Study of the magnetite to maghemite transition using microwave permittivity and permeability measurements

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Abstract

The microwave cavity perturbation (MCP) technique is used to identify the transition from magnetite (Fe₃O₄) to the meta-stable form of maghemite (γ-Fe₂O₃). In this study Fe₃O₄ was annealed at temperatures from 60 to 300 °C to vary the oxidation. Subsequent to annealing, the complex permittivity and magnetic permeability of the iron oxide powders were measured. The transition to γ-Fe₂O₃ was corroborated with x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and vibrating sample magnetometry (VSM). XRD, XPS and VSM implied that the starting powder was consistent with Fe₃O₄ and the powders annealed at more than 200 °C were transitioning to γ-Fe₂O₃. The MCP measurements gave large differences in both complex permittivity and magnetic permeability of the two phases in the frequency range of 2.5–10.2 GHz. Magnetic permeability decreased with annealing temperature, though magnetic losses showed frequency dependent behaviour. Complex permittivity measurements showed a large decrease in both dielectric constant and losses at all measurement frequencies, as well as a prominent loss peak centred around the phase transition temperatures. We interpret the loss peak as being a consequence of field effects due to an intermediate multi-phase mixture. Additionally, almost no frequency dependence was observed.

The reduction in complex permittivity implies that the Fe²⁺ cations in the lattice provide a significant contribution to polarization at microwave frequencies and the effects of Fe³⁺ are nominal in comparison. The change in loss can be explained as a combination of the differences in the effective conductivity of the two phases (i.e. Fe₃O₄ exhibits electron-hopping conduction whereas the presence of vacancies in γ-Fe₂O₃ nullifies this). This shows that the non-invasive MCP measurements serve as a highly sensitive and versatile method for looking at this phase transition in iron and potentially the effects of oxidation states on the polarization in other iron oxides.

Keywords: magnetite transition, maghemite determination, complex permittivity, complex permeability, microwave cavity perturbation, electron hopping conduction

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(Some figures may appear in colour only in the online journal)
I. Introduction

Magnetic particles have gained great interest recently in applications ranging from electromagnetic absorbers [1–4] to numerous biomedical applications including magnetic drug delivery [5] and treatment of hyperthermia [6, 7]. In particular, magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃) have been highlighted as suitable candidates for these applications due to the simplicity of their synthesis, biocompatibility and non-toxicity [8, 9]. Fe₃O₄ can be synthesized through coprecipitation of iron salts. Synthesis of γ-Fe₂O₃ is most commonly through subsequent oxidation of Fe₃O₄, with the exception of the dehydroxylation of iron oxide-hydroxides such as lepidocrocite (γ-FeOOH) or goethite (α-FeOOH) [10, 11]. Oxidation of Fe₃O₄ in air at temperatures around 200–300 °C induces the phase change to γ-Fe₂O₃ [12–14]. These two oxides are of interest due to their structural similarity but γ-Fe₂O₃ is the more thermally and chemically stable of the two [15, 16].

Current standard techniques to study the synthesis of γ-Fe₂O₃ include x-ray diffraction (XRD) [17, 18], x-ray spectroscopy (XPS), x-ray absorption near edge spectroscopy (XANES) [19], vibrating sample magnetometry (VSM), Raman and IR spectroscopy [20, 21], and Mössbauer spectroscopy [12, 22]. The most effective method is Mössbauer spectroscopy since it specifically probes the oxidation state of the iron from the sextet caused by Zeeman splitting from the different nuclear spin moments. XRD works by changes in lattice constant but since both oxides have the same inverse spinel lattice, identifying γ-Fe₂O₃ after oxidation is by no means trivial. The lattice constant of γ-Fe₂O₃ (8.34 Å) is slightly smaller than Fe₃O₄ (8.39 Å), resulting in a shifted diffraction pattern towards smaller angles for Fe₃O₄ when compared with γ-Fe₂O₃. A difference can be identified though from the shift in the (5 1 1) plane [23]. For a multiphase material, a convolution of two peaks with intensities dependent upon the concentrations of Fe₃O₄ and γ-Fe₂O₃ can be seen. XPS probes a difference in binding energy of the Fe 2p core electrons, as well as characteristic satellite peaks caused by particular oxidation states in materials. This technique is a very effective surface probe, but is less sensitive to the bulk. Raman Spectroscopy is able to identify the material phases through distinct differences in phonon scattering of the A₁g, E₂g and T₂g modes [20, 21]. However, due to the nature of the measurement it can induce the phase change to hematite, caused by heating from the laser and thus great care must be taken to measure these materials [21, 24, 25]. Though phase identification can be achieved, there are some drawbacks to all of these methods, including complicated analysis, low sensitivity, invasive (to the point of destruction) and the demand for complex, expensive experiments which sometimes involve ionizing radiation.

