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EXECUTIVE SUMMARY OF THE THESIS

Exploring the Frustrated Charge Density Wave in $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$ via Diffuse X-Ray Scattering and 3D-Delta Pair Distribution Function analysis

LAUREA MAGISTRALE IN ENGINEERING PHYSICS - INGEGNERIA FISICA

Author: NICOLA CAMPANIELLO

Advisor: PROF. MARCO MORETTI SALA

Co-advisor: DR. DANIEL ALEXANDER CHANEY

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1. Introduction

The physics of correlated disorder in quantum materials represents an exciting area of research currently receiving significant attention. Conventional single crystal diffraction is extremely powerful in determining the average structure of long-range ordered crystals, but it is intrinsically less sensitive to weak diffuse intensities coming from short-range atomic correlations. These correlations may nevertheless control important physical properties, especially in materials where electronic and structural degrees of freedom are strongly coupled. Diffuse X-ray scattering [4] is a particularly suitable technique for investigating local deviations from the average crystal structure, since it probes weak elastic scattering intensities distributed over large regions of reciprocal space. When combined with three-dimensional difference pair distribution function (3D- Δ PDF) analysis, diffuse scattering provides direct access to real-space pair correlations and can be used to identify the microscopic origin of disordered states.

This thesis focuses on the ruthenate system $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$. Previous studies on undoped

NaRu_2O_4 [5] reported a commensurate Charge Density Wave phase below 535K, with a doubling of the unit cell along the crystallographic b direction and the formation of Ru-Ru dimers. Unconventional Z-type bonding and charge ordering involving Ru^{3+} and Ru^{4+} states were also predicted. Despite this ordering tendency, NaRu_2O_4 remains metallic over the investigated temperature range, making it an unusual example of a material where charge ordering, Peierls-like distortions and metallic transport coexist. The main objective of this work is to characterize the structural disorder state in Ir-substituted $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$ and to clarify whether the observed diffuse scattering originates from sodium diffusion, substitutional Ru/Ir disorder or correlated Ru displacements. The thesis also aims to follow the temperature evolution of the disorder state from 80K to 650K, in order to understand whether the system undergoes a well-defined phase transition or instead displays a smooth crossover between different short-range correlated regimes.

2. Methodology

Single crystals of $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$ were synthesized at Harvard University and measured at the ID28 beamline of the European Synchrotron Radiation Facility. The selected crystal was needle-like, with an approximate size of $5\mu\text{m} \times 200\mu\text{m} \times 5\mu\text{m}$, reflecting the quasi-one-dimensional growth tendency of the structure along the $\mathbf{b}$ axis. The experiments were performed using hard X-rays with photon energy chosen to minimize Ru fluorescence from the sample, combined with a detector threshold adjusted to suppress Ir fluorescence.

Diffuse scattering measurements were collected at several temperatures: 80K, 285K, 400K, 470K, 535K and 650K. Additional measurements during cooling were performed at 400K and near room temperature to test reversibility and possible hysteresis effects. At each temperature, two independent 360° sample-rotation datasets were acquired at different detector angles, allowing a broad coverage of reciprocal space with several hundred main Bragg peaks and almost 7GB per temperature dataset. This was essential for reconstructing three-dimensional reciprocal-space volumes and for obtaining meaningful 3D- Δ PDFs.

The raw frames were normalized by the incoming photon flux and processed through a sequence of steps. First, the reciprocal-space volumes were reconstructed using the UB matrix obtained from CrysAlis Pro software. Then, the two detector-angle acquisitions were merged, and *mmm* Laue symmetry was used to increase reciprocal-space coverage and reduce incompleteness effects in the Fourier transform. A radial background was estimated and subtracted. Bragg peaks were removed through a punch-and-fill strategy, and the KAREN algorithm with the smallest moving window of 2 voxels was used to reduce sharp residual features, while preserving the superstructure reflections. The processed diffuse scattering intensity was finally Fourier transformed into the 3D- Δ PDF. Two complementary analyses were then performed. In real space, the 3D- Δ PDF was interpreted using Pair Displacement Maps and refined with Yell [1] models. In reciprocal space, the temperature evolution was studied using X-ray TEMperature Clustering (X-TEC) [2] and by fitting selected high-resolution two-

dimensional cuts of a representative superstructure feature.

