Comment on "Size-Dependent Curie Temperature in Nanoscale $MnFe_2O_4$ Particles"

A recent Letter [1] reported a size-dependent Curie temperature T_c of nanoscale $MnFe_2O_4$-ferrite particles, such that T_c *increases* by as much as 97 K with decreasing particle size. The influence of the microstructure on magnetic properties of ferrites has been studied in the past [2], and continues to receive attention [3]. The observation of Tang *et al.* is in contrast to all other investigations in films where T_c is seen to decrease with declining sample dimensions [1]. This anomalous behavior of nanoscale $MnFe_2O_4$ ferrite was argued to be related to the reduction of all three dimensions, and was discussed in terms of a finite-size scaling model [1].

We propose an alternative explanation for the anomalous behavior in the $MnFe_2O_4$ system. The assumption in Ref. [1] that in the preparation method used only the particle size is varied does not hold. Ferrites prepared by wet chemical methods (e.g., coprecipitation) are known [4–6] to display different cation distributions over the tetrahedral (A) and octahedral (B) sites than ferrites prepared by standard ceramic methods. For Mn-containing ferrites this distribution has been determined by Mössbauer spectroscopy [4], NMR [5], and neutron diffraction [6]. In all cases a higher inversion degree than Mn ferrite prepared by solid-state reactions [2] was found. Tang *et al.* [1,7] did not discuss the importance of the cation distribution in determining T_c. Furthermore, they could not determine the site occupation due to limited resolution in their Mössbauer experiment [7].

Inverse spinels $Fe_A{}^{3+}[Me_B{}^{2+}Fe_B{}^{3+}]O_4$ with $Me^{2+} = Co^{2+}$, Ni^{2+}, Fe^{2+}, and Cu^{2+} have a T_c between 728 and 858 K [2]. As the AA interactions are 10 times weaker than the AB and BB interactions in these ferrites, T_c depends on the respective exchange integrals J, with k Boltzmann's constant, n_{ij} the number of nearest exchange-coupled neighbors, and $|S|$ the absolute spin value, as [2]

$$\begin{aligned} T_c \approx (2/3k)[&(n_{AB}n_{BA})^{0.5}|S_{\mathrm{Fe}^{3+}}||S_{\mathrm{Fe}^{3+}}|J_{A\text{-}B}^{\mathrm{Fe}^{3+}\text{-}\mathrm{Fe}^{3+}} \\ &+(n_{AB}n_{BA})^{0.5}|S_{\mathrm{Fe}^{3+}}||S_{\mathrm{Me}^{2+}}|J_{A\text{-}B}^{\mathrm{Fe}^{3+}\text{-}\mathrm{Me}^{2+}} \\ &+n_{BB}|S_{\mathrm{Fe}^{3+}}||S_{\mathrm{Me}^{2+}}|J_{B\text{-}B}^{\mathrm{Fe}^{3+}\text{-}\mathrm{Me}^{2+}}]\,. \end{aligned}$$

The T_c of $MnFe_2O_4$, of 585 K, is so low because it is a near normal spinel with composition $Mn_{0.8}{}^{2+}Fe_{0.2}{}^{3+}$-$[Fe_{1.8}{}^{3+}Mn_{0.2}{}^{2+}]O_4$: Compared to inverse spinels, the $Fe_A{}^{3+}$-$Fe_B{}^{3+}$ exchange interaction is replaced by the factor 2 weaker $Mn_A{}^{2+}$-$Fe_B{}^{3+}$ interaction, and interactions between the ions on the B sites can be neglected [2]. Calculations [8] of the effect of differing degrees of inversion x in the system $Mn_{1-x}{}^{2+}Fe_x{}^{3+}[Mn_x{}^{2+}Fe_{2-x}{}^{3+}]O_4$ show that T_c depends strongly on x. This dependence was experimentally demonstrated [5,8]. Wet chemically prepared $Mn_{0.48}{}^{2+}Fe_{0.52}{}^{3+}[Mn_{0.06}{}^{2+}Mn_{0.46}{}^{3+}Fe_{1.02}{}^{3+}$-$Fe_{0.46}{}^{2+}]O_4$ is reported [5] to have a T_c of 770 K, due to the increased $Fe_A{}^{3+}$-$Fe_B{}^{3+}$ interaction, caused by the migration of Mn^{2+} ions from A to B sites and the inverse process for the Fe^{3+} ions. Thus, a nonequilibrium distribution of Mn^{2+} ions over the A and B sites can explain the considerably higher T_c observed in Ref. [1]. Also, the Fe^{2+} content influences the T_c of a ferrite. However, previous experiments [8,9] and the data in Table I of Ref. [1] suggest that the Fe^{2+} content of $MnFe_2O_4$ is too low ($\leq 3\%$) to account for the 97-K variation in T_c.

The origin of the increased T_c with decreasing particle size is related to the technique of preparation. Tang *et al.* [7] report that the particle growth is due to Ostwald ripening, i.e., the growth of larger particles at the cost of smaller ones. Their primary particles are formed very rapidly by coprecipitation and subsequent dehydration, and therefore will have a rather random cation distribution [4–6]. During Ostwald ripening the rate of particle growth is inversely proportional to the particle radius. This leads to a less random cation distribution for larger particles. Smaller particles should therefore exhibit an increased T_c, without the unexpected and unique finite-size scaling behavior suggested in [1].

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Received 22 January 1992
PACS numbers: 75.60.Jp, 05.70.Jk, 64.60.−i, 75.40.−s

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