

Multi- $L1_0$ Domain CoPt and FePt Nanoparticles Revealed by Electron Microscopy

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The atomic structure of CoPt and FePt nanoparticles (with a diameter between 2 and 5 nm) has been studied by transmission electron microscopy. The particles have been produced by a laser vaporization cluster source and annealed under vacuum in order to promote chemical ordering. For both alloys, we observe a coexistence of crystalline and multiply twinned particles with decahedral or icosahedral shapes. In addition to particles corresponding to a single $L1_0$ ordered domain, we put into evidence that even small particles can display several $L1_0$ domains. In particular, the chemical order can be preserved across twin boundaries which can give rise to spectacular chemically ordered decahedral particles made of five $L1_0$ domains. The stability of such structures, which had been recently predicted from theoretical simulations, is thus unambiguously experimentally confirmed.

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Although it has recently attracted considerable attention, the structure of bimetallic magnetic nanoparticles such as CoPt or FePt is still debated [1–28]. These nanoalloys are promising for applications, in particular due to the extremely high magnetocrystalline anisotropy (MCA) of the bulk face-centered tetragonal [29] (fct) $L1_0$ phase [30–33] where pure atomic Co (or Fe) and Pt planes are stacked along the [001] direction. At small sizes, these systems appear to be much more complex than single element metallic particles: in addition to the usual existence of peculiar symmetries (icosahedral and decahedral) when the size is reduced [34,35], the various possibilities of chemical ordering offer another degree of freedom. Despite this increased complexity, several theoretical investigations have tackled this question, predicting for nanoparticles smaller than 3 nm the stability (or metastability) of exotic structures displaying at the same time a fivefold symmetry and a chemical order [13–15,23,25]. However, even if the different types of cluster shapes has been experimentally observed [2,6,9,16,25,27,36,37], clear evidence of few nanometers chemically-ordered particles retaining a fivefold symmetry is still missing. Moreover, the question of a preferential surface segregation of one element [13–16,24,38], as well as the possible existence of a threshold particle size for chemical ordering [12,17,22,28,39–42] are still unclear, with sometimes conflicting reported results. Besides, while planar defects (twins and c -domain boundaries) are quite well known [43–45] both in the bulk phase and thin films, their possible occurrence in small CoPt and FePt nanoparticles had not been discussed until very recent observations in FePt particles [28]. An implicit assumption regarding $L1_0$ particles is that they should consist of a single $L1_0$ domain. If it is not the case, the magnetic properties, especially the MCA, should be strongly modified.

In this Letter, we discuss the atomic structure of CoPt and FePt nanoparticles (with a diameter between 2 and 5 nm). For both alloys, we show using transmission electron microscopy (TEM) that crystalline nanocrystals coexist with multiply twinned particles (MTPs) having decahedral or icosahedral symmetries. In addition to particles corresponding to a single $L1_0$ ordered domain, which are met down to a diameter of $D < 2.5$ nm, we put into evidence that even small nanoparticles can display several $L1_0$ domains. In particular, we show that the chemical order can be preserved across twin boundaries which can give rise to spectacular chemically ordered decahedral particles made of five $L1_0$ domains, as theoretically predicted.

CoPt and FePt clusters are synthesized by the mass-selected low-energy cluster-beam deposition technique described elsewhere [46–49]. The nanoparticles are produced by laser vaporization and subsequently size selected using a quadrupolar electrostatic deviator allowing us to adjust the diameter of the deposited clusters (typically between 2 and 5 nm). The particles are then deposited on a substrate (here the thin amorphous carbon film of a commercial TEM grid), under ultrahigh vacuum conditions and capped by amorphous carbon. Since the as-prepared particles are crystallized in the A1 phase, a 2 h annealing at 750 K is used to promote chemical ordering through an enhanced atomic diffusion [17,27]. The samples are then characterized by TEM either in a high resolution mode (HRTEM) or with a high angle annular dark field detector in a scanning TEM mode (STEM-HAADF). In addition to a JEOL 2010F microscope (operating at 200 kV and with a field emission gun), we have used a FEI Titan 80–300 microscope operating at 300 kV with a field emission gun and either a C_s corrector for the objective lens (for HRTEM images with highly

improved spatial resolution [50]) or an aberration corrected probe (for atomic resolution STEM-HAADF images).

