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# Measuring the $L1_0$ chemical order parameter of a single CoPt nanoparticle smaller than 4 nm

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We discuss the possibility of $L1_0$ chemical order parameter quantification for an individual particle of CoPt, using transmission electron microscopy. While "usual" approaches are found to be unapplicable for small particles (less than 4 nm in diameter), we present a method based on the comparison between an experimental high-resolution image and simulated ones with various degrees of chemical order.

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The chemical order phase transition in alloy nanoparticles such as CoPt or FePt has recently motivated a lot of experimental and theoretical studies.[1–11] In addition to its fundamental aspects, a good knowledge of this transition is relevant for the study of magnetic properties: in particular, the magnetic anisotropy is intimately related to the degree of chemical order,[12] and the extremely high magnetocrystalline anisotropy of the bulk $L1_0$ phase originates from the stacking of pure Co (or Fe) and Pt atomic planes in the [001] direction.[13] Even if this ordered phase is thermodynamically stable at room temperature, nanoparticles are generally synthesized in the face-centered-cubic (fcc) chemically disordered phase $A1$, which is metastable. Annealing is then required to promote atomic diffusion and reach a chemically ordered state; however, without exceeding the $L1_0 \rightarrow A1$ transition temperature. This temperature is very high for the bulk but must be significantly decreased by size reduction effects: this opens up a question on the existence of a lower size limit for $L1_0$ ordering in nanoparticles.[3,5,14] Moreover, the finite size is also expected to change the type of transition[5,8–10,14] from a first-order one, with a discontinuity in the long-range chemical order parameter $S$, to a second-order one, with a smooth transition from $S = 1$ for the perfectly ordered $L1_0$ phase at low temperatures to $S = 0$ for the completely disordered $A1$ phase at high temperatures. In this case, any value of $S$ (i.e., any degree of chemical order) may exist for nanoparticles: we cannot consider that a particle will simply be either "ordered" or "disordered." A quantitative determination of $S$ for individual nanoparticles will provide deeper insight on the chemical order transition and is thus highly suitable. Having an applicable method for that purpose will allow us to get rid of the averaging effects and the unavoidable inhomogeneous broadening met in the study of entire assemblies of size-distributed particles. In addition, the usual approach for the experimental determination of $S$, namely, the use of x-ray diffraction, becomes at the same time much more difficult to apply and much less reliable, or even unapplicable when very small particles are considered.

In this Brief Report, we show how high-resolution transmission electron microscopy (HRTEM) may be the most reliable or even the only method offering the possibility of an $S$ quantification for a small (with a diameter less than 4 nm) single CoPt particle. We have studied CoPt nanoparticles synthesized by the low-energy cluster-beam deposition technique described elsewhere,[11,15] where CoPt nanoparticles with an $\simeq$3 nm diameter are produced by laser vaporization and deposited on a substrate (here the thin amorphous carbon film of a commercial TEM grid), under ultrahigh vacuum conditions. Since the as-prepared particles are crystallized in the $A1$ phase, a 2 h 750 K annealing is used to promote chemical ordering.[11]

There have been a few reports of the chemical order parameter measurement for individual nanoparticles,[2,16,17] but not for CoPt, always using electron diffraction: the idea was to correlate the intensity of a chemical order (or sur-structure) peak, like [001], to the value of $S$. With a few small particles on a substrate, diffraction with a parallel incident beam is not possible and nanodiffraction or convergent beam electron diffraction is needed. Within such experimental conditions, particles are exposed to a very high fluence, which questions their stability both in orientation and in structure/composition. We have indeed noticed that (see Ref. 18), on one hand, the orientation of a particle observed in nanodiffraction changes on a 100 ms time scale, and on the other hand, with a nanoprobe, the chemical composition of a cluster varies within a few seconds (because of a Co evaporation, the Co/Pt ratio goes from 1 to $\simeq$0.5 in 40 s). The use of scanning transmission electron microscopy with a high-angle annular dark field (STEM-HAADF) detection may represent the most simple approach in terms of image interpretation: with a $Z$ contrast image, the intensity of an atomic column is almost directly related to its chemical content. However, a narrow probe is needed to reach the atomic contrast, and even if we have succeeded in observing an $L1_0$ contrast on our small CoPt particles, we have observed a very rapid degradation of particles exposed to the electron beam (see Ref. 18).

