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1 **AC susceptibility Studies in capped Ni/Ni(OH)₂ Core/Shell**
2 **nanoassemblies: Dual Peak Observations**

3
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13
14 **Abstract**

15 In the present study, the AC susceptibility (χ' and χ'') variation with
16 temperature (10-100K) for oleic acid capped Ni/Ni(OH)₂ core/shell nanoparticle
17 assemblies are reported at frequencies varying from 0.1 Hz to 1000 Hz. Nanoparticle
18 assemblies, with two average particle diameters of ~34 nm and ~14 nm were
19 synthesised using a wet chemical synthesis approach. Two peaks in the AC
20 susceptibility versus temperature curves are clearly discernable for each of the
21 samples. The first, occurring at ~22K was attributed to the
22 paramagnetic/antiferromagnetic transition of the Ni(OH)₂ present in the shell. The
23 second higher temperature peak was attributed to the superparamagnetic blocking of
24 the pure Ni situated at the core of the nanoparticles. The higher temperature peaks in
25 both the χ' and χ'' curves were observed to increase with increasing frequency. Thus

26 the Néel and the blocking temperatures for such core-shell nano-assemblies were
27 clearly identified from the AC analysis, where as they were not discernable
28 (superimposed) even from very low DC (FC/ZFC) field measurements. Interparticle
29 interactions within the assemblies were studied through the fitting of
30 phenomenological laws to the experimental datasets. It is observed that even with an
31 oleic acid capping layer, larger Ni/Ni(OH)₂ nanoparticles experience a greater degree
32 of sub-capping layer oxidation thus producing lower magnetic interaction strengths.

33 **I. Introduction**

34 To date magnetic nanoparticles have been successfully synthesised (Godsell et
35 al., 2010, Li et al., 2010, Banerjee et al., 2000, Donegan et al., 2011, Das et al., 2002)
36 and used in a variety of applications such as in magnetic resonance imaging
37 contrasting agents (Huh et al., 2005), ferro-fluids (Gomes et al., 2008), magnetic
38 storage devices (Speliotis, 1999), catalytic applications (Osaka et al., 2008),
39 hyperthermia treatment (Jordan et al., 1999), drug delivery (McGill et al., 2009) etc.
40 The effects of interparticle and surface interactions on magnetic properties has
41 continued to be a central issue in the study of magnetic nanoparticle systems.
42 Interparticle interaction effects between magnetic nanoparticles have previously been
43 analysed through the use of AC susceptibility measurements with the aid of the Néel-
44 Arrhenius and the Vogel-Fulcher laws. In such studies, the frequency of the AC
45 excitation field being applied to the nanoparticles is progressively incremented while
46 the complex susceptibility is measured across a varying temperature range to allow
47 for an exploration of the relaxation processes within the sample.

48 For the present study, a system of Ni/Ni(OH)₂ (core/shell), nanoparticles were
49 analysed. For Ni nanoparticles synthesised within an aqueous environment, it was
50 shown (Bala et al., 2009) that air drying post centrifugation could lead to the

51 formation of an amount of Ni(OH)₂ within the samples. In spite of the presence of an
52 oleic acid (OA) capping layer, a thin shell of Ni(OH)₂ was formed, to create a
53 Ni/Ni(OH)₂ core/shell type structure. Such a structure allows for an investigation of
54 how the strength of interactions between the particle cores is affected by the presence
55 of a Ni(OH)₂ shell around each of the nanoparticles comprising the assemblage. The
56 ability to slightly oxidise the surface of a Ni nanoparticle may be advantageous in
57 certain applications such as in protein separation (Lee et al., 2006), allowing for a
58 tailoring of the sample's magnetic properties. Such effects as a control of
59 magnetisation or the introduction of an exchange bias/pinning effect at lower
60 temperatures are easily achievable with such a core/shell structure. Indeed it has been
61 reported that an exchange bias effect in nanoparticles with antiferromagnetic shells
62 can overcome the superparamagnetic limit, which holds potential interest for the
63 magnetic data storage industry (Skumryev et al., 2003). The potentially interesting
64 control of the magnetic properties allowed by this bilayer Ni/Ni(OH)₂ nanostructure
65 were hence deemed worthy of further investigation as detailed in the subsequent
66 sections.

67 **II. Experiment**

68 Details of the particle synthesis technique have previously been reported (Bala
69 et al., 2009). In brief, an aqueous mixture of 1×10^{-2} M Ni(NO₃)₂·6H₂O was mixed
70 with 1×10^{-4} M oleic acid and 1×10^{-2} M (sodium dodecyl sulphate) SDS. To produce
71 sample 2 an amount of Pluronic block copolymer (P123) was added to keep the
72 concentration at 0.3% in the solution, however no P123 was added to produce sample
73 1. The solutions were reduced using 0.035g of NaBH₄ in solid form. Post addition of
74 the reducing agent to the solutions the liquid was seen to turn black almost
75 immediately. The solutions were allowed to stand for 30 minutes to ensure the

76 completion of the reduction reaction before repeatedly being centrifuged at 8000rpm
77 for 15 minutes to separate the pellets. The pellets were then washed using deionised
78 water, the resultant pellets were subsequently dispersed in water. The samples were
79 next fully dried in an air environment to produce a dry powdered sample for magnetic
80 analysis.

81 The reactions were seen to be perfectly reproducible with the as synthesised
82 particles being reasonably monodisperse. XRD analysis showed the presence of both
83 fcc Ni (PCPDF file no. 04-0850) and Ni(OH)₂ in the sample, figure 1. The presence of
84 peaks at 33.8 and 51.5 ensured the hydroxide to be α - Ni(OH)₂ (Subbaiah et al.,
85 2003). Figures 2 showed the TEM and HRTEM images of the images of samples 1.
86 A particle distribution analysis (inset, Figure 2A) revealed the size as ~34 nm in
87 diameter. Ni (111) planes could be identified in the HRTEM image (Figure 2C) but
88 no planes for Ni(OH)₂ were visible plausibly due to poor crystallinity of the thin
89 hydroxide layers. A detailed XPS analysis (Bala et al., 2009) for the same sample
90 demonstrated fairly good amounts of Ni(OH)₂ species. Considering the surface
91 sensitivity of the XPS technique and combining the HRTEM and XPS results, the
92 presence of the hydroxide layers on the surface of the nanoparticles was inferred..

93 While sample 1 displays particles ~34nm in diameter, sample 2 is seen to be
94 initially bimodal with a small fraction of the particles ~34nm in size but the
95 predominant portion of particles are ~14nm. With sample 2, repeated centrifugation
96 was used to remove the ~34nm particles from the bimodal sample to leave
97 predominantly ~14nm samples behind for magnetic analysis. For both samples,
98 magnetic measurements were performed using a commercial superconducting
99 quantum interference device, (Quantum Design - Model no. MPMS-XL5). For the AC

100 susceptibility measurements, a peak drive field amplitude of 2.5Oe was applied for all
101 frequencies, no DC offset magnetic field was applied during AC measurement.

102 **III. Theory**

103 With varying AC frequency, the percentage of magnetic nanoparticles which
104 follow the applied field's oscillations will change, inducing an associated
105 modification in the sample's magnetic response. For non-interacting nanoparticle
106 systems, which in turn are subjected to a slowly oscillating magnetic field
107 ($h=h_0\cos\omega_m t$), the real and imaginary parts of the ac susceptibility's components are
108 given by (Singh et al., 2009)

$$109 \chi' = \chi_0/[1+(\omega_m\tau)^2], \quad (1)$$

$$110 \chi'' = \chi_0\omega_m\tau/[1+(\omega_m\tau)^2], \quad (2)$$

111 where $\omega_m = 2\pi f_m$, with $f_m = 1/\tau_m$, the measuring frequency.

