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Deciphering chemical order/disorder and material properties at the single-atom level

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Perfect crystals are rare in nature. Real materials are usually composed of crystal defects and chemical order/disorder such as grain boundaries, dislocations, interfaces, surface reconstructions and point defects that disrupt the periodicity of the atomic arrangement and determine their properties and functionality¹⁻³. Although recent years have witnessed rapid development of quantitative material characterization methods^{1,4-18}, correlating 3D atomic arrangements of chemical

order/disorder and crystal defects with material properties remains a major challenge. On a parallel front, quantum mechanics calculations such as density functional theory (DFT) have made significant progress from modelling ideal bulk systems to “real” materials with dopants, dislocations, grain boundaries and interfaces^{19,20}. Presently, these calculations rely heavily on average atomic models extracted from crystallography. To improve the predictive power of first-principle calculations, there is a pressing need to use atomic coordinates of real systems beyond average crystallographic measurements. Here, we determined the 3D coordinates of 6,569 iron and 16,627 platinum atoms in an iron-platinum nanoparticle to correlate 3D atomic arrangements and chemical order/disorder with material properties at the single-atom level. We identified rich structural variety and chemical order/disorder including 3D atomic composition, grain boundaries, anti-phase boundaries, anti-site point defects and swap defects. We show for the first time that experimentally measured 3D atomic coordinates and chemical species with 22 pm precision can be used as direct input for DFT calculations of material properties such as spin and orbital magnetic moments and local magnetocrystalline anisotropy. This work merges the forefront of 3D atomic structure determination of crystal defects and chemical order/disorder with DFT calculations, which is expected to transform our understanding of structure-property relationships at the most fundamental level.

Intermetallic compounds such as FePt with an ordered face-centered tetragonal ($L1_0$) phase are among the most promising candidates for next-generation magnetic storage media and permanent magnet applications²¹⁻²⁵. As-synthesized, FePt thin films and nanoparticles have a chemically disordered face-centered cubic (fcc) structure (A1

phase). When annealed at high temperatures, they undergo a transformation from an A1 phase to an L1₀ or chemically ordered fcc (L1₂) phase depending on the chemical composition²²⁻²⁵. Due to the chemical ordering and strong spin-orbit coupling, L1₀ FePt exhibits extremely large magnetocrystalline anisotropy energy (MAE)²¹. DFT calculations have been performed to elucidate the roles of morphology, capping layers, and surface segregation of model FePt nanoparticles in relation to the spin, orbital magnetic moments and MAE^{24,26,27}, which were compared with experimental measurements from electron microscopy, magnetometry and x-ray magnetic circular dichroism^{24,28,29}. However, despite extensive studies of this material system, a fundamental understanding of 3D chemical order/disorder, crystal defects and resulting magnetic properties at the individual atomic level remains elusive. Here, we report the precise determination of the 3D coordinates and chemical species of 23,196 atoms in a single 8.4-nm Fe_{0.28}Pt_{0.72} nanoparticle using atomic electron tomography (AET)¹.

FePt nanoparticles were synthesized and annealed at 600°C for 25 minutes to induce partial chemical ordering (Methods). Using an aberration-corrected scanning transmission electron microscope (STEM) operated in annular dark-field (ADF) mode (Extended Data Table 1), we acquired tomographic tilt series from several FePt nanoparticles. A representative tilt series of 68 images with a tilt range from -65.6° to +64.0° was chosen for the detailed analysis due to its structural complexity (Extended Data Fig. 1). After image denoising and alignment (Methods), a 3D reconstruction was computed from the tilt series using a generalized Fourier iterative reconstruction (GENFIRE) algorithm (Methods). By iterating between real and reciprocal space, GENFIRE searches for a best-possible solution that is concurrently consistent with the measured images and the general physical constraints. GENFIRE can also automatically

refine all the tilt angles to improve the 3D reconstruction. Both numerical simulation and experimental results indicate that GENFIRE results in higher resolution and contrast and can tolerate a larger missing wedge than other iterative algorithms (Methods). Supplementary Video 1 shows the 3D reconstruction of the FePt nanoparticle with individual Fe and Pt atoms clearly distinguishable.

From the 3D reconstruction, we developed an atom tracing and classification method to determine the coordinates of all individual Fe and Pt atoms based on their local intensity distribution (Methods, Extended Data Figs. 2 and 3). This process resulted in a 3D atomic model of 16,627 Pt and 6,569 Fe atoms. To verify this atomic model, we applied multislice simulations to calculate 68 ADF-STEM images from the model using the same experimental parameters (Method). Extended Data Figs. 4a-c show good agreement between a measured and multislice image. Using the same reconstruction, atom tracing and classification procedures, we obtained a new 3D model consisting of 16,577 Pt and 6,747 Fe atoms. Compared to the experimental atomic model, 99.0% of all atoms are correctly identified in the new 3D model and a root-mean-square deviation of the common atom positions is 22 pm (Extended Data Fig. 4d). To further confirm the precision of our atomic position measurements, we performed a lattice and structural analysis of the experimental 3D atomic model and determined the atomic displacements of the nanoparticle (Extended Data Figs. 5 and 6). By comparing the atomic positions to an ideal fcc lattice, we estimated an average 3D precision of 21.6 pm (Extended Data Fig. 7a), which agrees with the multislice result.

Next, we classified the 3D chemical order/disorder of the FePt nanoparticle by determining the short-range order parameter (SROP) of all phases present in the 3D structure (Methods). The nanoparticle consists of two large $L1_2$ FePt₃ grains with

interlocking concave shapes (Fig. 1b). Seven smaller grains are located at the boundary between the two large $L1_2$ grains, including three $L1_2$ $FePt_3$ grains, three $L1_0$ $FePt$ grains and a Pt-rich A1 grain (Fig. 1b and Supplementary Video 2). This level of complexity of the 3D chemical order/disorder can only be fully revealed by AET¹. To illustrate this point, we used multislice ADF-STEM simulations to calculate 2D images from the 3D atomic model along the [100], [010] and [001] directions (Fig. 1c). Several ‘ $L1_0$ grain’ signatures appearing in the 2D images (magenta in Fig. 1c) are actually deceptive structural information, which derive from the overlapping of the two large $L1_2$ grains.

