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Symmetry breaking in Prussian Blue Analogues via growth–guided local ordering of hexacyanometallate vacancies

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ABSTRACT

We report Growth–Guided Local Ordering, a novel mechanism of symmetry reduction in disordered crystals. This mechanism operates through the directional ordering of point defects during crystal growth, where defect correlations develop preferentially along the growth direction, resulting in reduced symmetry that persists in the final structure through the spatial distribution of defects.

We demonstrate this phenomenon in Mn[Co]-Prussian Blue Analogues, disordered cyanide crystals containing numerous Co(CN)₆ vacancies. Single-crystal diffuse scattering reveals pronounced anisotropy in vacancy distribution: strong correlations along the [001] growth direction contrast with weak correlations perpendicular to it. This local ordering reduces the Laue symmetry to tetragonal $4/mmm$, evident in properties such as birefringence, while the average structure retains cubic $m\bar{3}m$ symmetry. When growth proceeds along [111] direction, the same mechanism produces domains with trigonal symmetry. Because this mechanism relies on fundamental aspects of crystal growth rather than specific material properties, it offers a general strategy for symmetry control in disordered crystals. Crucially, it transforms the complex task of altering crystal symmetry into the more manageable challenge of controlling growth direction, which can be achieved through various established techniques, such as using surfactants during crystallization.

Introduction

While symmetry is beautiful, breaking of symmetry often leads to the emergence of novel functional properties. This is fundamental across scales—from materials exhibiting birefringence¹, magnetism, and ferroelectricity², to phenomena in spintronics³, superconductivity⁴, and catalysis⁵, extending even to the emergence of mass in elementary particles^{6–8}.

In the synthesis of bulk crystals, symmetry reduction remains challenging as it typically relies on spontaneous symmetry-breaking mechanisms, such as octahedral tilts in perovskites or cooperative Jahn-Teller distortions^{9–12}, which are inherently difficult to control. By the very nature of structural phase transitions, a new symmetry is set by the long-range ordering of local distortions. Here we propose an alternative approach that can be employed in disordered crystals, where symmetry reduction is achieved through growth–guide short-range ordering of defects.

We demonstrate this method on the ordering of hexacyanometallate vacancies in a disordered Prussian Blue Analogue (PBA). In this system, while the average structure maintains cubic symmetry, the local structure is highly anisotropic. The vacancies order preferentially along the crystal growth

direction, resulting in a symmetry reduction from cubic to tetragonal (**Figure 1**). This symmetry reduction manifests itself in optical properties such as the appearance of birefringence, highlighting the potential of Growth–Guided Local Ordering for tailoring material properties.

Prussian Blue Analogues is a broad family of cyanide materials primarily investigated for their potential applications in gas storage¹³, gas purification¹⁴, as catalysts^{15,16}, and as electrode materials^{17,18}. Some PBA representatives also exhibit rare magnetic and electronic effects like charge transfer^{19,20} or humidity-sensitive magnetism²¹.

Extensive research using conventional Bragg diffraction has revealed that PBAs can adopt cubic, orthorhombic, or rhombohedral symmetries¹⁷. For instance, in PBA battery cathode materials, the symmetry is often reduced to orthorhombic or rhombohedral due to cooperative A-site ions displacements¹⁷, octahedral tilts, cooperative Jahn–Teller distortions, columnar shift, etc. However, in PBAs containing a large number of vacancies, like our model system, these vacancies are typically considered disordered and the symmetry is reported to be $Fm\bar{3}m$. Our study focuses on Mn[Co] Prussian Blue Analogue with a composition $\text{Mn}[\text{Co}(\text{CN})_6]_{2/3} \cdot n\text{H}_2\text{O}$, whose

average structure shows this canonical cubic symmetry with Co and Mn atoms occupying alternating sites, connected by cyanide linkers, as shown in Fig. S1 and Fig. 3a.

The rest of the paper is organized as follows. We first use optical measurements to reveal unexpected birefringence in cubic PBA crystals, demonstrating deviation from cubic symmetry. Through combined Bragg and diffuse X-ray scattering analysis, we show that while the average structure remains cubic, the local structure is tetragonal due to preferential ordering of Co(CN)_6 vacancies along the [001] growth direction. Finally, we demonstrate that by growing crystals with {111} faces, we can achieve domains with trigonal symmetry, establishing growth direction as a powerful parameter for controlling crystal symmetry.

Results

Optical Observations

We have grown single crystals of Mn[Co] Prussian Blue Analogue (Mn[Co]-PBA) in Agar gel media, resulting in well-formed cubes (Figure 1a). When placed between crossed polarizers, these cubic crystals show a distinct light contrast pattern resembling pyramids (Figure 1b). This optical property known as birefringence emerges only in non-isotropic media. Birefringence implies an anisotropic direction in the crystal and indicates that the real symmetry of the given crystals is lower than the previously assumed cubic symmetry.

Mn[Co]-PBA crystals in crossed polarizers show a four-triangle contrast pattern, independent of which side the crystal is placed on. Such a contrast in cube-shaped crystals suggests that each cube consists of six square-based pyramid-shaped twins, likely having tetragonal crystal symmetry (Figure 1c, d).

This observation apparently contradicts the well-known fact that disordered PBAs have $Fm\bar{3}m$ symmetry in their average structure. To reconcile this discrepancy, we first employed classical Bragg diffraction approach.

Average Structure

High-resolution single-crystal XRD

To investigate potential deviations of Mn[Co]-PBA from cubic symmetry, we performed high-resolution reciprocal space mapping around 18 different Bragg peaks. Any deviation from cubic symmetry would manifest through the formation of strain or ferroelastic domains, resulting in the corresponding splitting of the Bragg peaks.

