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Exploration of Antiferromagnetic CoO and NiO using Reverse Monte Carlo Total Neutron Scattering Refinements

Lisa Timm¹, Matthew G. Tucker,² David A. Keen,² Peter M. M. Thygesen,¹ Paul J. Saines^{1,3*} and Andrew L. Goodwin¹

¹*Inorganic Chemistry Laboratory, Department of Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom*

²*ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, United Kingdom*

³*School of Physical Sciences, University of Kent, Canterbury CT2 7NH, United Kingdom*
**P.Saines@kent.ac.uk*

Abstract: The atomic and magnetic structures of CoO and NiO have been probed using reverse Monte Carlo refinements of neutron total scattering data. The results obtained show that the known magnetic structure for NiO can be recovered by the reverse Monte Carlo process starting from random spin configurations, but it is insensitive to the spin direction in the {111} ferromagnetic planes. Refinements of the magnetic structure of CoO starting from random spin configurations result in collinear or non-collinear magnetic structure, consistent with those reported by other techniques. Starting from an ordered collinear spin structure for CoO and NiO leads to different results than when starting from a random arrangement of spins, evidence for configurational bias that highlights the need to take care when selecting a starting model for reverse Monte Carlo refinements of magnetic structures.

1. Introduction

Reverse Monte Carlo (RMC) refinements of neutron diffraction data have shown tremendous promise in recent years as a way of uncovering new information about low dimensional and frustrated magnets.¹ The RMC process involves fitting a large supercell of a structure to the data with the addition of magnetic spins to at least some of the atoms in this supercell required to fit magnetic scattering.²⁻⁴ In general two common approaches can be taken to this, depending on whether the compound of interest features significant magnetoelastic coupling, where the emergence of magnetic order causes substantial distortions to the crystallographic structure of a material. In cases where magnetoelastic coupling is minimal, and the local positions of the magnetic cations are well characterised by the average structure, it is possible to approach refinements by fixing the atomic positions and only allowing magnetic spin orientations to refine.^{4,5} In this case fits can be made simply to the magnetic scattering alone, ideally measured using polarised neutrons. This approach has been found to be useful for a large number of exotic low dimensional and frustrated materials, especially because it does not require the use of a preconceived magnetic structure.¹

Many important materials, however, feature very strong magnetoelastic coupling including magnetostriction alloys,⁶ multiferroic oxides,⁷ and even metal-organic frameworks, where it has been shown to cause negative thermal expansion⁸. In RMC refinements of such materials, it is necessary to refine both atomic positions and spin orientation while fitting to the total scattering from the sample.⁹ Such studies reported thus far have been largely restricted to binary systems, due to their challenging nature, including selected members of the antiferromagnetic transition metal rock salts MO (M = Mn, Fe, Co and Ni).^{2,10-12} The magnetic structures of these materials are well known, from the pioneering work of Shull¹³ more than fifty years ago, to have $\mathbf{k} = [\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]_c$ propagation vectors (note that subscript *c* will be used throughout when taking reference with regards to the parent cubic structure). This is consistent with a rhombohedral structure in which the dominant coupling is super-exchange interactions between next-nearest neighbour cations. In-line with this MnO, Fe_{1-x}O and NiO have large rhombohedral

structural distortions, which enable the next-nearest neighbour cations to get closer together, strengthening the interactions between them.^{13,14} The magnetic structures of these compounds contain $\{111\}_c$ sheets in which nearest neighbour cations are, unfavourably, ferromagnetically coupled. In Fe_{1-x}O the spins are perpendicular to the $\{111\}_c$ plane while in MnO and NiO they lie in plane of the sheets.^{13,14} The Bragg intensities of the essentially rhombohedral diffraction patterns of MnO and NiO are insensitive to the spin orientation in these planes, although at least for NiO other techniques suggest the spins are oriented along the $\langle 11\bar{2} \rangle_{\square}$ axis.¹⁵

The magnetic structure of CoO is somewhat more controversial, with both a collinear, essentially rhombohedral, structure and non-collinear magnetic structures fitting the magnetic Bragg reflections.¹⁶ The collinear structure of CoO, which is generally favoured is similar to that of the other rock salts, with spins close to the $[113]_c$ axis.^{16,17} It is, however, inconsistent with the large tetragonal structural distortion that accompanies its magnetic ordering at T_N , 289 K. While evidence that the crystallographic structure of CoO is monoclinic has emerged from high-resolution studies in recent years,^{18,19} resolving this discrepancy, additional weak magnetic reflections have been observed from single crystal neutron diffraction that are not consistent with a collinear structure²⁰.

Recent RMC refinements of MnO and $\text{Fe}_{0.90}\text{O}$ have provided new insights into these oxides. MnO has been confirmed to adopt a monoclinic magnetic structure, as long known to be required from theory, with evidence being found for the magnetic spins in MnO on average pointing along the $\langle 11\bar{2} \rangle_{\square}$ axis and featuring significant modulated out-of-plane component.¹¹ For $\text{Fe}_{0.90}\text{O}$, where the moment has long been known to be, on average, perpendicular to the $\{111\}_c$ planes RMC refinements have revealed that the reduced magnetic moment arises, at least in part, from a deviation of spins from the $\langle 111 \rangle_{\square}$ towards $\langle 110 \rangle_{\square}$ directions in three of the four distinct groups of ions related by the face-centering operation.¹² This, at least partially, lifts the magnetic frustration caused by unfavourable ferromagnetic nearest-neighbour coupling within the $\{111\}_c$ planes. In the light of these results we have, therefore, expanded our work on this series to CoO and NiO, to explore whether RMC refinements can provide new insights into these archetypical antiferromagnets. We have carried out fits starting from both the known collinear magnetic structures and random arrangements of spins to test what effect the starting model has on the magnetic structure refined using the RMC technique. For NiO our results confirm that, below its Néel temperature at 528 K, all spin orientations lie within the $\{111\}$ planes but we find no evidence to support a particular orientation of the spins within these planes. We also recover both collinear and non-collinear magnetic structures from our refinements of CoO. We find strong evidence that the results obtained from the magnetic refinement depends on whether ordered or random spin configurations are used as a starting point, a warning of the need to take care when selecting starting models for RMC magnetic refinements.

