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# A comparative study of the magnetic properties of bulk and nanocrystalline $\text{Co}_3\text{O}_4$

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## Abstract

A comparative study of the magnetic and electron paramagnetic resonance (EPR) parameters of bulk and  $\text{Co}_3\text{O}_4$  nanoparticles (NP), synthesized by a sol-gel process, is presented. Both samples possess the cubic phase with a slightly lower (by 0.34%) lattice parameter for the  $\text{Co}_3\text{O}_4$  NP. The average crystallite size  $D = 17$  nm determined by x-ray diffraction (XRD) for the  $\text{Co}_3\text{O}_4$  NP is quite consistent with the electron microscopic observations. The bulk  $\text{Co}_3\text{O}_4$  has particle size in the 1–2  $\mu\text{m}$  range. A Néel temperature of  $T_N = 30$  K (lower than the 40 K usually quoted in the literature) is determined from the analysis of the magnetic susceptibility versus temperature data for bulk  $\text{Co}_3\text{O}_4$ . This  $T_N = 30$  K is in excellent agreement with the  $T_N = 29.92$  K reported from specific heat measurements. The  $\text{Co}_3\text{O}_4$  NP powder exhibits a still lower  $T_N = 26$  K, possibly due to the associated finite size effects. The values of coercivity,  $H_c = 250$  Oe, and exchange bias,  $H_e = -350$  Oe, together with the training effect have been observed in the  $\text{Co}_3\text{O}_4$  NP sample (cooled in 20 kOe). Both  $H_c$  and  $H_e$  approach zero as  $T \rightarrow T_N^-$ . For  $T > T_N$ , the  $\chi$  versus  $T$  data for both samples fit the modified Curie-Weiss law ( $\chi = \chi_0 + C/(T + \theta)$ ). The magnitudes of  $C$ ,  $\theta$  and  $T_N$  are used to determine the following: exchange constants  $J_{1\text{ex}} = 11.7$  K,  $J_{2\text{ex}} = 2.3$  K, and magnetic moment per  $\text{Co}^{2+}$  ion  $\mu = 4.27 \mu_B$  for bulk  $\text{Co}_3\text{O}_4$ ; and  $J_{1\text{ex}} = 11.5$  K,  $J_{2\text{ex}} = 2.3$  K and  $\mu = 4.09 \mu_B$  for  $\text{Co}_3\text{O}_4$  NP. EPR yields a single Lorentzian line near  $g = 2.18$  in both samples but with a linewidth  $\Delta H$  that is larger for the  $\text{Co}_3\text{O}_4$  NP. Details of the temperature dependence of  $\Delta H$ , line intensity  $I_0$ , and disappearance of the EPR on approach to  $T_N$  are different for the two samples. These effects are discussed in terms of spin-phonon interaction and additional surface anisotropy present in  $\text{Co}_3\text{O}_4$  NP.

## 1. Introduction

Nanocrystalline materials derive their interesting and technologically useful properties with respect to bulk mainly from quantum confinement effects and the increasing role of surface atoms with the decrease in particle size  $D$  [1, 2]. A comparison of the specific properties of nanoparticles (NP) and the corresponding bulk sample is therefore likely to provide new insights into the associated differences.  $\text{Co}_3\text{O}_4$  is described by a formula unit  $\text{AB}_2\text{O}_4$  ( $\text{A} \rightarrow \text{Co}^{2+}$ ,  $\text{B} \rightarrow \text{Co}^{3+}$ ) and exhibits a normal spinel crystal structure with occupation of tetrahedral

A sites by  $\text{Co}^{2+}$  and octahedral B sites by  $\text{Co}^{3+}$ . Its magnetic moment arises due to  $\text{Co}^{2+}$  ions largely because of spins, with a small contribution from spin-orbit coupling [3]. On the other hand,  $\text{Co}^{3+}$  ions have no permanent magnetic moment as a consequence of the splitting of 3d levels by the octahedral crystal field and complete filling of  $t_{2g}$  levels.  $\text{Co}_3\text{O}_4$  behaves like an antiferromagnet (AF) with the Néel temperature  $T_N \approx 40$  K with each  $\text{Co}^{2+}$  ion in the A-site having four neighboring  $\text{Co}^{2+}$  ions of opposite spins [3]. Two paths for the superexchange interaction between  $\text{Co}^{2+}$  ions have been suggested: A–O–A with  $z_1 = 4$  neighbors and A–O–B–O–A with  $z_2 = 12$  neighbors (O stands for the oxygen  $\text{O}^{2-}$  ion) but without

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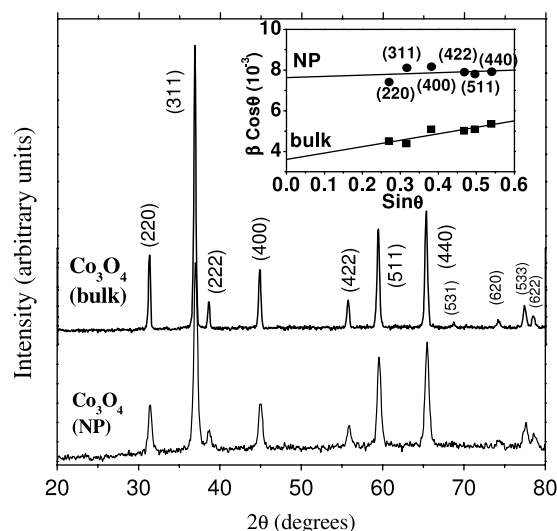
specifying their relative strengths [3]. Angelov *et al* [4] reported a nearly linear temperature dependence of the electron paramagnetic resonance (EPR) linewidth  $\Delta H$  in bulk  $\text{Co}_3\text{O}_4$ , prepared by decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at different temperatures (623–1073 K). Although the value of  $\Delta H$  was found to decrease with increase in the decomposition temperature [4], an appropriate interpretation of these results was not provided [4]. Of course, no EPR line was observed below  $T_N$ , as is generally the case for anisotropic antiferromagnets [5, 6].

