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Antiferromagnetic spin correlations in MnO nanoparticles

Tapan Chatterji [a,*], Yixi Su [b], Gail N. Iles [c], Yi-Cheng Lee [d], Amit P. Khandhar [d], Kannan M. Krishnan [d,*]

[a] JCNS, IFF, Forschungszentrum Jülich Outstation at Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex 9, France
[b] JCNS, IFF, Forschungszentrum Jülich, Outstation at FRMII, Lichtenbergstrasse 1, 85747 Garching, Germany
[c] Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex 9, France
[d] Department of Materials Science, University of Washington, Seatle, WA 98195-2120, USA

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ABSTRACT

We have investigated nearly monodispersive MnO nanoparticles of 10 nm diameter by polarised neutron diffraction with XYZ-polarisation analysis. We found no long-range ordering down to 3.5 K. A broad magnetic peak appeared close to $Q=(1/2,1/2,1/2)$ signifying short-range antiferromagnetic correlations. The correlation length was found to be about 2.4 nm at $T=3.5$ K. The correlation length decreases rapidly with increasing temperature and becomes about 0.7 nm at $T=250$ K.

Size-dependent scaling laws and the magnetic and optical properties of small particles and nanostructured assemblies, as a function of size, shape, dimensionality, morphology and inter-particle interactions, are increasingly of fundamental, technological and biomedical interest [1–8]. There are clearly two limits to the magnetic behavior as a function of size and dimensionality. At one end of the spectrum (bulk) the microstructure determines the magnetic (hard and soft) behavior. This is a function of the processing method and our understanding of it is qualitative and empirical at best. At the other end, as the length scales approach the size of domain wall-widths (nanostructures), lateral confinement (shape and size) and inter-particle exchange effects dominate, rendering classical descriptions grossly inadequate. Moreover for nanoscale structures, surface effects due to the lack of translation symmetry, reduced coordination number and broken bonds, possible at the particle boundary, can lead to surface spin disorder and frustration [9,10]. These surface effects can dominate the magnetic behavior of fine particles, especially with decreasing particle size (note that, for example, 60% of the atomic spins of a cobalt nanoparticle, 1.6 nm in diameter, are on the surface). As a result, the ideal model of a single domain particle or a giant superspin, with the same orientation and magnetic moment as the bulk material and reversing coherently is no longer valid. In other words, the combination of finite size, structural details of the core/surface and their interactions influence the magnetic ground state, including the non-uniform magnetization profile across the particle. Nanoparticles, prepared by chemical routes, are excellent materials to study such magnetic correlations on the nanometer scale, provided they can be synthesized with narrow size distributions. Beginning with cobalt as a model system, we have developed a comprehensive chemical method for the reproducible synthesis of monodisperse, passivated nanocrystals (metals [11], alloys [12], oxides [13] and core-shell structures [14]) with good size/shape control. The nanoparticles are well-characterized magnetically (a.c. and d.c magnetometry over a wide temperature range, high resolution electron holography and X-ray magnetic scattering), optically (VUV-VIS spectroscopy), structurally (transmission electron microscopy, dynamic light and small angle X-ray scattering) and chemically (electron energy-loss spectroscopy). However, there still remain fundamental questions about magnetic correlations in such materials. In order to get microscopic information about the magnetic correlations in magnetic nanoparticles in general and MnO nanoparticles in particular we have undertaken systematic neutron diffraction investigations.

Antiferromagnetic nanoparticles have been reported to have a net magnetic moment due to the uncompensated surface spins. The magnetic moment becomes larger with the decrease in particle size implying increase in the surface-to-volume ratio. This surface magnetism affects the magnetic properties such as the superparamagnetic blocking of the spin magnetisation direction of the nanoparticles. The resulting phenomenon is a shift of the peak T_p in the zero-field cooled (ZFC) magnetisation of MnO nanoparticles towards higher temperatures with decreasing particle size [15–18]. This temperature dependence is opposite to that of most other antiferromagnetic nanoparticles, including the isostructural NiO [19–21].

