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APPLIED FIELD DEPENDENCES OF LOCAL MAGNETIC FIELDS IN SINGLE FE304CRYSTALS

MORANTE, CARLOS
GHORBANI, ELAHEH
BOEKEMA, CAROLUS
DEPARTMENT OF PHYSICS & ASTRONOMY
SAN JOSE STATE UNIVERSITY
SAN JOSE, CALIFORNIA

Prof. Carolus Boekema
Mr. Carlos Morante
Dr. Elaheh Ghorbani
Department of Physics & Astronomy
San José State University
San José, California

Applied Field Dependences of Local Magnetic Fields in Single Fe_3O_4 Crystals

Synopsis:

The internal fields in single crystals of magnetite (Fe_3O_4) have been previously studied through muon-spin rotation (μSR). By Maximum-Entropy (ME) μSR, [2] we have analyzed μSR Fe_3O_4 data with external field parallel to the <111>, <110> or <100> axis. Our MEμSR field-dependent studies lead to a better understanding of the local magnetism and conduction mechanism in this Mott-Wigner glass.

Applied field dependences of local magnetic fields in single Fe_3O_4 crystals: a Maximum-Entropy μSR study.

C Morante, E Ghorbani and C Boekema,

Physics & Astronomy Department, San Jose State University, San Jose CA 95192 – 0106.

Abstract The internal fields in single crystals of magnetite (Fe_3O_4) have been previously studied through muon-spin rotation (μSR). By Maximum-Entropy (MaxEnt, ME) μSR, we have analyzed μSR data of single crystals of Fe_3O_4 with external fields parallel to the <111>, <110> or <100> axis. Several μSR time series indicate a beat pattern. By curve fitting and confirmed with improved precision by MEμSR second frequency signals are seen in the temperature range above the Verwey transition (T_V = ~123 K). Assuming one demagnetization field and one muon-probe-site set, we find for roomtemperature (RT) <111> Fe_3O_4 fields close to the maximum allowable. For <110> at RT Fe_3O_4, indicates a second μSR signal is seen. We compare our RT field-dependent results with those observed for 205 K <110> Fe_3O_4 to study a 2nd order phase transition observed at the Wigner temperature T_W (about twice T_V) **.** The existence of these secondary signals may be related to phonon-assisted 3d-electron hopping. Another possibility could be the existence of magnetically different muon-probe sites. Our MEμSR field-dependent studies lead to a better understanding of the local magnetism and conduction mechanism in this Mott-Wigner glass.

1. Introduction

Magnetite (Fe_3O_4) is a ferrimagnetic oxide. Fe_3O_4 has a fully spin-polarized band, making an ideal compound for studying basic spintronics. At the Verwey temperature ($T_V \sim 123$ K) Fe_3O_4 shows a semimetal-to-insulator transition, which is related to the properties of the "extra 3d" (3d*) electrons. The Verwey transition is a first order transition.[1-2] The Wannier states for these 3d* conduction electrons in Fe_3O_4 indicate a mixture of localized and delocalized electron/hole states [3-4]. Magnetic anomalies, observed between T_V and the Wigner temperature ($T_W \approx 247$ K), show Fe_3O_4 can be considered a Wigner electron glass [5]. The resistivity is a minimum at T_W suggesting glassy, precursor effects in the $T_V - T_W$ region.

Magnetite's physical-chemical formula reads: $(Fe^{3+})_A\,[Fe_2^{3+}\,e^{-1}]_B\,O_4^{2-}$. The Fe ions have two different configurations: in the tetrahedral site (A) the Fe^{3+} ion is surrounded by four O^{2-} ions, while in the octahedral site (B) the $Fe^{3+/2+}$ ion is surrounded by six O^{2-} ions [6-7]. The electron configuration of $(Fe^{3+})_A$ is $3d^5$ and all 5 spins are parallel. These spins on the A sublattice are antiparallel to those on the B sublattice; the 3d* electron has a spin-down orientation ($\downarrow e^{-1}$). The Magneto-chemical formula is: $(\downarrow Fe^{3+})_A[\uparrow Fe_2^{3+} \downarrow e^{-1}]_B O_4^{2-}$. The top energy band is half filled by 3d* electrons, which are fully spin polarized. Our studies support the phonon-assisted electron-spin hopping model and the Mott-Wigner glass description of Fe_3O_4.[5]

