Abstract

We report studies on temperature, field and time dependence of magnetization on cupric oxide nanoparticles of sizes 9 nm, 13 nm and 16 nm. The nanoparticles show unusual features in comparison to other antiferromagnetic nanoparticle systems. The field cooled (FC) and zero field cooled (ZFC) magnetization curves bifurcate well above the Néel temperature and the usual peak in the ZFC magnetization curve is absent. The system does not show any memory effects which is in sharp contrast to the usual behavior shown by other antiferromagnetic nanoparticles. It turns out that the non-equilibrium behavior of CuO nanoparticles is very strange and is neither superparamagnetic nor spin glass-like.

Keywords: A. CuO nanoparticles, D. magnetic relaxation, D. memory effects, D. spin glass
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1. INTRODUCTION

Magnetism in nanoparticles have been investigated intensively in the last few decades because of their technological importance as well as for understanding the physics involved in their many unusual properties vis-a-vis the bulk. [1] In a nanoparticle the magnetic properties are strongly affected by the large proportion of surface spins which face an entirely different environment in comparison to the particle’s core. Generally these systems show non-equilibrium behavior at low temperature with features such as a bifurcation in field cooled (FC) and zero field cooled (ZFC) susceptibility, slow relaxation of magnetization, aging and memory effects. [2–9] It is widely believed that such non-equilibrium behavior exhibited by magnetic nanoparticles can arise mainly due to three mechanisms. First, in non interacting nanoparticle systems one can have superparamagnetism which arises from anisotropy energy barrier of each nanoparticle moment. [1, 2, 5, 7, 10, 11] Second, in interacting nanoparticle systems, one can have superspin glass behavior which arises from the frustration caused by competing dipolar interactions of neighboring particles coupled with the randomness in particle positions and orientations of anisotropy axes. [1, 3, 5] A third mechanism for non-equilibrium behavior has been proposed based on spin glass behavior arising due to the freezing of surface spins in a nanoparticle caused by disorder at its surface. [3, 12, 14]

Transition metal monoxides such as NiO, MnO, CoO, CuO etc. are all antiferromagnetic and nanoparticles of most of them are claimed to show superparamagnetic or spin glass like behavior. [13, 15] Cupric oxide (CuO) is different from other transition metal monoxides magnetically and its magnetism is perhaps the least understood among them, showing some sort of magnetic order even above its Néel temperature. Because of this it was felt that a magnetic study of the nanoparticles of CuO may turn out to be very interesting.

Bulk CuO has attracted some attention due to its structural resemblance to high $T_c$ superconductors. It has been known experimentally by neutron scattering, specific heat and magnetic susceptibility studies...
that CuO undergoes a transition to an incommensurate antiferromagnetic state at its Néel temperature 230 K followed by a transition from the incommensurate to a commensurate antiferromagnetic state at 213 K. However, strangely, the magnetic susceptibility of CuO instead of peaking at its Néel temperature undergoes a change in slope there and shows a broad maximum at about 540 K. This behavior has been claimed by many authors as a manifestation of its quasi one dimensional nature and the related presence of some sort of short range order above the Néel temperature. There have been claims that CuO can be visualized to have a spin fluid state above the Néel temperature where the spins are thought to be dynamically correlated over several lattice spacings. The low temperature susceptibility of CuO shows diverse results and this has been attributed to the existence of paramagnetic defects like oxygen vacancies. 

There have been a few studies on the magnetism of CuO nanoparticles. The temperature dependence of magnetization and susceptibility as reported by various authors are usually somewhat different and sometimes even contradictory. Punnoose et al. have studied exchange bias in CuO nanoparticles of various sizes. They have shown that 6.6 nm particles show weak ferromagnetism below 40 K and that for particles above 10 nm in size the behavior is almost bulk-like with a reduction in the Néel temperature. Further they have done detailed studies on size dependence of exchange bias and hysteresis and have pointed out that the temperature dependence of susceptibility does not follow the usual superparamagnetic behavior. Various values of Néel temperatures have been estimated for various particle sizes using susceptibility, exchange bias and muon spin resonance studies. Bifurcation in FC and ZFC magnetization and hysteresis have been observed in CuO nanoparticles but no effort has been made to systematically study such non-equilibrium behavior. In this work we would like to make a detailed study on the non-equilibrium behavior of CuO nanoparticles and will try to address the following issues: (a) Does the system show magnetization relaxation? (b) Does it show memory effects? (c) Does it show superparamagnetic or spin glass-like behavior?

