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Cite as: AIP Advances **6**, 055007 (2016); https://doi.org/10.1063/1.4948798
Submitted: 17 December 2015 • Accepted: 26 April 2016 • Published Online: 03 May 2016

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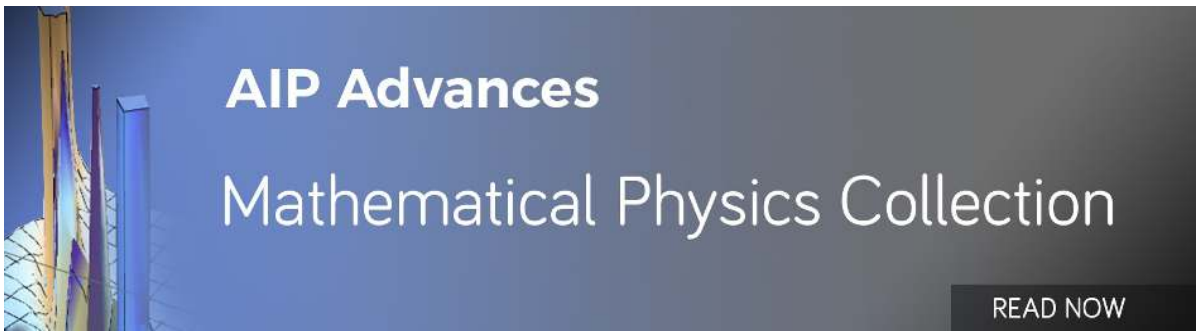

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Large tunneling magnetoresistance in octahedral Fe_3O_4 nanoparticles

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(Received 17 December 2015; accepted 26 April 2016; published online 3 May 2016)

We have observed large tunneling Magnetoresistance (TMR) in amine functionalized octahedral nanoparticle assemblies. Amine monolayer on the surface of nanoparticles acts as an insulating barrier between the semimetal Fe_3O_4 nanoparticles and provides multiple tunnel junctions where inter-granular tunneling is plausible. The tunneling magnetoresistance recorded at room temperature is 38% which increases to 69% at 180 K. When the temperature drops below 150 K, coulomb staircase is observed in the current versus voltage characteristics as the charging energy exceeds the thermal energy. A similar study is also carried out with spherical nanoparticles. A 24% TMR is recorded at room temperature which increases to 41% at 180 K for spherical particles. Mössbauer spectra reveal better stoichiometry for octahedral particles which is attainable due to lesser surface disorder and strong amine coupling at the <111> facets of octahedral Fe_3O_4 nanoparticles. Less stoichiometric defect in octahedral nanoparticles leads to a higher value of spin polarization and therefore larger TMR in octahedral nanoparticles. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4948798]

Magnetic nanoscale materials offer a promising platform for spintronic applications where spins along with their charges are modulated to fabricate devices.[1,2] Modern spintronics devices such as MRAM[3] and read head of magnetic memory devices[2] are based on magnetoresistance (MR), a change in electrical resistance under an applied magnetic field. Magnetoresistance which is observed across a magnetic tunnel junction (MTJ, defined as two ferromagnetic materials separated by a very thin insulating layer)[4] is called tunneling magnetoresistance (TMR). Magnetic materials in bulk form and thin films are generally used as the ferromagnetic layer in MTJ. However, nanoparticle based systems are not the conventional MTJs, because there are several magnetic grains which are separated by insulating layers attached to their surfaces. Among the magnetic nanoparticles, magnetite (Fe_3O_4) has been one of the most studied material due to its semi metallic nature with a band gap of 0.1–0.15 eV and a very high spin polarization at room temperature.[4] Fe_3O_4 nanoparticles which have a layer of organic molecules present on their surfaces acting as the surface functionalizing agent can be synthesized by various techniques.[5,6] Exploiting this surface monolayer as the insulating barrier, nanoparticle based MR devices could be designed.[4,7,8] Researchers have also synthesized magnetic core-shell nanoparticles whose core material has very high spin polarization and the shell material acts as an insulator.[9] There are a few reports in literature where a TMR has been observed in multiple tunnel junctions. For example, spin dependent tunneling in oleic acid stabilized Co nanoparticle superlattices was observed by Black *et al.*[10] Similarly Wang *et al.* reported 17% TMR at 115 K and 7% TMR at room temperature for oleic acid coated Fe_3O_4 nanoparticles.[11] In another report, Wang *et al.*[4] observed TMR of 22% at room temperature for