2. Previous μSR studies, using Fourier Transformation and Curve Fitting

Previous μSR studies [5, 8] studied the behavior of the internal magnetic field in Fe_3O_4 as a function of temperature and external field B_{ext} .These studies showed that at T_w there appears to be a 2nd order phase transition. Further, the local field B_{loc} can be approximated by $B_{loc} = B_{ext} - B_{dem}$ for $B > B_{dem}$ and $B_{loc} = B_{loc}(ZF)$ for $B < B_{dem}$. B_{dem} is the demagnetization field. For the <111> orientation at room temperature (RT) the external field dependence results indicated a field somewhat larger than the theoretical maximum allowed. These studies were done using Fourier transformation (FT) and curve fitting (CF). The CF results gave only a reasonable frequency values, with large error bars for its amplitudes and relaxation rates. A field dependency was observed for Fe_3O_4 at RT in the <110> orientation. See Fig 1. This trend differs from the one observed at 205 K at <110> orientation. See Fig 2.

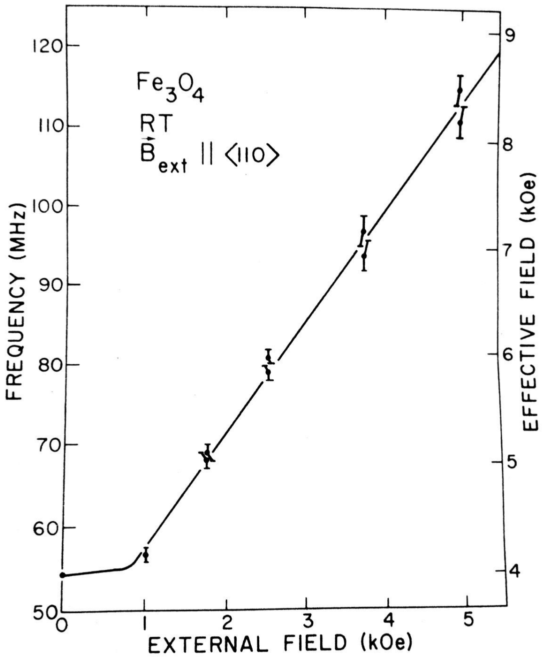

Figure 1: External field dependence observed for B// <110> magnetite at RT. The frequencies observed follow the expected linear trend with a slope of 13.55 MHz/kOe and B_{dem} = ~ 0.9 kOe. At 5 kOe, the highest field is somewhat larger than theoretically allowed.

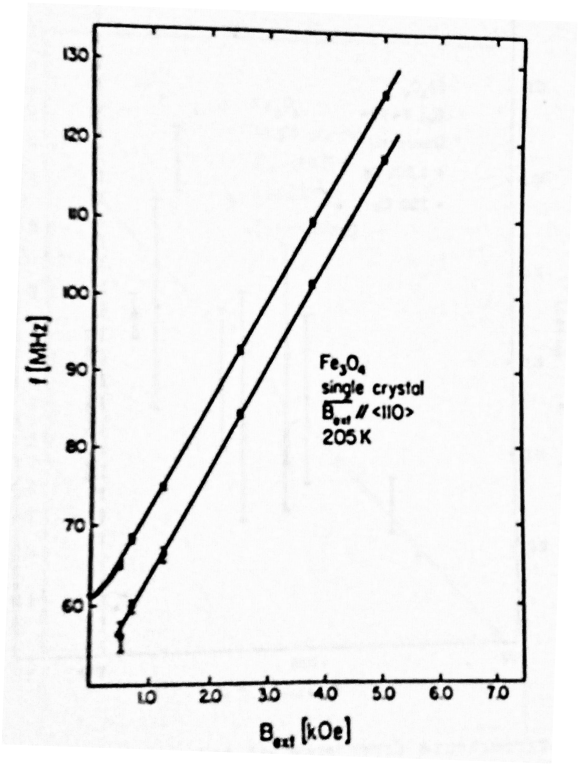

Figure 2. Observed μSR frequencies with B // <110>. At 205 K the two frequency signals clearly follow the expected linear trend with a slope of 13.55 MHz/kOe with both a B_{dem} of about 0.5 kOe. The lower frequency signal at zero field has not been seen by FT and CF analysis. At zero field, FT & CF studies [5, 8] indicated only one frequency signal.

