Non-Joulian Magnetostriction and Non-Joulian Magnetism

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Complementing volume-conserving Joule magnetostriction (JM), the non-Joulian magnetostriction (NJM) phenomenon has recently been discovered whose hallmark is change in volume of the crystals in magnetic fields. This article reviews the unique set of non-Joulian properties that are so non-conforming relative to conventional magnets that they merit the designation of a distinctly new class of (functional) magnets. This review distills key aspects of non-Joulian magneto-elasticity and magnetism, including the sign of volume change (contracting or expanding); the orientation dependence of volume change that is key to realizing large volume changes (remarkably, this volume-anisotropy coexists with a seemingly isotropic magnetization response for all crystal axes); and a digital coercivity landscape unlike that seen in conventional magnets. NJM lay undiscovered for nearly two decades because prior literature assumed, without experimental foundation, that iron-based alloys obeyed volume-conserving JM. Measurements now show that volume change is inherent across wide composition ranges, occurring in both quenched, metastable, and inexorably slow-cooled, equilibrated crystals. While not essential, quenching promotes long-range periodicity of magneto-elastic gradients with enhanced NJM. Another objective is to “frame” Joulian-to-non-Joulian behavior within a single framework of magnetically responsive, wave-like elastic medium in which approach to homogeneity yields the limiting case of JM; in fact, gradient magnet-elasticity is indispensable to describing non-Joulian magnetism. A consequential auxiliary finding is the large differences in intrinsic magneto-elastic constants for seemingly equivalent crystal axes, consistent with gradient magneto-elasticity. Consequentially, a sizeable literature that previously characterized these crystals using volume-conserving assumption and framework of phenomenological magnetostriction theory of homogeneous cubic crystals is rendered moot, and unreliable for high-fidelity applications.

1. Introduction

The focus of this topical review is the recently discovered phenomenon of non-Joulian magnetostriction,[1–3] (NJM) and the associated non-Joulian magnetism whose unique characteristics set it apart from behavior of conventional magnets as a distinctly new class of (functional) magnets.

The review is prefaced by a brief historical note on Joule magnetostriction (JM) to contextualize and outline the scope of this article.

In 1841, F. D. Arstall, a machinist with a keen sense of observation, thought of the possibility of magnetic-based mechanical engines, and urged Joule to explore whether there existed a connection between magnetism and elasticity (magneto-elasticity). Through a series of ingenious experiments, Joule concluded that iron and steel bars indeed changed their physical dimensions in magnetic fields. Joule quantitatively measured the magnitude of strain and found them to be on the order of few tens of parts-per-million (ppm). Over the course of these experiments, Joule noticed that the spontaneous elongation of the samples along one direction was always accompanied by transverse contractions. This behavior led him to further hypothesize that magnets obeyed the linear theory of deformation in responding to applied “magnetic” forces. By designing a water capillary system, Joule concluded that spontaneous field-induced deformations produced virtually zero volume change.

This spontaneous tendency of magnets to distort and change their physical dimensions in magnetic fields is now widely known as “Joule magnetostriction.” Its defining characteristic is volume conservation, of course, within approximations of negligible volume change one makes in linear theory of deformation. Since its discovery in 1842 (an abridged 1847 version of Joule’s work is given elsewhere[4]) magnets have been characterized on the basis of net zero volume change. Along with laying the foundation for “magneto-elasticity” as a new subject, remarkably, the idea of “functional” materials is explicit in Joule’s paper.

Thermodynamically, the magnetic energy of a ferromagnet is the sum total of its exchange, anisotropy, and magnetostatic energy. Each of these energy terms is a function of inter-atomic distance, that is, these energy terms are a function of strain. Therefore, a magnet will spontaneously deform if the distortions lower the overall energy (magnetic and elastic) of the crystal. A
2. Experimental Section

The growth of Fe-Ga, Fe-Ge, and Fe-Al single crystals, their heat-treatments, crystallography, sample orientation, and carving of the single crystal boules into discs was done at Ames Laboratory, IA. A previously grown boule of Fe-Si crystal was also characterized and carved into discs at Ames. Nominally, discs are 5 mm in diameter, 1 mm thick, with [001] axis as the disc normal. The orientation accuracy is better than 1°. Following elaborate steps were taken to ensure single crystallinity prior to characterization of magnetoelastic and magnetic properties to eliminate any possible heterogeneity (crystalline, structural, compositional, inclusions, cracks, etc.). Starting with high-purity elements, materials were arc-melted repeatedly into “buttons” in an argon-filled atmosphere to first form the base alloys. This is followed by drop-casting the buttons into copper molds. The resulting pellet are put into an alumina crucible and heated to a temperature just above melting of the alloy. The cast is typically 423 K (150°C) above the melting temperature. This melt is held for 1 h, after which the crucible is withdrawn at a rate of 5 mm h⁻¹. This elaborate single crystal growth protocol is followed by repeated polishing and chemical assay using scanning electron microscopy. As-grown boules are annealed at 1273 K (1000°C). Individually oriented discs may be additionally heat-treated and annealed in a sealed quartz tube in argon partial pressure. Crystals cooled in furnace are referred to as “slow-cooled” or “furnace cooled.” Samples that were placed in a furnace at a particular temperature and held for periods lasting up to 4 h before water quenching are referred to as “quenched.” Typical annealing temperatures for Fe-Ga, Fe-Ge, Fe-Si are 1043 K (770°C), whereas for Fe-Al it is 1273 K (1000°C).

High-resolution, high thermal stability magnetostriction measurements are made by attaching strain gauges on single crystal discs, using lock-in amplifier with Wheatstone bridge circuit.[10] Although it is relatively easy to set up a “basic” magnetostriction measurement system, it is non-trivial to measure these strains at high-resolution and without thermal drifts. This is because any factor (e.g., thermal fluctuations) that causes a change in length of the resistive grid of a strain gauge produces an artefact. For example, typical strain gauges have 2–10 ppm strain K⁻¹ change in temperature, which shows up as drifts. The same applies for pots and resistors in the accompanying circuit used to balance the Wheatstone bridge. These problems are overcome by using a circuit built with temperature-compensating features and by using resistors with exceptional thermal stability. The resulting resolution of the lock-in method is ≈0.04–0.1 ppm strain, and in typical measurements it is ≈0.1 ppm. Data are typically acquired at 100 scans s⁻¹, which yields sufficient data points that can further averaged and smoothed, if needed. A full loop may take ≈160–300 s to measure; typically, 5–7 loops are measured to eliminate the possibility of drifts and/or anelastic effects.

Through accurate placement of gauges, the observed large non-equivalence of magnetostriction strain for equivalent crystal axes is unambiguously ascertained. The nominal accuracy in aligning a strain gauge along a given axis is ≈1°, which may not fully convey the precision and accuracy of actual experiments, as demonstrated in the recent characterization of non-Joulian Fe-Si crystals, to an accuracy of ≈0.1 ppm between equivalent axes.[11]

The high-resolution magnetostriction measurements do not imply probing a small region of the crystal. The measurements described here use large gauge-length strain gauges to ensure maximal coverage of the flat disc surface, and it is these “bulk” measurements that are at the aforesaid resolution. In contrast, commercially available equipment or ad hoc laboratory setups often reported in literature rarely exceed a resolution of 1 ppm, and without any special efforts to minimize the contagion of thermal drifts. Our measurements also ensure that each measurement set is from the same large location of the sample, regardless of the orientation of strain gauges. Key measurements have been validated by using strain gauges of different gauge lengths, and the conclusions remain unchanged. To eliminate the possibility of any time-wise (history) dependence, key measurements have been repeated; even after a period of well over 1 year, and using a new set of strain gauges, conclusions remain the same. Key dataset is further validated by “blind tests” in terms of personnel handling the crystals, and conclusions remain the same. Strains normal to the 1 mm thick discs are measured by strain gauges of comparable length-scale (≈0.3 mm), by attaching them to the cylindrical surface of discs.[2]

