

Comment on "Size-Dependent Curie Temperature in Nanoscale MnFe₂O₄ Particles"

In a recent Letter, Tang *et al.* [1] reported the size dependence of the Curie temperature and saturation magnetization of manganese ferrite particles. They described the T_c enhancement by a finite-size-scaling formula and suggested that this increase in T_c is a mesoscopic effect, i.e., is due to the confined measures of the material in three dimensions. However, these changes can also be explained by a variation of the cation distribution [2-5].

In Table I, the Curie temperatures are listed of MnFe₂O₄ specimens, which were annealed in evacuated silica tubes between 380 and 420 °C. The fresh specimens were prepared at 1340 °C in $P_{O_2}=10^{-2}$ atm and quenched into water. Because of the quenching, part of the manganese ions are located on the octahedral sites (23%) [6]. By annealing at lower temperatures, the equilibrium state of the cation distribution will be restored (at 400 °C about 5%) [6]. As pointed out by Lotgering [2] the Curie temperature of MnFe₂O₄ increases with an increasing inversion of manganese to the octahedral sites, which was explained by a molecular-field approximation [7,8].

Using the empirical relation between the octahedral Mn concentration y and the Curie temperature T_c , $y=3.05 \times 10^{-3} T_c - 0.771$, the kinetics of the cation redistribution was analyzed; an activation energy of the order of 2.2 eV was found, and for the temperature dependence of the distribution, 0.3 eV, in good agreement with other experiments [4,5]. It is obvious that below 350 °C the slower redistribution does not affect the magnetization measurements. The increase in T_c of 97 K reported by Tang *et al.* (1) is twice as high as for the ceramic specimens. However, this large value can also be attributed to differences in cation distribution. The wet-chemical preparation of MnFe₂O₄ can result in a very high value for the octahedral Mn concentration, $y \geq 0.5$, and a Curie temperature as high as 500 °C [9-11].

Further, Tang *et al.* [1] used Mössbauer measurements in zero field to probe the atomic environment of the iron ions, from which it was concluded that the cation distributions in all samples are identical. Unfortunately, zero-field measurements are not reliable to detect the different inversion degrees as observed in ceramic and wet-prepared samples [12-14]. The decreasing saturation magnetization with decreasing particle size complies also with an increasing octahedral Mn concentration [2,13,14], although the reduction in magnetization might also partially be attributed to a nonmagnetic surface layer on the particles. Altogether, the changes in T_c and magnetization related to the particle size by Tang *et al.* can easily

TABLE I. Curie temperature in °C, determined from the temperature dependence of the saturation magnetization.

| Annealing time (h) | Annealing temperature (°C) | | | | |
|--------------------|----------------------------|-----|-----|-----|-----|
| | 417 | 405 | 398 | 394 | 388 |
| 0 | 318 | 318 | 317 | 320 | 319 |
| 0.5 | 308 | 312 | 312 | 314 | ... |
| 1.0 | 299 | 307 | 309 | 310 | 309 |
| 2 | 288 | 297 | 301 | ... | 304 |
| 4 | 285 | 288 | 290 | 301 | 298 |
| 8 | 279 | 280 | 281 | 290 | 292 |
| 16 | 277 | 278 | 280 | ... | 286 |
| 60 | 275 | 276 | ... | 275 | 277 |

be attributed to the physicochemical arrangement of the cations in their samples. Nevertheless, their results are very interesting from a technological point of view, because it seems that the cation distribution which is established during the wet-chemical formation of the spinel crystal depends on the size of the particle.

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