We have then chosen to use HRTEM because it allows observations without intense illumination, thus preserving the particles' integrity. Even if the observation of so small particles is highly challenging, CoPt clusters are found to be stable (good imaging conditions) for a few seconds. HRTEM dynamical simulations with the multislice method (JEMS software,[19] computational details are given in Ref. 18) have been used to successfully reproduce the observed chemical order contrast: such a contrast is, of course, only visible for correctly oriented particles, but even in such a case, it may not be detected if the objective lens defocus is not in some particular ranges (see Ref. 18). It has also been verified that a contrast with a periodicity corresponding to a [001] spatial frequency (peak in the diffractogram) is the signature of chemical order and cannot be an artifact appearing in images of chemically disordered particles. Images simulated with perfectly ordered clusters are found to be in good visual agreement with the experimental ones, but we would like to go further.

A first semiquantitative method is illustrated in Fig. 1, where we compare an experimental image to simulations with various chemical order parameters. This allows a visual comparison and provides a range of acceptable $S$ values (here, from 0.7 to 1). Let us remind the reader that to describe the $L1_0$ order, the original fcc lattice is split into two sublattices labeled $\alpha$ and $\beta$ corresponding to alternating planes in the (001) direction. The long-range order chemical parameter is then defined as $S = (n_\alpha - x)/(1 - f_\alpha)$, where $n_\alpha$ is the probability to have a Co atom on an $\alpha$ site, $x$ the Co concentration, and $f_\alpha$ the fraction of $\alpha$ sites. This definition ensures that $S = 0$ when the atoms are randomly distributed and $S = 1$ for a perfect order (which is only achievable when $x = f_\alpha$). Since $S$ is a global quantity, many different configurations of a cluster correspond to a same value and hence, there is, in fact, no unique HRTEM image corresponding to a given degree of chemical order. From a simulation point of view, we can randomly generate a single or several chemical configurations by setting the probability to have a Co atom on an $\alpha$ site to $p_\alpha = (S_0 + 1)/2$: this will result in a statistical set of particles[20] with $S \simeq S_0$ and $x \simeq 1/2$. This approach has been used for the simulations shown in Fig. 1, where a single configuration has been considered for each $S$. We can also construct an "average" cluster where each site is occupied at the same time by fractional Co and Pt atoms, with a probability of $p_\alpha$ and $1 - p_\alpha$, respectively (and the symmetrical occupations on $\beta$ site). This average configuration, where the chemical disorder is homogeneously spread in a particle, should provide a mean image correctly reflecting the one that would be obtained by averaging several randomly generated configurations.