3. Results

At 80K, the reconstructed diffraction pattern contains intense Bragg peaks and structured diffuse scattering planes at $K = 0.5, 1.5, 2.5$ and 3.5 as can be seen in Fig. 1. These positions coincide with the superlattice planes previously associated with the CDW modulation in undoped NaRu_2O_4 . However, for the Ir-substituted compound, the superstructure planes are not simply made of sharp superlattice peaks, but contain broad, highly structured diffuse intensities as shown in Fig. 2. In the low- H , low- L region, the diffuse scattering forms pseudo-triangular features connected by softened pinch points arranged in a Kagome-like pattern. These features indicate that the local disorder is not random but constrained by local rules or competing interactions.

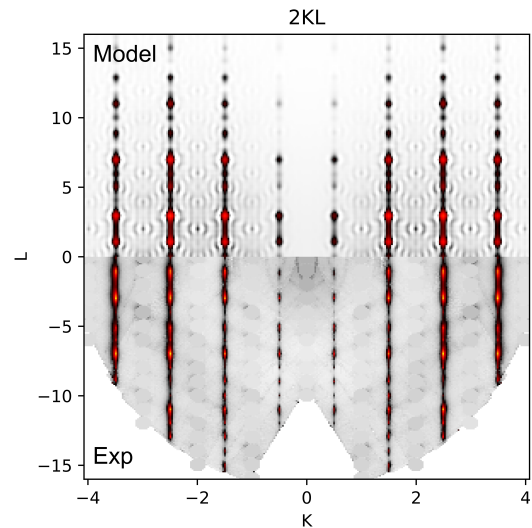


Figure 1: 80K reciprocal space dataset (experimental vs Yell model). The diffuse planes at $K = 0.5, 1.5, 2.5$ and 3.5 are visible from the $2KL$ layer.

The width of the diffuse scattering features is strongly anisotropic. In reciprocal space, the features are narrow along $\mathbf{K}$ and broader along $\mathbf{H}$ and $\mathbf{L}$. This is also reflected in the 3D- Δ PDF, where the signal extends over a long range along $\mathbf{v}$, but decays rapidly along $\mathbf{u}$ and $\mathbf{w}$. Quantitatively, the low-temperature correlation lengths extracted from Lorentzian fits are approximately $185\text{\AA}$ along $\mathbf{b}$, $36\text{\AA}$ along $\mathbf{a}$ and

53Å along $\mathbf{c}$. In real lattice units, this corresponds to about 65 unit cells along $\mathbf{b}$, 3.9 along $\mathbf{a}$ and 4.7 along $\mathbf{c}$. The system is therefore best described as almost long-range ordered along the longitudinal direction, where the CDW chains develop, but only short-range ordered between chains, along the transverse directions.

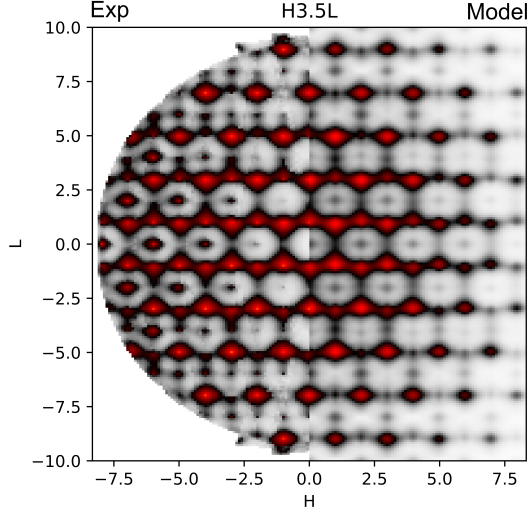


Figure 2: 80K reciprocal space dataset (experimental vs Yell model). The pseudo-triangular shape of the diffuse features and the pinch points are visible from the $H3.5L$ layer.

The 3D- Δ PDF reveals alternating-sign, y-y, second-order displacive correlations developing along $\mathbf{v}$. These correlations are naturally interpreted through an Ising-like displacement model in which each Ru atom is assigned a positive or negative displacement along $\mathbf{b}$. Along each chain, neighbouring Ru atoms displace in such a way as to form dimers, producing alternating positive and negative correlations depending on the parity of the interatomic vector along $\mathbf{b}$. This provides a direct real-space signature of the dimerization associated with the CDW modulation.