A number of studies have been reported recently for  $\text{Co}_3\text{O}_4$  NP: (a) Takada *et al* [7] dispersed 3 nm  $\text{Co}_3\text{O}_4$  particles in  $\text{SiO}_2$  and reported a superparamagnetic behavior with a blocking temperature  $T_B = 3.4$  K; (b) Li *et al* [8] studied  $\text{Co}_3\text{O}_4$  NP of (i) size 14 nm and (ii) of size 12 nm but capped by polymer decomposition residues and reported an increase in coercivity ( $H_c$ ) and exchange-bias ( $H_e$ ) for the capped NP; (c) Makhlof [9] reported  $T_B = 25$  K for  $\text{Co}_3\text{O}_4$  NP of size  $\sim 20$  nm and Curie–Weiss behavior of the magnetic susceptibility  $\chi = C/(T + \theta)$  for  $T > T_B$ ; (d) Salabas *et al* [10] prepared  $\text{Co}_3\text{O}_4$  nanowires of diameter 8 nm and lengths up to 100 nm (by the nanocasting route) and observed blocking temperature  $T_B = 30$  K and non-zero  $H_e$  for  $T < T_B$ .

In this work, a comparative study of the properties of bulk and nanocrystalline  $\text{Co}_3\text{O}_4$  is reported in terms of magnetic parameters (namely Néel temperature, magnetic susceptibility  $\chi$ , coercivity  $H_c$  and exchange bias  $H_e$ ) under different conditions and the temperature-dependent behavior of the EPR parameters (i.e. linewidth  $\Delta H$ , resonance field  $H_r$  and intensity  $I_0$ ) on approach to  $T_N$ . Substantial differences observed between the bulk and nanocrystalline samples are interpreted in terms of finite size effects and the dominant role of surface atoms in NP. The exchange constants for the two samples are also determined.

## 2. Experimental details

The bulk  $\text{Co}_3\text{O}_4$  powder obtained from Aldrich Chemicals was used as-received without any further modification. The nanocrystalline  $\text{Co}_3\text{O}_4$  was synthesized by a sol–gel process using cobalt acetate tetrahydrate [ $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ] and oxalic acid as precursors and ethanol as solvent. For this, 2 g of cobalt acetate tetrahydrate was dissolved in about 200 ml of ethanol under constant stirring and heating at 45 °C for 30 min to obtain a light pink color sol. A solution of 6 g of oxalic acid solution in 200 ml of ethanol was then added to the above warm sol to yield a thick gel. This product was then dried at 80 °C for 24 h to produce pink flakes/powder of cobalt oxalate hydrate  $\text{CoC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ . Thermogravimetric analysis (TGA) indicated complete decomposition of cobalt oxalate hydrate to  $\text{Co}_3\text{O}_4$  at temperatures above 400 °C. The product was therefore calcined at 500 °C for 2 h in air for further study. An x-ray powder diffractometer (Rigaku Model D/Max) with Cu  $K\alpha$  radiation ( $\lambda = 1.54185$  Å) was used for phase evaluation, and scanning and transmission electron microscopes (FEI Quanta 200 HV and FEI Tecnai 20 G2, respectively) were used for morphology. A commercial superconducting quantum interference device (SQUID) magnetometer with temperature capabilities of 2–380 K and magnetic field ( $H$ ) up to  $\pm 70$  kOe



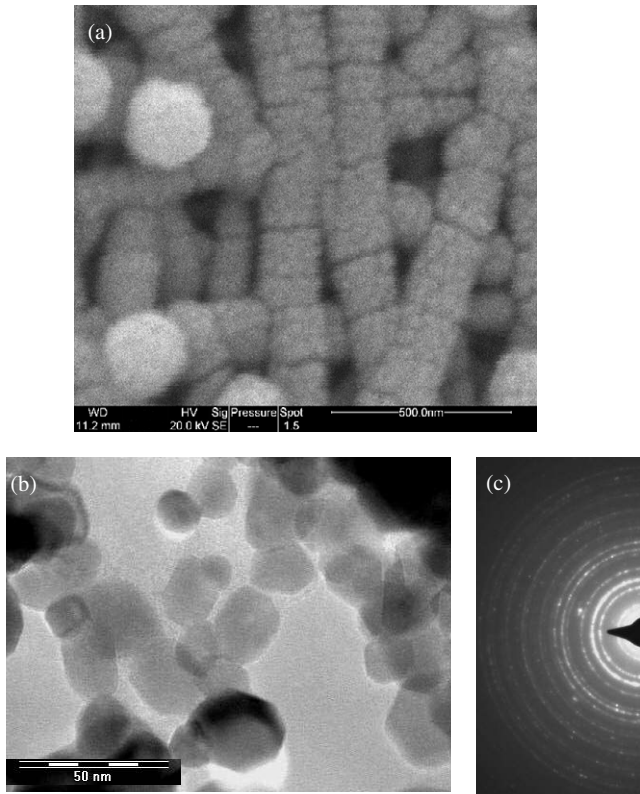
**Figure 1.** X-ray diffraction patterns of the bulk and  $\text{Co}_3\text{O}_4$  NP with Miller indices of the peaks marked. The inset shows  $\beta \cos \theta$  versus  $\sin \theta$  plots, whose fit to  $\beta \cos \theta = (0.89\lambda/D) + \eta \sin \theta$ , yields particle size  $D = 17 \pm 3$  nm and strain  $\eta = 6.3 \times 10^{-4}$  for  $\text{Co}_3\text{O}_4$  NP and  $D = 40 \pm 5$  nm and  $\eta = 3.4 \times 10^{-3}$  for bulk  $\text{Co}_3\text{O}_4$ .

was employed for measurements of the magnetization ( $M$ ). EPR measurements were made with a standard reflection-type spectrometer operating at 9.28 GHz in conjunction with a variable temperature cryostat (4.2–300 K).

