

Local Magnetoelectric Effects as Predictors of Surface Magnetic Order

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We use symmetry analysis and density functional theory to show that changes in magnetic order at a surface with respect to magnetic order in the bulk can be generically determined by considering local magnetoelectric responses of the crystal. Specifically, analysis of the local atomic-site magnetoelectric responses, or, equivalently, the corresponding atomic-site magnetic multipoles, can be used to predict all surface magnetic modifications arising purely from symmetry lowering via termination of the bulk magnetic order. This analysis applies even in materials with no bulk magnetoelectric response or net surface magnetization. We then demonstrate our arguments for two example antiferromagnets, topological semimetal CuMnAs and rocksalt NiO. We find that the (010) and (1 $\bar{1}$ 0) surfaces of CuMnAs and NiO, respectively, exhibit a series of antiferroically, as well as roughness-sensitive, ferroically ordered, modifications of the surface magnetic dipole moments, via canting or changes in sublattice magnitude, consistent with the bulk ordering of the magnetic multipoles. Our findings demonstrate a universal bulk-boundary correspondence allowing the general prediction of minimal possible surface and interface magnetic modifications, even in materials with no net magnetoelectric response. Furthermore, it paves the way for more accurate interpretations of a wide variety of surface-sensitive measurements.

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I. INTRODUCTION

The assumption that magnetic dipole moments on a vacuum-terminated surface or interface maintain the same orientation and magnitude as they would in the bulk is generically inaccurate. Because the creation of a surface leads to an inherent symmetry lowering, additional dipole components are often allowed at a surface despite being forbidden in the bulk. Furthermore, an elegant bulk-boundary correspondence exists between the symmetry of surface dipole magnetic order and that of the magnetoelectric (ME) effect in a bulk material, whereby an applied electric field $\mathbf{E}$ induces a net magnetization $\mathbf{M}$ [1,2]. More concretely, a magnetic crystal with a finite bulk ME response for a particular direction $\mathbf{r}$ of applied electric field develops the same components of magnetization on a surface perpendicular to $\mathbf{r}$, in the absence of an applied field [3–5].

The above argument implies that any bulk antiferromagnet (AFM) which has a nonzero ME response (at linear or

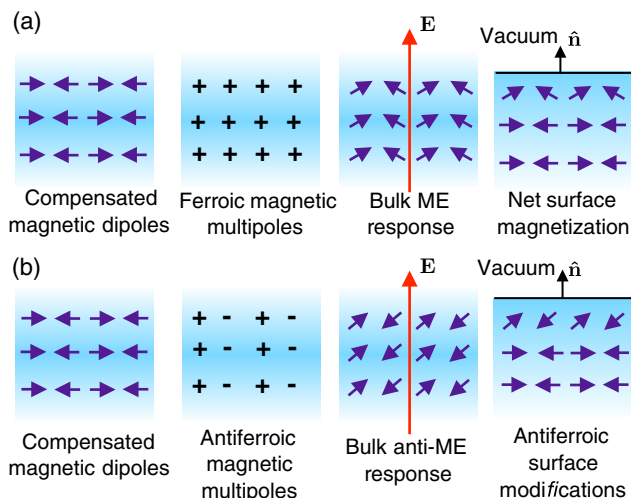


FIG. 1. Link between ordering of bulk atomic-site magnetic multipoles, bulk ME effects, and surface magnetic order. (a) Even for surfaces which are parallel to planes with compensated magnetic dipoles in the bulk (left), ferroic HOMMs (second panel) imply a net bulk magnetoelectric response (third panel) and a net induced surface magnetization (right). (b) HOMMs which are antiferroically ordered parallel to the surface plane of interest imply a bulk anti-ME effect and surface dipolar modifications which maintain the compensation of magnetic dipoles. Fadeout blue color represents continuing periodic bulk; the black line in right panels represents vacuum-terminated surface.

higher order) has a corresponding roughness-robust net magnetic dipole moment per unit area (“surface magnetization”), despite the vanishing bulk magnetization [5] [Fig. 1(a)]. Because the sign of surface magnetization is coupled to the sign of the underlying bulk staggered magnetization, or Néel vector, surface magnetization has utility as an experimentally detectable probe of the bulk Néel vector [4–9]. For example, many experimental techniques, such as nitrogen vacancy magnetometry, directly measure the stray magnetic field produced by the surface magnetization [10,11]. In addition, transport-based methods leveraging the so-called “layer-locked” anomalous Hall effect, whose sign couples to the sign of surface magnetization in many ME materials [12], have widened the experimental accessibility of surface magnetization even further.

Importantly, surface magnetization can arise even on surfaces parallel to atomic planes which are magnetically compensated in the bulk [Fig. 1(a)]. We showed in Ref. [5] that such “induced” surface magnetization in ME AFMs occurs when higher-order *local* bulk magnetic multipoles centered on the magnetic sites order ferroically in the unit cell [Fig. 1(a), second and fourth panels]. These atomic-site higher-order magnetic multipoles (HOMMs), which describe magnetic density asymmetries beyond the spherically symmetric magnetic dipole around individual atoms, are established as symmetry indicators for the local bulk ME responses of individual ions, based on the symmetries of their Wyckoff sites [13,14], with ferroically ordered magnetic multipoles implying macroscopic ME responses [Fig. 1(a)].

On the other hand, surfaces of AFMs parallel to planes which have antiferroically ordered HOMMs in addition to antiferroically ordered magnetic dipoles [Fig. 1(b), second panel] have no net surface magnetization (nor a net ME response for a field applied along the surface normal). But magnetic dipole order at the surface will *still* change due to the nonzero local HOMMs and the effective electric field of the surface. While the technological utility of antiferroic surface magnetic modifications is less obvious than cases where a net magnetization arises, predicting changes in magnetic order at a surface is crucial for properly interpreting surface-sensitive experiments [15,16].

In this work, we show using a combination of symmetry analysis and density functional theory (DFT) that the *minimal* set of surface magnetic dipole modifications, arising solely from vacuum termination of the periodic bulk, can be universally understood based on the ordering of the bulk atomic-site HOMMs or, equivalently, the *local* ME responses of individual atoms. We further map this local magnetic multipole or local ME response description to an alternative group-theory procedure based on the bulk Wyckoff magnetic point group of the atoms and the surface orientation of interest. Finally, we use DFT to test our generic arguments for two specific AFMs, topological semimetallic CuMnAs and rocksalt NiO.

II. THEORETICAL BACKGROUND

Most of the background necessary for our analysis was introduced in Ref. [5], where we focused exclusively on surfaces of bulk AFMs with a *net* dipole magnetization. Here, we restate the key points and then extend the analysis to allow for the prediction of antiferroic surface magnetic modifications.