Since the process is related to cations with unpaired electron spins, polarization (via permittivity) and permeability measurements may offer a complementary insight to the transformation. This can be achieved through impedance spectroscopy and magnetometry [26]. For the former this requires powdered samples to be compressed, shaped and physically built into the measurement system. Though this method infers the conductivity, repeatability becomes a problem as well as system contamination due to contact. For magnetic measurements, high precision field probes with large magnets or superconducting detectors require controlled cooling to support large fields. Our present study explores whether the conversion of Fe₃O₄ to γ-Fe₂O₃ can be observed using non-invasive dielectric and magnetic probing techniques, in particular MCP. The MCP approach may offer a simpler and highly sensitive measurement system for oxidation analysis, which could be applied to many other materials systems apart from iron oxides.

II. Principles of microwave characterization

Microwave cavity perturbation (MCP) provides a non-contacting electromagnetic probe through the simple perturbation of high density fields as opposed to contact measurements at DC (or low frequencies) and subsequent measurement of impedance through voltage and current. In MCP, the powder of interest is simply poured into a low microwave loss container and placed into the antinode of the appropriate standing wave (electric or magnetic) of a microwave cavity resonator. The greatest advantages of this approach are the non-contact nature of the measurement, as well as low power requirements (generally it uses input power levels of approximately 1 mW, with typically less than 10 μW dissipated in the sample). Microwave systems have been explored to measure some iron oxides through electron spin resonance (ESR) where a sample perturbs a microwave cavity resonator whilst subject to a DC magnetic field (often modulated by Helmholtz coils to increase the signal to noise ratio using lock-in amplifiers). The DC field aligns the electron spins parallel and anti-parallel, creating Zeeman splitting where the equivalent energy level difference lies in the microwave region through the Einstein relation $E = hf$. Maximum absorption occurs when the microwave frequency of the resonator matches that of the energy difference $E$. It has been shown that Fe₃O₄ and γ-Fe₂O₃ give different ESR responses, with γ-Fe₂O₃ giving a narrower linewidth at absorption [27–29]. If the differences in the materials’ properties can be expressed in a simple change in cavity resonance alone, there is no need for the additional instrumentation imposed by ESR. Hence we move from probing spin resonance to simple bulk complex permittivity and permeability measurements, which eliminates the need for a large DC electromagnet, field calibration procedures and other added complexities, reducing the system to just a resonator and a means of interrogating it. Whilst we use a vector network analyser for the measurements presented here, a simple system involving a voltage controlled oscillator and a power detector will suffice.

Complex permittivity (hence conductivity) and permeability measurements using MCP are very simple. The sample is placed inside a hollow metal cavity and the differences that arise in complex resonant frequency between the unperturbed and sample perturbed states (the real part being centre frequency and imaginary part being related to the quality factor,
Figure 1. Example of resonant traces from an MCP measurement. The procedure involves measuring the frequency and 3 dB bandwidth (BW) of the unperturbed state denoted by ‘0’ and the sample perturbed state denoted by ‘s’. These values can be related to real and imaginary parts of the complex permittivity or permeability.

