	503
Table A.109 Sample 001 Grain Size Distribution.....	538
Table A.110 Sample 004 Grain Size Distribution.....	541
Table A.111 Sample 006 Grain Size Distribution.....	544
Table A.112 Sample 012 Grain Size Distribution.....	547
Table A.113 Sample 018 Grain Size Distribution.....	550
Table A.114 Sample 023 Grain Size Distribution.....	553
Table C.1 Orifice C-1 calibration.....	588
Table C.2 Orifice H-10 calibration.....	589
Table C.3 Orifice H-11 calibration.....	590
Table C.4 Sample versus heater chamber temperatures.....	592
Table C.5 Thermocouple cross-calibration.....	593
Table C.6 TRM furnace field coil calibration.....	595

Table D.1 Unit conversions.....	598
Table E.1 FORTRAN routine for fitting data.....	612
Table E.2 Input data for Schmidt-Neél fit calculations.....	615
Table E.3 Schmidt-Neél fit results.....	616
Table F.1 Thermocouple characteristics.....	637

## LIST OF SYMBOLS

Symbol	Units	Description
<i>A</i>	$\text{kg m}^{-1} \text{A}^{-1} \text{s}^{-2}$	Constant in §3.2
<i>B</i>	$\text{kg m}^{-1} \text{s}^{-2}$	Constant in §3.2
<i>C</i>	$\text{s}^{-1}$	Frequency factor
<i>D</i>	$\text{kg m}^{-3} \text{s}^{-2}$	Constant in §3.2
<i>D</i>	-	Demagnetizing factor
<i>d</i>	m	Effective grain diameter
<i>E</i>	$\text{J} = \text{kg m}^2 \text{s}^{-2}$	Energy
<i>F</i>	-	Constant in §3.2.2
<i>H</i>	$\text{A m}^{-1}$	Magnetic field strength
<i>I</i>	A	Current
<i>J</i>	$\text{T} = \text{kg m}^2 \text{s}^{-2}$	Magnetic polarization ( <u>not</u> current density)
<i>K</i>	(as required)	Constant, as required, see text
<i>k</i>	$\text{J K}^{-1} = \text{kg m}^2 \text{K}^{-1} \text{s}^{-2}$	Boltzmann constant, $1.38 \times 10^{-23} \text{ J K}^{-1}$
<i>L</i>	m	Grain length in §3.2

<b>Symbol</b>	<b>Units</b>	<b>Description</b>
$L(x)$	-	Langevin function, $L(x) = \coth(x) - \frac{1}{x}$
$m(T)$	-	Reduced magnetization $m(T) = \frac{M_s(T)}{M_s(0)}$
$m$	$A\ m^2$	Magnetic dipole moment
$M$	$A\ m^{-1}$	Magnetization
$M_s$	$A\ m^{-1}$	Saturation magnetization
$p$	-	Exponent in §3.2
$q$	(as required)	Constant, as required, see text
$T$	K	Temperature
$T_c$	K	Curie temperature
$T_b$	K	Blocking temperature
$v$	$m^3$	Grain volume
$x$	m	Wall position in §3.2
$Z$	-	Partition function
$h$	m	Manometer height difference
	m	Defect spacing
	$s^{-1}$	Time constant
$(0, )$	$s^{-1}$	Alignment time constant in §3.1
$(, 0)$	$s^{-1}$	Misalignment time constant in §3.1

<b>Symbol</b>	<b>Units</b>	<b>Description</b>
$\mu_0$	$\text{H m}^{-1} = \text{kg m A}^{-2} \text{s}^{-2}$	Permeability of free space, $4 \times 10^{-7} \text{ H m}^{-1}$
	$\text{m}^3 \text{s}^{-1}$	Flow
a	(subscript)	Ambient (room) temperature
b	(subscript)	Blocking temperature
c	(subscript)	Curie temperature
s	(subscript)	Saturation
THB	(subscript)	Thermal-activation blocking
ub	(subscript)	Unblocking temperature

## 1.0 INTRODUCTION

Paleomagnetism occupies a unique position among geophysical techniques due to the ability of certain rocks to preserve a record of the local Earth's magnetic field throughout geologic times. Initially even first-order interpretations of the paleomagnetic record were significant, as evidenced by the substantial support paleomagnetism provided for plate tectonic theory. More recently, paleomagnetic studies have pushed toward obtaining higher temporal and spatial resolution. The success of these efforts is critically dependent on an understanding of the remanent mechanisms operating in rocks, and in particular on the mechanism of thermoremanent magnetization (TRM), which is the principal source of remanence in igneous rocks and a likely source for the original magnetization in detrital grains in sedimentary rocks.

A rigorous theory of TRM based on first principles appears to be presently unattainable. The accepted quantum mechanical model for ferromagnetism involves a primitive cubic array of atoms with an electron spin of  $s=\pm 1/2$  associated with each lattice site [Pathria, 1972]. Although the mathematical model [Heisenberg, 1928] is widely known, solutions have only been obtained for the Ising approximation in the one-dimensional [Ising, 1925] and the field free two-dimensional [Onsager, 1944] cases. Topological considerations [Kac and Ward, 1952] argue against obtaining three-dimensional solutions to the Ising problem by similar techniques. Considering physicists' failure to solve the Ising model despite six decades of trying, there is little reason to expect a



rigorous description of TRM in real materials at any time in the immediate future.

Practical TRM theories have taken a less rigorous approach. These theories can be divided into two categories. The classical approach involves developing simple analytical models of idealized magnetic particles. Néel's two classic papers on single-domain (SD) [Néel 1949] and multidomain (MD) [Néel, 1955] magnetic grains form the starting point for most of these studies. More recent studies have invoked an intermediate "pseudo-single-domain" (PSD) grain behavior to explain the continuity of experimentally measured parameters across the predicted SD-MD boundary, but to date these efforts have been inconclusive. Some of the competing explanations for pseudo-single domain mechanisms are:

1. Barkhausen discreteness of domain wall motions [Stacey, 1962]
2. surface domains [Stacey and Banerjee, 1974; Banerjee, 1977; Moskowitz and Banerjee, 1979]
3. domain wall moments with SD-like properties [Dunlop, 1977]
4. moments pinned by stress fields of dislocations [Verhoogen, 1959; Ozima and Ozima, 1965]
5. expected MD-size grains in metastable SD or SD-like states [Halgedahl and Fuller, 1980, 1983]
6. intrinsic SD-like properties of small MD grains [Fuller, 1984]

The TRM mechanism for SD grains is fairly well understood in terms of Néel's SD model, though some discrepancies remain. The agreement between experiment and the available Néel domain wall motion theories for MD grains is much less satisfactory, particularly for the small MD grains which in practice dominate the TRM of so many rocks. To date, explanations of the discrepancies have been less than satisfactory. Previous work indicates that Néel-type models of TRM are qualitatively useful but quantitatively

inaccurate. This study investigates the details of how Néel-type theories of MD TRM are violated for high quality synthetic magnetites produced by the glass-ceramic method of Worm and Markert [1987b].

