Precursor effects and field-induced short-range order above the Verwey transition in single Fe$_3$O$_4$ crystals

Carolus Boekema
San Jose State University, carolus.boekema@sjsu.edu

Carlos Morante
San Jose State University, carlos.morante@sjsu.edu

Follow this and additional works at: https://scholarworks.sjsu.edu/faculty_rsca

Recommended Citation
Carolus Boekema and Carlos Morante. "Precursor effects and field-induced short-range order above the Verwey transition in single Fe$_3$O$_4$ crystals" AIP Advances (2020). https://doi.org/10.1063/1.5130191
Precursor effects and field-induced short-range order above the Verwey transition in single Fe$_3$O$_4$ crystals

Cite as: AIP Advances 10, 025005 (2020); https://doi.org/10.1063/1.5130191
Submitted: 03 October 2019 • Accepted: 18 December 2019 • Published Online: 04 February 2020

Carolus Boekema and Carlos Morante

COLLECTIONS

Paper published as part of the special topic on 64th Annual Conference on Magnetism and Magnetic Materials

ARTICLES YOU MAY BE INTERESTED IN

Azetidinium as cation in lead mixed halide perovskite nanocrystals of optoelectronic quality
AIP Advances 10, 025001 (2020); https://doi.org/10.1063/1.5133042

Proton radiation effects on carrier transport in diamond radiation detectors
AIP Advances 10, 025004 (2020); https://doi.org/10.1063/1.5130768

A formula to calculate solid dielectric breakdown strength based on a model of electron impact ionization and multiplication
AIP Advances 10, 025003 (2020); https://doi.org/10.1063/1.5110271
Precursor effects and field-induced short-range order above the Verwey transition in single Fe₃O₄ crystals

Carolus Boekema and Carlos Morante

AFFILIATIONS
Physics & Astronomy, San Jose State University, San Jose, California 95112, USA

Note: This paper was presented at the 64th Annual Conference on Magnetism and Magnetic Materials.
*Carolus.Boekema@SJSU.edu and BoekemaC@AOL.com

ABSTRACT
The internal fields in single crystals of magnetite (Fe₃O₄) have been previously studied through muon-spin rotation (μSR). By Maximum-Entropy (ME) μSR, we analyze Fe₃O₄ μSR data with external fields parallel to the <111>, <110> or <100> axis. The ME peak-to-noise ratio is optimized by varying the filter time and time interval. Several μSR time series indicate a beat pattern. Using MEμSR, a second frequency signal is seen at non-zero fields in the temperature range above the Verwey transition (Tᵥ = ~123 K). At zero field, MEμSR confirms with much-improved precision the existence of one frequency signal found earlier by curve fitting (CF) and Fourier transformation (FT). We compare our room temperature (RT) field-dependent MEμSR transforms for <110> Fe₃O₄ with those found at 205 K to study a second order phase transition at the Wigner temperature (Tₘ = ~247 K). At RT and 205 K for fields below the demagnetization field and parallel to <110> Fe₃O₄, a second MEμSR frequency is observed, missed by CF and FT. These extra magnetic fields fall on the extended magnetization curves below and above Tw. At RT, a small field induces a short-range order similar to the precursor effects in the Tᵥ – Tₘ interval. At 205 K within that precursor T-interval, we observe a comparable RT-disordered state. The existence of these additional internal fields is likely related to phonon-assisted 3d-electron(-spin) hopping and short-range order behaviors. Our MEμSR studies lead to a better understanding of the local magnetism in this Mott-Wigner glass.

© 2020 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5130191

I. INTRODUCTION
Magnetite (Fe₃O₄) is a ferrimagnetic oxide. At the Verwey temperature (Tᵥ = 123 K) Fe₃O₄ shows a semimetal-to-insulator transition, which is related to the properties of the delocalized “extra 3d” (3d*) electrons. The Verwey transition is a first order transition. For the conduction of Fe₃O₄ two models are being considered: either phonon-assisted electron hopping with the 3d* being the only spin-current carries or a broad energy band (about 1 eV) conduction mechanism. The Wannier states of these 3d* conduction electrons in Fe₃O₄ indicate a mixture of localized and delocalized electron & hole states. Magnetic anomalies, observed between Tᵥ and the Wigner temperature (Tₘ = 247 K) show, Fe₃O₄ can be considered a Wigner electron glass. The resistivity is a minimum at Tₘ suggesting glassy, precursor effects in the Tᵥ – Tₘ region.

