Antiferromagnetism in NiO Observed by Transmission Electron Diffraction

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(Dated: May 2, 2014)

Neutron diffraction has been used to investigate antiferromagnetism since 1949. Here we show that antiferromagnetic reflections can also be seen in transmission electron diffraction patterns from NiO. The diffraction patterns taken here came from regions as small as 10.5 nm and such patterns could be used to form an image of the antiferromagnetic structure with a nanometre resolution.

Antiferromagnetic materials have opposed magnetic moments on adjacent atoms so produce no external magnetic field. They were identified in 1932 [1] and today their main application is for computer hard drive readers which use the exchange-bias effect [2, 3]. The arrangement of the atomic magnetic moments can be deduced by recording diffraction patterns using radiation sensitive to the magnetic flux density between the atoms. Neutrons have a magnetic moment due to the magnetic flux density between the atoms. By recording diffraction patterns using radiation sensitive to the magnetic moments can be deduced which use the exchange-bias effect [2, 3]. The arrangement of the atomic magnetic moments can be deduced by recording diffraction patterns using radiation sensitive to the magnetic flux density between the atoms. Neutrons have a magnetic moment of magnitude $\mu_n = 9.65 \times 10^{-27}$ Am$^2$ and so feel a force $F_n = \mu_n \nabla B$ on passing through a B-field with a velocity $v$. The effect of the Lorentz force is used extensively in electron microscopy to map B-fields in ferromagnets [6] but our literature survey found no evidence of its use to examine antiferromagnets [3].

Electrons should also be sensitive to antiferromagnetism as they are charged particles (with charge $-e = -1.602 \times 10^{-19}$ C) and so experience a Lorentz force $F_e = -e v \times B$ on passing through a B-field with a velocity $v$. The effect of the Lorentz force is used extensively in electron microscopy to map B-fields in ferromagnets [6] but our literature survey found no evidence of its use to examine antiferromagnets.

Antiferromagnetic domains have been imaged before using transmission electron microscopy but these images did not use magnetic scattering but relied on the fact that the domains observed were also structural twins [7]. In Electron Microscopy of Thin Crystals [8] it states ‘it is not clear whether the periodicity in the spins [of an antiferromagnet] can give rise to observable diffraction effects [in a transmission electron diffraction pattern]’. Here we show that antiferromagnetic reflections can be observed in electron diffraction patterns and are about $10^4$ times less intense than the structural Bragg peaks unlike neutron diffraction where both are of similar intensity [5].

The Lorentz force is the dominant force felt by electrons due to the magnetic flux density in the specimen at the energies used for transmission electron microscopy (300 keV here) as shown in Supp. Info. 1. Unlike neutrons, the magnetic force due to the electron’s dipole moment never dominates. At low energy, the exchange interaction dominates [4] and low energy (32 eV) electron diffraction patterns have been acquired from the first atomic layer of an antiferromagnet using this effect [10].

The advantage of transmission electron microscopy is its potential to examine features of the antiferromagnetic structure such as domain walls at high resolution. The diffraction patterns taken here came from regions as small as 10.5 nm and a 1 nm resolution should be possible. For comparison, the resolution of neutron imaging [11] is 60 µm; low energy electron diffraction, 10 nm [10] and photoemission electron microscopy, 20 nm [12].

In this experiment, we acquired electron diffraction patterns from single crystal NiO. It was one of the first antiferromagnets investigated by neutron diffraction so its magnetic structure is well characterised [13]. Its crystal structure is based on the face-centred cubic, sodium chloride structure [14] with a lattice parameter of $a = 4.18$ Å. Antiferromagnetic order occurs below the Néel temperature, $T_N = 523$ K and consists of the ferromagnetic alignment of the magnetic moments of the Ni ions in one set of (111)-type planes with the moments in alternate (111) planes being antiparallel [13] (see Supp. Info. 2). Experimental measurements of the magnetic moment give values between 1.77 and 2.2±0.2µB per Ni ion [15] and the usual picture is that each Ni$^{2+}$ ion has its spin-only magnetic moment of 2µB although this is questioned in ref. [16].

Antiferromagnetic order is accompanied by a slight rhombohedral distortion [14] which compresses the lattice along the [111] axis normal the ferromagnetic (111) planes. This distortion does not lead to extra reflections and we index diffraction patterns using the conventional cubic coordinates. In Supp. Info. 3, it is shown that if positions in reciprocal space of the structural Bragg reflections are denoted $\mathbf{G} = (hkl)$ and the antiferromagnetic modulation in the local magnetisation is written $\mathbf{M} = \mathbf{M}_0 \cos(2\pi \mathbf{q} \cdot \mathbf{r})$ (where $\mathbf{r}$ is a position vector, $\mathbf{q}$ is the wavevector of the modulation and $\mathbf{M}_0$ is the sublattice magnetisation), antiferromagnetic reflections occur at positions $\mathbf{Q} = \mathbf{G} \pm \mathbf{q}$ in diffraction patterns acquired using radiation sensitive to magnetism. For NiO, $h,k,l$ must all be odd or all even numbers. The antiferromagnetic wavevector points in one of four possible (111) directions and each will generate different antiferromagnetic reflections. For example, the lowest order reflections generated by $\mathbf{q} = \frac{1}{2}(111)$ will be $\mathbf{Q} = \pm \frac{1}{2}(111)$, $\pm \frac{1}{2}(1\bar{1}3)$, $\pm \frac{1}{2}(\bar{3}1)$ but not $\frac{1}{2}(113)$ as there is no allowed structural reflection, $\mathbf{G}$, from which this could
In the absence of an applied magnetic field, the magnetic moments of the Ni ions, \( \mathbf{\mu} \), point in one of the three \((1\overline{1}2)\) directions (called ‘easy axes’) which lie in the ferromagnetically aligned \((111)\) planes [15]. When the direction of the antiferromagnetic order changes, there are two types of domain boundary: a twin (T-type) boundary occurs when the magnetic order changes to a different set of \((111)\) planes and the accompanying distortion generates a crystallographic twin. The spin (S-type) domain boundary occurs where the same set of \((111)\) planes remains ferromagnetic but the magnetic moments point in a different direction (see Supp. Info. 2).

