

ANALOGY BETWEEN THE MAGNETIC DIPOLE MOMENT AT THE SURFACE OF A MAGNETOELECTRIC AND THE ELECTRIC CHARGE AT THE SURFACE OF A FERROELECTRIC

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In a linear magnetoelectric material, an applied electric field induces a magnetization linearly proportional to the field strength, and an applied magnetic field induces a corresponding linear electric polarization. The first mention of the phenomenon, to our knowledge, is in the original 1958 edition of the classic *Electrodynamics of Continuous Media* by Landau and Lifshitz [1], with the brief statement that an effect resulting from a linear relation between the magnetic and electric fields in a substance is possible in principle. Soon after, Dzyaloshinskii proved using symmetry arguments that the behavior should occur in chromia, Cr_2O_3 [2]. This was then the material of choice for the first experimental demonstration of the linear magnetoelectric effect by Astrov [3].

A symmetry requirement for the existence of a linear magnetoelectric response is that both time-reversal, T , and space-inversion, P , symmetries are broken. This condition is the same as that for a non-zero magnetoelectric multipole tensor, $\mathcal{M}_{ij} = \int r_i \mu_j(\mathbf{r}) d^3r$, which is the second order coefficient in the multipole expansion of the energy of a spatially varying magnetization, $\boldsymbol{\mu}(\mathbf{r})$, in a spatially varying magnetic field, $\mathbf{H}(\mathbf{r})$ [4–6]:

$$\begin{aligned} \text{Energy} &= - \int \boldsymbol{\mu}(\mathbf{r}) \cdot \mathbf{H}(\mathbf{r}) d^3r = \\ &= - \int \boldsymbol{\mu}(\mathbf{r}) \cdot \mathbf{H}(0) d^3r - \\ &\quad - \int r_i \mu_j(\mathbf{r}) \partial_i H_j(0) d^3r - \dots \quad (1) \end{aligned}$$

Here, the expansion in powers of the field gradients is calculated at some arbitrary reference point $\mathbf{r} = 0$, and i, j are Cartesian directions with summation over repeated indices implied. The usual magnetic dipole moment, $\mathbf{m} = \int \boldsymbol{\mu}(\mathbf{r}) d^3r$ appears in the first term of the expansion of Eq. (1); the \mathcal{M}_{ij} tensor appears in the second term. When appropriately normalized by the volume in the case of bulk, periodic systems we will call it the magnetoelectric multipolization, by analogy with the magnetization or polarization. It provides a bulk, thermodynamic quantity associated with “magnetoelectricity”, complementing the usual definition of magnetoelectricity as a response function.

One scenario in which this thermodynamic aspect manifests, which was pointed out by Dzyaloshinskii in 1992 [7], is in the power-law decay of the external magnetic field around an antiferromagnetic material with a net non-zero magnetoelectric multipolization. Power-law behavior is fundamentally different from the exponential field decay expected around a conventional centro- or time-reversal symmetric antiferromagnet [7]. In the particular case of the prototypical magnetoelectric Cr_2O_3 , which is uniaxial and has non-zero magnetoelectric multipolization below its Néel temperature, Dzyaloshinskii showed that the external field should have the angular form of a magnetic quadrupole. As in

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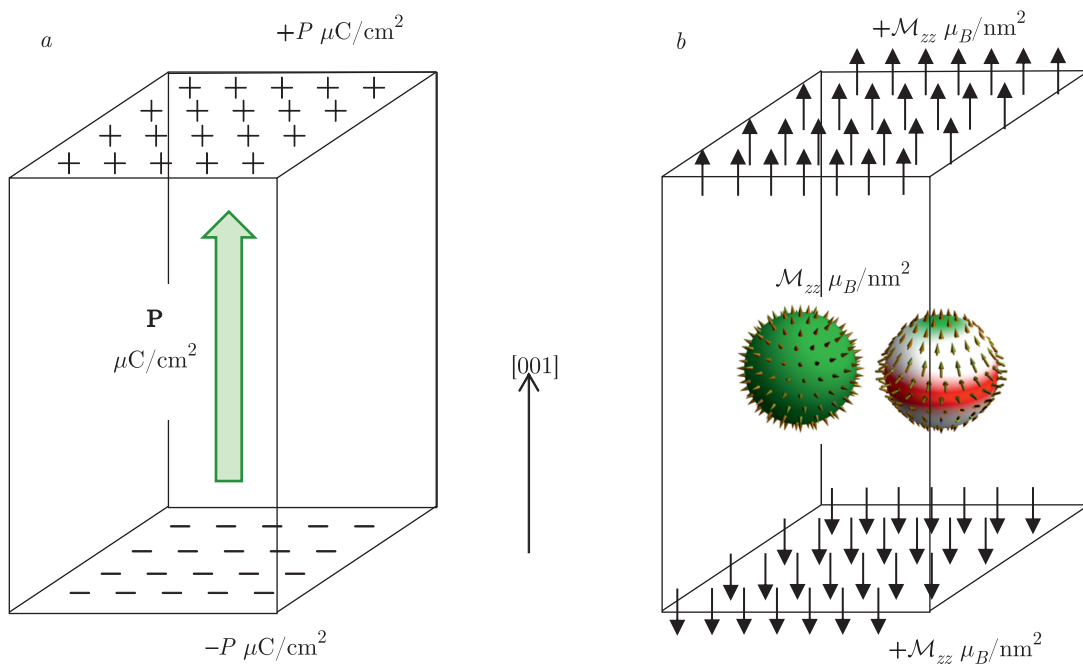