As illustrated in Fig. 1, the three types of particle structure (fcc crystal [51], decahedron, icosahedron) can be observed, both for CoPt and FePt [52]. Let us remind the reader that a decahedral cluster is a particular type of MTP made of five fcc domains joined by (111) twins and slightly deformed (it is then a noncrystalline structure). The particle surface consists of both (111) and (100) facets. On the other hand, an icosahedral cluster is made of 20 fcc domains, also joined by (111) twins and stressed, but only displays dense (111) facets. The stability of MTPs at small sizes, instead of truncated octahedral crystalline structures (corresponding to Wulff's equilibrium shape), is due to the gain in surface energy which is then larger than the cost of twins and internal strain. Among the CoPt and FePt particles studied here, we also observe fcc particles with one or a few twins. The relative abundance of each type of structure can hardly be determined in a reliable way, because in many cases the observed HRTEM contrast does not allow us to infer the particle geometry in a straightforward way [53]. Nevertheless, as a general trend, we find

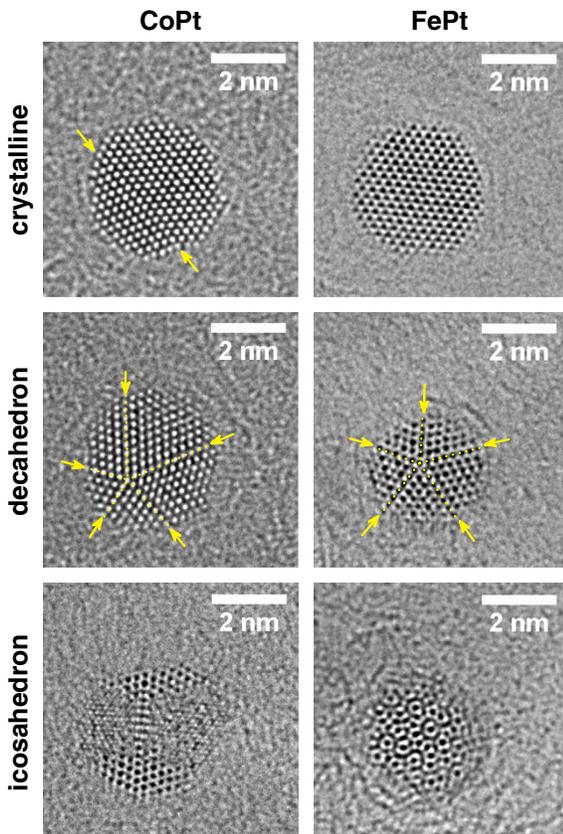


FIG. 1 (color online). C_s -corrected HRTEM images of CoPt (left) and FePt (right) nanoparticles. The three different types of structure are observed. The arrows indicate (111) twins, which are also highlighted by dotted lines in the case of decahedral particles, in order to emphasize the fivefold symmetry.

that the proportion of icosahedra is larger for CoPt particles than for FePt particles, which appears to often form decahedra. This must be related to a more favorable twinning in the case of CoPt [14,15,23]. The coexistence of a variety of structures is the result of kinetic trapping phenomena, which favor the formation of MTPs, during the sample preparation (annealing and subsequent cooling down [54] to room temperature). These experimental observations indicate that, in this size range, the energy differences between the different types of clusters are smaller or of the order of the thermal energy. This feature is consistent both with previous experimental studies [2,6,9,16,25], although the present particles are smaller, and with theoretical investigations [13–15,23,25].

Because we are dealing with bimetallic particles, the type of symmetry is not enough to characterize their structure and the question of the chemical order needs to be addressed [52]. Interestingly, both for FePt and CoPt, we observe crystalline particles with a single chemically ordered $L1_0$ domain all along the nanoparticle (see Fig. 2), down to $D = 2.3$ nm (the smallest diameter considered here). Contrary to what is sometimes reported [33,39,41,45] and in agreement with Delalande *et al.* [28], $L1_0$ particles smaller than 3 or 4 nm can exist. In the present case we do not observe any threshold size. Moreover, there is no indication of a preferential surface segregation of one element, contrary to what is often predicted by numerical calculations (especially for CoPt [14,15,55]). A full surface