For most of this experiment, the microscope was used in its normal operating mode where the objective lens applies a 2.8 T magnetic field to the sample parallel to the electron beam. Above 1.54 T, a ‘spin-flop’ takes place in single crystal NiO where the spins are realigned so they remain in the same zone as \( \mathbf{q} \) but point normal to the applied field [17]. For the \([112]\)-type zone axes used here, the direction of the magnetic moments in the spin-flopped configuration will be of the \([1\overline{1}0]\)-type. In addition, the spins will be canted in the direction of the field by an angle of 9° (calculated from the susceptibility measurements in ref. [18]). The induced spin flop is an advantage for the purpose of seeing antiferromagnetic reflections, as they have maximum intensity when the magnetic moments are normal to the incoming beam. The spin flop also avoids the possibility of the magnetic moments being parallel to the beam which would render the antiferromagnetic reflections invisible. We have also taken diffraction patterns in a low-field configuration as discussed later.

In Supp. Info. 3, the phase object approximation is used to derive the following formula for the intensity of an antiferromagnetic reflection at position \( \mathbf{Q} \), \( I_Q \), relative to the 000 beam, \( I_0 \), for electron scattering:

\[
\frac{I_Q}{I_0} = \left( \frac{e \mu_0 \mu_B t}{2 \hbar \Omega \mathbf{Q}} \left( \mathbf{\hat{z}} \times \mathbf{Q} \right) \hat{z} F(\mathbf{Q}) \right)^2
\]

where \( h \) is Planck’s constant, \( \Omega \) is the unit cell volume and \( t \) is the specimen thickness. \( \mathbf{\hat{z}} \) is a unit vector in the direction of the magnetic moments, \( \mathbf{Q} \) is a unit vector in the scattering direction and \( \mathbf{\hat{z}} \) is a unit vector in the direction of the incident electron beam. The structure factor is given by \( F(\mathbf{Q}) = \sum_j n_j f_j(\mathbf{Q}) e^{2\pi i \mathbf{Q} \cdot \mathbf{r}_j} \) where the sum is over all the atoms in one unit cell, \( n_j \) is the number of unpaired electrons associated with atom \( j \) and \( f_j(\mathbf{Q}) \) is the magnetic form factor for atom \( j \). The form factor is the same as for neutron diffraction because the same electrons generate the flux density. We use the values given in ref. [19]. The calculated intensity ratios are tabulated in Supp. Info. 4 for a 100 nm thick specimen in the \((112)\)-type zone axes for \( \mathbf{\mu} \) in \((1\overline{1}2)\)-type easy directions as well as the spin-flopped \([1\overline{1}0]\)-type directions.

The NiO single crystals used in this experiment were supplied by Pi-Kem Ltd and were of size \( 5 \times 5 \times 0.5 \) mm with the largest surface being \((111)\). They were prepared for electron microscopy by thinning in the \([111]\) direction by mechanical polishing followed by argon ion beam thinning using a Gatan Precision Ion Polishing System (PIPS). Electron microscopy was conducted using a Philips CM300 transmission electron microscope equipped with a field-emission gun operated at 300 kV.

The advantage of a crystal thinned in the \([111]\) direction is that the \([122], [121] \) and \([211] \) zone axes are accessible with a double-tilt holder as each lies at 19.5° to \([111]\). This ensures that antiferromagnetic reflections are seen in at least one of these zones for any \( \mathbf{q} \). The disadvantage is that the \((111)\) surface is unstable to surface reconstructions which can also produce extra reflections in a diffraction pattern [20].

Electron diffraction patterns were acquired using Ditabi imaging plates which have a high dynamic range of 2 million grey levels. They were not filtered to remove inelastic scattering as the Gatan Imaging Filter on this microscope does not allow energy-filtered images to be acquired on imaging plates. The patterns were acquired with exposures between 0.2 and 200 s at camera lengths of 740–3900 mm from regions 10.5–880 nm in diameter. The shortest exposure in which antiferromagnetic reflections could be seen was 0.24 s.

