Quantitative three-dimensional imaging of chemical short-range order via machine learning enhanced atom probe tomography

Yue Li (✉ yue.li@mpie.de)

Max-Planck-Institut für Eisenforschung GmbH <https://orcid.org/0000-0003-3377-6676>

Ye Wei

Max-Planck-Institut für Eisenforschung <https://orcid.org/0000-0003-1965-2298>

Zhangwei Wang

Central South University

Timoteo Colnaghi

Max Planck Computing and Data Facility

Liuliu Han

Max-Planck-Institut für Eisenforschung <https://orcid.org/0000-0002-2332-2868>

Ziyuan Rao

Max-Planck-Institut für Eisenforschung

Xuyang Zhou

Max-Planck-Institut für Eisenforschung GmbH <https://orcid.org/0000-0002-3789-4103>

Liam Huber

Max-Planck-Institut für Eisenforschung GmbH

Raynol Dsouza

Max-Planck-Institut für Eisenforschung GmbH

Jörg Neugebauer

Max Planck Institute for Iron Research

Andreas Marek

Max Planck Computing and Data Facility

Markus Rampp

Max Planck Computing and Data Facility

Stefan Bauer

Max Planck Institute for Intelligent Systems

Hongxiang Li

University of Science and Technology Beijing

Ian Baker

Dartmouth College <https://orcid.org/0000-0001-6347-6960>

Leigh Stephenson

Max-Planck-Institut für Eisenforschung GmbH, Germany <https://orcid.org/0000-0002-7852-2509>

Baptiste Gault

Max Planck Institute for Iron Research <https://orcid.org/0000-0002-4934-0458>

Physical Sciences - Article

Keywords:

Posted Date: January 7th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1092384/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Quantitative three-dimensional imaging of chemical short-range order via machine learning enhanced atom probe tomography

Yue Li^{1,}, Ye Wei¹, Zhangwei Wang^{2,*}, Timoteo Colnaghi³, Liuliu Han¹, Ziyuan Rao¹, Xuyang Zhou¹, Liam Huber¹, Raynol Dsouza¹, Jörg Neugebauer¹, Andreas Marek³, Markus Rampp³, Stefan Bauer⁴, Hongxiang Li⁵, Ian Baker⁶, Leigh T. Stephenson¹, Baptiste Gault^{1,7,*}*

¹ Max-Planck Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

² State Key Laboratory of Powder Metallurgy, Central South University, Changsha, 410083, China

³ Max Planck Computing and Data Facility, Gießenbachstraße 2, 85748 Garching, Germany

⁴ Max Planck Institute for Intelligent Systems, Max-Planck-Ring 4, 72076 Tübingen, Germany

⁵ State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, 100083, Beijing, China

⁶ Thayer School of Engineering, 14 Engineering Drive, Dartmouth College, Hanover, NH 03755, USA

⁷ Department of Materials, Imperial College, South Kensington, London SW7 2AZ, UK

**Corresponding authors, yue.li@mpie.de (Y. L.); z.wang@csu.edu.cn (Z. W.);*

b.gault@mpie.de (B. G.)

Abstract

Chemical short-range order (CSRO) refers to atoms of specific elements self-organising within a disordered crystalline matrix. These particular atomic neighbourhoods can modify the mechanical and functional performances of materials ¹⁻⁶. CSRO is typically characterized indirectly, using volume-averaged (e.g. X-ray/neutron scattering) ^{2,7,8} or through projection (i.e. two-dimensional) microscopy techniques ^{5,6,9,10} that fail to capture the complex, three-dimensional atomistic architectures. Quantitative assessment of CSRO and concrete structure-property relationships remain unachievable. Here, we present a machine-learning enhanced approach to break the inherent resolution limits of atom probe tomography to reveal three-dimensional analytical imaging of the size and morphology of multiple CSRO. We showcase our approach by addressing a long-standing question encountered in a body-centred-cubic Fe-18Al (at.%) solid solution alloy that sees anomalous property changes upon heat treatment ². After validating our method against artificial data for ground truth, we unearth non-statistical B₂-CSRO (FeAl) instead of the generally-expected D0₃-CSRO (Fe₃Al) ^{11,12}. We propose quantitative correlations among annealing temperature, CSRO, and the nano-hardness and electrical resistivity, supported by atomistic simulations. The proposed strategy can be generally employed to investigate short/medium/long-range ordering phenomena in a vast array of materials and help design future high-performance materials.

Main

Ordering is the preferential occupation of specific sites in crystalline materials by particular elements. The very early stage of thermally-activated ordering is referred to as chemical short-range order (CSRO)¹³⁻¹⁵, the occurrence of which has been reported to significantly change the mechanical^{4-6,16-21} and functional^{1,2,22} performances of materials. Fe-Al alloys, lightweight materials with excellent strength and corrosion/wear resistance, are good candidates for theoretical studies on such ordering transformations^{2,23,24}. Undeformed Fe-Al alloys with compositions close to the boundary of the disorder-order transition, annealed at a relatively low temperature (e.g. 523 K) and then quenched, often exhibit an anomalous increase in electrical resistivity^{22,25,26}. This unusual behaviour results from the so-called K-state initially reported at 1951²² and attributed to D0₃-CSRO (Fe₃Al), seen as the onset of long-range ordering reactions^{11,12}. The K-state was reported in a vast array of alloy systems, e.g. Ni-X (X=Cr, Co, Al, Fe), Fe-X (X=Si, Ga, Cr), Cu-X (X=Ni, Mn), Ni-Cu-Zn, Ni-Fe-Cr, Fe-Al-Cr^{22,25-28}. However, the underpinnings of the K-state are still unclear and the quantitative characterization of CSRO remains a formidable challenge. As alloys increase in complexity, the knowledge gap linking CSRO to material properties hinders exploiting it in material design to enhance material performance^{6,9,29}.

CSRO was conventionally characterized by indirect, volume-averaged bulk experimental techniques, such as X-ray or neutron scattering, or Mössbauer spectroscopy^{2,7,8,22}, leaving much room for interpretation on how CSRO proceeds at the atomic scale. Recently, transmission electron microscopy characterized CSRO in compositionally-complex alloys based on enhanced diffraction contrast or local compositional mapping^{6,9,10}. Transmission electron microscopy only provides two-dimensional, through-thickness projections of CSRO, leading to limitation in the measurement of size/morphology of CSRO domains. With near-atomic spatial resolution and high analytical sensitivity (10–100 ppm), atom probe tomography (APT) offers, in principle, a unique opportunity for quantifying the size and morphology of CSRO domains in three dimensions (3D)^{30,31}. However, its spatial resolution prevents it from precisely imaging atomic ordering processes, particularly domains below 1-nm in diameter^{15,30,32,33}.