In all cases, the observed Bragg peaks were distributed over several detector pixels without any apparent peak splitting. We analyzed the corresponding rocking curves, which represent the ω -dependencies of diffraction intensities integrated over the relevant detector area. Supplementary Figure S2 illustrates three such rocking curves from the 222, 026, and 080 Bragg peaks, corresponding to scattering angles of 30° , 55° , and 72° , respectively. The width of each rocking curve is below 0.02° , which is close to the instrument's resolution limit. For comparison, we included the rocking curves of the 111, 113,

and 133 reflections from a silicon crystal, measured at similar scattering angles.

These high-resolution measurements demonstrate the absence of peak splitting, strongly indicating the absence of strain domains and supporting the preservation of cubic symmetry in the average structure of Mn[Co]-PBA (Figure S1).

Single-crystal Bragg diffraction from untwinned portion

To further investigate the apparent discrepancy between optical observations and the average structure, we performed single-crystal X-ray diffraction (XRD) on an isolated section of the crystal. This section, approximately $40 \times 50 \times 40 \mu\text{m}^3$ in size, was carefully cut from a bigger crystal to correspond to only one of the six pyramidal domains observed optically. The measured dataset showed reliability factors $R_{\text{int}}(\text{cubic}) = 3.28\%$ and $R_{\text{int}}(\text{tetragonal}) = 3.16\%$, indicating negligible preference for tetragonal symmetry. The Bragg peak intensity distribution followed cubic symmetry, and automatic Laue group analysis resulted in the $m\bar{3}m$ point group, consistent with cubic symmetry.

Structure refinement in the cubic space group $Fm\bar{3}m$ yielded reliability factor $wR2(\text{cubic}) = 12.87\%$ (Tables S2 and S3 with the refined structure parameters in cubic and tetragonal settings respectively). After transforming the refined structure to a tetragonal $I4/mmm$ group and performing refinement with this lower symmetry, we obtained a marginally better $wR2(\text{tetragonal}) = 12.76\%$. The tetragonal structure revealed no significant displacements of the atomic positions (Table S4 and Fig. S5). The R-factor improvement (Table S5, Fig. S6) came from a slight change in anisotropic displacement parameters (ADPs) attributable to systematic errors of the experiment.

In short, conventional diffraction approaches do not detect any clear indications of symmetry breaking from cubic to tetragonal in the average structure, despite the optical evidence in the form of birefringence suggesting lower symmetry.

Local Structure

To resolve the apparent contradiction between optical properties and the symmetry suggested by diffraction experiments, we measured diffuse scattering as a probe of local structure from the untwinned portion of the crystal.

The Co(CN)_6 vacancies, though disordered on average, have a strong local order²². In diffraction experiments, this local order manifests itself as characteristic “squares” of diffuse scattering around the Bragg peaks (Fig. 2a). Unlike the Bragg peaks, which follow cubic symmetry, the diffuse scattering clearly shows tetragonal symmetry. Notably, the pattern is sharp along the c -axis — which corresponds to the crystal's growth direction — but broad in other directions.

This diffuse signal can be explained by correlations between Co(CN)_6 occupancies and indicates their non-random distribution in the network on the local scale. Anisotropy of diffuse scattering shape reflects a highly ordered arrangement of hexacyanometallate ions and vacancies along the growth direction, contrasting with weaker correlations along other