112 The characteristic relaxation time of each particle (τ), attributed to the
113 thermally assisted reversal of the magnetic moments over the anisotropy energy
114 barrier (KV) in the absence of an applied field and which is approximately valid for
115 small applied field strengths is given by a Néel-Arrhenius law (Goya et al., 2003)
116 (Néel-Brown expression (Bedanta and Kleemann, 2009)) as

$$117 \tau = \tau_0\exp(E_B/k_B T) = \tau_0\exp(KV/ k_B T). \quad (3)$$

118 Here V is the particle volume, T is the temperature, K is the effective uniaxial
119 anisotropy, k_B is the boltzmann constant and τ_0 is the inverse of the particle attempt
120 frequency ($f_0 = \tau_0^{-1}$) which represents the particle's attempt to jump between opposite
121 parallel directions to the magnetisation's easy axis (for superparamagnetic systems
122 typical values of τ_0 are $\sim 10^{-9}$ to $\sim 10^{-11}$) (Goya et al., 2003). The blocking temperature
123 (T_B) of the particles, below which the particle's moment will appear frozen on the

124 time scale of the experiment can be isolated by a rearrangement of equation (3) (with
125 $T = T_B$) as

$$126 \quad T_B = T_a / \ln(f_0/f_m) \quad (4)$$

127 where T_a is equal to KV/k_B and $\tau = \tau_m = 1/f_m$. It is known that as the effects of
128 interparticle interactions become increasingly prevalent, then equation (4) will
129 become modified into the form (Singh et al., 2009)

$$130 \quad T_B = T_a / \ln(f_0/f_m) + T_0 \quad (5)$$

131 known as Vogel-Fulcher law, where T_0 quantifies the effects of the interparticle
132 interactions. The aforementioned equations are based upon the assumption of
133 uniform particle size. For distributions of particle sizes as in real samples, an average
134 particle size is often assumed as in previous (Singh et al., 2009, Singh et al., 2008) as
135 well as in the present work. For improved accuracy the equations may alternatively
136 be modified appropriately to take account of particle size variation for improved
137 accuracy as previously reported (Gittleman et al., 1974). By fitting the Néel-Arrhenius
138 and the Vogel-Fulcher laws to the measured datasets, the effects of interparticle
139 interactions may be analysed and quantified.

140 **III. Results and Discussion**

141 $Ni(OH)_2$ is an antiferromagnetic material with a bulk Néel temperature of
142 $\sim 26K$ (Suzuki et al., 2000). While bulk antiferromagnetic materials have a roughly
143 equal numbers of spin-up and spin-down magnetic moments leading to a
144 compensation of the magnetic spins below the material's Néel temperature, on the
145 nanoscale this may not always be true. Nanoscale antiferromagnetic particles may in
146 fact acquire large magnetisations due to uncompensated magnetic spins, such as at the
147 surface. The effects on the magnetic properties of the present samples owing to the
148 presence of $Ni(OH)_2$ may hence be significant.

149 Figure 4 shows the hysteresis loops of the samples measured at 10K, 30K and
150 300K. It is seen that at 300K the samples appear to behave paramagnetically,
151 displaying no appreciable coercivity or retentivity. As the temperatures of the samples
152 are lowered to 30K and 10K from 300K, it is seen that the behaviours change from
153 that of a paramagnetic signature to one of a mixed ferromagnetic/paramagnetic type
154 of behaviour. In order to verify if the systems were behaving as ideal
155 superparamagnets, the reduced magnetisations (M/M_s) were plotted as a function of
156 (H/T). The classic law for superparamagnetism dictates that for a pure
157 superparamagnetic sample, the resultant curves would have superimposed onto a
158 universal curve (Knobel et al., 2008). As evident from figure 5, the reduced
159 magnetisation curves did not superimpose thus confirming the prevalence of a more
160 complex underlying mechanism. Additionally, the failure of the samples to fully
161 saturate with increasing field strength even at low temperatures is indicative of the
162 mixed magnetic phases of the sample with the nonmagnetic phase
163 (paramagnetic/antiferromagnetic) failing to achieve saturation even at 50 kOe applied
164 field strength.

165 In testing for the presence of an exchange bias system, a number of loop shift
166 measurements were conducted. At 300 K, the samples had a magnetic field of 10,000
167 Oe applied prior to the samples being cooled in the presence of the field down to 5 K.
168 Hysteresis loops were then measured from $\pm 10,000$ Oe. The resulting curves are
169 shown in Figure 6, in the insets of the figures an offset is discernable implying the
170 presence of an exchange bias affect. To facilitate the delineation of the contribution
171 from the different magnetic phases present, AC measurements were employed. To
172 facilitate the further probing of the characteristics of the system, a series of AC
173 susceptibility measurements were carried out at applied AC frequencies of 0.1 Hz, 2.5

174 Hz, 100 Hz, 500 Hz and 1000 Hz as shown in figure 7. Two peaks were clearly
175 discernable in each of the AC susceptibility measurements at all frequencies. The
176 perfect immobility of the lower temperature peaks with a changing measuring
177 frequency discounts the presence of a blocking temperature at this point in the AC
178 susceptibility measurements. The peaks may plausibly be attributed to the
179 antiferromagnetic Néel temperature of the Ni(OH)₂ present in the system. In contrast,
180 it is noted that the position of the higher temperature peaks in both the χ' and χ''
181 curves are observed to increase with increasing measurement frequency, a feature
182 characteristic of a superparamagnetic blocking temperature. The peaks in the χ (χ' and
183 χ'') versus temperature curves at higher temperatures may hence be attributed to the
184 blocking temperatures of the pure Ni centres at the cores of the core-shell Ni-Ni(OH)₂
185 structures.

186 In addition to the AC measurements a series of Field-Cooled/Zero-Field-
187 Cooled (FC/ZFC) measurements, with 1 Oe applied field strength were performed on
188 both samples as shown in Figure 8. For both samples, the irreversibility point of the
189 curves were observed at ~22K. A series of additional FC/ZFC measurements at
190 further magnetic field strengths (10 Oe and 100 Oe) were also carried out (not all
191 shown) and produced an similar irreversibility point at ~22K. It is noted that the slight
192 upturn in the ZFC curve of sample 2 was not observed at higher field strengths and as
193 such is likely attributed to the sample settling. The apparent invariance of the
194 temperature of this point with varying applied field strengths appears contrary to what
195 may be expected for a system containing superparamagnetic particles. In such a
196 system it is known that the blocking temperature's position in the ZFC measurement
197 will change with different applied field strengths. This effect has been attributed to the
198 non-linear field of the unblocked particle's magnetisation and has been described

199 elsewhere (Suzuki et al., 2000). As no appreciable changes in the ZFC peak positions
 200 were observed with varying applied field strengths, this suggests the possible presence
 201 of a Néel temperature without the implication of a blocking temperature at ~22K.
 202 However, with the blocking of the nanoparticle assemblages being evidenced in the
 203 AC susceptibility measurements, it is therefore likely that these affects are being
 204 masked by the Néel temperature peak in the static magnetic measurements. This
 205 observed phenomenon may be explained as follows, the blocking temperature can be
 206 defined using the following equation (Knobel et al., 2008).

$$207 \quad \ln \tau_m = \ln \tau_0 + \frac{KV_0}{k_B T_B} \quad (6)$$

208 Here it can be seen that T_B is dependent on the measurement time of the
 209 experimental apparatus and V_0 is the particle volume. T_B is defined as the temperature
 210 at which the characteristic measuring time is equal to the intrinsic relaxation time
 211 associated with the nanoparticle's energy barrier. Typically, the measuring time is
 212 given a value of 100sec as this is a good approximation for the measurement time
 213 scale in a DC magnetometer. With an AC susceptibility measurement, the measuring
 214 time will be the inverse of the measurement frequency . In the AC measurements
 215 undertaken here, the values of τ_m are therefore 10, 0.4, 0.01, 0.002 and 0.001 for the
 216 0.1, 2.5, 100, 500 and 1000 Hz measurement frequencies respectively. The effect of
 217 this reduction in the measuring time will be to increase the system's measured
 218 blocking temperature from $T_B = \frac{KV_0}{25k_B}$ in the DC case where $\tau_m = 100$ sec and $f_0 = 10^9$, to

$$219 \quad T_B \approx \frac{KV_0}{14k_B}$$

in the AC case where $\tau_m = \frac{1}{1000} = 0.001$. The reduction in the blocking

220 temperatures of the system with increased measuring time for the DC FC/ZFC
 221 measurement thus leads to a masking of the blocking temperatures as apparent in
 222 Figure 8.

223 If a simple Néel temperature was being observed at ~22K then the reasons for
224 an irreversibility point in the FC/ZFC curves may not be immediately apparent. It has
225 however additionally been reported that in a mixed ferromagnetic/antiferromagnetic
226 system an irreversibility point in the FC/ZFC curve may also be observed (Acet et al.,
227 2002, Duman et al., 2002). The reasons for this are that for systems with both
228 antiferromagnetic and ferromagnetic materials present, an irreversibility point in the
229 FC/ZFC curves can occur at the lower transition temperature of the two materials
230 present. Be that either the Néel temperature or the Curie temperature, in the present
231 case it occurs at the Néel temperature. The only stipulation for this effect is that the
232 applied field should be sufficiently small. This effect has been attributed to the
233 preferential pinning of the spins into different configurations by the anisotropy of the
234 antiferromagnetic phase. The FC/ZFC measurements can hence be used to determine
235 if different forms of coexisting long range magnetic phases are present in the samples.
236 While the aforementioned effect may be present in the current samples under
237 investigation, the FC/ZFC separation in figure 8 is sufficiently exaggerated. It is
238 therefore likely that a superposition of both effects (both a pinning at the material
239 boundary and a blocking of the centres) brought about by the coexistence of Ni
240 nanoparticles and a Ni(OH)₂ corona is being observed.