The fundamental problem of investigating magnetic ordering or short-range magnetic correlations in nanoparticles is the high

* Corresponding authors.
E-mail addresses: chatterji@ill.fr (T. Chatterji), kannank@uw.edu (K.M. Krishnan).

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incoherent background coming from the hydrogen atoms of surfactants with which the nanoparticles are coated in order to achieve narrow size dispersions and also to keep them apart. The incoherent background is so high that any reasonable determination of the relatively weak magnetic scattering becomes impossible by unpolarised neutron diffraction. However, magnetic information can be obtained by polarised neutron diffraction with proper analysis in magnetic fields. The XYZ-method using polarised neutrons for the separation of coherent, spin-incoherent, and magnetic scattering was developed by Schärpf et al. [22]. We exploited this method to extract magnetic scattering and determine magnetic correlations in MnO nanopartices.

We have prepared high quality, monodisperse, 10 nm dia., antiferromagnetic MnO nanoparticles. In the bulk, MnO is a cubic antiferromagnet with a Néel temperature, $T_N \approx 122$ K. We have extensively characterised structure and magnetic behavior of these nanoparticles [23]. Fig. 1 shows the X-ray $\theta-2\theta$ scans from the bulk as well as from the nanoparticles. One immediately notices that the Bragg peaks from the bulk sample has smaller 2θ values compared to those of the nanoparticles. This shows that the room temperature lattice parameter of the nanopartices is smaller than that of the bulk. The bulk lattice parameter is $a=4.436$ Å whereas that for nanoparticles is $a=4.37$ Å. The reduction of the unit cell volume with decreasing particle size is, by now, a well-known effect. This can naively be explained by the fact that the nanoparticle of diameter d is under effective pressure $P=2S/d$ due to surface tension S. The reduction of the cell volume in nanoparticles of half-doped manganites has been reported [24]. The inset of Fig. 1 shows a TEM picture of a single

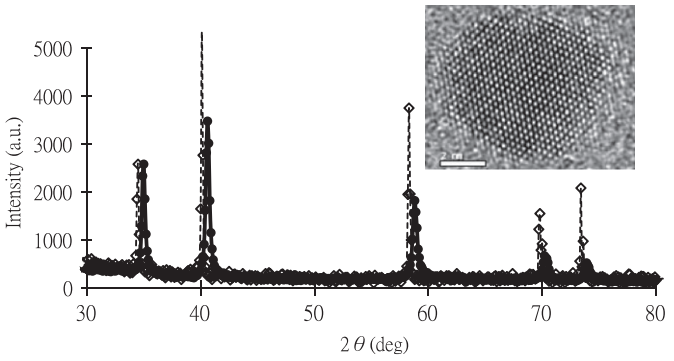

Fig. 1. X-ray diffraction diagram from bulk (dashed line) and nanoparticles (solid line) of MnO. The inset shows the TEM picture of a nanoparticle. The scale bar indicates 2 nm.

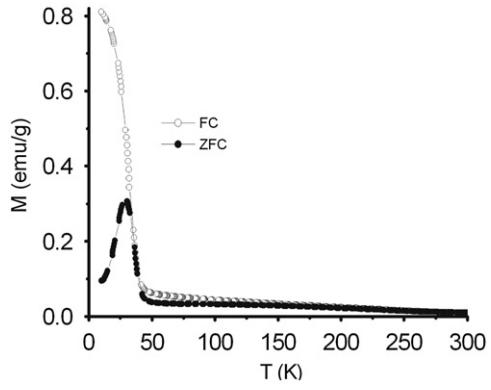

Fig. 2. Zero field cooled (ZFC) and field cooled (FC) magnetisation of MnO nanoparticles as a function of temperature. The magnetic field was 100 Oe.