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polystyrene coated magnetite nanoparticle assemblies, which increases to 40.9% TMR at 110 K. A 35% MR was observed by Zeng *et al*. at 60 K under 3.5 T in surfactant coated Fe_3O_4 nanoparticles.[8] Recently, Kohiki *et al*.[7] reported a MR of 60% for oleic acid coated Fe_3O_4 nanoparticles at 200 K. In most of these above mentioned studies, TMR values are poor, which is due to impurities and defects present in magnetite nanoparticles. Moreover, magnetite nanoparticles often have maghemite impurity, which further hinders the achievable 100 % spin polarization. Recently, it has been observed that octahedral nanoparticles are stoichiometrically more prefect as compared to spherical nanoparticles due to their low surface anisotropy.[12] The shape of the nanoparticle plays an important role in modulating various physical and chemical properties of nanoparticles.[13,14] Therefore, shape anisotropy could be exploited to obtain a better spin polarization in ultra-small size regime.

In this study, tunneling magnetoresistance (TMR) is measured in octahedral and spherical Fe_3O_4 nanoparticle assemblies at different temperatures. For octahedral nanoparticles, the TMR recorded at room temperature is 38% and reaches a maximum of 69% at 180 K, whereas, for spherical nanoparticles 41% TMR is observed at 180 K and 24% at room temperature. Octahedral nanoparticles are faceted with {111} planes; therefore, possessing minimum surface energy and lesser surface defects. Therefore, a better spin polarization is attained in octahedral particles as compared to the spherical particles.

Synthesis of octahedral and spherical Fe_3O_4 nanoparticles were performed using oleylamine as the solvent, reducing and surface functionalizing agent as described in earlier published literature.[6,12] The detailed synthesis, surface chemistry and morphological analyses are given in the supplementary material.[15] The powder samples were pressed into pellets (Fig. 1(a)) and annealed in argon gas flow at 150 °C for 2 hours to eliminate the moisture on the particle surface.

X-ray diffraction (XRD) measurements are performed in order to analyze the phase of octahedral nanoparticles before and after preparing the pellet (Fig. S1).[15] In both the cases nanoparticles exhibit six prominent diffraction peaks for (220), (311), (400), (422), (511) and (440) planes of spinel structure of magnetite (ICDD 19-0629). The comparative XRD spectra show the same position and full width half maxima (FWHM) of the peaks before and after pressing and annealing of nanoparticles which indicates that size as well as phase is retained after the pelletization.

Temperature dependent zero-field-cooled (ZFC) magnetization data of the octahedral and spherical Fe_3O_4 nanoparticles measured at 50 Oe in the temperature range of 10 K to 300 K is shown as Fig. S5a (supplementary material).[15] Spherical particles show conventional blocking temperature (T_B) in the ZFC curve while a kink of Verwey transition is observed near 120 K for octahedral nanoparticles.[16] Verwey transition is an indication of stoichiometric Fe_3O_4 phase formation and vanishes with a very little defect in stoichiometry.[17,18] Therefore, we can conclude that octahedral nanoparticles have better shoichiomety as compared to spherical nanoparticles.[12] Room temperature M-H curves of the spherical and octahedral Fe_3O_4 nanoparticles are shown in

