

# Magnetization-graded ferromagnets: The magnetic analogs of semiconductor junction elements

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Compositionally graded ferrites are formed as the magnetic analogs of semiconductor junction devices. The internal, or the “built-in,” magnetic field is intrinsic to the structure and is determined from ferromagnetic resonance microscopy. Magnetic analysis of a nickel–zinc–ferrite system in terms of its spatially dependent order parameter, the magnetization, yields a value for the internal magnetic field consistent with experimental observations. Our results are extended to the general class of ferroic and other “smart” materials via a spatially dependent free-energy potential. © 2005 American Institute of Physics. [DOI: 10.1063/1.2012526]

The studies of semiconductors, ferroelectrics, ferromagnetics, ferroelastics, and a wide variety of other, what are often referred to as ferroic materials and systems, have historically evolved quite independently of each other; resulting in their own separate terminology and experimental methodology. Semiconductor research, however, uniquely and quite rapidly expanded into the realm of compositionally graded structures; yielding tremendously important practical electronic components, such as junction diodes and transistors, both of which we find in virtually every modern electronic device. Research into nonhomogeneous ferroics, conversely, has primarily been confined to the study of bilayer and multilayer structures and has only very recently been expanded to include polarization-graded ferroelectrics. Thus, investigations of compositionally graded ferroics offer superb opportunities for discovering novel passive and active devices as analogs of their semiconductor counterparts.

A fundamental study of compositionally graded semiconductors usually begins by relating a space-charge inhomogeneity,  $\rho(\mathbf{r})$ , through Poisson’s equation to a *built-in internal potential*,  $V(\mathbf{r})$

$$-\nabla^2 V(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\epsilon}, \tag{1}$$

where  $\epsilon$  is the permittivity and  $\mathbf{r}$  is a position vector. It is from this potential that the interesting properties of transistor and diode elements are derived; such as asymmetric electrical conduction and power gain.

Quite similarly, for electrically insulating polarization-graded ferroelectrics (where the dielectric displacement,  $\mathbf{D}$ , obeys the relation  $\nabla \cdot \mathbf{D} = 0$ ), a straightforward application of Maxwell’s equations relates a spatial variation in polarization to a *dielectric-based internal electrostatic potential* according to:

$$\nabla^2 V(\mathbf{r}) = \frac{1}{\epsilon_0} \nabla \cdot \mathbf{P}(\mathbf{r}), \tag{2}$$

where  $\epsilon_0$  is the permittivity of free space and  $\mathbf{P}(\mathbf{r})$  is the position dependent dielectric polarization (induced and spontaneous). The presence of a spatially dependent potential in dielectrics also creates a “built-in” electric field similar to the semiconductor diode case and has yielded fundamentally new phenomena related to both active and passive “transcapacitive” devices.<sup>1,2</sup>

Intuitively, it follows that this approach should be extendable to other ferroic systems,<sup>3</sup> most particularly to magnetization-graded ferromagnets, the subject of this letter. From Maxwell’s equations (where  $\nabla \cdot \mathbf{B} = 0$ , with  $\mathbf{B}$  the magnetic induction), a gradient in magnetization,  $\mathbf{M}$ , yields an *internal magnetostatic potential* according to the relation:

$$\nabla^2 \phi(\mathbf{r}) = \nabla \cdot \mathbf{M}(\mathbf{r}). \tag{3}$$

The magnetic scalar potential,  $\phi$ , is defined through  $-\nabla \phi(\mathbf{r}) = \mathbf{H}_{\text{int}}(\mathbf{r})$ , where  $\mathbf{H}_{\text{int}}$  is the internal magnetic field. The spatial invariance of  $\mathbf{M}$  arises from both the permeability and the spontaneous magnetization.

Figure 1 shows a schematic of the three separate cases described above for the creation of internal potentials in three unrelated material systems as captured analytically by Eqs. (1)–(3). This letter extends the semiconductor junction

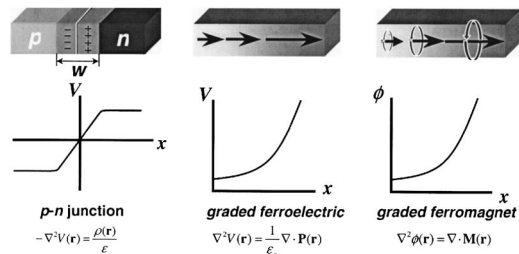


FIG. 1. Internal potentials of semiconductors, ferroelectrics, and ferromagnetics are created by gradients in charge density, polarization, and magnetization, respectively.