A major achievement of the thesis is the construction and use of Pair Displacement Maps (PDMs). These are obtained by first calculating the displacements of individual Ru atoms from the difference between distorted and undistorted positions, and then by taking the difference displacement of all Ru pairs. The calculated Pair Displacement vectors are then compared with the experimental 3D- Δ PDF, as shown in Fig. 3 and 4, providing an excellent match not only

for the Ru-Ru pair position, but also for the signs of the correlations. As a result, the low-temperature diffuse scattering is attributed primarily to correlated Ru displacements rather than to sodium diffusion, and a pattern with the same displacement arrangements as the undoped system, but decaying correlations, is found.

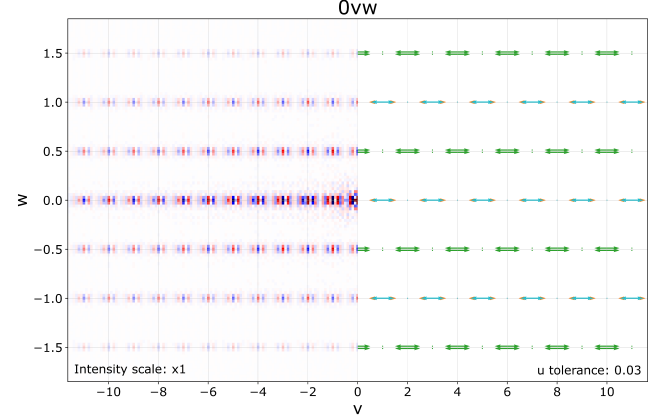


Figure 3: Comparison between 80K 3D- Δ PDF and PDMs in the $0vw$ plane. Orange, cyan and green indicate respectively Ru1-Ru1, Ru2-Ru2 and Ru1-Ru2 pairs. Null Pair Displacements map onto positive (blue-red-blue) displacive correlations, indicating in-phase displacements of the pair. Large Pair Displacements map onto negative (red-blue-red) displacive correlations, indicating either an increase or a decrease of the interatomic vector along $\mathbf{b}$.

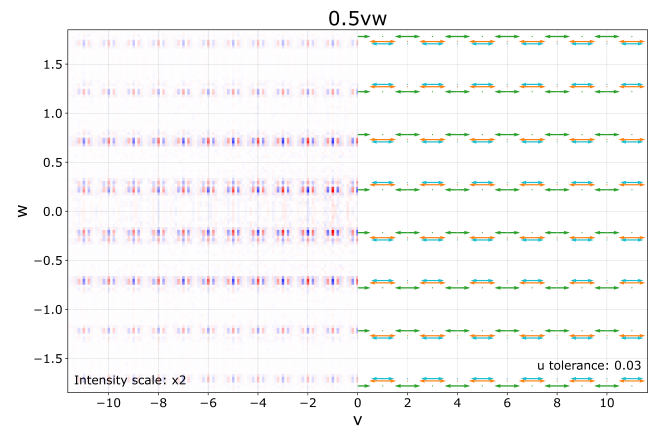


Figure 4: Comparison between 80K 3D- Δ PDF and PDMs in the $0.5vw$ plane. Strong correlations at $w = 0.21$ correspond to Ru1-Ru2 nearest-neighbour pairs of the triangular layers and always have the opposite sign to the weaker $w = 0.29$ correlations from Ru1-Ru1 or Ru2-Ru2 NN pairs in the same triangular layer.