Figure 2a shows the 3D grain boundaries (black lines) of the nanoparticle. The grains are more ordered in their cores and become less ordered closer to their surfaces. Four representative cut-outs of the atomic model are shown in Figs. 2b-e. The most chemically ordered region of the nanoparticle is at the core of a large $L1_2$ grain with the SROP close to 1 (Fig. 2b). Figure 2c shows a grain boundary between two large $L1_2$ grains with a varied grain boundary width. Anti-phase boundaries between the two $L1_2$ grains are also observed (Extended Data Fig. 7b). The largest $L1_0$ grain is shown in Fig. 1b (3rd grain from the left) and Fig. 2d. This $L1_0$ grain sits between the two large $L1_2$ $FePt_3$ grains with each of its two Fe sub-lattices matching the Fe sub-lattice of the neighbouring $L1_2$ grains (Extended Data Fig. 5), suggesting the shared Fe lattice with its neighbouring grains may have facilitated the nucleation of the $L1_0$ phase. The central region of the nanoparticle has the highest degree of chemical disorder, including a Pt-rich A1-phase grain (Fig. 2e), with much lower SROP values than those in the two large $L1_2$ grains.

To probe the 3D chemical order/disorder at the single-atom level, we analysed individual anti-site point defects in the 3D reconstruction of the nanoparticle. Figures 3a, b and Extended Data Fig. 7b show 3D atomic positions overlaid on the reconstructed intensity of several representative anti-site point defects (arrows) in the $L1_2$ grains, where an Fe atom occupies a Pt atom site or vice versa. The anti-site point defects in these figures are clearly visible by comparing their local peak intensity with that of the nearby Pt and Fe atoms. Furthermore, swap defects are also observed (Fig. 3c), where a pair of nearest-neighbour Fe and Pt atoms are swapped. Overall, the FePt nanoparticle contains a substantial number of anti-site defects and chemical disorder. Figures 3e and g show the anti-site defect density of the two large $L1_2$ grains (inset) as a function of the distance from the grain surface. Far outside of each grain, the anti-site defect density approaches ~50%, because two of the four sub-lattices in the two large $L1_2$ grains share the same composition (pure Pt), while the other two sub-lattices swap Fe for Pt and vice versa (Extended Data Fig. 5). The anti-site defect density drops to below 40% at the surface of the two grains and reduces to ~3% for sites deep inside each grain. Figures 3f and h show the SROP of the two large $L1_2$ grains as a function of the distance from the grain surface.

The striking similarities between the two large $L1_2$ grains, *i.e.* each having a concave shape with a highly-ordered core, a similar chemically disordered boundary and a consistent distribution of the anti-site defect density (Figs. 3e-h), suggest a potential pathway in the nucleation and growth process. We note that as-synthesized FePt nanoparticles show large chemical disorder with a Pt-rich core³⁰. Such a 3D Pt-rich core is observed in our measurement (Fig. 2e). During the annealing process, Pt atoms diffused out from the core³⁰ and the nucleation of the $L1_2$ phase likely occurred

simultaneously at multiple sites in the nanoparticle. The nuclei then grew and merged into larger grains by the Ostwald ripening process³¹. This process would continue until the nanoparticle became a single crystal if sufficiently high temperature/long time annealing was applied. However, if the annealing process was stopped at some intermediate stage, two or more larger grains with similar sizes could coexist since it was difficult for either to annihilate the others. The chemical ordering at the grain boundaries would then be frustrated by competition between neighbouring grains. However, determining the particle's chemical structure growth pathway with certainty will require adding the dimension of time to the AET measurements¹.

To correlate measured atomic coordinates and chemical order/disorder to magnetic properties, we performed DFT calculations of the atomic magnetic moments and MAEs. We focused on one of the grain boundaries between two large L1₂ grains, where the largest L1₀ grain is located, and computed the MAE of different local regions using two independent methods, namely full supercell and sliding local volume calculations (Methods). Figure 4a and Extended Data Fig. 8a show a good agreement of the MAE calculations by these two methods. The MAE decreases with the increase of the number of atoms because the embedded L1₀ grain mainly contributes to the MAE. Figure 4b and Extended Data Fig. 8b show a strong correlation between the local MAEs inside a 1,470-atom supercell and the L1₀ order parameter difference. The 3D distribution of the local MAEs matches well with that of the L1₀ order parameter difference (Fig. 4c and Extended Data Fig. 8c). The L1₀ grain embedded in two large L1₂ phases exhibits an fcc lattice rather than an fct of bulk L1₀ FePt with c/a ratio of 0.96. Together, these results confirm that the local chemical order rather than lattice distortion is the main source of MAE. Because there is no perfect L1₀ phase in the

nanoparticle, the largest local MAE in the region (0.95 meV/atom) is smaller than that of an ideal L1₀ phase (1.40 meV/atom). The smallest MAEs exist in the L1₂ grain and some sharp transitions from large to small MAEs are also observed. Fig. 4d and Extended Data Fig. 8d show the local MAE distribution at an L1₀ and L1₂ grain boundary, overlaid with measured atomic positions and species. The sharp grain boundary is responsible for a sudden transition of the local MAE, suggesting that MAE is highly localized and there is absence of “proximity effect” for MAE.

Our DFT calculations using the measured atomic coordinates and chemical species also yield the spin and orbital magnetic moments. Extended Data Figs. 9a-d show the histograms of the spin and orbital magnetic moments of the Fe and Pt atoms in the largest L1₀ grain. The average orbital magnetic moment of the Fe atoms is $0.08 \pm 0.01 \mu_B$, and the average spin and orbital magnetic moments of the Pt atoms are 0.31 ± 0.05 and $0.05 \pm 0.01 \mu_B$, respectively, which are consistent with those reported elsewhere²⁴. However, the average spin magnetic moment of the Fe atoms is $3.14 \pm 0.06 \mu_B$, slightly larger than that of ideal L1₀ FePt²⁴. The enhancement is attributed to two factors: i) the L1₀ grain is confined between two large L1₂ grains and has lower Fe coordination numbers, which enhances local magnetic moments (Extended Data Fig. 9e); ii) the L1₀ grain shares the fcc lattice parameters of the L1₂ grains. The expanded lattice constant along the c-axis leads to enhancement of Fe spin magnetic moment owing to the magneto-volume effect³². Both the enhanced spin magnetic moments and their distributions signify the importance of correlating structure and properties at the single atom level.

With the exponential growth of computing power and improvements in *ab initio* techniques, our measured atomic coordinates of the whole FePt nanoparticle with

23,196 atoms could be used as direct input for first-principle calculations. The local MAE and atomic magnetic moments extracted from the nanoparticle can then be used as parameters for micromagnetic simulations³³, whose precision is presently limited by parameters taken from either bulk or modelled values. Looking forward, the ability to determine the chemical order/disorder and crystal defects with high precision and to correlate their 3D atomic arrangements with material properties at the single-atom level is expected to find applications in materials science, physics, chemistry, nanoscience and nanotechnology.