We first used polarised light microscopy to visualise the rhombohedral (T-type) domains (Supp. Info. 5) showing they were 2–80 \( \mu \)m in size. We then acquired electron diffraction patterns and Fig. 1(a) shows a pattern taken at room temperature from the \([122] \) zone axis with superlattice reflections at \( \mathbf{Q} = \frac{1}{2}(11\overline{1}) \). The full-width-half-maximum of the superlattice reflections was the same as the structural reflections to an upper limit of 0.2% of \( |q_{11\overline{1}}| \) indicating very good long-range order. No superlattice reflections were seen in the same area from the \([121] \) and \([211] \) zone axes, consistent with the area being a single antiferromagnetic domain.

To investigate whether the reflections were generated by antiferromagnetism, the sample was heated above the Néel temperature \( (T_N = 523 \) K) using a Philips PW6592 heating holder. Fig. 1(b) was recorded at a temperature of 563 K and the superlattice reflections are now absent. This is strong evidence that they originate from antiferromagnetism.

At room temperature after heating above \( T_N \), the pattern of antiferromagnetic domains would be expected to change and this is what was observed. The reflections at \( \mathbf{Q} = \pm \frac{1}{2}(11\overline{1}) \) were no longer present in the region from which Fig. 1 was taken but an adjacent region 250 nm away showed \( \mathbf{Q} = \pm \frac{1}{2}(11\overline{1}) \) reflections which had not been there previously. Between these two regions was a line of contrast of the type identified in ref. [21] as a T-type antiferromagnetic domain wall.

The same experiment was performed in a different re-
FIG. 1. (a) Electron diffraction pattern from the [112] zone axis taken at room temperature from a region of diameter 880 nm with an exposure of 70 s. \( \pm \frac{1}{2}(11\bar{1}) \) superlattice are indicated by arrows. (b) Electron diffraction pattern from the same region taken at 563 K, above the Néel temperature \( T_N = 523 \) K, showing that the superlattice reflections are no longer present.

The data points in Fig. 2 show the variation of the intensity of the \( \pm \frac{1}{2}(11\bar{1}) \) reflections as a function of thickness. The x-errorbars show the uncertainty due to the extrapolation between thickness fringes. The error in the measured intensities is very small and the principal cause of data scatter is specimen bending which changes the deviation parameter so that the \( \pm \frac{1}{2}(11\bar{1}) \) reflections do not have the same intensity.

The behaviour in Fig. 2 is not consistent with a surface reconstruction. For a surface reconstruction, the intensity should be greatest at the smallest thickness and diminish as the thickness increases. Here the intensity is zero at zero thickness and oscillates as the thickness increases as expected for a reflection originating from the bulk.

The deviation parameter for the \( \pm \frac{1}{2}(11\bar{1}) \) reflections on the [112] zone axis is \( s = 4.23 \times 10^{-4} \) Å\(^{-1} \) so the intensity should oscillate with thickness with period \( 1/s = 237 \) nm. This prediction is shown by the solid line in Fig. 2 and the only fitting parameter used was the amplitude of the oscillation. It can be seen that the data points follow this trend.

Eqn. 1 predicts the intensity ratio of the antiferromagnetic \( \frac{1}{2}(11\bar{1}) \) beam relative to the 000 beam but makes use of the phase object approximation and so will only apply to the thinnest parts of the specimen. There are several comparisons one could make with experiment. The simplest is to look at the diffraction pattern from the thinnest region where superlattice reflections could be discerned, 57 nm. The measured intensity ratio here is \( 1.25 \times 10^{-4} \) for \( \frac{1}{2}(11\bar{1}) \) and \( 1.79 \times 10^{-4} \) for \( \frac{1}{2}(1\bar{1}1) \). The predicted ratio (accounting for the deviation parameter) is \( 0.50 \times 10^{-4} \). Alternatively one could state that the theory neglects the loss of intensity of the 000 beam due to scattering to the structural reflections and therefore one should divide not by the intensity of the 000 beam for 57 nm but by the intensity of 000 for the thinnest region at which data was recorded. This gives ratios of...
FIG. 3. Electron diffraction pattern taken from the [112] zone axis in a field of less than 10 mT. Antiferromagnetic reflections (indicated by arrows) are seen at $\pm \frac{1}{2}(11\bar{1})$.

0.54 $\times$ 10$^{-4}$ and 0.77 $\times$ 10$^{-4}$, closer to the predicted ratio of 0.50 $\times$ 10$^{-4}$. Finally, one could use the fitted curve to give the intensity ratio for the thinnest region of the sample from which data was recorded, 19 nm. This gives a ratio of 6.4 $\times$ 10$^{-6}$ as compared with a predicted ratio of 6.6 $\times$ 10$^{-6}$.

We consider the combined facts that the superlattice reflections are at the correct positions, originate from the bulk, disappear above the Neel temperature and have intensities in the range predicted by theory compelling evidence that they originate from antiferromagnetism.