2. Experimental

Data were collected on 7 and 8 g samples of NiO and CoO, respectively, which were used as purchased from Sigma-Aldrich. Their purity was checked by X-ray diffraction and thermogravimetric analysis was used to confirm the samples were single phase and stoichiometric with regards to oxygen content. High quality data suitable for neutron total scattering analysis were collected using the GEM diffractometer²¹ at the ISIS neutron source, Rutherford Appleton Laboratories over the range of $0.3 < Q < 50 \text{ \AA}^{-1}$ with counting times of 900 μA -hour. The samples were held in 8 mm diameter vanadium cans in a GEM low-temperature furnace at or above room temperature or in a closed-cycle refrigerator when cooled below room temperature. Measurements of the empty instrument, empty sample environments and empty vanadium can were also carried out to correct for the

instrumental background and scattering from a vanadium rod was used to produce a normalised total scattering structure factor $F(Q)$ (herein we use the terminology of Keen²²). To obtain $F(Q)$ for total scattering analysis for NiO the data from different detector banks were merged and normalised using the programme Gudrun²³. The stronger magnetic scattering from CoO required that self-normalisation and a “Top Hat” correction were performed manually after background subtraction and merging were carried out.

RMC fits to these total scattering data were carried out using the RMCProfile⁹ suite of programmes by similar methodology to that employed for MnO and Fe_{0.90}O to fit $F(Q)$ and Bragg data sets. The Bragg data were initially fitted in GSAS²⁴ via the EXPGUI interface²⁵ to obtain lattice parameters, and background and instrumental constants, using Chebyshev polynomials and an Ikeda-Carpenter function, respectively, which were kept fixed during the RMC refinements. The Rietveld fits were carried out using cubic and tetragonal models for NiO and CoO, respectively, as the additional splitting indicative of symmetry lowering to rhombohedral and monoclinic phases, respectively, could not be observed due to the moderate resolution data obtained. The models used for RMC refinements contained about 10,000 atoms in a $12 \times 12 \times 12$ supercell of the nuclear cubic unit cell of NiO or $14a \times 14a \times 10c$ supercells of the nuclear tetragonal supercell of CoO. It should be noted that RMCProfile⁹ does not apply any symmetry elements so refined models are allowed to have $P1$ symmetry. 16 distinct starting models were used for each material, 8 from an ordered arrangement of spins and pairs of refinements from 4 different random spin configurations. The ordered magnetic starting models for NiO had ferromagnetically coupled $\{111\}$ planes with spins pointing in the $[11\bar{2}]_c$ direction, as well established by magnetization measurements. For CoO the ordered magnetic starting models had magnetic spins oriented along the $[1,1,\bar{3}.4]_c$ axis, which was found to give an improved fit to the data in Rietveld refinements compared to the $[11\bar{3}]_c$ direction in previous models.¹⁷ In the RMC refinements the magnitude of the magnetic moments were fixed at $2.8 \mu_B$ for Ni²⁺, as calculated from the quantised spin-only formula, and $4 \mu_B$ for Co²⁺. Ni-O and Co-O bonds were constrained to lie between 1.60-2.60 Å and 1.50-2.50 Å, respectively using so-called “distance window” constraints. Similar constraints were placed on nearest neighbour metal-metal bonds and oxygen-oxygen bonds at 2.50-3.34 and 2.50-3.50 Å for NiO and CoO, respectively. Refinements allowed either atomic positions or the cation spin orientations to change, by moving atom positions or spin orientations by random fractions of a maximum move size, for four alternating periods in order to minimize the cost function:

$$\chi^2_{\text{total}} = \sum \chi^2_i$$

where the χ^2_i corresponds to the goodness of fit to the $F(Q)$, $\chi^2_{F(Q)}$, and Bragg, χ^2_{Profile} , datasets. The individual χ^2 functions being minimised were, where t is the neutron time-of-flight:

$$\chi^2_{F(Q)} = \sum_{\text{Q}} [\text{data}(Q) - \text{fit}(Q)]^2 w_{F(Q)}$$

$$\chi^2_{\text{Profile}} = \sum_{\text{Q}} [\text{data}(Q) - \text{fit}(Q)]^2 w_{\text{Profile}}$$

The Monte Carlo algorithm avoids local minima by accepting individual moves that degrade the fit to the data with a probability that is close to inversely proportional to the

magnitude of how worse they make the fit. Refinements were carried out with the Bragg and $F(Q)$ datasets weighted approximately equally and with σ values that ensured a reasonable proportion of moves, between 20 and 80 %, are accepted. For the σ values used in this study it was found to be necessary to allow atomic structure and magnetic structure refine for two and one days per period for NiO and CoO, respectively, in which time about 2.5 and 10 million moves were accepted, respectively. This led to RMC refinements for NiO and CoO taking a total of 8 and 4 days respectively at which point the change in χ_{RMC}^2 over several hours for each refinement was approximately an order of magnitude less than the variations between different refinements. These were carried out using a computer with 12 3.06 GHz Intel Xeon processors and 64 GB RAM, with refinements running on one processor each in parallel. Maximum move sizes for atomic positions were set at 0.054 Å and 0.100 Å for the cations and anions, respectively, with the maximum change in spin orientation vector set at 0.05; spin orientation changes are implemented by changing a unitary spin vector by a fraction of this maximum move and renormalizing to ensure the overall magnitude of the spin is retained. For refinements of the crystallographic and magnetic structure the Bragg dataset from banks at 50-75° (bank 4) and 24-45° (bank 3) were used respectively; the former contains data at higher Q, allowing atomic positions to be refined more precisely while the latter enabled all magnetic reflections to be observed at lower Q. For CoO due to the method used to normalize the $F(Q)$ data the scale for the Bragg and $F(Q)$ datasets had to be refined separately.