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Author contributions J.M. directed the project; F.S. and H.Z. prepared the samples; M.C.S., W.T., P.E. and J.M. discussed / acquired the data; Y.Y., C.-C.C., R.X., A.P.J., L.W., J.Z. and J.M. conducted the image reconstruction and atom tracing; C.O., Y.Y., H.Z., P.E., W.T., R.F.S., M.C.S. and J.M. analysed and interpreted the results; M.E., P.R.C.K., R.F.S., Y.Y., H.Z., C.O., W.T. and J.M. discussed / performed the DFT calculations; J.M., Y.Y., H.Z., P.E., C.O., W.T., M.E., P.R.C.K., R.F.S. wrote the manuscript.

Author information The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to J.M. (miao@physics.ucla.edu).

Data availability The experimental data, image reconstruction and data analysis source codes of the paper are freely available at www.physics.ucla.edu/research/imaging/FePt.

Figure legends

Figure 1. 3D determination of atomic coordinates, chemical species and grain structure of an FePt nanoparticle. **a**, Overview of the 3D positions of individual atomic species with Fe atoms in red and Pt atoms in blue. **b**, The nanoparticle consists of two large L1₂ grains, three small L1₂ grains, three small L1₀ grains and a Pt-rich A1 grain. **c**, Multislice images obtained from the experimental 3D atomic model along the [100], [010] and [001] directions,

where several 'L1₀ grains' (magenta) appearing in the 2D images are deceptive structural information. Scale bar, 2 nm.

Figure 2. 3D identification of grain boundaries and chemical order/disorder. **a**, Atomic coordinates and species of the FePt nanoparticle divided into one-fcc-unit-cell thick slices. The grain boundaries are marked with black lines. **b-e**, Four representative cut-outs of the experimental atomic model, showing the most chemically ordered L1₂ region of the particle (**b**), a grain boundary between the two large L1₂ grains (**c**), the largest L1₀ grain (**d**), and the most chemically disordered region of the particle centered on a Pt-rich A1 grain (**e**). The locations of the cut-outs are labelled in (**a**), and the SROP of each cut-out is averaged along the [010] viewing direction and displayed as the background colour.

Figure 3. Observation of anti-site point and swap defects and statistical analysis of the chemical order/disorder and anti-site density. **a-c**, 3D atomic positions overlaid on the 3D reconstructed intensity illustrating anti-site point defects: a Pt atom occupying an Fe atom site (**a**), an Fe atom occupying a Pt atom site (**b**), a pair of nearest-neighbouring Fe and Pt atoms are swapped (swap defect) (**c**). **d**, 3D atomic structure of an ideal L1₂ FePt₃ phase for reference. **e, f**, The anti-site defect density and SROP for a large L1₂ grain, inset in (**e**), as a function of the distance from the grain surface (unit cell size = 3.875Å). **g, h**, The anti-site defect density and SROP for the other large L1₂ grain, inset in (**g**), as a function of the distance from the grain surface. Smooth red trendlines are overlaid on the defect density distribution as a guide for the eye.

Figure 4. Local MAEs between the [100] and [001] directions determined by using measured atomic coordinates and species as direct input to DFT.

a, Black squares represent the MAEs calculated from six nested cubic volumes of 32, 108, 256, 500, 864 and 1,372 atoms. The blue curve shows the results of fitting a $L1_0$ sphere inside cubic $L1_2$ grains with different sizes. Red dots are the local MAEs averaged by sliding a 32-atom volume inside the corresponding six supercells. **b**, MAEs of all sliding 32-atom volumes inside a 1,470-atom supercell as a function of the $L1_0$ order parameter difference, where the order parameters were computed from the 32-atom volumes. The dots and error bars represent the mean and the standard deviation with the number of 32-atom volumes, $n = 2, 17, 63, 631, 284, 164, 92, 128, 45$ and 26 (from left to right). The negative MAE values indicate that their local magnetic easy axis is along the [100] instead of [001] direction. **c**, 3D iso-surface rendering of the local MAE (top) and $L1_0$ order parameter differences (bottom) inside the 1,470-atom supercell. **d**, Local MAE distribution at an $L1_0$ and $L1_2$ grain boundary, interpolated from the sliding local volume calculations and overlaid with measured atomic positions.

