Reciprocal space imaging of ionic correlations in intercalation compounds

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The intercalation of alkali ions into layered materials has played an essential role in battery technology since the development of the first lithium-ion electrodes. Coulomb repulsion between the intercalants leads to ordering of the intercalant sublattice, which hinders ionic diffusion and impacts battery performance. While conventional diffraction can identify the long-range order that can occur at discrete intercalant concentrations during the charging cycle, it cannot determine short-range order at other concentrations that also disrupt ionic mobility. In this Article, we show that the use of real-space transforms of singlecrystal diffuse scattering, measured with high-energy synchrotron X-rays, allows a model-independent measurement of the temperature dependence of the length scale of ionic correlations along each of the crystallographic axes in sodium-intercalated V_2O_5 . The techniques described here provide a new way of probing the evolution of structural ordering in crystalline materials.

he cathodes of the first lithium-ion batteries developed over 40 years ago were materials with van der Waals-bonded layers between which the lithium ions could be rapidly intercalated and deintercalated^{1,2}. Since the first tests on Li_xTiS₂, many other intercalation compounds have been investigated as potential electrodes because of their rapid charging rates and inherent stability over multiple charge-discharge cycles3. Insertion of alkali ions between such weakly bonded layers is highly reversible because the weak coupling of the intercalants to the host produces only minor structural modifications during the electrochemical cycle. The potential use of multivalent ions in batteries has renewed interest in such materials⁴⁻⁶, although weak coupling can compromise a battery's gravimetric and volumetric energy density. The transition metal oxides most frequently used as cathodes in consumer electronics, such as LiCoO₂ (ref.⁷), are also layered materials, albeit with stronger host-intercalant interactions8.

Even if the interactions of the alkali ions with the host lattice are weak, the Coulomb interactions between the intercalants cannot be ignored, especially at high concentrations⁹. Voltage anomalies as a function of lithiation in TiS_2 were quickly ascribed to correlations between the intercalants induced by Coulomb repulsion¹⁰, causing changes in the configurational entropy and consequently the chemical potential for ion insertion¹¹. Berlinsky et al. showed that order–disorder transitions can be inferred from extrema in the voltage derivatives versus composition⁹. Such anomalies have also been observed in transition metal oxide cathodes^{12,13}, where they have been modelled using both lattice gas^{13–15} and first-principles methods^{16–18}. Ordering of intercalants impacts battery performance by disrupting ionic mobility, and there is evidence that suppressing ordering can improve charging rates¹⁹.

Order-disorder transitions are usually associated with discrete stoichiometries, corresponding to commensurate ordering of the intercalant sublattice. In Li_xCoO_2 and other transition metal oxides, ordering occurs at $x = \frac{1}{2}$ and a number of other rational fractions^{11,20-22}. Although it is possible to infer order-disorder transitions at these values from bulk measurements, direct evidence can

only be obtained by the observation of (often weak) superlattice peaks from unit-cell expansion in diffraction measurements. The low cross section of lithium makes this difficult with X-ray scattering, unless associated changes in the host lattice space group are observable. For this reason, electron diffraction provided the first conclusive evidence of lithium-vacancy ordering in $\text{Li}_{0.5}\text{CoO}_2$ (ref. ²³), showing unit-cell doubling both within and perpendicular to the planes. However, conventional Bragg diffraction is only sensitive to long-range order and cannot be used to probe short-range correlations, which will also play a role in decreasing ionic mobility across the whole composition range. Understanding such correlations is important in modelling diffusion kinetics, for example as a function of concentration fluctuations close to the electrolyte interface.

The most powerful technique to probe short-range correlations is single-crystal diffuse scattering, using either X-rays or neutrons, which comprises all the scattering that results from nanoscale deviations from the average crystalline structure²⁴⁻²⁶. The average occupancies of all the atomic sites within the translationally invariant unit cell of a crystal can be determined from Bragg peak intensities using standard crystallographic techniques, but, apart from thermal diffuse scattering from lattice vibrations, all the scattering between (and under) the Bragg peaks results from the presence of local disorder, often in the form of point defects, such as interstitials and vacancies, or of short-range order from defect-defect correlations. When measured over a sufficiently large volume of reciprocal space, diffuse scattering contains a true thermodynamic average of disorder scattering from the entire sample and so is complementary to techniques that utilize X-ray coherence to reconstruct real-space images of atomic correlations over a limited coherence volume.