Fe₃O₄ has a fully spin-polarized band, making an ideal compound to study basic spintronics. The magneto-chemical formula is: \((\text{Fe}^{3+})_\lambda \left[\text{Fe}_3^{3+} \downarrow \text{e}^\uparrow\right]_\beta \text{O}_4^{2–}\). The Fe ions have two different configurations: in the tetrahedral site (A) the Fe³⁺ ion is surrounded by four O²⁻ ions, while in the octahedral site (B) the Fe ion is surrounded by six O²⁻ ions. The electron configuration of (Fe³⁺)_λ is 3d⁰ 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. The net magnetization is 4 μₜ per unit cell. The top energy band is half filled by the fully spin-polarized 3d* electrons. Our studies support the phonon-assisted electron-spin hopping model and the Mott-Wigner glass description of Fe₃O₄.
II. μSR studies using Fourier transformation and curve fitting

The behavior of the internal magnetic field in Fe$_3$O$_4$ as a function of temperature and applied magnetic field has been reported in previous μSR studies. At T$_w$, there appears to be a 2nd order phase transition. See Fig. 1. These studies have used Fourier transformation (FT) and curve fitting (CF). The CF fits have only produced reasonable frequency (or local field ($B_{loc}$)) values with large error bars for its amplitudes and relaxation rates. $B_{loc}$ can be written as $B_{loc} = B_{ext} - B_{dem}$ for B $<$ $B_{dem}$ and $B_{loc} = B_{ZF}$ for B $<$ $B_{dem}$. $B_{ext}$ is the internal field; $B_{dem}$ is the demagnetization field; ZF means zero field.

An external field ($B_{ext}$) dependency for Fe$_3$O$_4$ at RT for the B // <110> shows that the frequencies follow an expected linear trend with a slope of 13.55 MHz/kOe and $B_{dem} = \sim 0.9$ kOe. The broadening with increasing $B_{ext}$ was interpreted as two frequency signals. At $B_{ext} = 5$ kOe, $B_{loc}$ (high) is somewhat larger than theoretically allowed.

The frequency behavior at 205 K, B // <110> differs from the one observed at RT, B // <110>. External field dependence of μSR frequencies for B // <110> at 205 K shows that two frequency signals follow the expected linear trend with slopes of 13.55 MHz/kOe with both a $B_{dem}$ of about 0.5 kOe and a 5-MHz shift. The lower frequency at zero field and 100 Oe has not been seen by FT and CF analysis. At zero field, FT & CF studies indicated only one frequency signal. Note, the relaxation rates at 205 K are much smaller; thus, smaller errors in frequency are seen at 205 K compared to those at RT.

A. μεμSR Fe$_3$O$_4$ investigations

Our ME μSR study analyzes original Fe$_3$O$_4$ 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 ME-Burg μSR technique, we refer to Refs. 10 and 11.

![FIG. 1. μSR frequencies in magnetite at zero field. T$_v$ and T$_w$ are indicated. A potential secondary magnetization trend is added to suggest a 2nd internal field in the T$_v$ - T$_w$ region. To extrapolate the upper field line to RT & beyond is another possibility. Adapted and reproduced with permission from Boekema et al., Phys Rev B 31, 1233 (1985). Copyright 1985 American Physical Society. About one-half of the data points shown in Fig. 1 have been reported in Ref. 10.](image-url)

B. μεμSR Fe$_3$O$_4$ B // <111> field dependence at RT

The field-dependent μSR data of B // <111> Fe$_3$O$_4$ at RT have been analyzed using μεμSR. An optimized T$_f$ of 0.6 μs is found to be about twice the relaxation time of the frequency signal. The μεμSR <111> Fe$_3$O$_4$ transform observations are consistent and yet are more precise than those previously made by CF. In Fig. 2, 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 χ². In Table I, our fit parameters 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. 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. A slight misalignment of the B // <111> alignment causes the μ-O sites to be magnetically different, resulting in an asymmetric ME distribution.