## 3. Results and discussion

### 3.1. Phase evaluation and morphology

Figure 1 shows x-ray diffraction (XRD) patterns of both bulk and nanocrystalline  $\text{Co}_3\text{O}_4$  samples. These correspond to the cubic phase of  $\text{Co}_3\text{O}_4$  and space group  $Fd\bar{3}m$  [11] with lattice constants  $a = 8.09 \pm 0.02$  Å for bulk  $\text{Co}_3\text{O}_4$  and  $a = 8.06 \pm 0.02$  Å for  $\text{Co}_3\text{O}_4$  NP. The average crystallite size  $D$  and strain  $\eta$  are determined by making a Williamson–Hall ( $\beta \cos \theta$  versus  $\sin \theta$ ) plot (the relation being  $\beta \cos \theta = (0.89\lambda/D) + \eta \sin \theta$ ), using the values for the diffraction peak width ( $\beta$ ) obtained after correction for instrumental broadening [12, 13]. The values of  $D$  and  $\eta$  as deduced are given in the caption to figure 1. The XRD crystallite size of the  $\text{Co}_3\text{O}_4$  NP prepared by the sol–gel process is  $\sim 17$  nm. A typical scanning electron micrograph (figure 2(a)) recorded in secondary electron (SE) mode reveals the presence of nanorods (average diameter  $\sim 100$  nm and aspect ratio 20) each stacked like a bamboo stick. Also, each nanorod consists of a large number of tiny spherical particles. Figure 2(b) shows a bright field (BF) transmission electron micrograph of nanocrystalline  $\text{Co}_3\text{O}_4$  powder observed at 200 keV. It shows particles in the size range 15–20 nm in agreement with the size determined from XRD. The corresponding selected area diffraction (SAD) pattern given in figure 2(c) matches well with the cubic phase of  $\text{Co}_3\text{O}_4$  described above. For the bulk sample, the scanning electron micrograph shows particles of 1–2  $\mu\text{m}$  (figure 3), much larger than the size of 40 nm determined by XRD in figure 1. However, for  $D > 30$  nm, sizes determined by

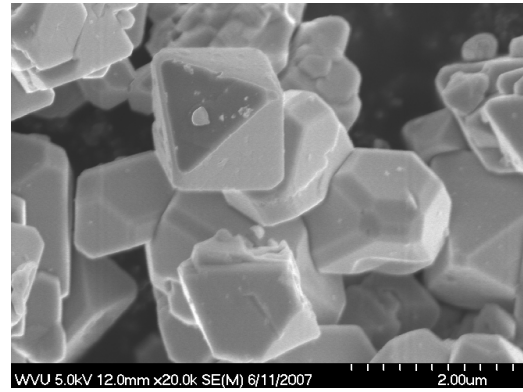


**Figure 2.** (a) Scanning electron micrograph of Co<sub>3</sub>O<sub>4</sub> NP showing nanorods of bamboo morphology with diameters  $\simeq 100$  nm and comprising many tiny particles of size about 20 nm. (b) TEM bright field image depicting particles in the size range 15–20 nm. (c) Electron diffraction pattern corresponding to (b) matching well with the cubic phase of Co<sub>3</sub>O<sub>4</sub>.

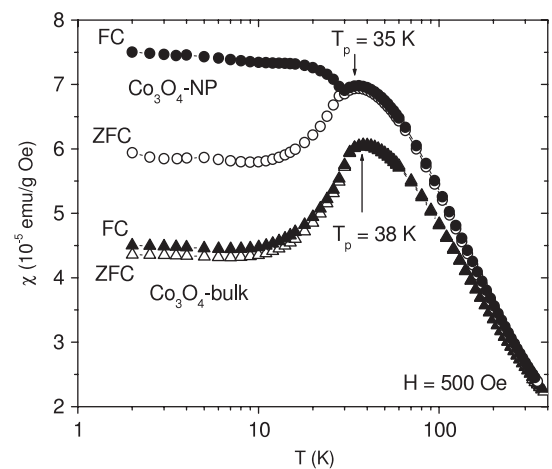
XRD line broadening are not reliable because the instrument corrected  $\beta$  is too small, yielding large errors in size  $D$ .

### 3.2. Temperature dependence of magnetic susceptibility

The magnetic susceptibility ( $\chi$ ) versus temperature plots for the bulk and nanocrystalline Co<sub>3</sub>O<sub>4</sub> samples are shown in figure 4. For the zero-field-cooled (ZFC) case, the sample was cooled from 300 to 2 K and then a magnetic field  $H = 500$  Oe was turned on for magnetization ( $M$ ) measurements with increasing temperature after ensuring stabilization at each temperature. Upon reaching 370 K, the data were similarly collected with decreasing temperature (FC mode) keeping the same applied field. The susceptibility ( $\chi$ ) versus temperature plots exhibit peaks at 38 and 35 K for the bulk and Co<sub>3</sub>O<sub>4</sub> NP, respectively. A clear bifurcation of the FC and ZFC plots, observed only for the NP case near 29 K, is a typical signature of superparamagnetic blocking in magnetic NP. Interestingly, the bifurcation occurs at a temperature (i.e.  $T_{\text{irr}} = 29$  K) lower than  $T_p$  (35 K). Also, flattening of  $\chi$  versus  $T$  plots at low temperatures (below  $T_{\text{irr}}$ ) is indicative of significant interaction among the NP [2]. For the bulk Co<sub>3</sub>O<sub>4</sub>, the  $\chi$  versus  $T$  plot is characteristic of an antiferromagnet such as CoO in that  $\chi$  becomes temperature-independent at the lower temperatures because the contribution from the orbital moment is partially



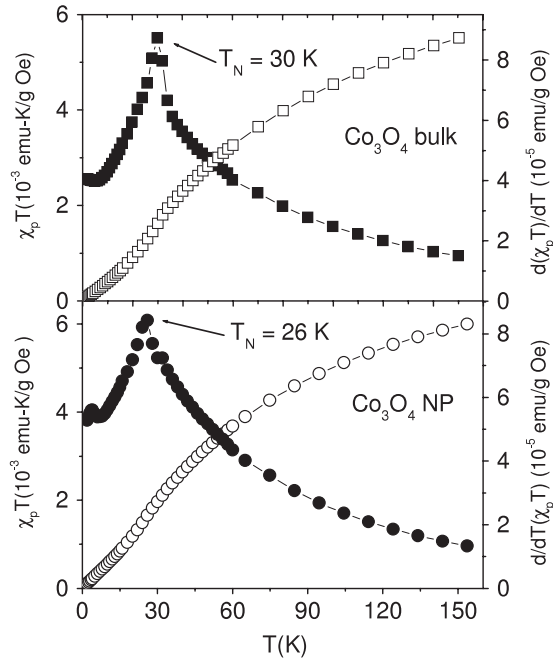
**Figure 3.** Scanning electron micrograph of bulk Co<sub>3</sub>O<sub>4</sub> showing particles with sizes 1–2  $\mu\text{m}$ .