Although it is an extremely powerful technique, single-crystal diffuse scattering has not been as widely utilized as, for example, pair-distribution-function (PDF) measurements of polycrystalline materials²⁷, because of the challenge of both measuring and modelling large volumes of reciprocal space (\mathbf{Q} space). By contrast, the PDF technique, which gives a one-dimensional spherical average of interatomic vector probabilities, has become a standard tool in

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materials science because the information can be interpreted intuitively and modelled effectively with existing software. In recent years, Thomas Weber and colleagues have shown that it is possible to extend the PDF technique to three dimensions by transforming single-crystal diffuse scattering into real space²⁸. The result is a Patterson function, containing the summed probabilities of interatomic vectors in the crystal with contributions from both the average structure and local disorder. By excluding Bragg scattering from the real-space transform, the resulting PDF function only includes those interatomic vectors whose probabilities differ from the average (3D- Δ PDF). This is not possible in polycrystalline data because of the substantial overlap of Bragg and diffuse scattering intensity, but in single crystals it allows a determination of the length scales of short-range order extending over 100 Å or more. By exploiting a new generation of fast area detectors, it is possible to measure sufficiently complete three-dimensional volumes of reciprocal space in under 20 min using high-energy X-rays at a synchrotron source, enabling the generation of robust $\Delta PDFs$ fast enough to allow detailed studies as a function of temperature.

We have applied this technique to measure ionic correlations in single crystals of V_2O_5 intercalated with sodium ions. In β -Na, V_2O_5 , the sodium ions are confined to two-leg ladders²⁹, but the configuration of ions within the partially occupied ladders cannot be determined by powder diffraction alone. The Δ PDFs reveal the tendency for sodium ions to form zigzag configurations within each ladder, which are in phase with those in neighbouring ladders, as well as the temperature dependence of the correlation length of this ordering in all three crystallographic directions, obtained from the exponential decay of the \triangle PDF intensities. It has previously been reported that this material undergoes a structural phase transition just above 200 K (ref. ³⁰), but our results show that this temperature marks a crossover from two- to three-dimensional correlations without true long-range order being established down to 30K. In the following Article, we describe the measurement process in more detail, the steps used to generate the 3D- Δ PDF results and the subsequent analysis to extract ionic correlation lengths, before discussing the implications of this technique for studying battery electrodes. Although the focus of this Article is on intercalation compounds, the techniques described here are applicable to any investigations of crystalline disorder.

The orthorhombic structure of pure V₂O₅ consists of both edgeand corner-shared square pyramids that form van der Waals-bonded planes, between which a variety of cations may be intercalated³¹. However, for some intercalants above a critical concentration, the structure transforms to a monoclinic β -phase (space group C2/m) with a more complex network of vanadium oxide octahedra and square pyramids that contain one-dimensional channels, into which the intercalated cations are inserted (Fig. 1)^{29,32,33}. It has recently been proposed that the tunnel framework improves structural stability during intercalation/deintercalation^{34,35}. In β -Na, V₂O₅ (0.2 $\leq x \leq 0.5$), the intercalants partially occupy a sublattice of two-leg ladders, whose legs are parallel to the crystal's b axis and whose rungs are parallel to the *c* axis. The ladder sites would be filled with a value of $x = \frac{2}{3}$, but stereochemical constraints prevent occupations much greater than 50% since the ladder rungs are too short (<2 Å). It has been postulated that the excess sodium ions would occupy additional octahedral and tetrahedral sites for x > 0.33 in a β' -phase³⁶, but these have never been conclusively observed (see Supplementary Fig. 15). In Supplementary notes, we discuss features in our data that provide evidence in favour of the octahedral site occupation preferred in ref.³⁶.

We measured diffuse X-ray scattering on single crystals of β' -Na_xV₂O₅ with x=0.45, corresponding to 68% occupation, using high-energy monochromatic beams at two synchrotron X-ray sources, the Advanced Photon Source (APS) and the Cornell High Energy Synchrotron Source (CHESS). Advances in the dynamic range and speed of X-ray area detectors now allow both the Bragg peaks and diffuse scattering to be measured efficiently, with



Fig. 1 | The monoclinic structure of Na_{0.45}V₂O₅ (space group C2/*m*), with a = 15.34 Å, b = 3.61 Å, c = 10.04 Å and $\beta = 109.6^{\circ}$ at 100 K, derived from the Crystallographic Information File of ref.³². The sodium ions (green) sit on two-leg ladders with rungs parallel to the crystallographic *c* axis in channels parallel to the *b* axis formed by the lattice of edge- and corner-shared vanadium oxide octahedra and square pyramids (blue). Neighbouring ladders along the *a* axis, that is, at $\pm \frac{1}{2}a$, are displaced by $\frac{1}{2}b$. Dashed lines show the unit-cell boundaries.

three-dimensional volumes of scattering in reciprocal space, $S(\mathbf{Q})$, collected in under 20 min at each temperature. More details are given in Methods and Supplementary methods.