Fig. 1. a) Surface charge associated with ferroelectric polarization, \mathbf{P} . b) Surface magnetic dipole moment associated with magnetolectric multipolization, \mathcal{M}_{zz} , which can be represented as the sum of a magnetolectric monopole and z^2 quadrupole. The $-$ signs, $+$ signs and small black arrows on the surfaces indicate negative charge, positive charge and magnetic dipole moments. The ferroelectric has negative charge on its lower surface and positive charge on its upper surface; the magnetolectric has positive magnetic dipole moments (pointing outwards from the sample) on both its upper and lower surfaces

the case of the original magnetolectric response prediction, this was subsequently confirmed by Astrov [8, 9], although the measured field strength was smaller in magnitude than predicted. The intrinsic bulk nature of the measured external field dependence was subsequently questioned, however, when it was pointed out that any antiferromagnet can in principle have a surface magnetization that, depending on the sample shape and choice of surface termination, could give rise to a magnetic field [10]. The discussion was further enriched by recent theoretical demonstrations that certain surfaces of a magnetolectric antiferromagnet will always have a surface magnetization [11] and associated external magnetic field [12] as a consequence of the bulk magnetolectric multipolization.

In this paper, we revisit Dzyaloshinskii’s pioneering work on the linear magnetolectric effect in light of the modern theory of ferroelectric polarization, and approach the description of the surface magnetism of magnetolectric antiferromagnets by making a correspondence with the surfaces of ferroelectrics. We show that the surface magnetic dipole moment associated with magnetolectric materials is analogous to the bound surface charge in ferroelectrics, in that it can

be conveniently described in terms of the bulk magnetolectric multipolization that is analogous to the ferroelectric polarization. We define the intrinsic surface magnetization to be this surface magnetic dipole moment per unit area, and provide a convenient recipe for extracting it for any surface plane, from knowledge of the bulk magnetic order. We demonstrate the procedure for the prototypical magnetolectric material, Cr_2O_3 , in which Dzyaloshinskii first identified the linear magnetolectric effect, and compare the value of the intrinsic surface magnetization to recent experimental measurements. Finally, we show that the description is also relevant for non-magnetolectric antiferromagnets, allowing a classification into one of two types with fundamentally different surface magnetic properties: the trivial case, in which the allowed magnetolectric multipolization values contains zero, and non-trivial antiferromagnets whose magnetolectric multipolization is non-zero, in spite of their not being magnetolectric.

From a quick glance at the units of electric polarization, which are dipole moment per unit volume or equivalently charge per unit area, it is clear that a surface perpendicular to the polarization direction in a ferroelectric material carries a bound charge per unit

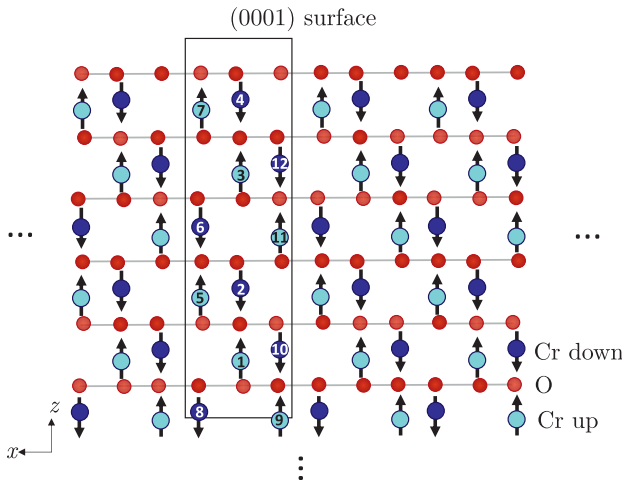


Fig. 2. (Color online) A semi-infinite slab of Cr_2O_3 with a (0001) surface, shown projected down the y axis. Cr and O ions are shown in blue and red respectively, and the arrows indicate the directions of the local magnetic moments on the Cr ions. The symbol ... (black dots) indicate continuation of the structure. The black rectangle shows a choice of hexagonal unit cell, which, in combination with the numbered Cr ions, can be periodically repeated to tile the slab

area equal to the value of the polarization, with the sign of the surface charge given by the direction of polarization, as shown in Fig. 1a. (For a rigorous derivation see Ref. [13].)