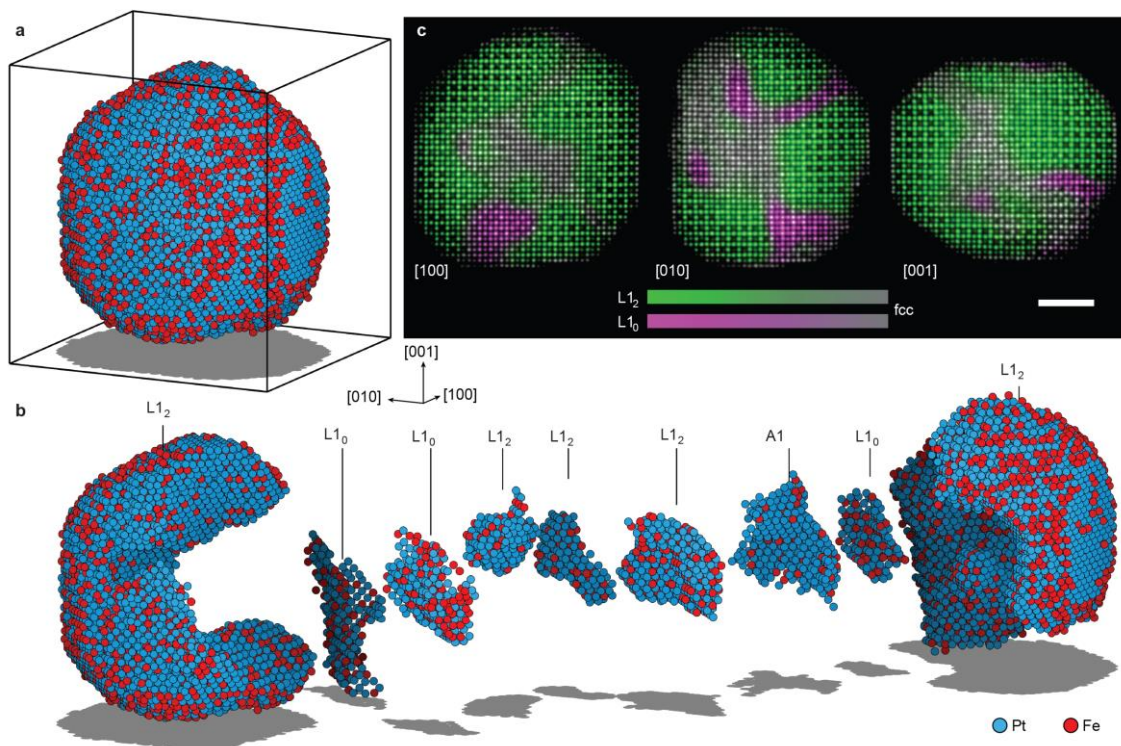


Figure 1

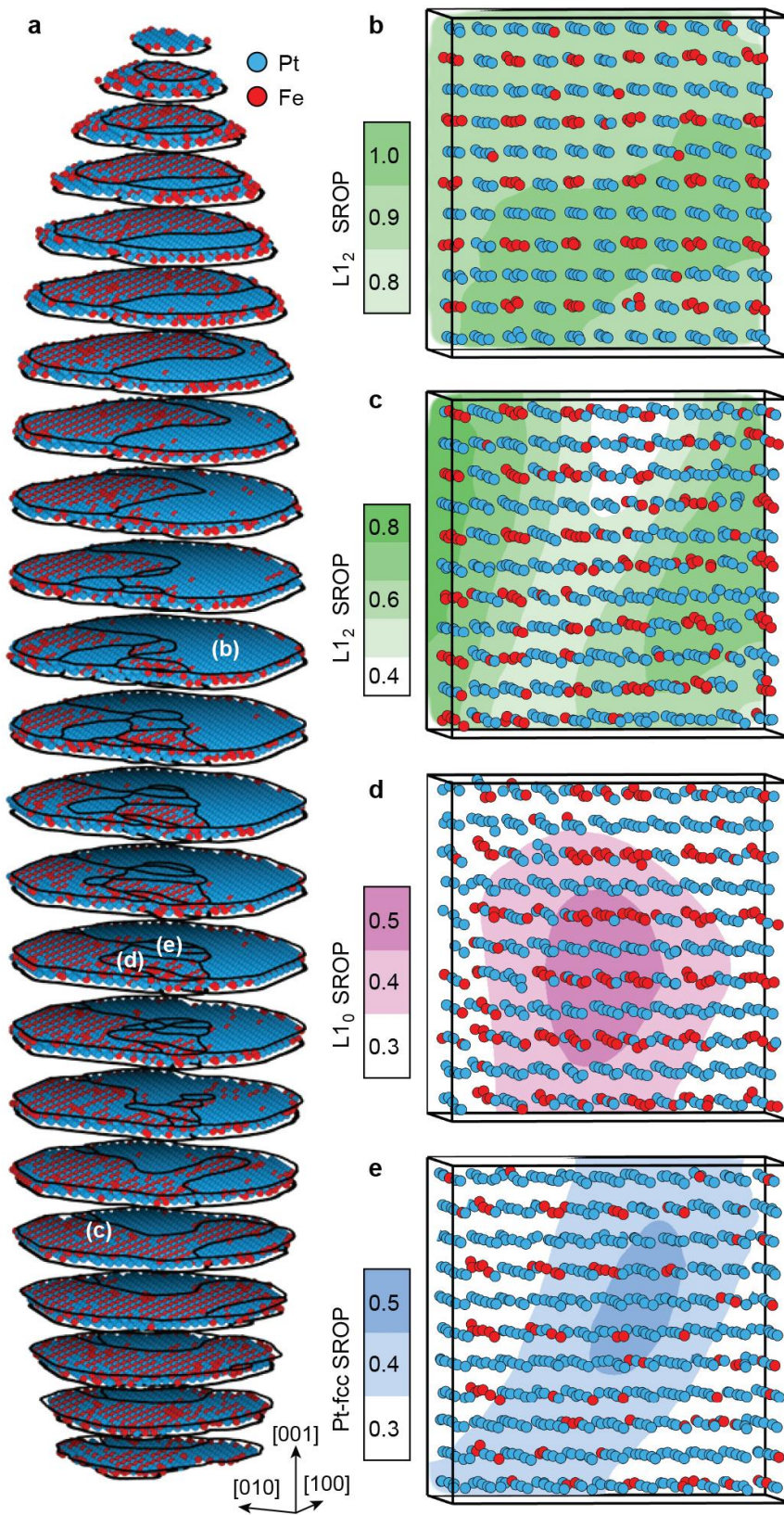


Figure 2

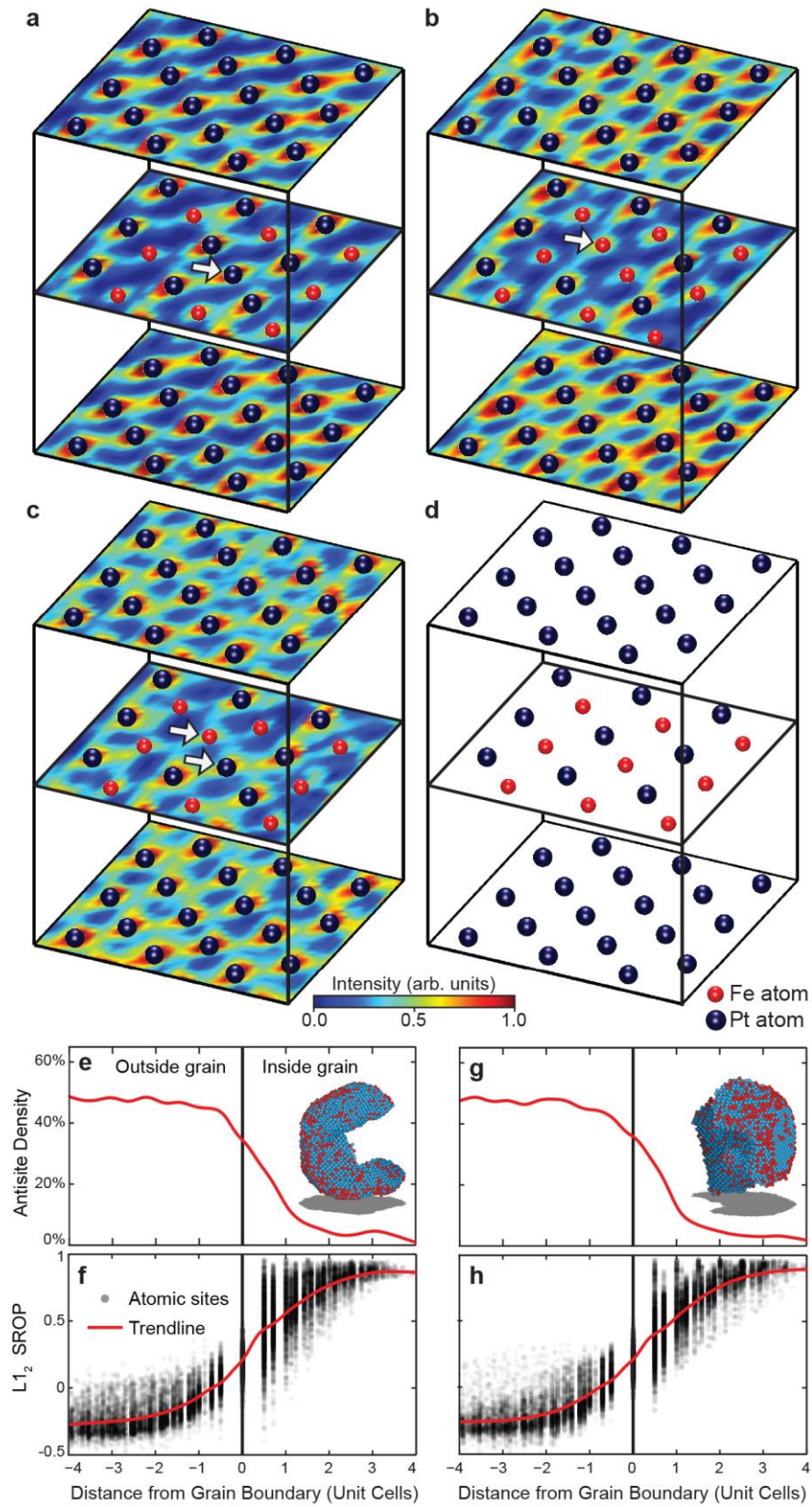


Figure 3

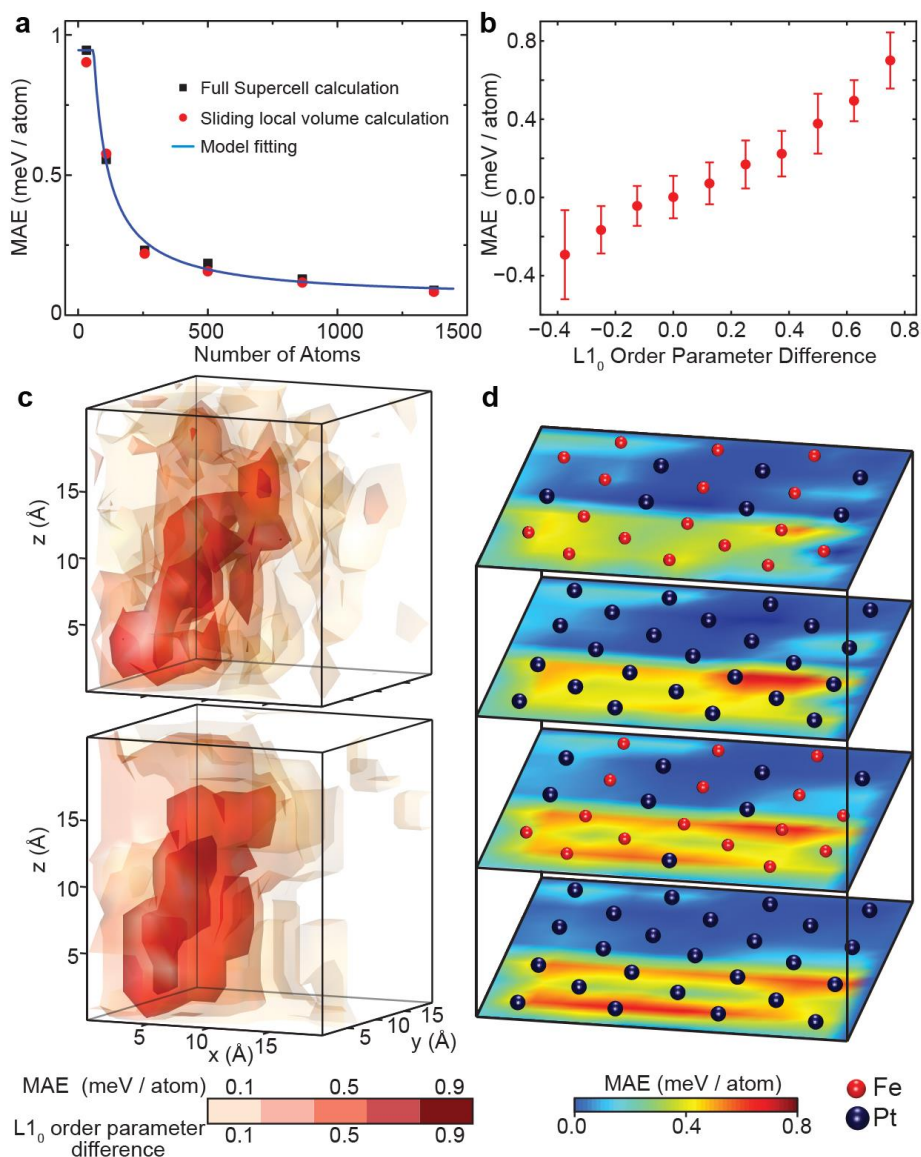


Figure 4

METHODS

Sample preparation. FePt nanoparticles were synthesized following procedures published elsewhere³⁴. Briefly, 0.5 mmol Platinum(II) acetylacetonate [Pt(acac)₂] was mixed with 20 ml phenyl ether under a gentle flow of nitrogen (N₂). The mixture was heated to 120°C, and kept at that temperature for 10 mins with magnetic stirring. Under nitrogen blanket, 1 mmol iron pentacarbonyl [Fe(CO)₅] was quickly injected, followed by sequential addition of 15 mmol oleic acid and oleylamine. The solution was heated

to 220°C in 20 mins and kept at that temperature for one hour. Then the mixture was further heated to 260°C and refluxed for another hour. After the solution was cooled down to room temperature, the nanoparticles were precipitated and purified by centrifugation. The collected nanoparticles were dispersed in hexane for storage.

Data acquisition. Samples were prepared by misting a solution of the FePt nanoparticles in ethanol onto a 5-nm-thick silicon nitride membrane using an atomizer. After the particles were applied to the silicon nitride membrane, they were annealed at 600°C for 25 minutes in high vacuum. A thin, ultra-pure carbon layer was then applied over the course of 5 minutes at 700°C to enhance the conductivity of the membranes and to protect the particles from damage under the electron beam. Several tomographic tilt series were acquired from FePt nanoparticles using the TEAM I microscope and TEAM stage³⁵ at the National Center for Electron Microscopy in the Molecular Foundry. Images were acquired at 300 kV in ADF-STEM mode with a 30-mrad convergence semi-angle (resulting in a probe size of $\sim 0.5\text{\AA}$), 48 and 251 mrad detector inner and outer semi-angles, and a beam current of 50-55 pA (Extended Data Table 1). A high-quality tilt series was selected for this study due to its rich structural variety (Extended Data Fig. 1). This tilt series was collected at 68 angles with a tilt range of -65.6° to $+64.0^\circ$. Ten images per tilt angle were measured with $3\mu\text{s}$ dwell time to minimize image blurring. Due to imperfections in the calibration of the x - and y - scanning coils in the microscope's STEM scanning system, an additional correction was applied to the images to ensure square pixels. This scan distortion was measured using a standard sample under the same imaging conditions, and corrected using Fourier methods³⁶.