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construct beyond polarization-graded ferroelectrics to magnetization-graded ferromagnetics, thereby setting the stage for an analogous discussion of active transinductive, “transductor”, and by further analogy to the general case of nonhomogeneous ferroics, “transponent” elements. We accomplish this by explicitly determining the magnitude and direction of the position-dependent internal (“built-in”) magnetic intensity,  $\mathbf{H}_{\text{int}}(\mathbf{r})$ , in a compositionally inhomogeneous ferrite, which is related through Eq. (3) to a spatial variation in magnetization, i.e.,  $-\nabla^2\phi(\mathbf{r}) = -\nabla \cdot \mathbf{M}(\mathbf{r}) = \nabla \cdot \mathbf{H}_{\text{int}}(\mathbf{r})$ . Finally, we show that the internal magnetic anisotropy is anticipated by a free-energy expansion in terms of the magnetization as a spatially dependent order parameter.

Reagent grades of the oxides of nickel, zinc, and iron were combined in appropriate proportions to produce nickel–zinc ferrites ( $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ) with  $x=0.5, 0.6, \text{ and } 0.7$ . The individual powders were calcined at  $850^\circ\text{C}$  for 3 h, ball milled for 16 h in water, then dried and screen meshed. The 0.7, 0.6, and 0.5 compositions were weighed and further ratioed to produce compositions having  $x=0.66, 0.633, 0.566, \text{ and } 0.533$ . Subsequently, 0.75 grams of each of the seven individual ferrites were combined with a cellulose binder and poured (sequentially) and lightly tamped into a 13 mm diameter steel die (to yield separate compositionally uniform layers, each 1.9 mm thick). The powder stackup was uniaxially pressed at 680 bars (10 000 psi) then sintered at  $1330^\circ\text{C}$  for 50 h so as to diffuse the components and make an approximately linear compositional gradient. The sintered ferrite was then sliced along the compositional gradient to yield a thin (1 mm thick) sheet approximately 1 cm in length by 0.6 cm in width. Electron probe microanalysis shows a linear variation in the Ni:Zn ratio over the length of the sample completely consistent with the variation in starting compositions and their local interdiffusion as a result of prolonged sintering.

Ferromagnetic resonance (FMR) microscopy at 9.45 GHz was performed to obtain a profile of the magnetic parameters, i.e., spectroscopic splitting factor  $g$  and the effective saturation induction.<sup>4</sup> A modified reflection-type cavity with a centered hole (1 mm diameter) at the bottom and at  $\lambda/4$  on the narrow side was used. The sample was placed *outside* the cavity and moved across the hole to obtain the profiles of the magnetic parameters. The first derivative of the power absorbed was recorded as a function of *applied* static field,  $H$ , for  $H$  parallel, antiparallel, and normal to the compositional gradient. “Magnetic mapping” by FMR was accomplished by determining  $g$  and the effective saturation induction,  $4\pi \cdot \mathbf{M}_{\text{eff}}$ :

$$4\pi \cdot \mathbf{M}_{\text{eff}} = 4\pi \cdot \mathbf{M}_s + \mathbf{H}_a, \quad (4)$$

where  $4\pi \cdot \mathbf{M}_s$  is the saturation magnetization and  $\mathbf{H}_a$  is the anisotropy field, from the resonance fields. The  $g$ -value was in the range of 2.5–2.6. Figure 2 reveals the mean position-dependent effective magnetization, which is related through Eq. (4) to the local spontaneous magnetization and the anisotropy field that may arise as a result of the compositional gradient, principally due to magnetostrictive effects in the material. Note, that in the experimental configuration, the “0” position corresponds to a Ni:Zn composition of 0.7:0.3 and the applied field is aligned toward increasing position. Not surprising, the effective magnetization increases with increasing Zn content. For, as Zn is substituted for Fe in the A site, the displaced Fe enters the B site, resulting in a net