The diffuse scattering is mostly confined to rods that are parallel to H, that is, orthogonal to the ladders, occurring at half-integer values of K (Fig. 2), from which we can infer that there is predominantly two-dimensional short-range order within the ladder planes generated by ionic correlations within the sodium sublattice that tend to double the unit cell along b. A sinusoidal modulation of the rod intensities as a function of L, parallel to the direction of the ladder rungs, whose periodicity is the inverse of the rung length, indicates that site occupations across each ladder rung are strongly correlated. At room temperature, there are no sharp peaks along the rods (Fig. 2c), which are broad laterally (~0.1 Å⁻¹ along K and ~0.13 Å⁻¹ along L), indicating that correlation lengths are of the order of 10-20 Å. However, below ~230 K, peaks start to appear at all integer values of H (Fig. 2b), growing steadily in intensity down to the lowest measured temperature of 30 K (Fig. 2a). These peaks are evidence of the development of longer-range three-dimensional correlations within the sodium sublattice below ~230 K, in agreement with previous X-ray measurements^{30,37}.

Most analyses of diffuse scattering require a calculation of the **Q** variation of the data using atomistic models that parametrize the disorder, but an alternative approach is to Fourier transform the data to generate real-space PDFs. This has the advantage of converting complicated intensity distributions in reciprocal space into discrete peaks in real space, whose positions and intensities are given by the interatomic vectors present in the disordered structure and their weighted probabilities, respectively. A further simplification is to include in the generated PDFs only those peaks whose probabilities deviate from the average structure. This is possible using the 'punch and fill' method pioneered by Weber and colleagues²⁸, which utilizes the fact that the total scattering can be separated into two components: one representing the average crystal, that is, the Bragg peaks, and the other representing the diffuse scattering from crystalline defects.

$$I_{\text{tot}}(\mathbf{Q}) = F(\mathbf{Q})F^{*}(\mathbf{Q}) = |F_{HKL}(\mathbf{Q})|^{2} + |\Delta F(\mathbf{Q})|^{2}$$
(1)

where $I_{tot}(\mathbf{Q})$ is the measured total scattering and $F(\mathbf{Q})$ is proportional to the Fourier transform of the electron density. The Fourier transform of this scattering function is also separable.

$$P_{\text{tot}}(\mathbf{r}) = \text{FT}[|F_{HKL}(\mathbf{Q})|^2] + \text{FT}[|\Delta F(\mathbf{Q})|^2]$$

= $P_{HKL}(\mathbf{r}) + \Delta P(\mathbf{r})$ (2)

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Fig. 2 | **Diffuse scattering and** Δ **PDF from Na**_{0.45}**V**₂**O**₅**. a**-**f**, Diffuse scattering is shown in the **Q** = $(H\frac{1}{2}L)$ plane at 50 K (**a**), 200 K (**b**) and 250 K (**c**), displayed in reciprocal lattice units (r.l.u.), and the resulting Δ PDF in the (0*yz*) plane at 50 K (**d**), 200 K (**e**) and 250 K (**f**), displayed in lattice units (l.u.), that is, units of *a*, *b* and *c* along the *x*, *y* and *z* directions, respectively (Fig. 1). See Supplementary Figs. 4 and 10 for larger versions of **a**-**c** and **d**-**f**, respectively.

 P_{HKL} is the Patterson function of the average structure while $\Delta P(\mathbf{r})$, or the 3D- Δ PDF, is the difference Patterson function due to the disorder. The punch and fill method isolates $\Delta P(\mathbf{r})$ by eliminating the Bragg peaks, that is, by removing the scattering in a small sphere around each Bragg peak and interpolating over the missing data, before performing the Fourier transform (Supplementary Fig. 7).