Image denoising. The 10 acquired images for each tilt angle were aligned by cross-correlation with 0.1 pixel steps and averaged. The ADF-STEM images collected with the TEAM I microscope exhibit Poisson-Gaussian mixed noise¹⁶, and follow the noise model of $Y = \alpha P(n_e) + N(\mu_b, \sigma_b)$, where Y is the measured counts of each pixel, α is the gain parameter (counts per electron), $P(n_e)$ is the Poisson distribution of n_e electrons, and $N(\mu_b, \sigma_b)$ is the normal distribution of the mean μ_b and the standard deviation σ_b . The noise parameters α , μ_b , σ_b were estimated from the local mean and the variance based on spatial averaging of acquired images. The images were denoised by sparse 3D transform-domain collaborative filtering³⁷, while Anscombe variance-stabilizing transformation and its inverse were applied to the images before and after denoising with estimated noise parameters³⁸. The robustness of this denoising method has been tested by other experimental data sets and multislice simulations¹⁶.

GENFIRE reconstruction. After denoising, the 68 images were projected onto the tilt axis (y -axis) to obtain 1D curves, and the images were aligned along the tilt axis by using cross-correlation among the 1D curves. During this process, the optimal background of each image was determined by maximizing the cross-correlation among the 1D curves and was subsequently subtracted from each image. Alignment along the x -axis was achieved by the centre of mass method with a step size of 0.1 pixel¹⁰.

From the aligned tilt series, a 3D reconstruction was performed using GENFIRE. GENFIRE started with assembling a rectangular 3D Fourier grid from the measured images. For each image, its Fourier transform represents a plane slicing through the origin of the 3D Fourier grid (*i.e.* the Fourier slice theorem³⁹). For any Fourier grid point (k_x, k_y, k_z) , a perpendicular distance (D_j) to the j^{th} Fourier plane and the foot of the perpendicular line, (u_j, v_j) , were calculated with $j = 1, 2, \dots, 68$. The value of (u_j, v_j) was computed from the j^{th} image using the discrete Fourier transform instead of the fast Fourier transform (FFT) as (u_j, v_j) are non-integer coordinates. By repeating the above procedure, we calculated the values of all the (u_j, v_j) points with D_j smaller than a predefined threshold D_{th} , from which the value of the grid point, $F(k_x, k_y, k_z)$, was computed

$$F(k_x, k_y, k_z) = \sum_{\{j \mid D_j < D_{th}\}} \frac{D_j^{-1}}{\sum_{\{j \mid D_j < D_{th}\}} D_j^{-1}} \sum_{x=-\frac{N}{2}}^{\frac{N}{2}-1} \sum_{y=-\frac{N}{2}}^{\frac{N}{2}-1} f_{obs}^j(x, y) e^{\frac{-2\pi i(xu_j + yv_j)}{NO}}, \quad (1)$$

where $f_{obs}^j(x, y)$ represents the j^{th} measured image with a size of $N \times N$ pixels ($N=256$ in this experiment) and O is the oversampling ratio^{40,41}. By properly choosing the oversampling ratio and the predefined threshold ($D_{th}=0.05$ voxels and $O=4$ in this case), we accurately computed the values of a small fraction of grid points from the images using Eq. (1). For the remaining grid points without any (u_j, v_j) point satisfying $D_j < D_{th}$, we set them as undefined. The algorithm then iterated between real and reciprocal space using the FFT and its inverse. In real space, a support and positivity were incorporated as constraints. In this case, a $256 \times 256 \times 256$ voxel cube with smoothed edges was used as a support. In each iteration, the values outside the support and the negative values inside the support were set to zero. In reciprocal space, the grid points with measured data were enforced as constraints in each iteration, while the values of the undefined grid points were iteratively updated by the algorithm. The algorithm was monitored by an error metric in each iteration, defined as the difference between the values of the

measured and calculated grid points. After 500 iterations, the error metric could not be further improved and an initial 3D reconstruction was obtained.

To identify atomic positions and species with high precision, we have implemented a method to refine the tilt angles from the initial 3D reconstruction, which is routinely used in single-particle cryo-electron microscopy^{42,43}. For each tilt orientation, we found the corresponding three Euler angles (φ , θ , ψ) and scanned each of the Euler angles with a small angular increment. At each increment, the 3D reconstruction was projected back to calculate a 2D image. An error metric, defined as the difference between the calculated and measured images, was computed. By scanning all the three angles, we obtained an optimal set of the Euler angles for the tilt orientation, corresponding to the minimum error metric. This procedure was repeated for all the tilt orientations (angles). In this experiment, since θ was very small, the φ and ψ axes were almost collinear to each other. Thus, we fixed ψ and scanned φ and θ for angle refinement. After refining all the angles of the images, we used GENFIRE with the updated angles to compute a new 3D reconstruction. The angle refinement and reconstruction procedure were repeated until there was no further improvement, producing a final 3D reconstruction. Our numerical simulation and additional experimental results have indicated that GENFIRE produces superior 3D reconstruction than other iterative tomographic methods^{44,45}. These results will be presented in a following paper.