While the ferroelectric polarization has units of charge per unit area, the magnetoelectric multipolization, or magnetoelectric multipole per unit volume, has units of magnetic dipole moment per unit area. Therefore, by analogy with the ferroelectric case, the surface of a magnetoelectric should have a magnetic dipole moment per unit area, whose size and orientation depends on the bulk magnetoelectric multipolization. We refer to this as the intrinsic surface magnetization, since it results from a bulk property of the material; it is this surface magnetization that was discussed in Ref. [11]. In Fig. 1b we illustrate the analogy with ferroelectricity for the case of a uniaxial magnetoelectric such as Cr_2O_3 in which the \mathcal{M}_{zz} component of the magnetoelectric multipolization tensor (which can be decomposed into the magnetoelectric monopolar and z^2 quadrupolar contributions shown) is non-zero. The \mathcal{M}_{zz} component results in a z -oriented magnetic moment pointing away from the sample on the (001) and (00 $\bar{1}$) surfaces in this example.

Our procedure for extracting the surface magnetization of a semi-infinite slab of an antiferromagnet from its bulk magnetoelectric multipolization follows that for determining the surface charge from the bulk ferro-

electric polarization [14, 15]. For a particular choice of surface plane orientation and atomic termination, we identify the unit cell that tiles the semi-infinite slab; an example for the (0001) surface of Cr_2O_3 is shown in Fig. 2. We then calculate the magnetoelectric multipole of that unit cell, and normalize it to the unit cell volume; by analogy with the ferroelectric case we call this \mathcal{M}^{bulk} . For the illustrated surface, domain and unit cell of Cr_2O_3 , only \mathcal{M}_{zz}^{bulk} is non-zero, and it has the value $-2.35\mu_B/\text{nm}^2$ (taking the atomic positions and lattice parameters from Ref. [16]). The surface magnetic dipole per unit area, which we define to be the intrinsic surface magnetization, can then be read off directly from the i, j components of the \mathcal{M}^{bulk} tensor, with the first index, i , indicating the x, y or z orientation of the surface magnetic dipole moments at the surface plane normal to the second index, j . For the case of Cr_2O_3 both (0001) surfaces shown have a surface magnetization of $2.35\mu_B/\text{nm}^2$ pointing into the sample.

In the full manuscript, the procedure is also applied to calculation of the interfacial magnetism in heterostructures of $\text{Fe}_2\text{O}_3/\text{Cr}_2\text{O}_3$, and to model non-magnetoelectric systems.

Summary and outlook. In summary, we reviewed the phenomenology of magnetoelectric multipolization in bulk, periodic solids, and provided an analogy with various aspects of the ferroelectric polarization. We showed that the analogy provides a particularly convenient picture of the surface magnetization that is associated with magnetoelectric materials [10, 11], and we provided the following straightforward recipe to extract it from the bulk magnetoelectric multipolization for a given surface plane:

- 1) for the surface plane and chemistry of interest, identify the unit cell and ionic basis that tiles a semi-infinite slab of the system;
- 2) calculate the components of the bulk magnetoelectric multipolization, \mathcal{M}_{ij}^{bulk} , using this unit cell and basis of ions, and normalizing it to the unit cell volume;
- 3) the non-zero components of \mathcal{M}_{ij}^{bulk} that have a contribution normal to the surface plane then give directly the size and orientation of the intrinsic surface magnetization.

We argued that such an intrinsic surface magnetization is possible even at the surface or interface of a non-magnetoelectric material, and distinguished two cases: In non-magnetoelectric materials whose multipolization lattice contains zero it is always possible to choose a stoichiometric termination with zero magnetic moment for any choice of surface plane, although this might not necessarily be the lowest energy termina-

tion. In non-magnetoelectric materials whose multipolization lattice contains the half-multipolization increment, in contrast, surface planes exist for which an intrinsic magnetic moment can not be avoided for stoichiometric terminations.

We mentioned some phenomena for which these concepts might be relevant and which could provide interesting directions for future work. In particular, the intrinsic surface magnetization arising from the magnetoelectric multipolization could have implications for the relative stability of antiferromagnetic surfaces and interfaces, the formation of antiferromagnetic domains, and the mechanism of exchange-bias coupling. Finally, we suggested some experiments that could be used to verify or disprove our proposals, and we hope, in the spirit of Igor Dzyaloshinskii, that this manuscript motivates future experimental work in these directions.

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