C. μεμSR Fe$_3$O$_4$ B // <110>

1. μεμSR Fe$_3$O$_4$ B // <110> RT

We have evaluated μεμSR transforms for low external fields for B // <110> and RT. As an approximation, a 1 μs T$_f$ is used. At zero field, we find only one peak of 54.4 MHz. The MEμSR transforms

![FIG. 2. Spectral density (SD) for B // <111> Fe$_3$O$_4$ at 5 kOe & RT, with a best fit of 2 Lorentzians. T$_f$ = 0.6 μs.](image-url)

| Fit function | $\chi^2$ × 10$^3$ | ME-BG Amplitude | 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) MHz | 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) |

| TABLE I. Fit values for B // <110> RT ME transform. The two Lorentzians give the best fit and lowest $\chi^2$. S (width) in MHz & K (inverse width) in MHz$^{-1}$. The substantial $\chi^2$ reduction for two Lor’s is caused by a much better fit in the 105 – 110 MHz interval, than that for two Gaus. |
for 500 Oe indicate a second signal. A two-Lorentzian fit reveals two peaks at 55.5 MHz and 58.0 MHz. If $B_{\text{dem}}$ is much less than 500 Oe, then we expect for $f(\text{high})$ about 61 MHz. Then, the $f(\text{low})$ peak may suggest a magnetically different set of muon sites, as $B \parallel <110>$.

With an optimized $T_f$ of 0.5 $\mu$s, two peaks become overlapping. See Fig. 3. The lower, less intense, frequency signal corresponds with those reported in the previous studies. The higher frequency signal (not found previously by CF an FT) is found below $B_{\text{dem}}$. This strong alternative interpretation suggests that a small field induces a short-range order, similar to what is seen in the $T_V - T_W$ interval.

2. ME$\mu$SR $\text{Fe}_3\text{O}_4$ $B \parallel <110>$ 205 K

In Fig. 4 an ME$\mu$SR transform for $B \parallel <110>$ $B = 100$ Oe and $T = 205$ K is shown. With an optimized signal ($T_f = 1.2$ $\mu$s) the distribution indicates two smaller signals (55 & 57 MHz) besides the main signal at 60 MHz. This sharp signal corresponds to the signal seen by CF. The 55 & 57 MHz signals were not seen in FT and CF analysis.

In Fig. 5, an ME$\mu$SR transform ($T_f = 0.5$ $\mu$s) is shown for $B$ (720 Oe) $B \parallel <110>$ at $T = 205$ K. Besides the peak at 68 MHz, a second signal is seen at 60 MHz. The frequency difference between the two signals is $\sim 8$ MHz which is in the order of the frequency shifts seen at $T_V$ and at $T_W$ in zero field. 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 comparable RT-disordered state has been induced by the small applied field. This may well be glassy, precursor effects.

A summary of our ME$\mu$SR $\text{Fe}_3\text{O}_4$ $<110>$ analysis is shown in Table II.

D. ME$\mu$SR $\text{Fe}_3\text{O}_4$ $B \parallel <100>$ field dependence at RT

We have evaluated the ME$\mu$SR transforms ($T_f = 1$ $\mu$s) in $\text{Fe}_3\text{O}_4$ for small $B \parallel <100>$ at RT. These ME$\mu$SR transforms for $B \parallel <100>$ indicate no substantial change up to 1 kOe. Only one frequency signal at zero field, 50 Oe and 1 kOe is seen. The fitted frequencies of about 55

| $f$ (ME$\mu$SR) MHz | Temperature K | $B$ (external) Oe | $f$ (expected) MHz |
|---------------------|---------------|-------------------|-------------------|
| 55.5                | RT            | 500               | 55                |
| 58.                 | RT            | 500               | 59                |
| 60.                 | 205           | 100               | 61                |
| 56. and 57.         | 205           | 100               | 56                |
| 68.                 | 205           | 720               | $61 + \Delta B$   |
| 60.                 | 205           | 720               | $57 + \Delta B'$  |
MHz are independent of $B \leq 1 \text{kOe}$, indicating for $B / / <100>$ $B_{\text{dem}}$ is larger than 1 kOe.