The above experiment was conducted with the microscope in its normal operating condition with a field of 2.8 T applied to the specimen so that its spins flop. Fig. 3 was taken from the same area using a ‘Lorentz lens’ instead of the objective lens so that the sample was in a field less than 10 mT. The same superlattice reflections are observed. Saito et al. showed that if the field inducing the spins to flop is removed, they return to point along their easy axes. Since the superlattice reflections are still visible in Lorentz mode, they must be aligned along either [2T1] or [T21] but not [112] (i.e. parallel to the electron beam) as they would then be invisible. The intensity ratios are 2.29 $\times$ 10$^{-4}$ and 2.74 $\times$ 10$^{-4}$ for the $\frac{1}{2}(11\bar{1})$ and $\frac{1}{2}(T1)$ reflections respectively and the diffraction pattern comes from a region 119 $\pm$ 10 nm thick. Supp. Info. 3 predicts an intensity ratio of 1.29, closer to the predicted ratio of 1.7.

In summary, antiferromagnetic reflections can be observed in transmission electron diffraction patterns from NiO with an intensity $\sim$ 10$^4$ times less intense than the structural reflections. We give a model to predict the intensities of the antiferromagnetic reflections which agrees with our observations, allowing deductions to be made about the direction of the magnetic moments. The diffraction patterns taken here came from regions as small as 10.5 nm in diameter and such patterns could be used to image the antiferromagnetic structure using spatially resolved electron diffraction with a nanometre resolution.

SUPPLEMENTARY INFORMATION 1: ESTIMATE OF THE FORCE ON AN ELECTRON AS IT PASSES THROUGH AN ANTIFERROMAGNET

For transmission electron microscopy, the Lorentz force is about 500 times larger than the force the electron feels due to its magnetic dipole moment as the following estimate shows. The maximum Lorentz force, $F_L = -ev \times B$ felt by an electron passing through an antiferromagnet is about 2.4 $\times$ 10$^{-11}$ N (using $v = 2.3 \times 10^8$ ms$^{-1}$ for 300 keV electrons and $B = \mu_0 M_0 = 0.64$ T where $M_0$ is the sublattice magnetisation for NiO) whereas the force due to the electron’s magnetic moment is $F_\mu = \mu_0 \nabla B$ and has a maximum value of $F_\mu \approx \mu_B(2B/d) = 4.9 \times 10^{-14}$ N (where $d = 2.4$ Å is the spacing between the (111) planes of antiparallel spins in NiO). A similar estimate shows that the energy of the electron beam would need to be 0.7 eV before the Lorentz and dipolar forces are equal.

In fact, unlike neutron diffraction, the dipolar force never dominates and at low energies, the dominant force is from the exchange interaction arising from the fact that the electrons in the beam and the antiferromagnet are identical particles as discussed by DeWames and Vredevoe. The exchange interaction is larger than the superlattice reflections are so weak. We have also attempted high resolution imaging which would give information on an atomic scale but with no success so far. We shall soon be conducting simulations to ascertain the effects of antiferromagnetism on high resolution images.

The most promising imaging technique is spatially resolved diffraction where a narrow, near-parallel electron beam is rastered across the specimen and a diffraction pattern recorded at each point. An image can be built up by plotting the intensity of a reflection as a function of position. This is not standard on most microscopes and its implementation will require modifying the software on our microscope. In our experiments, diffraction patterns showing antiferromagnetic reflections were obtained from regions as small as 10.5 nm in diameter. Tao et al. have used this technique to image charge-ordered domains in La$_{0.55}$Ca$_{0.45}$MnO$_3$ with a resolution of 1.7 nm.
dipole interaction by a factor of the rest mass energy of the electron (511 keV) divided by the kinetic energy of an electron in the beam. This ratio is 1.7 at 300 keV and so it is the Lorentz interaction which dominates at high energies.

Low energy (32 eV) electron diffraction patterns have been acquired from the first atomic layer of an antiferromagnet by Menon et al. and here the exchange interaction dominates the scattering process as it is about 16000 times greater than the dipolar interaction and 2300 times greater than the Lorentz force. Menon et al. have used these diffraction patterns to image antiferromagnetic domains in the first atomic layer of the sample with a resolution of 10 nm.

**SUPPLEMENTARY INFORMATION 2: ANTIFERROMAGNETIC DOMAINS**

In NiO, the magnetic moments are aligned ferromagnetically along one set of \{111\} planes with the moments in alternating planes being antiparallel as shown in Fig. 4(a). There are two types of antiferromagnetic domain boundary: a twin (T-type) boundary occurs when the magnetic order changes to a different set of (111) planes and the accompanying distortion generates a crystallographic twin (Fig. 4(b)). The spin (S-type) domain boundary occurs when the same set of (111) planes remains ferromagnetic but the magnetic moments point in a different direction (Fig. 4(c)).

**SUPPLEMENTARY INFORMATION 3: THEORY OF ELECTRON DIFFRACTION FROM AN ANTIFERROMAGNET**

Here we calculate the appearance of an electron diffraction pattern from an antiferromagnet and estimate the intensities of the antiferromagnetic reflections. To do this, we arrange Cartesian coordinates so that the electron beam is travelling in the \(z\)-direction before it hits the specimen and then the wavefunction of the electron \(\psi(x, y, z)\) at any point can be found using the Schrödinger equation for fast electrons:

\[
\frac{\partial \psi}{\partial t} = \frac{i}{\hbar} \left( -\frac{\nabla^2}{2m} - \frac{\gamma e}{\hbar} A_z \right) \psi - \frac{\lambda e}{\hbar} A \cdot \nabla \psi
\]

(2)

where \(V(x, y, z)\) is the electrostatic potential, \(A(x, y, z)\) is the magnetic vector potential, \(\lambda\) the electron wavelength and \(C_E = \frac{2\pi e}{\lambda} \left( \frac{E + mc^2}{2(E + mc^2)} \right)\) where \(E\) is the kinetic energy of the electrons, \(m\) the rest mass of the electrons and \(c\) is the speed of light in a vacuum.