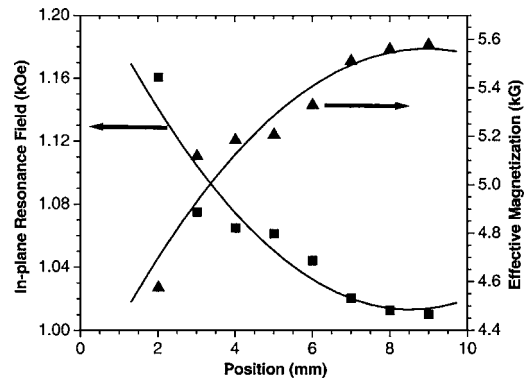


FIG. 2. In-plane resonant field and position dependent effective magnetization, the latter of which is related [through Eq. (4)] to the local spontaneous magnetization and any anisotropy field that arises as a result of the compositional gradient. The curves are guides for the eyes.

moment increase.<sup>5</sup> Indeed, separate measurements by us of homogeneous nickel–zinc ferrites reveal that the saturation magnetization  $4\pi \cdot \mathbf{M}_s$  varies from 4070 G for a Ni:Zn ratio of 0.7:0.3 to 4623 G for a ratio of 0.5:0.5; consistent with the above description.

The presence of a small built-in magnetic field aligned along the magnetization-gradient is revealed as a shift in the magnetic inflection point of the FMR signal; the shift coming from an alignment of the external field with the internal field ( $H=180$ ) versus antialigned ( $H=0$ ), see inset of Fig. 3. Figure 3 also shows that the magnitude of this internal field is dependent on the magnitude of magnetization gradient (see Fig. 2), which is itself a function of position.

To fully understand the origin of this internal field bias, we must go beyond Eq. (3) and account for the interdependence of the magnetization and the internal strains that arise as a result of the compositional gradient. Logically, the study of graded ferroics can be unified through a generalized free-energy functional:<sup>6</sup>

$$\begin{aligned} F[\eta_i(\mathbf{r})] = & \int_V [\alpha_{ij}\eta_i\eta_j + \beta_{ijkl}\eta_i\eta_j\eta_k\eta_l + A_{ijkl}(\nabla_i\eta_j \cdot \nabla_k\eta_l) \\ & + \dots + \delta_{ijk}x_{ij}\eta_k + q_{ijkl}x_{ij}\eta_k\eta_l - (\psi_i^D - \psi_i)\eta_i \\ & + F_{\text{El}}(\eta_i, q_{ijkl}, C_{ijkl})]dV, \quad (5) \end{aligned}$$

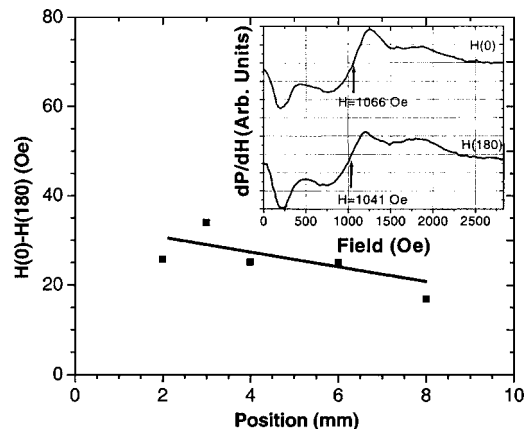


FIG. 3. Intrinsic field that arises as a result of the compositional gradient along the axis of the sample as revealed by the difference in resonant field obtained for an applied field parallel ( $H=0$ ) to and antiparallel ( $H=180$ ) to the gradient. The inset shows the shift in the FMR signal with externally applied field parallel and antiparallel to the compositional gradient at the zinc rich end (high magnetization) of the sample; the arrows designate inflection points in the power absorption.

where  $\eta_i(\mathbf{r})$  are position dependent order parameters,  $\alpha_{ij}$ ,  $\beta_{ijkl}$ , and  $A_{ijkl}$  are the Landau–Ginzburg expansion coefficients,  $\delta_{ijk}$  and  $q_{ijkl}$  are the bilinear and linear-quadratic coupling coefficients between the order parameter and the strain  $x_{ij}$ ,  $C_{ijkl}$  are the elastic moduli,  $\psi_i$  is an externally applied electrical or magnetic field, and  $\psi_i^D$  is the internal depolarization or demagnetization field for ferroelectric or ferromagnetic materials systems, respectively.  $F_{El}$  represents an internal elastic energy due to a built-in stress field. This field arises because of the coupling between the position dependent order parameter and self-strain<sup>7</sup> and can be analytically determined via theory of linear elasticity and the conditions of mechanical equilibrium.<sup>8</sup>

The generalized Landau–Ginzburg expression has been used extensively to characterize critical phenomena where spatial fluctuations in order parameter are important.<sup>9</sup> However, unlike fluctuation phenomena, where the  $\nabla_i \cdot \eta_j$  terms often oscillate about zero mean in homogeneous media,<sup>10</sup> graded ferroic systems fix these terms to nonzero values.