We have used this technique to produce Δ PDFs that eliminate any contribution from the framework V₂O₅ lattice to first order and leave only the sodium-sodium pair correlations. In the case of purely substitutional disorder, when local relaxations can be neglected, Weber and Simonov show that the 3D- Δ PDF consists of peaks at real-space vectors that connect the disordered sites (see, for example, equation (14) in ref.²⁸). The intensity of the peaks is given by the difference between the conditional probability that if one site is occupied the connected site is also occupied, and the average occupation. This means that Δ PDF peaks can have either positive or negative intensities. In the average structure determined by powder diffraction³² the sodium ladder sites are randomly occupied with a probability of ~0.5, so this difference can range from 0.5 to -0.5, but in a disordered structure the absolute peak intensities will in general decay with increasing distance as the correlated site occupations become increasingly random. The decay constant gives the correlation length of the substitutional ordering.

Figure 2d–f shows the Δ PDF in the *b*–*c* plane, displayed in a symmetric log plot, which consists of a repeating triplet pattern of peaks with positive (red) intensity and negative (blue) intensity. With increasing distance from the origin, the absolute intensity of these peaks diminishes as expected. At 250 K (Fig. 2f) these correlations extend over only a few neighbouring sodium ladders, but as the temperature is lowered the correlation length increases substantially,

as seen at 200 K (Fig. 2e). At 50 K, the correlations extend over more than 100 Å in all directions (Fig. 2d). This is the real-space corollary of the growing intensity and sharpness of the reciprocal space peaks shown in the insets to Fig. 2a-c.

Some immediate conclusions can be drawn by inspection of the Δ PDF without detailed modelling. We show in Fig. 3 a comparison of the two-leg ladders within the y-z plane and the corresponding 3D- Δ PDF. The triplets of red-blue-red and blue-red-blue peaks are entirely consistent with this ladder structure, producing threeleg ladders because the origin of each interatomic vector can be on either leg. This is a consequence of analysing scattering amplitudes without phase information, so that $\Delta P(\mathbf{r}) = \Delta P(-\mathbf{r})$. By choosing one of the sodium sites to be occupied, we can determine the other neighbouring sites that are occupied (unoccupied) by identifying all the interatomic vectors that have positive (negative) Δ PDF intensity. In Fig. 3, we show the resulting configuration of occupied sites by indicating atoms on unoccupied sites with lighter colour. This shows that all the nearest-neighbour sites within the ladder are likely to be unoccupied, but next-nearest-neighbour sites are likely to be occupied, leading to a zigzag configuration. This is to be expected from considerations of both stereochemistry and Coulomb repulsion, but the Δ PDF also makes clear that these zigzag configurations are in phase with neighbouring ladders, since the vectors connecting sites on the same leg (left or right), that is, with $\pm ma \pm nc$, where m and n are integers, have positive probability, whereas those connecting the opposite legs have negative probability.

There are weaker Δ PDF peaks in other planes that could be associated either with additional sodium sites, such as those proposed by Galy et al.³⁶, or with relaxations of the vanadium and oxygen ions. In the scattering data, additional superlattice peaks are also







Fig. 4 | a-**c**, Fits to the temperature dependence of Δ PDF peak intensities. Fits are shown along the *x* direction (**a**), *y* direction (**b**) and *z* direction (**c**). The model is the product of an exponential decay from the pair correlations and a Gaussian envelope from the finite **Q** resolution. The data are shown from 50 K (blue) to 250 K (red) in steps of 50 K.

observed at $K = \pm \frac{1}{6}$, below ~130 K, which is the temperature of a metal-insulator transition ascribed to V⁴⁺/V⁵⁺ charge ordering^{37,38}. These give rise to a weak modulation of the Δ PDF intensity along the *y* axis, but do not appear to affect the sodium correlations. The additional peaks are shown in Supplementary Fig. 5.

To quantify the growth in correlations, we have modelled the dependence of the absolute Δ PDF peak intensities on interatomic distance by analysing one-dimensional slices selected to eliminate all but allowed sodium-sodium vectors (Supplementary Figs. 11 and 12). Figure 4 shows that these intensities follow an exponential decay at high temperature, consistent with a one-dimensional Ornstein-Zernike function³⁹. At lower temperature, it is necessary to include the effect of the finite resolution in reciprocal space, which produces an envelope function that suppresses the real-space transform at large distances. Its Gaussian width can be estimated by fitting the total PDF, that is, the data transformed without eliminating the Bragg peaks, which represents long-range crystalline order (Supplementary Figs. 8 and 9). The Δ PDF intensities in Fig. 4 have been fitted to the product of this Gaussian envelope function with a temperature-dependent exponential decay function, whose decay constant is a direct measure of the correlation length, ξ .