3. Results and Discussion

3.1 NiO

Rietveld fits to diffraction data obtained from NiO in the paramagnetic phase at 548 and 673 K using all five detector banks did not significantly improve when the oxygen occupancies were allowed to refine, confirming the sample is stoichiometric. Lattice parameters of 4.194050(5) Å and 4.2101680(5) Å, were obtained at 548 K and 673 K, respectively. Fits to data collected at 300 K confirmed this result and a fit using a cubic model gave a lattice parameter of $a = 4.178349(6)$ Å, with the magnetic intensities being well fitted by the established model with spins oriented along the $\langle 112 \rangle_{\square}$ direction with a magnitude of 1.698(4) μ_B (see Fig. S1).¹⁴

RMC fits to total scattering patterns collected at 300 K, starting from both ordered and disordered magnetic structures, gave equally good fits to the data with the average and standard deviation of the eight fits of the χ^2 of each type of 11.7(1.1) % and 11.9(8) % (see Fig. 1). Examination of the RMC-refined crystallographic structure did not reveal any large structural distortions or clustering, with the distribution of atoms around any one position in the collapsed supercell being uniformly spherical (see Fig. S2). The average nearest neighbour distances obtained from the RMC refinements were equivalent for both refinements starting from ordered and random spin configurations with Ni-O, Ni-Ni and O-O distances of 2.075(14) Å, 2.942(14) Å and 2.941(16) Å for those starting from ordered structures compared to 2.075(13) Å, 2.942(12) Å and 2.941(15) Å for those starting from initially random magnetic structures; by comparison the distances obtained from the average structure were 2.089 Å, 2.954 Å and 2.954 Å (uncertainties for the bond distances obtained by the Rietveld method are not given as these are in the 7th significant figure).

The magnetic structures refined using RMC appear very disordered (see Fig. 2 for a typical example) but as the scale of the nuclear and magnetic phases in the refinement were fixed to be on the same scale the well-ordered nuclear structure suggest this is a reasonable representation of the spin orientation at ambient temperature. Analysis of the magnetic structures obtained from RMC refinements indicated that in all cases the

antiferromagnetic coupling of $\{111\}_c$ ferromagnetic planes is recovered from the data (see Fig. S3).

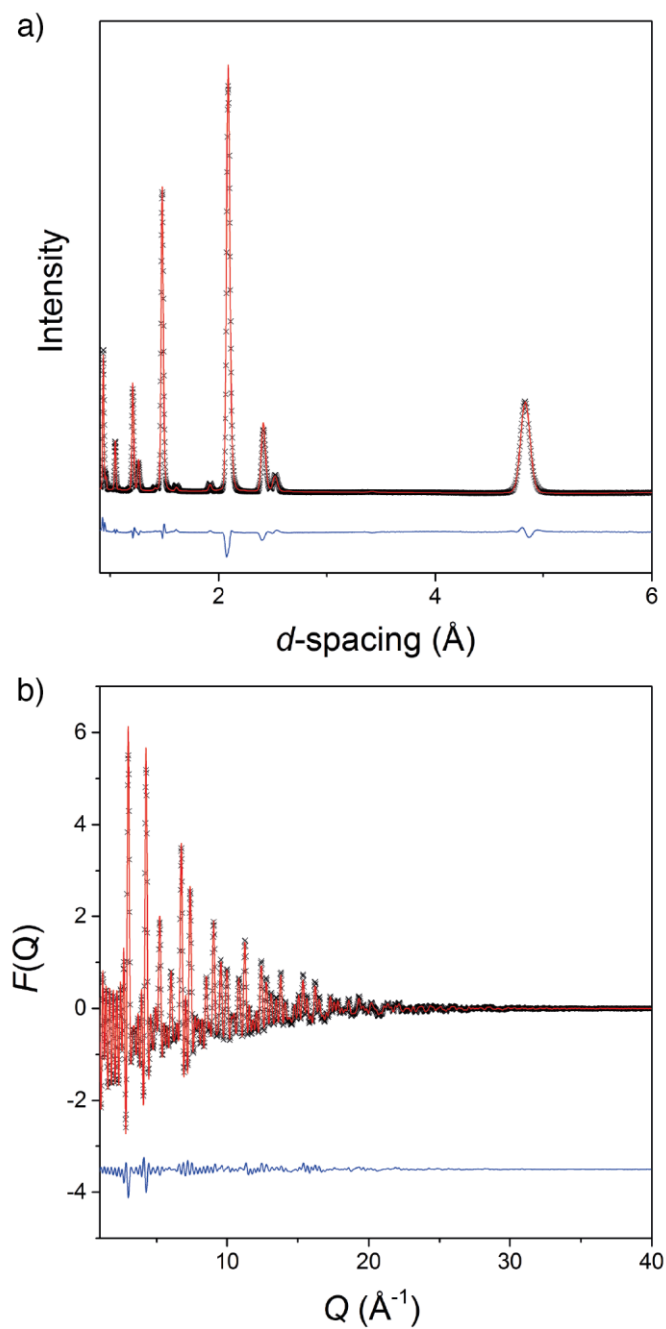


Fig. 1: Representative RMC fits to a) Bragg data from detector bank 3 of the GEM diffractometer and b) total scattering data, respectively, for NiO. The crosses and upper and lower lines represent the experimental data, calculated fits and the difference between them.