Here, to overcome this inherent limitation and unveil CSRO, we propose a machine learning (ML) enhanced approach based on a convolutional neural network (CNN) applied to spatial

distribution maps (SDMs) obtained from APT data. SDMs are statistical analyses of the interatomic distances used to reveal partial crystallographic information within APT data (Methods)³⁴⁻³⁶. ML, especially deep learning, has been used across microscopy and microanalysis to speed up and improve the repeatability of analyses and reveal elusive details^{37,38}. In APT, it has been used for crystallographic orientation identification and improving microstructural feature extraction³⁹⁻⁴¹. SDMs have been applied to long-range-ordered precipitates^{23,36,42-44} but not to analyse CSRO.

We performed APT on body-centred-cubic (BCC) Fe-18Al alloys annealed at two temperatures for 2 weeks (Methods, Extended Data Fig. 1). Fig. 1a is an example of a reconstructed APT analysis along the (002) zone axis. Fig. 1b is a detector hit map showing the corresponding symmetries of low-index sets of atomic planes⁴⁵, which are highlighted in Fig. 1c. A $2 \times 2 \times 2$ nm³ voxel was examined through SDMs along the depth, i.e. z-SDMs (Methods), for all possible pairs of elements, as plotted in Fig. 1d. The peak-to-peak distance is the same for all pairs, and the reconstruction was calibrated^{46,47} to have the interspacing of 0.144 nm as expected for this composition⁴⁸.

A dedicated search for CSRO has been applied to a similar Fe-18Al alloy, but no concrete information was reported^{2,23}. Other conventional analyses of APT data to extract CSRO include isosurfaces^{41,42}, 1st, 2nd, and 3rd nearest neighbours^{2,49}, and frequency distribution analysis^{30,50}. Results from the latter two are displayed in Fig. 1e-g, but they do not provide evidence for CSRO, which can be attributed to a high fraction of reconstructed atoms shift beyond their 1st nearest neighbours after field evaporation and data reconstruction³³. The lateral resolution of APT is hence too low to detect CSRO with approaches that probe the reconstructed data assuming an isotropic distribution of atomic species^{30,34}. However, most atoms at low-index planes do not shift beyond their 1st nearest neighbours along the depth direction³³, leaving an unexplored opportunity to analyse CSRO, as already achieved for long-range orders utilizing ML^{41,42}.

Fig. 1 APT data of Fe-18Al alloy annealing at 523 K for 14 days.

a APT reconstruction along the [002] zone axis. **b** two-dimensional detector hit map. Four crystallographic poles were indexed, corresponding to (002), ($\bar{1}02$), ($\bar{1}\bar{1}2$), ($1\bar{1}4$), respectively. **c** A close-up of a thin slice in **a** along [002]. **d** The z-SDMs of Fe-Fe, Fe-Al, Al-Al pairs in a $2 \times 2 \times 2 \text{ nm}^3$ voxel in **a**. This signature corresponds to the BCC structure. Typical APT analysis methods: **e**, **f** K-nearest neighbour (KNN) distance analysis ($k = 1, 2$, and 3) of Fe-Fe and Al-Al atoms, respectively, and Exp and Ran refer to the results obtained from experimental and random-labelled datasets, respectively; **g** Frequency distribution analysis of Fe and Al atoms in comparison to the theoretical binomial random distribution.

Fig. 2a summarises the complete framework of our proposed ML-classifier to distinguish the BCC matrix and different CSRO structures using z-SDMs. A synthetic bank of z-SDMs (Methods) was built for the three crystal structures expected from the Fe-Al binary phase diagram^{1,51}, namely BCC, D0₃, and B₂ (FeAl) as detailed in Fig. 2b-e. Each structure exhibits a specific pattern in the z-SDMs (Fig. 2e), which enables classification between BCC matrix, D0₃-CSRO and B₂-CSRO. A total of 10,000 data samples were generated (Methods, Extended Data Table 1). Then, we trained and validated a one-dimensional CNN (Methods, Extended Data Fig. 2a) with a five-fold cross-validation procedure using 90% of the synthetic dataset. The remaining 10% was used to test the CNN (Test I). For comparison, we also trained a random forest using the same synthetic data and five-fold cross-validation procedure to perform the same classification task. In parallel, we scanned the reconstructed APT data, and generated experimental z-SDMs for the Fe-Fe and Al-Al elemental pairs. Afterwards, the data were preprocessed with a pipeline of transformations including curve smoothing and background reduction (Methods). Two examples of the original and optimized experimental curves are presented in Extended Data Fig. 3.

Both algorithms exhibited almost 100% training, validation, and test (Test I) accuracies (Extended Data Fig. 2b-d). The two models were further tested using 148 optimized experimental data (Test II). Their classifications were evaluated by the area under the curve (AUC) of the receiver operating characteristic curve (ROC) (Methods). The CNN exhibited high AUC values and low uncertainties, i.e., 0.95 ± 0.01 , 0.95 ± 0.01 , 0.97 ± 0.01 for BCC, D0₃-CSRO, B₂-CSRO (Extended Data Fig. 4a), respectively. These scores suggest that the CNN is also able to successfully classify experimental data. In comparison, the random forest algorithm only led to low AUC and high uncertainties for each class (Extended Data Fig. 4b). Only CSRO based on CNN will be discussed in the following.

Fig. 2 Machine-learning-enhanced APT strategy to find CSRO and its application in large-scale APT simulation data.

a Flowchart of the proposed ML framework to find CSRO within APT data. Procedure to build three classes of crystal structures and generate relevant synthetic z-SDMs: **b** Generating supercell. **c** Atoms shift from theoretical sites in x, y, z directions. **d** Randomly discarding some of the atoms. **e** Examples of simulated z-SDMs of Fe-Fe and Al-Al pairs. Relevant crystal cells are enclosed. Test of the obtained ML-APT recognition model in large-scale Fe-Al APT simulation: **f** Morphology maps of the simulated CSRO domains and detected ones via the proposed model using 1 × 1 × 1 nm³ scanning cubes. The size and colour of one circle denote the number of atoms within one domain. **g** Number densities versus CSRO size range corresponding to simulated and recognized CSRO domains. The size refers to the APT-counted atoms. The result from the chemically-randomized dataset (Methods) is compared, and the Pearson's correlation coefficients (PCC) are listed in the inserted table.