The vector magnetization measurements were done using a low noise (5 × 10⁻⁷ emu noise) vector vibrating sample magnetometer (VVSM from MicroSense, Inc.) that is equipped with real-time field control. Magnetization measurements are made up to 1.8 T. The domain structure is imaged using the optical-based Interference-Contrast-Colloid (ICC) technique, which is described in several prior papers.[1,12–14]

Throughout this article, the term “homogeneous” strictly refers to a crystal with uniform spacing of adjacent planes. In
such a homogeneous medium, no elastic gradients exist. A crystal with wave-like or elastically modulated atomic planes naturally leads to elastic gradients, say, for example, a crystal with a charge density wave. When such periodic modulations vanish, its limiting state is described as a homogeneous crystal. Both forms of the crystals are non-heterogeneous, where the term “heterogeneous” is reserved solely to refer to defects such as inclusions, or variations in structure due to variations in composition, whose presence leads to macroscopic variations in physical properties. Crystals described in this article are free of such heterogeneities.

3. Non-Joulian Magnetostriction – An Overview

Complementing volume-conserving JM, non-volume conserving NJM phenomenon has recently been discovered.[11–13] Outlining the reproducible experimental facts of NJM phenomenon, through investigations on high-quality single crystals across a wide composition range, alloying elements (Ga, Ge, Al, Si), and thermal treatments that are known to yield equilibrium and metastable phases,[15,16] the volume change is found to be an intrinsic property of various phases in these alloys. Giant volume change and associated non-Joulian properties are observed in both quenched Fe-Ga with a compositionally long-range ordered D00 structure (metastable, ordered bcc)[17] with a weak iron-induced magnetism on Ga atoms through negative exchange,[18,19] as well as in slow-cooled, equilibrated crystals. Crystal structure studies on iron-based alloys have previously been described by the AMES group.[15,16] A robust volume change in inexorably slow-cooled (furnace-cooled) crystals further highlights that the effect is inherent to these crystals and cannot be erased simply by stress-annealing. Incidentally, the volume change and the myriad non-Joulian properties lay undiscovered for nearly two decades because prior literature measured, modeled, and theorized their behavior on the unfounded assumption of volume-conserving JM, and analyzed them within the inapplicable framework of phenomenological magnetostriction theory of a homogeneous medium. Hence, there was no motivation to probe either volume change, either as a function of field or load, or other non-Joulian properties, to understand physics of this phenomenon.

Note that quenching is not essential to observing volume change in these non-Joulian crystals, but there is unambiguous evidence that it promotes the formation of long-range periodic, magneto-elastic gradients spanning the entire physical dimensions of the crystal. These magneto-elastic gradients manifest as self-organized, highly periodic cellular domains, to produce enhanced NJM. In contrast, slow-cooling of crystals show large variations in the orientation and periodicity of magneto-elastic domains, presumably, due to the simultaneous nucleation and growth of multiple nuclei across the volume of the single crystal. A somewhat imprecise analogy would be the dependence of ferroelastic domains on heat-treatments in ferroelastic single crystals whereby the periodicity and orientation of domains can be altered.[13,20] Quenching is also not mutually exclusive to the condition of single crystallinity; examples of this abound, including crystals with charge density waves, and atomically modulated martensite crystals.[21–25]

The key characteristics of non-Joulian magnetism include:

- Non-volume conserving magnetostriction – crystals may either expand or contract. Section 3.1.
- Isotropy of magnetization (IoM) – linear, isotropic, virtually hysteresis free (coercivity less than ≈1 Oe) magnetization curves relative to crystal axes; no traditional magnetic “easy” axis exists. Section 3.2.
- Unique digital coercivity landscape. Section 3.2.
- Highly anisotropic orientation dependence of volume change. Section 3.3.
- Non-equivalent magneto-elastic response along equivalent crystal axes. Section 3.3.

The article also discusses:

- Domain structure and mechanistic model. Sections 3.4 and 3.5.
- Implications for past literature and predictions. Section 4.

Initially, NJM was reported in Fe-Ga alloys over a wide range of compositions and heat treatments, the role of thermal treatments pointing to the path dependence of the degree of perfection and coherence of the internally modulated magneto-structure essential to realizing volume change.[11–13] Since then, NJM has been observed in various iron-based binary bcc alloys (Fe-Ga, Fe-Al, Fe-Si).[11] Whereas the Fe-Ga alloys tend to expand and increase their volume, the Ge, Al, and Si-based alloys contract and decrease their volume. However, recent results indicate that the sign of NJM is not specific to a given alloy system but depends on the relaxation characteristics of long-wavelength elastic waves within these materials; contracting Fe-Ga crystals have been found.

One of the objectives of this review is to conjoin Joulia and non-Joulian magnetostriction phenomena – within this framework, the limiting case of zero volume change is JM. This viewpoint is useful for validating future theories of NJM, wherein, under certain parametric conditions, that is, when self-strain associated with elastic gradients abates or disappear, results would yield a homogeneous crystal with JM. Experimentally too, this viewpoint provides a powerful “diagnostic probe” by taking advantage of zero volume change in JM for all magnitudes of Joulia strain – deviation from zero volume change immediately signals the existence of a non-volume conserving mechanism. It also provides a means to assess the fidelity and quality of a given experimental dataset.

Another objective of this review is to provide an overview of the truly unique set of non-Joulian magnetic properties. The collage in Figure 1 highlights key differences vis-à-vis conventional magnetic properties and is assembled to “visualize” their discussion throughout this article. As Figure 1 shows, non-Joulian properties are so different from conventional magnets that they represent a new class of (functional) magnets. Moreover, some of the non-Joulian properties are even seemingly at odds with each other; for example, the observed isotropy of magnetization curves along all crystal axes versus magnitude of volume change that critically depends on the orientation of magnetization, both behaviors co-existing within the same crystal.
Brieﬂy, the schematics (a–d) in the left column of Figure 1 highlight key non-Joulian properties discovered so far; they are in sharp contrast to the response of conventional magnets, as shown by corresponding schematics (a’–d’) in the right column of Figure 1. Figure 1a shows that non-Joulian magnets are magneto-elastically modulated, whose origin has been attributed to charge/spin density waves.[1,21,26] The resulting magneto-elastic gradients self-organize into highly periodic domains spanning the entire macroscopic crystal, and such domains are magnetostatically and magneto-elastically “autarkic” or self-sufﬁcient.[1] The ﬁeld-assisted folding and unfolding of these elastic gradients causes a change in the inter-atomic spacing, leading to volume change. Depending on the alloy system and thermal treatment, the modulations may dilate or contract, resulting in either expanding or contracting NJM (e-NJM or c-NJM), respectively, as shown in Figure 1b. A signature of deformation of a medium with elastic gradients is “wrinkling.”

Non-Joulian crystals exist in a wrinkled state, as shown in Figure 1a; images of the wrinkled state and their ﬁeld dependence is shown previously.[1] In contrast, each domain in a conventional magnet, by the very deﬁnition of a domain, is a homogeneous volume, that is, free of magnetic gradients. Magnetic gradients exist only across domain walls separating adjacent domains. Moreover, each domain already exists in a state of saturation magnetostriction. The effect of magnetic ﬁeld is to rotate the magnetization, and thus, the direction of its self-strain. Hence, volume remains invariant in JM. Also, each microscopic region of a Joulian magnet experiences the exact same volume-conserving set of deformations, as shown in Figure 1a’, and macroscopically, these distortions yields zero volume change. An often forgotten and ignored but unyielding condition of JM is that the volume change is zero not only at saturation but at all ﬁelds leading to saturation, as shown in Figure 1b’; volume is zero regardless of whether all or just a few domains rotate. Incidentally, it is this very fundamental condition of zero-volume change at all ﬁelds for JM that serves as an excellent diagnostic tool to assess the quality and integrity of measurements.