III. Experimental methods

Fe2O4 powder (Bayoxide® E8712) initially exhibited a solid black colour consistent with Fe3O4. The particle sizes of this sample are quoted at approximately 0.3 μm. 500 mg of the powder was filled into an open vial and placed into a laboratory oven. Ten separate vials were prepared with each one annealed for 1 h at a different temperature, ranging from 60 to 300 °C, to vary the amount of oxidation of Fe2O3 to Fe3O4. The resultant powder changed to a brown colour which was initially subjectively identified as γ-Fe2O3. The identification of this phase was carried out using XRD, XPS, VSM and MCP measurements. XRD was conducted using Cu Kα radiation at 1.545 Å from 10 to 80°. Offsets were removed and Gaussian curve fitting was applied at the relevant peaks in the data to match the materials. XPS spectra were collected using a Kratos Axis Ultra DLD system with a monochromatic Al Kα x-ray source operating at 144 W. Data was collected with pass energies of 160 eV for survey spectra and 40 eV for high resolution scans. Due to the magnetic nature of the samples under analysis, the system was operated in the electrostatic operation mode with an acquisition area of approximately 300 × 700 μm². Spectra were analysed using CasaXPS (v2.3.17) with sensitivity factors supplied by the instrument manufacturer. All spectra were calibrated to the C1s line for adventitious carbon at 284.8 eV. Magnetic hysteresis loops were measured at room temperature using a LakeShore® 7400 Series VSM System calibrated to a 3 mm nickel standard. The maximum applied field on the samples was 640 kA m⁻¹. The samples were dispersed at a fixed weight concentration of 10% inside a non-magnetic adhesive and left to dry in silicone moulds approximately 3 mm in width.

The microwave complex permittivity data was collected using our aluminium TM cylindrical cavity setup (inner diameter φ = 92 mm and height h = 40 mm) which uses a selection of TM0np modes [30]. This cavity is designed to excite TM010, TM011, TM020, TM021, TM012, and TM022 modes at frequencies of 2.5, 4.5, 5.7, 6.8, 7.9 and 9.4 GHz, respectively. The complex permeability was measured using our aluminium TE cylindrical cavity setup (φ = 95 mm, h = 40 mm) which uses a selection of
TM and TE modes [31]. This cavity is designed to excite TM_{110}, TE_{011}, TE_{012} and TE_{022} modes at frequencies of 3.8, 5.4, 8.0, 8.4 and 10.2 GHz respectively. Both of these cavities are shown in figure 2. Microwave excitation and detection was provided by a Keysight Technologies PNA-L microwave network analyser using standard transmission measurements (i.e. S_{21}). Standard 3.5 mm flexible coaxial cables by Huber and Suhner were used to connect the PNA to SMA antennas on the cavity. Resonant trace data was logged using a program developed in National Instruments LabVIEW, which implements non-linear Levenberg–Marquadt curve fitting algorithms to a Lorentzian function to extract the parameters of resonant frequency, bandwidth and peak transmitted power.

The empty sample container was first placed at the sample location and measured to obtain the unperturbed frequency response. Quartz tubes (\( \phi = 1 \text{ mm}, h = 100 \text{ mm} \)) were used due to their low microwave loss. The quartz tubes were then filled to a height such that the ends of the sample protrude from the cavity (at least 60 mm) to avoid macroscopic depolarization effects and placed on a vibrating stage for 5 min to allow the particles to settle in the tube. This forms the main source of error in that the differences in particle packing gives rise to different depolarization effects each time the tube is filled (and hence the effective complex permittivity and permeability may vary). The tubes were then placed in the cavity to conduct a perturbed measurement. Multiple S_{21} measurements were taken over a period of approximately 30s at a sample rate of 1 Hz, with the average values of frequency and bandwidth used to calculate the permittivity/permeability and standard deviation used to provide random error (maximum of 5kHz deviation, resulting in a measurement error of less than 1% for resonant frequency and 2% for bandwidth). The sample was placed with the field (either electric or magnetic) parallel to the sample tube, as shown in figure 2, to minimize any macroscopic depolarizing fields caused by the geometry of the sample container, though individual particle depolarization would still be present hence we quote effective and not intrinsic values. The effective relative dielectric permittivity, magnetic permeability and their equivalent losses were calculated using the simple, first order cavity perturbation equations [32]:

\[
\alpha_{\text{eff,1}} - 1 \approx 2 \frac{\Delta f}{f_0} \frac{V_s}{V_e} 
\]

\[
\alpha_{\text{eff,2}} \approx - \frac{\Delta \text{BW}}{f_0} \frac{V_s}{V_e} 
\]

where \( \alpha_{\text{eff}} \) is the effective complex measurand, \( \Delta f \) and \( \Delta \text{BW} \) are the differences in resonant frequency and bandwidth, respectively, from the unperturbed values, \( f_0 \) is the unperturbed resonant frequency, \( V_s \) is the volume of the sample within the cavity and \( V_e \) is the effective mode volume of the cavity. The mode volume is a scalar quantity calculated by integrating the total electromagnetic energy inside of the cavity and normalising it to the field at the sample location. Calculated values of each mode used in this study are all given elsewhere [30, 31]. The effective conductivity can also be extracted using the measured dielectric losses using:

\[
\varepsilon_i = \varepsilon_1,i(\omega) - i \left[ \varepsilon_2,i(\omega) + \sigma_{\text{AC}}(\omega) / \omega \right] 
\]

where \( \sigma_{\text{AC}}(\omega) \) is the frequency dependent AC conductivity, \( \omega \) is the angular frequency and \( \varepsilon_1,i \) and \( \varepsilon_2,i \) are the polarization related contributions to the relative dielectric constant and losses, respectively. In most cases, either \( \varepsilon_2,i(\omega) \) or the
conducting term dominates (for example, in water ε ω₂,d dominates due to Debye relaxation caused by dipolar molecules whereas in semi-metallic powders it will more likely be conductivity related). Using these simple equations we can infer the dielectric, magnetic and conducting properties of powders.

IV. Results and discussions

IV.A. X-ray diffraction (XRD)

Diffraction patterns from 20 to 80° were collected, with data cropped to the significant peaks shown in figure 3. The diffraction patterns of the starting Fe₃O₄ powder and powders annealed around the inferred transition temperature from the microwave results were obtained. The pattern of the starting powder was matched to Fe₃O₄, with a strong (3 1 1) peak at approximately 35.4° accompanied with the (2 2 0), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) planes of the cubic cell at 30.0, 43.1, 53.5, 57.0 and 62.6°, respectively. The same planes are evident for the annealed samples, but are shifted upward with increasing temperature indicating that structurally these materials have a spinel cubic lattice but with a changing lattice constant. The average calculated lattice constant from the higher diffraction angles of planes (5 1 1) and (4 4 0) yielded 8.39 Å and 8.36 Å for the starting Fe₃O₄ and the 260 °C annealed samples, respectively. (see supplementary material regarding instrumentation errors with the Inorganic Crystal Structure Database (ICSD) match, stacks.iop.org/JPhysCM/28/106002/mmedia). A trend in decreasing lattice constant is evident.

The explanation behind the decreasing lattice constant may be due to the ionic radii of the Fe²⁺ and Fe³⁺ cations. Since Fe²⁺ cations have a larger ionic radius, the Fe–O spacing is greater. In γ-Fe₂O₃ the conversion of these cations to Fe³⁺, along with the formation of vacancies, decreases the spacing which results in the shifted 2θ pattern. This result is congruent with the transformation to γ-Fe₂O₃ as given in the aforementioned literature. However, a convolution of two peaks for the (5 1 1) plane, as reported by Kim et al (2012), was not noticed in this material. This may be more of a consequence of the low resolution from the Cu Kα line, and hence the presence...
of an intermediate phase may not be determined. Hence, from these results we can qualitatively conclude that structurally the phase change occurs at a temperature of at least 180 °C.