241 It is noted that the particle sizes studied here are below the single domain sizes
242 of Ni (below which the particle becomes a single, uniformly magnetized magnetic
243 domain, as the energy required to create and sustain domain walls is no longer
244 favourable) which are reportedly in the region of ~55 nm (Lu et al., 2007), ~43 nm
245 (Gong et al., 1991). Due to the proximity of the particles, the samples may experience
246 a degree of interparticle interactions. The effect of the capping layer and hydroxide
247 shell will likely be to lessen the likelihood of interactions somewhat by increasing the

248 inter-core distances. In a real system there are many possible types of interactions
249 which may be present such as exchange interactions, dipole-dipole, tunnelling
250 exchange etc. as outlined by Bedanta et al (Bedanta and Kleemann, 2009).

251 The degree of interparticle interactions within the two samples is more fully
252 analysed through the use of AC susceptibility measurements. Figure 7 shows the plots
253 of χ' and χ'' , against temperature. The higher temperature's peak positions, were
254 observed to shift to higher temperatures with increased measuring frequencies, an
255 effect also observed in other nanoparticle systems (Shim et al., 2006, Singh et al.,
256 2008, Goya et al., 2003). The frequency dependence of the blocking temperature for
257 isolated particles has been predicted by the superparamagnetic Néel model to follow
258 the Néel-Arrhenius law.

259 This law (which is equivalent to equation 3) may be expressed in the form
260 (Goya et al., 2003)

$$261 \quad f = f_0 \exp(-T_a/T) \quad (7)$$

262 where f is the relaxation frequency ($f=1/\tau$). This law may also be linearised into the
263 equation of a straight line of the form $\ln(f) = (-T_a)(1/T) + \ln(f_0)$ where f is left to equal
264 the measuring frequency f_m , and T is left to equal the blocking temperature T_B .
265 According to G.F.Goya et al, for both the in-phase and the out of phase components
266 of χ , the thermally activated Néel-Arrhenius model is followed. The fitting of this
267 equation to the measured datasets for χ'' is shown in figure 9. The steeper slope of the
268 fitted curve for sample 2 implies that the energy barrier increases from sample 1 to
269 sample 2, this is due to the fact that as the energy barrier E_a is increased then so too
270 does the blocking temperature. It is seen that $T_a = 747$ K while f_0 is 4.11×10^{11} Hz.
271 These values of T_a and f_0 can be compared to previously reported values for other Ni
272 nanoparticle systems, a T_a value of 270 K and an f_0 of 2.6×10^9 Hz have been reported

273 for ~ 4nm Ni (~15% loading) nanoparticles also embedded in a nonmagnetic SiO₂
274 matrix (Singh et al., 2008).

275 In examining the behaviour of sample 2, again the Néel-Arrhenius law is fitted
276 to the measured dataset as shown in figure 9. For sample 2, the calculated values of
277 T_a and f_0 are 1449 K and 3.34×10^{17} Hz respectively. As these values seem
278 implausibly high for the system under investigation, the results for sample 2 are likely
279 being affected by the presence of a degree of interparticle interactions which have
280 been reported to increase the f_0 of the system. The fittings hence imply that for sample
281 2 the interactions are not simply a perturbation to the anisotropy energy barriers, but
282 are in fact strong in relation to the barrier height.

283 The strength of the dipolar interactions between nanoparticles will fall relative
284 to the cube of the distance between the centres of the particles. The interaction
285 strength between two adjacent particles is approximately given by μ^2/r^3 , with μ being
286 the average magnetic moment of the particles and r being the distance between the
287 particles (Telem-Shafir and Markovich, 2005). One means of analysing the degree of
288 interparticle interactions lies in analysing the widths of the normalised χ'' curves. It
289 has been reported that for an ensemble of non-interacting nanoparticles, the
290 distribution of anisotropy energy barriers of the particles will typically determine the
291 normalized width of the AC susceptibility versus temperature curves (Telem-Shafir
292 and Markovich, 2005). The decrease in the scaled curve widths of the χ'' curves of
293 sample 2 relative to sample 1 are clearly visible in figure 10 for the 3 representative
294 frequencies shown demonstrating that dipolar interactions are more prevalent in
295 sample 2 than in sample 1. This seems to confirm the earlier conclusion from the
296 Néel-Arrhenius model fitting to the sample 2 dataset. A further indication of the
297 dipolar interaction strength lies in a comparison of the blocking temperatures of the

298 samples, which are expected to increase as the interactions strength increases. It is
299 seen in figure 7 that the blocking temperatures for sample 2 are higher than those of
300 sample 1 at similar frequencies. The reduced interactions from sample 1 may be
301 related to the increased surface area of the particles which in turn may result in a
302 thicker Ni(OH)₂ shell thus increasing the core interparticle distances.

303 To better quantify the effect of interparticle interactions the phenomenological
304 Vogel-Fulcher law has been fitted to the experimental datasets of samples 1 and 2.
305 For magnetically interacting particles, a Vogel-Fulcher law is used as a modification
306 of the Arrhenius law but this is only valid for the case where the blocking temperature
307 $\gg T_0$. The law implies a characteristic ordering temperature T_0 which arises from the
308 interactions within the system. If we consider the Vogel-Fulcher law and place $T_0 = 0$,
309 then the Vogel-Fulcher law will simply reduce to the Arrhenius law implying a
310 transition at $T_0 = 0\text{K}$. Previously, the Vogel-Fulcher law has also been successfully
311 applied to spin glass type systems, where it can be used to account for the observed
312 frequency dependence of the freezing temperature T_f . For the present
313 superparamagnetic system, T_0 is the temperature at which the relaxation time would
314 diverge, thus signalling a transition, the Vogel-Fulcher law is consequently only valid
315 across a restricted temperature range and breaks down in the proximity of T_0 . This
316 law is reported to take the form $T_B = T_0 + T_a / \ln(f_0/f_m)$ where T_0 measures the strength of
317 the interparticle interactions. For the present systems under investigation 4.11×10^{11} Hz
318 is taken as the likely magnitude of f_0 . For sample 2, this model fitting as shown in
319 figure 11 returns a value of 584 K for T_a and 14 K for T_0 . For sample 1, the value of
320 T_a is 750K (close to the 747K returned by the Néel-Arrhenius law) with T_0 being
321 0.17K (close to 0K), this shows the interparticle interactions to be negligible for
322 sample 1 while remaining substantial for sample 2. The smaller value of T_a for sample

323 2 is to be expected given the smaller particle sizes of sample 2 relative to sample 1,
324 thus helping to confirm the validity of the results.

325 Additionally, the parameter $\Phi = \Delta T_B / T_B \Delta \log_{10} f_m$ was calculated to examine
326 the nature of the interparticle interactions. Here ΔT_B is the shift in the blocking
327 temperature peak as determined from the χ'' curves, over the $\Delta \log_{10} f_m$ frequency
328 interval (Goya et al., 2003, Dormann et al., 1988). In the present study the calculated
329 value of Φ for sample 1 is 0.11 and is calculated to be 0.057 for sample 2. It has been
330 reported that $0.05 < \Phi < 0.13$ for coupled nanoparticles with increasing values of Φ
331 indicating a reduction in the coupling strength. For isolated nanoparticles, $\Phi = 0.13$
332 while for spin glasses Φ is reported to be very small (0.005-0.05).

333 The larger strength of interactions in sample 2 relative to sample 1 seems to
334 imply a thicker Ni(OH)_2 shell around the metallic core. The sizes of the Ni
335 nanoparticle cores could be anything up to the sizes identified using TEM microscopy
336 depending on the Ni(OH)_2 layer thickness. It has been reported that for a system with
337 cubic anisotropy and $K_1 < 0$, the value of K_a which is the effective uniaxial anisotropy
338 is related to K_1 through the relation $K_a = K_1 / 12$ (Goya et al., 2003). If it is assumed that
339 the value of K_1 for the system is actually the same as that of bulk Ni ($-8 \times 10^5 \text{ erg/cm}^3$)
340 then using the equation ($T_a = K_a V / k_B$) and assuming spherical particles, we can back
341 calculate the particle diameter for sample 1 to be 14.3nm. Since the TEM confirms the
342 particle size to be $\sim 32\text{nm}$ then this would suggest that approximately 9nm of the
343 particle's radius is in fact OA and oxidised Ni in the form of Ni(OH)_2 . For sample 2 a
344 particle diameter of 13nm is estimated using this approach implying an approximate
345 0.5nm inter-core distance. It is known that anisotropies well above that of bulk Ni can
346 become manifest in magnetic nanoparticle systems (Godsell et al., 2010) which would
347 likely have the effect of reducing the particle diameter as calculated above. In spite of

348 this, it still becomes apparent that the quantity of Ni(OH)₂ present is considerably
349 more substantial in sample 1 than in sample 2 leading to stronger interactions in
350 sample 2 as evidenced in the magnetic measurements. The increased surface area of
351 sample 1 would likely have led to an increased rate of oxygen diffusion through the
352 OA capping layer thus leading to an increased rate of sub-capping layer surface
353 oxidation of sample 1 relative to sample 2. Sub capping layer hydroxide shells of
354 Ni(OH)₂ fabricated using this method may hence provide a convenient and facile
355 means of controlling interparticle interactions in similar nanoparticle assemblages for
356 differing applications.