We then tested our ML-APT recognition model using large-scale Fe-Al APT artificial data as ground truth (Methods). D0₃ domains, with a minimum diameter of 0.7 nm, can be distinguished well from the BCC matrix with Pearson's correlation coefficients (PCC) above 0.8 when using 1×1×1 nm³ voxel (1-nm³ cube) with a 0.5 nm stride (Extended Data Fig. 5). The morphologies of the identified D0₃ domains, as described by their aspect ratio and oblateness reported in Fig. 2f, appear close to spheres. Some are slightly stretched or compressed, likely because of the voxelisation. Fig. 2g is a histogram of CSRO domains vs. size, which essentially follows the simulated data with a PCC of 0.67. The calculated number density of the identified D0₃ domains is $5.71 \times 10^{25} \text{ m}^{-3}$, which is within 11% of the actual value. Even in a truly random yet concentrated solid solution, some local environments similar to CSRO randomly form, with no specific ordering driving force. We also applied this ML-APT recognition model to a randomized dataset (Method, Fig. 2g), enabling the identification of randomly-occurring small CSRO domains. The PCC of 0.39, in this case, shows that our ML model prediction (PCC 0.67) can identify the underlying order and distinguish between CSRO and random structures.

Our ML-APT recognition model was subsequently applied to experimental datasets scanned with a 1-nm³ cube and 0.5-nm stride. Here, we take the data shown in Fig. 1a as an example. In total, 653,944 experimental z-SDMs were generated. The distributions of the predicted D0₃-CSRO and B₂-CSRO probabilities corresponding to these experimental z-SDMs from 1×1×1 nm³ voxels and corresponding uncertainties are close to zero (Extended Data Fig. 6b, d). The probability for a certain CSRO is then estimated from the sum of the predicted probabilities of the 8 overlapped 1-nm³ cubes since the stride was only 0.5 nm, and hence ranges between 0 and 8. The determined classification thresholds are 3.75 and 4 for D0₃-CSRO and B₂-CSRO, respectively (Methods, Extended Data Fig. 7).

Fig. 3a shows coloured regions individually identified with a D0₃-CSRO in the dataset shown in Fig. 1a (See also Supplementary Video 1), along with two close-ups viewed from two perpendicular directions. By using a cluster-finding approach and a best-fit ellipsoid (Methods), the aspect ratio of each CSRO domain is plotted against oblateness in Fig. 3b, evidencing an average near-spherical morphology. The statistical size distribution of D0₃-CSRO domains is given in Fig. 3c. Most of the D0₃-CSRO domains only contain less than 50 APT-counted atoms

corresponding to approximately 1-nm³ cube. Similarly, the obtained B₂-CSRO domains are also visualized (Fig. 3d, Supplementary Video 2) and their morphologies are also very close to spherical (Fig. 3e). Most of the B₂-CSRO domains also contain less than 50 APT-counted atoms (Fig. 3f). Note that previous studies did not observe B₂-CSRO in this alloy ^{11,12}.

We applied ML-APT to data obtained from Fe-18Al annealed for 14 days at either 873 K or 523 K (Methods). The results from the chemically-randomized datasets are compared. The statistical results are summarized in Fig. 4a and b, which compare the number density distributions of the two types of CSRO domains with different sizes for these annealing conditions. Both states exhibit a high PCC (0.99) for the detected D0₃-CSRO compared to random, suggesting no substantial ordering beyond homogenous, statistically-random CSRO in this concentrated alloy. For B₂-CSRO, there is no obvious deviation from random at 873 K (PCC is 0.99), but a distinct difference appears at 523 K (PCC is 0.96). The number densities of the smaller (≤ 50 atoms or 1-nm cube) and larger (> 50 atoms) domains increase by 8.74×10^{23} and $4.18 \times 10^{23} \text{ m}^{-3}$, respectively, as the annealing temperature decreases from 873 K to 523 K. The total number density of B₂-CSRO increases by $1.29 \times 10^{24} \text{ m}^{-3}$. This suggests the formation and growth of non-statistical B₂-CSRO at 523 K.

To confirm that the alloys we investigated exhibit the CSRO, i.e. the K-state in these Fe-18Al alloys ^{22,25}, we measured the nano-hardness and resistivity changes, shown in Fig. 4c. The former decreases from 3.1 ± 0.2 GPa to 2.8 ± 0.2 GPa when the annealing temperature is decreased from 873 K to 523 K, which is within measurement errors. Based on the classical strengthening model (Methods) using the size distribution of CSRO domains (Fig. 4a, b), we estimated their contributions to be approximately 20 MPa and 23 MPa, at 873 K and 523 K, respectively, matching with experimental observations considering the experimental uncertainty. The resistivity rises by 14%, and previous reports attributed this anomalous resistivity change ($\sim 4\%$ increase at 553 K for 1 day) only to D0₃-CSRO ^{2,11,52}. Our work proves that this resistivity change lies in the formation and growth of non-statistical B₂-CSRO ($1.29 \times 10^{24} \text{ m}^{-3}$) at 523 K.

Fig. 3 Two types of CSRO tomography in Fe-18Al alloys annealing at 523 K for 14 days.

a, d Part of $D0_3$ -CSRO and B_2 -CSRO tomography, respectively. Different CSRO domains are marked using different colours. For each tomography, two thin slices of thickness 2 nm are highlighted. The whole 3D images are provided in Supplementary Video 1 and 2. **b, e** Distributions of morphologies of $D0_3$ -CSRO and B_2 -CSRO domains, respectively. The size and colour of one circle denote the number of atoms within one domain. **c, f** Histograms of the size distributions of the identified $D0_3$ -CSRO and B_2 -CSRO domains, respectively. Another format with the logarithmic-scale x-axis is provided in the inserted image. This size refers to the APT-counted atoms.

Fig. 4 Quantitative CSRO evolutions and property changes of Fe-18Al alloys with different heat treatments as well as Fe-Al potential energy diagram at different temperatures.

a, b Number density distributions of different sizes of D0₃-CSRO and B₂-CSRO, respectively, for two annealing temperatures for 14 days. The results from the chemically-randomized dataset are compared with the PCC values. The detailed changes in number densities of smaller and larger B₂-CSRO are listed in the inserted table. The value of 50, ideally corresponding to 1-nm³ cube, is set as the dividing point. **c** Changes of nano-hardness and electrical resistivity at different annealing temperatures for 14 days. **d** Simulation values for Fe-Al potential energy/atom for each Fe-Al phases up to 50 at.% Al. Details can be found in the Supplementary Information.

To rationalise the observed CSRO (Fig. 4a, b), we performed Monte Carlo-Molecular Dynamics simulations with an empirical potential (Fig. 4d, Supplementary Information). While our calculations showed no evidence of B₂-CSRO forming at either temperature, we observed a strong tendency at 873 K to form many small D0₃-CSRO (<50 atoms) and some large D0₃-CSRO (>50 atoms). At 523 K, this tendency for CSRO was not observed and the system showed a full phase separation. A detailed analysis showed that at 873 K the small clusters are rather short-lived objects, i.e. the individual clusters are subcritical nuclei that form, exist for a short time, dissolve, and reform as new clusters with other atoms at another location in the matrix. In contrast, at 523 K the existing clusters show the expected behaviour of supercritical nuclei: they slowly ripen and grow larger. From the relative energetics of the competing phases shown in Fig. 4d, we see that at lower temperatures the miscibility gap between BCC solid solution and D0₃ widens, and this behaviour is expected as there is less Al available in the solution from which to form clusters. In our calculations, the lower annealing temperature tends to allow Ostwald ripening of precipitates, while the higher temperature is entropically driven to maintain more and smaller clusters. Despite the deficiencies of the potential, these calculations still provide insights into the temperature dependence of the experimentally observed B₂-CSRO: at the 523 K we can infer that the system is kinetically limited and small clusters do not have enough time to diffuse and ripen; at 873 K entropy has destroyed the CSRO and we have a solid solution again.