IV.B. X-ray photoelectron spectroscopy (XPS)

The high resolution XPS spectra are shown in figure 4. For the Fe3O4 starting material, the Fe2p3/2 peak is centred at 711.1 eV and is ascribed to the convolution of both Fe2+ and Fe3+ signals in Fe3O4 [33]. Since Fe3O4 comprises of both Fe3+ and Fe2+, the resultant peaks are a convolution of electron energies in both oxidation states and whilst the Fe3+/Fe2+ ratio can be obtained through rigorous curve fitting, for this experiment only a qualitative identification of the γ-Fe2O3 phase is required.

Annealing reveals a change in the O1s spectra, with loss of organic contamination and the development of clear oxide and hydroxide peaks, the latter coming from exposure of the samples to air during transfer to the vacuum chamber for analysis. More importantly, the Fe2p region exhibits a slight downward shift in energy from 711.1 eV to 710.7 eV and the clear development of a satellite peak at around 719.0 eV is characteristic of Fe2+ and other forms of Fe2O3. Hence, this measurement shows that the phase change can be noticed, beginning at 100 °C and becoming complete by 300 °C.

IV.C. Vibrating sample magnetometry (VSM) and magnetic properties

Magnetic hysteresis curves of the annealed Fe3O4 samples are given in figure 5 with numerical calculations given in table 1.

| Table 1. Summary of magnetic properties obtained from VSM measurements with errors over three different samples. |
|---------------------------------------------------------------|
| | 0 °C (Fe3O4) | 200 °C | 300 °C |
|-----------------|---------|-------|-------|
| Hysteresis area × 10^3 (J m^-3) | 34 ± 10 | 20 ± 30 | 8 ± 1 |
| Coercivity, Hc (kA m^-1) | 9.7 ± 0.9 | 10.2 ± 0.5 | 11.1 ± 0.8 |
| Magnetization, Ms (A m^-2 kg^-1) | 92 ± 2 | 87 ± 9 | 60 ± 3 |
| Remanence, Mr (A m^-2 kg^-1) | 9 ± 2 | 13 ± 9 | 11 ± 4 |
| Squareness, Ms/Ms | 0.1 ± 0.03 | 0.2 ± 0.2 | 0.18 ± 0.09 |

The difference in magnetism between the two materials is a consequence of the cations in the inverse spinel lattice. For Fe3O4, ferrimagnetism exists through two main mechanisms, as given in figure 6. The first is the anti-ferromagnetic super-exchange interactions between the Fe2+ and Fe3+ cations through the O2- anions [38]. The spin-up 5d electrons in the Fe2+ couple with the overlapping 2p orbitals in the O2- making them spin-down. The other 2p electron is thus spin-up which makes the Fe3+ 5d electrons spin-down. Thus Fe2+ and Fe3+ are antiparallel and cancel out each other’s unpaired spin magnetic moments. The second factor is related to the aforementioned double-exchange interaction [39]. The spin-down electron can only hop from Fe2+ to Fe3+ if the majority spins are the same. Hence they are coupled and aligned parallel. Therefore, all the Fe2+ cations contribute to the magnetic moment while all Fe3+ cations cancel each other out. However, in γ-Fe2O3 the conversion of 2/3 of the Fe2+ to Fe3+ balances some of the Fe3+ cations but not all of them since the rest are turned into vacancies, resulting in a finite magnetic moment. When calculated, Fe3O4 has a larger magnetic moment [40] which is implied in table 1, thus providing more evidence that the phase change has occurred.
IV.D. Microwave cavity perturbation (MCP)

MCP traces of two modes are given in figure 7. It is clear that the microwave properties of Fe$_3$O$_4$ change as it is annealed at different temperatures. This is shown by the changes in complex frequency, with a maximum in dielectric loss occurring at an annealing temperature of 200 °C. Taking the centre frequency and bandwidth of each trace of each resonant mode, the complex permittivity (thus conductivity) and permeability can be calculated.