2. EXPERIMENTAL DETAILS

2.1. Sample preparation
CuO nanoparticles were prepared by the precipitation-pyrolysis method using starting materials of 99.99% purity. 50 ml aqueous ammonium carbonate solution (0.3 M) was added to 300 ml of aqueous copper acetate solution (0.05 M). The precipitate was separated using a centrifuge and washed with distilled water and ethanol several times to remove possible remnant ions. This precipitate was dried at 60 °C in air to obtain a precursor. The precursor was then heated at temperatures 250°C (in nitrogen atmosphere), 300°C (in air) and 350°C (in air) to obtain CuO nanoparticles.

2.2. Characterization
The samples were characterized by X-ray diffraction (XRD) using a Seifert diffractometer with Cu Kα radiation. We have used cupric oxide (99.9999%) bought from Sigma Aldrich Pvt Ltd as the standard bulk sample. The crystallite sizes were calculated using Scherrer formula turned out to be 9 nm, 13 nm and 16 nm for samples heated at 250°C, 300°C and 350°C respectively. Transmission electron micrograph (TEM) and energy dispersive X-ray analysis (EDAX) of the sample prepared by heating the precursor at 250°C was taken with a FEI Technai 20 U Twin Transmission Electron Microscope. TEM image is shown in Figure 1. The inset of this figure shows the particle size distribution and the corresponding selected area diffraction (SAD) pattern of the sample. It can be seen that the particles are more or less spherical and we have estimated the particle size to be 9.8 nm with a standard deviation of 2.1 nm using the histogram shown in the inset (a) of Figure 1. The SAD pattern consists of concentric diffraction rings with different radii. The diameter of the diffraction ring in SAD pattern is proportional to \( \sqrt{h^2 + k^2 + l^2} \), where (hkl) are the Miller indices of the planes corresponding to the ring. Counting the rings from the center 1st, 2nd, 3rd... rings correspond to (110), (111), (002) planes, respectively. EDAX showed that the sample does not have any magnetic impurity.
2.3. Measurements

All measurements were performed in a SQUID magnetometer (Quantum Design Model MPMS XL5). The field cooled (FC) and zero-field-cooled (ZFC) magnetization measurements were done in the temperature range 10 K to 300 K. The FC measurements were done while cooling (FCC) as well as while heating (FCW). Hysteresis measurements were done at 10 K, 100 K and 300 K. Time dependence of thermoremanent magnetization was done at temperatures 10 K, 50 K, 100 K, 150 K, 225 K and 300 K for all the samples. Memory experiments were done in a field of 250 Oe in both FC and ZFC protocols.

3. RESULTS AND DISCUSSION

3.1. Temperature dependence of magnetization

The temperature dependence of magnetization was done under FC and ZFC protocols for all the samples at a field of 100 Oe. See Figure 2. It can be seen that the FC and ZFC magnetization curves bifurcate above 300 K for the nanoparticle samples, while they almost coincide for the bulk sample. No difference between FCC and FCW (same as FC) magnetization was seen in any of the samples. The magnetization for 16 nm particles is unexpectedly greater than that of 9 nm and 13 nm particles. The reasons for this are not clear, but perhaps this may be due to surface roughness which is not necessarily a monotonic function of particle size. [36]