**Figure 4.** Temperature dependence of the magnetic susceptibility ( $\chi$ ) for bulk and Co<sub>3</sub>O<sub>4</sub> NP under the zero-field-cooled (ZFC) and field-cooled (FC) conditions.  $T_p$  denotes the peak position in  $\chi$  versus  $T$  plots. Note the bifurcation of  $\chi_{\text{ZFC}}$  and  $\chi_{\text{FC}}$  curves of Co<sub>3</sub>O<sub>4</sub> NP below  $\sim 29$  K.

restored by the spin–orbit coupling [14, 15]. For the Co<sub>3</sub>O<sub>4</sub> NP, the magnitude of  $\chi$  is somewhat larger at all  $T$  as compared to bulk Co<sub>3</sub>O<sub>4</sub>, suggesting an additional contribution to  $\chi$ , perhaps due to uncompensated surface spins.

It is well known that the peak in the magnetic susceptibility in antiferromagnets usually occurs at a temperature few per cent higher than  $T_N$ ; instead,  $T_N$  is defined by the peak in the  $\partial(\chi T)/\partial T$  versus  $T$  plot [16, 17]. The  $(\chi_p T)$  versus  $T$  and  $\partial(\chi_p T)/\partial T$  versus  $T$  plots for the two samples (bulk and NP) are shown in figure 5, where  $\chi_p = (\chi - \chi_0)$  is the paramagnetic susceptibility of a polycrystalline sample corrected for the temperature-independent contribution  $\chi_0 = 3.06 \times 10^{-6}$  emu g<sup>-1</sup> Oe<sup>-1</sup> of Co<sub>3</sub>O<sub>4</sub> discussed later. These plots yield  $T_N = 30$  and 26 K for bulk and Co<sub>3</sub>O<sub>4</sub> NP, respectively. The value of  $T_N = 30$  K for bulk Co<sub>3</sub>O<sub>4</sub> is lower than the  $T_N \simeq 40$  K often quoted for Co<sub>3</sub>O<sub>4</sub> [3, 4]. However, measurements of the specific heat  $C_p$  for bulk Co<sub>3</sub>O<sub>4</sub> in the temperature range 5–307 K indicate a peak in  $C_p$  corresponding to  $T_N = (29.92 \pm 0.03)$  K [18]. Thus,  $T_N = 30$  K

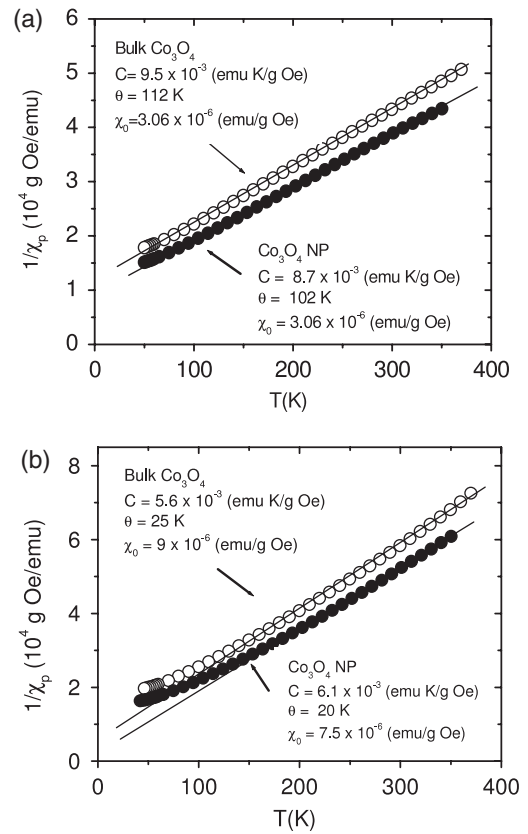


**Figure 5.** Plots of  $(\chi_p T)$  versus  $T$  and  $d(\chi_p T)/dT$  versus  $T$  plots for the bulk and  $\text{Co}_3\text{O}_4$  NP where  $\chi_p = \chi - \chi_0$  with  $\chi_0 = 3.06 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$  (see text). The peak in the  $d(\chi_p T)/dT$  versus  $T$  plot defines the Néel temperature  $T_N$ . Note the lower value of  $T_N$  for the  $\text{Co}_3\text{O}_4$  NP sample.

determined from two independent techniques (i.e.  $\chi_p$  and  $C_p$  measurements) is the characteristic value for bulk  $\text{Co}_3\text{O}_4$ . The decrease of  $T_N$  to 26 K for the  $\text{Co}_3\text{O}_4$  NP can be understood on the basis of the finite size effects (decrease in particle size  $D$ ) [19, 20]. Resnick *et al* [21] have reported  $T_N = 15 \pm 2 \text{ K}$  in  $\text{Co}_3\text{O}_4$  NP of still smaller size of 4 nm in line with the expected decrease of  $T_N$  with decrease in size  $D$ .