The complex permittivity is given in figure 8. At temperatures below 180 °C both the effective dielectric constant and losses show minimal change. At higher temperatures, the dielectric constant decreases greatly while the losses increase to a peak and then decrease to effectively zero. There is also very little frequency dependence, as implied by all of the different resonant modes being superimposed upon one another. This consistency in the loss measurements implies an increasing effective conductivity with frequency, as calculated using (4).

As more of the Fe$^{2+}$ cations are oxidized to Fe$^{3+}$, the dielectric constant decreases, showing that the presence of Fe$^{2+}$ cations provides a significant contribution to the polarization mechanism at microwave frequencies in Fe$3$O$_4$ most likely due to the double exchange interactions explained later. With the assumption that only Fe$^{3+}$ cations exist in the samples annealed above 200 °C as inferred by XPS, the permittivity measurements show that the contribution from the Fe$^{3+}$ cations is much less without the mixed valence Fe$^{2.5+}$ at microwave frequencies.

A similar decrease is noticed in the losses, which reduce from approximately 0.4 to 0, as shown in figure 8. A large loss peak, however, is exhibited at around 200 °C, which intriguingly is not manifested in any of the other measurement techniques. This can be explained by a consequence of measuring a multiphase mixture in a microwave electric field if the difference in complex permittivity between the two phases is significant. Consider an air porous medium ($\epsilon_b$) that consists of multiple spherical particles of radius $b$ representing the Fe$_3$O$_4$ phase. After annealing, the powders are filled into the tube with a fraction of the Fe$_3$O$_4$ now converted to γ-Fe$_2$O$_3$. This can be represented as a spherical volume ($\epsilon_a$) with radius $a$ growing within the main volume. This volume is not actually growing inside the individual Fe$_3$O$_4$ particles since the oxidation process is expected to permeate from the edges but represents a low loss volume growing within the bulk volume. The reason why the model has been considered in this way is because models for a lossy core and a low loss shell particle do not take into account the local field effects from other particles. In this model, the volume of the mixture remains the same, hence $a \leq b$. Eventually, all of the Fe$_3$O$_4$ phase disappears and the result is the γ-Fe$_2$O$_3$ phase or the low loss phase now occupies volume of the original particle so that $a \rightarrow b$. If this material is placed in an applied E-field ($E_0$), then the dipole moment per particle volume ($P_i$) of one of these inclusions can be calculated using the following formula [41]:

$$P_i = E_0 \frac{(\beta + 2)(\alpha - 1)\gamma^3 - (\alpha + 2)(\beta - 1)}{(\beta - 1)(\alpha + 2) - 2(\beta - 1)(\alpha - 1)\gamma^3}$$

where $\alpha = \epsilon_a / \epsilon_b$, $\beta = \epsilon_m / \epsilon_a$, $\gamma = a/b$. In this instance we assume that the porous spaces are air (hence $\epsilon_m = 1$). This formula can be incorporated into the well-known Maxwell-Garnett mixing law for multiple particles in a dielectric medium:

$$\epsilon_{\text{eff}} = \epsilon_m \left(1 + 2\delta_{i}P_i / (1 - 2\delta_{i}P_i)\right)$$

where $\delta_{i}$ is the volume fraction of the particles in the tube. In the case of a lossy particle with an increasing volume of a lossless dielectric, a loss peak can be exhibited at a certain volume fraction, as shown in figure 9. This loss peak only
occurs, however, if the difference in permittivity between the materials is significant. Hence, microwaves maybe a very useful tool for looking at dramatic phase changes in materials and these materials may have excellent microwave absorbing properties at certain volume fractions.