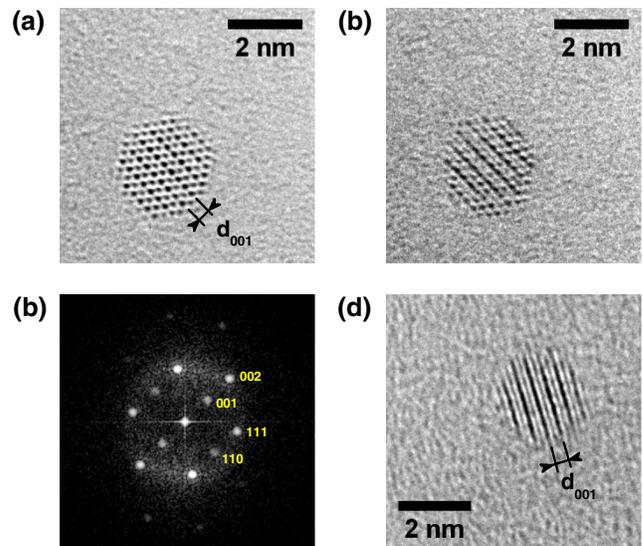


FIG. 2 (color online). C_s -corrected HRTEM images of a FePt cluster [(a) and (b)], corresponding to two different defocus values) and of a CoPt cluster (d). (c) Fast Fourier transform corresponding to image (a), with clear [001] and [110] peaks which are the signature of $L1_0$ order. In (a), the chemical order is evident from the difference in brightness and apparent size between two successive planes of atoms along the [001] direction, which is related to the difference in the scattering factors of Fe and Pt atoms.

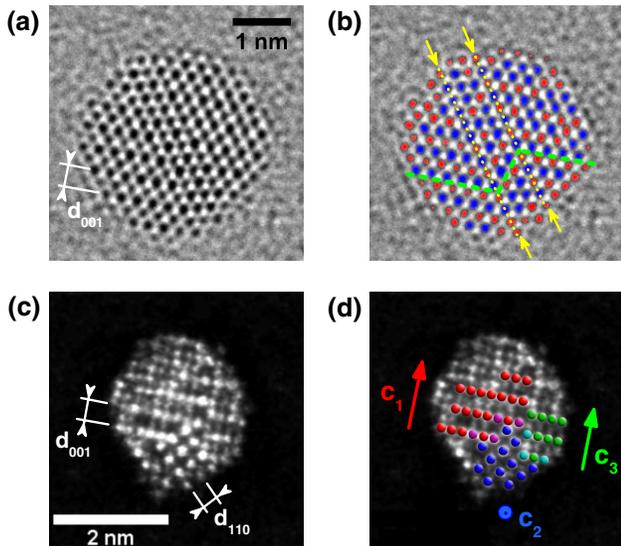


FIG. 3 (color online). (a) C_s -corrected HRTEM image of a CoPt particle displaying a continuous $L1_0$ chemical order over two (111) twins [indicated by arrows in (b)]. As a guide to the eyes, in (b) the atomic columns are colored according to their apparent size in the original image (a): the chemical order follows a “zig-zag” pattern (stressed by the green dashed line). (c) STEM-HAADF image (also called Z-contrast image) of a CoPt particle: the bright dots correspond to Pt-rich atomic columns. Three different $L1_0$ domains can be distinguished, as schematized in (d): the dots represent Pt-rich atomic columns, and are colored (in red, blue or green) according to their domain (intermediate colors correspond to dots common to two domains). The different c axis orientations are also indicated.

segregation would anyway be totally incompatible with the observation of a $L1_0$ order along a particle because for a size of around 2.5 nm, nearly 50% of the atoms are at the surface. The theoretical simulations may significantly overestimate the tendency for one element to segregate [13,14,24,55], or one may imagine that the amorphous carbon surrounding the particles prevents the segregation that would take place in the case of a free particle.