Numerous studies have examined magnetic properties of titanomagnetite particles in the SD, PSD, and small MD size range. Most of these studies were hampered by the difficulties involved in preparing uniform samples for study. Recently a glass-ceramic technique has been developed which provides well-dispersed titanomagnetite particles in a silicate matrix [Worm and Markert, 1987b]. Worm [1986] reports he has used samples prepared in this manner to verify Néel's SD theory. This study produced samples by this glass-ceramic method, then proceeded to magnetically characterize the samples with the intent of carefully understanding the details of how the MD Néel models are violated, thus providing guidance for modifying the Néel-type MD models.

Néel-type MD theories are based on domain wall motion only, and usually on that of only a single wall. They omit the demonstrable influence of domain wall nucleation [Boyd et al., 1984]. Theories incorporating domain wall nucleation have been proposed [Moon, 1985], but currently are formulated in a micromagnetic approach requiring extensive numerical calculation. A very simple demonstration of the inadequacy of Néel-type theories is that they predict that for MD particles TRM acquired in a strong field is more stable with respect to AF demagnetization than TRM acquired by the same sample in a weak field [Schmidt, 1976], whereas the converse is experimentally observed in small MD particles. This has been partially, but not fully, resolved by considering the interaction effects between walls when more than one wall is present [Schmidt, 1975], and by taking into account demagnetizing field effects [Bailey and Dunlop, 1983].

There is a need for a simpler model which incorporates domain wall nucleation without requiring the extensive calculations involved in the micromagnetic approach. One immediate suggestion is incorporating a potential barrier against nucleation into a Néel-type model such as Schmidt's

[1973], while introducing assemblages of different grains that may or may not contain walls. Another approach would allow multiple interacting walls in one grain, with nucleation effects determining the number. Clearly, experimental results are needed as a guide in the construction of such models.

It is generally understood that synthetic materials can provide simpler systems for theoretical modeling than natural titanomagnetites. Natural titanomagnetites are often both nonstoichiometric and impure. Most natural titanomagnetites do not lie upon the ulvöspinel-magnetite join, but are slightly oxidized towards the ilmenite-magnetite join [Nagata, 1961].  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$  and other cations are known to substitute for  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$ . Although numerous authors have investigated the effects of oxidation [Readman and O'Reilly, 1970; Ozima and Sakamoto, 1971; Rahman and Parry, 1978] and cation substitution [Özdemir and O'Reilly, 1978; Richards et al., 1973], natural systems still provide too many complications for convenient theoretical treatment and too much variability for comparison of results with theory. Synthetic materials can provide samples with fewer variations in composition and grain size distribution, and hence are more amenable to theoretical treatment.

Synthetic samples have been prepared by several methods:

1. Hydrothermal method [Lindsley, 1962; Pucher, 1969]
2. Grinding sintered titanomagnetites and dispersing sieved fragments in a nonmagnetic matrix [Day, 1977; Clauter, 1979]
3. Aqueous precipitation [Dunlop, 1973; Clauter, 1979]
4. Bridgman method [Syono, 1965; Hauptman and Stephenson, 1968]
5. Flux method [Hauptman et al., 1973]
6. Glass-ceramic method [Worm and Markert, 1987a]

The study samples were produced by the glass-ceramic method. The synthesis procedure consists of melting a mixture of oxides/carbonates of Ca, K, Na, Si, Fe and Ti under a controlled reducing atmosphere, then quenching the melt to a glass. Two heat treatment steps under controlled atmosphere allow nucleation and growth of titanomagnetite crystals respectively, and are followed by a final quench.

The glass-ceramic method has several advantages. First, it is amenable to crystal growth in a controlled atmosphere, and hence stoichiometry can be controlled. The resulting titanomagnetite crystals are dispersed throughout a magnetically inert matrix, minimizing the effects of intergrain interactions. The matrix acts as a barrier to oxygen, thus protecting the titanomagnetite crystals from chemical alteration. Crystals are easily produced in the grain sizes corresponding to the SD through MD transition. The heat treatment process allows one to maintain relatively close control over the size distribution for a wide range of crystal sizes. Stresses in the resulting crystals are less than those introduced by methods involving sample grinding. These advantages are illustrated by the first published results using the glass-ceramic titanomagnetites, where SD and MD hysteresis results disagree with previous studies, yet were found to be in better agreement with theory [Worm and Markert, 1987a].

Initially I proposed working with various-sized grains of a single titanomagnetite composition. I originally planned to use a moderately high-titanium titanomagnetite (approximately  $\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$ ) with a fairly low Curie temperature of  $\sim 200$  °C, thus reducing the probability of chemical alteration during the TRM experiments. Comments received during the NSF review of the research grant proposal, conversations with Dr. Worm, and the possibility of magnetite/ulvöspinel exsolution complicating the results convinced me to work with magnetite instead.

The heating and cooling for the TRM studies was performed in the TRM furnace built and described by Clauter [1979]. Although the TRM furnace is equipped for maintaining a controlled atmosphere and this feature was used

in this study, the process requires careful attention and is somewhat of a nuisance. Since I did not need to exceed the Curie temperature by much in these experiments, I could not rely on using equilibrium atmospheres to prevent sample oxidation since equilibration is unlikely to occur at such low temperatures. I tried to eliminating chemical change in the samples during the magnetic experiments by isolating the samples from the atmosphere. The method I chose was to seal the samples in evacuated quartz tubes to minimize the probability of chemical alteration and to provide self-buffering. The samples were then thermally cycled from room temperature to beyond their Curie temperature until their magnetic properties stabilized. The sample preparation furnace was used because the electronic temperature controller was easily programmed to automate the desired temperature cycling process.

An original fragment of each sample was preserved for comparison to determine the extent of chemical alteration during the thermal cycling process, and the characterization process was repeated after the magnetic experiments were completed to determine the extent and nature of any changes. The synthesized magnetites were characterized by x-ray diffraction, SEM, and electron microprobe. Magnetic hysteresis properties were measured on Material Engineering's vibrating sample magnetometer equipped with a temperature controlled sample holder. Isothermal remanent magnetization (IRM) curves were measured using the Paleomagnetism Laboratory's spinner magnetometer, while TRM, partial TRM (PTRM), and additional IRM properties were measured in the Paleomagnetism Laboratory's cryogenic magnetometer.