For ME materials having by definition broken time-reversal symmetry Θ , the induced bulk magnetization along direction $\hat{i}$ due to an applied electric field $\mathbf{E}$ can be written as an expansion in powers of $\mathbf{E}$ [17]:

$$M_i = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots, \quad (1)$$

with α , β , and γ being the linear, quadratic, and cubic ME response tensors, respectively, and summation over repeated indices implied. The various orders of the ME effect can be predicted via symmetry considerations based on ground state properties, namely, the previously mentioned bulk magnetic multipoles, which are the coefficients in a multipole expansion of the interaction energy of a bulk magnetization density $\boldsymbol{\mu}(\mathbf{r})$ with a spatially inhomogeneous magnetic field $\mathbf{H}(\mathbf{r})$ [18]. The coefficient of the first-order term, $\int \boldsymbol{\mu}(\mathbf{r})d^3\mathbf{r}$, gives the magnetic dipole per unit volume, and the next three coefficients, $\mathcal{M}_{ij} = \int r_j\mu_i(\mathbf{r})d^3\mathbf{r}$, $\mathcal{O}_{ijk} = \int r_jr_k\mu_i(\mathbf{r})d^3\mathbf{r}$, and $\mathcal{H}_{ijkl} = \int r_jr_kr_l\mu_i(\mathbf{r})d^3\mathbf{r}$, are HOMMs per unit volume known as the ME multipole, the magnetic octupole, and the magnetic hexadecapole, respectively. $\mathcal{M}_{ij}$, $\mathcal{O}_{ijk}$, and $\mathcal{H}_{ijkl}$ have the same symmetry-allowed forms as the linear, quadratic, and cubic ME response tensors α_{ij} , β_{ijk} , and γ_{ijkl} , respectively [5,13,18–20].

These bulk HOMMs, which are thermodynamic quantities obtained from integration over the magnetic unit cell, represent the symmetry-allowed multipole tensors of the full bulk crystal magnetic point group (MPG), which we call $\mathbf{G}$ for concreteness. They can alternatively be decomposed into a summation over magnetic atoms of two terms. For the example of the ME multipoles, this decomposition can be expressed as

$$\begin{aligned} \mathcal{M}_{ij}^{\mathbf{G}} &= \int r_i\mu_j(\mathbf{r})d^3\mathbf{r} \\ &\approx \sum_{\alpha} \int_{\Omega_{\alpha}} (r_i - R_{i,\alpha})\mu_j(\mathbf{r})d^3\mathbf{r} + \sum_{\alpha} \int_{\Omega_{\alpha}} R_{i,\alpha}\mu_j(\mathbf{r})d^3\mathbf{r} \\ &= \sum_{\alpha} \int_{\Omega_{\alpha}} (r_i - R_{i,\alpha})\mu_j(\mathbf{r})d^3\mathbf{r} + \sum_{\alpha} R_{i,\alpha}m_{j,\alpha} \\ &= \sum_{\alpha} \mathcal{M}_{\alpha,ij}^{\text{AS},\mathbf{G}^w} + \mathcal{M}_{ij}^{\text{LM},\mathbf{G}}. \end{aligned} \quad (2)$$

Here, $R_{i,\alpha}$ is the i th Cartesian component of the position of atom α in the magnetic unit cell, the sum is over magnetic atoms in the unit cell, $m_{j,\alpha}$ is the j th component of the

magnetic dipole moment on atom α , and Ω_α is a spherical region around atom α ; analogous decompositions can be made for multipoles at higher order than the ME multipoles. While this decomposition neglects contributions to $\mathcal{M}_{ij}^G$ due to interstitials, these are generally small and can be neglected. The second term $\mathcal{M}_{ij}^{\text{LM},G}$, which we refer to as the “local-moment” contribution to the ME multipole tensor, captures asymmetry of the bulk magnetization due to the arrangement of local dipole moments across all magnetic sites at the unit-cell level. In Ref. [5], we discussed this contribution and its connection to “uncompensated surface magnetization,” which, in contrast to induced magnetization, occurs due to vacuum termination of the bulk AFM order without requiring any further surface dipole modifications.

In the present work, however, we focus exclusively on the contributions to the summation in the first term in Eq. (2), where $\mathcal{M}_\alpha^{\text{AS},G^w}$ is the atomic-site ME multipole of atom α . This is because these “atomic-site” multipoles, as mentioned in the Introduction, capture bulk magnetic asymmetries centered around individual magnetic atoms. Thus, it is these types of multipoles that are the bulk symmetry markers for the local bulk ME responses of individual atoms, and correspondingly, as we shall soon see, for local magnetic dipole changes of individual atoms at a surface which we are interested in here [21].

Importantly, the nonzero elements on the individual atomic-site ME multipoles $\mathcal{M}_\alpha^{\text{AS},G^w}$ (as well as analogous higher-order atomic-site multipoles) are dictated not by the full bulk MPG $\mathbf{G}$ of the crystal but rather by the lower-symmetry MPG $\mathbf{G}^w$ of the Wyckoff site of α [22,23]. The Wyckoff MPG for a given atomic site is defined as the subgroup of bulk operations that map the site onto itself. If the (ij) element of the atomic-site HOMM of interest has the same sign on all magnetic atoms in the unit cell (ferroic ordering), from Eq. (2) we see that the (ij) component of the higher-symmetry HOMM for the full bulk crystal MPG will also be nonzero, and there will be a corresponding net ME response.

We now make the step from bulk ME effects and bulk magnetic multipoles to the equilibrium magnetic order at a surface. The MPG of a two-dimensional unreconstructed surface, whose orientation (hkl) is defined by the unit vector $\hat{\mathbf{n}}$ perpendicular to the surface, is identical to the MPG selected by an electric field applied in the bulk, parallel to $\hat{\mathbf{n}}$ [5]. This lower-symmetry MPG is defined as the subgroup of bulk MPG operations which leave the direction of the polar vector (either $\hat{\mathbf{n}}$ or $\mathbf{E}$) invariant [4,5]. Thus, if the MPG selected by $\mathbf{E}$ in the bulk allows for an induced bulk magnetization, then a surface cleaved such that $\hat{\mathbf{n}} \parallel \mathbf{E}$ will have the same symmetry-allowed components of magnetization in the absence of $\mathbf{E}$.

The allowed components of net magnetization in the surface MPG identified via the above formalism reflect the symmetry of ME responses at *all* powers of applied electric

field. Because of the mapping $\alpha_{ij} \Leftrightarrow \mathcal{M}_{ij}$, $\beta_{ijk} \Leftrightarrow \mathcal{O}_{ijk}$, $\gamma_{ijkl} \Leftrightarrow \mathcal{H}_{ijkl}$ between each power of ME effect and the corresponding bulk magnetic multipole, determining which HOMMs are ferroically ordered in the unit cell immediately tells us which orders of the bulk ME effect are reflected in the symmetry-allowed components of induced surface magnetization.

We now extend the above analysis by noting that, even if the full bulk MPG forbids any net ME response (that is, there is no HOMM which is ferroically ordered throughout the unit cell), or, equivalently, the surface MPG has no roughness-robust surface magnetization, the individual atomic-site HOMMs referenced in Eq. (2) can still be nonzero, as long as the corresponding local ME tensor is allowed by the lower-symmetry bulk Wyckoff MPG of the atom. Recent theoretical work [24] demonstrated that atomic-site HOMMs which are nonzero but antiferroically ordered in the bulk lead to anti-ME effects, whereby an applied electric field induces changes in individual magnetic moments which cancel across the unit cell [Fig. 1(b), third panel].

Starting from the bulk Wyckoff MPG $\mathbf{G}^w$ for the magnetic atom in question, we can identify the *surface* Wyckoff MPG $\mathbf{G}_\hat{\mathbf{n}}^w$ for a specific surface orientation characterized by $\hat{\mathbf{n}}$ as the subset of operations in $\mathbf{G}^w$ which leave the direction of $\hat{\mathbf{n}}$ invariant:

$$\mathbf{R}_i \in \mathbf{G}_\hat{\mathbf{n}}^w \Leftrightarrow \mathbf{R}_i \hat{\mathbf{n}} = \hat{\mathbf{n}}, \quad (3)$$

where $\mathbf{R}_i$ is the i th element of the bulk Wyckoff MPG $\mathbf{G}^w$. Then, we examine which components (m_x, m_y, m_z) are allowed in $\mathbf{G}_\hat{\mathbf{n}}^w$ to deduce the possible modifications of the surface magnetic dipole moment compared to its symmetry-allowed components in $\mathbf{G}^w$ [Fig. 2(a)].