In summary, we managed to overcome the current limitation in imaging CSRO by APT by using ML. Our approach precisely reveals the morphology and size distributions of multiple types of (non-)statistical CSRO, in 3D and with the near-atomic resolution, thereby enabling us to rationalise their origin and microstructural influence. We showcase this strategy on the open question in the context of the K-state Fe-Al system by establishing relationships between the compositions, processing, CSRO and properties. In this case, the functional property is more sensitive to the formation of a limited number of non-statistical B₂-CSRO as compared to the mechanical property. However, whether abundant CSRO can affect the mechanical properties is still controversial, especially in compositionally-complex alloys^{6,53} and we are now poised to characterise the CSRO in such complex alloy systems, and exploit short/medium/long-range ordering phenomena in newly designed advanced metallic materials.

Methods

Sample preparation

An alloy with a nominal composition of Fe-18Al (at.%) was arc-melted from pieces of raw metals with high purity (> 99.8 wt.%) in a water-chilled copper crucible under an argon atmosphere. Then, the as-received sample was cut into pieces and annealed at 873 K and 523 K for 14 days, respectively, under argon atmosphere, followed by water quenching. The annealed samples were ground and polished for microstructure analysis as well as mechanical and functional properties tests.

APT experiments

Electron backscatter diffraction was first applied to determine the desired grain site along the [002] zone axis. Then, the needle-like specimens for APT along [002] were prepared using a FEI Helios focused ion beam (FIB) with a Xenon plasma ion source. Note that using a FIB with the more commonly-utilized Gallium source was excluded because of the potential Gallium pollution in the Fe-Al alloy. The APT measurements were performed on a CAMECA Inc. LEAP 5000XR with a 52% detection efficiency. The APT experiments were carried out in voltage pulsing mode at 40-60 K, a detection rate of 0.2%, a pulsing fraction of 20%, and a pulsing rate of 200 kHz. Note that a temperature range from 80 K to 30 K was tried to adjust the evaporation field to avoid the peak overlap between $^{54}\text{Fe}^{2+}$ and Al^+ at 27 Da according to the bulk composition analysis (Extended Data Table 2)^{2,23}. For each state, three APT datasets were collected for statistical analysis. AP suite 6.1 was used to make initial reconstruction and visualization. Two important reconstruction parameters, i.e., the field factor and image compression factor, were calibrated using the method suggested by Gault et al.^{46,47}.

Spatial distribution maps

SDMs are produced by establishing the vectors between each atom and its surrounding neighbours in 3D space³⁴⁻³⁶. These vectors are then accumulated into two-dimensional (2D) histograms (projected onto a plane, commonly the xy, or xz plane), or one-dimensional (1D) histograms (along the z-axis). Here, the 1D z-SDMs (see Fig. 1d) were employed to focus on the depth-direction structural information.

Synthetic z-SDMs bank

Various possible configurations were simulated, around BCC, D0₃, and B₂ (Fig. 2b-e) using the following approach. First, a supercell with 3×3×3 nm³ was generated (the lattice constant was set as 0.287 nm⁴⁸). Second, the atoms were shifted in x, y, z reconstruction directions according to Gaussian distributions to simulate the anisotropic spatial resolutions (depth resolution is better than the lateral direction). Third, a certain fraction of atoms were randomly discarded to simulate the imperfect detection efficiency met in APT data. Finally, 5,000 z-SDMs of three structures were generated. The differences in the peak-to-peak distances of the Fe-Fe and Al-Al pairs allow one to make classification (Fig. 2e). The peak positions of the experimental z-SDMs were not always at their theoretical sites. Thus, we augmented the dataset by adding additional 5,000 synthetic samples in which the peak-to-peak distance was randomly modified by ±0.06 nm. All parameters for generating simulated z-SDMs are listed in Extended Data Table 1.

Experimental data preprocessing

The data preprocessing procedure includes using the Savitzky-Golay filter⁵⁴ to smooth the original z-SDM curve and make a background reduction. For the Savitzky-Golay filter, the length of the filter window and the order of the polynomial are set as 15 and 8, respectively, obtained by a tuning procedure in which different values are set and their performances on real data are evaluated. The background curve was calculated using³⁵

$$y_p(i) = \min \left\{ y_{p-1}(i), \frac{y_{p-1}(i+1) + y_{p-1}(i-1)}{2} \right\} \quad (1)$$

where $y_{p=0}$ is the smoothed z-SDM curve, and $y_p(i)$ is the value of the i th discrete point of the z-SDM at the p th iteration. The iteration is stopped when the first local minimum value of the smoothed z-SDM (after x-axis is above 0) is lower than the maximum of $y_p(i)$ within the shade zone (Extended Data Fig. 3). The background as defined above was subtracted from the smoothed z-SDM curve to obtain the optimized z-SDM.

CSRO recognition model based on 1D CNN and random forest algorithms

As detailed in Extended Data Fig. 2a, the 1D CNN^{55,56} consists of a convolutional layer with filter number, kernel size and stride of 64, 10 and 1, respectively, followed by a dropout layer with the rate of 0.5 used to avoid overfitting. Then, a max-pooling layer⁵⁵ with a pool size of 2 is added to highlight the most important features. A fully-connected layer with 256 neurons is employed to generate an output corresponding to the three crystal structures. All layers used

the activation function of ReLu, except the output layer which used softmax for classification purposes. The categorical cross-entropy was chosen as the loss function, which is commonly used to train a multi-classifier. We used a batch size of 32 and an optimized learning rate of 0.001 during training, and the Adam optimizer was used to minimize the loss function. Note that the reported hyperparameters' values in the 1D CNN are the result of a thorough tuning procedure based on the training, validation, and test results on synthetic and real datasets (like the tested convolutional layer number: 1~5; filter number: 8~64; kernel size: 3-20, neurons of full layer: 64~1000; learning rate: 0.001~0.1). For the random forest classifier⁵⁷, the number of trees in the forest was set to 200 based on the training, validation, and test results on synthetic and real datasets (the tested number of trees: 100~300). The CNN was implemented using Keras 2.2.4 with the TensorFlow 1.13.1 backend on Python 3.7. The random forest was performed using scikit-learn 0.23.2 using the default parameters except for the number of trees. The uncertainty was calculated based on the five models obtained by five-fold cross-validation.

