

Comment on "Particle-size effects on the value of T_C of MnFe_2O_4 : Evidence for finite-size scaling"

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We show that a nonequilibrium cation distribution is the likely explanation for the 47-K rise in the Curie temperature of ultrafine MnFe_2O_4 particles found by Kulkarni *et al.* This nonequilibrium cation distribution is argued to be caused, in part, by oxidation of Mn^{2+} to Mn^{3+} due to heating of the particles during the experiments performed by Kulkarni *et al.* to determine the Curie temperature.

Recently, Kulkarni *et al.* reported a 47-K rise in the Curie temperature T_C of ultrafine MnFe_2O_4 particles compared to the T_C of bulk MnFe_2O_4 . They claimed that this effect was due to finite-size scaling.¹

Previously, Tang *et al.*² arrived at the same conclusion for the rise in T_C of ultrafine MnFe_2O_4 particles prepared by wet-chemical methods (e.g., coprecipitation). We have commented on this issue that a nonequilibrium cation distribution was a more likely explanation for the observed rise in T_C .^{3,4} Specifically, it is well documented by NMR,⁵ neutron diffraction,⁶ and Mössbauer spectroscopy⁷ that wet-chemically prepared Mn-containing ferrites have a different cation distribution over the tetrahedral (*A*) and octahedral (*B*) sites than ferrites prepared by standard, solid-state ceramic methods. Due to a higher inversion degree, i.e., a larger octahedral Mn concentration, the $\text{Mn}_A^{2+}\text{-Fe}_B^{3+}$ superexchange interaction is replaced by the $\text{Fe}_A^{3+}\text{-Fe}_B^{3+}$ interaction with double strength, which raises T_C .^{3,8} Also a more recent report by Tang *et al.*⁹ demonstrates that a nonequilibrium cation distribution causes a rise in T_C as large as those found in Refs. 1 and 2. Moreover, a neutron diffraction study on ZnFe_2O_4 particles found deviations from a standard cation distribution which increases with decreasing particle size.¹⁰

Fortunately, Kulkarni *et al.* made an effort to determine the cation distribution of the wet-chemically prepared MnFe_2O_4 particles made by them, following the method of Tang *et al.*^{2,11} They found that the Mn inversion degree was 32% in their 33-nm particles, which is close to, but certainly not identical to the 20% found for MnFe_2O_4 prepared by solid-state reactions.⁸ Moreover, the Fourier transforms of the Mn *K*-extended x-ray-absorption fine structure (EXAFS) at 300 K of their 12- and 33-nm particles are similar, but *not identical* [see Fig. 3(a), Ref. 1, in particular the deconvoluted peak intensities]. The latter is needed to rule out any variations in the initial cation distribution of the samples. More seriously, around T_C , at temperatures of 573 and 653 K, an even higher Mn inversion degree of 60% is reported.¹

Heating of the samples during the measurement is therefore established to cause a major change in the cation distribution. The modified cation distribution will alter the magnetic properties of the ferrite particles, including the T_C . Therefore, the relationship of the experimentally determined T_C to any scaling effect is ambiguous as the magnetic properties of the particle will vary during the measurement. Inspection of Fig. 4 of Ref. 1 even suggests that the rate of cation redistribution with increasing temperature, is different for larger than for smaller particle size.

We suggest that the high octahedral Mn concentration reported by Kulkarni *et al.* is related to the particulate nature of their samples. Normally, in single-crystalline or ceramic MnFe_2O_4 the equilibrium octahedral Mn concentration at 650 K is about 0.10.¹² The maximum inversion degree which can be reached by quenching ceramic samples is 25–30%.¹² Higher inversion degrees can only be reached through oxidation of Mn^{2+} .¹³ Due to the enhanced surface area, Mn^{2+} ions located at or near the surface will be prone to oxidation to Mn^{3+} . As shown by Tailhades *et al.*,¹³ the latter process predominantly occurs in the temperature range 570–670 K, resulting in a defect spinel structure with an enhanced octahedral Mn^{3+} concentration, an increased Fe occupancy of the tetrahedral sites, and the presence of cation vacancies at the octahedral sites. The ratio of the octahedral to tetrahedral Fe sites of 0.57, found in Ref. 1, is also in accordance with such a cation-deficient structure. Thus, due to oxidation, the Mn inversion degree is increased. Consequently, the overall superexchange interaction is raised and T_C will increase, as observed.¹ We think that the prolonged heating needed to perform the Mössbauer experiments at 573 and 653 K, from which T_C has been determined in Ref. 1, causes the oxidation of Mn^{2+} to octahedral Mn^{3+} . Oxidation may occur more rapidly and completely in the 12-nm particles than in the 33-nm particles, due to the larger surface area. The differences in the Fourier transforms of the Mn *K* EXAFS at 573 and 653 K of the 33-nm particles [see Fig. 4(a), Ref. 1],

whereas these Fourier transforms appear identical for the 12-nm particles, seem to bear this out.

Finally, it has been demonstrated that fresh, unannealed MnFe_2O_4 particles of 12 to 27 nm showed a uniformly increased T_C compared to bulk MnFe_2O_4 , but *no* particle size dependence of T_C .⁹ Also on theoretical grounds a reduction rather than an increase in T_C is expected in finite-size systems.¹⁴ Consequently, physicochemical effects such as a nonequilibrium cation dis-

tribution and a redox process seem to be the cause for the rise in T_C seen in Ref. 1, rather than a unique finite-size scaling effect.

In conclusion, ultrafine ferrite particles, although being interesting in themselves for various aspects,¹⁵ are poor systems for the study of finite-size scaling effects due to the complications arising from nonequilibrium cation distributions and possible surface chemistry phenomena.

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