Alternatively, we can determine all symmetry-allowed local ME tensors within $\mathbf{G}^w$ and from this deduce the atomic-site magnetic multipoles which have nonzero values for the components with all spatial indices $r_j, r_k, r_l \dots \parallel \hat{\mathbf{n}}$ (since these are the components mapping to the local bulk ME response for $\mathbf{E} \parallel \hat{\mathbf{n}}$). The full set of these HOMMs tells us the allowed components of induced magnetization for the individual atoms at a surface [Fig. 2(b)].

While the HOMM method [Fig. 2(b)] is more involved than determining the local surface dipole components directly from the surface Wyckoff MPG [Fig. 2(a)], finding the full set of HOMMs and corresponding local ME tensors for the bulk Wyckoff MPG has two advantages. First, it tells us the *order* of response to the surface’s effective electric field at which a particular surface atom dipole component arises. This information can aid in making educated guesses about the relative magnitudes of different components of local surface dipole modifications. Second, atomic-site HOMMs of the bulk Wyckoff MPG can be readily computed in DFT, so we can determine the *relative* ordering of induced surface dipole components for all

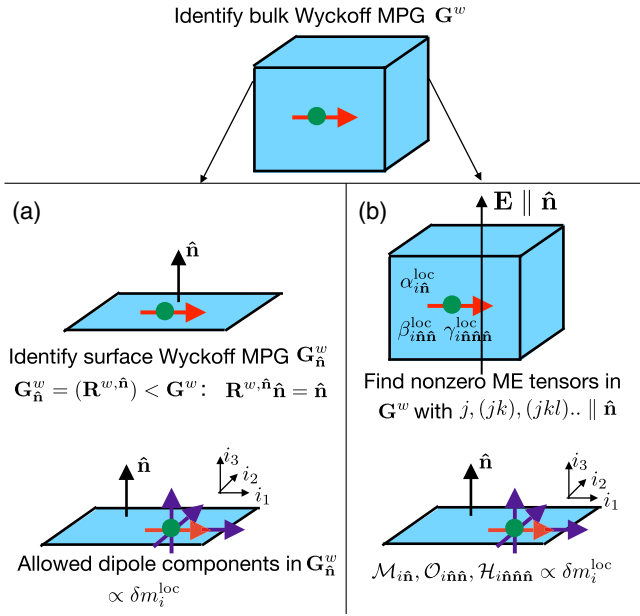


FIG. 2. Summary of two possible methods to determine changes in magnetic dipole components (shown in the bottom by purple arrows superimposed on the bulk direction and magnitude of the local bulk dipole, indicated with a red arrow) of an individual atom (green circle) at a surface with orientation $(hkl) \perp \hat{n}$. (a) Method in which symmetry-allowed components of the local magnetic dipole are determined by finding the surface Wyckoff MPG. (b) Method in which the symmetry-allowed bulk ME tensors in G^w for an electric field along the surface normal, and, consequently, the nonzero HOMMs, are identified, thus determining the components of the local magnetic dipole at the surface. Note that magnetic octupole $\mathcal{O}_{i\hat{n}\hat{n}}$ with i parallel to the bulk direction of magnetic dipole in G^w , corresponding to a change in magnitude along i , is always present. Note that, in this and all subsequent figures, we omit the “AS” superscript, which we do include in the main text, for atomic-site HOMM labels in order to reduce clutter.

atoms in the magnetic unit cell. In contrast, the surface Wyckoff MPG method tells us the surface dipole modifications for a given atom of a particular bulk Wyckoff MPG but cannot tell us the relative ordering of these dipole components between different atoms at the surface.

The allowed magnetic dipole components for an atomic site at a surface based on the analysis above, in general, depend on the specific symmetries maintained in $G_{\hat{n}}^w$. There is, however, one set of nonzero HOMMs, and a corresponding local magnetic modification, that is *always* present at a surface. Recall that the bulk Wyckoff MPG must allow for at least one equilibrium component of local magnetic dipole m_i in a magnetically ordered material. Interestingly, one can prove (see Supplemental Material [25]) that if a local magnetic dipole is symmetry allowed along direction i for G^w , then all second-order magnetic octupoles with diagonal spatial indices, that is, $\int d^3\mathbf{r} \mu_i(\mathbf{r}) r_j r_{k=j}$ for $j = (x, y, z)$, are also symmetry allowed.

This means that, for both ferromagnets and AFMs, any magnetically ordered site must also have a local second-order ME response, with the induced magnetization parallel to the bulk direction of the dipole, for *any* direction of applied electric field. It also follows that, for any surface orientation, the magnetic dipole of a surface atom has a symmetry-allowed magnetization change parallel to its direction in the bulk, which manifests as a change in its dipole moment magnitude. This omnipresent coexistence of atomic-site magnetic dipoles m_i and atomic-site magnetic octupoles $\mathcal{O}_{ijj}^{\text{AS}}$ is consistent with the widely reported magnitude changes of dipole moments at surfaces and interfaces, often by tenths of a μ_B , with respect to their bulk values [26,27].

We emphasize that the formalism in this manuscript based on Wyckoff MPGs is a generalization of our analysis in Ref. [5], where the full surface MPG, or, alternatively, the nonzero ME tensor components, corresponding to *ferroically ordered* atomic-site HOMMs of the full bulk MPG, were discussed. However, the formalism in Ref. [5] identifies only the presence and Cartesian components of any *net* dipole magnetization arising from summing the dipole moments of all surface atoms. In contrast, by focusing on the surface Wyckoff MPGs of individual atoms [Fig. 2(a)], or, alternatively, by analyzing the atomic-site HOMMs and local ME tensors of bulk Wyckoff MPGs [Fig. 2(b)], the present manuscript also reveals information on the *microscopic* surface magnetic configuration. In particular, the Wyckoff-based analysis both captures the ferroic surface dipole changes also identified in Ref. [5] and, additionally, reveals *antiferroic* dipole moment cantings and changes in magnitude, which were missed by our prior analysis. For the following two material examples, we briefly mention the symmetry predictions obtained by using the method in Ref. [5] in order to highlight the new insights revealed by the present formalism.

We now apply these generic arguments to the analysis of surfaces of two specific AFMs: CuMnAs and NiO. These two materials were chosen in part because of their highly contrasting properties. Orthorhombic CuMnAs is a metallic AFM with topological bulk Dirac points and a nonzero bulk linear ME tensor; NiO, on the other hand, is a large-gap Mott insulator and, in Ref. [5], was revealed to be a “null” case of an AFM whose bulk MPG forbids any net ME response and a *net* induced magnetization on any surface. By showing with first-principles DFT calculations that our theoretical predictions for local surface magnetic modifications hold true for both compounds, we demonstrate the broad predictive power of the above analysis.

III. CuMnAs

Orthorhombic CuMnAs is a semimetal with a collinear AFM order. It crystallizes in space-group $Pnma$. In the past decade, it has garnered interest based on theoretical proposals that it hosts gapless topological Dirac fermions

if the Néel vector is oriented along the [001] direction, whereas the Dirac crossings gap out for other Néel vector orientations [28,29]. Furthermore, like its better-known tetragonal counterpart, the efficient reorientation of the Néel vector via current-induced spin-orbit torque should be possible based on symmetry arguments [29], thus enabling an electrically controlled tuning of the topology.