By Neumann’s principle in crystal physics, the magnetocrystalline anisotropy must possess the symmetry of the underlying crystal.[27] Thus, a conventional magnet must possess a set of easy axes overlapping the underlying crystalline symmetry. Along these directions of spontaneous magnetization, the crystal internal energy is a minimum. When a crystal is magnetized along one of its easy axes, reversal primarily occurs by domain wall motion and the well-known hysteretic curves are observed, as shown in Figure 1c’. The easy axes are punctuated by hard axes, which are the energetically unfavorable axes for magnetization. Magnetization along the hard axes occurs by rotation, resulting in linear magnetization curves, also shown in Figure 1c’. In sharp contrast, a key feature of non-Joulian magnets is their virtually identical magnetization curves regardless of the crystal direction along which such curves are measured, as shown in Figure 1c. Moreover, they are all linear, hard-axis type curves. In other words, these crystals have far greater (inﬁnite) rotational symmetry compared to the crystal symmetry.

All non-Joulian magnets exhibit a miniscule or zero coercivity in the measured linear magnetization curves, regardless of the crystals axis. Careful analysis of their magnetization curves has recently revealed the existence of an exquisite coercivity landscape that is unlike that seen in conventional magnets. Measured as a function of crystal orientation, the coercivity remains constant for a large angular swathe until it changes abruptly to a different value at a critical angle, as shown in Figure 1d. Moreover, this digital coercivity landscape bears no relationship to the underlying crystallographic axis. Instead, it is
an emergent phenomenon, reflecting the exquisite balance of local and global magneto-elastic energy terms across periodic magneto-elastic gradients. In contrast, conventional magnets display maximum coercivity along the easy axes, which gradually drops to zero or a minimal value along hard axes, as shown in Figure 1d'.

While aforesaid non-Joulian effects have only recently been discovered, non-Joulian magnetism remains a complex phenomenon and its complete understanding eludes. Therein lies the excitement and the challenge is to fully decipher the causal relationships. For instance, in the presence of magneto-elastic gradients, the digital coercivity landscape of these crystals is clearly an emergent phenomenon that, by the very definition of emergence, cannot be derived from first principle calculations and/or from atomic information alone. The temperature dependent effects are beginning to be investigated. Some unusual behavior is predicted.

Implications for past literature that characterized similar iron-based alloys on the basis of homogeneous medium is discussed in Section 4. The electron transport behavior and temperature dependent effects of non-Joulian magnets are beginning to be investigated; several properties are predicted in Section 4.

Finally, characterization protocols are highlighted throughout the text to avoid the pitfalls of assumptions that are typically carried over from characterization of homogeneous crystals of cubic symmetry but are found inapplicable to non-Joulian magnets.

A key takeaway in studying non-Joulian magnets is that while differences in response along various crystals directions are subtle, the exciting challenge is to make those distinctions obvious.

3.1. Joulian Versus Non-Joulian Magnetostriction

Figure 2a–c exemplifies NJM, using Fe-Ga, Fe-Ge, and Fe-Al crystals, respectively; the respective schematics in Figure 2a'–c' shows saturation strains along various axes. Unless otherwise stated, all crystals are circular disks \( \approx 5 \) mm in diameter and \( \approx 1 \) mm thick, with [001] axis as the disc normal. The quenched Fe\_71\_Ga\_29\_9 crystal in Figure 2a illustrates expanding NJM (e-NJM) behavior, whereas the Fe\_80\_Ge\_19\_2 and Fe\_70\_Al\_33 crystals in Figure 2b,c, respectively, display contracting NJM (c-NJM). The magnetostriction curves in Figure 2a for Fe-Ga crystal were measured by applying strain gauges along various axes, with applied field directed along the [110] axis; similarly, for the Fe-Ge sample in Figure 2b. For Fe-Al, the curves in Figure 2c are measured with \( H || [110] \) axis.

First consider the response of Fe-Ga crystal in Figure 2a-a'. Remarkably, the crystal simultaneously expands in all in-plane directions; the [110] axis by \( +25 \) ppm, the [110] axis by \(+46 \) ppm, and [110] and [010] axes by \(+70 \) and \(+48 \) ppm, respectively. The strain normal to the disc is non-existent, \( \approx -1 \) ppm at saturation field of \( \approx 2 \) kOe; a small additional strain beyond saturation is due to conventional exchange striction and does not pertain to NJM. A large volume expansion, that is, e-NJM is readily seen by imagining a small cube within the disc with edges along [100], [010], and [001]. At saturation, the volumetric expansion of the cube, \( SV/V \), is proportional to \( \lambda_{100} + \lambda_{010} + \lambda_{001} \). It is equal to \( +70 + 48 - 1 \) or \(+117 \) ppm. In contrast, Fe-Ge in Figure 2b, and Fe-Al in Figure 2c, contract and decrease their net volume. The data for Fe-Ge, \( SV/V \), at saturation is \( (-21 -26 + 3) \) or \(-44 \) ppm; whereas for Fe-Al, it is \(-36 \) ppm. Their behavior exemplifies c-NJM.

For the three crystals described in Figure 2, the change in volume as a function of field is quantified in Figure 3a; also shown is the volume change of a long-term “aged” (at room temperature for \( \approx 30 \) years) single crystal of Fe\_70\_Si\_30. The data for Fe-Si crystal is included because it is near the crossover between c-NJM \( \rightarrow \) e-NJM, with only a small volume change at saturation, on the order of \(-9 \) ppm. To-date, this crystal is closest to conforming Joulian and non-Joulian magnetostriction, using a measurement resolution of 11 parts-per-billion (ppb), as shown in Figure 3c. The ultra-high stability of measurements against thermal drifts is illustrated in Figure 3d.

In Figure 3a, notice that for non-Joulian crystals the volume change is non-zero at all fields, and not just at saturation. Here, it is especially instructive to contrast NJM with the response of a conventional, that is, Joulian magnet, which by its very definition, conserves its volume regardless of magnitude of strain – if the distortions are Joulian no matter how small, volume is always conserved. This is shown in Figure 3b for an annealed polycrystalline nickel disc. Nickel is a negative magnetostriction material, that is, it contracts along the field direction while expanding along the transverse directions. Its net distortions are such that the sum of longitudinal and transverse strains add to zero, that is, \( \lambda_{long} + \lambda_{trans} = 0 \), as shown by the green curve in Figure 3b. Notice the stringent volume conserving condition of JM from Figure 3b – in JM, the volume change is zero independent of the magnitude of strain, and not just at saturation field. Incidentally, this data is plotted “raw” without a special effort to account for a finite coercivity on a point-by-point basis, which would yield a “flat line” shown in Figure 1b.

Consistently, it is found that non-Joulian response is sensitive to prior thermo-mechanical-magnetic treatments; even rough mechanical handling of crystals can degrade the internal structure, such as due to high stresses at the tips of tweezers used to handle the crystals. While all these crystals change their volume, thermal treatments cause crystals of similar composition to deviate in the degree to which various axes expand and/or contract. This is illustrated in Figure 4b-b’ by a slow-cooled Fe-Ga crystal whose composition (Fe\_70\_Ga\_30) is comparable to the sample in Figure 2a-a’; for ease of comparison, the curves for the quenched sample are reproduced again in Figure 4a-a’. While the slow-cooled crystal in Figure 4b-b’ still displays a robust net increase in volume, the volume change is reduced by half. From Figure 4b-b’, its volume change at saturation, \( \lambda_{100} + \lambda_{010} + \lambda_{001} \) is only \(+44 + 33 - 16 = +61 \) ppm versus \(+117 \) ppm for the quenched crystal in Figure 4a-a’. Later, analysis of another degraded versus a near-ideal sample helps explain the origins of NJM.