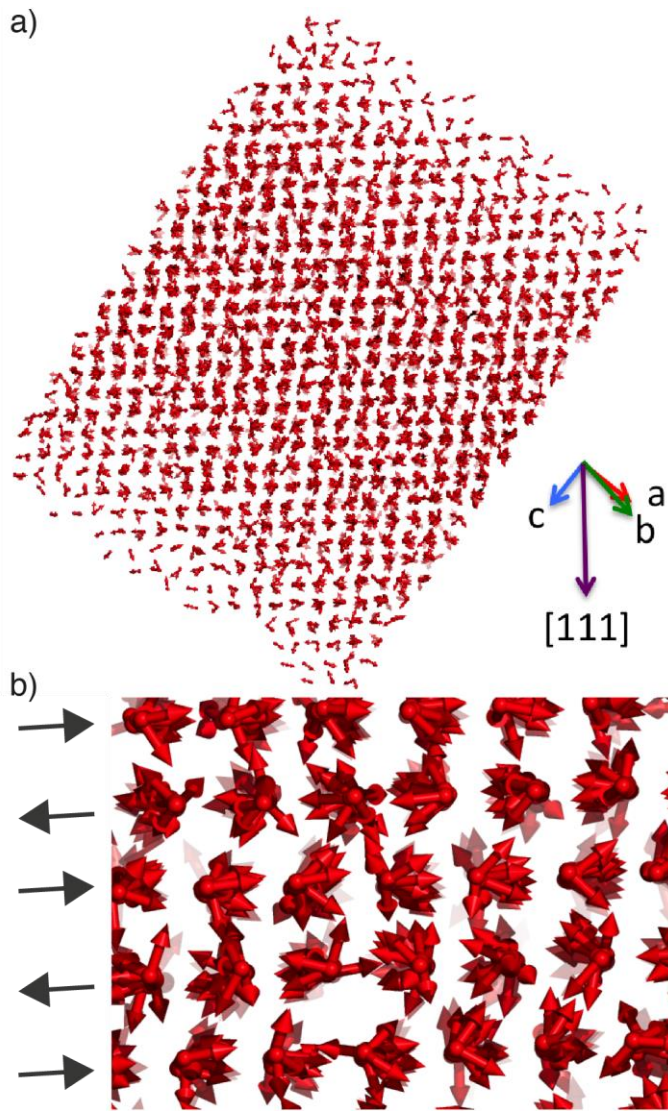


Fig. 2: Spin orientations of Ni in RMC refined structures of NiO are shown as arrows. This refinement started from an ordered spin configuration and the oxygen atoms are omitted for clarity. a) Shows the entire magnetic configuration while b) magnifies on a small section highlighting the $\{111\}$ ferromagnetic planes.

In the case of those refinements starting from ordered magnetic structures the spins remained oriented along the $\langle 11\bar{2} \rangle_{\square}$ directions, mostly along the $[11\bar{2}]_{\square}$ axis although some refined to the symmetry equivalent $[\bar{1}1\bar{2}]_{\square}$ axis (see Fig. 3). The moments in those refinements starting from boxes of random spins were significantly more disordered with it not always being possible to determine a clear spin direction. The moments in these models were found to remain confined along the $\{111\}_c$ planes, without a clear preference for the $\langle 11\bar{2} \rangle_{\square}$ directions. Configurations starting from random orientation are not biased towards any kind of order but will select a random direction within the $\{111\}_c$ planes, providing the most disordered results that fit the data. This suggests the data are quite insensitive to any particular spin direction within the $\{111\}_c$ planes. Refinements starting with spins oriented along various directions in the 60° crystallographically distinct range of orientations in the $\{111\}_c$ planes of a monoclinic magnetic structure for NiO may indicate some subtle improvement for particular directions indicative of a preferred orientation, as found in the previous study of Goodwin *et al.*¹¹ for MnO, but such refinements are beyond the scope of this study. Those starting from ordered magnetic structures exhibit initial configurational bias due to the difficulty in reorienting spins

away from their ordered direction since these are close to values required for a good fit to be obtained. Attempts were made to probe whether the spin orientations of different atoms in the $2a_c \times 2a_c \times 2a_c$ magnetic unit cell could be distinguished from each other, including those groups identified by our previous study of Fe_{1-x}O . Stereographic projections showed no particular variations in spin orientations beyond that required for the known collinear antiferromagnetic structure, however, suggesting an absence of systematic deviations of the spin orientations of different sites in NiO (see Fig. S4).

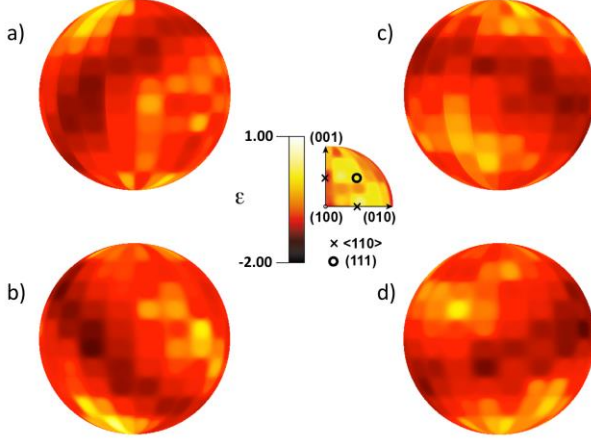


Fig. 3: a) and b) are stereographic projections from a fully refined ordered starting configuration rotated by 180° relative to each other, along the c -axis; c) and d) represent the same for a refinement completed from a random spin configuration. The relative spin density $\epsilon(\theta, \phi) = \ln \left[\frac{n(\theta, \phi)}{n_d(\cos \theta) d\phi} \right]$, where $n(\theta, \phi)$ is the number of spins with orientations within the range $d(\cos \theta), d\phi$.