We focus on the (010) surface of orthorhombic CuMnAs, which is parallel to bulk atomic layers having one Mn atom of each sublattice; thus, with the bulk collinear AFM order, these layers have completely compensated magnetic dipoles [Fig. 3(a)]. We mention here that there is some discrepancy between experiment and theory regarding the ground-state orientation of the bulk Néel vector [30,31]. Our DFT calculations indicate that the [100] orientation of the Néel vector is lower in energy by 0.05 (0.1) meV per formula unit than the [010] ([001]) orientation, also in agreement with prior first-principles studies [29]. Thus, for

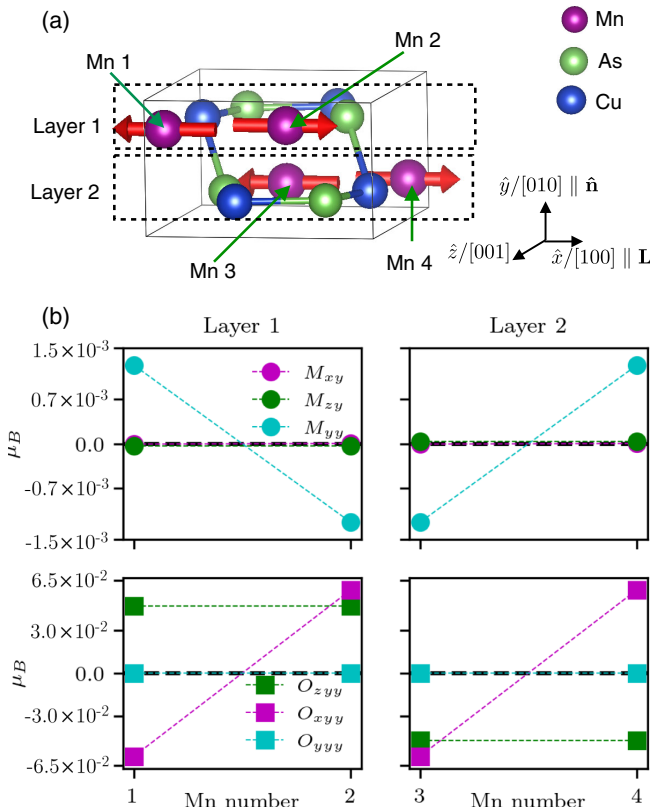


FIG. 3. Crystal structure and multipoles for CuMnAs. (a) Bulk crystal structure of orthorhombic CuMnAs. Each atomic layer parallel to the (010) surface of interest contains two oppositely oriented Mn sublattices (the bulk magnetic unit cell contains two layers, a total of four Mn atoms). (b) Calculated bulk magnetic multipoles for the four Mn atoms, with the bulk dipole orientations shown in (a). The left column is layer 1; the right column is layer 2. Labeling of Mn atoms is the same as in (a). Top: ME multipoles. Bottom: magnetic octupoles. The dashed lines serve as visual aids to connect the set of HOMMs and are not meant to imply a linear relation between the atoms in each layer.

concreteness, we perform the following analysis assuming that $\mathbf{L} \parallel [100]$ (with $\mathbf{L}$ being the bulk Néel vector) as in Fig. 3(a).

First, we use the surface Wyckoff MPG method [Fig. 2(a)] to identify the symmetry-allowed magnetic dipole components for individual Mn atoms on the (010) surface. With $\mathbf{L} \parallel [100]$, the full bulk magnetic space group (MSG) of CuMnAs is $Pnm'a$ [62.444] [32]. The Mn moments sit at the Wyckoff site $4c$, and with this MSG the Wyckoff site corresponds to the bulk Wyckoff point group $\mathbf{G}^w = m'$. m' contains two symmetry operations: the trivial identity $\mathcal{E}$ and a mirror plane $\sigma'_{[010]}$ perpendicular to $\hat{y}/[010]$ coupled to time reversal, $\sigma'_{[010]}$. These operations allow for bulk magnetic dipole components parallel to $\hat{x}/[100]$ and $\hat{z}/[001]$ on the individual Wyckoff sites. Although a local dipole component along $\hat{z}$ is already symmetry allowed in the bulk, according to our DFT calculations, the magnetoanisotropy energy of CuMnAs constrains the bulk Néel vector to point purely along $\hat{x}/[100]$.

Now, to find the (010) surface Wyckoff MPG, we consider which operations in m' leave the surface normal $\hat{n}$ invariant. Under the operation $\sigma'_{[010]}$, spatial coordinates transform as $(x, y, z) \rightarrow (x, -y, z)$. Thus, since $\sigma'_{[010]}$ flips the sign of $\hat{n} \parallel [010]$, it is forbidden in the surface Wyckoff MPG, and we are left with the trivial group having only the identity, $\mathbf{G}_n^w = 1$, which allows for a net magnetic dipole along all three Cartesian directions, in contrast to the bulk Wyckoff MPG, which forbids any local dipole component along $\hat{y}/[010]$. This indicates that on the (010) surface, in addition to an atomic-site magnetic dipole m_x along the bulk Néel vector direction, we can also expect cantings along $\hat{y}/[010]$ and $\hat{z}/[001]$ of the individual Mn surface dipole moments.

We now use the alternative HOMM method [Fig. 2(b)], where, instead of finding the surface Wyckoff MPG, we identify the symmetry-allowed ME tensors within the bulk Wyckoff MPG m' which have nonzero components for an electric field along $\hat{y}/[010]$. Adopting a Cartesian coordinate system where the $\hat{y}$ coordinate (perpendicular to the mirror plane) is parallel to $\hat{n}$ and $\hat{x}$ is parallel to $\mathbf{L}$, the local linear ME response tensor for $\mathbf{G}^w$ takes the form

$$\alpha^{\text{loc}} = \begin{pmatrix} \alpha_{xx} & 0 & \alpha_{xz} \\ 0 & \alpha_{yy} & 0 \\ \alpha_{zx} & 0 & \alpha_{zz} \end{pmatrix}. \quad (4)$$

From this, we can immediately conclude that atomic-site ME multipoles $\mathcal{M}_{yy}^{\text{AS}}$ on individual atoms are nonzero, and, thus, for the relevant surface normal direction $\hat{n} \parallel \hat{y}$, this means that Mn moments at the (010) surface have a symmetry-allowed out-of-plane canting. We can compare Eq. (4) to the form of the linear ME tensor for the *full* bulk MPG of orthorhombic CuMnAs, which is $mm'm$. α in this

MPG has vanishing components on the diagonal. Thus, the atomic-site ME multipoles $\mathcal{M}_{yy}^{\text{AS}}$ must be ordered antiferroically across the four Mn atoms in the unit cell. This is exactly what we see in the top in Fig. 3(b), where we have explicitly calculated using DFT the three atomic-site ME multipoles with spatial indices along $\hat{y}$ for the orientation and domain of bulk magnetic dipoles shown in Fig. 3(a). As expected, $\mathcal{M}_{xy}^{\text{AS}}$ and $\mathcal{M}_{zy}^{\text{AS}}$ vanish, while $\mathcal{M}_{yy}^{\text{AS}}$ values on Mn1 and Mn4 are equal and opposite to those on Mn2 and Mn3. From this, we know that the Mn atoms for layers near a vacuum-terminated (010) surface (for example, Mn1 and Mn2) should experience antiferroically ordered out-of-plane cantings.