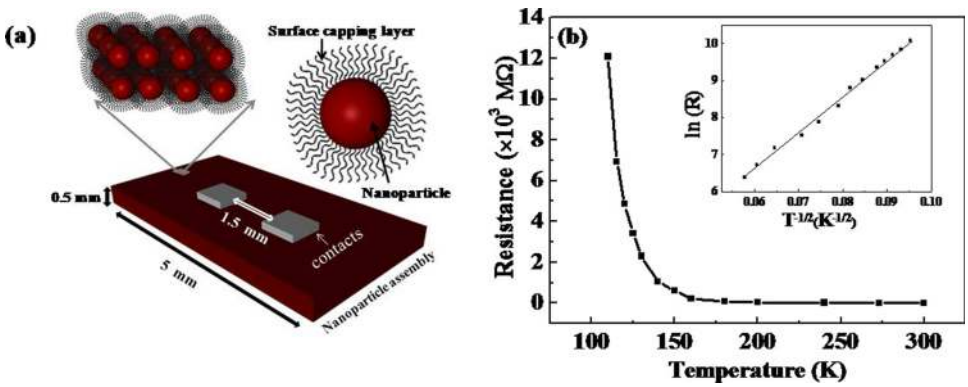

FIG. 1. (a) Schematic of a Fe_3O_4 nanoparticle pellet (thickness 0.5 mm); nanoparticles form a multiple junction (MTJ) system where intergranular tunneling is plausible. Surface capping amine layer between particles acts as the insulating dielectric layer. (b) Resistance as a function of temperature for 8 nm octahedral particles. Inset: A linear relationship between $ln\ R$ and $T^{-1/2}$ indicates the tunneling between the nanoparticles.

Fig. S5b.[15] At room temperature, both the octahedral and spherical nanoparticles exhibit superparamagnetic behavior without magnetic hysteresis and remanence. The saturation magnetization (M_S) value of the octahedral particles is 77 emu/g while for spherical nanoparticles it is 71 emu/g. Higher M_S value for octahedral particles indicates lesser surface spin disorder[14] and better stoichiometry in octahedral shape.[12]

The resistance *vs*. temperature curve (Fig. 1(b)) depicts an exponential decrease of resistance with temperature, as expected for Fe_3O_4.[19] The electrical transport measurements are performed in a temperature range of 100–300 K. Intergranular tunnelling in the nanoparticle system is examined by the relationship between R and $T^{-1/2}$ as shown in the inset of Fig. 1(b). The straight line fit indicates that the tunnelling dominates the electron conduction between the adjacent Fe_3O_4 nanoparticles.[4,7] Fig. 2(a) shows the electrical transport measurement curves of 8 nm sized octahedral particles under magnetic field of 0, 0.2, 0.5 and 1.0 T at room temperature. The resistance at different fields is calculated from the slope of the curves. The magnetoresistance (MR) is calculated as MR $= (R_H - R_0)/R_0$, where R_H and R_0 are the resistance under an applied magnetic field and zero field. As the applied magnetic field is increased, more spins are polarized; therefore TMR value is also increased very rapidly. We have observed 38% TMR at room temperature under 1.0 T magnetic field. This large value of TMR at room temperature is a result of high spin polarization in octahedral nanoparticles. Fig. 2(b) and S6 a–b in supplementary material[15] depict the current versus voltage plots in different fields at the temperature of 273 K, 200 K and 180 K. The calculated MR values are 40% at 273 K, 49% at 200 K and 69% at 180 K. As the degree of spin polarization near the Fermi level enhances with the decreasing temperature, the TMR value increases at low temperature.[7]

For spherical particles of 8 nm, 24% TMR is observed at room temperature (Fig. 2(c)). With a decrease in temperature, the MR value increases and reaches to 41% at 180 K (Fig. 2(d)). Table I in the supplementary material[15] summarizes the TMR values of spherical and octahedral particles at different temperatures under an applied field of 1.0 T. In addition to measuring the TMR from transport characteristics at three different magnetic fields, we have also measured TMR as a function