MnO nanoparticle. The particle has a defect-free core and a surface layer that may contain defects. Fig. 2 shows the zero field cooled (ZFC) and field cooled (FC) magnetisation of MnO nanoparticles as a function of temperature. The ZFC curve shows a peak at ≈ 30 K but the magnetisation in both the ZFC and FC measurements persists up to 300 K. Further, careful measurements of the spontaneous magnetization and coercivity of the MnO nanoparticles as a function of temperature show a magnetic transition at $T_{SG} \approx 30$ K. This transition has been shown to be associated with the freezing of a spin-glass [25,26]. Details are published elsewhere [23] and therefore will not be repeated here.

Neutron diffraction experiment has been performed on MnO nanoparticles on the polarized diffractometer DNS at the FRM II (Garching, Germany). The neutron wavelength was 4.74 Å. We placed about 200 mg of MnO nanoparticles in an Al foil that was wrapped into a hollow cylindrical shape. We then put the wrapped nanoparticles inside an Al container under He atmosphere. We measured diffraction intensities as a function of temperature in the range 3.5–310 K. The diffracted intensity could be separated by the polarization analysis into the following three contributions: (1) coherent nuclear scattering, (2) spin-incoherent nuclear scattering and (3) magnetic scattering. The nanoparticles were covered with surfactants that contained H atoms that are strong spin-incoherent scatters. However, we were able to separate out the spin incoherent scattering from the H atoms by polarization analysis. The intensity in the coherent nuclear scattering channel gives structural information, however, using a neutron wavelength of 4.74 Å we could not access any nuclear Bragg peaks and therefore no structural information was obtained from the present experiment. We were mainly interested in the diffracted intensity in the paramagnetic channel containing scattering from the short-range ordered spins of Mn ions. Fig. 3 shows the short-range correlations at $Q=$ (1/2,1/2,1/2). A strong antiferromagnetic Bragg peak corresponding to the type-II AF structure appears at this position in bulk MnO samples. But for the MnO nanoparticles we observe only broad scattering due to short-range spin correlations. We fitted the broad peaks with Lorentzian functions. The half-width at half-maximum (HWHM) derived from these fits gave the inverse correlation length, which has been plotted in Fig. 4. The magnetic correlation length is very short and is 2.4 nm at $T=3.5$ K. The correlation length decreases rapidly with increasing temperature reaching 0.7 nm at $T=250$ K. The magnetic correlation length estimated is shorter than the particle size and probably represents the core antiferromagnetic part and does not include the outer part of the particles that are not strictly antiferromagnetic. In any case the estimation of correlation length is very rough.

Bulk MnO orders in an antiferromagnetic structure at $T_N \approx 122$ K. It is expected that both a bulk and a nanoparticle system will develop antiferromagnetic correlations in increasing length scales on approaching this temperature from above. In a bulk sample the magnetic correlation length diverges at T_N. In the nanoparticle system the finite size of the particles sets an upper limit to the correlation length ξ. In the present system the upper limit of correlation length is about $\xi = 10$ nm. The magnetic correlation length may reach this limit at low temperature. It is thus expected that the measure 1/HWHM should increase on approaching T_N of the bulk MnO, and on further decreasing temperature remain constant on a length scale of order 1–10 nm. The results exemplified in Fig. 3 could be interpreted to support this anticipation or at least the results are not contradictory to this interpretation. The particles are antiferromagnetically ordered (short range—due to finite size) at low temperatures with an uncompensated excess moment. The neutron data do not allow us to estimate the temperature for this ordering.