Some additional features of the data in figures 4 and 5 deserve further discussion. First  $\chi$  for bulk  $\text{Co}_3\text{O}_4$  in figure 4 becomes essentially temperature-independent for  $T < 10 \text{ K}$ . This is similar to other  $\text{Co}^{2+}$  antiferromagnets such as  $\text{CoO}$  [15] and  $\text{CoF}_2$  [22] in which the orbital contribution to the magnetic moment of  $\text{Co}^{2+}$  has been shown to result in non-zero easy-axis or parallel susceptibility  $\chi_{11}$  in the limit of  $T \rightarrow 0 \text{ K}$ . This also leads to temperature-independent  $\chi_{11}$  and hence  $\chi_p$  at lower temperatures. A similar effect is probably present in  $\text{Co}_3\text{O}_4$ . The weak anomalies in the plots of  $\partial(\chi_p T)/\partial T$  observed in figure 5 near 10 K are simply related to this change in the slope of  $\chi_p$  versus  $T$  data near 10 K in figure 4.

For  $T > T_p$ , the data of  $\chi$  versus  $T$  of figure 4 are fitted to the modified Curie–Weiss law  $\chi = \chi_0 + [C/(T + \theta)]$  with  $C = N\mu^2/3k_B$ ,  $\mu^2 = g^2 J(J + 1) \mu_B^2$ ,  $\theta$  the Curie–Weiss temperature and  $\chi_0$  contains the temperature-independent orbital contribution mentioned earlier and the diamagnetic contribution of  $\chi_d = -3.3 \times 10^{-7} \text{ emu g}^{-1} \text{ Oe}^{-1}$  [23]. Usually  $\chi_0$  is estimated from the plot of  $\chi$  versus  $1/T$  in the limit of  $1/T \rightarrow 0$  using the high temperature data. In [3],  $\chi_0 = 3.06 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$  was estimated for bulk  $\text{Co}_3\text{O}_4$  using the  $\chi$  versus  $T$  data up to 1000 K. A similar procedure for our data up to 380 K in figure 4 yields  $\chi_0 =$



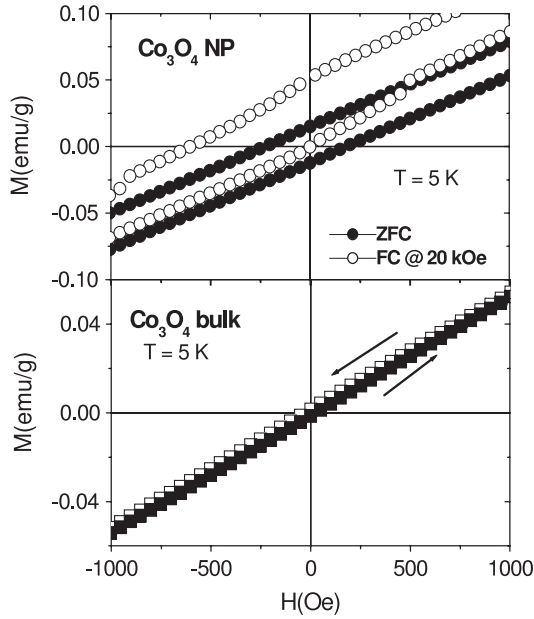
**Figure 6.** (a)  $1/\chi_p$  versus  $T$  plot for the bulk and  $\text{Co}_3\text{O}_4$  NP with  $\chi_0 = 3.06 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$ . The solid lines represent linear fit to the Curie–Weiss law:  $\chi_p = C/(T + \theta)$ . (b) The same except for different  $\chi_0$  listed in the figure and discussed in the text.

$9 \times 10^{-6}$  ( $7.5 \times 10^{-6}$ )  $\text{ emu g}^{-1} \text{ Oe}^{-1}$  for the bulk (NP)  $\text{Co}_3\text{O}_4$ . We argue later that  $\chi_0 = 3.06 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$  is a more reliable estimate, partly because extrapolation of the limit of  $1/T \rightarrow 0$  is expected to be more accurate near 1000 K than near 380 K. The plots of  $1/\chi_p$  versus  $T$  are shown in figures 6(a) and (b) using the two sets of the magnitudes discussed above. The magnitudes of  $C$  and  $\theta$  determined from these fits to the modified Curie–Weiss law are listed in the figures. It is evident that the plots of figure 6(a) using  $\chi_0 = 3.06 \times 10^{-6} \text{ emu g}^{-1} \text{ Oe}^{-1}$  yield the expected linear variation over a wider temperature range, pointing to greater reliability of these fits. For these reasons, we have used the magnitudes of  $C$  and  $\theta$  listed in figure 6(a) to estimate the exchange constants for  $\text{Co}_3\text{O}_4$ .

### 3.3. Exchange constants

As mentioned in section 1, there are two possible paths for superexchange interaction between  $\text{Co}^{2+}$  ions: A–O–A and A–O–B–O–A with  $z_1 = 4$  and  $z_2 = 12$ , respectively. If the corresponding exchange constants are represented by  $J_{1ex}$  and  $J_{2ex}$ , the expression for  $T_N$  and  $\theta$ , using the molecular field theory [24], can be written as:

$$T_N = \frac{J(J + 1)}{3k_B} (J_{1ex}z_1 - J_{2ex}z_2) \quad (1)$$



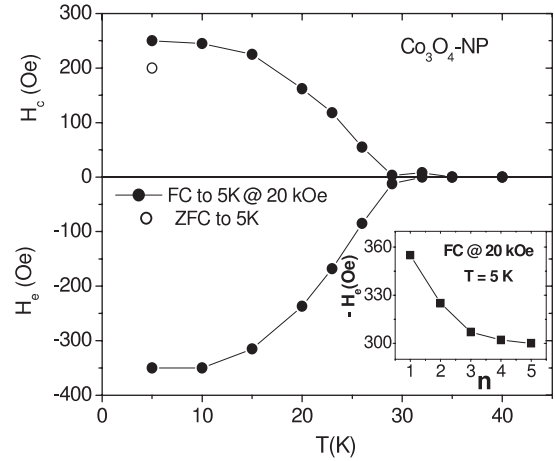
**Figure 7.** Hysteresis loops of bulk and  $\text{Co}_3\text{O}_4$  NP recorded at 5 K in the lower field region of  $\pm 1$  kOe. The minute irreversibility observed for the direct and reverse field scans for bulk  $\text{Co}_3\text{O}_4$  is within the experimental uncertainty of the SQUID magnetometer. A shifted hysteresis loop with enhanced coercivity can be clearly noticed for the  $\text{Co}_3\text{O}_4$  NP field cooled (FC) in  $H = 20$  kOe.