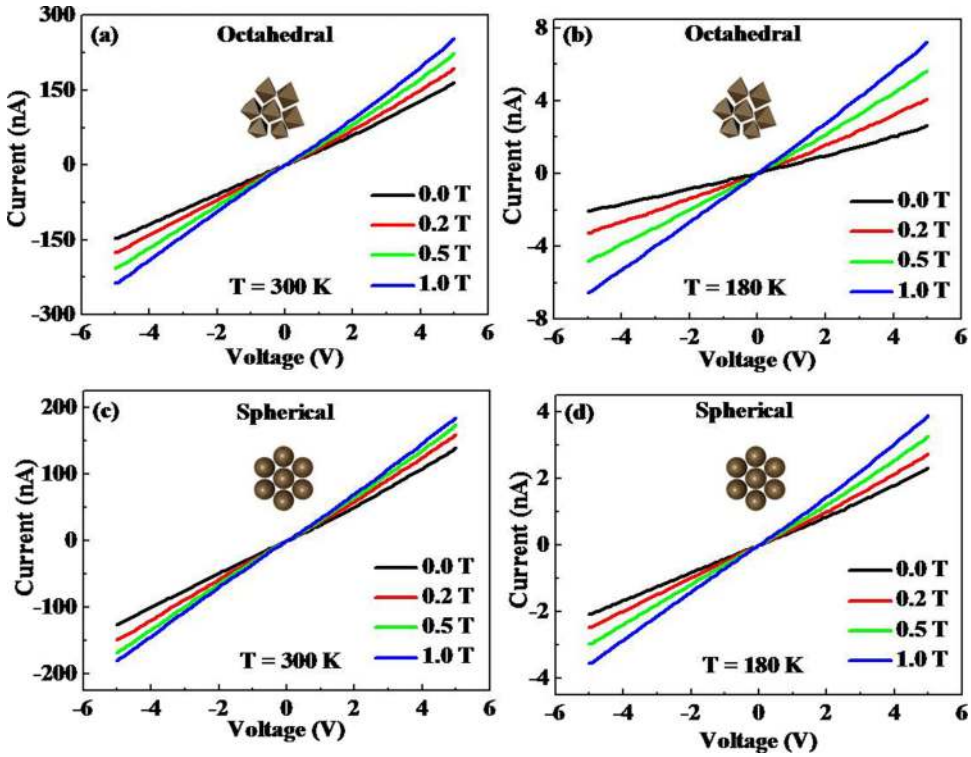

FIG. 2. Current-voltage measurements of octahedral particles conducted under different magnetic fields as indicated at (a) 300 K (b) 180 K. Current voltage measurements for spherical particles conducted under different magnetic fields as indicated at (c) 300 K and (d) 180 K.

TABLE I. Comparison of TMR values of octahedral Fe_3O_4 nanoparticles with other Fe_3O_4 systems reported in literature.

Studied system	TMR at 300 K	TMR highest	Reference number
Oleylamine coated octahedral Fe_3O_4	38 %	69 % (180 K)	This work
oleic acid-coated Fe_3O_4	46 %	58 % (200 K)	8
Polystyrene-coated Fe_3O_4	22.8 %	40.9 % (110 K)	5
Fe_3O_4 superlattice	12 %	35 % (60 K)	9
oleic acid-coated Fe_3O_4	7.3 %	17.5 % (115 K)	13