3.2 CoO

Rietveld fits to the neutron diffraction patterns of CoO above 289 K, in the paramagnetic phase, were well fitted by the cubic rock salt structure with $a = 4.26599(4)$ Å and $4.28903(13)$ Å, for 300 K and 673 K respectively. Refinement of the oxygen occupancy did not significantly improve the fit, confirming the sample is also stoichiometric with respect to oxygen content. The medium resolution of the diffractometer used in this study only reveals splitting consistent with symmetry lowering to tetragonal in the ordered phase, instead of the recently reported monoclinic structure. Fits to data at 100 K, gave $a = 3.014315(9)$ Å and $c = 4.21685(3)$ Å for the nuclear cell with magnetic reflections well fitted by the known $2a \times b \times 2c$ magnetic structure with spins parallel and antiparallel to the $[1, 1, \sqrt{3}\bar{60}(11)]_c$ with an overall moment of $3.864(5) \mu_B$ (see Fig. S5).¹⁷

RMC refinements started from both ordered and disordered arrangements of spins both gave equivalent fits to the total scattering patterns obtained at 100 K, with final average χ^2 of $19.45(6)$ % obtained over eight refinements of each type (see Fig. 4). As was the case for NiO examination of the refined atomic positions did not reveal any major defects or clustering of atoms with both cobalt and oxygen atoms having a uniform distribution around their average positions (see Fig. S6). The average nearest neighbour distances for Co-O, Co-Co and O-O were very similar with $2.10(2)$ Å, $2.94(2)$ Å and $2.991(15)$ Å obtained from the ordered starting configurations and $2.12(2)$ Å, $2.99(2)$ Å and $2.991(15)$ Å obtained from starting with random spin orientation.

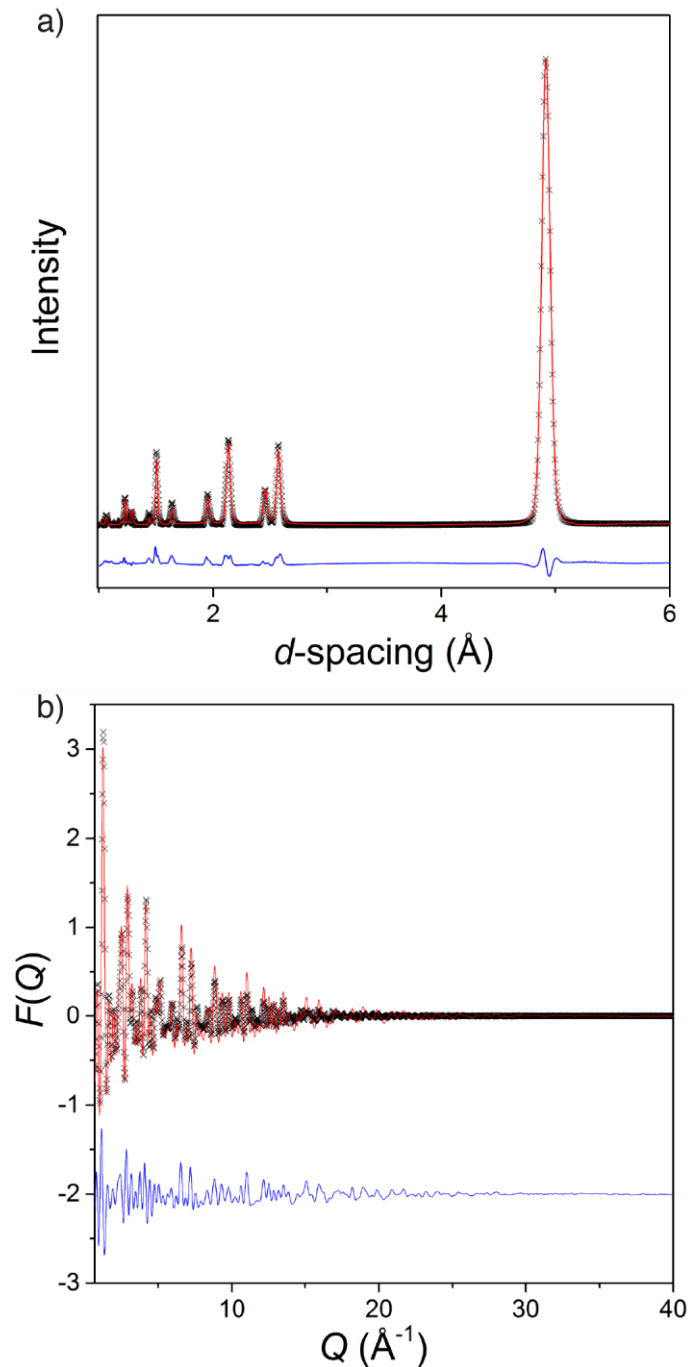


Fig. 4: Representative RMC fits to a) Bragg data from detector bank 3 of the GEM diffractometer and b) total scattering data, respectively, for CoO. The format is the same as for Fig. 1. The fit shown is that obtained with a collinear model; fits obtained from non-collinear models were of visually identical quality.