Evaluation of classification ability based on ROC analysis

The ROC analysis^{58,59} was applied to evaluate the performance of the multi-label classifier. In Extended Data Fig. 4, one curve is plotted based on two critical evaluation parameters: true positive rate and false positive rate. The top left corner of this curve is an ideal point, i.e., the true positive rate and false positive rate are 1 and 0, respectively. For each label, we plot its ROC curve regarding each element of the label indicator matrix as a binary prediction. Five models from five-fold cross-validation provide five ROC curves for each class, and the mean value and standard deviation are plotted. The mean AUC and its standard deviation of each class are also provided.

Large-scale Fe-Al APT simulation

We built a perfect BCC supercell ($10 \times 10 \times 50 \text{ nm}^3$) with D0₃-type domains (the diameters vary from 0.7 to 2.0 nm). Then, the atoms were shifted in lateral and depth reconstruction directions according to Gaussian distributions. According to the previous APT evaporation simulation in alloys and concentrated solid solutions³³, the maximum atoms shift in the lateral and depth directions were set as 5th and 1st nearest neighbour distances, respectively. The detection efficiency was set to 52%. Finally, the simulated D0₃-type domains are shown in Extended Data Fig. 5a. The ML-APT recognition model obtained was applied to the simulated APT data

using different scanning strategies (Extended Data Fig. 5b, c). The 3D recognition results were compared via the 2D distribution of the number of atoms along Z and Y directions (Extended Data Fig. 5d, e), morphology and size distributions (Fig. 2f, g).

To figure out the impact of the randomly-formed CSRO from the truly random solid solution, we randomly swapped the elemental identities of data points while retaining the original x, y, and z coordinates. Then, the same ML-APT recognition model was applied to the random dataset to obtain the randomly-formed CSRO domains. This is compared with the results above using Pearson's correlation coefficient (PCC). PCC is a statistic that evaluates the linear correlation between variable X and Y, given by ⁶⁰:

$$\text{PCC} = \frac{\sum_{i=1}^N (x_i - \tilde{x})(y_i - \tilde{y})}{\sqrt{\sum_{i=1}^N (x_i - \tilde{x})^2} \sqrt{\sum_{i=1}^N (y_i - \tilde{y})^2}} \quad (2)$$

where N is the data size. x_i, y_i are the individual data points. $\tilde{x}, \tilde{y}$ are the mean values. PCC varies from -1 to 1, suggesting the linear correlation extent of the two variables. 1 represents a complete positive linear correlation, 0 is no linear correlation, and -1 is a complete negative linear correlation.

Classification thresholds

Extended Data Fig. 7a, b presents the frequency distributions of two kinds of CSRO structure probabilities of the 0.5-nm³ voxels (named P_{0.5}). The data from three zones (1, 2, 3) in Extended Data Fig. 7a were analysed and the corresponding z-SDMs are shown in Extended Data Fig. 7c. For the z-SDMs of Fe-Fe pairs, the peaks are unclear, which also occurs in the large-scale APT simulation data. This is attributed to the imperfect lateral and depth resolutions. For the z-SDMs of Al-Al pairs, there is an obvious trend to be close to the signature of D0₃-CSRO except zone 1. Thus, the separating line between zones 1 and 2 was regarded as the threshold between D0₃ and others, i.e., 3.75. Similarly, zones 1-3 in Extended Data Fig. 7b were also analysed and the corresponding z-SDMs are plotted at Extended Data Fig. 7d. The B₂ signature becomes clear after zone 1, and, thus, 4 was seen as the threshold. Finally, the z-SDMs of each kind of CSRO based on the chosen threshold exhibits a clear signature (zone 4), suggesting the excellent CSRO classification ability.

Quantification of CSRO domains

We made a quantitative analysis of the identified CSRO domains based on the cluster analysis algorithm included in AP suite 6.1. The approach consists of choosing a maximum separation distance between the clustered elements ($d_{\max}$) and a minimum number of ions in the cluster ($N_{\min}$)^{49,61}. After getting the optimized parameters in the simulated APT dataset (Fig. 2f, g) these values were further fine-tuned in the real APT dataset by visual observation. The determined values of $d_{\max}$ and $N_{\min}$ are 0.4 nm and 3 ions, respectively, which was applied to all real APT datasets. Then, the obtained count of CSRO domains was divided by the total volume to calculate the number density of CSRO, N_v .

To describe the shape of each CSRO domain, we first define its centre of mass in a best-fit coordinate system, r_{com} , by

$$r_{\text{com}}(x_{\text{com}}, y_{\text{com}}, z_{\text{com}}) = \frac{\sum_{i=1}^{N_c} m_i r_i(x_i, y_i, z_i)}{\sum_{i=1}^{N_c} m_i} \quad (3)$$

where m_i and r_i denote the mass and coordinates (in the best-fit coordinate system) of each atom in the domain and N_c is the total number of atoms in the domain. Then, the three radii of gyration in the best-fit ellipsoid system, ($R_{g1} > R_{g2} > R_{g3}$), were calculated. The shape of the domain is expressed by the plot of the oblateness vs aspect ratio, defined by

$$\text{Oblateness} = \frac{R_{g3}}{R_{g2}} \quad (4)$$

$$\text{Aspect ratio} = \frac{R_{g2}}{R_{g1}} \quad (5)$$

Nano-hardness and electrical resistivity measurements

The Nano-hardness tests were performed using the G200 nanoindenter at a strain rate of 0.1 s⁻¹ and an indentation depth of 1000 nm. The grains close to {110} were selected and the hardness values from 50 measurements within the specific grains were measured to calculate the statistical results for each sample. The electrical resistivity corresponding to each annealing temperature was measured on a Quantum Design Physical Property Measurement System with a temperature of 300 K and zero Tesla magnetic field. The resistivity values from 50 measurements were obtained to calculate the statistical results for each sample.

Strength model

The main strength contribution can be divided into the intrinsic strength from the BCC matrix, solid solution strengthening, and precipitation strengthening from CSRO. The two formers are almost identical for the studied states. The precipitation strengthening from CSRO, σ_p , is estimated by the previously-developed precipitation strength model in terms of spherical precipitates ⁶²⁻⁶⁵:

$$\sigma_p = 0.9M\mu b\sqrt{2\bar{r}N_V}\bar{f}^{\frac{3}{2}}\left(1 - \frac{1}{6}\bar{f}^5\right) \quad (6)$$

$$\bar{f} = \left(\frac{1}{r_c^{2k}}\int_0^{r_c} r^{2k+1}\varphi_r dr + \int_{r_c}^{\infty} r\varphi_r dr\right)\frac{1}{\bar{r}N_V} \quad (7)$$

where M is the Taylor factor. μ is the BCC-Fe shear modulus, and b is the Burgers vector. N_V is the total number density of CSRO. $\bar{r}$ is the mean particle radius and r_c is the critical radius that the precipitates transform from shearable to non-shearable. k is an empirical model parameter. φ_r is the statistical distribution of the number of particles per volume as a function of the particle radius, r . Here, $M=3$, $\mu=80$ GPa, $b=0.25$ nm, $k=1$, and $r_c=5$ nm were used ⁶⁶.