Thus, consider a compositionally graded ferromagnetic bar of length  $L$ . The grading is along the length  $L$  ( $z$  direction) which coincides with the easy magnetization direction of a ferromagnet with  $\mathbf{M}=[0, 0, M(z)]$ . If there are no external fields acting on the sample, Eq. (5) reduces to:

$$F[M(z)] = \int_0^L \left[ \alpha(z)M(z)^2 + \beta(z)M(z)^4 + \frac{1}{2}A \left( \frac{dM(z)}{dz} \right)^2 - \frac{1}{2}N_D M(z)^2 + F_{El}[M(z), C_{ijkl}(z), \lambda_{ijkl}(z)] \right] dz, \quad (6)$$

where  $(1/2) \cdot N_D \cdot M(z)^2 = H_D \cdot M(z)$  is the magnetostatic energy due to the demagnetization,  $H_D$  is the demagnetizing field, and  $N_D$  is a demagnetization factor that depends only on the geometry of the sample,  $C_{ijkl}$  are elastic moduli at constant magnetization, and  $\lambda_{ijkl}$  are the magnetostrictive coefficients. The demagnetization is negligible in our case, as the samples were purposely made in sheet form with the magnetization gradient along the length of the sheet, not normal to its surface.

The elastic energy can be blended into the first two terms of the Landau expansion via renormalized coefficients  $\bar{\alpha}$  and  $\bar{\beta}$  (Refs. 6 and 11) yielding:

$$F[M(z)] = \int_0^L \left[ \bar{\alpha}[C_{ijkl}(z), \lambda_{ijkl}(z)]M(z)^2 + \bar{\beta}[C_{ijkl}(z), \lambda_{ijkl}(z)]M(z)^4 + \frac{1}{2}A \left( \frac{dM(z)}{dz} \right)^2 \right] dz. \quad (7)$$

The equilibrium magnetization profile is then given by the equation of state,  $\partial F / \partial M = 0$ , in the form of a Euler–Lagrange equation:

$$A \frac{d^2 M(z)}{dz^2} = 2\bar{\alpha}M(z) + 4\bar{\beta}M(z)^3. \quad (8)$$

For the nickel–zinc–ferrite system, the composition (and thus the position) dependence of the thermodynamic coefficients

and magnetoelastic parameters are not known at this point. However, the order of magnitude of the internal field can be determined approximately from Eq. (3), utilizing the relation  $-\partial^2 \phi / \partial z^2 = \partial H_{int} / \partial z$  for a variation in the magnetic potential in one dimension, and our knowledge of the variation of the saturation magnetization with composition of the homogeneous samples, to yield:

$$H_{int} = - \int_0^L \frac{dM(z)}{dz} dz \cong 44 \text{ Oe}, \quad (9)$$

a remarkable confirmation of our findings (factor of 2) considering that the saturation magnetization may dependent upon the internal stress within the material [Eq. (8)].

Magnetization-graded structures can also be realized by subjecting a homogeneous ferromagnetic material to either temperature or stress gradients. However, we distinguish these *extrinsic* magnetization-graded constructs from their compositionally graded counterparts discussed in this report as the internal magnetic fields of the extrinsic devices vanish once the external stress or temperature gradients are relaxed or removed. In keeping with our semiconductor junction device analogy, internal fields are intrinsic to the structures and are established solely through spatial variations of the composition.

While this research was aimed at understanding graded ferromagnetic systems as the magnetic analogs of semiconductor junction devices, our findings are quite general and extendable, via Eq. (5), to other ferroics, including ferroelastics, ferromagnetics, superfluids, superconductors, and many other “smart” materials.<sup>1–3,6</sup> Thus, *graded* ferroic systems, in which the order parameter has a spatial dependence, have nonconstant free-energy potentials that result in internal bias fields that drive their dynamic properties. Such structures promise to yield whole new classes of transponant devices with potentially rich new phenomena to explore.

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