3.0 MaxEnt- μSR Fe_3O_4 in progress

Our MaxEnt [8-10] study analyzes original Fe_3O_4 μSR data to investigate these T_V & T_W transitions and potential precursor effects in the T_V - T_W region. For more detail on our MaxEnt-Burg technique applied to μSR, see the Appendix.

3.1 MEμSR Fe_3O_4 B//<111> field dependence

The field-dependent μSR data of B // <111> Fe_3O_4 at RT have been analyzed using MaxEnt. A filter time T_f of 0.6 μs is found to be about twice the relaxation time of the frequency signal. The MEμSR <111> Fe_3O_4 results are consistent with, yet are more precise than the CF results. [5, 8] In Fig 3, we show the <111> ME transform at 5 kOe, RT fitted with two Lorentzians (Lor) that describes the asymmetric broad peak best. A fit with two Gaussians (Gau) or a Gau/Lor combination gave a higher χ^2. In Table 1 below, our fit results are given. The fact that the Lor fits are better implicates exponential μ-spin relaxation, caused by the muons moving among the μ -O sites within the empty O octahedrons at RT. [8, 10]

Note, for a perfect alignment B/ /<111> the six muon-stop sites within an empty O-octahedron are magnetically and electrically equivalent, due to rotation symmetry around the <111> axis. Assuming one μ-site and one B_{dem}, the highest 111-MHz frequency is about the maximum allowable. [5, 8] A slight misalignment of the B // <111> alignment causes the μ -O sites to be magnetically different, resulting in an asymmetric ME distribution.

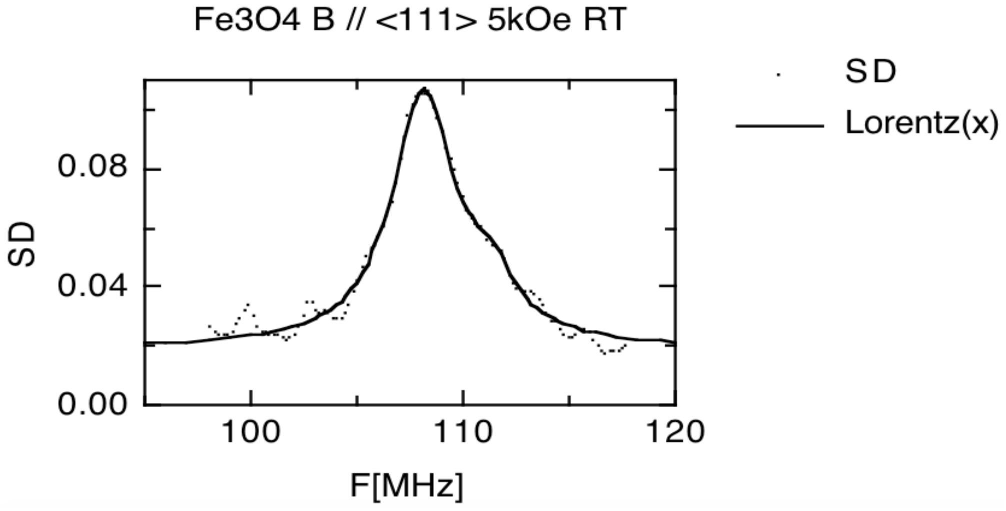

Figure 3. Spectral density for B <111> Fe3O4 at 5kOe, RT, with a best fit of 2 Lorentzians.

Table 1: Fit parameters for B // <111> RT MaxEnt transform. The two Lorentzians give the best fit parameters and lowest χ^2. S in MHz & K in MHz^{-1}. The substantial χ^2 reduction for two Lor*s is caused by a much better fit for the 105 – 110 MHz interval, than that for two Gau*s.