3D identification of atomic coordinates and chemical species. The 3D atomic positions and species of the FePt nanoparticle were determined using the following procedure.

i) All local intensity maxima were identified from the final 3D reconstruction. Starting from the highest intensity peak, a 3D Gaussian function of $5 \times 5 \times 5$ voxels was fit to the peak¹⁶. If this peak was satisfied with a minimum distance constraint (i.e. the distance between two neighbouring atoms $\geq 2\text{\AA}$), it was added to a peak position list. This minimum distance constraint is justified as the covalent diameter of an Fe atom is 2.52\AA . Repeating this step for all the local intensity maxima resulted in 28,800 peaks. These peaks were also manually checked to ensure there were no misidentifications. During this process, 446 peaks in the list were adjusted and 525 new peaks were added by using manual Gaussian fitting of some local intensity maxima, producing a total of 29,325 peaks.

ii) Extended Data Figure 2a shows a histogram of the identified peaks. Each peak should belong to one of the three categories: potential Pt atoms, potential Fe atoms and potential non-atoms. To separate

these peaks, we developed an unbiased atom classification method using the following steps. a) We selected a small fraction (0.6%) of peaks with the lowest intensity and obtained an average non-atom distribution ($5 \times 5 \times 5$ voxels) from them. We then chose an initial threshold between the Pt and Fe peaks. For all the remaining peaks, those larger or smaller than the threshold were used to calculate an average Pt or Fe atom, respectively, each with a size of $5 \times 5 \times 5$ voxels. b) For each identified peak, three error functions were calculated,

$$E_{Pt} = \sum_i |P_i - A_i^{Pt}| \quad E_{Fe} = \sum_i |P_i - A_i^{Fe}| \quad E_{NA} = \sum_i |P_i - A_i^{NA}| \quad (2)$$

where P_i is the i^{th} voxel intensity of the peak, A_i^{Pt} , A_i^{Fe} and A_i^{NA} are the i^{th} voxel intensity of the averaged Pt, Fe and non-atom, respectively. Using Eq. (2), all the peaks were re-classified into three categories based on the minimal error function. c) From the updated three categories, we re-calculated the average Pt and Fe atoms. Based on the updated average Pt and Fe atoms, we used Eq. (2) to classify all the peaks again to produce another three categories. This step was repeated until there was no change of the belonging of each peak to one of the categories, resulting in 13,917 Pt and 9,519 Fe atom candidates and 5,889 non-atoms (Extended Data Figs. 2b-d). This method is unbiased as we obtained very consistent results using a different fraction number from 0.6% and a different initial threshold value between the Pt and Fe peaks.

iii) Carefully examining the 5,899 non-atom peaks identified from step ii) suggested that some potential atoms might be incorrectly classified into this category. To mitigate this problem, we implemented a less aggressive method to re-classify the non-atom category. For every peak identified in step i), we quantitatively compared it to an average Fe atom obtained from step ii) and a constant background. If it matched more with the average atom, it was selected as an atom candidate. Otherwise, it was classified as a non-atom. Repeating this step for all 29,325 peaks with some minimal manual intervention produced 23,804 atom candidates and 5,521 non-atoms. Using the unbiased atom classification method [step ii)], we classified 23,804 atom candidates into 14,216 Pt and 9,588 Fe atom candidates (Extended Data Figs. 2e-g).

iv) Next, we quantified the peak intensity of the atoms in the missing wedge direction and found the average atom intensity is lower than that in the other regions. To mitigate this problem, we selected 5,445 atom candidates in the missing wedge region and applied the unbiased atom classification method

[step ii)] to separate these atoms. Collectively, steps i-iv produced 17,087 Pt and 6,717 Fe atom candidates.

v) To validate the robustness of our method with regard to the choice of the minimum distance, we repeated steps i-iv) using a minimum distance of 1.6Å and obtained 16,551 Pt and 6,639 Fe atom candidates. The two different atomic models with a minimum distance of 1.6 Å and 2.0Å were quantitatively compared, resulting in 23,145 common pairs and 659 non-common atoms. Among the 23,145 common pairs, 22,304 pairs were identified as the same species and 841 atom candidates were opposite species. To examine these non-common atoms and opposite atomic species, we used the 68 measured images with the following procedure. a) Each of the measured images was converted to a Fourier slice by the FFT. b) 68 Fourier slices were calculated from an atomic model by

$$F_{calc}^j(\mathbf{q}) = \sum_{n=1}^N H_{A_n} f_e(q) e^{\frac{-B'_{A_n} q^2}{4} - 2\pi i \mathbf{r}_n \cdot \mathbf{q}}, \quad (3)$$

where j is number of images, N is the number of atoms, $A_n=1$ if the n^{th} atom is Fe, $A_n=2$ if the n^{th} atom is Pt, H_1 and H_2 are the scaling factors for Fe and Pt atoms, respectively, $f_e(q)$ is a normalized electron scattering factor, \mathbf{r}_n is the position of the n^{th} atom, and B'_1 and B'_2 account for the electron probe size (50 pm), the thermal motions, and the reconstruction error of the Fe and Pt atoms, respectively. c) An error function between the measured, $F_{obs}^j(\mathbf{q})$, and calculated Fourier slices were computed,

$$E = \sum_{j,q} |F_{calc}^j(\mathbf{q}) - F_{obs}^j(\mathbf{q})|^2. \quad (4)$$

d) The 659 uncommon atom candidates were sorted from the highest to lowest intensity. Using the 23,145 common atoms as an initial model, the uncommon atoms, starting from the highest intensity, were cumulatively added one by one as Fe atom candidates to produce different models. For each model, the error function E was minimized by adjusting H_1 , H_2 , B'_1 , and B'_2 . By selecting the minimum error from all the models, we identified 37 uncommon atoms as real atoms. e) For the 841 atom candidates with opposite species, we used the similar procedure described in previous steps to confirm that 240 are Pt atoms and 601 are Fe atoms.

vi) Based on the atomic coordinates and species identified through steps i-v), we examined every atom and manually adjusted 37 atoms, producing a 3D model of 23,196 atoms with 6,569 Fe and 16,627

Pt atoms. Note that manual adjustment of a very small fraction of atoms is routinely used during the atom tracing and refinement process in protein crystallography⁴⁶.

v) The 3D atomic model was refined¹⁶ and then linearly projected back to calculate 68 images at the experimental angles. An R_I factor was computed between the j^{th} measured, $f_{obs}^j(x, y)$, and calculated, $f_{calc}^j(x, y)$, images,

$$R_I = \frac{\sum_{x,y} |f_{obs}^j(x, y) - f_{calc}^j(x, y)|}{\sum_{x,y} |f_{obs}^j(x, y)|} \quad (5)$$

The average R_I for 68 pairs of images was 9.6%.