3.2. Isotropy of Magnetization and Discovery of Exquisite Digital Coercivity Landscapes

In addition to their ability to change volume, a remarkable property of non-Joulian magnets is their “isotropy of magnetization” (IoM) – linearly reversible, near hysteresis-free magnetization curves
that are virtually identical irrespective of the crystals axis.\cite{1,11} This is shown in Figure 5a–e for various alloys. By comparison, conventional magnets show hysteresis along the easy axis and are linear only along the magnetic hard axes,\cite{29} as shown schematically in Figure 5f. The linear curves of non-Joulian magnets resemble a hard axis of a conventional magnet, implying rotation. If it was not specified that these curves were from bcc Fe-rich single crystals, they might have been taken for an amorphous system; in fact, even amorphous or nanocrystalline magnetostriction materials show distinct easy and hard axes due to stress-induced anisotropy.\cite{30} The IoM is found to exist regardless of the choice of alloy composition, alloy system, or thermal treatments.\cite{1,11}

It is worth pointing out that before the discovery of NJM,\cite{1} prior literature spanning nearly two decades never measured the orientation dependence of magnetization in similar crystals; the reported curves for a few specific axes were oddly referred to as “soft” magnets (contrary to the definition of a soft magnet—square loops of low coercivity\cite{29}) instead of what they are—linear curves resembling a hard-axis; some literature show isolated curves with far higher coercivity\cite{31} (\wedge 12 Oe, implying precipitates or low-quality crystals) instead of 0 to \wedge 1 Oe coercivity that is typical of crystals described here. The unusual coercivity behavior of non-Joulian magnets has recently been discussed as a means to understand the origins of coercivity in magnets.\cite{32} A facet of paradoxical properties of non-Joulian crystals is the recent discovery of discrete or “digital” coercivity landscapes as a function of crystal orientation, as shown in Figure 6a–f. To illustrate and explain, consider the angular-dependence of coercivity of the Fe-Si single crystal in Figure 2.

Figure 2. Expanding and contracting non-Joulian magnetostriction. Set of magnetostriction curves along various directions in (a) quenched Fe\textsubscript{71.1}Ga\textsubscript{28.9} single crystal; (b) quenched Fe\textsubscript{90.6}Ge\textsubscript{19.2} crystal; and (c) Fe\textsubscript{82}Al\textsubscript{18} crystal. a’–c’) Schematics showing saturation strains along various axes corresponding to (a–c), respectively. The direction of magnetization of each sample is also shown. (b,c) and (b’,c’) Reprinted with permission.\cite{11} Copyright 2017, American Physical Society.

Figure 3. Field dependence of volume change in NJM. a) Field-dependence of volume change, \(\delta V/V\), in various non-Joulian single crystals. Direction of magnetic excitation in each case is also indicated. b) Magnetostriction of an annealed Ni disc, 1 cm \(\phi\), 0.1 mm thick. Measurement offset error in \(\lambda_{long} + 2\lambda_{trans}\) (green curve) is \wedge 1 ppm. c) The resolution of the lock-in based magnetostriction measurement method is \wedge 100 parts-per-billion, as shown using an annealed polycrystalline Ni foil that is slowly cycled between 40 and 50 Oe. d) Stable, drift-free magnetostriction loops in a quenched Fe\textsubscript{81.7}Ga\textsubscript{18.3} in measurement lasting over 25 min. (a) Adapted with permission.\cite{11} Copyright 2017, American Physical Society.
Figure 6a. Measured as a function of angle within the plane of the disc-shaped sample, the coercivity value divides the disc into yellow and green sectors. Within a given sector (say, yellow or green), the coercivity is independent of the angle until it changes stepwise to a different value across the sector boundary; the same data is re-plotted in linear coordinates in Figure 6b to emphasize this discrete change across the sector boundary. Such a digital coercivity landscape, schematized in Figure 6c, stands in stark contrast to all conventional magnets (not only single crystals, but also thin films, multilayers, amorphous systems, etc.), where coercivity varies gradually, it being maximum along the easy axes and minimum along the hard axes, and for which magnetization reversal models are well developed.[33,34]

A quenched Fe\textsubscript{73.9}Ga\textsubscript{26.1} single crystal used to first report NJM\textsuperscript{[1,3]} shows a profile similar to Fe-Si except for the presence of additional discrete intermittent steps, as shown in Figure 6d; in a slow-cooled (degraded) Fe-Ga sample of exactly the same composition, the discrete coercivity landscape is replaced by a gradually varying coercivity (shown later in Section 3.5).

Results show that the sector geometry varies with the alloy system and heat-treatments, and crystals may spontaneously exhibit quad-

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Figure 4. Path-dependence of non-Joulian magnetostriction. a-a') Set of magnetostriction curves along different directions in a quenched Fe\textsubscript{71.1}Ga\textsubscript{28.9} (same curves as in Figure 2a) and saturation strains corresponding to (a), b-b') Behavior of a slow-cooled crystal of comparable composition (Fe\textsubscript{70.4}Ga\textsubscript{29.6}) and saturation strains, respectively.

Figure 5. Isotropy of magnetization in non-Joulian magnets. a) Quenched Fe\textsubscript{73.9}Ga\textsubscript{26.1}. b) Slow-cooled Fe\textsubscript{73.9}Ga\textsubscript{26.1}. c) As-grown Fe\textsubscript{67}Al\textsubscript{33}. d) Slow-cooled Fe\textsubscript{81.1}Ge\textsubscript{18.9}. e) Aged Fe\textsubscript{94}Si\textsubscript{6} single crystal (Fe-3.1 wt%Si). Only selected angles are shown; in-plane angles (measured every 3° to 5°) show the same isotropic behavior. f) Anisotropy of magnetization in conventional magnets, which show distinct easy and hard magnetic axes. (c) Reprinted with permission.© 2018 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
sectors, hex-sectors, etc. For example, Figure 6e shows the angular dependence of coercivity measured from magnetization curves of an aged Fe₉₄Si₆ single crystal (Fe-3.1 wt% Si). The green and yellow sectors represent regions of constant coercivity that change stepwise across the sector boundaries. The geometry of disc-shaped samples with [001] normal is shown schematically in the lower-right corner. b) Same data as in (a), plotted in linear coordinates to emphasize the stepwise change in coercivity. c) Schematic showing the emergence of macro-sectors within which coercivity has a fixed value. d) Digital coercivity in a quenched Fe₇₃.₉Ga₂₆.₁ single crystal that was annealed at 1033 K for 1h followed by rapid quenching. e) Angular dependence of in-plane coercivity in Fe₉₀Al₃ single crystal. Yellow sectors have zero coercivity. f) Angular dependence of coercivity in a quenched Fe₈₀.₈Ge₁₉.₂ single crystal.

Figure 6. Digital coercivity landscapes of non-Joulian magnets. a) Angular dependence of coercivity measured from magnetization curves of an aged Fe₉₄Si₆ single crystal (Fe-3.1 wt% Si). The green and yellow sectors represent regions of constant coercivity that change stepwise across the sector boundaries. The geometry of disc-shaped samples with [001] normal is shown schematically in the lower-right corner. b) Same data as in (a), plotted in linear coordinates to emphasize the stepwise change in coercivity. c) Schematic showing the emergence of macro-sectors within which coercivity has a fixed value. d) Digital coercivity in a quenched Fe₇₃.₉Ga₂₆.₁ single crystal that was annealed at 1033 K for 1h followed by rapid quenching. e) Angular dependence of in-plane coercivity in Fe₉₀Al₃ single crystal. Yellow sectors have zero coercivity. f) Angular dependence of coercivity in a quenched Fe₈₀.₈Ge₁₉.₂ single crystal.