$$\theta = \frac{J(J+1)}{3k_B} (J_{1\text{ex}}z_1 + J_{2\text{ex}}z_2). \quad (2)$$

To determine  $J_{1\text{ex}}$  and  $J_{2\text{ex}}$ , the magnitude of effective  $J(J+1)$  for  $\text{Co}^{2+}$  is needed. The Curie constant  $C = N\mu^2/3k_B$  with  $\mu^2 = g^2J(J+1)\mu_B^2$ ,  $g$  being the Landé factor and  $J$  the total angular momentum. Using the magnitudes of  $g = 2$  and  $C$  as given in figure 6(a) one finds  $\mu = 4.27 \mu_B$  for bulk  $\text{Co}_3\text{O}_4$  and  $\mu = 4.09 \mu_B$  for the  $\text{Co}_3\text{O}_4$  NP. The spin contribution to the above magnitudes of  $\mu$  is  $3.87 \mu_B$  for  $\text{Co}^{2+}$  with spin  $S = 3/2$ . Obviously, there is some additional contribution resulting from the partially restored orbital angular moment for the  $^4F_{9/2}$  ground state of  $\text{Co}^{2+}$  [24]. Using equations (1) and (2) and the values of  $\theta$ ,  $T_N$  and  $\mu$  for the two cases yields  $J_{1\text{ex}} = 11.7$  K and  $J_{2\text{ex}} = 2.3$  K for bulk, and  $J_{1\text{ex}} = 11.5$  K and  $J_{2\text{ex}} = 2.3$  K for  $\text{Co}_3\text{O}_4$  NP. Thus, both the exchange constants  $J_{1\text{ex}}$  and  $J_{2\text{ex}}$  correspond to antiferromagnetic coupling. From the magnitudes of  $C$  in figure 6(b),  $\mu = 3.28 \mu_B$  ( $3.43 \mu_B$ ) is obtained for bulk(NP)  $\text{Co}_3\text{O}_4$ . We consider these magnitudes of  $\mu$  to be unphysical for  $\text{Co}^{2+}$  since they are even lower than the spin-only value of  $\mu = 3.87 \mu_B$ . Consequently the magnitudes of  $\theta$  in figure 6(b) are also considered to be incorrect. Of course, the use of the molecular field theory to determine exchange constants has its own limitations since higher-order spin correlations are neglected in this model.

### 3.4. Coercivity and exchange bias

For a bulk antiferromagnet below  $T_N$ , magnetization is expected to vary linearly with applied field  $H$  below the spin-flop field, with zero  $H_c$  and  $H_e$ . This indeed is observed in bulk  $\text{Co}_3\text{O}_4$  (figure 7). However, for the  $\text{Co}_3\text{O}_4$  NP, the data at 5 K



**Figure 8.** Temperature dependence of coercivity ( $H_c$ ) and exchange-bias ( $H_e$ ) for the  $\text{Co}_3\text{O}_4$  NP in the 5–40 K FC case at 20 kOe and at 5 K under ZFC conditions. Note the zero values of  $H_c$  and  $H_e$  above  $T_N$ . The inset shows the progressive decrease of the magnitude of exchange-bias ( $H_e$ ) after successive scans denoted by  $n$  at 5 K. The lines joining the data points are a visual aid.

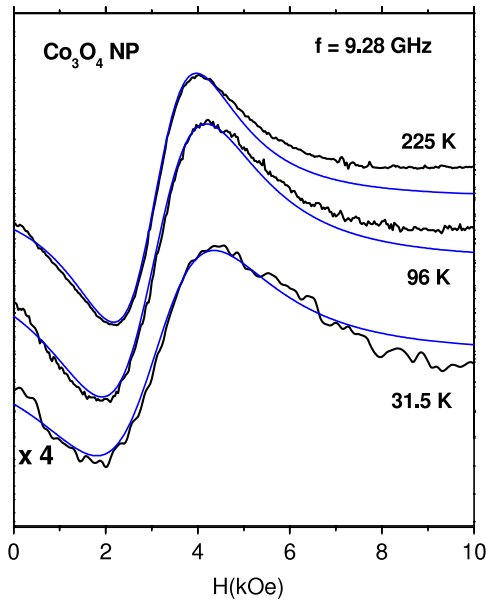
show a symmetric hysteresis loop with  $H_c = 200$  Oe for the ZFC sample and a shifted hysteresis loop with  $H_c = 250$  Oe and  $H_e = -350$  Oe for the sample cooled in  $H = 20$  kOe from 300 to 5 K (figure 8). Thus, cooling the sample in a magnetic field produces an exchange-bias and leads to enhancement of  $H_c$  as well.

The temperature dependence of  $H_c$  and  $H_e$  for the  $\text{Co}_3\text{O}_4$  NP cooled under  $H = 20$  kOe from 300 K to the measuring temperature is shown in figure 8. Both  $H_c$  and  $H_e$  become zero above  $T_N$ . The inset to figure 8 depicts the training effect, namely change in  $H_e$  for the sample cycled through several successive hysteresis loops (designated by ' $n$ ' at 5 K). A similar effect was reported recently by Salabas *et al* [10] in  $\text{Co}_3\text{O}_4$  nanowires of 8 nm diameter, although the magnitudes of  $H_e$  and  $H_c$  in their case are somewhat smaller.