of constantly varying magnetic field. Fig. 3 shows the room temperature TMR measurements in a magnetic field range of -2.5 kOe to +2.5 kOe. Octahedral nanoparticles have shown a TMR of 36% at room temperature while for spherical nanoparticles 23% TMR is obtained under identical experimental condition. According to Slonczewski[20] and MacLaren *et al.*[21] the nature of the insulating barrier also influences the effective spin polarization if the barrier height is small. But as oleylamine is an insulator, the effect of the barrier on the spin polarization would be negligible. So the difference in the spin polarization between the two shapes is due to the difference in stoichiometric purity, surface / interface coordination. The stoichiometric superiority of octahedral nanoparticles could be explained using shape anisotropy. Octahedral nanoparticles have facets of {111} planes as their surface, which possess minimum surface energy among all the planes of magnetite; therefore, as compared to spherical particles octahedral particles have less surface defects and broken symmetry.[14] Spherical nanoparticles with a curved surface have all the planes at their surface which results in higher surface anisotropy and stoichiometric defects. Therefore, octahedral shape has a higher degree of spin polarization as compared to spherical particle. Recently, Kurahashi *et al.* reported that spin polarization in Fe_3O_4 varies at different crystal planes and becomes minimum for {100} planes due to the hybridization of oxygen surface states and Fe d_{x2-y2} surface state.[22] Therefore absence of {100} plane at the surface could be a reason for higher spin polarized current in octahedral Fe_3O_4 nanoparticle assemblies.

In three dimensional assemblies, Fe_3O_4 nanoparticles get magnetized in [111] direction (easy axis) under an applied magnetic field. If we consider the angle between two adjacent magnetization (m) is θ, then θ relates to m as $m^2 = \langle\cos\theta\rangle$.[23] Therefore, when magnetizations in the system align parallel (θ = 0) under a strong magnetic field, m becomes unity. Inoue *et al.*[23] formulate TMR in a

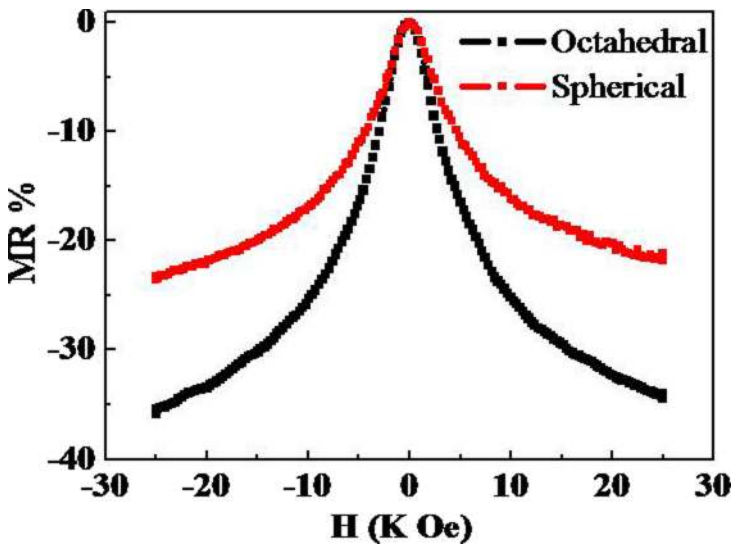

FIG. 3. TMR measured in the magnetic field range of -25 KOe to +25 KOe at 300 K, for spherical and octahedral Fe_3O_4 nanoparticles of 8 nm.

three dimensional multiple tunnel junctions as

$$MR = \frac{P^2m^2}{1 + P^2m^2} \, (where \; P = magnetic \; polarization) \tag{1}$$

therefore, consideration of P = 100% and m = 1 maximize the TMR value.[7] Substituting the maximum achievable value of P and m, a 50% TMR is foreseen using equation (1). However, similar to our results, an enhanced TMR (>50%) is reported for intergranular tunneling in literature.[7,24] Inter-granular tunneling is a complex phenomenon and several deviations occur from theoretical calculation because of spin independent conduction between the nanoparticles via hopping and scattering of electrons.[4] Ziese *et al.*[25] had developed an equation for MR in intergranular tunneling using a modified spin hopping model in discontinuous manganite ($La_{0.7}Ca_{0.3}MnO_3$) films. He considered the multiple tunnel junctions as equivalent circuits of resisters in series. The expression for MR was obtained as

$$MR = \frac{\left(1 + P^2\right) P^2 \operatorname{arctanh}\left(P^2\right) - 1}{\left(1 + P^2\right) P^2 \operatorname{arctanh}\left(P^2\right)} \tag{2}$$