357 **IV Conclusions**

358 Ni/Ni(OH)₂ core/shell nanoparticles have been shown to represent a potentially
359 interesting nanomaterial. This morphology was observed to facilitate varying degrees
360 of interparticle interactions within the nanoparticle assemblage. The presence of
361 hydroxides within the material also leads to a more complex magnetic system with a
362 combined antiferromagnetic/ferromagnetic signature. Static (DC) and dynamic (AC)
363 magnetic properties of the synthesised samples were compared and the degree of
364 interactions within the individual nanoparticle assemblages were investigated. The
365 phenomenological Néel-Arrhenius and Vogel-Fulcher laws were successfully fitted to
366 the experimental datasets to analyse the interparticle interaction strengths. A clear
367 transition temperature peak was visible for both of the samples in the AC
368 susceptibility as well as DC FC/ZFC measurements and was attributed to the
369 antiferromagnetic Ni(OH)₂ corona around the metallic particle cores. The degree of
370 oxidation of the Ni cores was also linked to the nanoparticle surface area. This implies
371 that more accurate control of the hydroxide layer thickness is achievable which in turn

372 may facilitate a more precise control of the magnitude of interparticle interactions
373 within similar nanocomposite assemblages.

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381

382

383 **Figure Captions**

384

385 **Figure 1: X-ray diffractograms of air dried Ni nanoparticles, peaks marked with**
386 **a * correspond to the Ni(OH)₂ present in the systems.**

387 **Figure 2: TEM and HRTEM image of Sample 1 - 34nm.**

388 **Figure 3: TEM image of Sample 2 – bimodal 34/14nm particle size, .**

389

390 **Figure 4: Hysteresis curves for samples 1 and 2 at 10K, 30K and 300K, inset**
391 **shows zoomed in image about the origin for the 10K measurements.**

392

393 **Figure 5: Reduced magnetisation curves (M/Ms) plotted as a function of**
394 **Ms(H/T) for samples 1 and 2 inset shows zoomed in image about the origin for**
395 **the measurements.**

396

397 **Figure 6: Loop Shift measurements for samples 1 and 2, inset shows zoomed in**
398 **image about the origin.**

399 **Figure 7: Temperature variation of χ' and χ'' for samples 1 and 2.**

400 **Figure 8: Field-Cooled and Zero-Field-Cooled curves for samples 1 and 2 with 1**
401 **Oe applied field strength. Inset of 8(b) shows Field-Cooled and Zero-Field-**
402 **Cooled curves for sample 2 with 10Oe applied field strength.**

403 **Figure 9: Néel-Arrhenius model fitting to the blocking temperatures obtained**
404 **from the χ'' dataset peaks for sample 1 and sample 2.**

405 **Figure 10: Scaled χ'' vs temperature for samples 1 and 2 at varying frequencies.**

406 **Figure 11: Vogel-Fulcher model fitting to the blocking temperatures from the χ''**
407 **dataset for sample 2.**

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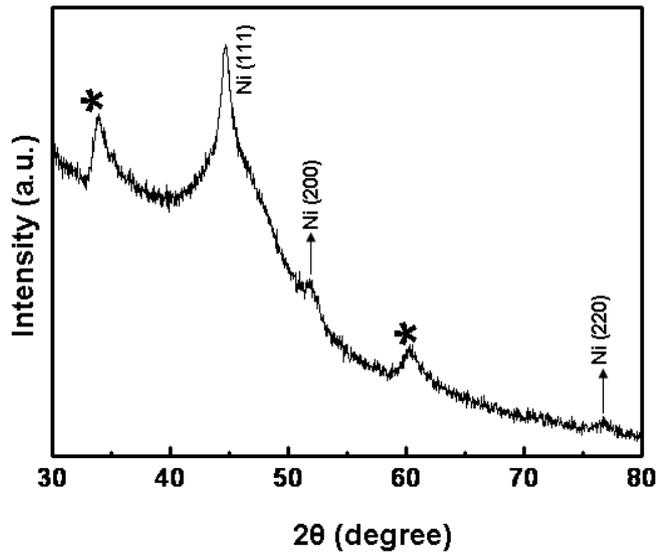
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Figure 1 : J. Godsell et al.



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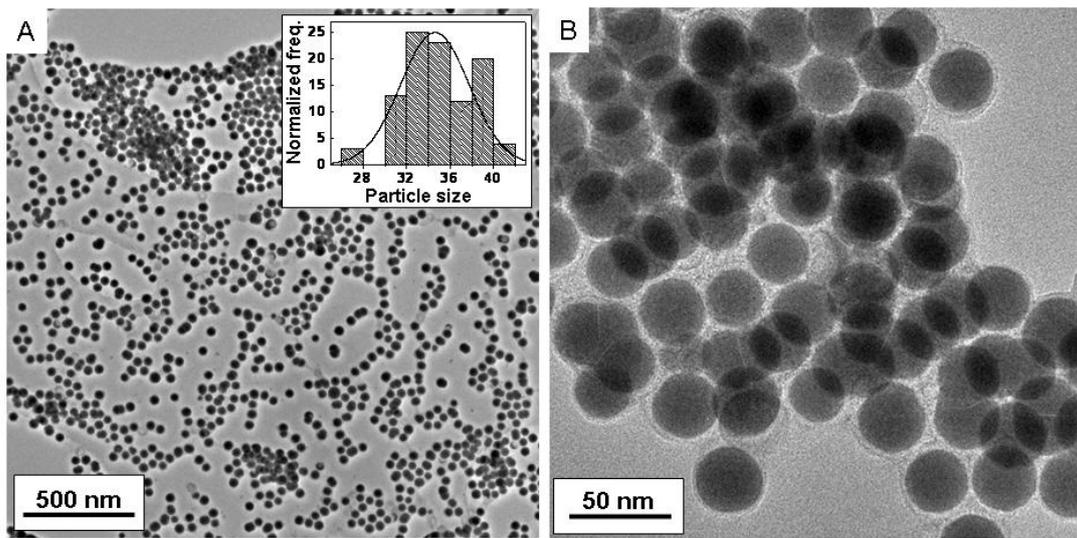
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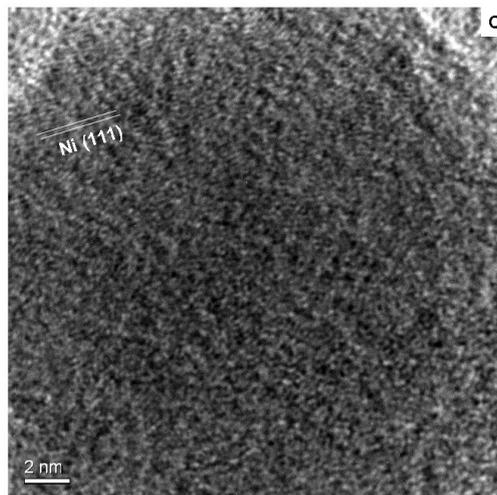
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429 **Figure 2: J. Godsell et al.**