Analysis of the magnetic structures obtained from RMC refinements starting from ordered spin configurations indicated they retained a similar magnetic structure, with $\{111\}_c$ ferromagnetic planes coupled antiferromagnetically to each other. In these cases the spin orientation remained close to the orientations present in the ordered starting configurations (see Fig. 5 and Fig. S7). Examination of the stereographic projections calculated for each site in the $2a_t \times 2a_t \times 2c_t$ magnetic unit cell for the random configurations showed that while half of the refinements starting from random spin configurations led to a similar structure the other half gave rise to a more complex structure that did not contain simple $\{111\}_c$ ferromagnetic planes or collinear magnetic

moments. This structure can be described on the basis of a $2a_t \times 2a_t \times 2c_t$ magnetic unit cell (here, subscript t indicates we are referring to the tetragonal setting) but only the spins on atoms related to each other by the body-centred operation maintain the same spin direction (see Fig. 5 and Fig. S8). The spin orientations still remain close to the $\langle 102 \rangle_{\square}$ directions but these are arranged in such a way that, while still satisfying the antiferromagnetic next-nearest neighbour coupling required by the dominant superexchange, spins on nearest neighbour sites that would otherwise be ferromagnetically coupled to each other are offset by about 30° (see Fig. 6). Qualitatively it is very similar to the non-collinear model proposed by Van Laar, whose model also lacked $\{111\}$ planes.¹⁶ As found in a similar result for Fe_{1-x}O this model would minimise the frustration inherent in these rock salt oxides by at least partially satisfying the desire for nearest neighbour spins to be antiferromagnetic.¹² That the non-collinear structure does not emerge from any of our refinements starting from a collinear phase again highlights the potential for configurational bias in magnetic RMC refinements. This highlights the important effect the starting model selected has on the results obtained from magnetic RMC refinements and, therefore, the need to be careful when selecting a starting model. Interestingly pairs of identical random starting spin configurations both lead to the emergence of either collinear or non-collinear structure. This suggests that even the precise of the random spin configuration influenced which of these emerged, although the number of pairs of refinements performed was relatively small so we are reluctant to draw any definitive conclusions here.

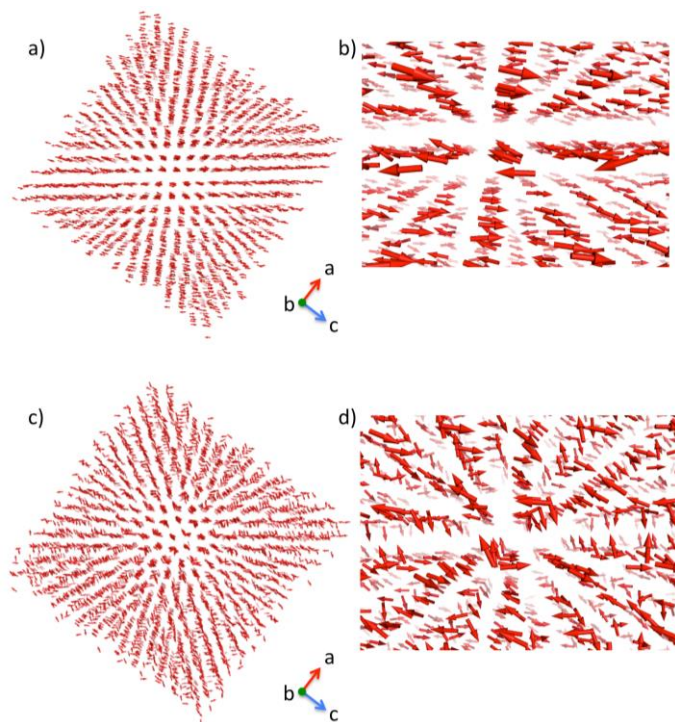


Fig. 5: Spin orientations of Co in RMC refined structures with collinear, a) and b), and non-collinear configurations, c) and d). The format is the same as Fig. 2. a) and c) show the entire magnetic configuration while b) and d) highlight the presence and lack of $\{111\}$ planes.

We have fitted our diffraction patterns of the antiferromagnetic phase to the non-collinear model using the Rietveld method to compare to the fit we obtain using the collinear structure. Unfortunately, as established by the work of Van Laar¹⁶ using low resolution data, we get almost identical fits. The non-collinear models give a fit with R_p , and R_{wp} and χ^2 of 3.50 % and 3.40 %, which is very similar to the values of 3.51 % and 3.42 % that we get from the collinear structure. The Rietveld refinements of the non-

collinear model give Co magnetic moments of $3.853(6) \mu_B$ with spins pointed along the $\langle 1.00(2), 0, 2.61(3) \rangle_{\square}$ directions. While neither of these fits are ideal the recently reported monoclinic model^{18,19} surprisingly gave a slightly worse fit to the data with R_p , R_{wp} and χ^2 of 4.24, 4.88 and 0.633. This is not to say that the magnetic structure of CoO is not monoclinic, merely there is no direct evidence for this in our moderate resolution data.