## 2.0 STATEMENT OF PROBLEM

Two classic experiments were performed. The first was to measure TRM acquisition versus the strength of an externally applied field. The second was to measure the shift in blocking temperature versus applied field by making a series of PTRM measurements. The first reaction of the reader may well be that this appears to be a rather old-fashioned approach, and it is, at least in its initial stages. The problem with the newer theoretical models that are being used is that they have tended to a micromagnetic approach. While obviously desirable, they have the disadvantage of requiring detailed knowledge of grain size and shape. Also, at present they are not easily generalized to bulk properties, which is what one must work with in the laboratory.

The strength of the Néel models has always been their simplicity. They clearly err in the direction of being generalizations that are too broad, and the MD model in particular may be faulted as missing the mark entirely if, for instance, domain nucleation is a more important process than domain wall displacement, or if moments intrinsic to the domain structure such as wall moments are of overriding importance. What one needs are experimental results that show just which predictions of the old Néel models are correct and which are not, for the new class of glass-ceramic synthetic titanomagnetites.

In two early papers, Schmidt [1973, 1976] pointed out the critical role that the variation of blocking temperature plays in both the SD and MD Néel models. It is evident that the broad behavior demonstrated in the 1976 paper

of  $T_B(H)$  must in fact be operational. Only if  $T_B(H)$  decreases with increasing field  $H$  can one obtain the observed and universal rule that TRM approaches IRM in all its properties as  $H$  becomes large compared to microscopic coercivity. From this, it is easy to show that the MD Néel model predicts that unblocking should take place at a lower temperature than blocking. The formal argument is summarized in Section 3.2.

Worm et al.'s [1988] recent work shows that the synthetic glass-ceramic samples support the earlier work reported by Bolshakov and Shcherbakov [1979], which was carried out on traditionally prepared samples, in which a partial TRM acquired in a moderate temperature range is not demagnetized in zero field until a much higher temperature. This appears to fly in the face of the  $T_B(H)$  behavior just discussed, but may reflect instead complications that are not present in the basic Néel models, such as interactions between domain walls and nucleation effects.

Thus, one of the highest priorities was to repeat some of the experiments of Clauter [Clauter, 1979; Clauter and Schmidt, 1981] in which it was shown that the partial TRM spectrum did in fact shift to lower temperatures as the field  $H$  increases. Note that this is not the same experiment done by Worm et al. [1988], which tests the relation between blocking and unblocking temperatures, but directly tests the  $T_B(H)$  dependence. If Clauter's results are borne out in the synthetic samples, then there would be a basis for extending the original Néel MD model, based on the  $T_B(H)$  dependence, but searching for additional terms that would reverse the blocking-unblocking relation.

First, I made measurements of TRM acquisition versus applied field. Previous workers [Dunlop, 1975; Day, 1977] have reported power-law dependencies in TRM( $H$ ) acquisition curves, while Clauter [1979] failed to find such a dependence for carefully-sized synthetic samples. A problem in interpreting these results is that grain size and shape variation within each bulk sample tends to smear out the breaks between the three segments of the acquisition curve predicted by the Néel MD theory (low-field linear during thermal fluctuation blocking, approach to saturation in which the effect of the

demagnetizing field is dominant, and finally saturation). The relatively uniform sizes and shapes of the dispersed magnetite grains produced by the glass-ceramic method yield much clearer and more reliable results, perhaps at last settling in the negative a very old question as to whether these power-law segments are in fact real.

Second, I investigated the variation of the blocking temperatures versus applied field, along the lines used by Clauter and Schmidt [1981]. This was accomplished through a series of PTRM acquisitions. Worm et al. [1988] performed some thermal demagnetization of PTRMs as part of a viscous magnetization study, but their experiments were limited to low field strengths (0.05-0.5 mT) and included only a single PTRM temperature interval. This work included more complete PTRM study and provides valuable data on the effect of applied field on blocking and unblocking temperatures, and hence provides valuable insight on the TRM mechanism in small MD grains. To this end, the PTRM acquisition spectra were supplemented by alternating-field demagnetization curves for individual PTRMs as well as for total TRMs.

In each case past work has indicated violation of the quantitative predictions of Néel-type models; by carefully measuring these deviations I hoped to gain some insight into the mechanisms not considered in the Néel models. These are summarized in Sections 7 and 8.



### 3.0 REVIEW OF ROCK MAGNETIC THEORIES

#### 3.1 SD theories

##### 3.1.1 The Néel SD model

The TRM mechanism for small particles must treat the particles as a single domain, for the simple reason that there is insufficient room in a small particle for a domain wall to form. More precisely, formation of a domain wall in small particles carries an energy penalty that can not be offset by a corresponding reduction in magnetostatic energy. A domain wall can only form in grains that are large enough for the change in magnetostatic energy (which is roughly proportional to grain volume) to exceed the increase in exchange energy associated with wall motion (roughly proportional to grain diameter). For this reason, theories of SD behavior have been developed. These theories all consider uniformly magnetized grains, and attribute changes in bulk magnetization to changes in the distribution of the magnetization directions of the individual grains

Néel [1955] proposed a theory of SD TRM that explains the observed linear dependence of TRM on the applied field  $H$  for low fields. Noting that an explanation based on the coercive force  $H_c$  approaching zero as temperature approaches the Curie temperature  $T_c$  fails to account for any field dependence, he introduced a model where thermal agitation acted to demagnetize a grain if the temperature was high enough. Specifically, the remanent moment  $m(t)$  of an assemblage of identical grains will decay to zero exponentially with time  $t$  as

$$\tau(t) = \tau_0 e^{-\frac{t}{\tau}}. \quad (3.1.1-1)$$

The time constant  $\tau$  is given by

$$\tau = C^{-1} e^{\frac{v\mu_0 M_s(T)H_c(T)}{2kT}}, \quad (3.1.1-2)$$

where  $C$  is a constant on the order of  $10^{10} \text{ s}^{-1}$  whose form does not concern us here,  $v$  is the grain volume,  $H_c(T)$  is the microscopic coercive force at temperature  $T$ ,  $M_s(T)$  is the saturation magnetization, and  $k$  is Boltzmann's constant. In an applied field  $H$ , Néel derived two relaxation times  $\tau(0, H)$  and  $\tau(H, 0)$  for alignment and misalignment, respectively. These were given by

$$\tau(0, H) = C^{-1} \left[ 1 + \frac{H}{H_c(T)} \right] \left[ 1 - \frac{H^2}{H_c^2(T)} \right]^{\frac{1}{2}} e^{\frac{v\mu_0 M_s(T)(H_c(T) + H)^2}{2H_c(T)kT}} \quad (3.1.1-3)$$

and

$$\tau(H, 0) = C^{-1} \left[ 1 - \frac{H}{H_c(T)} \right] \left[ 1 - \frac{H^2}{H_c^2(T)} \right]^{\frac{1}{2}} e^{\frac{v\mu_0 M_s(T)(H_c(T) - H)^2}{2H_c(T)kT}}, \quad (3.1.1-4)$$

respectively, and the effective relaxation time constant for the assemblage is given by

$$\frac{1}{\tau} = \frac{1}{\tau(0, H)} + \frac{1}{\tau(H, 0)}. \quad (3.1.1-5)$$

The time constant's exponential dependence on temperature shows that there is a narrow temperature range over which the time constant changes from a large time at low temperature to a small time at high temperature. This motivates defining a blocking temperature  $T_b$ , and making the simplifying assumption that equilibration is reached instantaneously for  $T > T_b$ , while no relaxation occurs for  $T < T_b$ . In practice, the blocking temperature is defined by first selecting a blocking time  $\tau_b$  corresponding to

the time scale for the experiment in question. The blocking temperature is then defined as the temperature at which  $\tau = \tau_b$ .