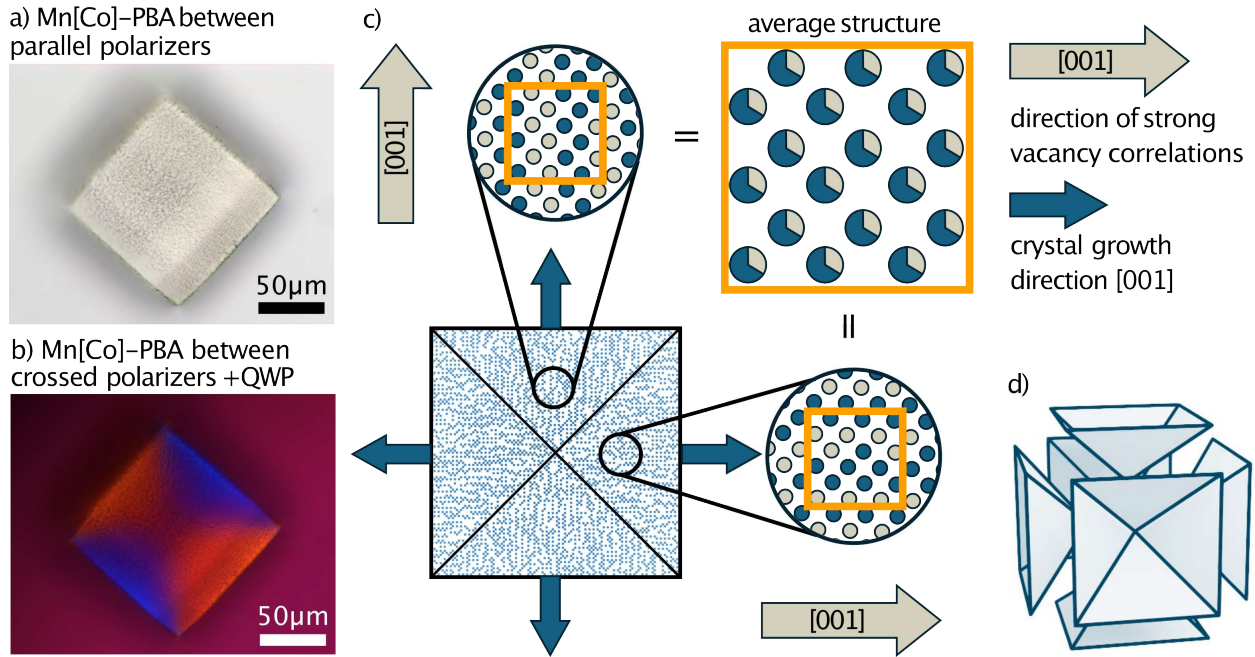


Figure 1. Mn[Co]-PBA crystals grow in the shape of cubes (a). When placed between crossed linear polarizers, these crystals show weak optical birefringence and two-color contrast when, in addition to crossed polarizers, a quarter-wave plate (QWP) is inserted (b). Such optical contrast suggests that each crystal cube consists of six square-pyramidal domains (c,d). Using Bragg and diffuse scattering analysis, we show that all six domain states share the same average structure with the cubic spacegroup $Fm\bar{3}m$. However, their optical properties are dictated by the local structure, which is tetragonal. This symmetry lowering is caused by the anisotropic ordering of hexacyanometallate vacancies with a strong correlation along the [001] growth directions (c).

axes Figure 1c). This alignment pattern likely reflects the crystal assembly process. During growth, the incomplete surface layer necessarily exhibits lower (tetragonal) symmetry. In ordered crystals, subsequent layer formation typically restores full bulk symmetry. However, in our system, the initial surface-imposed arrangement of defects becomes locked in, preserving a memory of the growth surface symmetry within the cubic average structure.

3D- Δ PDF Analysis

To quantify the degree of local order, we employed three-dimensional difference pair distribution function analysis (3D- Δ PDF). This method provides information about the spatial correlations in the distribution of $\text{Co}(\text{CN})_6$ clusters and their vacancies (Fig. 3b), as well as correlations in static displacements around these vacancies. To obtain this 3D- Δ PDF map, we first refined all substitutional and displacive correlations simultaneously for all the pairs available in the direct space (Figs. S8). Afterward, we separated the signal into two portions: the diffuse signal arising due to the substitutional correlations and to the displacive correlations (Fig. S9). Among these, the analysis of displacive correlations is not covered in this work and can be found in ²³.

The 3D- Δ PDF map, Fig. 2b, reveals a non-random distribution of vacancies characterized by short-range vacancy-

vacancy avoidance. This ordering pattern is most pronounced for the first-neighbor distance, corresponding to interatomic vectors such as $1/2\ 0\ 1/2$. Specifically, if a certain site is vacant, its nearest neighbors are more likely to be occupied than would be expected from a random distribution of vacancies.

For second-nearest neighbors, we observe positive correlations, with slightly stronger correlations along the [001] direction compared to the [100] and [010] directions. Beyond this range, the decay of correlations exhibits significant anisotropy: along the [001] direction, correlations persist up to a length of approximately 18 unit cells, while in the [100] and [010] directions, the correlation length is only about 8 unit cells (Fig. 2c).

This anisotropy in vacancy ordering induces statistically tetragonal $4/mmm$ Laue symmetry in the crystal, which manifests macroscopically as birefringence. Furthermore, this directional ordering has implications for the pore network characteristics: vacancy channels exhibit slightly better connectivity within planes perpendicular to the c -axis than along the c -axis itself.

Here, we clarify the discrepancy in symmetry identified by Bragg diffraction and diffuse scattering. According to Von Neumann's principle, any crystal's property will be at least as symmetric as the underlying structure⁸. Since diffuse