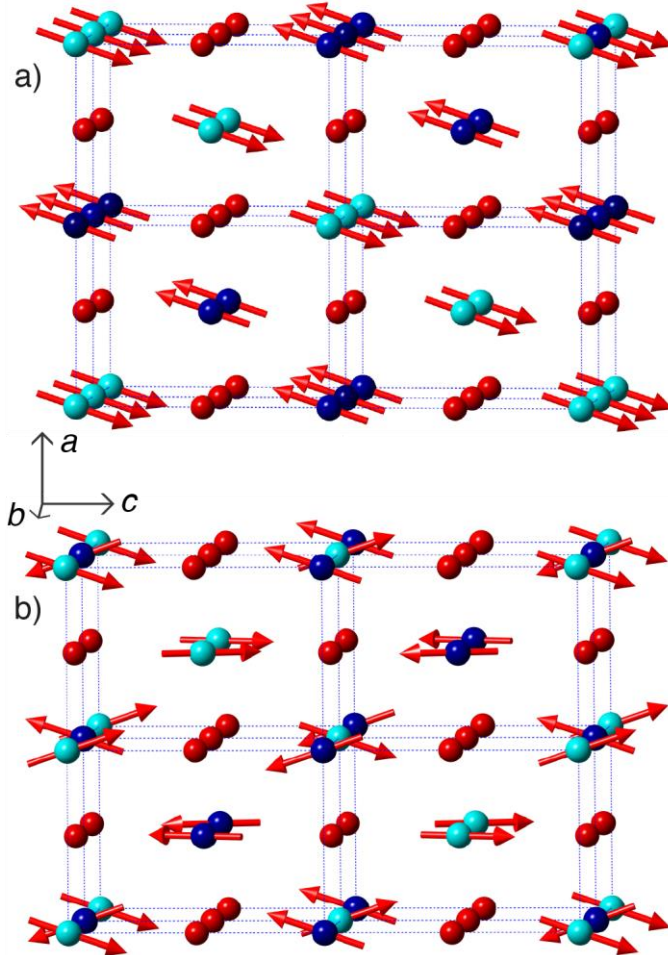


Fig. 6: Average magnetic structures of the a) collinear and b) non-collinear magnetic structures of CoO.

Using the group-theoretical analysis package ISODISTORT²⁶ we have examined how the two magnetic structures relate to the parent $\square\square\bar{3}\square$ structure. The FINDSYM²⁶ programme in this package identifies that the non-collinear magnetic structure has I_c4_1/acd symmetry in a structure containing a single unique Co cation at the $16e$ $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$ position with freely refineable magnetic moments along the c -axis and perpendicular to it. The collinear structure, on the other hand, is in magnetic space group C_c2/c with the Co at the $4d$ $(0, \frac{1}{2}, 0)$ position, with refineable magnetic moment along the a - and c -axes. Removal of the magnetic spins from this latter structure leads to the $C2/m$ crystallographic structure first proposed Jauch *et al.*,¹⁸ consistent with their similar magnetic structures. The modes active for these two magnetic structures are similar, with group-theoretical analysis suggesting that a transition to either structure would involve symmetry lowering via primary distortion modes at both the Γ , $(0,0,0)$, and Λ -points, $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, with the former allowing the distortion of the lattice while the latter describes the magnetic order. In the I_c4_1/acd non-collinear structure, however, there are secondary distortions allowed at the X-point, $(0,1,0)$, which is consistent with the weak reflections observed in the work of Tomiyasu *et al.*²⁰ On this basis they proposed a different non-

collinear model, which does not emerge in any of our RMC refinements, but we agree that such distortions would not be allowed by the C_c2/c collinear structure. We do not observe any X-point reflections in our data but, as Tomiyasu *et al.*²⁰ suggest these have very weak intensities, 1×10^{-3} of the order of the (001) reflection and would be in the noise of our data.

Since both the collinear and non-collinear fits to the data are equivalent, and indeed both emerge from non-configurationally biased RMC refinements starting from random spin arrangements, we are unable to distinguish between these two on the basis of our data. We suggest that in-order to distinguish clearly whether the magnetic structure of CoO is collinear or non-collinear patterns would need to be obtained that have both the extremely high resolution required to resolve the subtle monoclinic splitting of CoO^{18,19}, but also have low enough background to confirm the presence of the very weak X-point reflections detected by Tomiyasu *et al.*²⁰ The approach used for this analysis would need to allow for the likely possibility that the symmetry of CoO will have to be lowered further than either of the models encountered in this work, to allow both these features to be accounted for. Only an approach that can confirm and then reconcile these two observations will provide a satisfying solution to the continuing debate over the magnetic structure of CoO. Furthermore that the results obtained from these compounds are so heavily influenced by the chosen starting configurations, however, may suggest implications for RMC studies of other materials. It emphasises the importance of considering starting from a number of different random arrangements of spins, ideally alongside configurations of more-ordered configurations thought to be likely candidates for the magnetic structure of a material. Only when a magnetic structure appears from the vast majority of starting points for the refinement is it likely to be a trustworthy solution.

4 Conclusions

In this study we have carried out RMC refinements of the strongly magnetoelastically coupled CoO and NiO rock salt antiferromagnets. We have found that regardless of whether an ordered or disordered starting point is used for the magnetic structure of NiO, we are able to recover the known antiferromagnetic structure for this material,¹⁴ with its ferromagnetic $\{111\}_c$ planes that couple antiferromagnetically to each other. While the spin orientations that emerge from our models remain in the $\{111\}_c$ planes we find no clear evidence that our data are sensitive to a particular orientation within them. Configurational bias from the ordered starting points, however, ensures the spins in these refinements remain along the $\langle 11\bar{2} \rangle_{\square}$ directions. In CoO we find that both collinear and non-collinear models emerge from our RMC refinements, which give an equally good fit to our data. Evidence for configurational bias again is found as all the refinements starting with collinear models as starting points yield collinear structures at the end of their refinements. We have confirmed the magnetic symmetry of these two structures, showing that the collinear structure is C_c2/c and the non-collinear structure is $Ic4_1/acd$, each of which account for a different observation regarding CoO observed in recent diffraction studies.¹⁸⁻²⁰ Further studies are required to confirm and reconcile these two observations to enable the true magnetic symmetry of CoO to be uncovered.