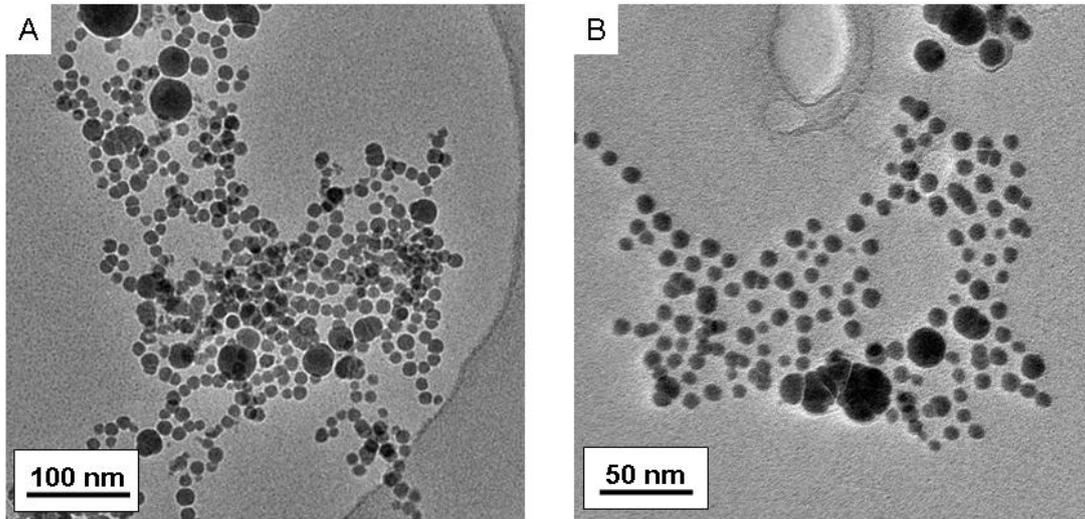
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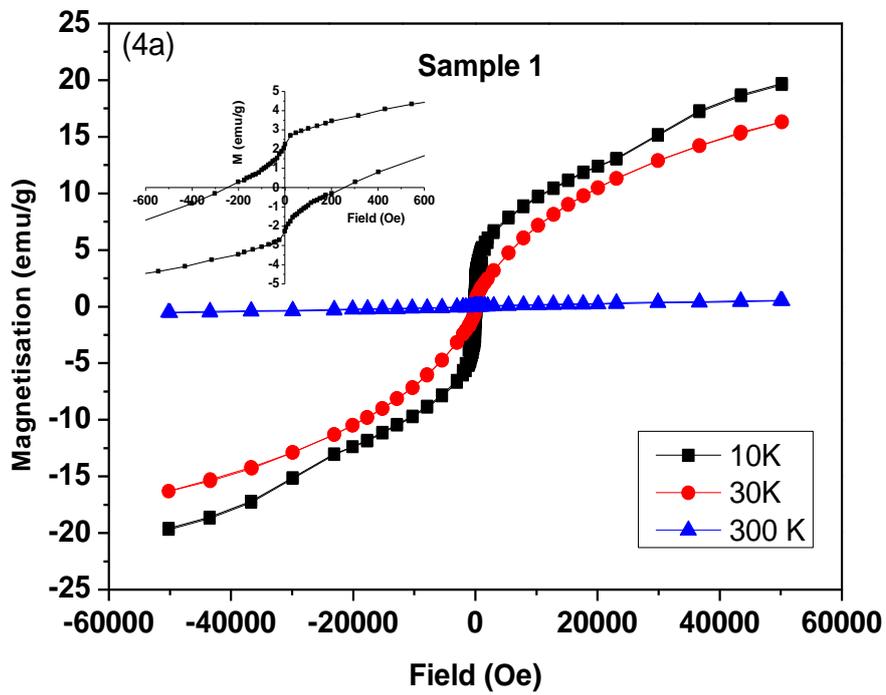
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Figure 3 : J. Godsell et al.

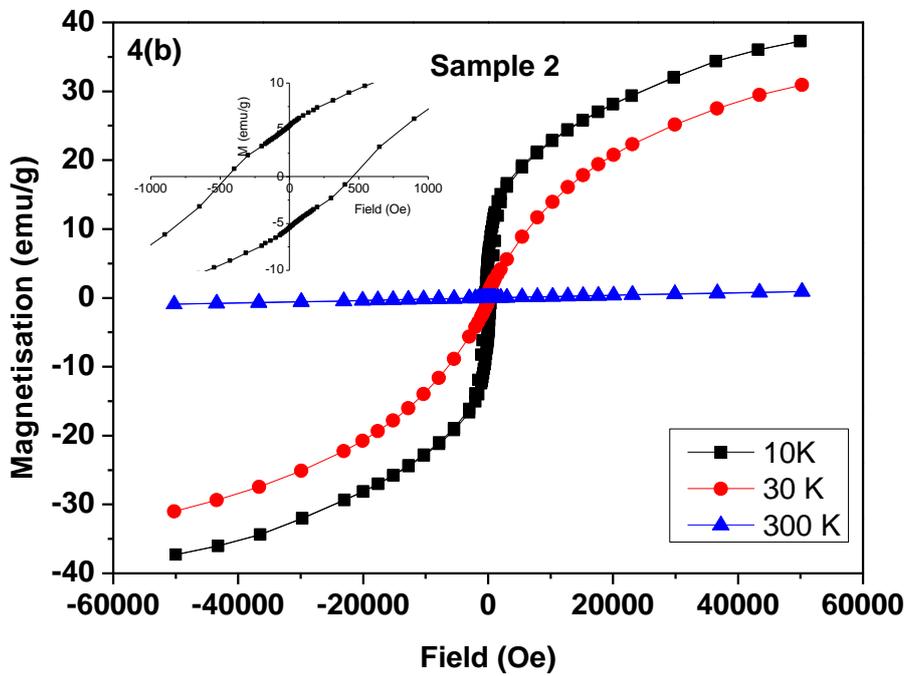


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439 Figure 4 : J. Godsell et al.
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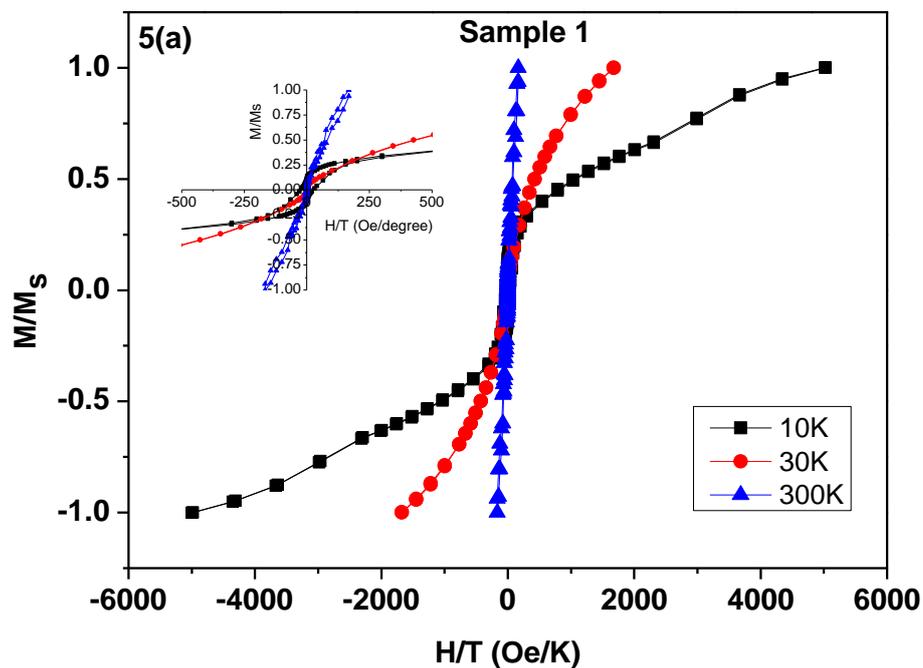
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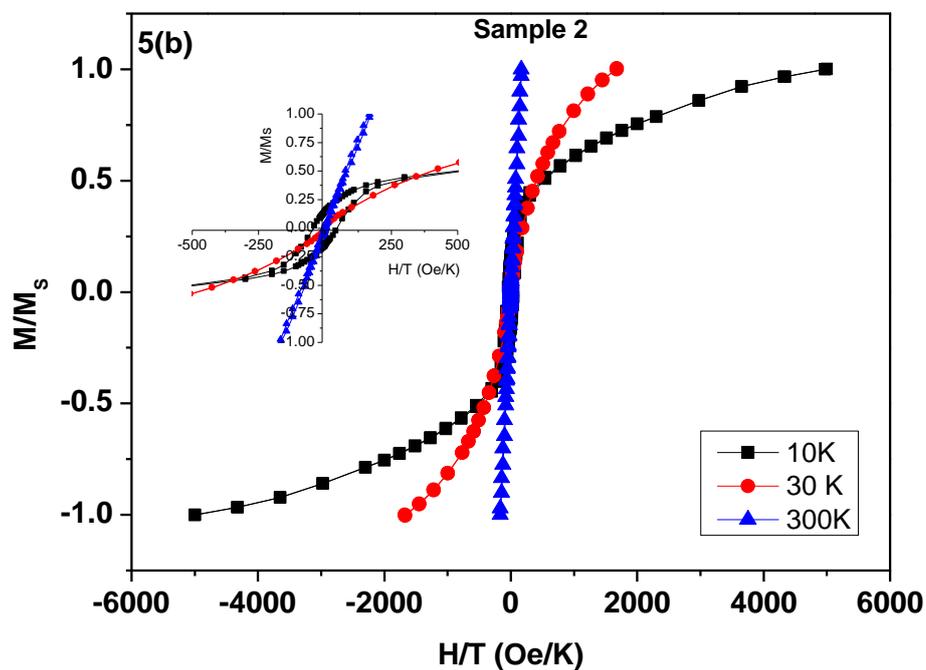
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Figure 5 : J. Godsell et al.



