Local crystal structure of Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$ in commensurate and incommensurate phases described by Pair Distribution Function (PDF) and Reverse Monte Carlo (RMC) modeling

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Supplementary References.
Section S1:

A typical diffraction pattern will contain contributions from both Bragg scattering from long-range order and diffuse scattering from short-range order. Careful normalization of the scattering data gives the total-scattering structure factor as a function of momentum transfer, \( Q \):

\[
F(Q) = \sum_{i,j=1}^{n} c_i c_j \overline{b}_i \overline{b}_j [A_{ij}(Q) - 1] \tag{1}
\]

where \( i \) and \( j \) represent atomic species, \( n \) is the number of distinct chemical species, \( c_{i,j} \) are the proportion of species in the material, \( \overline{b}_{i,j} \) are the coherent bound neutron scattering length and \( A_{ij}(Q) \) are the Faber-Ziman partial structure factors.\(^1\) The coherent bound neutron scattering length may be positive or negative. For the present system of study \( \overline{b}_{\text{Mn}} \) 8.5532 fm, \( \overline{b}_{\text{Ni}} \) −3.73 fm, \( \overline{b}_{\text{O}} \) 5.803 fm; this gives excellent contrast between the scattering power of the B site cations Mn and Ni, however the contribution of for example Mn-O and Ni-O bonds to the pair distribution function will have opposite signs, resulting in partial cancellation of the observed intensity. In such situations, additional information is typically needed to extract reliable distributions and chemically sensible constraints are typically introduced to the observed data (see Experimental Method and Data Analysis section).

Fourier transformation of \( F(Q) \) gives the pair distribution function (PDF) as a function of real space distance, \( r \). The PDF is usually defined by the total radial distribution function, \( G(r) \), or total correlation function, \( T(r) \), which are expressed in equations (2) and (3), respectively:\(^2\)

\[
G(r) = \frac{1}{(2\pi)^3 \rho_0} \int_0^{\infty} 4\pi Q^2 F(Q) \frac{\sin Qr}{Qr} dQ \tag{2}
\]

\[
T(r) = 4\pi r \rho_0 [G(r) + (\sum_{i=1}^{N} c_i \overline{b}_i)^2] \tag{3}
\]

where \( \rho_0 \) is the average number density of the material. Both \( G(r) \) and \( T(r) \) functions describe the probability of finding two atoms separated by distance \( r \) within a given volume.\(^2\) The PDF data also contains information about coordination numbers which can be determined by integrating the intensity under the peaks. Individual contributions to the PDF for two atoms \( i \) and \( j \), known as the partial distribution function is given by:

\[
g_{ij}(r) = \frac{n_{ij}(r)}{4\pi r^2 dr \rho_j} \tag{4}
\]

where \( n_{ij}(r) \) is the number of \( j \) particles between distances \( r \) and \( r+dr \) from particles \( i \), and \( \rho_j \) represents the number of density of particle \( j \).

Reverse Monte Carlo (RMC) modeling is a powerful method for the analysis of total scattering data.\(^3,4\) The RMC method can be used to generate a three-dimensional atomistic
model which simultaneously matches the Bragg profile, total-scattering structure factor and the PDF data. The starting model consists of a supercell of the average structure. During the RMC refinement the atomic coordinates of the atoms in the supercell are improved using a Monte Carlo algorithm to fit calculated functions to experimental data. Random movements of the atoms in the RMC modeling are accepted with the probability \( \exp(-\Delta \chi^2_{RMC}/2) \) where \( \chi^2 \) is made up of contributions from Bragg scattering (\( \chi^2_{l(\theta)} \)), the total-scattering structure factor (\( \chi^2_{F(Q)} \)) and the PDF (\( \chi^2_{G(r)} \));

\[
\chi^2_{l(\theta)} = \sum_f [I_{\text{calc}}(\theta_j) - I_{\text{exp}}(\theta_j)]^2 / \sigma^2(\theta_j)
\]

\[
\chi^2_{F(Q)} = \sum_k \sum_f F_{\text{calc}}(Q_j)_k - F_{\text{exp}}(Q_j)_k]^2 / \sigma^2_k(Q_j)
\]

\[
\chi^2_{G(r)} = \sum_i [G_{\text{calc}}(r_j) - G_{\text{exp}}(r_j)]^2 / \sigma^2(r_j)
\]  

(5)

where \( \sigma \) represents the experimental uncertainty. RMC modeling is repeated until there is no further improvement in the quality of the fit and the final 3-dimensional configuration is consistent with the experimental data: the Bragg profile, total scattering structure factor and the PDF. Fitting to the Bragg scattering ensures that the model is consistent with the long-range average structure, while the inclusion of diffuse scattering information and the PDF ensures that medium- and short-range order information is also reflected in the model.
Section S2:

Starting atomic configurations for RMC modeling were created from supercells of the long-range average structures. The starting RT supercell was generated from a commensurate $2\sqrt{2}a_p \times 4a_p \times \sqrt{2}a_p$ subcell ($a = 11.1496$ Å, $b = 15.5302$ Å and $c = 5.5092$ Å) in the polar orthorhombic space group $P2_1mn$, previously identified as the best commensurate approximation to the incommensurate structure. $^7$ A $5 \times 4 \times 10$ expansion of this subcell produced a supercell of dimensions $55 \times 62 \times 55$ Å$^3$ containing 16,000 atoms (Figure 1a). The crystallographic directions of the RMC model remain the same as in the applied commensurate subcell. All of the supercells are therefore aligned with $x$ oriented along $\langle 1\bar{1}0 \rangle_p$, the direction of the Bi displacement giving rise to polarity in the incommensurate subcell, whereas $y$ and $z$ are oriented along the non-polar directions $\langle 001 \rangle_p$ and $\langle 110 \rangle_p$ respectively.

In order to directly compare the RT results from RMC modeling to the incommensurate structure, supercells of the incommensurate structure with a similar size to the RMC configurations were generated from the subcell ($Ibmm(a00, 0\beta0)mm.ss$) using Jana. $^8$ A multiplicity $10a \times 7b \times 10c$ of lattice parameters $a = 5.5729$ Å, $b = 7.7686$ Å and $c = 5.5091$ Å give an incommensurate supercell with approximate dimension $55 \times 55 \times 55$ Å$^3$ (Figure 1b). Ten supercells were generated with different origins of the incommensurate modulation (e.g. $t = 1/10$, $u = 1/10$; $t = 1/10$, $u = 2/10$) where $t$ and $u$ correspond to the initial phase of two modulation vectors (0.4930 0 0) and (0 −0.4210 0) along $\langle 1\bar{1}0 \rangle_p$ and $\langle 001 \rangle_p$ respectively. Results presented are an average from the ten supercells in order to remove any bias from the starting point of the modulation, and therefore represent the “complete” average incommensurate model. The incommensurate cell is aligned with $x$ and $y$ oriented along $\langle 1\bar{1}0 \rangle_p$ and $\langle 001 \rangle_p$ respectively in the primitive cubic perovskite cell and $z$ oriented along $\langle 110 \rangle_p$. Thus both RMC and average incommensurate model supercells have the same settings in relation to the crystallographic directions presented on Figure 1c.

The RMC supercell for the commensurate HT structure was generated from the non-polar $Pcmn$ space group with lattice parameters $a = 5.4513$ Å, $b = 7.8058$ Å and $c = 5.5893$ Å as it gave the best fit to the neutron diffraction data. An RMC model built of $10a \times 7b \times 10c$ unit cells gave a HT supercell with dimensions $55 \times 55 \times 55$ Å$^3$ and 14,000 atoms (Figure 1d). The HT supercell has the same settings and orientation as the RT structure.

RMC refinements were carried out using RMCPProfile $^9$ to simultaneously fit the Bragg profile, total-scattering structure factor $F(Q)$ and the PDF $G(r)$. The RMC models are not constrained by space group symmetry as structures are during Rietveld refinement; in order to keep a model physically feasible during RMC refinement it is often necessary to use constraints and restraints such as distance windows, bond valence sums and interatomic potentials. Distance window (DW) hard constraints define the maximum and minimum separations between atoms. Bond valence sums (BVS) constrain bond distribution to empirical bond valence distances $R_0$ between the cations and oxygen atoms. $^{10,11}$ Initial RMC refinements gave a reasonable fit for the RT structure using only DW constraints, but sharp cut-off features caused by the DW minimum separation boundary were observed for the shortest distances in the partial Mn/Ni-O pair distribution functions. The application of BVS constraints for each cation-oxygen pair improved these cut-off features and, in combination with interatomic potential constraints, helped to distinguish the Mn and Ni atoms which occupy the same crystallographic B site. Final RT RMC refinements were performed with DW constraints, BVS constraints and an interatomic potential restraint for Ni-O which allowed the

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preservation of a regular Ni-O environment. Final HT RMC refinements required only BVS constraints in order to protect the configuration from unphysically large distortions during the refinement.