Above equation shows that TMR can reach up to 80% when the value of P approaches 1 (Fig. S7).[15] Sheng Ju *et al.*,[26] had done a rigorous study on spin dependent transport in manganite nanoparticles considering the multiple tunnel junctions as the bond-disordered resistor network (both charging energies (E_C) and spin-polarized tunneling are considered as the means of magnetotransport) and estimated a 60% of TMR in the theoretical calculations. We have calculated spin polarization values of spherical and octahedral particles using Zisse model (Equation (2)). Spin polarization for octahedral nanoparticles is calculated as 68% at room temperature and 94% at 180 K, whereas for spherical nanoparticles, spin polarization values are 51% and 72% at room temperature and 180 K, respectively. As compared to different Fe_3O_4 nanoparticulate systems reported in literature[4,8,11] (table-I), we observe higher value of MR in octahedral Fe_3O_4 nanoparticle assemblies. Better stoichiometry and lesser surface defects in octahedral particles result in higher degree of spin polarization and hence a better TMR in octahedral particles.

Mössbauer spectra analysis is performed to study the oxidation states and stoichiometry of octahedral and spherical Fe_3O_4 nanoparticles.[27,28] Room temperature Mössbauer spectra of octahedral and spherical nanoparticles deconvoluted into three sextets are shown in Fig. 4(a) and 4(b), respectively. The isomer shift (I_S), quadrupole moment (Q_f) and hyperfine fields (H_{hf}) of sextet A and B are given in the Table II. Isomer shift for Fe^{3+} (tetrahedral), Fe^{3+} (octahedral), Fe^{2+} (octahedral) are 0.25, 0.4, 1.00 at 300 K respectively.[28] As there are no Fe^{2+} (octahedral) ions in maghemite, stoichiometric defect can be easily identified from I_S value. The isomer shift of sextet B for spherical and octahedral particles are 0.405 and 0.571 respectively, which shows that higher amount of Fe^{2+} present in octahedral particles.[28,29] As the maghemite content is the most prominent source for stoichiometric defect in magnetite, it can be clearly inferred that octahedral nanoparticles

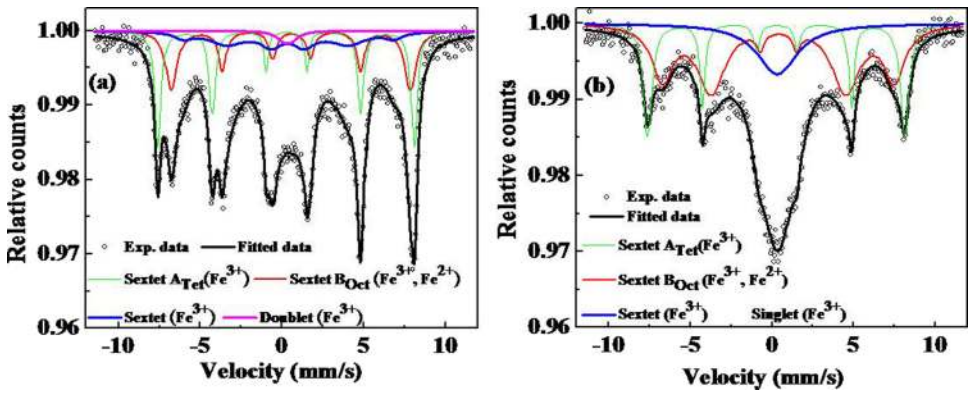

FIG. 4. Mössbauer Spectra recorded at 300 K for: (a) octahedral and (b) spherical nanoparticles of size 8 nm.

TABLE II. Mössbauer parameters: hyperfine field (H_{hf}), quadrupole splitting (Q_S) and isomer shift (I_S) for octahedral and spherical nanoparticles.