3.3. Magnitude of Volume Change Is Orientation Dependent – Non-Equivalent Response of Supposedly Equivalent Axes

This section describes the orientation dependence of volume change and the non-equivalence of magneto-elastic response for seemingly equivalent axes.

First, results show that the magnitude of volume change critically depends on the direction along which a crystal is magnetized; this coexists with the IoM in these crystals. With this fundamental understanding between crystal axes and its magneto-elastic response, four-times larger volume changes are realized by applying the field along certain “preferred” orientations. Consistently, a relatively smaller volume change is observed for fields along (at least) one of the cubic axis. It also means that if samples are being screened for their NJM by energizing them along a cubic axis that yields a small volume change ($\approx 10–20$ ppm), the full potential of the crystal may be missed, especially when using measurement systems with low or unknown resolution, and/or large thermal drifts; such as, the curves shown in Figure 12 by Clark.[31]

A second finding is that the measured magnetostriction constants for these cubic crystals is non-equivalent, that is, $\lambda_{100} \neq \lambda_{010}$. This asymmetry is the hallmark of gradient magneto-elasticity that causes otherwise symmetric tensors to become asymmetric.[35,36]

Third, a simple mechanistic model emerges that explains various manifestations of non-Joulian magnets, including its sign and non-equivalence of response.

Fourth, the large difference in intrinsic magnetostriction coefficients has implications for prior literature that is based on the assumptions of zero volume change (JM) and the framework of phenomenological magnetostriction theory of homogeneous cubic crystal. This aspect is separately discussed in Section 4.

It has previously been shown that domain walls separating adjacent domains in Fe-Ga crystals are not straight line segments but are in fact zigzagged segments at the micron to sub-micron scale; see for example, “Figure 3E” of ref. [1]. The origin of these zigzagged walls was pointed out to be an elastically modulated crystal structure in the form of charge/spin density waves. These highly periodic elastic gradients couple to the magnetic medium, whose spacings can then be changed by applied fields. Recent work using nano-X-ray scanning diffraction microscopy point to the existence of such periodic gradients,[17–19] as was first predicted,[1] and that the quenched Fe-Ga crystal has an ordered $DO_3$ structure.[17] Independently, charge and spin density waves have also been reported in the Fe-Ga system.[22] In the presence of magneto-elastic gradients, no assumptions should be
made regarding the equivalence of magneto-elastic response (or any other physical properties for that matter) along seemingly equivalent crystallographic directions. This is because the condition of equivalence of physical response is derived from crystal symmetry whose foundation is a homogeneous medium. \cite{27} In contrast, existence of (long-range) elastic gradients renders those constants asymmetric, that is, non-equivalent. Therefore, the intrinsic saturation magnetostriction constants, $\lambda_{100}$, $\lambda_{010}$, and $\lambda_{001}$, must be explicitly measured. Experimentally, this is done by keeping track of fiducial alignment marks on the samples. In non-Joulian magnets it is found that, in general, $\lambda_{100} \neq \lambda_{010}$ and this difference can become quite large (e.g., over 300\% for the Fe-Al crystal in Figure 2c).

Figure 7c–e\textsuperscript{'} for $H \parallel [110]$, and Figure 7f–h\textsuperscript{'} for $H \parallel [110]$ axis shows that the crystal expands along all in-plane directions in either case. However, the magnitude of various magneto-strains for $H \parallel [110]$ axis is not equivalent to response when $H \parallel [110]$. Figure 7g–g\textsuperscript{'} shows, respectively, the schematics of saturation strains. In all cases shown in Figure 7c–h, the strain normal to the disc, the [001] direction, is negligible. For each case shown in Figure 7c–h, the volume change is positive, that is, $\lambda_{100} + \lambda_{010} + \lambda_{001} \neq 0$.

The implication is that experimentally, dependence of NJM on applied field direction must be measured by placing a series of strain gauges along various key axes. In a disc-shaped sample, directions of interest include [100], [010], [001], [110], and [110], as shown schematically in Figure 7a. For example, when a crystal is magnetically excited along the [110] axis, see schematic in Figure 7a, a set of magneto-strains are obtained, as shown in Figure 7e for the quenched Fe\textsubscript{71.1}Ga\textsubscript{28.9} crystal. Similarly, Figure 7f–h for $H \parallel [110]$, $H \parallel [100]$, and $H \parallel [010]$, respectively. Figure 7e\textsuperscript{'}–h\textsuperscript{'} shows, respectively, the schematics of saturation strains. In all cases shown in Figure 7c–h, the strain normal to the disc, the [001] direction, is negligible. For each case shown in Figure 7c–h, the volume change is positive, that is, $\lambda_{100} + \lambda_{010} + \lambda_{001} \neq 0$.

Examination of Figure 7e–e\textsuperscript{'} for $H \parallel [110]$, and Figure 7f–h\textsuperscript{'} for $H \parallel [110]$ axis shows that the crystal expands along all in-plane directions in either case. However, the magnitude of various magneto-strains for $H \parallel [110]$ axis is not equivalent to response when $H \parallel [110]$. Figure 7g–g\textsuperscript{'} for $H \parallel [100]$, and Figure 7h–h\textsuperscript{'} for $H \parallel [010]$, show that a large longitudinal strain is accompanied by a transverse contraction. Again, magnitude of various strains for magnetic excitation along supposedly equivalent $<100>$-type axes is non-equivalent.

The most remarkable and consequential feature of Figure 7 is that the magnitude of volume change is sensitive to the direction of magnetic excitation. This is highlighted in Figure 7b for the Fe-Ga crystal, and in Figure 7c for the Fe-Ge crystal. With respect to the Fe-Ga crystal, the volumetric change is maximum when the crystal is specifically magnetized along the [110] axis (green curve), yielding $8\text{V/V}$ of +120 ppm. This is three-times higher volume change versus magnetization along [100] (cyan curve). Equally significant is the fact that the volumetric change for seemingly equivalent axes is non-equivalent. Thus, $8\text{V/V}$ for [110] versus [110] excitation differs by a giant factor of 2.3 (133\%); whereas for [100] versus [010], it differs by 1.7-times (70\%).

For homogeneous cubic crystals, $\lambda_{100}$ is exactly equal to $\lambda_{010}$, or $\lambda_{001}$. Thus, measuring either one suffices. A well-established method to determine $\lambda_{100}$ for a homogeneous cubic crystal is as follows\cite{29} A strain gauge is placed along [100] axis, and the longitudinal strain, $\lambda_{L1}$, is measured, see Step-I of Figure 7d. To
eliminate any uncertainty associated with a non-ideal demagnetized state, that is, to eliminate the uncertainty associated with the baseline relative to saturation longitudinal strain, \( \lambda_{\text{L}} \). Magnetic field is then applied parallel to the [010] axis, while measuring the strain along [100] axis. This gives the transverse strain, \( \lambda_{\text{T}} \), as shown in Step-II of Figure 7d. For homogeneous crystals of cubic symmetry, \( \lambda_{100} = (2/3)(\lambda_{\text{L}} - \lambda_{\text{T}}) \). In the same manner, \( \lambda_{010} \) can be determined by attaching a strain gauge along the [010] axis. It is expected that its value would be precisely identical to \( \lambda_{100} \).

