Magnetic Nanoparticles: When atoms move around

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The degree of atomic ordering in magnetic nanoparticles decreases strongly with the particles' size. The origin of such a phenomenon has been determined by high-resolution transmission electron microscopy and tomography, which shows how correct heat treatment can lead to atomic order also in very small nanoparticles.

Considerable attention has recently been given to nanoparticles of magnetic alloys, such as FePt, CoPt or FePd with the CuAu I-type (defined as $L1_0$-type) ordered structure, because of their potential applications in future ultrahigh-density magnetic-storage media. In binary $L1_0$-ordered alloys, two kinds of sublattices are occupied by either Fe(Co) or Pt(Pd) atoms (Fig. 1a). The tetragonal $L1_0$-ordered structure gives rise to high magnetocrystalline anisotropy along the crystallographic c-axis. However, as-synthesized nanoparticles, typically produced by wet-chemical methods or physical vapour deposition, are in most cases disordered solid solutions with a face centred-cubic (fcc) structure. To recover the atomic order and therefore their excellent magnetic properties, a high-temperature annealing step is required (typically above 600 °C), so that the $L1_0$-ordered phase can be recovered by atomic diffusion. However, on its own the procedure is not enough to attain order in small nanoparticles (that is, below 5 nm in diameter), as confirmed by several experiments that reveal large disordered phase components. This strange dependence of atomic ordering on the nanoparticles' size has been the subject of considerable debate. On page 940 of this issue, Damian Alloyeau and coauthors report their results on atomic ordering of equiatomic 2–3-nm sized CoPt nanoparticle alloys[1], which is an important step forward in determining the origin of this so-called size-dependent ordering effect.

Alloyeau et al. found that the transition temperatures (T_C) of these nanoparticles are between 500–650 °C, which is lower than that of the bulk alloy, which can be as high as 825 °C. The researchers annealed disordered CoPt nanoparticles at 500 °C for up to a maximum of 16 h. They found the ordered lattice inside a 2.4-nm-sized particle by high-resolution transmission electron microscopy (HRTEM). However, when the same sample of nanoparticles was annealed for 1 h at 650 °C followed by quenching to room temperature, this caused the disordering of nanoparticles less than 3 nm in diameter, implying a T_C lower than 650 °C. The difference between these two results proves that atomic ordering can take place even in very small nanoparticles when the annealing temperature (T_a) is lower than the size-dependent reduced T_C. The present study is then the first to prove experimentally and unambiguously the view of Chepulskii and Butler, who argued that the experimental absence of relatively high $L1_0$ order in 3.5-nm-diameter nanoparticles annealed at 600 °C or below is mainly a problem of kinetics rather than equilibrium[2].

Figure 1b shows the temperature dependence of the degree of order for different sized nanoparticles (labelled NP1, NP2, NP3 and NP4) based on recent Monte Carlo simulations[1–4]. As can be seen, the T_C is reduced as the particle size decreases. This is owing to the fact that as the

nanoparticles become smaller, coordination at the surface is progressively reduced. The $L1_0$–fcc transition is known to be first-order in the bulk alloy, whereas a continuous transition has been predicted for nanoparticles less than about 5 nm in diameter. The continuous disordering has been attributed to the surface-induced disorder related to platinum segregation onto the particle surface[3,4]. In fact, surface induced disorder has very recently been found in strained nanoparticles by means of aberration-corrected HRTEM[5]. Here, the relationship between T_a and the reduced T_C is of fundamental importance. When the reduced T_C is lower than the typical annealing temperature (T_a ~ 600 °C; NP2 in Fig. 1b), the following two situations can be considered. First, if the particles are cooled slowly to ambient temperature after annealing above T_C, the nanoparticles will be annealed, and eventually atomic ordering will take place. In contrast, if the particles are cooled rapidly (that is, quenched) to room temperature just after annealing, a metastable disordered phase will remain. Therefore, the rate of cooling is one of the key issues when considering atomic ordering during the cooling process. As T_C decreases (NP3 in Fig. 1b), atomic migration requires a longer annealing time for ordering (annealing at $T_a < T_C$ NP3 is required), and consequently the disordered phase may dominate the nanoparticles. Furthermore, it is practically impossible to attain the ordered state for NP4 by heat treatment, for which T_C is well below room temperature. Indeed, an ordered phase is not always attainable by heat treatment, as in the case of 2–4-nm-sized Cu_3Au nanoparticles, where the reduced T_C is well below room temperature[6,7].

As well as the experimental proof of atomic ordering described above, the study further showed the essential aspect of the size effect: T_C is uniquely determined by the smallest characteristic length of a nanoparticle, that is, only one dimension of the particle (in-plane diameter or thickness) smaller than 3 nm is sufficient to induce a considerable decrease of T_C. This work therefore emphasizes the fact that to understand the nanoparticles' structural properties, their three-dimensional morphology needs to be considered. Understanding the effect of size and shape on ordering, which was made possible in this study through the use of basic methodologies in materials science (that is, by controlling annealing time and temperature, HRTEM and three-dimensional electron tomography), sheds light on the order–disorder transition in small nanoparticles. It also presents some fresh perspectives for designing nanoparticles for industrial applications, such as ultrahigh-density magnetic-storage media.

References

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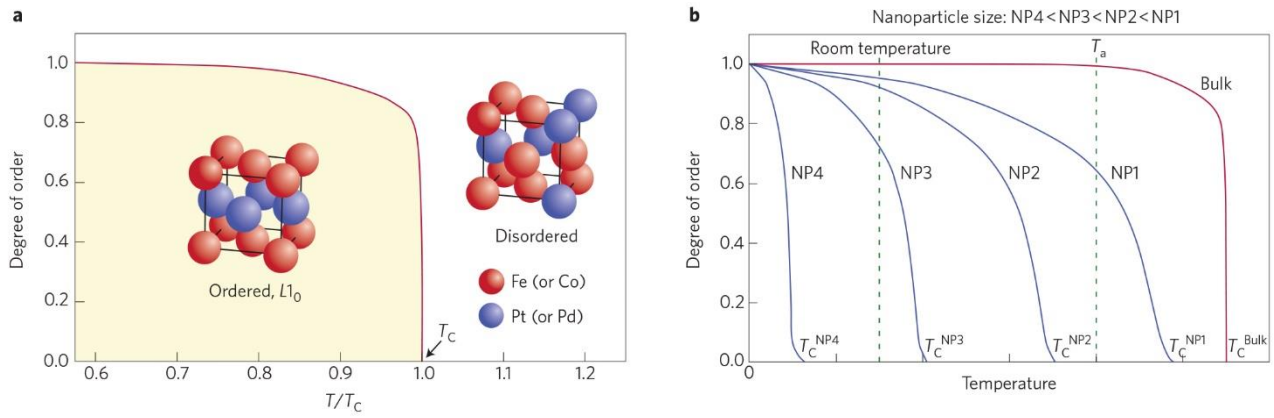

Figure 1. Temperature dependence of the degree of order. **a**, The $L1_0$–fcc order–disorder transition in a bulk alloy, with structural models shown in the insets. **b**, The effects of size on T_C. As the nanoparticles' size decreases there is an associated decrease in T_C. Note that NP2, NP3 and NP4 are not ordered by annealing the alloys at T_a followed by quenching to room temperature. The stability of an ordered phase in a nanoparticle will also be affected by external parameters, such as substrates or protective layers.