Most of the nanoparticles of antiferromagnetic materials have been known to show superparamagnetic or spin glass-like behavior, well below the Néel temperature of the bulk material, both of which are characterized by a peak in the ZFC magnetization at low fields without a corresponding peak in the FC magnetization. [13, 16, 35, 38] As can be seen from Figure 2, there is no peak in the ZFC magnetization of CuO nanoparticles. Initially the magnetization decreases with decreasing temperature and then it increases at low temperatures showing a clear minimum, for all particle sizes. We would like to check whether this system shows any signatures of superparamagnetic or spin glass-like behavior. For this purpose, FC and ZFC magnetization measurements were done at fields of 100 Oe, 500 Oe, 1000 Oe and 1 T for 16 nm particles. For superparamagnets, the field dependence of the peak temperature, \( T_p \), is given by \[ T_p \propto \left( 1 - \frac{H}{H_K} \right)^2, 0 \leq H \leq H_K \] \[
\text{(1)}
\]
where $V$ is the volume of a particle and $H_K$ is a positive constant depending on anisotropy of the system. For spin glasses the corresponding relation is [41]

$$H \propto \left(1 - \frac{T_p}{T_f}\right)\frac{3}{2}, \quad 0 \leq T_p \leq T_f$$

(2)

where $T_f$ is the spin glass transition temperature in zero applied field. We see that for a superparamagnetic system $T_p$ is linearly related to $H$ whereas for a spin glass system $T_p$ decreases linearly with $H^{2/3}$.

In our case, the CuO nanoparticles do not show any peak in the ZFC curves. Now, in the case of canonical spin glasses, the bifurcation temperature ($T_{bf}$) between the FC and ZFC curves and the peak temperature of the ZFC magnetization are very nearly the same. [42] In superparamagnetic particles it is generally seen that $T_{bf} > T_p$. [43] $T_{bf}$ can be considered as the onset of superparamagnetic blocking or spin glass freezing and so it is expected that $T_{bf}$ will behave in a manner similar to peak temperature. This has been shown to be the case for NiO nanoparticles. [13] Thus, following the example of NiO we shall consider $T_{bf}$ as a good enough replacement for $T_p$ for further analysis.

![Figure 2](image1.png)

Figure 2: (Color online) FC and ZFC magnetization for (a) bulk, (b) 13 nm, (c) 9 nm and (d) 16 nm samples at 100 Oe. Clear bifurcation in FC and ZFC curves can be seen in all the nanoparticle samples.

![Figure 3](image2.png)

Figure 3: (Color online) Difference between FC and ZFC susceptibility for 16 nm nanoparticles for various fields: (1) 100 Oe, (2) 1000 Oe, (3) 5000 Oe and (4) 1 T. The insets show the plot of (a) $T_{bf}$ vs $H^{2/3}$ and (b) $T_{bf}^{1/2}$ vs $H$. The error bars are of the size of the data points.
| Particle size (nm) | T(K) | Coercivity (Oe) | Remanence (emu/g) |
|-------------------|------|----------------|------------------|
| 1                 | 9    | 38             | 1.83E-4          |
| 2                 | 9    | 42             | 1.80E-4          |
| 3                 | 9    | 55             | 2.30E-4          |
| 4                 | 13   | 28             | 1.08E-4          |
| 5                 | 13   | 32             | 1.09E-4          |
| 6                 | 13   | 30             | 9.3E-5           |
| 7                 | 16   | 15             | 6.85E-5          |
| 8                 | 16   | 60             | 2.26E-4          |
| 9                 | 16   | 24             | 1.25E-4          |

Table 1: Hysteresis parameters for various particle sizes.

In Figure 3 we show the difference between FC and ZFC susceptibilities, $\chi_{FC-ZFC}$, of the 16 nm sample at various applied fields. It is clear that the bifurcation temperature decreases as the applied field increases. For operational reasons, we shall define the bifurcation temperature as the temperature at which $\chi_{FC-ZFC}$ is 1% of its maximum value. From the insets of Figure 3, where we look at the functional dependence of $T_{bf}$ on $H$, we find that CuO nanoparticles neither follow superparamagnetic nor spin glass behavior.

3.2. Hysteresis measurements

We have done hysteresis measurements for all the samples at temperatures 10 K, 100 K and 300 K. The bulk sample does not show any hysteresis at any of the above temperatures but the nanoparticle samples do show hysteresis. We show the coercivity and remanence data for all the nanoparticle samples in Table 1. They show a small hysteresis at temperatures below as well as above the Néel temperature of the bulk sample.