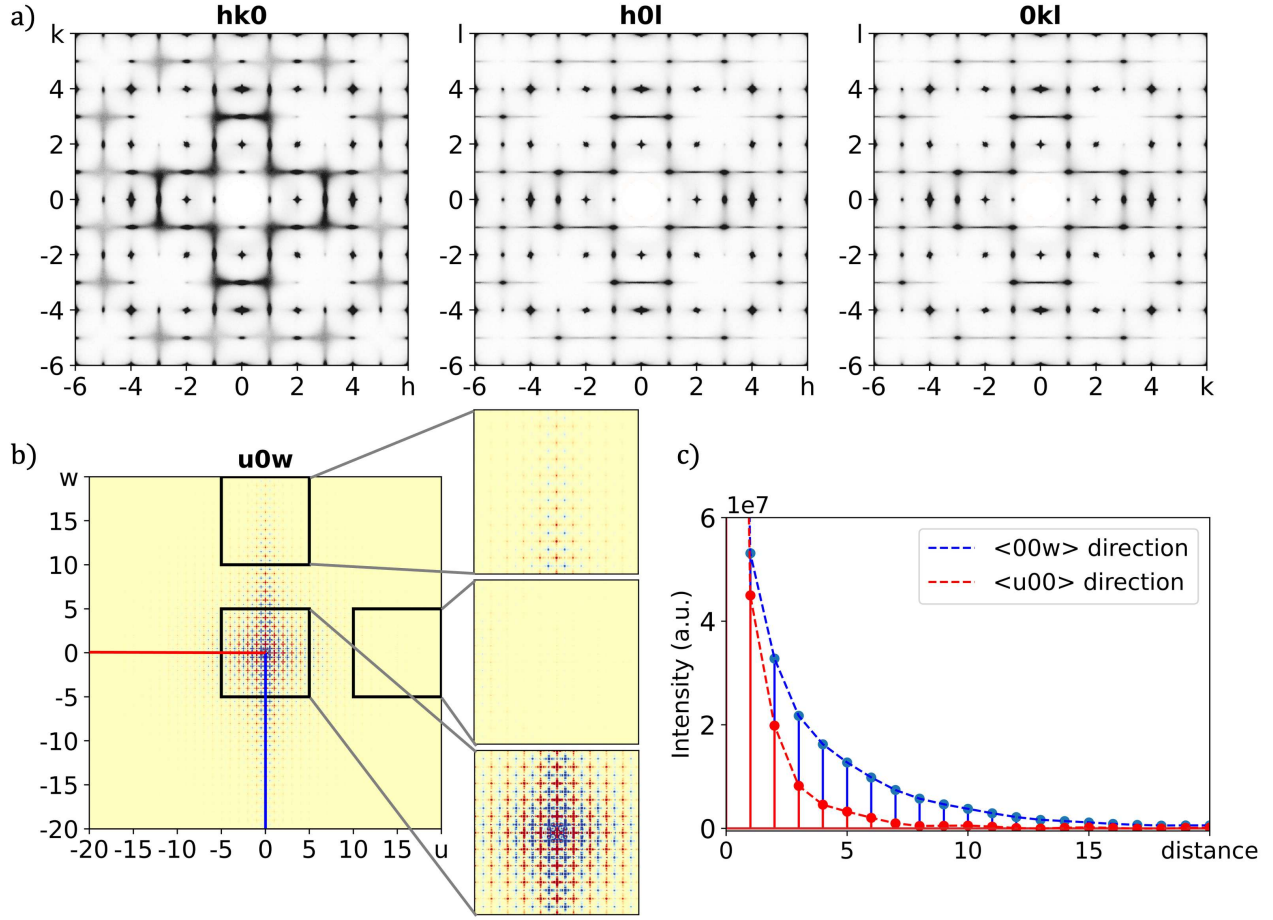


Figure 2. Single crystal diffuse scattering from Mn[Co]-PBA. (a) Three cross-sections, $hk0$, $h0l$, and $0kl$, of the reconstructed three-dimensional-diffuse-scattering dataset. This dataset contains Bragg peaks at even h, k, l , and diffuse-scattering located in between. The characteristic diffuse scattering on a border of the Brillouin zone can be explained by non-random $\text{Co}(\text{CN})_6$ distribution. The intensity distribution of this diffuse scattering follows tetragonal symmetry, indicating anisotropic vacancy distribution in Mn[Co]-PBA. The difference in diffuse-scattering symmetry can be seen well by comparing the diffuse feature around $(h+1, k+1, 0)$, with $h, k = \text{odd}$ on the $hk0$ plane versus the $h0l$ plane. Diffuse scattering becomes sharp along the l direction, which breaks the three-fold rotation along $\langle 111 \rangle$ directions. We demonstrate the difference in the length of vacancy correlations along two perpendicular directions (c) by plotting the profiles of 3D- Δ PDF signals, which indicate the strength of vacancy correlations. The color code is the same as in (b).

scattering reveals tetragonal symmetry ($4/mmm$), the crystal's true symmetry must be tetragonal. The apparent cubic symmetry seen in Bragg diffraction reflects the fundamentally different roles of local and average structure: symmetry reduction is driven by local vacancy ordering during growth, while changes in the average structure remain too subtle for conventional diffraction to detect. Throughout this paper, we use 'cubic average structure' and 'tetragonal local structure' as convenient shorthand, acknowledging that the average structure's deviation from cubic symmetry, while mathematically necessary, is experimentally undetectable.

Real-Space Model

To obtain a real-space representation of the local ordering, we performed Monte Carlo simulations based on a model similar

to that described in our previous work by Simonov *et al.*²². The MC model incorporates two terms:

- J_1 : The nearest-neighbor interaction enforcing electrostatic neutrality and driving the main feature of local order – negative correlations between nearest-neighbor vacancies.
- J_2 : A weak next-nearest-neighbor interaction describing positive vacancy correlations along cubic $\langle 100 \rangle$ directions. To account for the observed tetragonal symmetry, we split this parameter into $J_{2,x} = J_{2,y}$ and $J_{2,z}$.

To reproduce the observed diffuse-scattering pattern, we found that the strength of $J_{2,z}$ must be set approximately six times that of $J_{2,xy}$.

Fig. 3 illustrates the resulting real-space vacancy configurations in three perpendicular cross-sections. In the xy plane, vacancies exhibit no preferential ordering direction but tend to avoid one another in a checkerboard-like pattern, resulting in diagonally connected pore channels. In contrast, the xz and yz cross-sections reveal strong vacancy ordering along the $[001]$ direction, with the enhanced $J_{2,z}$ interaction ensuring weaker vacancy connectivity along this axis (Fig. 3d).

Figure S10 compares the calculated diffuse scattering from these simulated structures with experimentally measured diffuse scattering, demonstrating good agreement.

The $[001]$ direction, characterized by longer vacancy correlations, corresponds to the crystal growth direction. This suggests that during crystal formation, incoming Co(CN)_6 building blocks are more strongly influenced by the already-incorporated blocks beneath them than by neighboring blocks on the surface. Such behavior is consistent with a layer-by-layer growth mode.

As the crystal grows simultaneously in all six directions, the resulting cube comprises six square-based pyramids. Each pyramid has a tetragonal direction with a high degree of vacancy order pointing outward from the cube face. This represents a highly unusual type of twinning: while traditional twins comprise domains with the same low-symmetry average structure in different orientations, here all domains share an identical cubic average structure but differ in the orientation of their local vacancy ordering. The twin boundaries at cube edges form more defective regions where these different ordering patterns meet, explaining the previously observed selective etching along cube edges in Fe[Fe]-PBA microcrystals²⁴.