Perhaps the simplest model of the field-dependence of TRM assumes an assemblage of identical, noninteracting SD particles where each grain has a uniaxial magnetic anisotropy aligned parallel to the applied field. The partition function  $Z$  for such an assemblage in equilibrium is

$$Z = e^{\frac{v\mu_0 M_s(T)H}{kT}} + e^{-\frac{v\mu_0 M_s(T)H}{kT}}, \quad (3.1.1-6)$$

and the average magnetization when  $T > T_b$  is given by

$$M(T) = \frac{1}{v\mu_0} kT \frac{\ln(Z)}{H} = M_s(T) \tanh \frac{v\mu_0 M_s(T)H}{kT}. \quad (3.1.1-7)$$

Below the blocking temperature, the relaxation time of the assemblage is long compared to the experiment, so the magnetization is assumed to be fixed at a value determined by past history. The TRM process fixes the past history in a manner that the TRM can be easily calculated. After heating to the Curie temperature and cooling in a weak field  $H$ , the TRM of an assemblage of such grains below the blocking temperature is given by

$$M_{\text{TRM}}(T) = M(T_b) \frac{M_s(T)}{M_s(T_b)} = M_s(T) \tanh \frac{v\mu_0 M_b(T_b)H}{kT_b}, \quad (3.1.1-8)$$

where  $M_b = M(T_b)$  and  $H(T_b)$  is written explicitly to emphasize that the TRM is caused by the applied field at the time the grains cool below their blocking temperature.

The preceding discussion neglects the blocking temperature's dependence on the applied field. In Néel's formulation, the variation in thermal relaxation time with applied field makes the blocking temperature a function of the applied field. Schmidt [1976] combined equations (3.1.1-3), (3.1.1-4), and (3.1.1-5) for  $T = T_b$  to give the following implicit formula for the blocking temperature:

$$M_b = \frac{2H_{C_b} kT_b}{v\mu_0 (H_{C_b} - H)^2} \ln \left[ \frac{1 - \frac{H^2}{H_{C_b}^2}}{1 - \frac{H}{H_{C_b}}} + 1 + \frac{H}{H_{C_b}} e^{-\frac{2v\mu_0 M_b H}{kT_b}} \right]. \quad (3.1.1-9)$$

This can be solved numerically for  $M_b(T)$  once the temperature dependence of  $H_C$  is known. Schmidt recommends using

$$H_{C_b} = KM_b^{q-1}, \quad (3.1.1-10)$$

where  $K$  is a constant in the range of 0 to 1 and  $q$  can be varied in the range of 2 to 10 to accommodate various types of magnetic anisotropy (e.g., shape, crystalline, and magnetostrictive). He recommends using a value close to 2 for the common case when shape anisotropy dominates. Substituting (3.1.1-10) into (3.1.1-9) allows one to numerically determine  $M_b$  and  $T_b$ , which are then substituted into (3.1.1-8) to give the TRM field dependence for SD grains.

Luce [1980] questioned the assumptions leading to (3.1.1-7). He preferred using the Langevin function as a starting point, rather than the hyperbolic tangent. The Langevin function  $L(x) = \coth(x) - x^{-1}$  arises when one considers a Boltzmann assemblage of uniaxial particles that may move and take any orientation with respect to the field. The partition function for this condition is given by

$$Z = \int_0^\pi e^{\frac{v\mu_0 M_s(T) H \cos(\theta)}{kT}} \sin(\theta) d\theta, \quad (3.1.1-11)$$

the corresponding average magnetization above the blocking temperature is given by

$$M(T) = \frac{1}{v\mu_0} kT \frac{\ln(Z)}{H} = M_s(T) L \left( \frac{v\mu_0 M_s(T) H}{kT} \right), \quad (3.1.1-12)$$

and the TRM is given by

$$M_{\text{TRM}}(T) = M(T_b) \frac{M_s(T)}{M_s(T_b)} = M_s(T) L \frac{v\mu_0 M_b H(T_b)}{kT_b} . \quad (3.1.1-13)$$

As before,  $M_b$  is given by (3.1.1-9) and  $T_b$  is calculated using (3.1.1-3), (3.1.1-4), and (3.1.1-5). Luce's reasons for preferring this model will be given after the next model is discussed.

Stacey and Banerjee [1976] introduced a model that accounted for a randomly-oriented distribution of identical noninteracting particles, each of which possessed a uniaxial magnetic anisotropy. The partition function for a particle aligned with the easy direction at angle  $\theta$  to the applied field is given by

$$Z = e^{\frac{v\mu_0 M_s(T) H \cos(\theta)}{kT}} + e^{-\frac{v\mu_0 M_s(T) H \cos(\theta)}{kT}} . \quad (3.1.1-14)$$

For these grains, the corresponding average magnetization above the blocking temperature is given by

$$M(T) = \frac{1}{v\mu_0} kT \frac{\ln(Z)}{H} = M_s(T) \cos(\theta) \tanh \frac{v\mu_0 M_s(T) H \cos(\theta)}{kT} . \quad (3.1.1-15)$$

Integrating over all orientations gives the average magnetization for all grains. The corresponding TRM is given by

$$M_{\text{TRM}}(T) = M(T_b) \frac{M_s(T)}{M_s(T_b)} = M_s(T) \int_0^{\pi/2} \cos(\theta) \tanh \frac{v\mu_0 M_b H(T_b) \cos(\theta)}{kT_b} \sin(\theta) d\theta . \quad (3.1.1-16)$$

As before,  $M_b$  is given by (3.1.1-9) and  $T_b$  is calculated using (3.1.1-3), (3.1.1-4), and (3.1.1-5).

Luce extended Stacey and Banerjee's approach by considering a cubic magnetite crystal with eight easy directions of magnetization. The resulting field-dependence was obtained numerically, and found to be closer to the

Langevin model than either the hyperbolic tangent model or the Stacey-Banerjee model. For this reason, he preferred the Langevin model.