For the Fe-Ga crystal in Figure 7, \( \lambda_{100} \) and \( \lambda_{010} \) can be determined using the saturation strains in Figure 7g′–h′. For instance, from Figure 7g′, \( \lambda_{\text{L}} \) along [100] axis is +129 ppm, and from Figure 7h′, the transverse strain \( \lambda_{\text{T}} \) is equal to −90 ppm. Therefore, \( \lambda_{100} = (2/3)(\lambda_{\text{L}} - \lambda_{\text{T}}) \) is equal to 2/3(129 + 90) or +146 ppm. Similarly, when the value \( \lambda_{010} \) is derived from Figure 7g′–h′, it is found to be equals to 2/3(151 + 89) or 160 ppm.

Therefore, \( \lambda_{010} \neq \lambda_{100} \), and these two intrinsic constants differ markedly by \( \pm 10\% \).

It is necessary to minimize errors in placing a strain gauge along a given axis; for the measurements shown in Figure 7, it is \(< 1\% \), and orientation-related errors are negligible. Simply stating this nominal accuracy in aligning a strain gauge may not fully convey the precision and accuracy of actual experiments; in the recent characterization of non-Joule Fe-Si crystals, an accuracy of \( \pm 0.1 \) ppm between equivalent axes is measured.[11]

The asymmetry of magnetostriction constants for equivalent cubic axes is generic to non-Joule crystals. For example, in the slow-cooled Fe-Ga crystal in Figure 4b, \( \lambda_{100} \) and \( \lambda_{010} \) differ by \( \approx 7\% \). Figure 7c shows the orientation dependence of volume change in the Fe-Ga crystals. Again, notice the large anisotropy of volumetric change with respect to the axis of magnetization. For this crystal, \( \lambda_{010} \neq \lambda_{100} \), and the two intrinsic constants differ by \( \approx 9\% \). These results emphasize that evaluating the behavior of these crystals based on coefficients derived from phenomenological theory of homogeneous crystals,\(^1\) is untenable.

### 3.4. Simple Mechanistic Model Based on Gradient Magneto-Elasticity

A mechanistic understanding of NJM and its sign (expanding or contracting) emerges. The model is based on the experimentally observed long-wavelength, magneto-elastic gradients stemming from internally modulated, charge density waves that get organize itself microscopically as long-range periodic domain structure.[1] as shown schematically in Figure 8a. In this model, the bulk magnetostriction occurs by atomic-level “coiling” and “uncoiling” of such elastic waves, as explained in detail elsewhere.[1] Incidentally, this change in inter-planar distances produces the volume change in NJM.

In the presence of these elastic waves, macroscopically, the crystal can be viewed as an assembly of “giant adaptive cells” (GACs). Two other observations seem to corroborate their existence. First, a sizeable rotational hysteresis exists in these crystals even at fields as high as 18 000 Oe, which is well in excess of fields required to saturate them by a factor of 4–10. Second, a natural consequence of elastic modulations is that strain at a given point depends on its position along the wavelength. This spontaneous “wrinkling” of the crystal has also been observed.[1]

The rich variety of NJM behavior can be qualitatively explained by the ability of GACs to relax and realize their self-strain in magnetic fields. Differences arise from the ability of GACs to either remain frozen, or to redistribute themselves by rotating (fully or partially) in a field: these adaptive features depend on thermal treatments. Whereas complete rotation of the domain pattern has been previously observed in a quenched Fe-Ga crystal,[1] an example of a frozen domain pattern is shown in Section 3.5 using a slow-cooled Fe-Ga crystal.

First consider the Fe-Ge sample in Figure 8b. When \( H \parallel 100 \), its longitudinal and transverse magneto-strains are \( (−52 \text{ ppm}; +17 \text{ ppm}) \), respectively. When the field is directed along [010] axis, the sign and magnitude of the strain along [100] and [010] remains unchanged, as shown in Figure 8b′: strains normal to the disc are negligible. Such a behavior cannot be explained by a homogeneous elastic medium and epitomizes completely frozen GACs – they only relax in response to applied field. In contrast, Figure 8c′–c″ shows the case of Fe-Si crystal where GACs rotate completely. As shown in Figure 8c, when \( H \parallel 100 \), the longitudinal and transverse strains are \( (−20 \text{ ppm}; +7 \text{ ppm}) \), respectively. When \( H \parallel 010 \) axis, Figure 8c′, the sign of longitudinal and transverse strains changes but the magnitude remains the same, \( (+20 \text{ ppm}; −7 \text{ ppm}) \). Figure 8d′–d″ shows the intermediate case where the sign of strain remains negative along [100] and [010] for \( H \parallel 100 \) and \( H \parallel 010 \), but the amplitude (i.e., degree of relaxation of GACs) changes.

Within the GAC model, the sign of NJM (positive or negative) can also be qualitatively explained. Previously, it was thought that Fe-Ga alloys only increase their volume. A quenched Fe\(_{81}\)-Ga\(_{18}\) crystal in Figure 8e′–e″ disproves this notion. In this crystal, when \( H \parallel 100 \), it exhibits an unusually small longitudinal strain of \( +35 \text{ ppm} \). The transverse strain along [010] for \( H \parallel 100 \) is negative \( (−55 \text{ ppm}) \). Also, strain normal to the disc, the [001], is \( −27 \text{ ppm} \). Therefore, for \( H \parallel 100 \), \( \lambda_{100} + \lambda_{010} + \lambda_{001} \) is equal to \( (35-57-27) = −47 \text{ ppm} \). For \( H \parallel 010 \), the longitudinal strain is +154 ppm, but the transverse strain is −168 ppm. The measured strain along [001] was −18 ppm. Therefore, for \( H \parallel 010 \), \( \lambda_{100} + \lambda_{010} + \lambda_{001} \) equals \( (154-168-18) = −32 \text{ ppm} \). This behavior is closest to the schematic shown in Figure 8c′–c″ (rotatable GACs).

The non-equivalent response of equivalent crystal axes can be explained by the mechanistic model. First, the possibility of these results as being measured from different locations, or arising from any historical time-dependence, is thoroughly ruled out by the various experimental precautions described in the Experimental Methods section. In addition to ensuring that measurements are made on the same location and are devoid any history-wise time-dependence, the exceptional uniformity of physical properties across the entirety of the crystal has been highlighted in the “Extended Dataset Figure 4” of ref. [1] where a collage of the 5 mm diameter sample shows long-range periodic domains spanning the entire crystal. Similar long-range periodicity is exhibited in a Fe-Ga sample across a wide composition range.

Consider a magnetostriction strain due to applied field along [110], described by the strain tensor \( \lambda_0 \). The strain along a given
direction $\mathbf{n}_i$ is given by $\lambda_{ij} \mathbf{n}_i \mathbf{n}_j$ (using dummy notation).\cite{27} In a conventional crystal, the following equality for volume change holds: $\lambda_{100} + \lambda_{010} + \lambda_{001} = \lambda_{110} + \lambda_{110} + \lambda_{001}$, representing the special case of the first invariant of the strain tensor. Rather than attempting to fit the framework of tensor relations to the data showing non-equivalence of axes, a straightforward reasoning that can be universally agreed upon shows that this tensor framework and its underlying assumptions are not applicable to the behavior of this new class of magnets: following that, the observed non-equivalence of equivalent axes is explained by the mechanistic model. This point is illustrated by examining, for example, Figure 7e′–h′, where each figure corresponds to the set of spontaneous deformations along different directions experienced by the initially circular disc for different applied field directions. For example, Figure 7e′ shows the set of spontaneous saturation deformations along various axes when the field is along [110]; Figure 7f′ shows the deformation set for field along [110], etc. Regardless of any theoretical framework, the volume change, $\delta V/V$, of an initially circular disc is equal to (change in area, $\delta A/A$)×(change in thickness, $\delta h/h$). Inspecting Figure 7e′ versus f′, volume change is distinctly different for these two equivalent axes. Hence the tensor relations used to describe the response of a conventional material are inapplicable.