Acknowledgements

This work was primarily supported by the Max Planck research network on big-data-driven materials science (BiGmax). We also acknowledge the research fellowship provided by the Alexander von Humboldt Foundation and the Open Foundation of State Key Laboratory of Powder Metallurgy at Central South University, Changsha, China. I.B. was supported by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences # DE-SC0018962. J. Rao and M. J. Duarte are acknowledged for their great help with nano-hardness tests.

Author contributions

Y. L., Z. W., and B. G. conceived the project. Y. L. was the lead experimental/data scientist of the study. Z. W., I. B., and Y. L. proposed the Fe-Al system and prepared the materials, samples and heat treatments. Y. L., Z. W., and X. Z. performed the PFIB/APT experiments with the help of L. S. and B. G.. Y. L. analysed the APT data with the help of L. S. and B. G.. Y. L. programmed the machine learning framework with the help of Y. W. and T. C.. Y. L. conducted APT simulations and strength modelling. L. Ha. and Z. R. performed the electrical resistivity measurements. L. Hu. and R. D. carried out the atomistic simulations. Y. L., Z. W., and B. G. wrote the manuscript. All authors contributed to the discussion of the results and commented on the manuscript.

Data availability

All data that support the findings are involved in this paper. Other data are available from the corresponding authors upon reasonable request.

Code availability

The software used for the simulation of z-SDMs and 1D CNNs model is available at GitHub address <https://github.com/a356617605>. The codes for fully reproducing the atomistic results can be found on GitHub at https://github.com/liamhuber/FeAl_solution. Further codes are available from the corresponding authors upon reasonable request.

Competing interests

The authors declare no competing interests.

Supplementary information

Supplementary Video 1 Entire 3D image of D0₃-CSRO in Fe-18Al APT data annealing at 523 K for 14 days.

Supplementary Video 2 Entire 3D image of B₂-CSRO in Fe-18Al APT data annealing at 523 K for 14 days.

Supplementary Information Atomistic simulations to explain experimentally-observed CSRO in Fe-18Al alloys upon different annealing temperatures.

References

- 1 Guruswamy, S., Garside, G., Ren, C., Saha, B. & Ramanathan, M. Ordering and magnetostriction in Fe alloy single crystals. *Prog. Cryst. Growth Charact. Mater.* **57**, 43-64 (2011).
- 2 Marceau, R. K. W. *et al.* Atom probe tomography investigation of heterogeneous short-range ordering in the ‘komplex’ phase state (K-state) of Fe–18Al (at.%). *Intermetallics* **64**, 23-31 (2015).
- 3 Radecka, A. *et al.* The formation of ordered clusters in Ti–7Al and Ti–6Al–4V. *Acta Mater.* **112**, 141-149 (2016).
- 4 Dumitraschkewitz, P., Uggowitzer, P. J., Gerstl, S. S., Löffler, J. F. & Pogatscher, S. Size-dependent diffusion controls natural aging in aluminium alloys. *Nat. Commun.* **10**, 1-6 (2019).
- 5 Zhang, R. *et al.* Direct imaging of short-range order and its impact on deformation in Ti-6Al. *Sci. Adv.* **5**, eaax2799 (2019).
- 6 Zhang, R. *et al.* Short-range order and its impact on the CrCoNi medium-entropy alloy. *Nature* **581**, 283-287 (2020).
- 7 Owen, L. R., Playford, H. Y., Stone, H. J. & Tucker, M. G. A new approach to the analysis of short-range order in alloys using total scattering. *Acta Mater.* **115**, 155-166 (2016).
- 8 Zhang, F. X. *et al.* Local Structure and Short-Range Order in a NiCoCr Solid Solution Alloy. *Phys. Rev. Lett.* **118**, 205501 (2017).
- 9 Chen, X. *et al.* Direct observation of chemical short-range order in a medium-entropy alloy. *Nature* **592**, 712-716 (2021).
- 10 Seol, J. B. *et al.* Short-range order strengthening in boron-doped high-entropy alloys for cryogenic applications. *Acta Mater.* **194**, 366-377 (2020).
- 11 Warlimont, H. & Thomas, G. Two-Phase Microstructures of α -Fe–Al Alloys in the K-State. *Met. Sci. J.* **4**, 47-52 (1970).
- 12 Watanabe, D., Morita, H., Saito, H. & Ogawa, S. Transmission Electron Microscopic Study on the “K-State” in Iron-Aluminium Alloys. *J. Phys. Soc. Jpn.* **29**, 722-729 (1970).
- 13 E P George, M Yamaguchi, K S Kumar, a. & Liu, C. T. Ordered Intermetallics. *Annu. Rev. Mater. Sci.* **24**, 409-451 (1994).
- 14 Schönfeld, B. Local atomic arrangements in binary alloys. *Prog. Mater Sci.* **44**, 435-543 (1999).
- 15 Wu, Y. *et al.* Short-range ordering and its effects on mechanical properties of high-entropy alloys. *J. Mater. Sci. Technol.* **62**, 214-220 (2020).
- 16 Gray, G. T., Luetjering, G. & Williams, J. C. The influence of oxygen on the structure, fracture, and fatigue crack propagation behavior of Ti-8.6 Wt Pct Al. *Metall. Trans. A* **21**, 95-105 (1990).
- 17 Gerold, V. & Karnthaler, H. P. On the origin of planar slip in f.c.c. alloys. *Acta Metall.* **37**, 2177-2183 (1989).
- 18 Han, D., Guan, X. J., Yan, Y., Shi, F. & Li, X. W. Anomalous recovery of work hardening rate in Cu-Mn alloys with high stacking fault energies under uniaxial compression. *Mater. Sci. Eng., A* **743**, 745-754 (2019).
- 19 Ding, J., Yu, Q., Asta, M. & Ritchie, R. O. Tunable stacking fault energies by tailoring local chemical order in CrCoNi medium-entropy alloys. *Proc. Natl. Acad. Sci. U.S.A.* **115**, 8919-8924 (2018).