The existence of the exchange-bias  $H_e$  suggests the presence of a ferromagnetic/antiferromagnetic (F/AF) interface with F-like surface spins covering the core of the antiferromagnetically ordered spins in  $\text{Co}_3\text{O}_4$  NP. Furthermore, the observation of the training effect and open loops up to 55 kOe suggests the surface spins to be in an unstable spin-glass-like state [10]. Such a spin-glass ordering results from the weaker exchange-coupling experienced by the surface spins due to reduced coordination at the surface. These effects, however, disappear above  $T_N$  when the spins in the core become disordered. The observation of a somewhat lower magnetic moment per  $\text{Co}^{2+}$  ion, smaller values of exchange constant  $J_{1\text{ex}}$  and lower  $T_N$  observed for the  $\text{Co}_3\text{O}_4$  NP compared with bulk  $\text{Co}_3\text{O}_4$  may all be due to the weak exchange coupling and reduced coordination of the surface spins.

### 3.5. Temperature dependence of paramagnetic resonance

For both the NP and bulk  $\text{Co}_3\text{O}_4$  samples, EPR spectra were recorded from 300 K down to  $T_N$  (below which the EPR line disappears) at 9.282 GHz. At all temperatures, only a

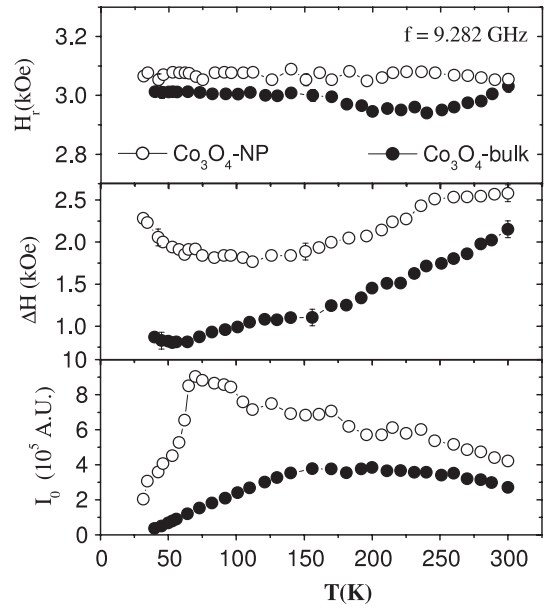


**Figure 9.** The standard derivative EPR spectra at several representative temperatures. The smooth solid lines are Lorentzian fits.

(This figure is in colour only in the electronic version)

single line near  $g = 2.19$  is observed for both bulk and NP  $\text{Co}_3\text{O}_4$ . In figure 9, we show representative line spectra at three temperatures (225, 96 and 31.5 K) and their fits to the Lorentzian lineshape for NP  $\text{Co}_3\text{O}_4$ . The fits are good except for some departures at the higher  $H$  well above the resonance field  $H_r$ . In addition to  $H_r$ , the linewidth  $\Delta H$  (peak-to-peak separation in the absorption derivative) and the line intensity  $I_0 = \alpha (\Delta H)^2 \ell$  were measured where  $\ell$  is the peak-to-peak height and  $\alpha = 3.63$  (1.033) for the Lorentzian (Gaussian) lineshape. Since the lineshape is essentially unchanged with temperature,  $(\Delta H)^2 \ell$  provides a good measure of relative change in  $I_0$  with  $T$ . In figure 10, the temperature dependences of  $H_r$ ,  $\Delta H$  and  $I_0$  are plotted for both bulk and NP  $\text{Co}_3\text{O}_4$ . The following observations are noteworthy:

- All the EPR parameters namely,  $\Delta H$ ,  $H_r$  and  $I_0$ , have higher values for the  $\text{Co}_3\text{O}_4$  NP.
- The line intensity  $I_0$  decreases rapidly whereas  $\Delta H$  increases on approach to  $T_N$  for both samples so that resonance is not observed at  $T_N$  as expected and as observed in other anisotropic antiferromagnets [5].
- For the  $\text{Co}_3\text{O}_4$  NP, the line intensity  $I_0$  peaks near 75 K and  $\Delta H$  reaches a minimum value near 100 K, signaling the onset of short range magnetic ordering. For the bulk  $\text{Co}_3\text{O}_4$  similar changes in  $I_0$  are observed below 150 K with only a change in the slope of  $\Delta H$  versus  $T$  variation.
- For bulk  $\text{Co}_3\text{O}_4$ , there is some temperature dependence of  $H_r$  above 150 K. This is the paramagnetic region since intensity  $I_0$  decreases with increase in temperature. This change in  $g$ -value is not yet understood.
- Significantly larger values of  $\Delta H$  observed at all temperatures for the  $\text{Co}_3\text{O}_4$  NP are related to size effects in NP. As discussed below, this finding is in agreement with



**Figure 10.** Temperature dependence of the EPR parameters, namely resonance field  $H_r$ , linewidth  $\Delta H$  and intensity  $I_0$ , for the bulk and  $\text{Co}_3\text{O}_4$  NP.

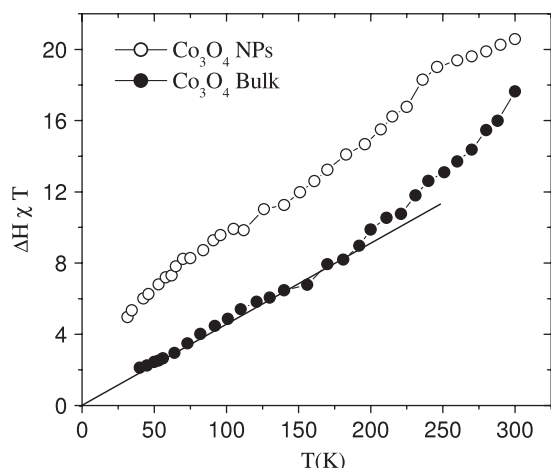
the reported EPR studies of Angelov *et al* [4] on a number of  $\text{Co}_3\text{O}_4$  samples prepared by the decomposition of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at different temperatures (623–1073 K). In this work, the samples synthesized at a lower decomposition temperatures showed higher  $\Delta H$  without affecting the  $g$ -value.