Now, we examine the components of the local second-order ME tensor in $\mathbf{G}^w$ which correspond to an electric field along $\hat{y}$. In MPG m' , the symmetry-allowed components β_{iyy}^{loc} are β_{xyy}^{loc} and β_{zyy}^{loc} , with β_{yyy}^{loc} constrained to zero. This contrasts with the case of the full bulk MPG $mm'm$, for which the second-order ME tensor is null. Thus, the corresponding individual atomic-site magnetic octupoles $\mathcal{O}_{xyy}^{\text{AS}}$ and $\mathcal{O}_{zyy}^{\text{AS}}$ are nonzero but, like the $\mathcal{M}_{yy}^{\text{AS}}$ ME multipoles, are antiferroically ordered in the unit cell. We confirm this by explicitly calculating the atomic-site magnetic octupoles in the bottom in Fig. 3(b). We see that the $\mathcal{O}_{xyy}^{\text{AS}}$ octupoles vanish for all Mn atoms, whereas both $\mathcal{O}_{zyy}^{\text{AS}}$, corresponding to a local in-plane canting of (010) Mn surface moments perpendicular to the Néel vector, and $\mathcal{O}_{xyy}^{\text{AS}}$, corresponding to a change in magnitude at the (010) surface parallel to $\mathbf{L}$, are nonzero and antiferroically ordered on the four Mn atoms in the unit cell. Thus, the alternative method for local surface magnetic modifications based on analysis of the ME tensors of the bulk Wyckoff MPG brings us to the same conclusion as directly finding the surface Wyckoff MPG. That is, at the (010) surface, individual Mn dipole moments have symmetry-allowed components along all three Cartesian directions.

There is one difference of note between the pattern of antiferroic ordering of the $\mathcal{O}_{xyy}^{\text{loc}}$ and $\mathcal{O}_{zyy}^{\text{loc}}$ octupoles, which is not immediately apparent from the surface Wyckoff MPG method. Figure 3(b) shows that the $\mathcal{O}_{xyy}^{\text{AS}}$ octupoles, like the $\mathcal{M}_{yy}^{\text{AS}}$ ME multipoles, are antiferroically ordered in the two Mn atoms in each layer parallel to (010), such that the changes in magnitude of the magnetic dipoles for the two sublattices in each layer will be of opposite sign. On the other hand, the $\mathcal{O}_{zyy}^{\text{AS}}$ octupoles are positive for both atoms Mn1 and Mn2 in layer one and equal magnitude but negative for both atoms Mn3 and Mn4 in layer 2. This means that (010) CuMnAs, in fact, has a nonzero, *roughness-sensitive* induced surface magnetization along $\hat{z}/[001]$, which will be finite in the atomically flat limit but in the presence of atomic steps at the surface will average macroscopically to zero.

To illustrate the additional insights gained by the analysis of the Wyckoff MPGs of individual atoms, we mention the

results we would obtain for (010) CuMnAs using the analysis of Ref. [5], which considers bulk and surface MPGs of the full crystal. We refer the reader to our prior work for further elaboration. Starting with the bulk magnetic space group $Pnm'a$, we identify the full surface MPG *in the atomically flat limit* by finding space group operations in $Pnm'a$ whose point group operations leave the [010] surface normal invariant *and* whose translations have no component perpendicular to the surface. We end up with the trivial identity and a (001) mirror plane coupled to an in-plane half-lattice translation: $(\sigma_{(001)}|1/2, 0, 1/2)$. The MPG corresponding to this space group operation is m , which, if the mirror plane lies in the (001) plane, allows for a net dipole moment along z or [001], with x and y components forced to vanish. Thus, for a perfectly flat (010) surface, our earlier analysis identifies a net magnetization along [010]. Now, if we return to the bulk $Pnm'a$ space group and look for operations which leave the direction of the [010] surface normal invariant but contain a translation component parallel to the surface normal, we find an additional operation comprised of a twofold rotation about [010] and half-lattice translation parallel to the rotation vector: $(2_{[010]}|0, 1/2, 0)$. This operation connects degenerate atomic steps on a (010) surface with finite roughness. Notably, however, under this operation, the sign of magnetization along z switches. Thus, the sign of surface magnetization switches between atomic steps, corresponding to a “roughness-sensitive” surface magnetization. In summary, by considering the point group operations of the full bulk crystal as well as translations, the analysis in Ref. [5] is able to identify the roughness-sensitive surface magnetization we also find in this work based on ferroic in-plane order of the atomic-site $\mathcal{O}_{zyy}^{\text{AS}}$ octupoles. However, it provides no information about the local, antiferroic out-of-plane cantings along [010] or the changes in dipole magnitude along [100] for Mn moments on the (010) surface, which the present analysis also reveals.

While symmetry considerations tell us which types of local magnetic modifications *can* occur, they do not prove that they are energetically favorable with respect to the bulk collinear AFM order. To demonstrate that our symmetry predictions actually manifest for the (010) surface of orthorhombic CuMnAs, we perform constrained magnetic total energy calculations within DFT + U , including spin-orbit coupling (see Supplemental Material [25] for computational details). Figure 4(a) shows the vacuum-terminated slab configuration used in the calculations, consisting of ten layers or five unit cells. Figure 4(b) shows the atomic magnetic dipole magnitudes (the two oppositely oriented dipole moments in each layer have equal magnitudes as required by symmetry) as a function of layer number. We see that, consistently with the nonzero $\mathcal{O}_{xyy}^{\text{AS}}$ octupoles, the moments on the two top and bottom layers closest to vacuum change on the order of $0.1\mu_B$ with respect to the moments in the central, bulklike layers.

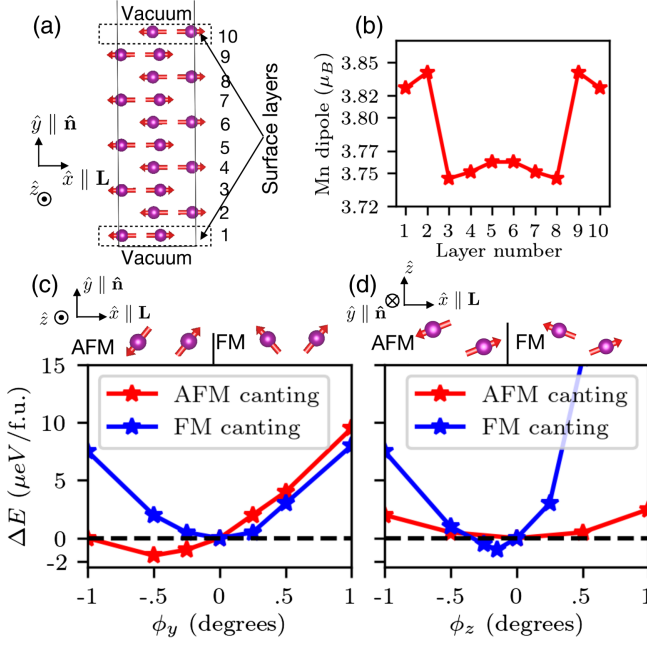


FIG. 4. (a) (010)-oriented slab of CuMnAs consisting of ten layers of two Mn atoms each. Cu and As atoms removed for ease of viewing. (b) Magnitude of Mn sublattice dipole moments along the bulk Néel vector direction $\hat{x}/[100]$ as a function of layer number. (c) Change in energy with respect to zero canting for rotating surface moments out of plane along $\hat{y}/[010]$. The cartoons above the plot show the symmetry-allowed AFM canting (left) and symmetry-disallowed FM canting (right) for one surface layer when looking along the surface. (d) Change in energy with respect to zero canting for rotating surface moments in plane along $\hat{z}/[001]$. The cartoons above the plot show the symmetry-disallowed AFM canting (left) and symmetry-allowed FM canting (right) for one surface layer when looking down on the surface.