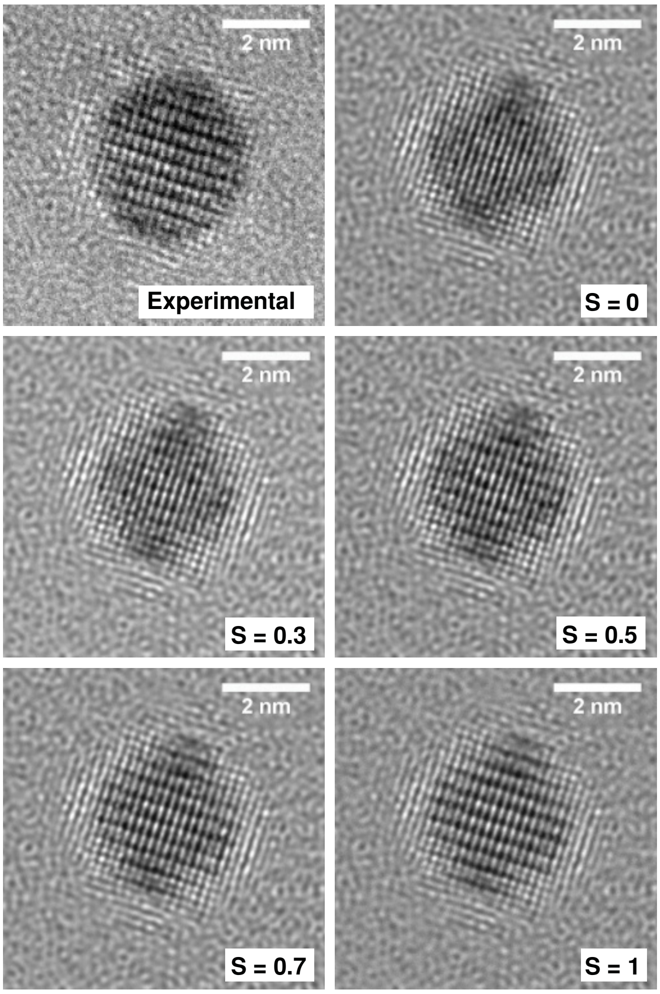

FIG. 1. Comparison between the experimental HRTEM image of a CoPt cluster and simulated images with various values of the chemical order parameter $S$.

To go further, we need a numerical criterion to find which the $S$ value corresponds to the best agreement between HRTEM observation and simulation. As the degree of chemical order is directly related to the intensity of the sur-structure [001] peak, we have chosen to consider the intensity ratio $R = I_{001}/I_{200}$ (we use [200] as a structure peak since in the experimental image the [002] peak is cut by a dark ring of the microscope contrast transfer function). Note that the intensities are not those of electron diffraction, but those of the corresponding spatial frequency on the HRTEM image: they are obtained from its fast Fourier transform (FFT), which we will call in the following its "diffractogram." Our method is thus based on the use of HRTEM images, but through an analysis in the reciprocal (Fourier) space. Preliminary steps

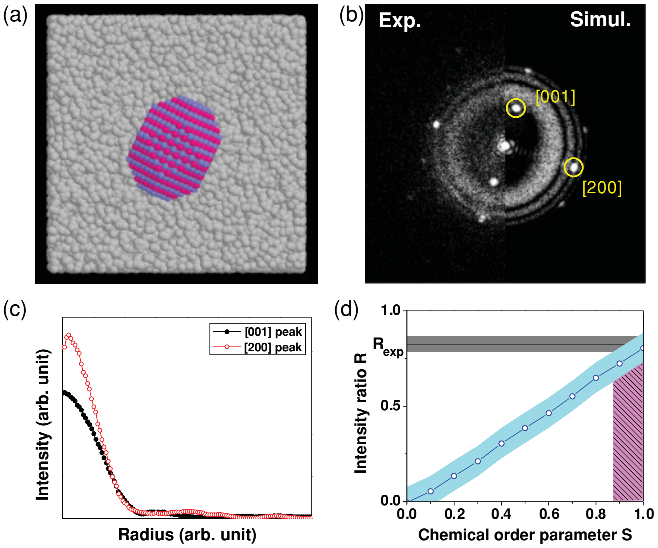

FIG. 2. (Color online) a) Schematic view of the structure used for HRTEM simulations: the truncated octahedral CoPt cluster (here, with a perfect $L1_0$ order) lies on an amorphous carbon film. b) Montage showing the FFT of the experimental HRTEM image (left side) and of a simulated one, with $S = 1$ (right side). The peaks used for the determination of $R$ are indicated. c) Peak profiles determined from the FFT of a simulated HRTEM image (here with $S = 1$): the ratio $R = I_{001}/I_{200}$ is calculated from the integrated intensities. d) Theoretical $R(S)$ curve computed for various degrees of chemical order. The experimental value $R_{exp}$ is indicated and provides an interval of $S$ values (hatched area) which are compatible with the HRTEM observations. The shaded areas correspond to the uncertainties.