This equation is used throughout electron microscopy to simulate images and diffraction patterns but usually with only the electrostatic terms. Here we have retained the magnetic terms and inserting a suitable expression for the vector potential from an antiferromagnet would allow very accurate simulations of images and diffraction patterns. This equation can only be solved iteratively, however, usually using the multislice or Bloch wave approaches and to give an analytic solution, we make the phase object approximation where only the second term on the right hand side equation 2 is retained. This approximation is valid for very thin specimens but gives a physical insight into the situation and provides an estimate of the intensities expected in a diffraction pattern. Having made this approximation, equation 2 is readily solved to give the wavefunction of the electron as it emerges from a sample of thickness \(t\) (called the ‘exit-plane wavefunction’) as \(\psi(x, y) = e^{i \phi(x, y)}\) where

\[
\phi(x, y) = \int_{-t/2}^{t/2} \left( C_E V(x, y, z) - \frac{2\pi e}{\hbar} A_z(x, y, z) \right) dz
\]

(3)

(We have assumed that both potentials are zero outside the specimen which is very reasonable for an antiferromagnet.)

We now show that the magnetic contribution to the phase is small by taking the case where the antiferromagnetic wavevector \(\mathbf{q}\) points in the \(x\)-direction and the flux...
density oscillates in \( y \). This will give the largest possible phase shift as the B-field is normal to the electron beam direction \( z \). If we write \( B_0 = B_0 \cos(2\pi q_x x) \), a suitable vector potential is \( A_z = -(B_0/2\pi q_x) \sin(2\pi q_x x) \) and this gives a phase shift \( \phi(x) = (eB_0/\hbar q_x) \sin(2\pi q_x x) \). For NiO, \( B_0 = 0.64 \) T and \( q_0 = \sqrt{(3)/2a} = 0.207 \ \text{Å}^{-1} \), the maximum phase shift for a 100 nm thick specimen is \( 7.5 \times 10^{-3} \) radians.

Returning to the general case, this means that we can make the weak phase object approximation for the magnetic contribution to the phase, \[ \exp[-i2\pi e/\hbar \int_{-\infty}^{\infty} A_z dz] \approx 1 - i2\pi e/\hbar \int_{-\infty}^{\infty} A_z dz \] and if the electrostatic contribution to the wavefunction is denoted \( \psi_V \equiv \int_{-\infty}^{\infty} \exp[iCEV(x,y,z)dz] \), the exit-plane wavefunction is

\[
\psi(x,y) = \psi_V \left( 1 - i\frac{2\pi e}{\hbar} \int_{-t/2}^{t/2} A_z dz \right) = \psi_V \left( 1 - i\frac{2\pi e}{\hbar} \int_{-\infty}^{\infty} A_z h(z) dz \right)
\]

where \( h(z) \) is a top hat function which is 1 for \(-t/2 < z < t/2\) and zero otherwise.

The diffraction pattern is the squared modulus of the Fourier transform of the exit plane wavefunction, \( |\Psi(k_x, k_y)|^2 \), and so, using the Fourier transform convention \( \Psi(k) = \int_{-\infty}^{\infty} \psi(r) e^{2\pi i k \cdot r} d^2r \), we obtain

\[
\Psi(k_x, k_y) = \Psi_V \left( \delta(k_x)\delta(k_y) - i\frac{2\pi e}{\hbar} \right) \times (\tilde{A}_z(k_x, k_y, k_z) * tsinc(\pi k_z t))_{k_z=0}
\]

where \( \tilde{A}_z \) denotes the three dimensional Fourier transform of \( A_z \), \( \text{sinc}(X) \equiv \sin(X)/X \), * denotes a convolution and we have made use of the convolution and Fourier projection theorems.

We now calculate the magnetic vector potential for an antiferromagnet basing our method on that used to derive the intensities for neutron diffraction described in ref [23]. The result could be used in equation [2] but here we apply it for the phase object approximation. If we assume that the contribution from the orbital angular momentum of the electrons in the antiferromagnet is quenched, the magnetic vector potential can be found by summing the fields due to the magnetic moments generated by the spin of the unpaired electrons on each atom. A single electron at position \( R_i \) with magnetic moment \( \mu_i \) will generate a vector potential at position \( r \) of

\[
A_i(r) = \frac{\mu_0}{4\pi} \frac{\mu_i \times (r - R_i)}{|r - R_i|^3} = \frac{\mu_0}{4\pi} \frac{\mu_i \times r}{r^3} \ast \delta(r - R_i)
\]

The vector potential for the entire crystal is then the sum over all the unpaired electrons

\[
A(r) = \sum_i \frac{\mu_0}{4\pi} \frac{\mu_i \times r}{r^3} \ast \delta(r - R_i)
\]