Several RMC refinement stages were applied to both RT and HT structures. For the RT structure, first the B site atoms in the starting configurations were randomly swapped in the absence of data to obtain a completely random Mn/Ni distribution on the B site. In the next step the RMC fit to the data was initiated in which only swapping of B site atoms was allowed, with no permitted translation steps. The refinement was continued until no further improvement in $\chi^2$ was observed. In the last stage of RMC refinement the B site atom swapping was replaced by atomic translation moves. The application of interatomic potential restraints, necessary to maintain chemical sensible Ni-O bond environments, was not possible during B site swapping and so atom swapping and translations were limited to separate RMC refinements. During the RMC refinement of the HT structure, the starting RMC B site configuration was first randomized, and then refined with simultaneous swapping of B site cations and translations until a very good fit to all experimental data was obtained. 20 RMC configurations were refined for both RT and HT structures; the results presented herein are a summation of results from the 20 individual configurations in order to improve the statistical accuracy of the analyses. A further 10 RMC refinements were refined for the RT and HT structures using the same stages described above, but without the observed data contributing to the $\chi^2$; these “data-free” refinements allowed for the contribution of the applied constraints and restraints on the refinement results to be assessed and separated out from results due to the experimental data.
Section S3:

The displacements of the Bi cations can be partially affected by local short-range order of the B site cations, presented in the main text as $n(r)$ results. In order to understand how the B site cations interact with the Bi cations we investigated the possible correlations between Bi and B site cations, and between the B site cations themselves. Displacement correlation functions (DCF) were calculated according to the method outlined in the main text.

The calculations of DCFs within a spherical volume were first performed for B site cations, which revealed only weak short-range correlations of first neighbour Mn-Mn homopairs along $(\overline{1}10)_p$, as indicated by the broad peak at 4 Å in Figure S1a. No equivalent correlation was observed for the Ni-Ni homopair (Figure S1b). DCFs calculated for Bi-Mn (Figure S1c) and Bi-Ni (Figure S1d) show that the RT local structure possesses only weak short-range correlations along $(110)_p$ as a possible effect of strong antiparallel displacement of Bi$^{3+}$ cations. These correlations are suppressed after the first nearest neighbour.

In conclusion, DCFs calculated for B-B and Bi-B displacements indicate at best only very weak correlations. The correlated displacements observed in the Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$ structure are dominated by the Bi-Bi displacements, as presented in the main text.

Comparison of the instantaneous B-O-B bond angle distributions ($g_{O-B-O}(\theta)$, Figure S2) reveals comparable tilting of octahedra centered on Mn and Ni cations in both the RT and HT RMC local structures, with a narrower distribution of O-Ni-O than O-Mn-O angles (Table S2).
**Section S4:**

We probed the different behavior of the B site cations by calculating the displacement of each B cation from the centroid of its oxygen coordination environment. The magnitude of the displacement was separated out into contributions along different crystallographic directions. The observed displacement distribution (Figure S5 b-d) along the polar $\langle 1\overline{1}0 \rangle_p$ and two non-polar $\langle 001 \rangle_p$ and $\langle 110 \rangle_p$ directions shows less displaced Ni atoms in comparison to Mn. This may be expected as the Mn site contains contributions from both distorted Mn$^{3+}$ and regular Mn$^{4+}$. However, data-free RMC refinements also displayed a sharper, less displaced distribution for Ni when compared to Mn, and as such we cannot draw conclusions about the relative magnitude of displacements observed for Mn and Ni. What is clear from the Mn data (which is not influenced by the potential restraint) is that the B site cations do not show an net displacement in any one direction and that they are readily displaced from the centroid of their coordination environment.
Table S1. Comparison of Bi-B site bond distances between the average crystallographic structure and the RMC local structure at RT and HT.

| Bond       | Average structure / Å | Local structure / Å |
|------------|------------------------|---------------------|
| Bi – Mn    | 3.32(4) 3.435(14)      | Bi – Mn 3.412(1)    |
| Bi – Ni    | 3.273(1)               | Bi – Ni 3.358(14)   |

| Bond       | Average structure angle / ° (RT) | Local structure (RT) |
|------------|----------------------------------|----------------------|
| Mn-O-Mn    | 157.1                            | Angle / ° 154.77(5)  |
|            |                                  | FWHM / ° 24.19       |
| Mn-O-Ni    | 151.48(4)                        | Angle / ° 151.52(8)  |
|            |                                  | FWHM / ° 25.28       |
| Ni-O-Ni    | 151.52(8)                        | Angle / ° 89.66(5), 165.57(14) |
|            |                                  | FWHM / ° 26.61, 20.31 |
| O-Mn-O     | 92.03                            | Angle / ° 88.91(7), 168.38(34) |
|            |                                  | FWHM / ° 18.37, 19.51 |
| O-Ni-O     | 173.89                            | Angle / ° 89.66(5), 165.57(14) |
|            |                                  | FWHM / ° 26.61, 20.31 |