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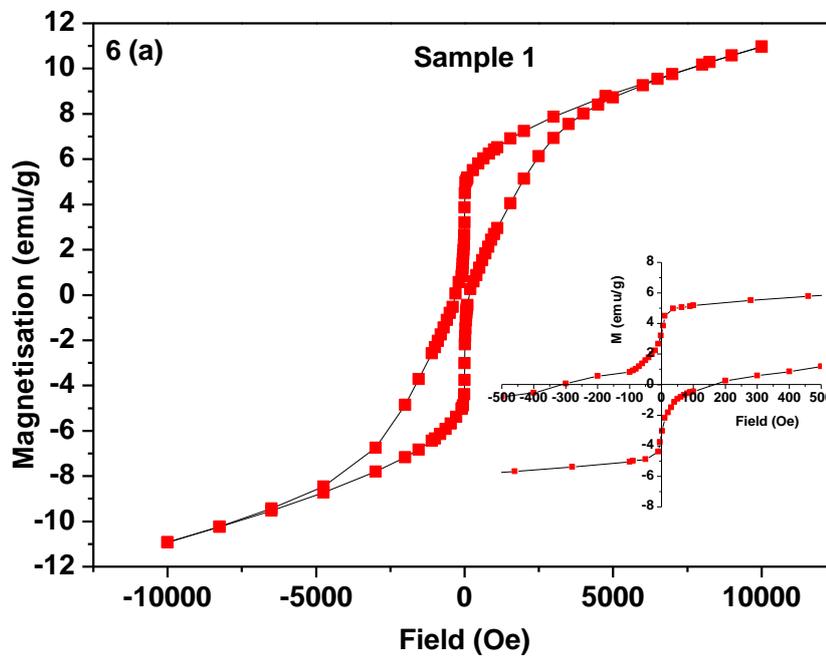
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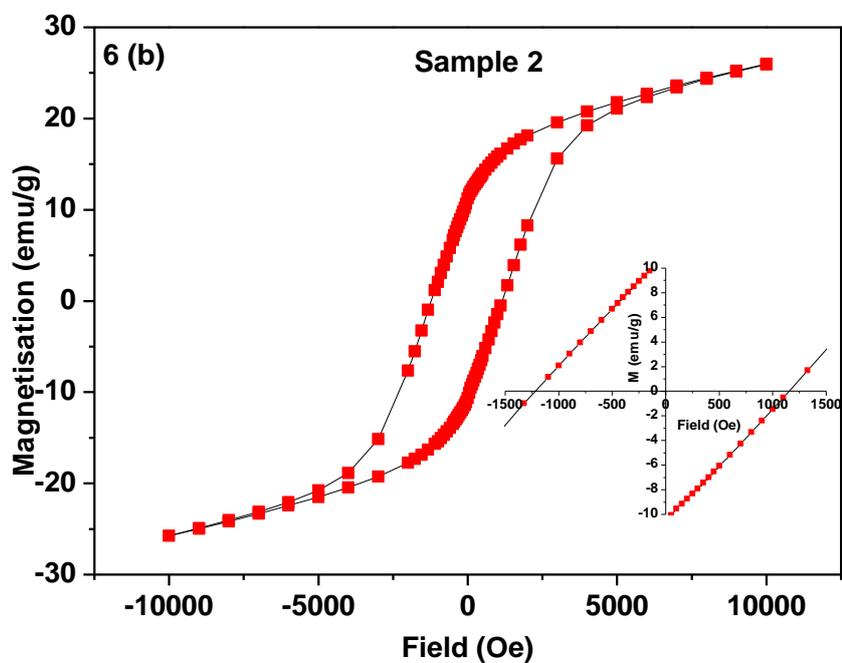
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453 Figure 6 : J. Godsell et al.

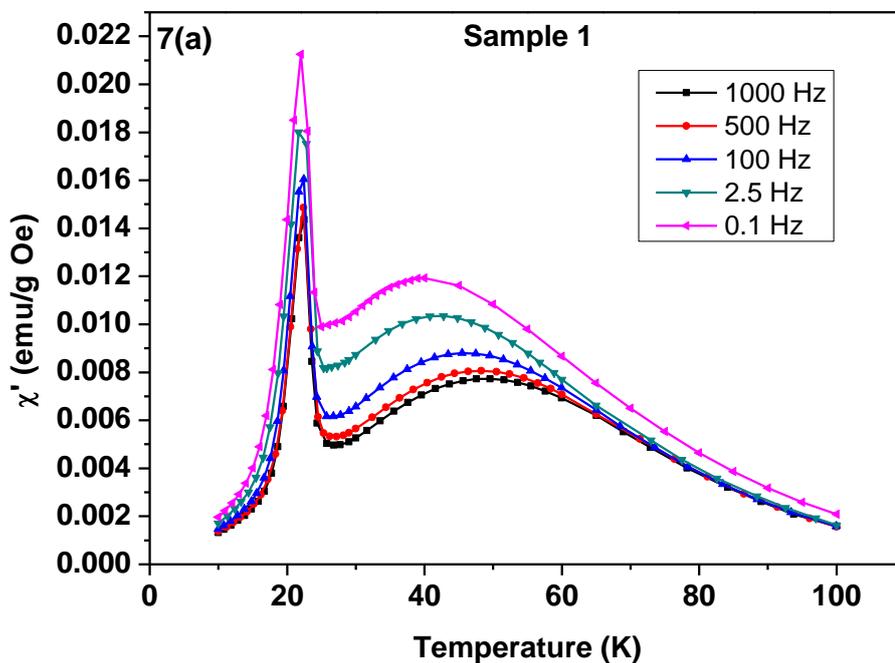


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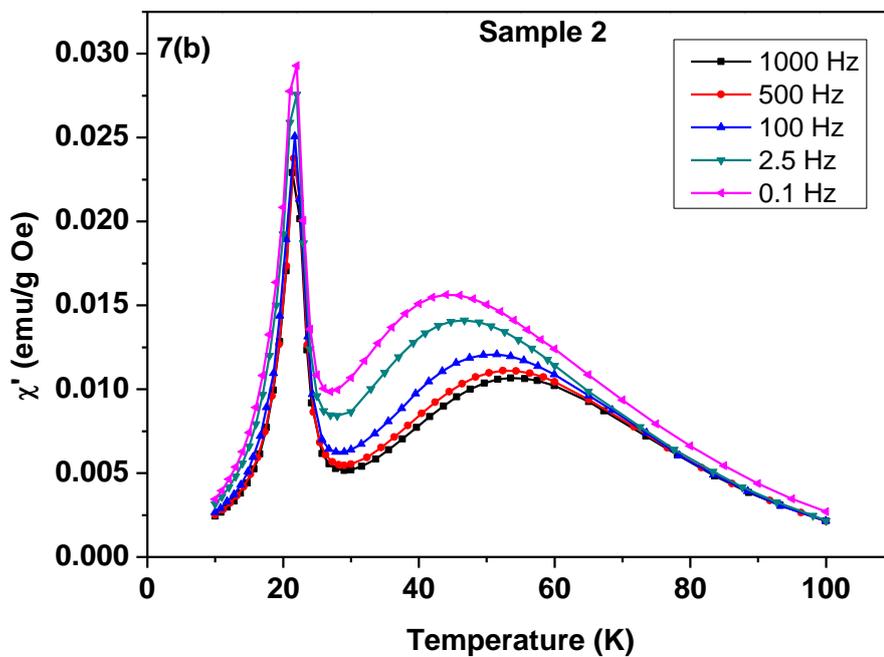
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456 **Figure 7 : J. Godsell et al.**