- 20 Ding, Q. *et al.* Tuning element distribution, structure and properties by composition in high-entropy alloys. *Nature* **574**, 223-227 (2019).
- 21 Hou, S., Zhang, D., Ding, Q., Zhang, J. & Zhuang, L. Solute clustering and precipitation of Al-5.1Mg-0.15Cu-xZn alloy. *Mater. Sci. Eng., A* **759**, 465-478 (2019).
- 22 Thomas, H. Über widerstandslegierungen. *Z. Phys.* **129**, 219-232 (1951).
- 23 Marceau, R. K. W., Ceguerra, A. V., Breen, A. J., Raabe, D. & Ringer, S. P. Quantitative chemical-structure evaluation using atom probe tomography: Short-range order analysis of Fe–Al. *Ultramicroscopy* **157**, 12-20 (2015).
- 24 Li, L.-L., Su, Y., Beyerlein, I. J. & Han, W.-Z. Achieving room-temperature brittle-to-ductile transition in ultrafine layered Fe-Al alloys. *Sci. Adv.* **6**, eabb6658 (2020).
- 25 Adunka, F., Zehetbauer, M. & Trieb, L. Heterogeneous short-range order as an origin of the K-state in α -FeAl. *Phys. Status Solidi A* **62**, 213-222 (1980).
- 26 Davies, R. An X-ray and dilatometric study of order and the “k-state” in iron-aluminum alloys. *J. Phys. Chem. Solids* **24**, 985-992 (1963).
- 27 Zhang, Y. *et al.* Atomic-level heterogeneity and defect dynamics in concentrated solid-solution alloys. *Curr. Opin. Solid State Mater. Sci.* **21**, 221-237 (2017).
- 28 Zhao, S., Osetsky, Y. & Zhang, Y. Preferential diffusion in concentrated solid solution alloys: NiFe, NiCo and NiCoCr. *Acta Mater.* **128**, 391-399 (2017).
- 29 Yin, S. *et al.* Atomistic simulations of dislocation mobility in refractory high-entropy alloys and the effect of chemical short-range order. *Nat. Commun.* **12**, 4873 (2021).
- 30 Gault, B., Moody, M. P., Cairney, J. M. & Ringer, S. P. *Atom probe microscopy*. Vol. 160 (Springer, 2012).
- 31 Gault, B. *et al.* Atom probe tomography. *Nature Reviews Methods Primers* **1**, 51 (2021).
- 32 De Geuser, F. & Gault, B. Metrology of small particles and solute clusters by atom probe tomography. *Acta Mater.* **188**, 406-415 (2020).
- 33 Gault, B. *et al.* Reflections on the spatial performance of atom probe tomography in the analysis of atomic neighbourhoods. *Microsc. Microanal.*, 1-11 (2021).
- 34 Gault, B. *et al.* Spatial Resolution in Atom Probe Tomography. *Microsc. Microanal.* **16**, 99-110 (2010).
- 35 Moody, M. P., Gault, B., Stephenson, L. T., Haley, D. & Ringer, S. P. Qualification of the tomographic reconstruction in atom probe by advanced spatial distribution map techniques. *Ultramicroscopy* **109**, 815-824 (2009).
- 36 Geiser, B. P., Kelly, T. F., Larson, D. J., Schneir, J. & Roberts, J. P. Spatial Distribution Maps for Atom Probe Tomography. *Microsc. Microanal.* **13**, 437-447 (2007).
- 37 Shen, Y.-F., Pokharel, R., Nizolek, T. J., Kumar, A. & Lookman, T. Convolutional neural network-based method for real-time orientation indexing of measured electron backscatter diffraction patterns. *Acta Mater.* **170**, 118-131 (2019).
- 38 Aguiar, J. A., Gong, M. L., Unocic, R. R., Tasdizen, T. & Miller, B. D. Decoding crystallography from high-resolution electron imaging and diffraction datasets with deep learning. *Sci. Adv.* **5**, eaaw1949 (2019).
- 39 Wei, Y. *et al.* Machine-learning-based atom probe crystallographic analysis. *Ultramicroscopy* **194**, 15-24 (2018).
- 40 Zelenty, J., Dahl, A., Hyde, J., Smith, G. D. W. & Moody, M. P. Detecting Clusters in Atom Probe Data with Gaussian Mixture Models. *Microsc. Microanal.* **23**, 269-278 (2017).
- 41 Li, Y. *et al.* Convolutional neural network-assisted recognition of nanoscale L12 ordered structures in face-centred cubic alloys. *npj Comput. Mater.* **7**, 8 (2021).
- 42 Gault, B. *et al.* Atom probe microscopy investigation of Mg site occupancy within δ' precipitates in an Al–Mg–Li alloy. *Scripta Mater.* **66**, 903-906 (2012).

- 43 Meher, S. & Banerjee, R. Partitioning and site occupancy of Ta and Mo in Co-base γ/γ' alloys studied by atom probe tomography. *Intermetallics* **49**, 138-142 (2014).
- 44 Tu, Y., Mao, Z. & Seidman, D. N. Phase-partitioning and site-substitution patterns of molybdenum in a model Ni-Al-Mo superalloy: An atom-probe tomographic and first-principles study. *Appl. Phys. Lett.* **101**, 121910 (2012).
- 45 Gault, B., Moody, M. P., Cairney, J. M. & Ringer, S. P. Atom probe crystallography. *Mater. Today* **15**, 378-386 (2012).
- 46 Gault, B. *et al.* Estimation of the Reconstruction Parameters for Atom Probe Tomography. *Microsc. Microanal.* **14**, 296-305 (2008).
- 47 Gault, B. *et al.* Advances in the calibration of atom probe tomographic reconstruction. *J. Appl. Phys.* **105**, 034913 (2009).
- 48 He, Y., Li, Y., Chen, C. & Yu, H. Diffusion coefficient of hydrogen interstitial atom in α -Fe, γ -Fe and ϵ -Fe crystals by first-principle calculations. *Int. J. Hydrog. Energy* **42**, 27438-27445 (2017).
- 49 Stephenson, L. T., Moody, M. P., Liddicoat, P. V. & Ringer, S. P. New Techniques for the Analysis of Fine-Scaled Clustering Phenomena within Atom Probe Tomography (APT) Data. *Microsc. Microanal.* **13**, 448-463 (2007).
- 50 Hu, R., Jin, S. & Sha, G. Application of atom probe tomography in understanding high entropy alloys: 3D local chemical compositions in atomic scale analysis. *Prog. Mater. Sci.*, 100740 (2020).
- 51 Kubaschewski, O. *Iron—Binary phase diagrams*. (Springer Science & Business Media, 2013).
- 52 Rossiter, P. & Wells, P. The dependence of electrical resistivity on short-range order. *J. phys., C, Solid state phys.* **4**, 354 (1971).
- 53 Yin, B., Yoshida, S., Tsuji, N. & Curtin, W. Yield strength and misfit volumes of NiCoCr and implications for short-range-order. *Nat. Commun.* **11**, 1-7 (2020).
- 54 Schafer, R. W. What is a Savitzky-Golay filter?[lecture notes]. *IEEE Signal processing magazine* **28**, 111-117 (2011).
- 55 Albawi, S., Mohammed, T. A. & Al-Zawi, S. in *2017 International Conference on Engineering and Technology (ICET)*. 1-6.
- 56 Kiranyaz, S. *et al.* 1D convolutional neural networks and applications: A survey. *Mech. Syst. Signal Process.* **151**, 107398 (2021).
- 57 Torrisi, S. B. *et al.* Random forest machine learning models for interpretable X-ray absorption near-edge structure spectrum-property relationships. *npj Comput. Mater.* **6**, 109 (2020).
- 58 Saito, T. & Rehmsmeier, M. Precrec: fast and accurate precision–recall and ROC curve calculations in R. *Bioinformatics* **33**, 145-147 (2017).
- 59 Kannan, R. & Vasanthi, V. in *Soft Computing and Medical Bioinformatics* 63-72 (Springer, 2019).
- 60 Van Den Berg, R. G. *Pearson correlations—quick introduction*, <https://www.spss-tutorials.com/pearson-correlation-coefficient/> (2020).
- 61 Hyde, J. M., Marquis, E. A., Wilford, K. B. & Williams, T. J. A sensitivity analysis of the maximum separation method for the characterisation of solute clusters. *Ultramicroscopy* **111**, 440-447 (2011).
- 62 Holmedal, B. Strength contributions from precipitates. *Philos. Mag. Lett.* **95**, 594-601 (2015).
- 63 Li, Y. *et al.* Precipitation and strengthening modeling for disk-shaped particles in aluminum alloys: size distribution considered. *Materialia* **4**, 431-443 (2018).