Next, in Figs. 4(c) and 4(d), we examine the energetics of the noncollinear out-of-plane (along $[010]$) and in-plane (along $[001]$) canting, respectively, of (010) surface Mn moments. We constrain the directions of Mn dipole moments in the central bulklike layers 2–9 to the collinear $[100]$ direction and systematically cant the moments on the top and bottom surface layers (see Supplemental Material [25] for details). For both directions of rotation, we check the change in energy for both antiferroic and ferroic canting of the two moments in a single surface layer. In Fig. 4(c), when canting the surface moments out of plane, we see an energetic stabilization for a finite value of ϕ_y (about -0.5° for the selected bulk AFM domain; note that switching the bulk domain results in the opposite angle of energetically favored out-of-plane rotation) when we cant the Mn moments in a single surface layer in opposite directions (red curve). This is in agreement with the in-plane antiferroic pattern of $\mathcal{M}_{yy}^{\text{AS}}$ ME multipoles [Fig. 3(b)]. In contrast, a symmetry-disallowed, ferroically ordered pattern of out-of-plane canting (blue curve) leads to a

symmetric increase in energy with respect to $\phi_y = 0$ for either positive or negative out-of-plane canting.

We see the exact opposite for in-plane canting along $[001]$ in Fig. 4(d). In this case, an antiferroic pattern of canting leads to a symmetric increase in energy for either sign of rotation of the Néel vector. On the other hand, a ferroic pattern of canting leads to an asymmetric profile about $\phi_z = 0$ with an energy stabilization at a small angle of 0.15° . This implies a nonzero, roughness-sensitive surface magnetization along $[001]$ of about $-0.01\mu_B$ per Mn atom, in agreement with the in-plane ferroic, and out-of-plane antiferroic, ordering of the $\mathcal{O}_{zyy}^{\text{AS}}$ octupoles. It is interesting to note that the in-plane canting angle ($\phi_z \sim 0.15^\circ$) of the Mn moments, which is directly proportional to the magnitude of induced local dipole components along $\hat{z}$, is smaller than the out-of-plane canting angle ($\phi_y \sim 0.5^\circ$) by about a factor of 3. This is consistent with the fact that the out-of-plane antiferroic canting along $\hat{y}$ stems from the first-order atomic-site ME multipoles, whereas the smaller, in-plane canting along $\hat{z}$ is due the higher-order magnetic octupoles.

We briefly summarize our findings for CuMnAs. We have shown that, despite having no net ME response for an electric field along $[010]$ and no corresponding roughness-robust magnetization on its (010) surface, semimetallic, orthorhombic CuMnAs should exhibit local changes in Mn magnetic dipole moments on its (010) surface along all three Cartesian directions. By examining the relative signs of bulk HOMMs on Mn atoms, we predict antiferroic out-of-plane cantings of the Mn (010) surface dipole moments, antiferroic changes in surface dipole magnitudes, and a roughness-sensitive $[001]$ -oriented surface magnetization. We confirm these symmetry-based predictions by constrained magnetic DFT calculations. The induced changes we find in the local dipole moments, between 0.1 and $0.01\mu_B$ per Mn depending on the Cartesian component, are over an order of magnitude larger than typical bulk-induced moments for insulating ME AFMs subjected to an applied electric field [24,33]. Thus, the physical consequences of such surface-symmetry-induced magnetic modifications, however objectively small, may be non-negligible. Further explorations of the consequences of these surface magnetic dipole changes for the topological surface states of CuMnAs, in particular, could be interesting.

We now give one final material example, rocksalt NiO, which, in contrast to CuMnAs, is an insulating AFM with *no* symmetry-allowed induced surface magnetization.

IV. NiO

Having worked through the example of (010) CuMnAs in some detail, we more briefly describe the analysis of surface magnetic modifications in NiO. NiO is a rocksalt structure, insulating AFM, with the Néel vector oriented along the $[\bar{1}\bar{1}2]$ cubic direction. NiO has attracted interest

for decades due to its myriad energy-related applications in batteries, chemical sensors, catalytic processes, and more [34,35]. Notably for our focus, NiO's bulk MSG, C_c2/c [15.90], is a so-called type-IV MSG; that is, it contains time-reversal Θ coupled to one or more translations as symmetry elements. For NiO, in particular, any two oppositely oriented Ni magnetic moments in the primitive unit cell are connected by time reversal coupled to a translation. Because every magnetic multipole is odd under Θ , it directly follows that *all* HOMMs adhere to the bulk antiferromagnetic pattern of the magnetic dipoles. Thus, a surface of NiO which is parallel to magnetically compensated planes in bulk can never have a net, induced magnetization; all surface magnetic modifications on nominally compensated surfaces *must* be antiferroic.

We show this explicitly for the $(1\bar{1}0)$ surface. Figure 5(a) shows a bulk supercell of NiO with in-plane orthogonal lattice vectors along the $\hat{x}/[111]$ and $\hat{y}/[\bar{1}\bar{1}2]$ directions and out-of-plane lattice vector along the $[\bar{1}\bar{1}0]$ surface normal of interest. Note that the three indices for each

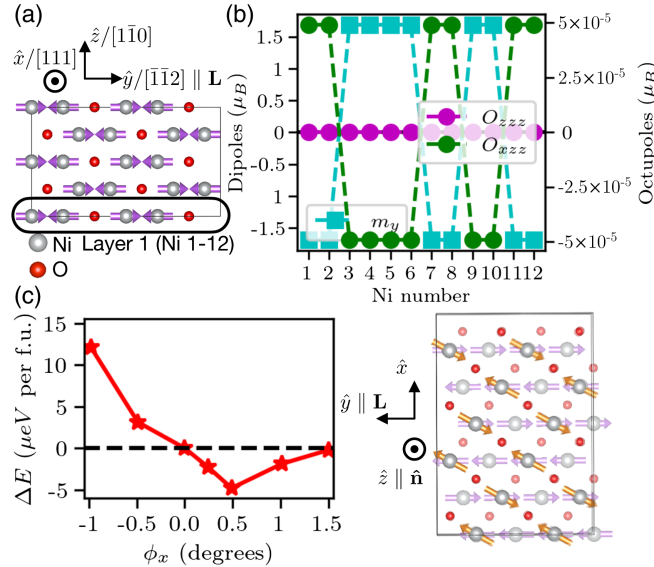


FIG. 5. (a) Bulk supercell of NiO oriented such that it tiles the $(1\bar{1}0)$ surface. Each layer parallel to the surface contains 12Ni moments (example bottom layer is circled in black), and the layers are magnetically compensated in bulk. Some atoms along the $[111]$ direction (into the page) deleted for clarity of plot. (b) Bulk atomic-site magnetic dipoles and magnetic octupoles $\mathcal{O}_{zzz}$ and $\mathcal{O}_{xzz}$ corresponding to a surface normal along $\hat{z}/[\bar{1}\bar{1}0]$ for the 12Ni moments in a single layer parallel to $(1\bar{1}0)$. Labeling 1–12 of the moments is taken directly from the structure file. (c) Constrained magnetic DFT calculations showing change in energy with respect to zero canting for the symmetry-allowed antiferroic canting along $\hat{x}/[111]$ (symmetry allowed). The right-hand cartoon shows the in-plane rotation ϕ_x of the dipole moments in the top surface layer (orange arrows) performed in the constrained magnetic calculations, corresponding to Ni 1–12 in (b). Faded purple arrows are Ni dipole moments of lower layers.

lattice vector of the supercell refer to the $[100]$, $[010]$, and $[001]$ directions, respectively, of the rocksalt cubic structure, as opposed to the primitive monoclinic vector directions. The bulk Néel vector $\mathbf{L} \parallel [\bar{1}\bar{1}2]$ lies in plane, and each layer of 12Ni atoms parallel to the $(\bar{1}10)$ surface has six positively and six negatively oriented dipole moments and is, thus, magnetically compensated.