To our knowledge, examples of such symmetry breaking due to local ordering in crystals are extremely rare. This scarcity is particularly striking given that computational growth models of disordered crystals consistently predict symmetry reduction along the growth direction²⁵. Theory suggests that, unless the model is specifically constructed²⁶, the symmetry of disordered crystals must always reflect the growth process. Yet experimental observations of this effect have remained elusive. Hulliger et al. described similar effects in host-guest organic molecular crystals^{27–30}. However, in their work, the low symmetry arises from the alignment of asymmetric molecules within the host network, directly affecting the average structure. Our work demonstrates symmetry lowering in a crystal with a cubic lattice and highly symmetric cubic building blocks. The symmetry of these crystals is defined solely by the arrangement of Co(CN)_6 building blocks during the crystal assembly process.

We propose that this apparent scarcity of experimental observations may be due to the inherent difficulty in detecting these effects: since these crystals invariably grow as twins, their structural anisotropy is effectively masked in average structure measurements. The symmetry reduction only becomes apparent when examining diffuse scattering from individual twin components, as we have done here. This suggests that growth-guided symmetry breaking may be far more preva-

lent than previously recognized, but has simply gone undetected due to the limitations of conventional characterization approaches.

Symmetry Control Through Growth Direction

So far we have shown how growth along the $[100]$ direction results in crystals with tetragonal symmetry, but we can use it to achieve different symmetries by selecting another growth direction. When grown with excess MnCl_2 , Mn[Co] PBAs develop into cubeoctahedra with both $\{111\}$ and $\{100\}$ faces. The relative size of the $\{111\}$ faces can be controlled through the $\text{Mn}^{2+}:\text{Co(CN)}_6^{3-}$ concentration ratio.

Mueller polarimetry microscopy provides evidence for new symmetry domains in these cubeoctahedral crystals (Figure 4). The false colors in the crystal images indicate the direction of the fast optical axis, i.e., the orientation where polarized light experiences the lowest refractive index and thus travels fastest through the material, and the intensity of the color is proportional to the value of retardance (the brighter colors relate to more retardant, black – to non-retardant areas). In each domain of the cube-shaped crystal, the fast axis points along the growth direction, toward the nearest $\{100\}$ face. In crystals with small $\{111\}$ faces (Figure 4), in addition to four $\{100\}$ -type domains, one can see additional thin domains stretching along the cube diagonals. These new domains correspond to growth toward the $\{111\}$ faces. In crystals with larger $\{111\}$ faces, these diagonal domains become more pronounced, and the $\{100\}$ faces show a more complex color gradient that likely reflects the interaction between signals from different domain types through the crystal depth (Figure 4). Interestingly, Mueller matrix analysis shows that in contrast to $\{100\}$ -type domains, in which the fast axis was pointing towards the growth direction, in $\{111\}$ -type domains their *slow* axis is oriented along the growth direction.

Symmetry analysis shows that $\bar{3}m$ is the highest symmetry subgroup of the cubic structure that could describe $\{111\}$ domains, a prediction strongly supported by our optical measurements. This indicates that growth along $\langle 111 \rangle$ directions likely produces domains with trigonal symmetry, analogous to how $\langle 100 \rangle$ growth yields tetragonal domains. Unfortunately, the crystals exhibiting these $\{111\}$ domains are quite small and possess complex overlapping domain patterns. These limitations currently prevent us from performing a detailed diffuse-scattering analysis that would reveal the three-dimensional distribution of vacancies within these domains. However, future diffuse-scattering tomography studies would be valuable in mapping out these vacancy distributions and fully understanding how growth direction controls the symmetry of the resulting domains.

These findings demonstrate that growth direction serves as a powerful parameter to engineer crystal symmetry. This represents an entirely new approach to symmetry control – one that operates through the organization of defects during crystal growth. The method is remarkably practical, as growth direction for bulk crystals can be controlled through