Fit *f* *	χ^2 *10^3	ME-BG	A	S / K	f [MHz]
Gaussian	2.54	.026(1)	.182(3)	4.1(2) MHz	108.41(5)
2 Gau	1.31	.025(1)	.193(3)	2.7(2)	108.1(1)
			.045(5)	1.5(5)	111.9(2)
Lorentzian	1.75	.018(1)	.089(2)	.20(1)MHz^{-1}	108.34(2)
2 Lor	1.00	.019(1)	.085(2)	.30(2)	108.13(4)
			.016(2)	.5(2)	111.3(2)

3.2 MEμSR Fe_3O_4 External Field in <110> orientation

3.2.1 MEμSR Fe_3O_4 B // <110> RT

We have evaluated MaxEnt transforms for low external fields for B // <111> & RT. As a zero approximation for T_f, a 1μs filter time is used. At zero field, we find only one peak of 54.4 MHz The MEμSR transforms for 500 Oe indicate a second signal. A two-Lorentzian fit reveals two peaks at 55.5 MHz and 59.0 MHz. See Fig 4. If B_{dem} is much less than 500 Oe, then we expect for f(high) about 61 MHz. The f(low) peak indicates a magnetically different set of muon sites, as B //<110>.

b)

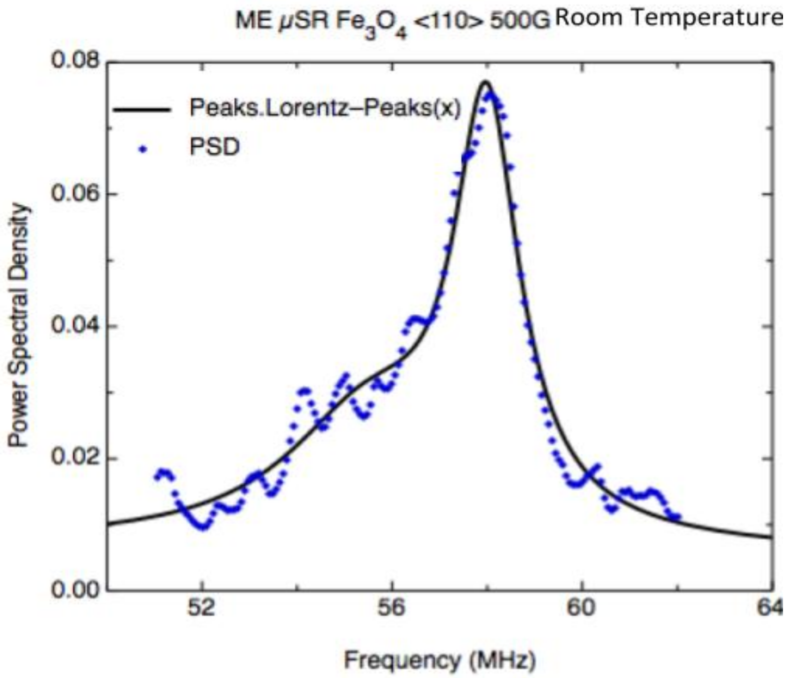

Figure 4: A two-Lor fit is shown in the MEμSR transform (T_f = 1μs)

for B (500-Oe) // <110> Fe_3O_4

3.2.2 MEμSR Fe_3O_4 B // <110> 205 K

In Fig 5 MEμSR tranforms for B // <110> B = 100 Oe and T = 205 K is displayed. With an optimized signal (T_f = 1 μs) the distribution indicates two smaller signals (55 & 57 MHz) besides the main signal at 60 MHz. This is different behavior than observed at RT and 500 Oe (Fig 4). The 55 & 57 -MHz signals were not seen in CF analysis – see also Fig 2.