We already discussed this surface in Ref. [5] in the context of a “null” case with no net surface magnetization. To facilitate comparison, we summarize here the results discussed in our prior work which are obtained by focusing exclusively on the full bulk and surface MPGs rather than the local analysis of this manuscript. From the bulk magnetic space group C_c2/c , operations that leave the surface normal direction invariant and contain only translations parallel to the surface are the identity, $(2_{[\bar{1}\bar{1}0]}|1, 1, 1)$, $(2'_{[\bar{1}\bar{1}0]}|0)$, and $(\Theta|1, 1, 1)$, where again we use the cubic basis rather than the primitive monoclinic basis, and Θ is the time-reversal operation. Because Θ reverses all components of magnetization, we can immediately conclude that, even in the atomically flat limit, no net surface magnetization is allowed, consistent with the above-mentioned generic absence of induced surface magnetization in type-IV MSGs.

We now focus instead on possible antiferroic magnetic modifications at the $(1\bar{1}0)$ surface which would be missed by our prior analysis. Having worked through both methods depicted in Fig. 2 in detail for the example of CuMnAs, for NiO we focus on the HOMM method in Fig. 2(b), where we identify the allowed magnetic $(1\bar{1}0)$ surface modifications by analyzing the local ME tensors for the bulk $\mathbf{G}^w$. The Ni moments sit at bulk Wyckoff position $4c$, and for the bulk MSG C_c2/c this corresponds to Wyckoff MPG $\mathbf{G}^w = 2'/m'$. $2'/m'$ contains inversion as a symmetry. Thus, because the linear ME tensor as well as the atomic-site ME multipoles are odd under $\mathcal{I}$, the linear ME tensor must be null for this MPG. So we instead examine the symmetry-allowed components of the local second-order ME tensor β^{loc} . Rotating β^{loc} such that $\hat{x}$, $\hat{y}$, and $\hat{z}$ are along the $[111]$, $[\bar{1}\bar{1}2]$, and $[\bar{1}\bar{1}0]$ crystallographic directions, respectively, as in Fig. 5(a), the quadratic ME tensor elements corresponding to an electric field along $\hat{z}$, that is, β_{izz}^{loc} , are nonzero for β_{xzz}^{loc} and β_{yzz}^{loc} but zero for β_{zzz}^{loc} .

Figure 5(b) shows the calculated corresponding bulk magnetic octupoles $\mathcal{O}_{zzz}^{\text{AS}}$ and $\mathcal{O}_{xzz}^{\text{AS}}$ for the 12Ni moments in a layer parallel to $(1\bar{1}0)$, together with the magnetic dipoles. As expected, the $\mathcal{O}_{zzz}^{\text{AS}}$ octupoles are zero, while the $\mathcal{O}_{xzz}^{\text{AS}}$ octupoles corresponding to an in-plane canting of the surface Ni moments are antiferroically ordered and follow exactly the pattern of the sign of the dipoles (though with opposite sign). Thus, we expect antiferroic in-plane cantings to be energetically stable, whereas both antiferroic and ferroic out-of-plane cantings along $\hat{z}/[\bar{1}\bar{1}0]$ are symmetry forbidden. Note that for clarity of the plot we do not

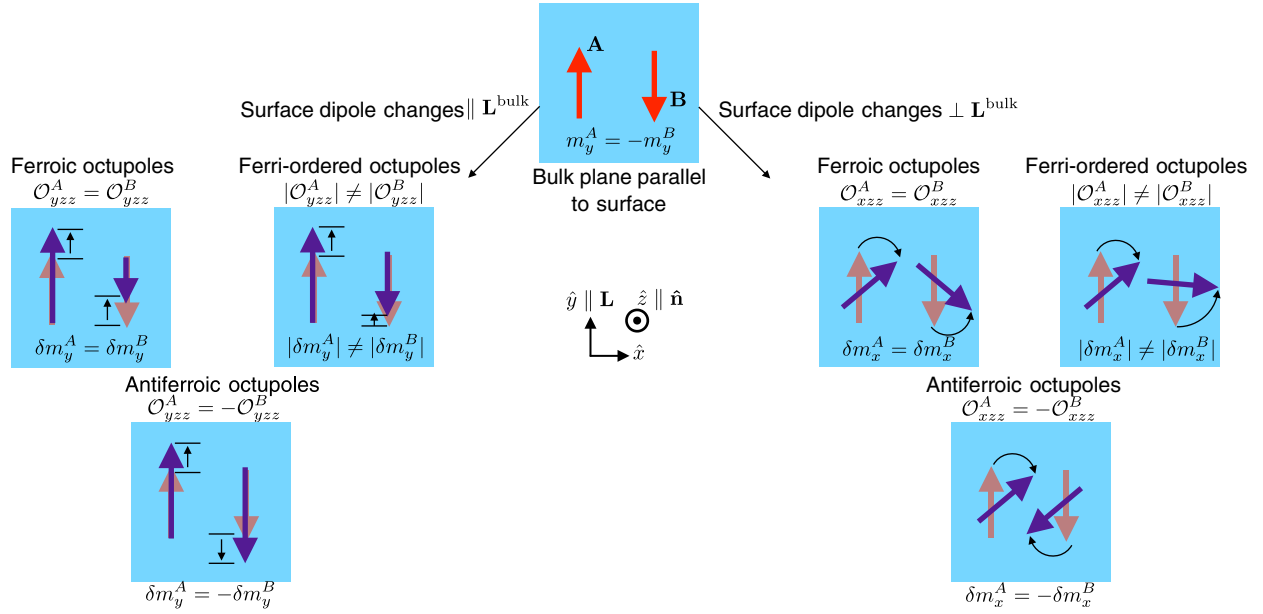


FIG. 6. Link between different relative orderings of bulk HOMMs and the corresponding surface magnetic dipole modifications. The top shows a bulk atomic plane parallel to the surface of interest (perpendicular to $\hat{z}$) containing two atoms **A** and **B** which have collinear antiparallel magnetic dipoles along $\hat{y}$ with the bulk AFM order. We assume that the only nonzero bulk atomic-site HOMMs for atoms **A** and **B** corresponding to the (001) surface are second-order magnetic octupoles. The left-hand side shows the possible dipole changes $\delta m_y^{A/B}$ (with modified surface dipole moments in purple and original bulk orientation in red faded out) parallel to the bulk Néel vector for the two atoms at a vacuum-terminated (001) surface due to ferri-ordered, ferroic, and antiferroic ordering of the atomic-site $\mathcal{O}_{yzz}$ octupoles. The right-hand side shows the same for the three possible orderings of the $\mathcal{O}_{xzz}$ octupoles, which correspond to surface dipole changes perpendicular to the bulk Néel vector. Small black arrows depict the changes $\delta m^{A/B}$ relative to the original bulk AFM ordering along $\hat{y}$.

show the $\mathcal{O}_{yzz}^{\text{AS}}$ octupoles corresponding to a change in magnitude along the direction of the bulk Néel vector but have confirmed that, as expected, these octupoles are nonzero and follow the dipole ordering pattern. We also see a corresponding change in the surface magnetic moment magnitudes in our DFT calculations.