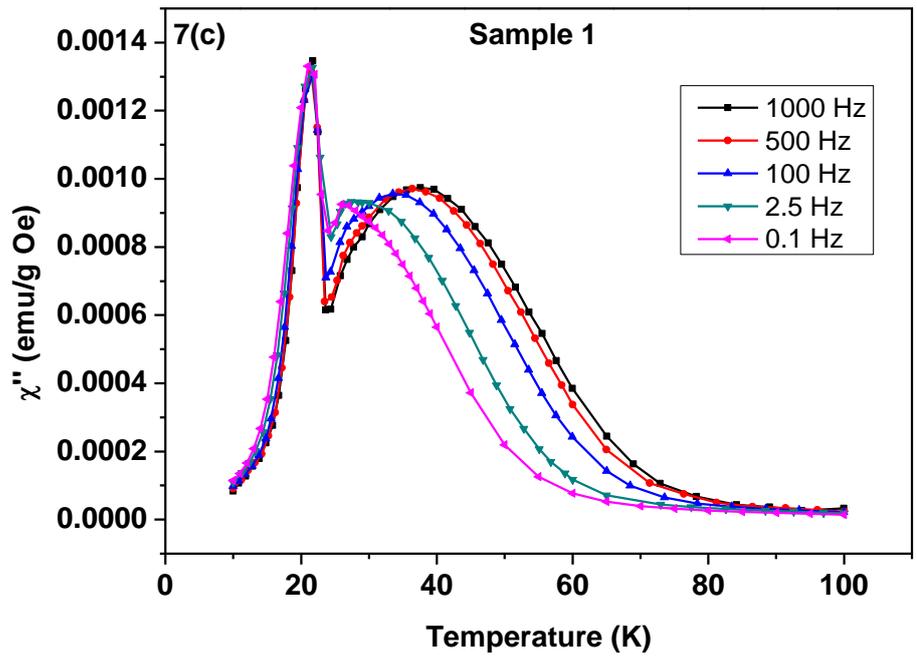
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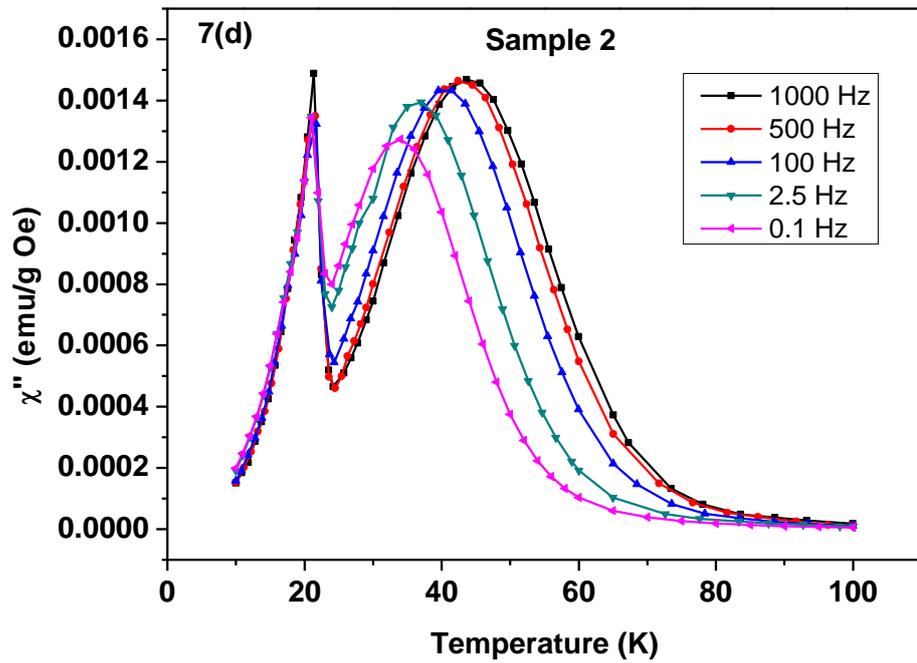


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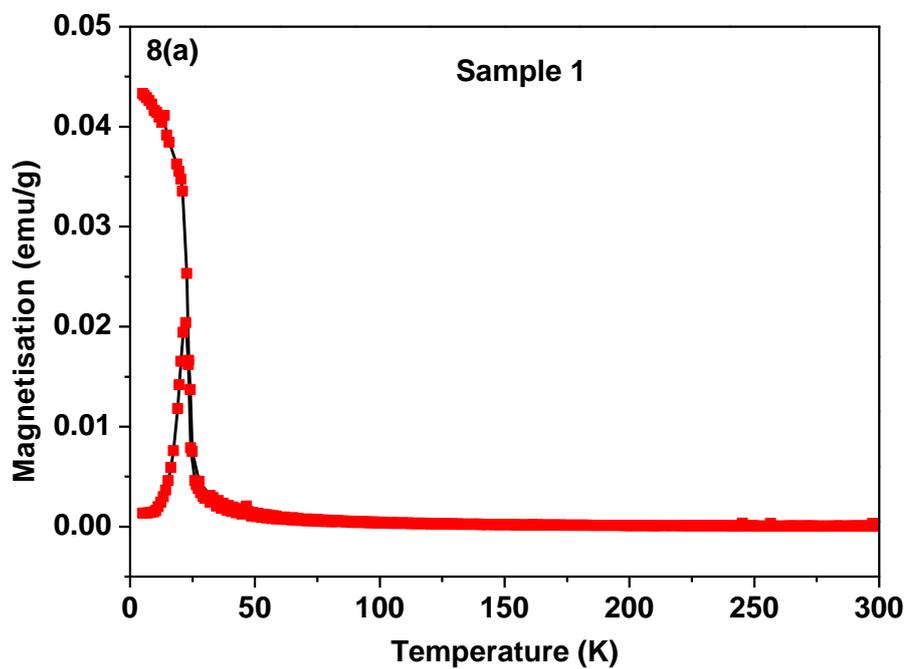


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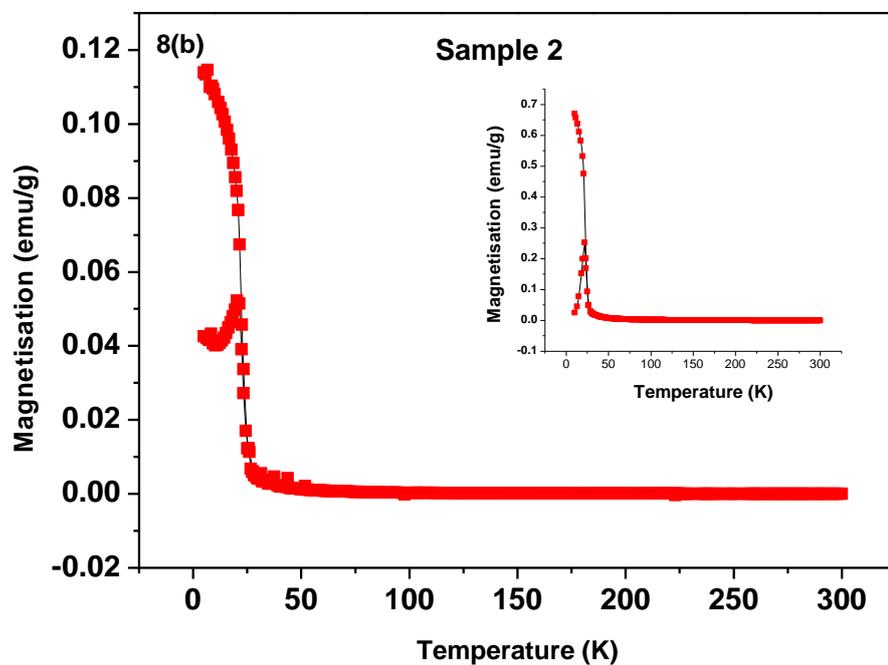
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Figure 8: J. Godsell et al.