Remarkably, we also observe a chemical order in crystalline particles consisting of several $L1_0$ domains. In some cases, the different c orientations are due to (111) twins [see Figs. 3(a) and 3(b) for CoPt and Figs. 4(a) and 4(b) for FePt] which can preserve a coherent chemical order, as recently reported [28] for small FePt particles. Even more surprisingly, it is also possible to find different $L1_0$ domains in a 2 nm CoPt particle free of twins [Z-contrast image, see Figs. 3(c) and 3(d)]. In this case, one domain has a c axis at 90° with respect to two other domains that are joined by an antiphase boundary (APB). The 90° angle is reminiscent of a (011) c -domain boundary (CDB), which is frequently met in bulk materials and thin films but which was unexpected [45] and had never been reported for such small particles. The two domains with the same c axis direction must be separated by a (010) APB [a “tilted” APB such as a (111), (110) or (011) APB can also be

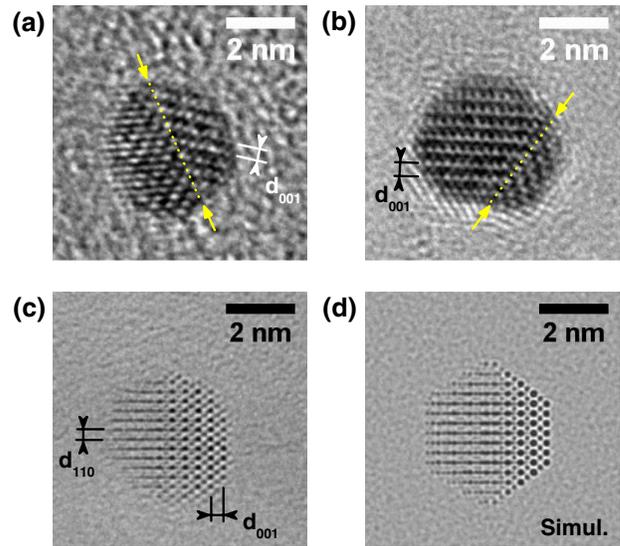


FIG. 4 (color online). (a), (b) HRTEM images of FePt particles with two $L1_0$ domains joined by a (111) twin. (c) C_s -corrected HRTEM image of a FePt particle with a (001) periodicity visible only on one side. This contrast corresponds to a chemically ordered decahedral particle [see Fig. 5(b)] viewed from the side, and is well reproduced by multislice HRTEM simulations (d) [53].

possible] which is also astonishing [40]. Another unusual contrast is often met in CoPt and FePt particles [see Fig. 4(c)], where the $L1_0$ order is clearly visible on one side with a (001) and (110) periodicity which are signatures of the chemical order, while on the other side only the (110) periodicity remains. This means that the chemical order is still present, but with the c axis pointing in another direction. We can also tell that the angle between the distinct domains is not 90° (otherwise we would still observe two families of atomic planes), which dismisses the possibility of a (011) CDB. In fact, what is not trivial and as can be shown with HRTEM simulations [see Fig. 4(d)], this particular contrast corresponds to decahedral particles (see following) indeed made of several $L1_0$ domains sharing the same (110) planes.

Finally, as illustrated in Fig. 5(a), particles showing a striking pentagonal pattern can also be found. They consist of decahedral clusters made of five $L1_0$ domains joined by (111) twins [see Fig. 5(b)]. The c axis of each domain are in the same plane, but are distributed according to a fivefold symmetry. Such a spectacular contrast can only be obtained when a particle is viewed along its fivefold symmetry axis [Fig. 5(b), top view]. Then, the shell-like structure is made self-evident and can manifest itself with different contrasts (see Fig. 6). Multislice image simulations have been performed [53], considering a particle with a perfect chemical order, and are in excellent agreement with the experimental C_s -corrected HRTEM images [Fig. 6(b)]. The “small gray” or “large dark” dots observed for small defocus values (the left side images

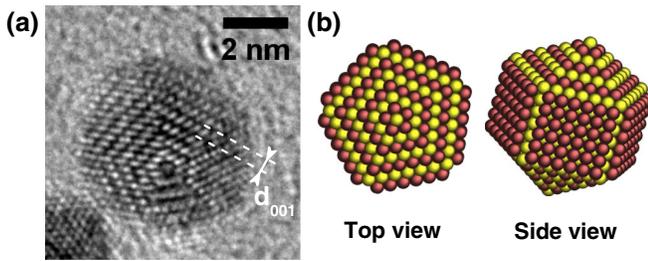


FIG. 5 (color online). (a) HRTEM image of a FePt particle displaying simultaneously a fivefold symmetry and $L1_0$ ordered domains. (b) schematic view of the corresponding chemically ordered decahedral structure, predicted by theoretical calculations.