In a conventional crystal, a 90° rotation would have superimposed the [110] axis onto [110], and one expects the same deformation behavior. Of course, in a conventional crystal, $\delta V/V$ would also be equal to zero in JM, whereas, a large volume change is evident in these crystals.

The mechanistic model can now be used to explain this behavior based on the ability of GACs to relax and realize their self-strain in magnetic fields. Differences in observed behavior arise from the ability of GACs to remain frozen or to redistribute themselves by rotating (fully or partially) in a field; these adaptive features are dependent on past thermo-magnetic treatments. The degree of flexibility of magneto-elastic gradients to rotate governs the crystal’s response to field. Indeed, crystals are found where the GACs are fully rotatable and the non-equivalence for a given set of axes disappears. As validation, the aforesaid Fe$_{94}$Si$_6$ crystal is fully rotatable, Figure 8c–c′, and indeed, in this crystal, $\lambda_{100}$ becomes equal to $\lambda_{010}$ ($=19$ ppm).

In conclusion, strains realized for applied field along these equivalent axes differ because the response is governed by gradient magneto-elasticity and cannot be analyzed by usual relations that are strictly applicable to a homogeneous medium, and where volume is assumed to be conserved.

### 3.5. Domain Structure in Non-Joulian Magnets

Ironically, the realization that magneto-elastic gradients may play a role in governing the emergent properties of non-Joulian magnets has come from a comparison between the domain structure in a slow-cooled Fe$_{73.9}$Ga$_{26.1}$ crystal. Figure 9, versus those of quenched crystals, Figure 10. Figure 9a is a collage of the domain structure of a slow-cooled Fe$_{73.9}$Ga$_{26.1}$ crystal; its NJM behavior is shown in the Extended Dataset in ref. [1] and in ref. [2]. Its domain structure vertically bisects the entire 5 mm $\phi$ crystal into two mirror-symmetric sectors, see schematic in the inset of Figure 9a; the bisector is approximately along the in-plane [010] axis. Figure 9b shows this structure at a higher magnification, revealing its mirror symmetry across the bisector, as well as large variations in the size and orientation of the cellular structure (contrast this with the highly periodic cellular structure in the quenched Fe-Ga crystal in Figure 10a).

The elements of magnetic symmetry across the bisector are shown at high-magnification in Figure 9c.

The domain structure in Figure 9 was imaged using the interference-contrast-colloid (ICC) method\cite{1,12,13}. In this technique, a wall segment appears dark when flux lines penetrate the sample surface (labeled as “−” in Figure 9c) due to accumulation of ferrofluid particles at that segment; conversely, a segment appears light if the flux lines are emanating out of the sample (labeled as “+”), which causes ferrofluid particles to be repelled away from such segments. In Figure 9c, every dark (−) and light (+) segment in the left sector has a corresponding mirror-image light and dark segment, respectively. This occurs by Bloch walls...
changing their chirality across the vertical bisector. Also, within a sector, say the left sector in Figure 9c, chirality of the walls oscillates from top to bottom. This local, short-range efficient flux closure via changes in chirality of Bloch walls across the bisector is schematized in Figure 9d. When this degraded sample is saturated and brought back to zero field, the sample remains bisected along the vertical direction regardless of the number of magnetic cycling, only the relative arrangement of cells within each sector changes. This is a picture of what could be called a “frozen” GAC structure referred earlier in Figure 8.

In contrast, the quenched Fe-Ga crystals exhibit highly periodic cellular chains spanning the entire disc, as discussed in detail in ref. [1] for a quenched Fe$_{73.9}$Ga$_{26.1}$ crystal. Another similar example of highly periodic cellular domains is shown in Figure 10a in a quenched crystal with widely different composition, Fe$_{72.9}$Ga$_{17.1}$, to emphasize the generic aspects of domain structure over a wide composition range. Its entire pattern across the bulk sample is concatenated and coupled together by the oscillating chirality flux lines. The implication being, the entirety of these flux linkages has to be ruptured for reversal.

Superimposed on such domain structures would be the periodic elastic modulation with alternating regions of tension and compression that cancel out any long-range stresses from developing. In the quenched state, the self-strain and periodicity would not vary spatially across the disc, Figure 10b$'$. As a result, additional nodes of zero-stress would appear parallel to the central bisector, Figure 10b$'$. Horizontally, going from left to right in Figure 10b$'$. these elastic waves would cross the vertical cellular bands at the point of their maximum gradient (stress $\sigma = 0$), and vertically, from top to bottom of the bisector, the elastic waves phase-shifts to cancel out long-range stresses. In other words, the maximum stress gradient, and flux gradient, coincides at the vertical boundaries of cellular chain. Degradation of the domain cellular structure in the slow-cooled sample, Figure 10c, suggest the same for the elastic waves, and the resulting variations in wavelength and/or self-strain of the elastic wave, Figure 10d-d$'$, would be manifested as variation in size and orientation of the magnetic cells, Figure 10c.

Within this GAC model, isotropy of magnetization or IoM also has a consistent and simple explanation. In conventional magnets, linear magnetization curves are observed along the hard axis due to rotation. In these alloys, linear curves along all directions implies a rotation-based mechanism, and additionally, this mechanism is the same regardless of the crystal direction. Domain studies on Fe-Ga based alloys reveal this reversal process involves rotation of the cells.[1] Measured as a function of orientation, it is the relative population of cells along a given direction that changes leading to linear magnetization curves along all crystal directions.

4. Implications for Past Literature and Predictions

A sizeable literature over the past two decades has ignored the existence of gradients, in preference to the convenience of adopting the well-known framework of phenomenological magnetostriction theory for homogeneous crystals. In light of non-equivalence of coefficients for equivalent axes, such literature becomes moot and unreliable for high-fidelity applications due to the uncertainty in the characterization of their samples and data.[31,37–54]

Figure 9. Domain structure of a slow-cooled Fe$_{73.9}$Ga$_{26.1}$ crystal. a) Collage of the domain structure. Schematic in the inset of (a) shows that the domain structure bisects the entire 5 mm diameter crystal into two symmetrical halves along the vertical [010] axis. b) Zoom-in view of a section of the collage. c) High magnification image (from inside the dotted rectangle in (b) reveals change in chirality of Bloch walls across the bisector, and (d) its schematic. e) Gradual, as opposed to digital, change in coercivity in this degraded crystal.
would cause problems even when measuring magnetostriction in conventional magnets with small strains, like Ni or Fe.

The aforesaid literature also seems to have primarily focused on the magnitude of magneto-strain. These past reports simply attach a strain gauge along one of the cubic axes, say, [100] and measured λ_{100}, by rotating the field, the thrust being to report as high values as possible. In this context, an inflated value of magnetostriction, \((3/2)\lambda_{100}\) is frequently reported,^16,31,37,39,42,48,51,52,54 even though \(\lambda_{100} \neq (3/2)\lambda_{100}\) is the intrinsic constant of a homogeneous cubic crystal reported in handbooks, textbooks, and literature.\(^{5,6,9,29,35–39}\)

By illustrating the most basic (but often forgotten) requirement of volume conservation in Joulian magnets, Figure 3b, the fallacy of some questionable recent results suggesting that NJM is not general to all Fe-Ga alloys^60 is revealed. A simple digitization of curves in such literature shows a large volume change for all fields \(\lambda_{100} + \lambda_{110} + \lambda_{001} \neq 0\), but this sum inexplicably changes in a near stepwise manner to zero when saturation is reached.\(^{60}\) The volume conserving condition of JM provides a simple method to identify questionable data or specious claims. As exemplified in Figure 3b, Joule magnetostriction conserves volume for all magnitudes of Joulian strain, and not just at saturation field. It is the same useful volume-conserving condition of JM that provides a “diagnostic tool” for discovering new non-Joulian magnets and phenomena, as well as assessing the fidelity and reliability of data reported in literature.