The temperature dependence of these fits is shown in Fig. 4 along all three crystallographic directions. As the correlation length approaches 200 Å, the effect of the finite resolution leads to an increase in the error bars, although ξ and the r=0 amplitude of the Δ PDF correlations is measurable down to 30 K.

The elimination of the interatomic vector probabilities of the average structure from the PDF allows short-range order to be determined over length scales that exceed 100 Å, which means that the correlation of ions undergoing an order-disorder transition can be monitored as a function of temperature from well above to well below the transition (Fig. 5). In β -Na_{0.45}V₂O₅, there is a gradual increase in the correlation lengths along the y and z directions, ξ_y and ξ_z , from 275 K to 230 K, which is easier to see in plots of ξ^{-1} versus temperature (Fig. 5c). At ~230 K, this induces a sharp increase in correlation length of the sodium pair correlations along the x axis, ξ_r , perpendicular to the sodium ladder planes, marking a crossover from two- to three-dimensional correlations (Fig. 5b). However, it does not appear to be a true second-order phase transition, since ξ_x saturates at 190 K with a value of only 170 Å, corresponding to approximately 10 unit cells or 20 ladder planes. The increase in ξ_x in turn generates a more rapid increase in ξ_{ν} and ξ_{z} , again without

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Fig. 5 | The results of fitting the Δ PDF peak intensities to a decaying exponential as a function of temperature along the three crystallographic axes. **a**, The amplitude of the Δ PDF exponential decays at *r* = 0 along the *x*, *y* and *z* directions. **b**, The correlation length of sodium pair correlations derived from the decay constant. **c**, The inverse correlation length. A beam failure prevented measurements between 60 and 110 K. Reliable fits along the *x* direction were not possible above 230 K because the Δ PDF intensities were too weak.

leading to a true divergence. The maximum correlation length at 30 K is still under 200 Å. Instead of a discontinuity in the slope of ξ_y^{-1} and ξ_z^{-1} , defining a unique transition temperature, there is a crossover between two temperature regimes at ~200 K close to where ξ_x saturates (Fig. 5c).

We propose that the saturation in ξ_x is a consequence of frustration. Due to the body-centring of the monoclinic structure, the ladder sites in the *y*-*z* planes at *x*=0 and *x* = $\frac{1}{2}a$ are shifted by $\pm \frac{1}{2}b$, which makes the strength of the Coulomb interactions

independent of the relative phase of the zigzag site occupations between two neighbouring planes. This degeneracy implies that the phase must be stabilized by next-nearest-neighbour interactions along the *x* axis, which may be weak enough to allow stacking faults that inhibit true long-range order. Disorder of the excess sodium ions that cannot be accommodated on the ladder sites would contribute to this frustration by locally pinning the zigzag phase in each plane. The fall in ξ_x below 190 K indicates that any such frustration mechanism is increased by the growth in intraplanar correlations. This could be tested by further measurements on β -Na_{0.33}V₂O₅ corresponding to precisely 50% occupation of the ladder sites.

The intensities of the \triangle PDF peaks increase monotonically with decreasing temperature (Fig. 5a). Along the *x* axis, the temperature dependence of the amplitude resembles an incipient order parameter, with a value close to 0 above the transition (Supplementary Fig. 6). However, along the *y* and *z* directions, there is a much weaker temperature dependence, reflecting the strong nearest-neighbour correlations at all temperatures.

Transforming X-ray diffuse scattering data into $3D-\Delta PDFs$ produces a remarkable simplification in how the data are represented. It is possible to interpret the short-range order in the crystal structure without a detailed simulation of the disorder, which has in the past required the optimization of a large number of parameters over a substantial volume of reciprocal space. In fact, the PDF intensities directly determined from the transformed data are related by simple analytic functions to the Warren–Cowley parameters that are frequently used to parametrize diffuse scattering models²⁴. Even without a well defined model of the underlying disorder, our results show that the spatial dependence of the PDF intensities provides a method of extracting correlation lengths as a function of temperature or other parametric variable. We believe that this method will be of value in investigations of the evolution of structural ordering in many crystalline materials.