Each of these models shares the following characteristics:

1. TRM is a continuous, smooth, monotonic, increasing function of the applied field.
2. TRM is a linear function of the applied field at low fields, and saturates at high fields.

These characteristics will be compared to those for MD particles in Section 3.2.1.

### 3.1.2 Unblocking in the Néel domain-reversal mechanism

Schmidt [1976] examined (3.1.1-9) and (3.1.1-10) for the case with  $q = 2$ . By neglecting the variation in the argument of the logarithm, he was able to show that  $H_{c_b} > H$  and  $T_b$  decreases with increasing  $H$ . For unblocking, as measured in the laboratory with  $H = 0$ , we can define an unblocking temperature  $T_{ub}$ . The unblocking temperature is given by the same equation as the blocking temperature (with  $H = 0$ ), and so immediately we see that  $T_{ub} < T_b$ , and the difference  $T_b - T_{ub}$  increases as  $H$  increases. A somewhat different result will be obtained for MD grains in Section 3.2.2.

## 3.2 MD theories

### 3.2.1 The Néel-Schmidt MD model

Schmidt [1972] constructed a model of MD TRM from first principles. His model is physically equivalent to Néel's [1955] MD model. Néel based his model on the temperature dependence of a secondary characteristic, the microscopic coercive force. Schmidt's model is based on the interaction of a single domain wall with the applied field, the demagnetizing field of the

grain, and a periodic array of pinning sites within the grain. The model assumes a grain of width  $L$  with a single  $180^\circ$  wall of area  $A$  offset a distance  $x$  from the grain center. The external field is applied parallel to the axis of domain magnetization. Defining the reduced magnetization  $m(T) = \frac{M_s(T)}{M_s(0)}$

for convenience, Schmidt gives the energy relation

$$\frac{E}{v} = -Hmx + \frac{1}{2}m^2x^2 - m^p \cos \frac{2\pi x}{\lambda} \quad (3.2.1-1)$$

The first term describes the magnetostatic interaction between the grain and applied field, where  $H = 2\mu_0 M_s(0)/L$ . (This differs from Schmidt's usage by a factor of  $\mu_0$ ). The second term represents the self-energy  $\mu_0 DM^2 v/2$  of the grain demagnetizing field where  $D$  is the demagnetizing factor and  $\lambda = 2D/2\mu_0$ . The coefficient  $D$  can be assumed to be constant since  $D$  is not a strong function of  $x$  [Dunlop, 1983b; Merrill, 1981 is in error]. The third term represents the interaction between the wall and a periodic array of pinning centers as a sinusoidal variation with wavelength  $\lambda$ . The temperature dependence of each term is contained in the reduced magnetization  $m$ .

Schmidt determines the possible stable wall positions by taking the derivative of (3.2.1-1) with respect to  $x$  and setting the result equal to zero. He shows that the extreme value for a stable wall position occurs at

$$S = -\frac{m^{p-2}}{2} + \frac{H}{m}, \quad (3.2.1-2)$$

and that the blocking temperature occurs when  $S$  is a minimum, yielding

$$m_b = m(T_b) = \frac{M(T_b)}{M(0)} = \frac{H}{2(p-2)} \frac{1}{\lambda^{p-1}} \quad (3.2.1-3)$$

As in the SD case, the blocking temperature is found to be a function of the applied field. At the blocking temperature the wall is pinned at or near  $x_b = S_{\min}$  where

$$M_b = \frac{{}^2H}{2\mu_0} \frac{p-1}{p-2} = \frac{p-1}{p-2} \frac{H}{D}. \quad (3.2.1-4)$$

With further cooling,

$$M(T) = M(T_b) \frac{M_s(T)}{M_s(T_b)} = M_b \frac{m(T)}{m(T_b)}. \quad (3.2.1-5)$$

The resulting TRM obtained by Schmidt is

$$M_{\text{TRM}} = m(T) \frac{{}^2(p-1)}{2\mu_0 (p-2)} \frac{2(p-2)}{H^{\frac{1}{p-1}} H^{\frac{p-2}{p-1}}}. \quad (3.2.1-6)$$

The coercive force is obtained by setting (3.2.1-2) equal to zero, giving

$$H_c(T) = \frac{2}{m^{p-1}(T)}. \quad (3.2.1-7)$$

This matches Néel's assumed variation of  $H_c$  with  $M_s$  if  $p = 3$ . Other workers have obtained values of  $p$  ranging from 2 to 10. The TRM can be written in terms of the coercive force as follows:

$$M_{\text{TRM}} = \frac{{}^2(p-1)}{2\mu_0 (p-2)} ((p-2)H_c)^{\frac{1}{p-1}} H^{\frac{p-2}{p-1}}. \quad (3.2.1-8)$$

These arguments hold provided the maximum stable wall position given by (3.2.1-2) does not decrease when we remove the field at room temperature; otherwise, the wall will move to the maximum stable room-temperature position. The limiting case occurs for the applied field  $H_2$  determined by setting  $S(T_a, H=0) = S(T_b, H_2)$ , using (3.2.1-2) and (3.2.1-3), and solving for  $H_2$ . Saturation will occur if the applied field  $H > H_2$ , where



$$H_2 = \frac{2}{p-1} \frac{p-2}{p-1} \frac{1}{p-1} m^{p-1}(T_a) = \frac{p-2}{p-1} \frac{1}{p-1} H_c(T_a). \quad (3.2.1-9)$$

The magnetization saturates at

$$M_s(T) = \frac{2}{\mu_0} m^{p-1}(T) = \frac{2H_c}{2\mu_0} = \frac{H_c}{D}. \quad (3.2.1-10)$$

Schmidt argues that thermal activation blocking will dominate in the low-field region where

$$H < H_1 = \frac{2}{p-2} \frac{(p-2)}{p-2} \frac{p-1}{p-2} m_{\text{THB}}^{p-1} = (p-2) \frac{p-1}{p-2} H_c(T_{\text{THB}}) \quad (3.2.1-11)$$

where  $m_{\text{THB}}$  must be determined numerically from

$$m_{\text{THB}}(T_{\text{THB}}) = \frac{kT_{\text{THB}} \ln(C_b)}{2v}^{\frac{1}{p}} \quad (3.2.1-12)$$

where  $C'$  is a constant that is analogous to  $C$  in (3.1.1-2) (see Appendix E). Since  $m_{\text{THB}}$  is independent of  $H$  in the low field limit, so is  $T_{\text{THB}}$ , and by (3.2.1-4) and (3.2.1-5)

$$M_{\text{THB}}(T) = \frac{2H}{2\mu_0} \frac{p-1}{p-2} \frac{m(T)}{m(T_{\text{THB}})} = \frac{p-1}{p-2} \frac{m(T)}{m(T_{\text{THB}})} \frac{H}{D}. \quad (3.2.1-13)$$

This model has the following characteristics:

1. TRM is a continuous, monotonic, increasing function of the applied field.
2. TRM is a linear function of the applied field at low fields (3.2.1-13), proportional to  $H^{\frac{p-2}{p-1}}$  for intermediate fields (3.2.1-6), and saturates at high fields (3.2.1-10). If Néel's suggestion of  $p=3$  is taken, the intermediate-field TRM is proportional to  $H^{1/2}$ .