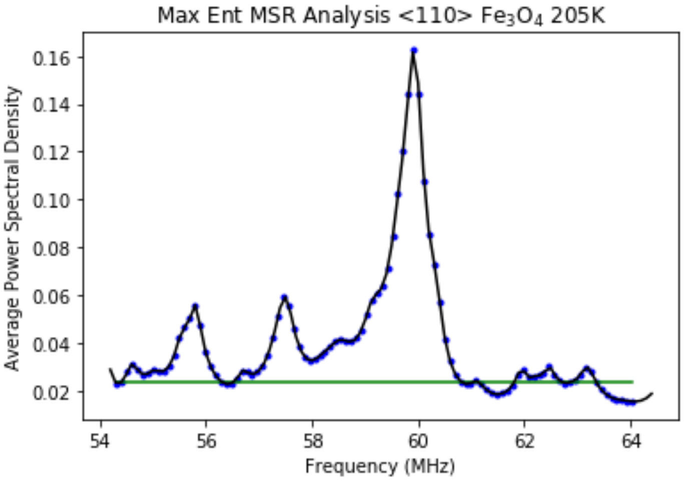

Figure 5. MEμSR transform ($T_f = 1$ μs) for B (100 Oe) // <110> Fe_3O_4 at 205 K. The curve is an interpolation to guide the eye; the line is an estimate for the ME background.

In Fig 6 MEμSR transform is shown for B // 720 Oe, T = 205 K, $T_f = 0.5$ μs. Besides the peak at 68 MHz, a second signal is seen at 60 MHz, possibly split as also the 100-Oe transform (Fig 5) indicates. The frequency difference between the two signals is about 8 MHz which is about equal to the observed frequency shifts seen at T_V and at T_W in zero field. [5, 8] This suggests that in the T_V - T_W region, two magnetically different subregions in the B sublattice exists: one following the normal magnetization curve, and one for which a Verwey-like structure and phase transition has been induced by the applied field. This may well be glassy, precursor effects.

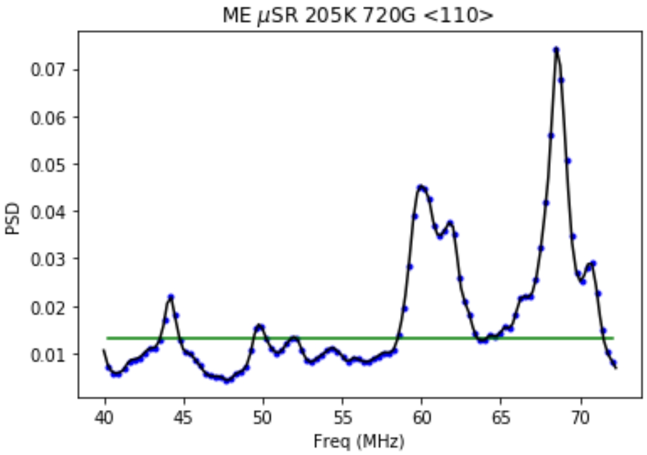

Figure 6. MEμSR transform ($T_f = 0.5$ μs) for B (720 Oe) // <110> at 205 K. The curve is an interpolation to guide the eye; the line is an estimate for the ME background

3.3 **MEμSR Fe_3O_4 B // <100> orientation field dependence.**

We have evaluated the MEμSR results in Fe_3O_4 for B // <100> for small fields. These RT transforms for B// <100> orientation indicate no substantial change up to 1 kOe. Only one peak signal at zero field, 50 Oe and 1 kOe is seen. The fitted frequencies of about 55 MHz are independent of $B \leq 1$ kOe, suggesting for B//<100> B_{dem} is larger than 1 kOe.

4. Conclusive Remarks

Using MEμSR, we find with improved precision the local magnetic fields in Fe_3O_4 crystals. Observation of two signals close in frequency is consistent with the beat patterns seen in the μSR time series.

We have observed two frequencies for the <111> orientation at 5 kOe, RT; the smaller signal indicates a slight misalignment of the <111> Fe_3O_4 crystal.

For the <110> orientation, a second signal is observed. These B-dependent μSR signals indicate a much different behavior at RT than they do at 205 K. The μSR signals at 205 K suggest a splitting in the magnetization, plausibly caused by glassy precursor effects above T_V.

Thus Fe_3O_4 is more like a narrow-band (degenerate) semiconductor than a semimetal.

3d* electrons appear to be important ingredients of the conduction mechanism in Fe_3O_4, supporting the phonon-assisted electron hopping model. [5,8]

Acknowledgements

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References

1. A Chainani *et al,* J Electron Spect & Rel Phen **78** (1996) 99;

   JH Park *et al,* Phys Rev **B55** (1997) 12813.