For a simple antiferromagnet where all the electron spins are collinear, we can write \( \mu_i = \mu_i \hat{\mu} \) where \( \hat{\mu} \) is a unit vector pointing in the direction of the magnetic moment and \( \mu_i \) expresses the magnitude and sign of the moment. Then

\[
A(r) = \frac{\mu_0}{4\pi} \frac{\hat{\mu} \times r}{r^3} \ast \sum_i \mu_i \delta(r - R_i)
\]

We recognise the last term as the local magnetisation, \( M(r) \) so we can write:

\[
A(r) = \frac{\mu_0}{4\pi} \frac{\hat{\mu} \times r}{r^3} \ast M(r)
\]

The magnetisation is the product of the electron number density and the magnetic moment of each electron \( M(r) = \rho(r)\mu(r) \). To model an antiferromagnet, we allow the magnetisation to vary depending on its position in the crystal. For NiO, this is conventionally done by using a ‘magnetic unit cell’ which is twice the size of the structural unit cell but allow the magnetisation to vary in the crystal. For NiO, this is conventionally done by using a ‘magnetic unit cell’ which is twice the size of the structural unit cell but allow the magnetisation to vary in the crystal. For NiO, this is conventionally done by using a ‘magnetic unit cell’ which is twice the size of the structural unit cell but allow the magnetisation to vary in the crystal.

It turns out to be convenient to write the number density of electrons in terms of the number density of electrons for one atom. If the atom is labelled \( j \) and the unperturbed electron density with the origin at the centre of the atom is denoted \( \rho_j(r) \), we can write:

\[
\rho_0(r) = \sum_n \sum_j \rho_j(r - R_n - R_j)
\]

where \( R_j \) is the position of atom \( j \) within its unit cell and \( R_n \) is the position of the unit cell within the crystal. Thus, the vector potential becomes:

\[
A(r) = \frac{\mu_0 \mu_B}{4\pi} \frac{\hat{\mu} \times r}{r^3} \ast \sum_n \sum_j (\rho_j(r) \ast \delta(r - R_n - R_j)) \times \cos(2\pi q \cdot r)
\]
The $z$-component of the vector potential can be selected by multiplying by a unit vector in the $z$-direction, $\hat{z}$ thus:

$$A_z(r) = \frac{\mu_0 \mu_B}{4\pi} \hat{\mathbf{\mu}} \times \mathbf{r} \cdot \hat{z} \sum_n \sum_j (\rho_j(r) \star \delta(r - R_n - R_j)) \times \cos(2\pi \mathbf{q} \cdot \mathbf{r})$$

(12)

The Fourier transform of this expression is

$$\tilde{A}_z(k) = \frac{\mu_0}{4\pi k} (\hat{\mathbf{\mu}} \times \hat{k}) \cdot \hat{z} \sum_n \sum_j (\tilde{\rho}_j(k)e^{2\pi i \mathbf{R}_j} e^{2\pi i \mathbf{k} \cdot \mathbf{R}_n})$$

$$\times \frac{\mu}{2}(\delta(k - q) + \delta(k + q))$$

(13)

where we have used the result that the Fourier transform of $[\hat{z}]$ is $-2(\hat{\mathbf{\mu}} \times \hat{k})$ and introduced a unit vector so that $\mathbf{k} = \hat{k}$. Recognising that the Fourier transform of the density of unpaired electrons is $n_j$, the number of unpaired electrons associated with atom $j$ multiplied by the magnetic form factor, $f_j(k)$ (identical to that used in neutron diffraction) we can now write

$$\tilde{A}_z(k) = -\frac{\mu_0 \mu_B}{4\pi k} (\hat{\mathbf{\mu}} \times \hat{k}) \cdot \hat{z} \sum_j n_j f_j(k)e^{2\pi i \mathbf{R}_j} \sum_n e^{2\pi i \mathbf{k} \cdot \mathbf{R}_n}$$

$$\times (\delta(k - q) + \delta(k + q))$$

(14)

Using the result that $\sum_n e^{2\pi i \mathbf{R}_n} = \frac{1}{V} \sum_G \delta(\mathbf{k} - \mathbf{G})$ where $\mathbf{G}$ is a reciprocal lattice vector of the structural unit cell and $\Omega$ is the unit cell volume, we obtain

$$\tilde{A}_z(k) = -\frac{\mu_0 \mu_B}{4\pi k} (\hat{\mathbf{\mu}} \times \hat{k}) \cdot \hat{z} \sum_j n_j f_j(k)e^{2\pi i \mathbf{R}_j}$$

$$\times \frac{1}{\Omega} \sum_Q \delta(k - Q)$$

(15)

where $Q = \mathbf{G} + q$. So the Fourier transform of the exit-plane wavefunction is

$$\Psi(k_x, k_y) = \Psi_V(k_x, k_y) \star \left( \delta(k_x) \delta(k_y) \right)$$

$$+ \frac{e}{2h} \frac{\mu_0 \mu_B}{\Omega} \hat{\mathbf{\mu}} \times \hat{k} \cdot \mathbf{\hat{z}} \sum_j n_j f_j(k)e^{2\pi i \mathbf{R}_j}$$

$$\times \sum_Q \delta(k_x - Q_x) \delta(k_y - Q_y) \text{sinc}(\pi Q_z t)$$

(16)