Fe_3O_4	Iron Sites	Hyperfine field, (H_{hf}) Tesla	Quadrupole splitting, (Q_S) mm/s	Isomer shift, (I_S) mm/s
Octahedral	Sextet B	45.36	-0.04	0.571
(8 nm)	Sextet A	48.69	-0.026	0.267
Spherical	Sextet B	44.13	-0.005	0.405
(8 nm)	Sextet A	48.91	-0.04	0.272

are of better stoichiometry. Magnetite as compared to maghemite has much higher spin polarization; therefore octahedral nanoparticles can achieve a higher degree of spin polarization and as a result higher TMR value.

If the temperature is decreased further on ($\leq$ 140 K), a step like nature is observed in the current versus voltage characteristics which is believed to be the Coulomb staircase (Fig. 5). This phenomenon could be observed in a tunnel junction when the charging energy exceeds the thermal energy k_BT, and the tunneling resistance is larger than the quantum resistance ($\frac{h}{e^2} = 26\,k\,\Omega$).[30] In an assembly of amine coated nanoparticles, resistance is much greater than the above mentioned value. Capacitance (C) of the nanoparticles coated by the tunnel barrier is calculated using the expression $C = 4\pi\varepsilon\varepsilon_0 r$,[31] where ε_0 is free-space and ε is relative permittivity. Assuming the radius (r) of the nanoparticle as 4 nm, and relative permittivity (ε) of oleylamine as 3, charging energy ($E = \frac{e^2}{C}$) is calculated around 75 meV, which is much higher than the thermal energy at 140 K (12 meV); therefore a nanoparticle can behave as the coulomb island at low temperature regime (<150 K).[32]

Oleylamine coated octahedral nanoparticle assemblies show a large TMR value of 38% at room temperature, which further increases to 69 % at 180 K. This large value of MR is due to the high degree of spin polarization in octahedral magnetite nanoparticles. As the temperature drops below 140 K, Coulomb staircase in current versus voltage characteristics is observed because the charging energy exceeds the thermal energy. Conventional spherical nanoparticles show a comparatively lower value of TMR (24%) at room temperature as well as at lower temperatures. Mössbauer spectroscopy and magnetic measurements reveal that octahedral nanoparticles have better stoichiometry and less surface defects as compared to spherical nanoparticles. Therefore, octahedral nanoparticles can achieve a higher degree of spin polarization which enhances the TMR value. Such nanoparticle based systems

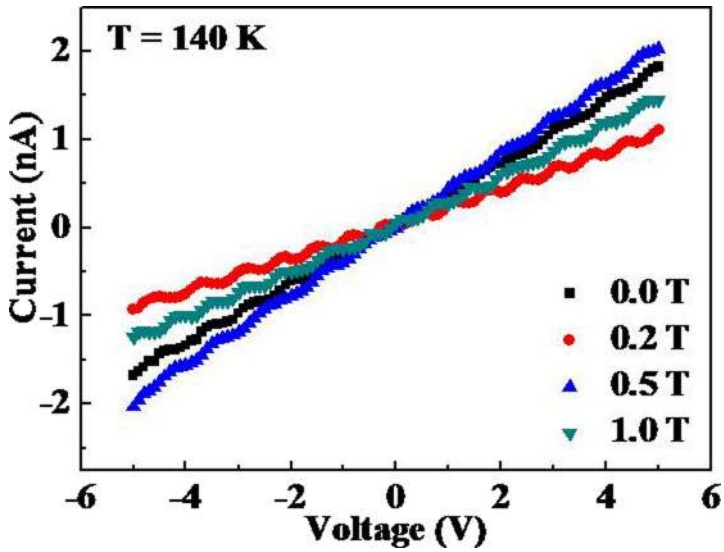

FIG. 5. Current voltage curves under different magnetic fields at 140 K shows Coulomb staircase (CS).

which show a large value of MR even at room temperature, have potential in applications of future generation spintronics devices.

We are thankful to CRNTS, IIT Bombay for microscopy measurements and IRCC, IIT Bombay for magnetic measurements. We are thankful to Prof. C.V. Tomy and Prof. S. Dhar for their assistance and permission in transport and magnetoresistance measurements.

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