2. W Shchennikov *et al*, Solid State Comm **149** (2009) 759.

3. T Her and C Boekema, J Appl Phys **76** (1994) 5772;

   P Sakkaris *et al,* APS Bulletin March 2014.

4. JR Cullen and E. R. Callen, Phys Rev **B7** (1973) 397.

5. C. Boekema, K.C. Chan, D.W. Cooke *et al*, Phys Rev **B33** (1986) 2102;

   C. Boekema, D. W. Cooke *et al*, Phys Rev **B31** (1985) 1233.

6. ME Fleet, Acta Crystallography **B37** (1981) 917.

7. S Sasaki, Acta Crystallography **B53** (1997) 762.

8. C Boekema *et al*, Hpf Interactions **31** (1986) 487; **17-19** (1984) 305.

9. C Boekema and MC Browne, MaxEnt 2008, AIP Conf Proc #1073 p260.

10. C Boekema *et al*, Proc 11th Int M2S Conf (2015) and references therein.

Appendix

MaxEnt Muon-Spin Research

Muon-Spin Rotation (μSR) is a magnetic resonance technique, in which an implanted positive muon (μ+) act as a magnetic probe. To measure the local magnetic fields in Fe_3O_4, we use μSR. The muon-decay distribution [a, b] is described by:

$$N(t) = N_0 e^{-t/\tau}[1 + S(t)] + BG$$

where N(t) is the number of muons decayed at time t, N_0 the initial muon-decay events at t = 0, τ the muon-decay time of 2.2 μs, S(t) the oscillatory signal and BG the background noise. The time histogram of the muon-decay events shows the Larmor muon-spin precession superimposed on the exponential muon decay [a, b]. The observed frequencies in S(t) are proportional to the magnetic fields.

These μ+ probes bond with O^{2-} ions at ~0.1 nm away from the O-ion. For Fe_3O_4, our preliminary calculations indicate, there are six equivalent muon-stop sites located in an empty oxygen octahedron between the A and B sites. Electrically, these sites are all equivalent.

Maximum Entropy (MaxEnt, ME)

The muon-spin polarization and time series S(t) can be transformed into a frequency domain to find the magnetic field distribution. To reduce Poisson noise, we optimize the ME signal-to-noise ratio by varying T_f the filter time. [a] On average, we've found T_f is about twice the 'lifetime' of the μSR signal.

MaxEnt is an advantageous method that produces sharper signals in a frequency transform, while reducing noise and eliminating sinc wiggles, commonly seen in Fourier analysis. Also, for weak and/or broad signals, Fourier analysis and curve fitting are less effective.

The MaxEnt-Burg technique is an auto-regressive method that assumes a correlation between the muon-spin signal, S(i) at any time i, and previous times, S(i-k) [a]. The Burg algorithm assumes each data point for S(i) can be expressed as:

$$S(i) = \sum_{k=1}^{p} S(i-k)c_k + n_i$$

The optimal number of auto-regression coefficients (p) lies between N/3 and N/5, where N represents the number of data points [a]. The MaxEnt transformation or spectral density is obtained by taking the square root of the power of the spectral density, P(f) given by:

$$P(f) = \frac{2\sigma^2}{\left|1 - \sum_{k=1}^{p} c_k e^{-2\pi i k f}\right|^2}$$

The μSR signal provides information about the frequency distribution. The spectral density or the frequency distribution is a direct measure of the local magnetic field distribution.

Muon-spin rotation in conjunction with Maximum Entropy technique is a sensitive tool [a] to search for the predicted (weak) magnetic effects. MaxEnt μSR has been proven useful for probing magnetism in cuprates by: (1) indicating d-wave symmetry for cuprate superconductivity, and (2) pointing toward extra condensate near the CuO-chain layers of $RBa_2Cu_3O_7$-δ (RBCO) below about $T_c/3$. [b]

[a] C Boekema and MC Browne, MaxEnt 2008, AIP Conf Proc #1073 p260;
JC Lee *et al*, J Appl Phys 95 (2004) 6906.
[b] R Santiago *et al*, Phys Rev B63 (2001) 132509;
C Boekema *et al*, J Appl Phys 83 (1998) 6795.