Thus if the structural Bragg reflections occur at $\mathbf{G}$, the antiferromagnetic reflections occur at $Q = \mathbf{G} \pm q$. It can be seen that the scattering amplitude is proportional to a geometric factor $G_z(k) = ((\hat{\mathbf{\mu}} \times \hat{k}) \cdot \mathbf{\hat{z}}/k)$ multiplied by the structure factor for magnetic scattering, $F(k) \equiv \sum_j n_j f_j(k)e^{2\pi i \mathbf{R}_j}$. For neutron diffraction, there is a similar expression where the structure factor is the same but the geometric factor $G_z(k) = |\mathbf{k} \times \mathbf{\mu} \times \mathbf{k}|$.

We use this expression for $\Psi(k_x, k_y)$ to calculate the intensities of the antiferromagnetic reflections $I_Q$ in an electron diffraction pattern for a 100 nm thick specimen relative to the 000 beam, $I_0$. The results are shown in Table I for various directions of $\mathbf{\mu}$. In its construction we made the further approximation that the 000 beam is much stronger than the other structural Bragg peaks (in the diffraction patterns acquired here it was typically 3–4 times more intense than the neighboring peaks) so that as far as magnetic scattering is concerned, $\Psi_V$ is simply a delta function at 000 and the intensity ratios are given by

$$\frac{I_Q}{I_0} = \left( \frac{e}{2h} \frac{\mu_0 \mu_B}{\Omega} \hat{\mathbf{\mu}} \times \hat{Q} \cdot \hat{z} \cdot \hat{F}(Q) \right)^2$$

(17)

**SUPPLEMENTARY INFORMATION 4: TABLE OF CALCULATED INTENSITIES OF ANTIFERROMAGNETIC REFLECTIONS**

Table I gives the intensities of the antiferromagnetic reflections for 100 nm thick NiO for the [112]-type zone axes investigated in this experiment calculated according to the method in Supp. Info. 3. The form factors used in its construction were $f(\frac{1}{2}(111)) = 0.92 \pm 0.03$, $f(\frac{1}{2}(113)) = 0.82 \pm 0.02$ and $f(\frac{1}{2}(333)) = 0.58 \pm 0.02$ derived using neutron diffraction in ref [12]. The symbols used are as follows: $\mathbf{z}$ is the direction of the electron beam relative to the crystal, $\mathbf{q}$ is the wavevector of the antiferromagnetic modulation, $\mathbf{Q}$ gives the reciprocal-space coordinates of the reflection being examined, $\mathbf{\mu}$ gives the direction of the magnetic moments and $I_Q/I_0$ gives the intensity of the reflection relative to the central beam. The intensity is given both for the case that $\mathbf{\mu}$ points in one of the [112]-type easy directions and for the [100]-type ‘flooded’ directions.
TABLE I. Calculated Intensity Ratios for Antiferromagnetic Reflections in an Electron Diffraction Pattern from 100 nm thick NiO.

| z   | q       | Q    | µ  | \(I_q/I_0\)        |
|-----|---------|------|----|-------------------|
| 211 | \(\frac{1}{2}(1\bar{1}1)\) | \(\frac{1}{2}(1\bar{1}1)\) | 211 | 0                  |
|     | 12T     | 12T  | 140 ± 0.08 | \(10^{-4}\) |
|     | \(\frac{1}{2}(333)\) | \(\frac{1}{2}(333)\) | 211 | 0                  |
|     | 12T     | 12T  | 6.0 ± 0.4  | \(10^{-6}\) |
|     | 01T     | 01T  | 6.0 ± 0.4  | \(10^{-6}\) |
|     | 01T     | 01T  | 8.4 ± 0.4  | \(10^{-6}\) |
| 121 | \(\frac{1}{2}(1\bar{1}1)\) | \(\frac{1}{2}(1\bar{1}1)\) | 211 | 6.0 ± 0.4  | \(10^{-6}\) |
|     | 12T     | 12T  | 6.0 ± 0.4  | \(10^{-6}\) |
|     | 01T     | 01T  | 8.4 ± 0.4  | \(10^{-6}\) |
| 112 | \(\frac{1}{2}(11\bar{1})\) | \(\frac{1}{2}(11\bar{1})\) | 211 | 1.04 ± 0.04  | \(10^{-7}\) |
|     | 12T     | 12T  | 1.2 ± 0.04  | \(10^{-5}\) |
|     | 01T     | 01T  | 1.2 ± 0.04  | \(10^{-5}\) |

SUPPLEMENTARY INFORMATION 5: OPTICAL MICROSCOPY

We assessed the size of the antiferromagnetic domains using optical microscopy. Fig. 5 is a transmission optical micrograph taken with crossed polars. This does not pick out the antiferromagnetic domains per se but the twins associated with each antiferromagnetic domain so only the T-type domains are visible. (Kondoh et al. have reported that S-domains can also be imaged with optical microscopy due to their associated lattice strain but the contrast is much fainter.) This shows that the sizes of the T-domains range from 2–80 μm.