Finally, the non-equivalence of saturation magnetostriction and volume change for equivalent axes makes a straightforward relation between them versus Ga concentration (or other alloying elements) difficult at present, and extensive studies are suggested in light of these results. In a conventional cubic crystal, the magnitude of saturation magnetostriction, say, \(\lambda_{100}\), can be empirically plotted versus an alloying element; in such a crystal it is implicit that the same relation holds for other equivalent axes, namely, \(\lambda_{110}\) and \(\lambda_{001}\). A Ga-dependence of \(\lambda_{100}\) with multiple peaks and valleys is frequently reported in the literature.\(^{16,38,39,42,47}\) Tellingly, the reported empirical behavior does not fit the equilibrium phase diagram.\(^{15}\) Instead, a metastable phase diagram is often cited to qualitatively explain the observed trends.\(^{15}\) In light of non-equivalent properties, extensive work has to be done to replot the behavior to account for multi-valued axes for these crystals. Hume Rothery first reported the phase diagrams for Fe-Ga, which have subsequently been refined.\(^{61}\) It is likely that the various phases have to be further refined to incorporate the existence of elastic waves. With the advent of new techniques, such as nano-scanning X-ray diffraction microscopy with pico-
level resolution,\textsuperscript{[62]} it should be possible to characterize this structure. As to predictions, the existence of atomic scale gradients suggests the possibility of large magnetoresistance (MR) effects. Indeed, our preliminary results show MR peaking to \(\approx 3\%\) at cryogenic temperatures in Fe-Ge.

Typically, Arrott plots are used to determine Curie temperature of magnets.\textsuperscript{[63]} When the sample is cooled across the Curie temperature, the curvature of magnetization curves changes from positive to negative, the linear curve at the crossover being at the Curie transition temperature. The magnetization curves of these samples are linear from cryogenic to room temperature.\textsuperscript{[1]} On heating these alloys, if the elastic gradients persist beyond the Curie temperature, one may observe a situation where the curves remain linear at all temperatures, below and above Curie point. On the other hand, if the gradients gradually dissipate on heating, one would observe transition from NJM to JM, and result in a conventional set of Arrott curves. In this context, it would also be of interest to identify new alloy systems with relatively low Curie transition to test these hypotheses.

5. Conclusions

The unique non-Joulian properties defines a new class of functional magnets and magnetism.

Non-Joulian properties include volume change in magnetic fields and its strong orientation dependence; isotropic magnetization; and a digital coercivity landscape.

Volume change is intrinsic to iron-based alloys, occuring in phases across a wide composition range, in quenched, metastable, and slow-cooled crystals. Volume change in slow-cooled crystals shows that the effect cannot be erased by stress-annealing.

Non-equivalent magneto-elastic response exists for equivalent crystal axes. A mechanistic model based on magneto-elastic waves explains the non-Joulian behavior.

Due to the non-equivalent magneto-elastic response for equivalent crystal axes and/or field induced volume change, a sizeable literature over the past two decades is rendered questionable, and unreliable for high-fidelity critical applications since it has characterized these crystals using volume-conserving magnetostriction theory, and moreover, inflated (1.5-times) the intrinsic magnetoelastic constants.\textsuperscript{[31,37–54]}

The most fundamental but often forgotten condition of Joule magnetostriction is zero-volume change at all fields, regardless of the magnitude of strain (not just at saturation). Ironically, this unyielding condition of JM becomes a “diagnostic tool” to identify recent specious data claiming zero volume change in these alloys;\textsuperscript{[60]} indeed, digitization of this group’s magnetostriction curves reveals a large volume change below saturation, following which, the sample inexplicably “jumps” back to strain values that somehow roughly adds close to zero.

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Conflict of Interest

The authors declare no conflict of interest. H.D.C. has a pending patent application (May 2015) on non-Joulian materials, whose assignee is the author’s academic institution, Temple University.

Keywords

functional materials, gradient elasticity, Joule magnetostriction, magneto-elasticity, non-Joulian magnetostriction

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[1] H. D. Chopra, M. Wuttig, Nature 2015, 521, 340.
[2] H. D. Chopra, M. Wuttig, Nature 2016, 538, 416.
[3] H. D. Chopra, M. Wuttig, in Proc. of the MSE Conference, Symposium A03, Darmstadt, Germany, September 2014.
[4] J. P. Joule, Philos. Mag. 1847, 76-87, 225.
[5] C. Kittel, Rev. Mod. Phys. 1949, 21, 541.
[6] J. H. van Vleck, Phys. Rev. 1937, 52, 1178.
[7] F. Bloch, G. Gentile, Z. Phys. A: Hadrons Nucl. 1931, 70, 395.
[8] E. W. Lee, Rep. Prog. Phys. 1955, 18, 184.
[9] S. Chikazumi, S. H. Charap, Physics of Magnetism, Wiley, New York, NY, USA 1964.
[10] M. Sullivan, Rev. Sci. Instrum. 1980, 51, 382.
[11] T. M. Saurav, M. L. Forst, J. A. Boligitz, H. D. Chopra, Phys. Rev. B 2017, 95, 174425.
[12] H. D. Chopra, C. Ji, V. V. Kokorin, Phys. Rev. B 2000, 61, R14913.
[13] M. R. Sullivan, H. D. Chopra, Phys. Rev. B 2004, 70, 094427.
[14] H. D. Chopra, M. R. Sullivan, A. Ludwig, E. Quandt, Phys. Rev. B 2005, 72, 054415.
[15] Q. Xing, Y. Du, R. J. McQueeney, T. A. Lograsso, Acta Mater. 2008, 56, 4536.
[16] T. A. Lograsso, E. M. Summers, Mater. Sci. Eng. A 2006, 416, 240.
[17] W. Yang, R. U. Chandrasena, M. L. Forst, J. A. Boligitz, A. Arab, M. V. Holt, A. Scholl, E. Arenholz, H. Ebert, J. Minár, T. A. Lograsso, A. X. Gray, 2017 (private communication).
[18] R. Chandrasena, W. Yang, A. Scholl, J. Minár, P. Shafer, E. Arenholz, H. Ebert, A. X. Gray, H. D. Chopra, in 13th Joint MMM/Intermag Conference, San Diego, CA, January 2016.
[19] A. X. Gray, R. Chandrasena, H. D. Chopra, in 63rd Annual AVS International Symposium and Exhibition, Nashville, TN, November 2016.
[20] H. D. Chopra, C. Bailly, M. Wuttig, Acta Mater. 1996, 44, 747.
[21] G. Gruner, Rev. Mod. Phys. 1988, 60, 1129.
[22] A. Blachowski, K. Ruebenbauer, J. Zukrowski, J. Przewoznik, J. Phys. A: Math. Gen. 2001, 34, 527.
[23] L. E. Tanner, A. R. Pelton, R. Gronsky, J. Phys. Condens. Matter 2000, 12, 539.
[24] V. Kiryukhin, B. Keimer, Phys. Rev. B 1995, 52, R704.
[25] S. Kaufmann, U. K. Röbler, O. Heczko, M. Wuttig, J. Buschbeck, L. Schultz, S. Fähler, Phys. Rev. Lett. 2010, 104, 145702.
[26] G. Gruner, Density Waves in Solids, Perseus Publishing, Cambridge, MA, USA 2000.
[27] J. J. Nye, Physical Properties of Crystals – Their Representation by Tensors and Matrices, Clarendon Press, Oxford, UK 1957.