Hysteresis has been observed in transition metal monoxide nanoparticles such as NiO, MnO, CoO etc. at temperatures below the bulk Néel temperature. It has been attributed to small ferromagnetic contributions due to uncompensated surface spins. It can be seen that hysteresis is present even at temperatures above the Néel temperature in CuO nanoparticles, which is quite unusual, and the origin of this is most likely the low dimensionality of CuO and a short range magnetic order which is present above the Néel temperature.

The fact that this short range order does not lead to any hysteresis in the bulk material means that it is antiferromagnetic in nature. This short range antiferromagnetic order gives rise to a weak ferromagnetism in the nanoparticles, which in turn causes the observed hysteresis even at room temperature, by the mechanism suggested by Néel. This also gives us a lower limit on the scale of the short range order; since this order exists over a region of the size of the nanoparticles the length scale of the short range order should be at least 16 nm, the maximum particle size where we have seen magnetic hysteresis.

3.3. Time dependence of thermoremanent magnetization

Time dependence of thermoremanent magnetization has been measured in all the samples at various temperatures (10 K, 50 K, 100 K, 150 K, 225 K, and 300 K). For this measurement a magnetic field of 1.0 kOe was applied and the sample was cooled to the temperature of interest. The magnetic field was now reduced to zero and the magnetization was measured as a function of time. We find no time dependence for the bulk sample, but all the nanoparticle samples show time dependence at all the temperatures at which the measurements were done. In Figure 4 we present the time dependence data for the 9 nm particles and it is seen to be more or less a logarithmic decay. In the inset of Figure 4 the magnetic viscosity ($dM/dlnT$) is plotted, which shows a maximum at 100 K. Such behavior of magnetic viscosity has been observed in other nanoparticle systems as well.
Figure 4: (Color online) Time dependence for 9 nm particles at various temperatures. The data have been smoothened by median filtering.

Figure 5: (Color online) Memory experiments done during FC for 16 nm nanoparticles with stops of one hour taken at 200 K and 100 K during the cooling process. The magnetic field was kept zero during the stop period and resumed for further cooling. Inset shows the curve for memory experiments during ZFC with stops of one hour taken at 200 K and 100 K while cooling. Solid lines are reference curves measured while heating, the preceding cooling process being performed without any stops.

3.4. Memory Experiments

Both superparamagnets and spin glasses are known to show memory effects. Superparamagnets are expected to show FC memory while spin glasses are expected to show memory in both ZFC and FC protocols. Memory experiments were done on the 16 nm sample according to the following protocol. Apply 3 T field to the sample for 5 minutes at 300 K to, hopefully, wipe out all memory to begin with. For ZFC memory, cool the sample in zero field to 10 K with intermittent stops of one hour at 200 K and 100 K. Measure the magnetization in a field of 250 Oe while warming up to 300 K. For FC memory, cool the sample in an applied field of 250 Oe with intermittent stops of one hour duration at 200 K and 100 K, with the field switched off. Cool to 10 K finally and then measure the magnetization in an applied field of 250 Oe as the temperature is ramped up to 300 K. In Figure 5 we show the results of our memory experiments. It is clear that no memory effects are present in either FC or ZFC protocols. This behavior is in sharp contrast to superparamagnetic or spin glass systems which are expected to show memory.
4. Conclusion

The magnetic properties of CuO nanoparticles are entirely different from other antiferromagnetic nanoparticles, for instance, the usual peak present in ZFC magnetization is absent. However there is a bifurcation between FC and ZFC magnetization curves which starts, surprisingly, well above the Néel temperature and the system shows hysteresis even at room temperatures. We have shown that this bifurcation does not have anything to do with the usual spin glass-like or superparamagnetic behavior shown by other magnetic nanoparticles. No memory has been observed in either FC or ZFC protocols which again leads to the very strange conclusion that this system behaves neither as a superparamagnet nor as a spin glass. Still, the observation of relaxation of magnetization and the associated peak in magnetic viscosity is similar to such behavior shown by other nanoparticle systems.

6. References

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