Table S2. Comparison of B-O-B and O-B-O bond angle distributions between the average incommensurate model and the RMC local structure at RT. Values were obtained by fitting Gaussian peaks to the angle distribution functions.
Table S3. Comparison of B-O-B and O-B-O bond angle distributions between the average crystallographic structure and the RMC local structure at HT. Values were obtained by fitting Gaussian peaks to the angle distribution functions.

|                  | Average structure angle / ° (HT) | Local structure (HT) | FWHM / ° |
|------------------|----------------------------------|----------------------|----------|
|                  |                                  | Angle / °            | FWHM / ° |
| Mn-O-Mn          |                                  | 152.82(2)            | 19.10    |
| Mn-O-Ni          | 153.14(8)                        | 150.18(2)            | 19.07    |
| Ni-O-Ni          |                                  | 147.64(5)            | 19.92    |
| O-Mn-O           | 89.84(6)                         | 89.97(2), 169.94(6)  | 17.50, 14.37 |
| O-Ni-O           | 179.96(0)                        | 89.55(4), 169.76(13) | 17.38, 16.34 |
**Figure S1.** Differential spherical displacement correlation functions (DCF) calculated from RMC models of Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$ at RT for (a) Mn-Mn (b) Ni-Ni, (c) Bi-Mn and (d) Bi-Ni.
Figure S2. Bond angle distributions for the B site environments: (a) B-O-B and (b) O-B-O for the RMC local structure at RT; (c) B-O-B and (d) O-B-O for the RMC local structure at HT. The intensity of the distribution is normalized by sinθ.
Figure S3. The partial pair correlation functions $g_{B-B}(r)$ for the RMC local structure at RT.
Figure S4. Differential displacement correlation functions calculated for Bi-Bi cations for the RMC local structure of Bi$_2$Mn$_{4/3}$Ni$_{2/3}$O$_6$ along $\langle 1\bar{1}0 \rangle_p$, $\langle 001 \rangle_p$ and $\langle 110 \rangle_p$ directions at HT.
Figure S5. (a) Total absolute displacements of the B site cations from the centroid of the coordinating oxygens for the RMC local structure at RT. Distribution of displacements of B site cations from the oxygen centroid along (b) \(\langle 1\overline{1}0\rangle_p\), (c) \(\langle 001\rangle_p\) and (d) \(\langle 1\overline{1}0\rangle_p\).
Supplementary References.

(1) Keen, D. A. *J. Appl. Crystallogr.* 2001, 34, 172.
(2) Egami, T. B., S. J. L. *Underneath the Bragg peaks: structural analysis of complex materials.* Pergamon: Amsterdam; Boston., 2003.
(3) McGreevy, R. L. *Nucl. Instrum. Methods Phys. Res. Sect. A-Accel. Spectrom. Dect. Assoc. Equip.* 1995, 354, 1.
(4) McGreevy, R. L. *J. Phys.-Condes. Matter* 2001, 13, R877.
(5) Dove, M. T.; Tucker, M. G.; Keen, D. A. *Eur. J. Mineral.* 2002, 14, 331.
(6) Proffen, T.; Kim, H. *J. Mater. Chem.* 2009, 19, 5078.
(7) Claridge, J. B.; Hughes, H.; Bridges, C. A.; Allix, M.; Suchomel, M. R.; Niu, H.; Kuang, X.; Rosseinsky, M. J.; Bellido, N.; Grebille, D.; Perez, O.; Simon, C.; Pelloquin, D.; Blundell, S. J.; Lancaster, T.; Baker, P. J.; Pratt, F. L.; Halasyamani, P. S. *J. Am. Chem. Soc.* 2009, 131, 14000.
(8) Petricek V, D. M. a. P. L. Institute of Physics of the ASCR, Prague, Czech Republic, 2006.
(9) Tucker, M. G.; Keen, D. A.; Dove, M. T.; Goodwin, A. L.; Hui, Q. *J. Phys.-Condes. Matter* 2007, 19, 335218.
(10) Norberg, S. T.; Tucker, M. G.; Hull, S. *J. Appl. Crystallogr.* 2009, 42, 179.
(11) Brese, N. E.; Okeeffe, M. *Acta Crystallogr. Sect. B-Struct. Commun.* 1991, 47, 192.