There are three distinct regions in this model, versus a smooth variation in the SD models. Assuming that this model is correct, these three regions should be observable. In practice, this is very difficult because variations in grain size and microscopic coercivity act to smooth the  $M_{\text{TRM}}(H)$  curve. Even if the observations showed three regions with the predicted  $H^1$ ,  $H^{1/2}$ , and  $H^0$  dependencies, that alone could not be cited as supporting the model for the simple reason that any reasonable smooth, monotonic, increasing model showing  $H^1$  dependence at low fields and  $H^0$  dependence at high fields would be expected to show  $H^{1/2}$  dependency at some intermediate field.

Schmidt [ca. 1976] studied a two wall, two coercivity model developed along the lines of the model just presented. The two wall, two coercivity model cannot be solved analytically, so computer simulations were used to examine its behavior. One of the more interesting results is the prediction of a low-field  $H^{0.7}$  dependence for  $M_{\text{TRM}}(H)$ . This was obtained without resorting to thermal-agitation blocking. This result merits further investigation.

### 3.2.2 Unblocking in the Néel wall-motion mechanism

In Schmidt's [1973] model of thermoremanence, the location of the domain wall at the blocking temperature is given by

$$x_b = \frac{m_b^{p-2}}{2} + \frac{H}{m_b}. \quad (3.2.2-1)$$

For the unblocking condition,  $H = 0$  and so the extreme location for the energy minimum is given by

$$S_{\text{ub}} = \frac{m_{\text{ub}}^{p-2}}{2}. \quad (3.2.2-2)$$

Now if  $S(T) > x_b$  then unblocking does not occur, whereas if  $S(T) < x_b$  it does. Setting  $S(T) = x_b$  gives

$$\frac{m_{ub}^{p-2}}{m_b^{p-2}} = \frac{m_b^{p-2}}{2 m_b} + \frac{H}{2 m_b}. \quad (3.2.2-3)$$

Immediately we see that  $m_{ub}(T) > m_b(T)$  for  $H > 0$ , and hence  $T_{ub} < T_b$ . The difference between  $T_{ub}$  and  $T_b$  widens as  $H$  increases, but slower than  $H$  since  $\frac{H}{m_b}$  is controlling. We can rearrange the preceding equation to give

$$m_{ub}^{p-2} = m_b^{p-2} + \frac{H}{2 m_b} = m_b^{p-2} + (p-2)m_b^{p-2}, \quad (3.2.2-4)$$

or

$$m_{ub} = (p-1)^{\frac{1}{p-2}} m_b. \quad (3.2.2-5)$$

The leading coefficient ranges from 1 for  $p \rightarrow 2^+$  to  $e = 2.718\dots$  for  $p \rightarrow \infty$ .

Thermal activation blocking replaces Néel blocking when  $x_{th} < S_{min}$ . It will be unblocked in zero field only when  $x_{th} = S_{H=0}$ . So

$$\frac{m_{ub}^{p-2}}{m_{THB}^{p-2}} = \frac{H}{2 m_{THB}}, \quad (3.2.2-6)$$

or

$$m_{ub}^{p-2} = \frac{H}{2 m_{THB}} = \frac{(p-2)}{H_1} \frac{p-1}{p-2} m_{THB}^{p-1} \frac{H}{m_{THB}} = \frac{H}{H_1} (p-2) \frac{p-1}{p-2} m_{THB}^{p-2}, \quad (3.2.2-7)$$

where  $H_1$  is the highest field at which thermal activation blocking takes place (see 3.2.1-11). So

$$\frac{m_{ub}}{m_{THB}} = (p-2)^{\frac{1}{p-2}} \frac{p-1}{p-2} \frac{H}{H_1} \frac{1}{p-2} = \frac{H}{H_1} \frac{1}{p-2}, \quad (3.2.2-8)$$

where  $F$  defined in this equation ranges from  $\frac{1}{p-2}$  to 1 as  $p$  ranges from 2 to  $\infty$ , and has typical values of 4 to 10. If we define  $H = H_3$  as the field at which

unblocking occurs at the same temperature as thermal activation blocking ( $m_{ub} = m_{THB}$ ), we can solve for  $H_3$  to obtain

$$H_3 = \frac{2}{p-1} \frac{m_{THB}^{p-1}}{H_{C_{THB}}} = H_{C_{THB}}. \quad (3.2.2-9)$$

Now  $H_3$  is just  $H_C$  due to Néel blocking at  $T = T_{THB}$ . If  $H$  is less than this coercive force, then Néel unblocking is not possible and thermal activation unblocking takes over. So for  $H < H_3$  we have  $m_{ub} = m_{THB}$  and hence  $T_{ub} = T_{THB}$ . So for all  $H$ ,  $T_{ub} = T_b$ .

To summarize,  $T_b - T_{ub}$  is zero for  $H < H_3$ , increases smoothly with increasing  $H$  until  $H = H_1$ , at  $H_1$  it decreases substantially as  $H$  is increased through  $H_1$ , and then it increases with  $H$  above  $H_1$ .

### 3.2.3 Other MD theories

There are several other MD models; however, examination shows that they are merely variations of the same model. Schmidt's [1972] formulation was presented in Section 3.2.1 because it provides the clearest explanation in terms of fundamental, easily understood concepts. Schmidt's model starts with an energy expression, whereas Néel [1955] began by assuming the following expression for the coercive force:

$$\frac{H_c(T)}{H_c(0)} = \left( \frac{M_s(T)}{M_s(0)} \right)^2. \quad (3.2.3-1)$$

Schmidt notes that his model is physically equivalent to Néel's [1955] model if  $p = 3$ . Dunlop and Waddington [1975] follow Néel, but generalize the coercive force relation to

$$\frac{H_c(T)}{H_c(0)} = \left( \frac{M_s(T)}{M_s(0)} \right)^n. \quad (3.2.3-2)$$