of Fig. 6), respectively, correspond to Fe and Pt atomic columns. The chemical atomic structure can then be inferred from a HRTEM image and we find that the particle central column can be made as well of Pt as of Fe atoms [see Figs. 6(a) and 6(c)]. Furthermore, no tendency is observed concerning the nature of the outermost atoms [i.e., the (100) facets]: once more, there is no sign of a preferential surface segregation of one element. This

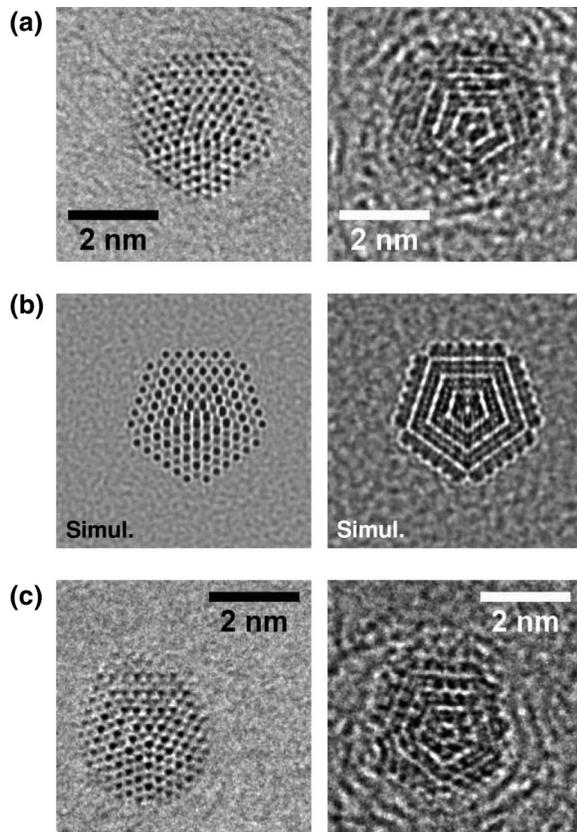


FIG. 6. (a), (c) C_s -corrected experimental HRTEM images of two different chemically ordered decahedral FePt particles, for two defocus values. (b) Multislice image simulation, using the geometry shown in Fig. 5(b) with Fe atoms at the center, to be compared to images (a). Note the reverse contrast of the central atomic column which is made of Fe in (a) and of Pt in (c).

remarkable particle structure is precisely the one predicted by theoretical calculations [13–15,25]. It is frequently met for FePt particles and also exists for CoPt particles, though in this case icosahedral clusters are more often observed. In spite of its predicted stability [14,15], we have not seen any indication of a chemical order in FePt or CoPt icosahedral particles. However, given the complexity of the presumed chemical arrangements for this geometry, extensive HRTEM simulations are needed because it is not evident how such an order could be visible.

Our HRTEM observations experimentally confirm the stability (or at least the metastability) of chemically ordered decahedral particles for a diameter between 2 and 5 nm. Besides, our results also contradict the statement of Andreatza *et al.* [25] that “the noncrystallinity of nanoparticles (Ih or Dh) is a limiting factor to achieve the chemical order.” From a magnetic point of view, it is expected that the MCA of these decahedral particles will be very low, despite that they are exclusively formed of $L1_0$ ordered domains. In the same way, for crystalline particles, twinning and the coexistence of several domains having different c orientations will certainly drastically reduce the MCA as compared to mono- $L1_0$ domain fct particles. This could explain why an assembly of particles can display a quite low MCA [17,56] simultaneously with a local $L1_0$ order (as can be, for instance, inferred from EXAFS [57], or indirectly from the magnetic moments evolution). Additional theoretical calculations are needed to fully apprehend the magnetic properties of these exciting nanoalloy systems.

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- [52] Note that, even if it is present, the chemical order may not be visible in HRTEM images when a particle is not favorably oriented or if the defocus is not in a suitable range (see, for instance, Ref. [27]).
- [53] See the Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevLett.110.055501> for HRTEM images with nontrivial contrasts, computational details on HRTEM images simulations, and HRTEM images of chemically ordered CoPt decahedra.
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