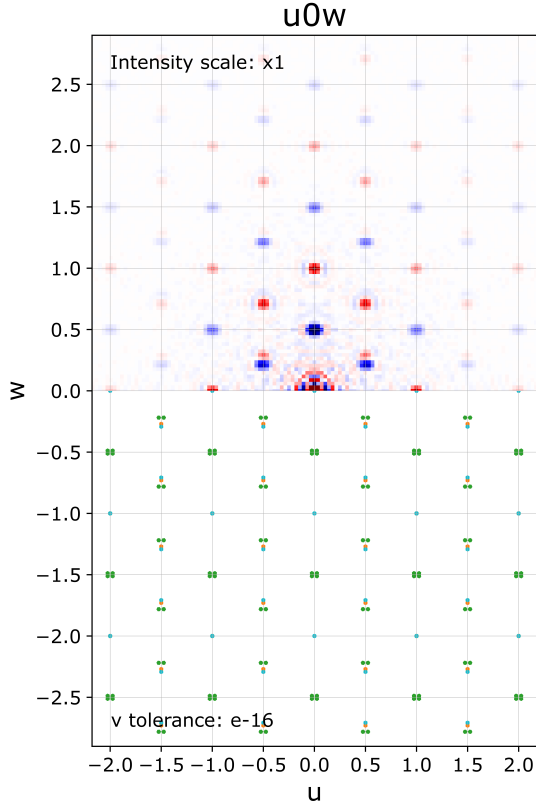


Figure 5: Comparison between 80K 3D- Δ PDF and PDMs in the $u0w$ plane. All $\alpha - \alpha$ and $\beta - \beta$ intra-layer correlations are visible. The structural distortions made it possible to distinguish the negative (blue) $w = 0.21$ from the positive (red) $w = 0.29$ correlations. The sign of further-neighbour correlations are consistent with the sign expected by propagating the nearest-neighbour correlation pattern along a path connecting the pair. In other words, the correlation function is characterized by an oscillation-free, monotonic envelope.

The inter-chain correlations are organized in two offset and staggered distorted triangular layers, named α and β . The 3D- Δ PDF and its Yell modelling show that intra-layer $\alpha - \alpha$ and $\beta - \beta$ correlations are stronger than inter-layer $\alpha - \beta$ correlations. The dominant intra-layer correlations, appearing in the $u0w$ section of the 3D- Δ PDF in Fig. 5, can be described by a local tendency in which Ru1-Ru2 nearest-neighbour pairs in a triangle favour antiparallel displacements, while the remaining pair of the triangle, either Ru1-Ru1 or Ru2-Ru2, shows a weaker tendency toward parallel displacements. This resembles the local constraint of an antiferromagnetic Ising model on a triangular lattice, where

frustration prevents all pair interactions from being simultaneously satisfied. In particular, the structural distortions that lower the symmetry of an equilateral triangular lattice suggest anisotropic inter-chain interactions that could eventually explain the intensity imbalance of the signal associated with the nearest-neighbour intra-layer correlations. The "one parallel, two antiparallel pairs of displacements" local rule could be applied for each triangle and, if combined with anisotropic interactions that favour Ru1-Ru2 antiparallel alignment, could explain the correlation pattern as shown in Fig. 6.

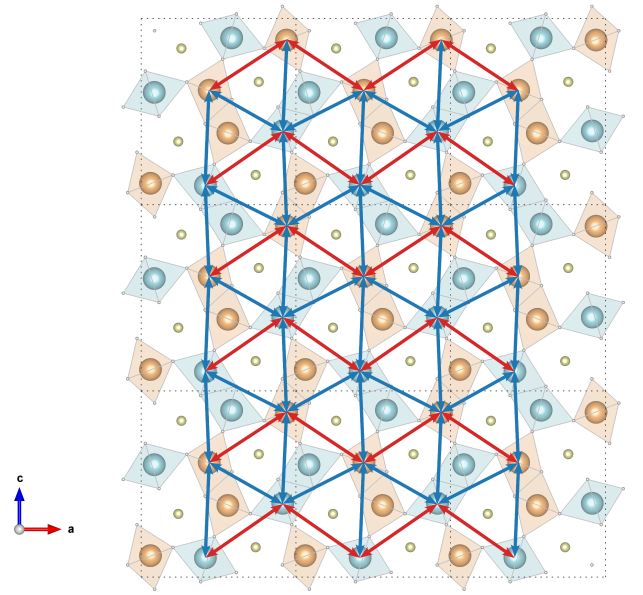


Figure 6: Mapping of the low-temperature nearest-neighbour $\alpha - \alpha$ correlations $(0,0,0.5)$, $(0.5,0,0.21)$ and $(0.5,0,0.29)$ onto the α transverse triangular layer. Orange and cyan are used for Ru1 and Ru2 sites, while red and blue links for positive and negative correlations.

Yell refinements using second-order y-y displacive correlations reproduce both the narrow extension of the diffuse planes along K and the structured intensity distribution within the HL planes. When the weaker $\alpha - \beta$ correlations are switched off, the main low- H , low- L pseudotriangular features and pinch points remain unchanged. This indicates that the dominant contribution to the characteristic diffuse scattering pattern comes from intra-layer correlations. The thesis also explores whether the Ir atoms introduce correlated substitutional disorder. A model including occupational correlations can

reduce the intensity of the $H0.5L$ layer, but the refined occupational correlations are weak and not fully reliable. The safer conclusion is that Ir substitution may contribute to local disorder, but the data do not provide clear evidence for a correlated Ru-Ir ordering pattern. Random or weakly correlated substitutional disorder remains a plausible scenario.