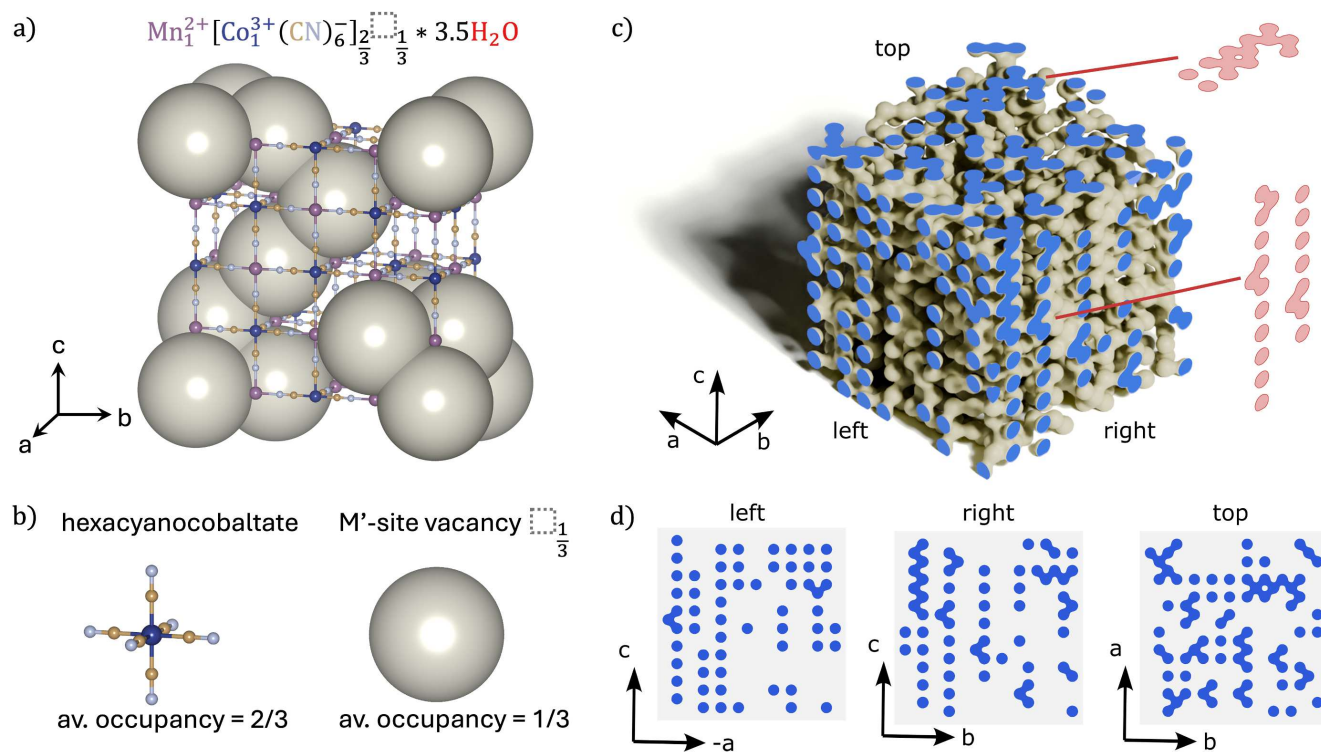


Figure 3. (a) The Mn[Co]-PBA structure consists of Mn and Co ions linked by cyanides. (b) Due to the electroneutrality condition, one-third of the hexacyanocobaltate clusters are absent and replaced with large vacancies, which we represent as beige spheres. (c) MC simulations of a supercell of Mn[Co]-PBA show highly anisotropic distribution of the vacancies. For clarity we remove all atoms and only show the vacancies, moreover three vacancy planes which are facing the viewer are colored in blue. In red, we present characteristic motifs of the vacancy distributions: long chains of ordered vacancies along the z axis evident on the “left” and “right” faces and symmetric distribution on the top face. (d) The same pattern can be seen in the cross-sections of the model: on the left and right faces, the predominant motif is a one-dimensionally ordered chain of vacancies stretched along the z axis, while on the top face, the vacancies are distributed symmetrically. Note that we use the term “vacancy” to indicate an empty hexacyanocobaltate site. In reality, these vacancies are filled with water molecules.

standard crystallization techniques, like surfactant addition or geometry of growth vessel geometry; for epitaxial thin films the growth direction can be controlled by a substrate. This provides a straightforward yet powerful way to tailor symmetry-dependent properties in disordered materials.

Discussion

Crystal symmetry is conventionally understood through the lens of average structure, but local structural correlations can independently drive symmetry reduction. Here we demonstrate how the spatial distribution of point defects can become a powerful tool for symmetry control, even in materials where the average structure maintains high symmetry. We demonstrate this effect in Mn[Co]-Prussian Blue Analogues. While classical crystallographic approaches indicate that the average structure is cubic with space group $Fm\bar{3}m$, our diffuse scattering analysis reveals a different picture at the local scale. Vacancies exhibit strong correlations along the crystal growth direction and shorter-range correlations in the perpendicular planes. In cubic crystals this anisotropic vacancy distribution

effectively reduces the local symmetry to tetragonal $4/mmm$ and results in enhanced pore connectivity within the planes perpendicular to the growth direction. In cubeoctahedral crystals, alongside tetragonal domains, this leads to the formation of domains with trigonal symmetry.

This observation exemplifies a broader effect we term ‘Growth-Guided Local Ordering’ which can control symmetry in disordered crystals. The effect relies on two key conditions: first, the crystal must exhibit a disordered average structure; second, the growth process must lock in the arrangement of disordered atoms or molecules, preventing subsequent reorganization. When the disordered building blocks are highly symmetric, as in Mn[Co]-PBA, this mechanism leads to symmetry reduction solely in the local structure while preserving the high symmetry of the average structure. In our case, the insoluble nature of the material ensures that once the building blocks attach during growth, they do not rearrange, thus preserving the growth-induced anisotropy.

The straightforward requirements suggest broad applicability of the principle across various material systems, par-

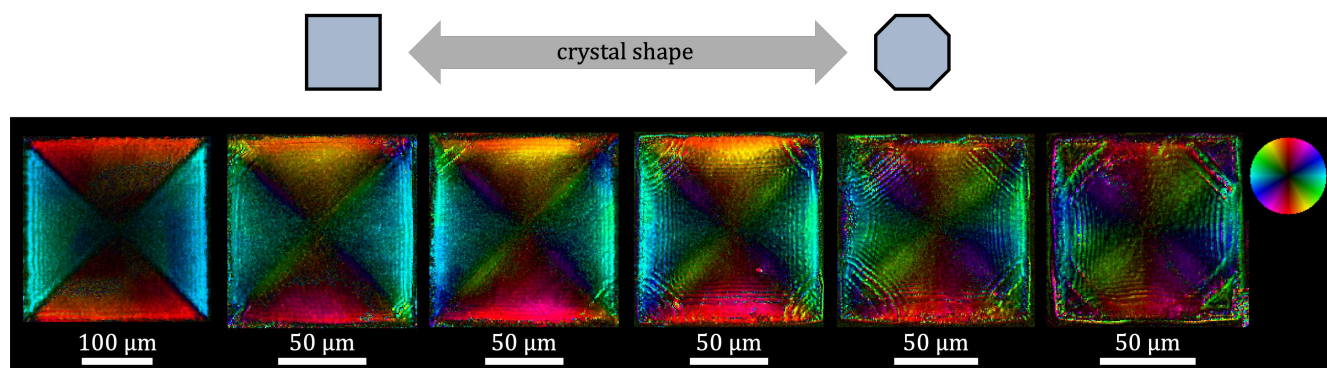


Figure 4. Mueller polarimetry of Mn[Co]-PBA crystals reveals the relationship between crystal morphology and domain structure. The color wheel (top right) indicates the direction of the fast optical axis, while color saturation represents retardance. Cubic crystals (left) exhibit four clearly visible triangular domains, with light blue domains indicating left-right fast axis orientation and red domains showing top-bottom orientation. Together with two domains along the viewing direction, this forms a pattern of six square-pyramidal domains, each with its fast axis aligned along the respective growth direction. Crystals with increasing degrees of truncation develop additional diagonal domains. These appear as thin lines at domain boundaries, colored bright pink and green, indicating fast axes oriented perpendicular to cube diagonals. The size of these diagonal domains increases with the degree of crystal truncation, proportional to the size of 111 faces.