Since Fe₃O₄ is a multi-valence oxide, it has a significant electrical conductivity which has been explained as a consequence of electron hopping from double exchange interactions through a chain of Fe²⁺ and Fe³⁺ cations [39]. This occurs because, being high spin [42], the cations only differ by one spin down electron, which is effectively delocalized due to minor overlapping between τ₂g orbitals. In the transformation to γ-Fe₂O₃, 2/3 of the Fe²⁺oct cations are oxidized to Fe³⁺ while the remaining 1/3 diffuse of out of the lattice leaving behind vacancies [43]. The hopping dependent conductivity effectively explains why γ-Fe₂O₃ is an inferior conductor when compared to Fe₃O₄, as the conduction path through the cations is disrupted by the presence of vacancies and, assuming that the spin states in γ-Fe₂O₃ are high [42], there is no longer a delocalized spin-down electron. Hence, it is seemingly a case of one phase showing electron hopping conductivity and the other showing none. Now, as for the microwave methods, the hopping conduction mechanism will contribute to the loss as given by (4). The general model for hopping mechanisms in conductivity follows the Jonscher power law (JPL) [44]:

\[ \sigma_{AC}(\omega) = \sigma_{DC} + A\omega^k \]  

Figure 9. Abstract representation (a) of the annealing process resulting in a multi-phase mixture with a volume of the low loss phase inside the bulk mixture. Effective complex permittivity (b) is shown for a dielectric mixture (εᵣ = 0.6) as a function of particle radius ratio.

Figure 10. Calculated complex permeability of annealed Fe₃O₄ samples using five different modes of the resonator (a) as a function of annealing temperature with error bars given as the standard deviation of the measurement of two separately filled powder tubes for a given annealed temperature and as a function of frequency (b).

where \( \sigma_{DC} \) is the DC conductivity, \( A \) is a pre-exponential constant and \( k \) is the exponent of the power law. This law includes the restriction of \( 0 < k \leq 1 \), while larger values indicate a super-linear power law (SLPL). The measured slopes are given in figure 8 where Fe₃O₄ gives a SLPL in this frequency range with an exponent \( k \) of approximately 1.12. For γ-Fe₂O₃ (annealed at 300 °C) the dielectric loss (and hence conductivity) is effectively zero at microwave frequencies. Taking the slopes of 200 and 260 °C annealed samples we find that the SLPL tends towards a regular JPL with \( k \) values of 0.94 and 0.66 respectively. Therefore, this implies that the SLPL characteristic may also be a figure of merit for identifying the phase transition.

The complex permeability or magnetic permeability and losses are given in figure 10. From this study and previous work [31], the microwave magnetic permeability of Fe₃O₄ decreases with frequency while the losses have a broad peak over the 5.0–8.5 GHz range. As the powder is annealed, the overall magnetic permeability decreases with frequency, congruent with the VSM measurements. The losses, however, increase in the lower GHz range while decreasing in the higher range. This implies that the broad peak may have either disappeared, or has shifted to lower frequencies. The magnetic permeability is merely a tail of the natural ferromagnetic resonance peaks occurring at lower frequencies as given by the negative slopes. The greatest differences occur in the TE₀₂₀ (10.2 GHz) mode in the losses,
and in the permeability in the TE011 mode (5.4 GHz) as shown in figure 10. From the TM110 mode, the losses give a similar response as for the permittivity measurements, with a decrease in the real part and a large loss peak at 200 °C. Contrary to the permittivity measurements, the losses at 300 °C do not go to zero and are of similar values to the starting material. This may be explained by the fact that in Fe3O4 the dielectric and magnetic loss mechanisms are a consequence of the double-exchange interaction (i.e. electron hopping gives rise to conduction loss and the ferrimagnetism from coupled electron spins will have an associated magnetic alignment loss with an applied field). With the diffusion of Fe2+ cations and the formation of vacancies, the dielectric loss mechanism is eliminated but the magnetic mechanism is now due to the imbalance of tetrahedral Fe3+ and octahedral vacancies, or an absence of the super-exchange interaction (which caused the anti-ferrimagnetism in Fe2O3) and hence the losses are associated with this. The TE022 mode shows little changes in the real part but a large decrease in loss from 140 °C. The TE011 mode shows some change in the losses but larger changes in the real part, again occurring at 140 °C. The transition is somewhat less clear-cut than for the permittivity measurements, but when looking at the frequency dependent data the change can be clearly seen.