are necessary in order to establish a reliable theoretical curve of $R$ as a function of $S$, which will then be compared to the experimental ratio $R_{\mathrm{exp}}$. These steps are the following: (1) determination of the zone axis from the experimental image; (2) determination of the particle shape (truncated octahedron with additional facets); (3) determination of the microscope parameters (defocus and astigmatism); (4) determination of the lattice tetragonalization; and (5) determination of the tilt angle, with respect to the perfect zone axis orientation. These adjustments are made empirically or with the help of a computer analysis (step 3, for instance), in the direct (steps 2 and 5) or Fourier space (steps 1, 3, and 4). We then compute the value of $R$ from the diffractogram of HRTEM images simulated with different $S$ parameters (see Fig. 2). We use here the "average" configuration approach described above. The peak intensities are determined by the integration of their radial profile [see Fig. 2(c) that displays the one-dimensional profile obtained by the rotational average of the pixel intensities around the peak center position], after a background subtraction.[21] We find a theoretical $R(S)$ curve which is almost a perfect line.

Of course, we have to put error bars on this line, first because of the statistical spread due to the multiplicity of configurations having the same order parameter $S$. Interestingly, we have verified with "statistical" calculations on a bulk supercell ($8 \times 8 \times 8$, corresponding to an $\simeq$3.1 nm thickness) that the mean $R$ value coincides with the value obtained with the average method: this was not trivial, since $R$ is not at all linked in a linear way to the electron-scattering atomic potentials. The standard deviation of $R$ is evaluated to be around 0.04 and is decreasing for high degrees of chemical order (since the number of different arrangements is reducing). In addition, there is a small uncertainty on the precise tilt angle ($\pm 1^\circ$) and defocus value ($\pm$2 nm): we have verified that it has only a very limited impact on the value of $R$ (see Ref. 18). In the end, we can estimate the uncertainty around the theoretical curve to be $\simeq$0.08 (upper bound). We also consider a 5% relative uncertainty on the experimental value $R_{\mathrm{exp}}$ to account for the various signal processing errors. Finally, as illustrated in Fig. 2, we find that the particle under investigation is almost perfectly ordered: with a confidence interval, we can conclude that $S \in [0.85, 1]$.

The quantification method we propose has been successfully applied to a particle displaying a strong $L1_0$ contrast (and consequently, a large $S$). Note, however, that for particles with a less pronounced contrast, a certain ambiguity may remain: for instance, a tilted particle with a large $S$ can correspond to the same $R$ as a poorly ordered particle with an "ideal" orientation. To resolve possible ambiguities, a solution might be to use more peak intensities or, if possible, different images of the same particle at different defocus values. Finally, we should also keep in mind that by using a single parameter $S$ to describe the chemical order of a particle, we somehow assume that it is homogeneous: according to theoretical studies, this is not granted as a surface disorder or segregation can exist in such nanosystems.[8,9,22,23] For the particle we have studied, there was no sign of such effects (which should, in addition, decrease the $R$ value), but they may be extremely subtle and hard to detect using HRTEM.

In conclusion, we have presented and applied a method of $L1_0$ chemical order parameter quantification using HRTEM, which is adapted to the investigation of small individual CoPt and FePt particles, where the "usual" approaches are no more applicable.

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[20] $S$ is the actual chemical order parameter of a particle, while $S_0$ is the target value used for random generation of a chemical configuration.

[21] The background intensity is removed by subtraction of a rotated diffractogram: the entire FFT is rotated around its center by a few degrees (typically 20°); the rotated image is then subtracted from the original image. The effect is to remove the amorphous carbon contribution at the peak positions we are interested in.

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