ticularly those grown out of equilibrium where post-growth annealing (which would allow rearrangement) is avoided. In this paper, we demonstrated it for the crystal grown from solution, but we expect it to also work for electrochemical growth and growth from flux. Crucially, it transforms the complex task of altering crystal symmetry into the more manageable challenge of controlling growth direction, achievable through various established techniques such as the use of surfactants during crystallization, and thus provides an elegant solution to the complex task of engineering local symmetry in disordered crystals.

Methods

Synthesis

The single crystals of Mn[Co]-PBA were grown by the slow counter-diffusion of aqueous solutions of manganese (II) chloride, MnCl_2 (Fluka), and potassium hexacyanocobaltate (III), $\text{K}_3[\text{Co}(\text{CN})_6]$ (Sigma-Aldrich), in Agar gel media at 2°C . The growth was performed in 15 ml centrifuge tubes: first, the MnCl_2 (500 μmol) was dissolved in 1 % Agar gel (10 ml) and poured into the centrifuge tube. After the gel was set, the water solution of $\text{K}_3[\text{Co}(\text{CN})_6]$ (500 μmol in 5 ml H_2O) was added on top. The salts diffused through the gel, resulting in the precipitation of insoluble transparent cubic crystals over the course of two weeks. The cube-shaped crystals used for the measurements have a side length of around 100–200 μm and were extracted from the gel in the lower part of the centrifuge tube. The crystals shaped as truncated cubes were extracted from the very top gel layer; these crystals have sizes of 40–80 μm . Chemical analysis of these crystals was performed using EDX and yielded chemical formula $\text{K}_{0.15}\text{Mn}[\text{Co}(\text{CN})_6]_{0.71} \cdot x\text{H}_2\text{O}$ (for the cube-shaped crystals, Table S7) and $\text{K}_{0.16}\text{Mn}[\text{Co}(\text{CN})_6]_{0.73} \cdot x\text{H}_2\text{O}$ (for truncated

cubes, Table S8).

Single crystal XRD and Single crystal diffuse scattering measurements

Preliminary diffraction measurements of the Mn[Co]-PBA crystals were performed at the Swiss-Norwegian beamline (BM01)³¹ at the European Synchrotron Radiation Facility (ESRF), while the final datasets were collected at the beamline I19 at the Diamond light source. The datasets were measured at a wavelength $\lambda = 0.71 \text{ \AA}$ and beam size $260 \times 73 \mu\text{m}^2$ with Eiger2 4M CdTe detector. Bragg- and diffuse-scattering datasets were collected with full and attenuated beams (1 %), respectively. Each collection consisted of a single 360° rotation scan around the ϕ axis with a 0.1° step per frame.

Single crystals of 150 μm thickness were cut with a scalpel under a polarizing microscope to get the untwinned portion of a crystal. Using two-component epoxy glue, the crystals were glued to the Mitegen loops³².

Crystal orientation, indexing, and integration of the Bragg peaks were performed using the program XDS³³ and Dials³⁴; the reconstruction of diffuse-scattering-reciprocal-space maps was carried out using the program Meerkat³⁵.

Average structure analysis

Structure solution and refinement of Mn[Co]-PBA were done using the SHELX software suite³⁶ in conjunction with the Olex2 graphical interface³⁷. Using the same Bragg reflections, we performed refinements using cubic $\text{Fm}\bar{3}\text{m}$ and tetragonal $I4/mmm$ space groups. We took special care to ensure that the scaling in XDS³³ was made in tetragonal symmetry and the tetragonal axis is pointing along the unique $00l$ direction (which can be seen from the reconstructed $hk0$ plane in Fig. S3).

High-resolution single-crystal X-ray diffraction

High-resolution single crystal X-ray diffraction measurements were conducted using a custom-built four-circle X-ray diffractometer at Tel Aviv University³⁸ using a PILATUS 1M pixel area detector. The diffractometer is equipped with a double-crystal monochromator and was specifically designed to combine standard single-crystal X-ray diffraction measurements with high-resolution reciprocal space mapping capabilities. Various benchmarks^{38–40} demonstrate that the horizontal and vertical divergence of the beam is approximately 0.01° , with a relative wavelength dispersion of $2 \cdot 10^{-4}$.

A crystal of approximately $100\ \mu\text{m}$ thickness was attached to a double-sided tape and a flat-based metal holder, which provided better stability compared to the more standard Miti-Gen loops. The measurements began with the determination of the crystal orientation matrix, followed by high-resolution scans around specific Bragg peaks of interest. These peaks were chosen to represent a wide range of scattering angles (16° – 99°) and various combinations of the reflection hkl indices.