This is equivalent to Schmidt's model with  $p = n + 1$ . Stacey [1958] proposed a model based on setting the internal field of the grain equal to zero. Dunlop and Waddington showed that this is equivalent to their model, and hence Schmidt's, when  $p = n + 1$ . Everitt [1962] proposed a model based on the relations

$$\frac{H_c(T)}{H_c(0)} = \frac{T_c - T}{T_c} \quad (3.2.3-3)$$

and

$$\frac{M_s(T)}{M_s(0)} = \frac{T_c - T}{T_c}^m \quad (3.2.3-4)$$

and also allowed the applied field  $H$  to make an angle  $\theta$  with the domain wall. The predictions of Everitt's model are equivalent to Schmidt's in the high field limit if  $p = \frac{1+m}{m}$ . Everitt derived the following expression for the TRM:

$$M_{\text{TRM}} = \frac{\mu_0 H \sin \theta}{N} \frac{H_c(0)}{aT_b}^{\frac{m}{1+m}} \left[ 1 - \frac{m}{1+m} \frac{H \sin \theta}{H_c(0)} \frac{H_c(0)}{aT_b}^{\frac{1}{1+m}} \right] \quad (3.2.3-5)$$

where

$$a = \frac{k \ln \frac{b}{a}}{cS \mu_0 M_s(0)}, \quad (3.2.3-6)$$

$S$  is the area of the wall,  $b$  is the width of the energy barrier that the wall must pass, and  $c$  is a factor determined by the shape of the barrier. Although this model brings in some geometric refinements that are not incorporated in Schmidt's model, the physical processes involved are the same.

Day [1977] provides a nice summary of each of these models.

The kinematic model of McClelland and Sugiura [1987], expanding on the model of Sugiura [1981], should be mentioned in passing. Their model is based on the assumption that when a rock is cooled in a magnetic field through the Curie temperature, the magnetization at any temperature is in a state equivalent to the total TRM, except the spontaneous magnetization is smaller at higher temperature. This can be written as follows:

$$\text{PTRM}_T^T(T) = \text{TRM}(T) \frac{M_s(T)}{M_s(0)} \quad (3.2.3-7)$$

Note that there is no field dependence in this model other than the field dependence of the TRM. This model is unique in that it gives the PTRM spectrum without explicitly assuming a grain size or microscopic coercivity spectrum. This model was developed to explain TRM properties observed in large ( 200  $\mu\text{m}$ ) magnetite grains, and does not appear to apply to the 1 to 2  $\mu\text{m}$  grains studied here.

### 3.3 PSD theories

The transition between SD and MD particles is expected to occur at a particle size where the reduction in magnetostatic energy achieved by taking on a domain structure offsets the increase in exchange energy associated with a domain wall. Calculated sizes for the transition depend somewhat on the assumptions made. Day [1977] summarized the work of several authors, showing that most estimates place the transition at about 0.03 to 0.1  $\mu\text{m}$  for equidimensional magnetite grains. The critical size increases as the length to width ratio of the particle increases.

Multidomain particles are expected to have low coercivities and low remanence; however, this is not observed for small MD grains. The discontinuities in various magnetic properties (e.g.,  $H_c$ ,  $\frac{H_c}{H_c^{\text{max}}}$ ,  $\frac{M_{rs}}{M_s}$ ) have not been observed (see Dunlop [1981]). Instead, there appears to be a gradual transition between the magnetic properties at the SD to MD transition size and the properties predicted by MD theory, which become dominant at about

20  $\mu\text{m}$ . Stacey [1962] postulated the existence of pseudo-single domain moments in small MD particles, with properties approaching those of true SD particles. Since then, several candidates have been suggested for the origin of these moments. The following sections describe the principal candidates.

### 3.3.1 Barkhausen discreteness of domain wall movements

Stacey [1962] introduced the concept of pseudo-single-domain moments, and explained them in terms of the Barkhausen discreteness in the position of the domain walls. He obtained the following expression for the spontaneous grain moment:

$$M = \frac{9 r d_0^3 M_s}{16 (1 + D)} \frac{d}{d_0} \frac{1}{2\sqrt{3}} \frac{d}{d_0} \tanh \frac{1}{2\sqrt{3}} \frac{d}{d_0} \quad (3.3.1-1)$$

where  $d_0$  is the critical minimum SD size,  $M_s$  is the intrinsic low-field susceptibility, and  $r$  is the net number of incremental moments in one direction. By assuming that the net alignment of the spontaneous moments of an assembly of grains in a field  $H$  is given by Boltzmann's distribution, and that blocking occurs as in Néel's [1955] SD theory, Stacey obtains

$$M_{\text{TRM}} = \bar{v} \tanh \frac{\bar{\mu}_0 m_b(T_b) H}{kT_b} \quad (3.3.1-2)$$

where  $\bar{v} = 0.85$  is the mean direction cosine between domain directions and the applied field. This gives essentially the same  $T_b(H)$  dependence as in the single domain model (see equation 3.1.1-8). Stacey concludes that "there is nothing fundamental about the transition from PSD to MD behavior, since the grain size at which it occurs is a function of the applied field," (see figure 1). This fact appears to have been overlooked by later workers.

Dunlop [1977] argues that Barkhausen discreteness cannot account for PSD behavior because the moments cannot reverse independently from the

domain moments. In addition, he felt that the interaction between the moments in larger grains would minimize their resultant moment.



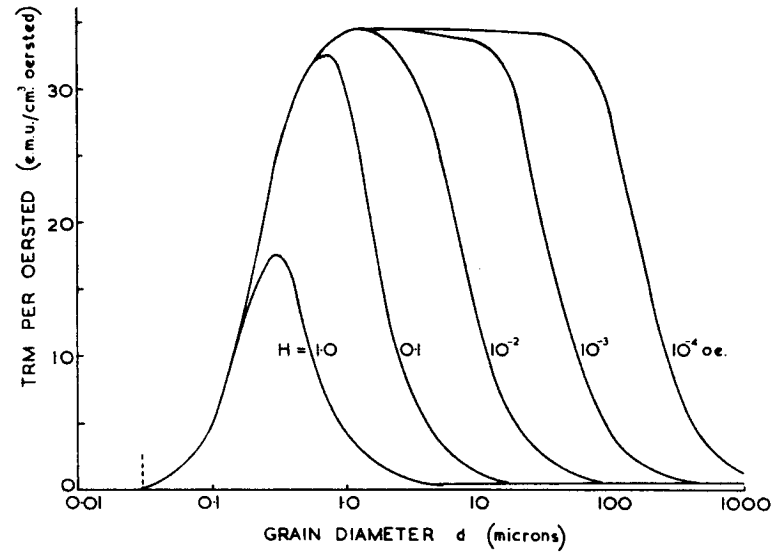


Figure 1 TRM versus grain size and applied field in Stacey's [1962] model of PSD behavior.

### 3.3.2 Surface domains

Stacey and Banerjee [1974], Banerjee [1977], and Moskowitz and Banerjee [1979] appeal to surface moments controlled by local surface anisotropy. This model immediately gives a  $M_{\text{TRM}} \propto d^{-1}$  dependence. Day [1977] collected the available data and obtained  $M_{\text{TRM}} \propto d^{-0.7}$ , which is consistent within the limits of the available data.