The temperature dependence of the diffuse scattering is one of the most important parts of the thesis. In contrast to undoped NaRu_2O_4 , where a sharp CDW transition was reported around 535K, $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$ does not show a sharp critical point in the measured temperature range. Instead, the diffuse scattering intensity decreases gradually upon heating with major temperature variations measured between 400K and 470K, as clearly visible from Fig. 7. The fact that the structured diffuse scattering weakens with temperature strongly supports a static correlated-disorder origin, rather than a purely thermal diffuse scattering origin. At 650K, diffraction rings appear, indicating partial sample degradation or chemical/structural changes induced by high temperature and high photon flux. Upon cooling, weaker intensities are measured, suggesting an hysteretic transition.

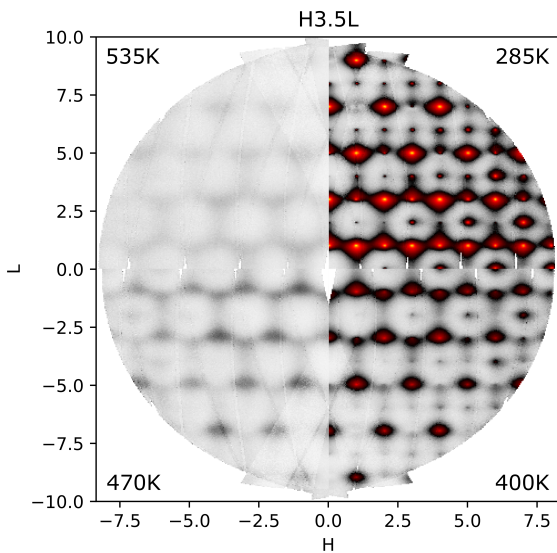


Figure 7: Temperature evolution of the diffuse scattering in the $H3.5L$ layer. At high temperatures all intensities become equal, removing the pinch points and favouring an hexagonal-like pattern.

As shown in Fig. 8, the 3D- Δ PDF confirms the gradual loss of correlations, eventually leading to a high-temperature regime in which only the very short-range correlations survive. Some correlations persist even at high temperature, while others seem to change sign around 470K and above. This suggests that the high-temperature state may not simply be a scaled-down version of the low-temperature correlation pattern. A possible phenomenological interpretation is that the correlation function develops a damped oscillatory component, with a temperature-dependent characteristic length or wave vector. This interpretation is qualitatively consistent with frustrated anisotropic Ising-like systems, where monotonic and oscillatory short-range correlation regimes can be separated by a disorder line [3]. However, in this thesis it should be treated as a hypothesis rather than a demonstrated result, because sign changes in the 3D- Δ PDF can also arise from overlapping pair contributions, symmetrization effects, incomplete reciprocal-space coverage or high-temperature artefacts.

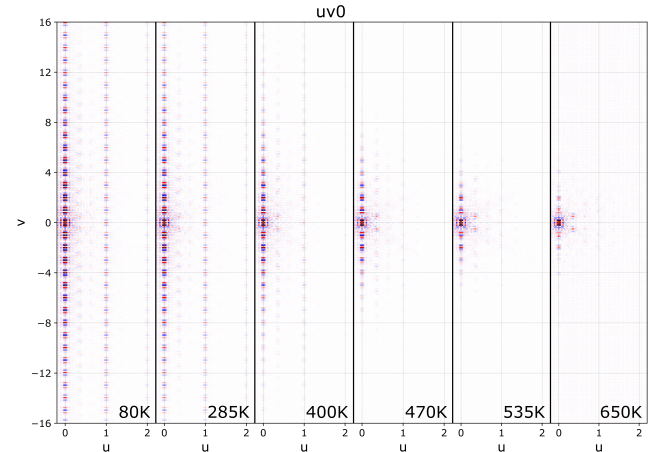


Figure 8: Temperature evolution of the 3D- Δ PDF in the $uv0$ section. The correlation length decreases until only first-neighbour pairs are correlated.