Three-dimensional pair distribution function analysis

Correlated disorder in Mn[Co]-PBA crystals was analyzed using Yell software⁴¹, which relies on the 3D- Δ PDF approach⁴². 3D- Δ PDF is a Fourier Transform of diffuse scattering and can be understood as the difference between the pair distribution function of the real crystal structure and the Patterson function calculated from its average structure. 3D- Δ PDF allows local structure analysis and refinement, expressed in pair probabilities of two atoms being found at a given lattice vector. Each signal in the 3D- Δ PDF at a position uvw corresponds to a pair of atoms ij in the structure such that $x_j - x_i = u$, $y_j - y_i = v$ and $z_j - z_i = w$. Signals in the 3D- Δ PDF can be positive or negative: for positive (negative) signals, the interatomic pairs appear more (less) frequently in the real structure than in the average structure. For a more in-depth introduction, see⁴².

For Fig. 2, the 3D- Δ PDF was calculated by punching out the Bragg peaks alongside the broad diffuse around Bragg peaks with large spheres and applying the Fourier Transform to get a three-dimensional map of interatomic lattice vectors with a slowly decaying signal, which indicates the strength of vacancy correlations. The reconstruction was done on the fine grid ($801 \times 801 \times 801$ pixels) to get access to long interatomic vectors.

For 3D- Δ PDF quantitative refinement, we have prepared a coarser reconstruction of diffuse scattering. We cleaned it from Bragg peaks by subtracting the area of three voxels centered at each Bragg peak by a punch-and-fill procedure, and subtracted the spherically symmetric background. We used the refined average structure from Bragg diffraction as the basis for the model. We refined all substitutional and displacive correlations simultaneously (Fig. S8) for all the pairs available in the direct space. The separated portions of the diffuse signal arising due to the substitution correlations

and the displacive correlations are represented in Fig. S9. The analysis of displacive correlations is not covered in this work and can be found in²³.

Monte Carlo modelling

The models of vacancy distribution for Mn[Co]-PBA were generated using Monte Carlo modeling. The custom scripts are included as supplementary files. The pair interaction parameters for this Monte Carlo simulation were calculated using the mean-field approximation. The details about this procedure are provided elsewhere²³.

The model is represented by an Ising-like Hamiltonian with pair-wise interactions. We include nearest-neighbor and second-nearest-neighbor interactions: $J_1 = 0.605$, $J_{2,x} = J_{2,y} = -0.0135$, and $J_{2,z} = -0.11$, while the temperature is set to 1.3. We generate 5,000 structures for the given parameters; each structure is represented by a $16 \times 16 \times 16$ supercell. Configurations are initialized with a random distribution of the vacancies such that one-third of the sites are vacant. Monte Carlo steps involve swap moves: one occupied and one vacant site are selected at random, and their contents are swapped. The configurations were equilibrated for 500 epochs (one epoch corresponds to the number of steps required to visit each site twice on average) with 20 epoch steps in between each produced structure.

The model of the structure is approximate, as the aim is not to represent an optimal model but the model that captures the essence of the ordered structure. The comparison between experimental diffuse scattering and the diffuse scattering calculated from the structures generated by Monte Carlo simulation is shown in Fig. S10.

Scanning electron microscopy and elemental composition

Images were taken using a Hitachi SU-70 scanning electron microscope (SEM, Schottky-type field emission gun) equipped with an X-Max energy dispersive X-ray (EDX) detector (Oxford Instruments) operated at 1 keV. EDX measurements were performed using a 15 keV accelerating voltage and Inca software. Point measurements were performed on at least three different crystals for each condition, and the values are reported as the average and standard deviation.

Mueller polarimetry microscopy

The polarimetric measurements were conducted with a custom-built Mueller polarimeter based on the inverted microscope Olympus IX73 (Fig. S12). The probing of the crystal was performed using a non-polarized diode at 625 nm, Thorlabs MCS103, coupled with an optical fiber (Thorlabs M122L02) and collimated with Thorlabs PAF2P-A15A. The polarization of the probe, referred to as polarization state generated (PSG), is controlled by a linear polarizer, PSG LP (Newport - 10LP-VIS-B), at 0° to enforce a linear state of the source, followed by a quarter-wave plate, PSG quarter-wave plate (Newport 10RP04-24), on a rotating stage (Thorlabs K10CR1/M) to control the PSG ellipticity through the PSG

QWP angle Θ_{PSG} . The samples were placed on a glass slide with index-matching oil to prevent scattering due to surface roughness and to minimize lensing effects caused by the sample geometry. The exit light is collected by an objective (depending on the measurement, Olympus UPLFLN4XP-2 x4/NA 0.13 or Olympus UPLFLN10XP-2 x20/NA 0.3). Polarization analysis is performed between the objective and the microscope frame tube lens to have parallel beams and to avoid angular artifacts on the polarization elements. The polarization states of the crystal (denoted PSA) are arranged in a symmetrical way with respect to the PSG using a quarter-wave plate on a rotating stage (Thorlabs K10CR1/M). The sensor, a CCD camera of 12-bit 1920×1200 pixels with 5.86 μm square pitch (IDS U3-3060CP-M-GL), is placed at the image plane of the tube lens to collect the resulting intensity images after the microscope's built-in dielectric mirror at 45°.

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Data availability

The raw data, along with the scripts used to produce the figures in this paper, are shared on the following doi:10.3929/ethz-b-000719385, <https://www.research-collection.ethz.ch/handle/20.500.11850/719385>.

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Author contributions statement

A.S. and Y.K. conceived the experiments, Y.K., T.W., J.B., A.S., D.C., and M.W. performed synchrotron diffraction experiments, Y.K., A.B., and M.L. performed Mueller microscopy experiments, T.A. performed scanning electron microscopy and EDX elemental composition measurements, S.G. and I.B. performed high-resolution diffraction experiments, Y.K., A.S., and A.B. performed data analysis. Y.K. and A.S. wrote the manuscript. All authors reviewed the manuscript.

Additional information

The authors declare no competing interests.

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