- 64 Zhang, Z. *et al.* ICME guided design of heat-treatable Zn-modified Al–Mg alloys. *Calphad* **74**, 102298 (2021).
- 65 Li, Y. *et al.* Towards high-throughput microstructure simulation in compositionally complex alloys via machine learning. *Calphad* **72**, 102231 (2021).
- 66 Deschamps, A., Militzer, M. & WJ, P. Precipitation kinetics and strengthening of a Fe–0.8 wt% Cu alloy. *ISIJ Int.* **41**, 196-205 (2001).

Extended Data

Extended Data Fig. 1 Atom probe mass spectra (voltage mode) of Fe–18Al (at.%) alloy annealing at 523 K for 14 days.

The peak at 27 Da was assigned to $^{54}\text{Fe}^{2+}$ according to the bulk composition analysis (Extended Data Table 2). No Fe^{1+} and Fe^{3+} peaks were found regardless of single or multiple hit map.

a Details of the used 1D convolutional neural network

Layer type	Specifications
1D CNN layer	Kernel size: 10; 64 filters; stride: 1; padding: Valid; Relu
Dropout layer	Rate: 0.5
1D Max pooling layer	Pool size: 2; stride: 2; Valid
Fully connected layer	Size: 256
Output layer	Size: 3

Extended Data Fig. 2 Details of the optimized 1D CNN structure and the training, validation, and test I results.

a The 1D CNN configuration. **b, c** The evolutions of the training and validation losses and accuracies. **d** The confusion matrix of the test results using the 10% simulated data. Note that the random forest algorithm exhibited almost the same training, validation, and test I performance (not shown here).

Extended Data Fig. 3 Typical experimental z-SDMs before and after data preprocessing. **a, b,** Curves with BCC matrix and CSRO signals, respectively. The original curve was initially smoothed using a Savitzky–Golay filter, and then its background was subtracted (Methods). The blue circles highlight the sites of the first local minimum after x-axis is above 0, which was taken as a criterion to stop the iterative background estimation.

Extended Data Fig. 4 ROC analysis of the 1D CNN and random forest algorithms obtained using 148 experimental data.

a, b ROC curves of the 1D CNN and random forest with uncertainties, respectively, corresponding to three kinds of structures. The relevant AUC values and standard deviations are given.

Extended Data Fig. 5 Test of the obtained ML-APT recognition model in large-scale Fe-Al APT simulation.

a Simulated D0₃-CSRO APT data. **b, c** Recognized CSRO domains via the proposed recognition model using $1 \times 1 \times 1$ and $2 \times 2 \times 2 \text{ nm}^3$ scanning cubes, respectively. **d, e** Distributions of counts of atoms in **a-c** along Z and Y directions, respectively. **f** The Pearson's correlation coefficients (PCC) in **d, e** are listed.

Extended Data Fig. 6 Frequency distributions of the predicted two types of CSRO structures probabilities and uncertainties of 653944 1-nm³ voxels generated from APT data shown in Fig. 1a.

a, c Distributions of the predicted D0₃-CSRO and B₂-CSRO structures probabilities. 1 represents the highest D0₃-CSRO and B₂-CSRO structures probabilities. **b, d** Distributions of the uncertainties obtained from five-fold cross validation of the D0₃-CSRO and B₂-CSRO structures.

Extended Data Fig. 7 Predictions of two kinds of CSRO structures in Fe-18Al data.

a, b Frequency distributions of two kinds of CSRO structure probabilities of the 0.5-nm³ voxels ($P_{0.5}$) obtained from Fig. 1a. The line divided by different colours indicates the determined threshold for classification. **c, d** The z-SDMs generated by the data corresponding to zone 1, 2, 3, and 4 in **a** and **b** (before data preprocessing).

Extended Data Table 1 Parameters for building the crystal structure library and generating the corresponding z-SDMs bank.

Note that “ σ ” represented the standard deviation of the Gaussian function.

Category	Number of z-SDMs	$\sigma_x = \sigma_y$, nm	σ_z , nm	Detect efficiency	Peak shift, nm
BCC	3000	0.2~0.8	0.02~0.05	0.2~0.7	-0.06~0.06
D03	4000	0.2~0.8	0.01~0.05	0.2~0.7	-0.06~0.06
B ₂	3000	0.2~0.8	0.03~0.06	0.2~0.7	-0.06~0.06

Extended Data Table 2 Bulk composition of APT data of Fe-18Al (at.%) alloy corresponding to the mass spectra in Extended Data Fig. 1.

The composition related to further analysis refers to the assignment of the peak at 27 Da to Al⁺.

Element	Peak decomposed, at.%	Composition related to further analysis, at.%
Fe	80.619±0.019	77.414
Al	17.116±0.018	22.327
C	0.030±0.002	0.029
O	0.103±0.002	0.102
H	0.132±0.003	0.129

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [FeAlsupplementaryfinal.pdf](#)
- [Supplementaryvideo2.avi](#)
- [Supplementaryvideo1.avi](#)