To obtain a more quantitative description of the temperature evolution, the thesis applies X-ray Temperature Clustering [2]. This unsupervised machine-learning method groups reciprocal-space voxels according to similar temperature trajectories. Six clusters were initially used, although two were later considered less physically meaningful because they were asso-

ciated with limited data coverage or negligible voxel populations.

The physically relevant clusters reveal a spatial organization within each diffuse feature. Each diffuse scattering feature encompasses contributions from multiple clusters, indicating that different regions of reciprocal space within the same feature can exhibit distinct temperature evolutions. Importantly, none of these clusters shows a clear critical behaviour. Their intensities, shown in Fig. 9, fade gradually with temperature, supporting the interpretation of a short-range ordered state rather than a conventional long-range phase transition.

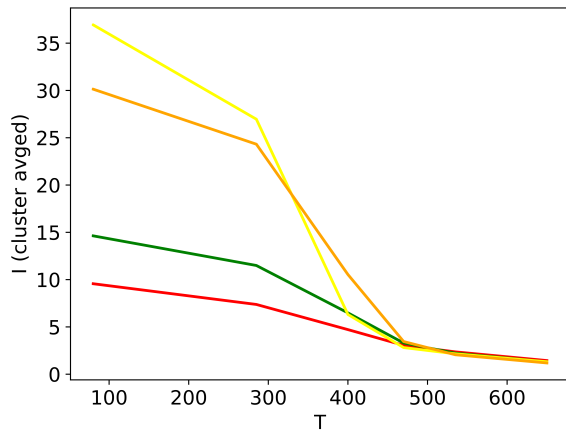


Figure 9: Temperature dependence of the average intensity for the four meaningful clusters. Each feature is composed, in order from the superlattice peak position to the most peripheral region, of yellow, orange, green and red voxels.

A selected superstructure feature, located at $(-1, 3.5, -5)$, was further analysed using high-resolution two-dimensional cuts. Lorentzian, Voigt and pseudo-Voigt profiles were tested, and the simpler Lorentzian profile was found to be sufficient in most cases. The peak areas, in Fig. 10, follow the X-TEC averaged intensities, while the extracted correlation lengths, in Fig. 11, confirm the strong anisotropy already observed in the 3D- Δ PDF.

However, a simple Lorentzian does not perfectly reproduce the line shapes of the central H and L sections. Two alternative models were therefore explored. The first is a two-component model with a sharp component and a broader diffuse one. In this picture, the sharp component could represent a long-range ordered

dimerized superstructure whose intensity vanishes near 400K, while the broad component represents short-range diffuse correlations that evolve smoothly with temperature, as reported in Fig. 12. The second model, instead, is a generalized Lorentzian, or regularized power law, which improves the description of the peak tails and suggests algebraic-like transverse correlations over a finite range. In particular, the short-range behaviour of the correlation function (for $r \ll 100\text{\AA}$) is estimated:

$$C(r) \sim |r|^{-0.8} \quad (1)$$

Both models are compatible with the data, but neither provides definitive proof of a unique microscopic scenario.

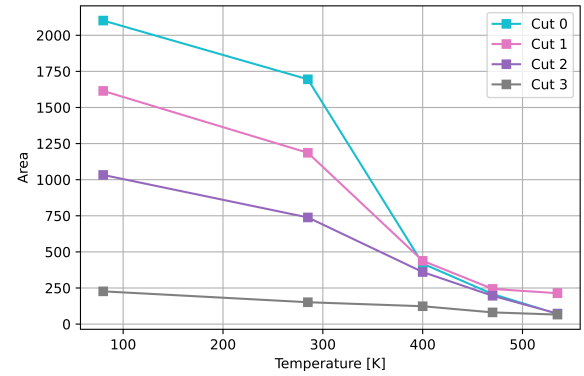


Figure 10: Temperature dependence of the peak area from the Lorentzian function fitting. The different colours refer to various H sections of the $(-1, 3.5, -5)$ feature. Cyan is taken at $L = -5$, pink at $L = -4.93$, purple at $L = -4.82$ and grey at $L = -4.5$.