III. CONCLUSIVE REMARKS

Using MEμSR, we find with improved precision and sensitivity the local magnetic fields in Fe$_3$O$_4$ single crystals and find frequency signals not seen by FT nor CV. Two signals close in frequency is consistent with the beat patterns seen in the μSR time series. We have found two frequencies for the $<111>$ orientation at 5 kOe and RT; the smaller signal indicates a slight misalignment of the $<111>$ Fe$_3$O$_4$ crystal. For the $<100>$ orientation and fields less than 1 kOe, one peak with no change in frequency is found. Thus, the $<100>$ $B_{\text{dem}}$ is larger than 1 kOe; effectively zero field exists for $B < 1 \text{kOe}$.

For the $<110>$ orientation: at RT and 500 Oe, two frequency signals are observed. These two broad signals suggest two separate magnetizations at RT. These B-dependent MEμSR peaks reveal a much different behavior at RT than at 205 K. The sharp MEμSR signals at 205 K suggest also two separate magnetizations. The difference between the two frequencies and the expected values is below 3%. See Table II. In both cases, these effects are plausibly caused by glassy, precursor effects above $T_V$ and induced by small magnetic fields below $B_{\text{dem}}$.

Our new MEμSR outcomes are consistent with the single crystal diffuse scattering findings of short-range correlations in Fe$_3$O$_4$ above $T_V$. Further, analysis of interatomic pair distribution derived from x-ray scattering data has revealed that short-range order can be observed even up to the ferrimagnetic Neél temperature of $\sim 850$ K. These short-range correlations may also explain the spontaneous magnetization reversals seen in a low field and in the $T_V - T_W$ region.

In sum, Fe$_3$O$_4$ is more likely a narrow-band (degenerate) semiconductor than a semimetal at RT. The 3d$^*\text{ electrons are important ingredients of the conduction mechanism in Fe$_3$O$_4$, supporting the phonon-assisted electron(-spin) hopping model.}$^5$ Through MEμSR analysis, a clearer picture of the magnetic environments in Fe$_3$O$_4$ is found. This new interpretation indicates two magnetization trends, reflecting different short-range orders in the ZF phase diagram.

ACKNOWLEDGMENTS

Research is supported by Department of Energy – Los Alamos National Laboratory & Ad Fysi Care.

REFERENCES

1. A. Chainani et al., J Electron Spect & Rel Phen 78, 99 (1996); J. H. Park et al., Phys Rev B55, 12813 (1997).
2. W. Shchennikov et al., Solid State Comm 149, 759 (2009).
3. T. Her and C. Boekema, J Appl Phys 76, 5772 (1994); P. Sakkaris et al., APS Bulletin 2014.
4. J. R. Cullen and E. R. Callen, Phys Rev B 7, 397 (1973).
5. C. Boekema et al., Phys Rev B 33, 2102 (1986); Phys Rev B 31, 1233 (1985).
6. G. S. Parkinson et al., Advanced Magnetic Materials (2012) https://www.intechopen.com/books/advanced-magneticmaterials/tailoring-the-interface-properties-of-magnetite-for-spintronics.
7. M. E. Fleet, Acta Crystallography B 37, 917 (1981).
8. S. Sasaki, Acta Crystallography B 53, 762 (1997).
9. C. Boekema et al., Hpf Interactions 31, 487 (1986); 17-19, 305 (1984).
10. C. Boekema and M. C. Browne, AIP Conf Proc 1073, 260 (2008).
11. C. Boekema et al., Proc 11th Int M2S Conf (2015) and references therein. C Morante et al, APS Bulletin March 2018; SJSU Physics Internal report (2019).
12. A. Bosak et al., Phys Rev X 4, 011040 (2014).
13. G. Perversi et al., Nature Comm 10, 2857 (2019).
14. R. A. Buchwald et al., Phys Rev Lett 35, 878 (1975).
15. A. A. Hirsch and G. Galeczki, J Phys Collo 40(C2), 320 (1979).
16. C. Boekema, Philos Mag B 42, 409 (1980).