

Tang *et al.* Reply: In their Comments [1,2] van der Zaag *et al.* and Brabers correctly raise the issue that the manganese cation distribution between the *A* and *B* sites of the ferrite lattice can affect the Curie temperature T_c , and that wet preparation methods can lead to a nonequilibrium distribution of the cations which causes MnFe_2O_4 to have a higher T_c than when in the equilibrium configuration. They then propose that our [3] observed enhancement of T_c was due to our wet preparation method, perhaps the size dependence being in some manner related to the Ostwald ripening process [1].

In response we show that our observed enhancement in T_c with declining particle size shown in Fig. 5 of our Letter [3] was found for samples that had been annealed and hence should have an equilibrium cation distribution with a particle-size-independent $T_c \approx 570$ K. To demonstrate this we replot in Fig. 1 the results of Fig. 5 of our Letter. We now add to this new data for freshly prepared, unannealed samples. One sees for the fresh samples a size-independent $T_c \approx 640$ K. This is larger than the cation equilibrium value in accord with the Comments and the literature cited. It is equally well known that annealing of fresh wet prepared ferrite samples will lead to the equilibrium cation distribution and the concomitant bulk T_c . Upon annealing at ca. 500°C for 1 h our samples show a size-dependent T_c as seen in Fig. 1 and originally demonstrated in our Letter. Under the assumption that this is sufficient annealing to obtain the same, equilibrium Mn cation distribution for all particle sizes, we stand behind our contention in our Letter that T_c is size dependent and the best description of the size dependence is given by finite-size scaling. We must take heed, however, of this assumption and the fact that the system now displays more complexity in that the size dependence is lacking in the nonequilibrium samples.

Brabers [2] further argues that the decreasing saturation magnetization with decreasing particle size is consistent with an increasing Mn concentration on the *B* sites, the suggested reason for increasing T_c . This is a qualitatively reasonable proposition, but it fails quantitatively. As Brabers points out, if y is the Mn *B* site concentration and T_c the Curie temperature, then an empirical relation is $y = 3.05 \times 10^{-3} T_c - 0.771$. This combined with another empirical relation [4] $\sigma_s \approx 90(1 - 0.4y)$ (emu/g) can yield a relation between T_c and the saturation magnetization, σ_s . For our smallest particles $T_c = 668$ K $= 395^\circ\text{C}$ from which the combined empirical relations would yield $\sigma_s \approx 74$ emu/g, much greater than the observed 40 emu/g. Hence we continue to support our original contention of a thin, magnetical dead surface lay-

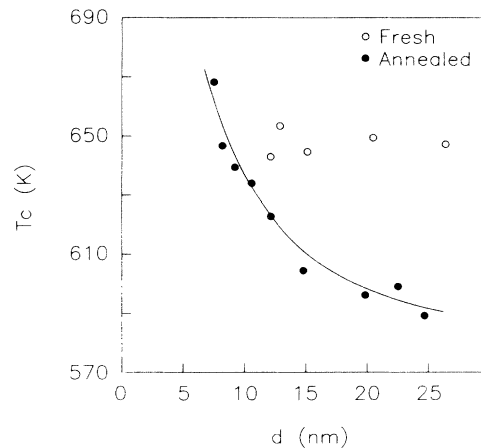


FIG. 1. Curie temperature vs particle size.

er on the particles.

The crux of the problem is whether the Mn distribution between the *A* and *B* sites changes with particle size. We believe our annealing leads to a size-independent distribution and had thought our Mössbauer measurements supported this. We now agree with both Comments that our Mössbauer measurements may not be precise enough to conclude this, but the annealing is still an argument in favor of a size-independent distribution. Further work is underway to resolve this situation.

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