In Fig. 5(c), we now use constrained-magnetic DFT calculations to demonstrate that the symmetry-allowed antiferroic canting along the in-plane [111] direction is energetically favorable. We focus exclusively on antiferroic canting of oppositely oriented Ni sublattices, as we already addressed the absence of ferroic canting and a corresponding induced surface magnetization in Ref. [5]. As shown in Fig. 5(c), we confirm a clear energetic preference for a nonzero, in-plane canting (corresponding to $\phi_x \approx 0.5^\circ$) ordered antiferroically in the surface plane. When we enforce symmetry-disallowed out-of-plane canting, on the other hand (corresponding to ϕ_z rotation), the total energy oscillates noisily with respect to its value at $\phi_z = 0$ and does not exhibit a systematic energy lowering for finite canting [36].

Before moving to broader conclusions, we summarize our material-specific findings for NiO. In contrast to our primary material example of CuMnAs, whose ordering of HOMMs corresponds to both ferroic and antiferroic

changes in its surface magnetic dipoles, the type-IV MSG of NiO constrains all HOMMs to follow the pattern of its bulk magnetic dipoles. In general, therefore, the allowed magnetic modifications for a given surface of NiO will always be ferroic (antiferroic) if the surface is parallel to uncompensated (compensated) layers of bulk dipoles. Further investigations of the possible ramifications of these magnetic modifications for NiO, both for experimental characterizations and for its myriad possible applications, are desirable.

V. CONCLUSIONS

In this work, we have demonstrated that the correspondence between bulk ME responses and surface magnetic order extends beyond the cases where we have a net surface magnetization. Rather, by analyzing the symmetry-allowed local bulk ME responses on individual magnetic ions and the corresponding bulk atomic-site HOMMs, we can universally determine how magnetic dipole moments at a surface are modified with respect to their bulk ordering, even in cases where no net surface magnetization or net bulk ME responses exist. As an overarching summary of the correspondence between bulk HOMMs and surface dipole changes, in Fig. 6, we depict the simplified case of magnetic dipole changes at a surface perpendicular to $\hat{z}$

with a pair of atoms **A** and **B** that have collinear AFM order along $\hat{y}$ in the bulk, due to three possible relative orderings of bulk atomic-site octupoles on **A** and **B**. Note that the qualitative results would be the same regardless of the specific type of HOMM (ME multipole, magnetic octupole, magnetic hexadecapole, etc.) responsible for the surface dipole modifications. The three possible HOMMs orderings are (i) ferroic ordering $\mathcal{O}_{izz}^A = \mathcal{O}_{izz}^B$; (ii) ferri ordering $|\mathcal{O}_{izz}^A| \neq |\mathcal{O}_{izz}^B|$; and (iii) antiferroic ordering $\mathcal{O}_{izz}^A = -\mathcal{O}_{izz}^B$. We give illustrations for both $i = y$ (induced atomic-site magnetic dipole parallel to the bulk dipoles, manifesting as a change in surface dipole magnitude) and $i = x$ (induced atomic-site magnetic dipole perpendicular to the bulk dipoles, manifesting as a surface dipole canting). Ferroic and ferri ordering of the bulk octupoles both result in a net surface magnetization which is collinear for $i = y$ and noncollinear for $i = x$, and material examples were discussed extensively in Ref. [5].

In contrast, the surface magnetic dipole modifications in Fig. 6 that correspond to antiferroic ordering of HOMMs (bottom), which are the primary focus of the present manuscript, do not result in any net surface magnetization. Instead, these modifications manifest as either a change in length or a rotation of the surface Néel vector compared to the bulk Néel vector. We emphasize that, despite their vanishing net magnetization, these surface magnetic changes can, in principle, be detected with established experimental techniques. Two promising techniques of note are spin-polarized scanning tunneling microscopy (STM) [16] and x-ray magnetic linear dichroism [37]. Both measurements are sensitive to local magnetic texture, rather than a net magnetic moment, and can, thus, give information about the direction and length of the surface Néel vector. The results of these surface-sensitive measurements can be compared with bulk measurements, such as neutron spectroscopy, to verify *changes* in the AFM dipole order at the surface due to the bulk HOMMs.

Given that the surface magnetic dipole changes, even when antiferroic, can be experimentally detected, we note two ways in which measurements of surface dipole order could serve as pointers for more subtle underlying bulk magnetic order. First, assuming the bulk AFM configuration is known, the symmetry mapping between atomic-site dipole changes at the surface and local ME responses in the bulk allows us to immediately determine the nonzero components, and in-plane ordering, of bulk HOMMs from the measured surface magnetic dipole modifications. Thus, probing the surface magnetic *dipole* order could be a promising method for identifying hidden bulk *multipolar* order. While direct detection of bulk HOMMs using techniques such as Compton [14] and neutron [38] scattering have been proposed, indirect detection via probing of the surface dipolar order could be more straightforward. As a second example, in analogy to the established protocol of measuring net surface magnetization to detect the sign of

the underlying bulk Néel vector, by monitoring the pattern of surface AFM magnetic order, such as by a spin-polarized STM map, one can similarly detect the reversal of the zero-magnetization bulk Néel vector by a reversal of the AFM surface dipole pattern [39].

Overall, the formalism introduced here, based on analysis of bulk atomic-site HOMMs, serves as an important starting point for predicting qualitatively the realistic magnetic reordering at arbitrary surfaces, since it identifies the *minimal* set of symmetry-allowed magnetic changes that occur even for ideal surfaces. We emphasize that, even when further symmetry lowering occurs with respect to the pristine bulk-terminated surface, via, for example, reconstructions, the nonzero local dipole components allowed by the surface Wyckoff MPG of the higher-symmetry, unreconstructed surface will persist. On top of these minimal surface magnetic changes that are predicted directly from the bulk-boundary correspondence described in this manuscript, one can then predict *additional* changes from the bulk magnetic order in a similar manner by identifying the subgroup of the pristine surface Wyckoff MPG that describes magnetic atoms on the reconstructed surface.

Going forward, it will be important to better understand the material properties (atomic elements, bulk symmetries, orbital composition) that influence the quantitative magnitudes of these symmetry-allowed modifications, in order to determine the cases in which these surface magnetic reorderings will be most experimentally relevant. It will also be interesting to investigate the potential consequences that the predicted modifications of the surface Néel vector will have on macroscopic properties like surface electronic structure or surface propagation of magnons.

Finally, we emphasize that the antiferroic surface magnetic dipole changes, as well as the underlying antiferroic bulk HOMMs, that we introduce in this work are both new types of “hidden order,” analogous to the original example of bulk antiferroic dipole order, or antiferromagnetism, identified by Néel almost a hundred years ago [40]. At this point, the broader consequences for physical observables and macroscopic properties related to these novel hidden orders are an open question. To that end, we hope our work stimulates further discussions in the theoretical community and can eventually lead to more nuanced interpretations of surface-sensitive experimental probes, such as spin-polarized STM, angle-resolved photoemission spectroscopy, and beyond.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [41].

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- [41] [10.24435/materialscloud:fz-1s](https://doi.org/10.24435/materialscloud:fz-1s)