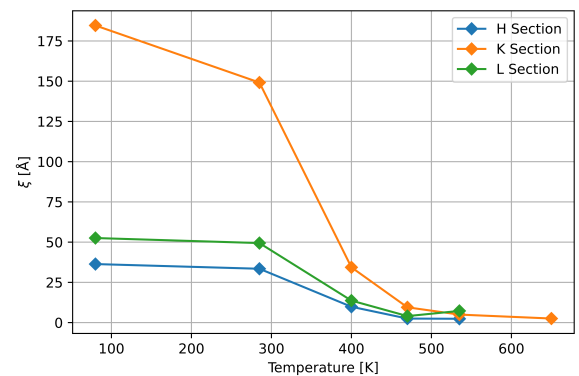


Figure 11: Temperature dependence of the anisotropic correlation length from the Lorentzian function fitting.

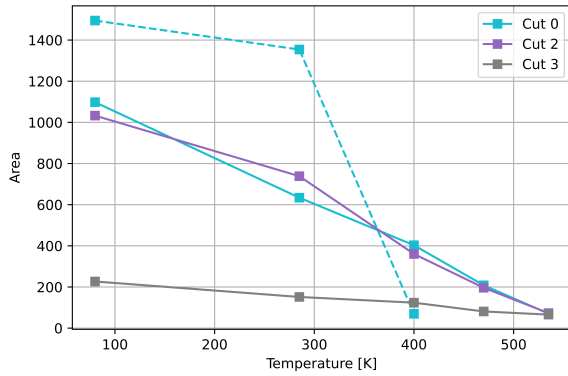


Figure 12: Temperature dependence of the $(-1, 3.5, -5)$ peak area from the double lorentzian function fitting along H . The dashed cyan line is for the sharp component, while the continuous cyan line is for the broad component. Purple and grey lines refer to single lorentzian fits in peripheral L regions away from the superlattice position.

4. Conclusions

This thesis provides a comprehensive investigation of the structural disorder state in $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$. The main conclusion is that the low-temperature diffuse scattering is dominated by correlated Ru displacements associated with a commensurate dimerization along the $\mathbf{b}$ direction and short-range inter-chain correlations in the transverse distorted triangular layers.

The temperature dependence does not show a sharp critical point comparable to the CDW transition reported in undoped NaRu_2O_4 . Instead, the diffuse scattering and the 3D- Δ PDF evolve smoothly, indicating the gradual weakening of a short-range ordered state.

Two main interpretations remain open and should not necessarily be regarded as mutually exclusive. In the first, the short-range transverse correlations are intrinsic to the material but too weak to have been detected by previous non-dedicated measurements. They would arise from geometrical frustration in distorted triangular Ru layers and possibly produce a Coulomb-like constrained disordered phase. In the second, Ir substitution locally perturbs the CDW phase, breaks long-range coherence and generates finite correlated domains. Pinch-point-like features favour the frustrated-disorder interpretation, whereas the finite low-temperature longi-

tudinal correlation length and the reduced transition temperature are more naturally explained by impurity effects. The available data are therefore consistent with a picture in which geometrical frustration and substitutional disorder coexist and jointly determine the rich phenomenology of $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$.

Future work should therefore focus on determining the actual Ir content and distribution, for example through energy-dispersive X-ray spectroscopy (EDX) or related chemical mapping techniques; performing Monte Carlo or modelling of candidate interaction models; analysing lower-symmetry 3D- Δ PDFs; and comparing the doped and undoped compounds using the same dedicated diffuse-scattering setup. These steps would make it possible to determine the relative role of intrinsic frustration and impurity-induced disorder and to clarify how their interplay governs the correlated-disorder state of $\text{Na}(\text{Ru}_{1-x}\text{Ir}_x)_2\text{O}_4$.

5. Acknowledgements

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References

- [1] T. Weber A. Simonov. Yell: a computer program for diffuse scattering analysis via three-dimensional delta pair distribution function refinement. *Journal of Applied Crystallography*, 47:1146–1152, 2014.
- [2] K. Mallayya J. Venderley et al. Harnessing interpretable and unsupervised machine learning to address big data from modern x-ray diffraction. *Proceedings of the National Academy of Sciences*, 119, 2022.
- [3] John Stephenson. Ising-model spin correlations on the triangular lattice. iv. anisotropic ferromagnetic and antiferromagnetic lattices. *Journal of Mathematical Physics*, 11:432–448, 1970.
- [4] T. Weber T. R. Welberry. One hundred years of diffuse scattering. *Crystallography Reviews*, 22:2–78, 2016.
- [5] A. K. Yogi et al. Coexisting z-type charge and bond order in metallic NaRu_2O_4 . *Communications Materials*, (3), 2022.