The average particle size  $D$  for the oxide NPs such as NiO and CuO is found to increase with increase in the annealing temperature during the preparation stage [25–27]. If a similar behavior is assumed for  $\text{Co}_3\text{O}_4$  samples, the progressive increase in  $\Delta H$  values observed by Angelov *et al* [4] with decrease in decomposition temperature can be attributed to a correspondingly smaller average particle size, although these authors did not measure the particle size of their samples. The observations of larger values of  $\Delta H$  found in  $\text{Co}_3\text{O}_4$  NP is thus a general phenomenon which can be qualitatively explained by the presence of enhanced anisotropy in NP as discussed below.

EPR linewidth  $\Delta H$  is broadened by anisotropic spin interactions and narrowed by exchange interaction such that  $\Delta H \sim H_a^2/H_{\text{ex}}$ , where  $H_a$  and  $H_{\text{ex}}$  are the equivalent anisotropy and exchange fields, respectively [28, 29]. Also, the effective anisotropy constant  $K_{\text{eff}}$  for a spherical nanoparticle of diameter  $D$  is given by [30, 31]:

$$K_{\text{eff}} = K_b + (6/D)K_s \quad (3)$$

where  $K_b$  is the bulk anisotropy constant,  $K_s$  is the surface anisotropy constant, and  $6/D$  stands for the surface area to volume ratio for spherical particles. According to equation (3), the anisotropy for a nanoparticle is invariably enhanced because of the additional contribution arising from its surface. The corresponding increase in  $H_a$  combined with a slight reduction in the effective exchange field  $H_{\text{ex}}$  (lower  $J_{1\text{ex}}$



**Figure 11.** Temperature dependence of the product ( $\Delta H\chi T$ ) for the bulk and  $\text{Co}_3\text{O}_4$  NP. The solid line depicts linear variation at lower temperatures.

observed) should cause an increase in EPR linewidth for  $\text{Co}_3\text{O}_4$  NP as observed in this work.

For systems with spin  $S \geq 1$  and with some orbital contribution to their magnetic moment (such as  $\text{Co}^{2+}$  in  $\text{Co}_3\text{O}_4$ ), spin–phonon interaction also contributes to  $\Delta H$  [32, 33]. While the one-phonon process yields a contribution proportional to  $T$  and is applicable at lower temperatures, the two-phonon process shows  $T^2$  dependence and dominates at higher temperatures. The linewidth  $\Delta H$  at a temperature ( $T$ ) for a polycrystalline sample in such cases is given by [32, 33]

$$\Delta H = \frac{C}{T\chi} \{K(T) + f(\varepsilon)\}, \quad (4)$$

where  $C$  is the Curie constant,  $K(T)$  is the non-critical term arising because of spin–phonon interaction and  $f(\varepsilon)$  is the critical contribution near  $T_N$  (with  $\varepsilon = (T - T_N)/T_N$ ) resulting from magnetic short range ordering. Accordingly, the product ( $\Delta HT\chi$ ) is expected to show temperature dependence in consonance with  $K(T)$  and  $f(\varepsilon)$ . For  $\text{CrBr}_3$  ferromagnet with  $T_c = 32$  K, the product  $\Delta HT\chi$  varies linearly with temperature for  $T > 3T_c$  [32, 33] whereas for  $\text{NiCl}_2$ , an antiferromagnet with  $T_N = 49.5$  K, there is linear dependence at lower temperatures and  $T^2$  dependence at higher temperatures [34]. In  $\text{R}_{1-x}\text{B}_x\text{MnO}_{3+\delta}$  manganites ( $\text{R} = \text{La}, \text{Pr}, \text{Br}, \text{Ca}, \text{Sr}$ ), data fitted to equation (4) indicated linear variation of  $K(T)$  with temperature [35].

For the bulk and  $\text{Co}_3\text{O}_4$  NP samples, the product  $\Delta HT\chi$  versus  $T$  plots are shown in figure 11. There is evidence of  $T$  ( $T^2$ ) dependence at the lower (higher) temperatures, signifying the role of spin–phonon interaction. The critical broadening of  $\Delta H$  on approach to  $T_N$  represented by the  $f(\varepsilon)$  term in equation (4) is more dominant for the  $\text{Co}_3\text{O}_4$  NP than for bulk  $\text{Co}_3\text{O}_4$ . Angelov *et al* [4] also reported more dominance of the  $f(\varepsilon)$  term in those samples which were prepared at the lower decomposition temperatures (apparently having smaller particle size  $D$ ). So, the short range magnetic order above  $T_N$  represented by  $f(\varepsilon)$  is felt over a wider temperature range for the  $\text{Co}_3\text{O}_4$  NP.

#### 4. Concluding remarks

The analysis of the magnetic susceptibility data presented here for bulk  $\text{Co}_3\text{O}_4$  has shown its Néel temperature  $T_N = 30$  K to be significantly lower than the  $T_N \simeq 40$  K usually quoted in literature. This value of  $T_N$  is in excellent agreement with  $T_N = 29.92 \pm 0.03$  K determined from the heat capacity  $C_p$  versus  $T$  measurements [18]. A still lower  $T_N = 26$  K observed for nanocrystalline  $\text{Co}_3\text{O}_4$  is due to associated finite size effects. A comparison of the magnetic properties and EPR parameters presented here revealed: (a) the existence of coercivity and exchange bias due to weakly coupled surface spins in NP, (b) antiferromagnetic ordering of spins in the core below  $T_N$ , (c) higher anisotropy in NP and (d) the important role of the spin–phonon interaction. The exchange-constants reported here, based on the molecular field theory approximation and an extrapolated value of  $\chi_0$ , need to be verified by direct methods such as neutron diffraction [36]. The results presented here also suggest the need for additional studies on the particle size dependence of exchange-bias,  $T_N$  and EPR linewidth in  $\text{Co}_3\text{O}_4$  NP. Such studies in well-characterized  $\text{Co}_3\text{O}_4$  NP are planned for the near future. A theory for the temperature dependence of EPR parameters in antiferromagnetic NP is also needed along the lines of that for bulk antiferromagnets [5, 37].

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