Multislice STEM simulations. A tilt series of 68 images with refined experimental Euler angles were calculated using multislice simulations⁴⁷. A total of 68 cubic super cells with $a=100 \text{ \AA}$ were created. The final 3D atomic model were placed within the super cells. Individual super cells were divided into multiple 2.0- \AA -thick slices along the z -axis, with 1800×1800 pixels sampling in the x and y axes for both the specimen and probe. The experimental parameters (300 keV electron energy, 0 mm C_3 aberration, 5 mm C_5 aberration, 30 mrad convergence semi-angle, 48 and 251 mrad detector inner and outer semi-angles) were used for the simulations, resulting in a tilt series of ADF-STEM images with 255×255 pixels per image and a pixel size of 0.37 \AA . For each tilt angle, 16 frozen phonon configurations were simulated and averaged to obtain a calculated image. Each multislice image was convolved with a Gaussian function, whose width was determined by minimizing the error between the measured and simulated images. This procedure was used to account for the electron probe size and other incoherent effects. Extended Fig. 4 compares the measured and multislice simulated images at 0° tilt. A 3D volume was then reconstructed from the simulated tilt series with GENFIRE, and a new 3D model was obtained by using the same atom tracing procedure. A total of 23,324 atoms were traced, comprising 16,577 Pt and 6,747 Fe atoms. 23,043 common pairs of the atoms between experimental and multislice 3D model were selected based on the criterion that each pair should be within the radius of the Fe atom. Among the common pairs, 6,401 common pairs were identified as Fe atoms (97.4%), and 16,562 common pairs were identified as Pt atoms (99.6%), resulting in 99.0% of all atoms having been correctly identified. A histogram of the atomic deviation between the common pairs is shown in Extended Fig. 4d, indicating a root-mean-square deviation of 22.2 pm.

Determining the short-range order parameter (SROP) of all phases present in the FePt nanoparticle. We used the atomic positions and species to classify the chemical order/disorder of the nanoparticle. This was done with the SROP of all possible phases present^{48,49}. SROPs are typically over a shell of equivalent neighbouring atomic sites, and scale linearly with the number of sites that are correctly occupied for a given phase. Normalization parameters were used to set the SROP equal to one for a perfectly ordered phase, and zero for a disordered phase with completely random chemical occupancies. Our analysis procedure was to calculate a weighted SROP, defined as a 3D-Gaussian sum using cross-validation to determine the standard deviation⁵⁰, over a given length scale for each phase. Then, each atomic site was assigned to the phase with the highest SROP. The FePt nanoparticle was therefore divided up into grains of different phases, with a measurement of the SROP at all atomic sites. In this study, we considered 16 possible ordered phases from the fcc lattice in the 3D FePt reconstruction: FePt₃ L₁₂ (4), Fe₃Pt L₁₂ (4), FePt L₁₀ (6), Pt-rich A1 (1), and Fe-rich A1 (1), where the number in the parentheses represents the possible phase orientations. Atomic sites with a SROP below a threshold, determined with cross-validation⁵⁰, were initially assigned to disordered boundaries. After the initial grain location determinations, these disordered sites were then assigned to neighbouring grains according to their highest SROP values. This step was carried out to prevent disordered regions in thin “pancake” regions between grains or at the nanoparticle surface from being classified as grains due to small SROP fluctuations.

DFT calculations. We used experimentally determined atomic coordinates and species as direct input for DFT calculations of magnetic properties. We implemented the local spin-density approximation of the exchange-correlation functional^{51,52} to calculate the MAEs using two independent approaches. First, we cut out a 1,470-atom supercell from a grain boundary between two large L₁₂ grains, where the largest L₁₀ grain is located. We then slid a 32-atom volume (2×2×2 unit cells) inside the supercell with a half-unit-cell per step along each direction and produced 1,452 32-atom volumes. The electronic structure calculations of these 32-atom volumes were performed using projector augmented-wave method⁵³ within the Vienna *ab-initio* simulation package (VASP)⁵². We used a plane-wave energy cut-off of 300eV and applied periodic boundary conditions. The integration over Brillouin zone was performed using 6×6×6 k-point sampling and the spin-orbit coupling was included in the calculations. Because the easy axis and hard axis of the nanoparticle were not known *a-priori*, we calculated the energies along three high

symmetry axes ([001], [010] and [100]) of the underlying cubic structure. In a system with substitutional and topological defects, the easy axis can be locally distributed. Furthermore, the local symmetry may cause the system to develop bi-axial anisotropy. Because we observed mainly $L1_0$ and $L1_2$ phases with substitutional defects, the uniaxial anisotropy energy was computed as the energy difference between the [100] and [001] directions as well as between the [010] and [001] directions.

Second, we validated the sliding local volume calculation by using a different approach. We cropped six nested supercells from the same region, containing 32 ($2 \times 2 \times 2$ unit cells), 108 ($3 \times 3 \times 3$ unit cells), 256 ($4 \times 4 \times 4$ unit cells), 500 ($5 \times 5 \times 5$ unit cells), 864 ($6 \times 6 \times 6$ unit cells) and 1,372 atoms ($7 \times 7 \times 7$ unit cells). The MAEs of these six supercells were calculated using the real-space locally self-consistent multiple scattering (LSMS) code⁵⁴. We performed fully relativistic calculations by solving the Dirac equation for all electrons in the sample⁵⁵ and constrained the magnetic moment directions along the [001], [010] and [100] axes⁵⁶. The Dirac equation was solved by directly calculating the Green's functions of the scattered electrons inside the material in real space. To achieve scalability to large systems, for each atomic site in the calculation cell we considered scattering within a finite volume only (i.e. local-interaction zone). For all the calculations presented here, we chose this local-interaction zone as a sphere with a radius of 12.5 Bohr radii and an angular expansion cut-off of $L_{\max} = 3$. Using this approach, we calculated the MAEs of the six nested supercells, which are consistent with those obtained from the sliding local volume calculation (Fig. 4a and Extended Data Fig. 8a). These results validated our sliding local volume approach to calculate the 3D distribution of the local MAE. Meanwhile, we also calculated the magnetic moment associated with each atomic site in the six supercells using the fully relativistic LSMS method⁵⁴. The self-consistent calculations of the magnetic moments used the same parameters as the MAE calculation and we solved the Dirac equations with a constraint that the magnetic moments on all sites point along the [001] direction. We assigned the spin and orbital magnetic moment to each atomic site by calculating the expectation value of the spin density operator and integrating the resulting magnetization density over the atomic sphere assigned to each site. Extended Data Fig. 9 shows the spin and orbital magnetic moments of the Fe and Pt atoms in the largest $L1_0$ grain.

Finally, to estimate the influence of the uncertainty in the measured atomic coordinates, we selected four 32-atom, one 256-atom and one 500-atom volumes and relaxed their atomic positions with DFT. The structural relaxation was performed using the VASP with a $2 \times 2 \times 2$ k-point mesh⁵². The atomic

positions were relaxed until forces were below $0.01\text{eV}/\text{\AA}$. The root-mean-square deviation between the measured and relaxed atomic positions is 24.7 pm, which agrees with our precision estimation (22 pm). The MAEs of these six relaxed volumes were calculated by using the LSMS code⁵⁴. The average MAE difference between the measured and relaxed volumes is 0.064 meV/atom.

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