Qualitative information of the transition is apparent in all of the MCP measurements, however, it can be shown that quantification of the Fe3O4 to γ-Fe2O3 ratio can be achieved using the plateau responses given in the effective dielectric constant measurements and if the air gaps caused by the packing density are considered. However, measuring the density of the samples for a given mass and volume will require accurate determination of the fill height in the tube. In this case, there were no noticeable differences in mass but this was due to the very small sample volume and hence the associated measurement error of the mass was too large. Nonetheless, assuming that the starting and ending powders consist of 0% and 100% γ-Fe2O3 respectively, and the theoretical density of Fe3O4 and γ-Fe2O3 is similar at 5.2 and 4.8 kg m⁻³ respectively [46], the effective resolution (Δε eff,1,max) in determining the concentration can be achieved from the maximum sample error given in figure 8(a). These values are given in table 2. Hence, for this particular MCP system and only with the assumption that the packing density is similar, the TM020 mode is potentially able to measure γ-Fe2O3 in concentrations of 6% only when it is mixed with Fe3O4 in these quartz tubes. This value is likely to increase if the packing density is significantly different amongst the samples but demonstrates the potential for MCP to extract this phase ratio.

V. Conclusion

We have shown that the MCP method is excellent for high-sensitivity, non-invasive materials characterization for the Fe3O4 to γ-Fe2O3 transition in annealed powders. We have also presented data from the standard methods of XRD, XPS and VSM techniques on these powders to corroborate the findings found with MCP. Each technique bears its own figure of merit for the characterization of the phase change. XRD results indicated the changing lattice constant from the upward shifting pattern in 2θ. XPS showed differences in binding energy caused by the different Fe cations at the surface of the material. Also Fe3+ satellite peaks associated mainly with the γ-Fe2O3 verified the change. VSM measurements provided hysteresis curves which showed that the starting material had a saturation magnetization very similar to Fe3O4, which decreased as the sample was annealed, again congruent with the change since γ-Fe2O3 is less magnetic. MCP measurements gave large frequency dependence for the effective permeability, with 3.8 and 10.2 GHz giving the most sensitive results, but with opposite behaviours of increasing and decreasing trends, respectively, with increased annealing temperature. Collectively looking over a broad microwave frequency range provides a better indication of the change qualitatively. Complex permittivity measurements, however, showed no frequency dependence but very large changes in both dielectric constant and loss. One cavity mode is sufficient for measuring the changes at microwave frequencies. The calculated conductivity of the powders showed a SLPL which may be due to the double-exchange hopping conduction caused by octahedral Fe2+ and Fe3+ cations. A loss peak was found at 200 °C, a consequence of field being focused at locations of inhomogeneity due to a multi-phase core-shell mixture. This insinuates that the phase change may occur around this temperature, with full transformation being reached at 300 °C. The γ-Fe2O3 phase has a smaller dielectric constant and negligible microwave losses when compared to Fe3O4. We conclude that the effects from Fe2+ cations can be probed very effectively using MCP and Fe3+ rich materials are likely to give minimal response. The presence of the loss peak in permittivity is a significant result for the applications of microwave absorber materials, as high loss tangents can be achieved through simple annealing of Fe3O4 at this temperature. This result shows that microwave dielectric measurements for all intents and purposes provide highly sensitive characterization of this oxidation process.

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| Mode  | Frequency (GHz) | Δε eff,1,max (%) |
|-------|----------------|-----------------|
| TM001 | 2.5            | 9               |
| TM002 | 4.5            | 12              |
| TM010 | 5.7            | 6               |
| TM011 | 6.8            | 9               |
| TM012 | 7.9            | 12              |
| TM020 | 9.4            | 10              |

*Resolution calculated by taking the largest measurable error caused by sample packing differences for each mode and dividing it by the difference in the effective dielectric constant between the starting powder and the powder annealed at 300 °C.*