Stacey and Banerjee assume that the PSD moments are random effects arising from imperfections in surface domain structures. They arbitrarily assume that there are  $n$  ( $\propto d^{-1}$ ) such moments per unit volume, with magnitudes that are uniformly distributed between 0 and  $M_{\text{psd}}^{\text{max}}$ . By assuming a constant blocking temperature, they obtain the following expression for the TRM:

$$M_{\text{TRM}} = n \int_0^{M_{\text{psd}}^{\text{max}}} dy \int_0^y xy \tanh \left( \frac{H}{kT_b} \frac{M_s(T_b)}{M_s(0)} xy \right) dx = n \int_0^{M_{\text{psd}}^{\text{max}}} f(H) dy \quad (3.3.2-1)$$

This is superimposed on the TRM obtained by MD theory. Dunlop, et al [1974] compared the TRM acquired by magnetite particles in the 0.04  $\mu\text{m}$  to 0.22  $\mu\text{m}$  range to an equation of the form

$$M_{\text{TRM}} = aH + bf(H) \quad (3.3.2-2)$$

where the linear term is typical of low-field MD theories. They obtained good agreement for  $300 \mu\text{T} < H < 2 \text{ mT}$ . Systematic deviations in higher fields were qualitatively attributed to the known nonlinearity of MD TRM on  $H$ , and the field dependence of  $T_b$ . Deviations observed for lower fields were not explained.

### 3.3.3. Domain wall moments

Dunlop [1977] argued that only the net moments of domain walls could qualify as subdomain moments with true SD-like behavior. He argues that equation (3.1.1-2) can be applied to these moments, which he called “psarks.”

Dunlop found evidence for psarks in 0.05 to 0.26  $\mu\text{m}$  magnetite grains by isolating part of the initial susceptibility and weak-field TRM that is not controlled by the internal demagnetizing field, and by determining the volume activated in TRM and high-temperature IRM and comparing it to the volume of a domain wall. There has been less success with larger grains. Dunlop and Bina [1977] analyzed the high-temperature hysteresis and alternating field demagnetization of 1.0 to 5.0  $\mu\text{m}$  magnetite grains. No evidence for psarks was found, despite the fact that PSD moments appear to exist in this size range. Dunlop [1977] concludes that the PSD moments are “either coupled to the main domains (i.e., not SD-like) or, if independent, too large to respond noticeably to thermal agitation.” He concludes that psarks cannot explain the PSD behavior observed in magnetite grains larger than 1.0  $\mu\text{m}$ .

### 3.3.4 Moments pinned by dislocation stress fields

Verhoogen [1959] felt that the stress fields introduced by dislocations in the crystal structure were the only mechanism likely to result in coercive forces in excess of about 300  $\text{kA m}^{-1}$  for MD magnetite. Ozima and Ozima [1965] felt that small regions isolated from the surrounding matrix by submicroscopic grain boundaries of at least several tens of interatomic distances were a more likely cause. Kobayashi and Fuller [1968] assumed that the moments associated with stress centers had a higher blocking temperature than the remainder of the grain, and obtained the following expression:

$$M_{\text{TRM}} = \frac{nv_0M_s(T_a)}{3(1 + D_m)} \tanh \frac{v_b\mu_0M_s(T_b)H}{kT_b} , \quad (3.3.4-1)$$

where  $n$  and  $v_b$  are the number and volume of in-phase stress centers at  $T_b$ ,  $v_0$  is the volume of the individual pinned domains at temperature  $T_0 \ll T_b$ , and  $\chi_m$  is the susceptibility of the matrix at the temperature at which the volume of the pinned regions reaches the final value  $v_0$ . This gives essentially the same  $T_b(H)$  dependence as in the single domain model (see equation 3.1.1-8).

Dickson, et al [1966] argued that Verhoogen's model could not apply to magnetite because the magnetostatic energy of a SD region would completely dominate the magnetocrystalline anisotropy and magnetostatic strain energies, making it impossible for such a region to behave independent of the matrix. Dunlop [1977] pointed out that the moments associated with stress-pinning of spins can only be reversed when traversed by a  $180^\circ$  domain wall, and hence could not be the source of independent SD-like behavior.

### 3.3.5 Metastable SD-like states

Halgedahl and others (e.g., Halgedahl and Fuller [1980, 1983]; Boyd, Fuller and Halgedahl [1984]) monitored the magnetic domain patterns for various titanomagnetite grains under varying fields, and concluded that the difficulty of nucleating domain walls can explain several aspects of PSD behavior. They identified two processes by which domain walls can be nucleated: creation of walls at surface imperfections, and unpinning of minute wall fragments from strong potential energy traps at the grain surface.

There seems to be little doubt that the difficulty of nucleating domain walls has important implications for explaining PSD behavior; however, no quantitative models have been proposed that can predict the observed TRM behavior of PSD grains.

### 3.3.6 Intrinsic SD-like properties of small MD grains

Fuller [1984] argued that PSD behavior was in part due to an intrinsic grain size dependence of  $\frac{J_R}{J_S}$ , in addition to the variation in  $\frac{J_R}{J_S}$  caused by the

difficulty in nucleating domain walls. His model was primarily based on attempts to fit empirical data, rather than derivations from first principles. This model was not developed to the point where it could be used to make significant predictions about TRM behavior.

### 3.4 Micromagnetic models

An entirely different approach is to perform calculations at the micromagnetic level where spin arrangements, not domain arrangements, are calculated. Domain patterns appear automatically when the spin configurations that minimize the total grain energy are determined. The energy minima found may be either global or local, with the latter being necessary to account for the thermal behavior of TRM.

The ideas of the micromagnetic approach are quite old, having first appeared in Landau and Lifshitz's [1935] article on domain theory. Early analytical calculations include those of Bitter [1937], Elmore [1938], and Brown [1940, 1959], but the complexity of the calculations limited progress until recent advances in computer technology made the problem more tractable. Recent studies examined both the one-dimensional (e.g., Moon and Merrill [1984, 1985], Moon [1985]) and three-dimensional (e.g., Schabes and Bertran [1988], Williams and Dunlop [1988, 1989, 1990], Shcherbakov et al [1990]) cases. Surprisingly, the typical octahedral form for magnetite has not yet been modeled, nor have most micromagnetic models considered the fact that, in magnetite, [111] are the easy directions and [100] are the hard directions.

The micromagnetic approach can give insight on the detailed magnetic structure of a perfect crystal, but is less suited to modeling assemblages of imperfect grains. The method suffers from its inability to express any final results in an analytical form, and the corresponding need for tremendous computer resources to predict quantitative trends.