The ability to generate a real-space 'image' of interatomic vectors from reciprocal space data, albeit one without phase information, makes this an especially powerful tool in the investigation of intercalation compounds, as it is especially suited to the measurement of ionic correlations on a sublattice that is distinct from the host structure. Although we have not yet tested this technique on lithiated compounds, we believe that the elimination of the average structure of heavier elements will allow lithium–lithium correlations to be measured in spite of their low cross section. In this Article, the method has allowed us to show that the apparent order–disorder transition reported in Na_xV₂O₅ is actually a crossover from twodimensional to three-dimensional correlations, with interplanar correlations saturating at only ~150 Å, probably because of frustration. Such detailed insight into intercalant disorder is not possible by any other method.

Although we have focused on layered materials, the technique can be utilized in more three-dimensional insertion compounds such as the oxide spinels¹⁵, as well as other disordered materials. The principal limitation of this technique is the need for single crystals, which makes in operando experiments within electrochemical cells challenging, although not impossible. Sample thicknesses can be less than 100 µm, and provided the rest of the cell is polycrystalline the real-space transform will only contain discrete peaks that correspond to the crystalline electrode. Measuring the phase diagram of order-disorder transitions as a function of both temperature and intercalant concentration will allow the strength of interionic interactions to be determined and improve our understanding of the how they limit ionic mobility. Such measurements could also be used to evaluate the effectiveness of strategies for mitigating these limitations, for example by co-intercalation with aliovalent cations⁴⁰ or substitution of transition metals on the vanadium sites⁴¹, to disrupt ordering phenomena.

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Any methods, additional references, Nature Research reporting summaries, source data, statements of code and data availability and associated accession codes are available at https://doi.org/10.1038/ s41563-019-0500-7.

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Author contributions

Samples were prepared by J.T.V. and prepared for measurement by M.J.K. The experiments were devised by M.J.K., S.R. and R.O. The X-ray experiments were performed by M.J.K., S.R., J.P.C.R., J.M.W. and R.O. The data were analysed by M.J.K., R.O., J.M.W. and G.J., using software written by G.J., M.J.K., R.O. and J.M.W. The manuscript and Supplementary information were written by R.O. with input from all the authors.

Competing interests

The authors declare no competing interests.

Additional information

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NATURE MATERIALS

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Methods

Synthesis. Na_xV₂O₅ crystals were grown using a self-flux technique. Five grams of V₂O₅ (Aldrich, >98%) in a nickel crucible was placed in an oven inside an Ar-atmosphere glovebox. The sample was heated to 720 °C. While the sample was liquid, the crucible was removed from the furnace and a stoichiometric amount of NaI (Aldrich, 99.5%) was added to the liquid. The sample was then put back in the furnace and cooled to 650 °C over 1 h, then radiatively cooled to room temperature. Single crystals were isolated from the flux. EDX analysis showed that the sodium concentration, when normalized to the nominal vanadium stoichiometry, was $x = 0.45 \pm 0.02$.

X-ray scattering. Three-dimensional volumes of diffuse X-ray scattering were collected at APS and CHESS. The APS data were measured on sector 6-ID-D using an incident energy of 87.1 keV and a Dectris Pilatus 2M with a 1-mm-thick CdTe sensor layer. The CHESS data were measured on beamline A2 using an incident beam energy of 27.3 keV and a Dectris Pilatus 6M detector with a 1-mm-thick Si sensor layer. The data were collected from 30 K to 300 K, with samples cooled by flowing He gas below 100 K and N₂ gas above 100 K. During the measurements, the samples were continuously rotated about an axis perpendicular to the beam at 1° s⁻¹ over 370°, with images read out every 0.1 s. Three sets of rotation images were collected for each sample at each temperature to fill in gaps between the

detector chips. The resulting images were stacked into a three-dimensional array, oriented using an automated peak search algorithm and transformed in reciprocal space coordinates using the software package CCTW (Crystal Coordinate Transformation Workflow)⁴², allowing *S*(**Q**) to be determined over a range of ~ \pm 15 Å⁻¹ in all directions. Further details are given in Supplementary methods.

Data availability

Files containing the datasets used in this Article are available for download from the Materials Data Facility¹³ (https://doi.org/10.18126/ooin-ce23) as NeXus files stored in the HDF5 format⁴⁴. The files for each measured temperature contain $S(\mathbf{Q})$, Δ PDF and, at three temperatures, the total PDF results. The data can be plotted using the Python package NeXpy (http://nexpy.github.io/nexpy/).

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