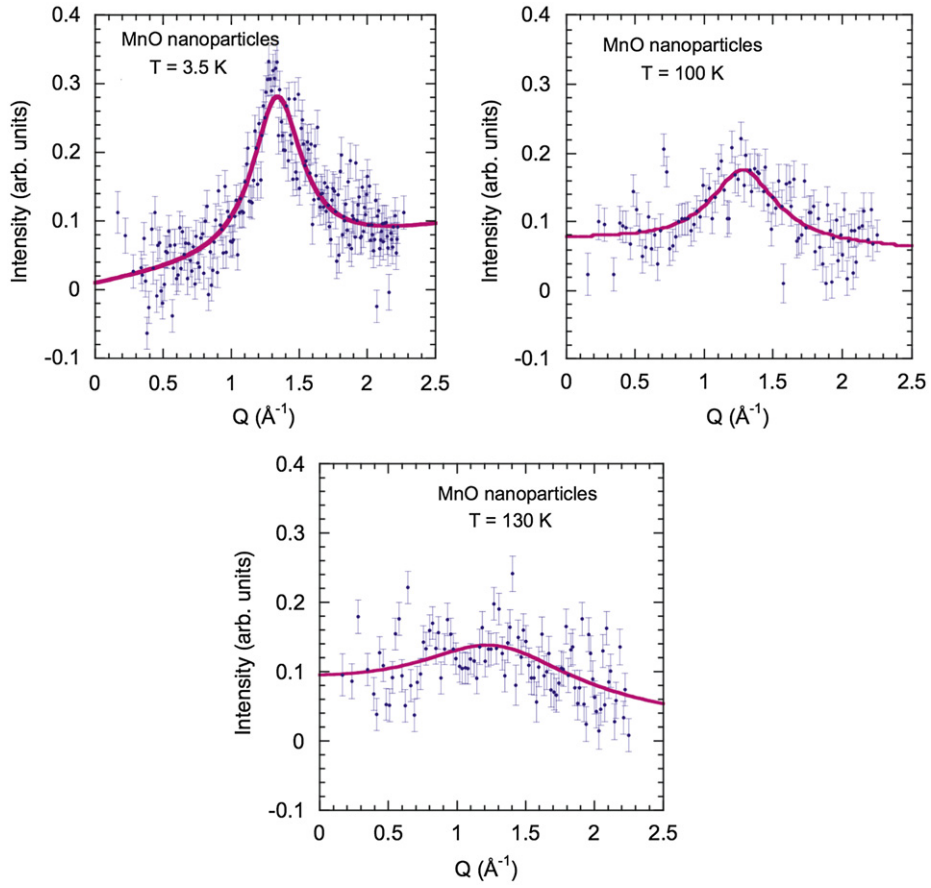

Fig. 3. Short-range antiferromagnetic correlations in MnO nanoparticles of average diameter 10 nm at different temperatures. The continuous red curves are the results of fit with a Lorentzian function. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

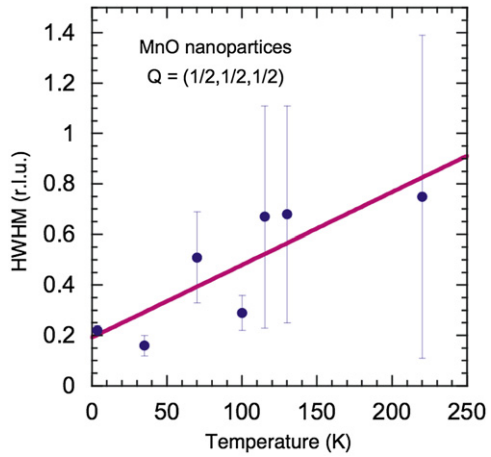

Fig. 4. Temperature variation of the half-width at half-maximum (HWHM) of the short-range antiferromagnetic correlations in MnO nanoparticles of average diameter 10 nm. The red line is just a linear fit. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The present data measured with cold neutrons of wave length $\lambda = 4.74$ Å do not show any convincing evidence for the ferromagnetic spin correlations. We do not see any obvious increase in magnetic intensity at small scattering angles, i.e. at a very small Q at which ferromagnetic correlations if it existed should have been present. (The two data points of the scan at $T = 3.5$ K of Fig. 3 show some tendency to increase but are hardly significant within counting statistics.) One should also observe broad magnetic scattering due to ferromagnetic spin correlations surrounding the nuclear Bragg peaks. However, due to the large wavelength of the cold neutrons used we could not access any nuclear Bragg peak. In order to probe short range ferromagnetic correlations we plan to do a similar polarised neutron diffraction experiment on MnO nanoparticles by using thermal neutrons with wave length of about 2.4 Å.

In conclusion the polarized neutron diffraction with XYZ-polarisation analysis has given important information about the short-range magnetic correlations in MnO nanopaticles.

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