FIG. 5. Transmission optical micrograph taken with crossed polars looking down the [111] zone axis. The arrow shows a hole caused by ion-beam irradiation around which was the electron transparent material used for transmission electron microscopy.

SUPPLEMENTARY INFORMATION 6: SUPERLATTICE REFLECTIONS DUE TO SURFACE RECONSTRUCTION

We have shown that antiferromagnetic reflections can be seen in electron diffraction patterns when the wavevector of the modulation \(q = \frac{1}{2}(1\bar{1}1)\) is normal to the electron beam, producing reflections at \(Q = \pm \frac{1}{2}(1\bar{1}1)\). However, when \(q = \frac{1}{2}(111)\), i.e. parallel to the thin direction of the crystal, superlattice reflections should be produced at the \(\pm \frac{1}{2}(1\bar{1}1)\) positions. We have acquired diffraction patterns showing such superlattice reflections but have found that they can also be generated by surface reconstructions which inevitably occur on the (111) surfaces which terminate the sample.

Fig. 6 shows the results of a heating experiment identical to the that shown in Fig. 1 but from a different region of the sample where \(\frac{1}{2}(311)\)-type superlattice reflections were observed. (a) was taken at room temperature and
FIG. 6. (a) Electron diffraction pattern from the [112] zone axis taken at room temperature from a region of diameter 880 nm with an exposure of 70 s showing superlattice reflections near $\pm \frac{1}{2}(311)$, $\pm \frac{1}{2}(131)$, $\pm \frac{1}{2}(153)$, $\pm \frac{1}{2}(513)$ etc., some of which are indicated by arrows. (b) Electron diffraction pattern from the same region taken at 563 K, above the Néel temperature of 523 K, showing that the superlattice reflections are still present and are therefore not caused by antiferromagnetism.

(b) at 563 K, above the Néel temperature of 523 K. In this case, however, the superlattice reflections do not disappear in the high temperature image showing that they are not related to antiferromagnetism.

Fig. 7 shows that the $\frac{1}{2}(311)$-type superlattice reflections are likely to be the result of a surface reconstruction. (b) shows superlattice reflections near the $\frac{1}{2}(311)$-type positions in the [112] zone axis but (a) shows very similar reflections in the [111] zone axis near the $\frac{1}{2}(422)$ positions. A surface reconstruction is only about 2 monolayers thick and so will produce a rod in reciprocal space running in the (111) direction. This rod can cause both the reflections in the [111] and [112] zone axes as $\frac{1}{3}(422) + \frac{1}{3}(111) = \frac{1}{2}(311)$.

FIG. 7. (a) Electron diffraction pattern from the [111] zone axis taken at room temperature with a 5 s exposure. Superlattice reflections (circled) can be seen near $\frac{1}{2}(422)$. (b) Electron diffraction pattern from the [112] zone axis taken from the same region as (a) with a 70 s exposure. Superlattice reflections can now be seen at $\frac{1}{2}(311)$.

Ciston et al. [20] have investigated the surface ordering in NiO using transmission electron diffraction using an ultra-high vacuum microscope which allows in situ annealing. Prior to annealing, their samples were thinned in the [111] direction using a very similar method to that used here. The authors do not report whether any surface order was observed prior to annealing but show that after annealing at temperatures between 1220 and 1470 K, two types of reconstruction were produced. Both the $\sqrt{3} \times \sqrt{3}R30^\circ$ and $p2 \times 2$ reconstructions produce reflections at $\frac{1}{2}(422)$-type positions in the [111] zone but they also produce additional reflections not observed in the present experiments. In addition the reflections observed here are frequently split, indicating an incommensurate surface reconstruction whereas those observed by Ciston et al. [20] are all commensurate. The splitting of the $Q = \frac{1}{2}(113)$-type reflections seen in the [112]-type zone...
axes, $\Delta Q$, ranged in magnitude from 0–0.07$a^*$ (where $a^*$ is the reciprocal lattice vector) and there seems to be no restriction on the angle of $\Delta Q$ with respect to the rest of the pattern.

The characteristics of the superlattice reflections caused by surface ordering are very different to those of the $\frac{1}{2}(11\overline{1})$-type antiferromagnetic reflections described in the main paper. The antiferromagnetic reflections are very sharp whereas those from the surface reconstruction are frequently streaked. Also, the intensity of the antiferromagnetic reflections falls very rapidly with increasing wavevector so that, for example, $\frac{1}{2}(33\overline{3})$ is very much dimmer than $\frac{1}{2}(11\overline{1})$ and the same should be true for the $\frac{1}{2}(311)$-type reflections. In contrast, the higher order reflections which can be seen in Figs. 6 and 7 resulting from the surface reconstruction have a similar intensity to the low order reflections.

Whilst we believe that some of the diffraction patterns we have recorded do show antiferromagnetic reflections at the $\frac{1}{2}(311)$-type positions, we are not able to demonstrate this definitively. In the future, we shall look at samples terminated at a stable surface, preferably (110) although this has the slight disadvantage that only two of the three possible $\frac{1}{2}(111)$-type superlattice reflections will be accessible. None of this alters the main conclusion that the effects of antiferromagnetism can be observed in electron diffraction patterns.

This work was funded by the Royal Society.

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