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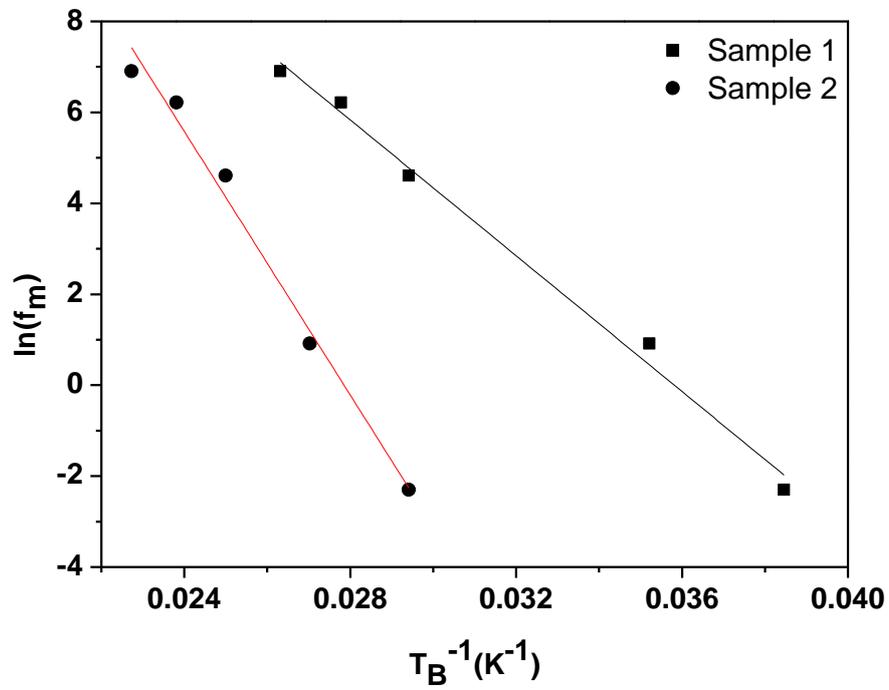
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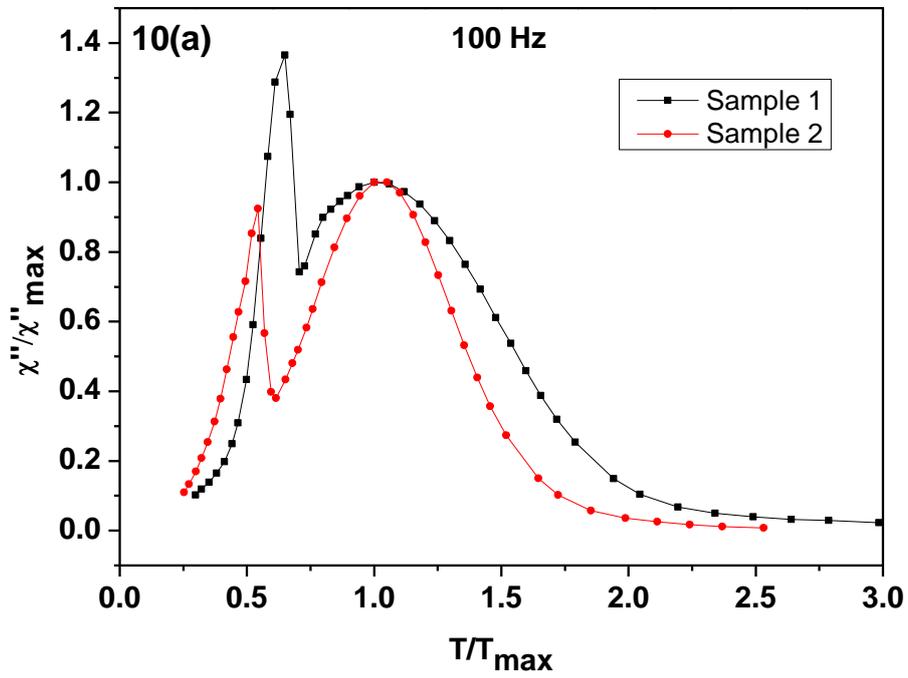
Figure 9 : J. Godsell et al.



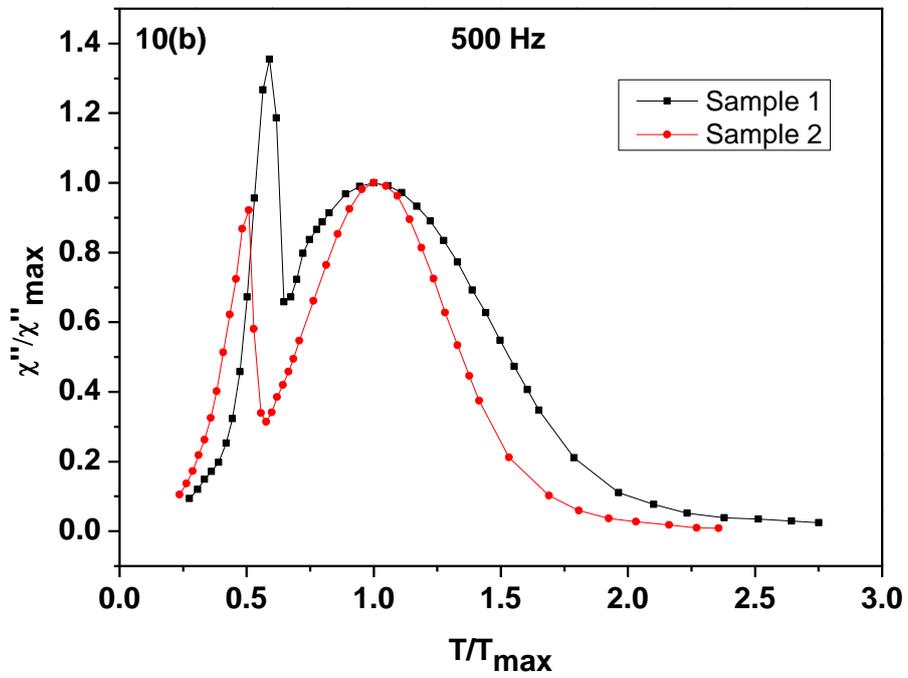
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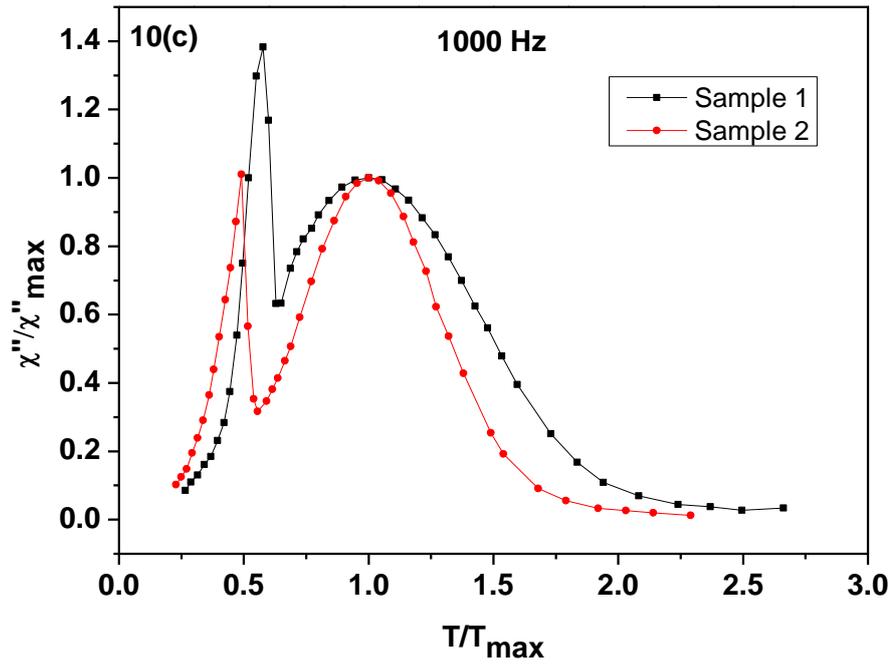
Figure 10 : J. Godsell et al.



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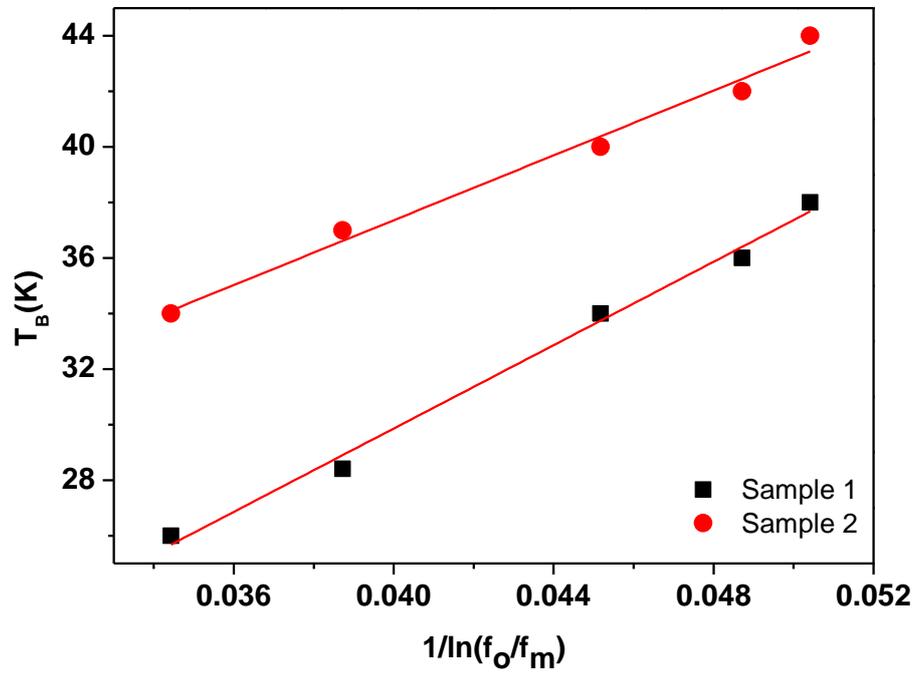
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Figure 11 : J.Gosdell et al.



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