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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

Online supplementary data available from stacks.iop.org/JPhysCM/28/106002/mmedia

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

Magnetic nanoparticles 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]. Fe₂O₃ 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 ions 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, E₆g 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 magnets 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,
2.501 are the relative permittivity and permeability of
21
2.5
2.502

These weaknesses however can be addressed. The sparse
unknown material is very challenging since many materials
powder grains. Finally the definite identification of an
factors associated with the specific shapes of the individual
is known. This is coupled with the uncertain depolarization
measurement parameter is in the frequency domain, giving
spectral information. The big advantage of MCP is that the
measurements at different frequencies [30] to provide some
utilizing different modes allows permittivity and permeability
for TE modes). Equation (1) is used to geometrically tune

\[
 f\text{,}_1 = \frac{c}{2\pi\sqrt{\mu_r \varepsilon_r}} \sqrt{\left(\frac{\rho_{\text{tm}}}{a}\right)^2 + \left(\frac{\rho_{\text{tm}}}{l}\right)^2}
\]  

(1)

where \( f\text{,}_1 \) is the resonant frequency in Hz, \( c \) is the speed of
light, \( \mu_r \) and \( \varepsilon_r \) are the relative permeability and permeability
of the cavity respectively, \( a \) and \( l \) are the cavity radius and
height respectively, \( n \), \( m \) and \( p \) are integers representing the standing
wave mode numbers and \( \rho_{\text{tm}} \) is the \( m \)th root of the
\( n \)th order Bessel function (either \( J_n(x) \) for TM modes, or \( J_x^n(x) \)
for TE modes). Equation (1) is used to geometrically tune
the frequency at which the measurement will be performed.
Utilizing different modes allows permittivity and permeability
measurements at different frequencies [30] to provide some
spectral information. The big advantage of MCP is that the
measurement parameter is in the frequency domain, giving
extremely high sensitivity when the resonant frequencies
are in the GHz range. There are also small sample require-
ments (typical volumes of 200 mm³) and for powders they can
simply be filled into a tube with minimal preparation.

The main drawback of the MCP technique is that measure-
ments can only be performed at spot frequencies defined
by the cavity dimensions. The measurement is also volum-
etric, and thus an accurate determination of sample volume
is required. Powders will have some air gaps and hence the
measured quantity is not intrinsic unless the packing density
is known. This is coupled with the uncertain depolarization
factors associated with the specific shapes of the individual
powder grains. Finally the definite identification of an
unknown material is very challenging since many materials
may have a similar absorption response at these frequencies.
These weaknesses however can be addressed. The sparse
data points in the frequency domain are not so much an
issue since microwave relaxation phenomena such as Debye
type behaviour is not expected as dipolar molecules do not
exist. Frequency dependent data will only provide qualitative
analysis on conduction mechanisms as described later. The
solution to packing density and particle shapes is to quote an
effective value of both permittivity and permeability which are
less than the intrinsic values due to the volume of air gaps and
field depolarization. Also, weighing of samples allows appro-
priate comparison measurements of materials with different
densities. Finally, for the identification issue, in this applica-
tion it is the characterization of a known precursor material
and determination of a different product; a simple before
and after experiment. The MCP technique in this respect is a
much simpler and non-invasive method when compared to the
aforementioned techniques although, they should be used as a
complementary procedure.

III. Experimental methods

\[ \text{Fe}_2\text{O}_3 \text{ powder (Bayoxide® E8712) initially exhibited a solid} \]
black colour consistent with \( \text{Fe}_2\text{O}_3 \). The particle sizes of this
sample are quoted at approximately 0.3 \( \mu \text{m} \). 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 \( \text{Fe}^{3+} \) to \( \text{Fe}^{3+} \). The resultant
powder changed to a brown colour which was initially subjec-
tively identified as \( \gamma\text{-Fe}_2\text{O}_3 \). The identification of this phase
was carried out using XRD, XPS, VSM and MCP measure-
ments. XRD was conducted using Cu K\( \alpha \) 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 K\( \alpha \) 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 \( \times \) 700 \( \mu \text{m}^2 \). Spectra
were analysed using CasaXPS (v2.3.17) with sensitivity fac-
tors 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 diam-
eter \( \phi = 92 \text{ mm} \) and height \( h = 40 \text{ mm} \)) which uses a selection of
tM0np modes [30]. This cavity is designed to excite TM010, 
TM011, TM020, TM021, TM042, and TM042 modes at frequencies
of 2.5, 4.5, 5.7, 6.8, 7.9 and 9.4 GHz, respectively. The complex
permittivity was measured using our aluminium TE cylindrical
cavity setup (\( \phi = 95 \text{ mm} \), \( h = 40 \text{ mm} \)) which uses a selection of

\[ \begin{align*}
\text{Figure 1. Example of resonant traces from an MCP measurement.} \\
\text{The procedure involves measuring the frequency and 3 dB} \\
\text{bandwidth (BW) of the unperturbed state denoted by ‘0’ and} \\
\text{the sample perturbed state denoted by ‘s’. These values can be related to} \\
\text{real and imaginary parts of the complex permittivity or permeability.} \\
\end{align*}
\]
TM and TE modes [31]. This cavity is designed to excite TM$_{110}$, TE$_{011}$, TE$_{021}$ 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 30 s 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 5 kHz 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]:

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

\[
\alpha_{\text{eff,2}} \approx \frac{\Delta BW}{f_0} \frac{V_s}{V_e} \quad (3)
\]

where $\alpha_{\text{eff}}$ is the effective complex measurand, $\Delta f$ and $\Delta BW$ 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:

\[
\varepsilon_\varepsilon = \varepsilon_{d1}(\omega) - j \left[ \varepsilon_{d2}(\omega) + \sigma_{AC}(\omega) / \omega \varepsilon_0 \right] \quad (4)
\]

where $\sigma_{AC}(\omega)$ is the frequency dependent AC conductivity, $\omega$ is the angular frequency and $\varepsilon_{d1}$ and $\varepsilon_{d2}$ are the polarization related contributions to the relative dielectric constant and losses, respectively. In most cases, either $\varepsilon_{d2}(\omega)$ or the
conducting term dominates (for example, in water $\varepsilon_{\omega}$ 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

IVA. 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 Fe$_3$O$_4$ powder and powders annealed around the inferred transition temperature from the microwave results were obtained. The pattern of the starting powder was matched to Fe$_3$O$_4$, 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 Fe$_3$O$_4$ 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 Fe$^{2+}$ and Fe$^{3+}$ cations. Since Fe$^{2+}$ cations have a larger ionic radius, the Fe–O spacing is greater. In $\gamma$-Fe$_2$O$_3$ the conversion of these cations to Fe$^{3+}$, along with the formation of vacancies, decreases the spacing which results in the shifted 2θ pattern. This result is congruent with the transformation to $\gamma$-Fe$_2$O$_3$ 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

Figure 3. XRD patterns of the starting Fe$_3$O$_4$ powder and subsequent annealed powders (a). Close inspection of the relevant peaks (b) show upward shifts with increasing annealing temperature. The dotted lines show the angle positions of the ICSD pattern.

Figure 4. XPS patterns of the Fe2p (a) and O1s (b) core-level photoelectron spectra for Fe$_3$O$_4$ and subsequent annealing temperatures, both charge corrected to the C1s peak.

Figure 5. Hysteresis curves obtained using VSM of the starting Fe$_3$O$_4$ powder and annealed powders at 200 and 300 °C. Error bars given for three samples prepared separately and scaled based upon a powder weight concentration of 10%.
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 the Fe3+ in γ-Fe2O3 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. The calculated saturation magnetization for the starting Fe3O4 phase is 92 A m² kg⁻¹, which is the same as those reported in the literature [34] of approximately 92 A m² kg⁻¹. As the powder is annealed at higher temperatures, this value decreases to approximately 60 A m² kg⁻¹ which is less than measured values [15] of 72 A m² kg⁻¹ for γ-Fe2O3. The decrease in saturation is congruent with the change to the γ-phase and not the α-phase (since the saturation of hematite is two orders of magnitude less [34] and any signs of the α-phase should appear in the XRD patterns due to the hexagonal structure). Coercivity after annealing has very little change; starting at approximately 9.7 kA m⁻¹ and increasing to 11.1 kA m⁻¹ (see table 1 for the associated errors). The significance of this value may infer the average particle size [35] and that it does not change by much during the phase transition since the particles retain their overall shape and simply decrease in magnetic moment. The magnetic losses inferred by the integrated areas of the hysteresis curves show a large decrease with annealing temperature. Intrinsically relating this magnetic loss property to Fe3O4 and γ-Fe2O3 is not easy as it varies greatly with particle size and shape [36]. However, Fe3O4 has been shown to have larger magnetic losses than γ-Fe2O3 for micron sized particles [37].

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 Fe3+oct and Fe3+tet cations through the O2- anions [38]. The spin-up 5d electrons in the Fe3+oct 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+oct 5d electrons spin-down. Thus Fe3+oct and Fe3+tet are antiparallel and cancel out each other’s unppaired spin magnetic moments. The second factor is related to the aforementioned double-exchange interaction [39]. The spin-down electron can only hop from Fe3+oct to Fe3+tet 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 Fe3+oct to Fe3+tet balances some of the Fe3+tet 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.

<table>
<thead>
<tr>
<th>Table 1. Summary of magnetic properties obtained from VSM measurements with errors over three different samples.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 °C (Fe3O4)</td>
</tr>
<tr>
<td>Hysteresis area × 10¹ (J m⁻³)</td>
</tr>
<tr>
<td>Coercivity, Hc (kA m⁻¹)</td>
</tr>
<tr>
<td>Magnetization, M (A m² kg⁻¹)</td>
</tr>
<tr>
<td>Remanence, Mr (A m² kg⁻¹)</td>
</tr>
<tr>
<td>Squareness, Mr/Ms</td>
</tr>
</tbody>
</table>

![Double-exchange](image1.png)

![Super-exchange](image2.png)

Figure 6. Conceptual representations of double and super-exchange interactions in Fe3O4 through d orbitals of Fe2+ and Fe3+ cations.
Eventually, all of the Fe$_3$O$_4$ particles are converted to Fe$_2$O$_3$. This can be represented as a spherical volume ($\varepsilon_a$) 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 Fe$_2$O$_3$. This can be represented as a spherical volume ($\varepsilon_a$) 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 $\gamma$-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 described using the following formula [41]:

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

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

$$\varepsilon_{\text{eff}} = \varepsilon_m \left(1 + 2\delta_i P_i \right) \left(1 - 2\delta_i P_i \right)$$

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 Fe₃⁺oct and Fe₂⁺oct 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 τₙg orbitals. In the transformation to γ-Fe₂O₃, 2/3 of the Fe₂⁺oct cations are oxidized to Fe³⁺ while the remaining 1/3 diffuse 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 [16], 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]:

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

\[ (7) \]

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 (ε₁ = 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).
(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\(_{\text{eff,1}}\)) 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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References

[34] Cornell R M and Schwertmann U 2003 The Iron Oxides (Weinheim: Wiley)
[38] Gilio M A 1958 Phys. Rev. 109 777