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References

1. a) A. M. Hallas *et al.*, *Phys. Rev. B*, 2012, **86**, 134431; b) J. A. M. Paddison, S. Agrestini, M. R. Lees, C. L. Fleck, P. P. Deen, A. L. Goodwin, J. R. Stewart and O. A. Petrenko, *Phys. Rev. B*, 2014, **90**, 014411; c) G. J. Nilsen, C. M. Thompson, G. Ehlers, C. A. Marjerrison and J. E. Greedan, *Phys. Rev. B*, 2015, **91**, 054415; d) J. A. M. Paddison, H. Jacobsen, O. A. Petrenko, M. T. Fernández-Díaz, P. P. Deen and A. L. Goodwin, *Science*, 2015, **350**, 179; e) P. J. Saines, J. A. M. Paddison, P. M. M. Thygesen and M. G. Tucker, *Mater. Horiz.*, 2015, **2**, 528; f) A. K. Bera, S. M. Yusuf, A. Kumar, M. Majumder, K. Ghoshray and L. Keller, *Phys. Rev. B*, 2016, **93**, 184409.
2. a) D. A. Keen, R. I. Bewley, R. Cywinski and R. L. McGreevy, *Phys. Rev. B*, 1996, **54**, 1036; b) A. Mellergård, R. L. McGreevy, A. Wannberg and B. Trostell, *J. Phys. Condens. Mat.*, 1998, **10**, 9401; c) A. Mellergård, R. L. McGreevy and S. G. Eriksson, *J. Phys. Condens. Mat.*, 2000, **12**, 4975; d) A. K. Azad, A. Mellergård, S.-G. Eriksson, S. A. Ivanov, J. Eriksen, H. Rundöf, *Appl. Phys. A*, 2002, **74**, s763.
3. R. L. McGreevy and L. Pusztai, *Mol. Simulat.*, 1988, **1**, 359.
4. J. A. M. Paddison and A. L. Goodwin, *Phys. Rev. Lett.*, 2012, **108**, 017204.
5. J. A. M. Paddison, R. J. Stewart and A. L. Goodwin, *J. Phys.: Condens. Mat.*, 2013, **25**, 454220.
6. a) L. Sandlund, M. Fahlander, T. Cedell, A. E. Clark, J. B. Restorff and M. Wun-Fogle, *J. Appl. Phys.*, 1994, **75**, 5656; b) A. E. Clark, J. B. Restorff, M. Wun-Fogle, T. A. Lograsso and D. L. Schlagel, *IEEE T. Magn.*, 2000, **36**, 3238.
7. a) X. Fabrèges, S. Petit, I. Mirebeau, S. Pailhès, L. Pinsard, A. Forget, M. T. Fernandez-Diaz and F. Porcher, *Phys. Rev. Lett.*, 2009, **103**; b) J. Park *et al.*, *J. Phys. Soc. Jap.*, 2011, **80**, 114714.
8. P. J. Saines, P. T. Barton, M. Jura, K. S. Knight and A. K. Cheetham, *Mater. Horiz.*, 2014, **1**, 332.
9. M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin and Q. Hui, *J. Phys. Condens. Mat.*, 2007, **19**, 335218.
10. L. Karlsson, R. L. McGreevy and J. D. Wicks, *J. Phys. Condens. Mat.*, 1999, **11**, 9249.
11. A. L. Goodwin, M. G. Tucker, M. T. Dove and D. A. Keen, *Phys. Rev. Lett.*, 2006, **96**, 047209.
12. P. J. Saines, M. G. Tucker, D. A. Keen, A. K. Cheetham and A. L. Goodwin, *Phys. Rev. B*, 2013, **88**, 134418.
13. C. G. Shull, W. A. Strauser and E. O. Wollan, *Phys. Rev.*, 1951, **83**, 333.
14. W. L. Roth, *Phys. Rev.*, 1958, **110**, 1333.
15. a) T. Yamada, S. Saito and Y. Shimomura, *J. Phys. Soc. Jap.*, 1966, **21**, 672; b) J. Baruchel, M. Schlenker, K. Kurosawa and S. Saito, *Philos. Mag. B*, 1981, **43**, 853; c) E. Ressouche, N. Kernavanois, L.-P. Regnault and J.-Y. Henry, *Phys. B Condens. Mat.*, 2006, **385–386**, 394.
16. B. van Laar, *Phys. Rev.*, 1965, **138**, A584.
17. D. A. O. Hope and A. K. Cheetham, *J. Solid State Chem.*, 1988, **72**, 42.
18. W. Jauch, M. Reehuis, H. J. Bleif, F. Kubanek and P. Pattison, *Phys. Rev. B*, 2001, **64**, 052102.
19. S. Lee, Y. Ishikawa, P. Miao, S. Torii, T. Ishigaki and T. Kamiyama, *Phys. Rev. B*, 2016, **93**, 064429.
20. K. Tomiyasu, T. Inami and N. Ikeda, *Phys. Rev. B*, 2004, **70**, 184411.
21. A. C. Hannon, *Nucl. Instrum. Meth. A*, 2005, **551**, 88.

22. D. Keen, *J. Appl. Crystallogr.*, 2001, **34**, 172.
23. A. K. Soper, *Technical Report No. RAL-TR-2011-013*, Rutherford Appleton Laboratory, 2011.
24. A. C. Larson and R. B. Von Dreele, *General Structure Analysis System (GSAS)*, LAUR 86-748, Los Alamos National Laboratory, Los Alamos, 1994.
25. B. Toby, *J. Appl. Crystallogr.*, 2001, **34**, 210.
26. B. J. Campbell, H. T. Stokes, D. E. Tanner and D. M. Hatch, *J. Appl. Crystallogr.*, 2006, **39**, 607.