Proposal for methods to measure the octupole susceptibility in certain cubic Pr compounds

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Direct means of measuring the susceptibility toward an octupole order parameter are proposed via a sixth-rank tensor property. Equivalent derivatives of more conventionally measured tensor properties, including elastic stiffness, magnetic susceptibility, and elastoresistivity, are written in full, as constrained by the symmetry of the experimentally motivated O_h point group. For simplicity, we consider the specific case of Pr^{3+} ions in a cubic point symmetry with a Γ_3 crystal-field ground state, but the ideas are somewhat general. The experimental feasibility of measuring these various derivatives of tensor quantities is discussed.

I. INTRODUCTION

Quantum states of localized electrons can have a variety of well-defined electromagnetic multipole moments; indeed, within higher angular-momentum states, particularly those that often arise from f-orbitals, higher-order multipolar moments frequently have some nonzero expectation value in the presence of simple magnetic (dipole) order. Of course, multipolar moments are subject to higher-order interactions among themselves, and they can thus order independently of any dipole moment, but this is uncommon: the dipole typically dominates in energy scale whenever a variety of multipoles are present or allowed. This motivates the use of the associated multipole susceptibility as a powerful tool for analyzing these higher-order multipoles, as the strength and character of specific multipolar interactions can be probed without requiring a simple ordered state of such a multipole. For higher-rank multipoles, however, it is a nontrivial task to relate the multipole susceptibility to physically measurable quantities.

It is well established that a ($q = 0$) magnetic susceptibility may be measured via an applied uniform magnetic field. Specifically, a magnetic field couples bilinearly to the magnetization (magnetic dipole moments per unit volume), and hence it is an appropriate conjugate field. Similarly, antisymmetric strain couples bilinearly to electric quadrupoles, providing access to the quadrupole strain susceptibility [1]. Here, we focus on the magnetic octupole, the next in the multipole series [2].

Magnetic octupole order has been proposed for many f-orbital systems, but it is often hard to verify or probe directly [3–5]. Given the time-reversal symmetry breaking inherent in a magnetic moment (of any rank), a bilinear coupling of an octupole to strain, like that of the electric quadrupole, is not possible; similarly, a magnetic field will couple bilinearly only to the magnetic dipole moments, with symmetry forbidding a bilinear octupole coupling. As shown in the work of Patri *et al.* [6], however, the combination of the two provides a conjugate field which, by symmetry, can couple directly to the octupole, allowing one to define and measure a susceptibility. This susceptibility most naturally manifests itself in a sixth-rank tensor, in contrast to the second-rank (magnetic susceptibility) tensor for dipoles and the various fourth-rank tensor components representative of quadrupole susceptibilities; the octupole susceptibility can thus be measured independently of the behavior of the lower-order multipoles in the system, at least under certain restrictions.

Measurement of an octupole susceptibility is then possible whenever the specifics of the system render it finite, but it may be quite difficult if lower-order multipoles are present. In particular, lower-order terms in a material's tensor properties invoking the strain or magnetic field individually could potentially drown out any higher-order effects associated with the octupolar degrees of freedom. Thus, the use of Neumann's principle [7] to significantly constrain the symmetry-allowed tensor terms is motivated, as terms can potentially be identified that have fewer lower-order components or other possible experimental impediments.

Furthermore, we choose to restrict our focus to intermetallic compounds with Pr^{3+} ions in a cubic point symmetry, and for which the crystalline electric field ground state is a Γ_3 doublet. The specific symmetries of this system forbid all magnetic dipoles and three of the five electric quadrupoles, allowing the octupole's conjugate field to be applied without inducing any lower-order multipoles. This system has been theoretically shown to allow and potentially favor an octupole order parameter [6], and it has been experimentally shown to order in a manner suggestive of an octupole order parameter [6,8]. Further compounds with the same crystalline electric field ground state have various exotic behaviors [9,10]; these may not have explicit octupole phases, but they may have relevant octupolar fluctuations that could be probed via a susceptibility. A measurement of the octupole susceptibility is then of interest and almost certainly feasible for a variety of compounds with this Γ_3 doublet ground state.

TABLE I. Effects of various mirror planes (σ) and rotations (C) contained in O_h on a generic second-rank tensor.

Symmetry	Effect(s)	Implied equality
σ_i	$i \rightarrow -i$	$F_{ij} = -F_{ij}(=0)$
$\sigma_{i=\pm j}$	$i \rightarrow \mp j \rightarrow i$	$F_{ij} = F_{ji}$
C_{4k}	$i \rightarrow j \rightarrow -i$	$F_{ij} = -F_{ji}$
$C_{3(111)}$	$i \rightarrow j \rightarrow k \rightarrow i$	$F_{ij} = F_{jk}$

Thus, herein we propose and elucidate the measurement of various tensor components to identify the associated susceptibility of a given octupole, separating it from the susceptibilities of other multipoles and probing interaction strengths of the octupole directly.

II. BACKGROUND

A. Introduction to the O_h point group

While any cubic point group can give rise to a Γ_3 doublet ground state, the most prominent experimentally realized case for an octupole order parameter has an O_h point group [8,11]. The O_h point group, being the most highly symmetric cubic point group, contains 48 symmetry elements, many of which are redundant in constraining the various tensor properties (see Appendix A for a full list of symmetries via a character table). A convenient, less redundant basis to work in is then shown in Table I, where σ_i represents a mirror plane defined by the i axis, C_{xi} represents an x-fold rotation about the i axis, and F_{ij} represents some generic second-rank material property tensor.

These symmetry elements of the point group place constraints on tensor properties of the material via Neumann's principle: the tensor properties must be invariant under the symmetry operations of the point group. In the absence of perturbative fields, these are calculated trivially by applying the symmetries to a given tensor element and observing how they affect the various indices; for example, under $C_{3(111)}$ rotation, $x \rightarrow y$, so

$$F_{xx} = C_{3(111)}F_{xx} = F_{yy},$$
$$F_{xx} = F_{yy}. \tag{1}$$

Additional examples are shown in Table I. The presence of additional perturbative fields, such as a magnetic field in the elastic tensors or elastic strains in the magnetic susceptibility, breaks the symmetries of the material and allows otherwise forbidden terms. This can be accounted for by simply incorporating the symmetry transformations of the perturbative fields [12]. The symmetries of the strain tensor and magnetic field are then relevant to all other tensors, and worth some brief discussion. The strain tensor is defined in a manifestly symmetric manner,

$$\epsilon_{ij} \equiv \frac{\partial \mu_i}{\partial x_j} + \frac{\partial \mu_j}{\partial x_i}, \tag{2}$$

where μ_i represents the displacement of an atom along the i axis from the unstrained position x_i. The inherent symmetry of the strain tensor then requires $\epsilon_{ij} = \epsilon_{ji}$, but otherwise elements of the strain tensor will transform similarly to any other

tensor, via applications of the symmetry operations to their indices [13]. Magnetic field, on the other hand, is a pseudovector, invariant under inversion; thus, it transforms as expected under the various rotations, but under mirror planes, which can be considered as a combined rotation and inversion, it effectively experiences only the rotation. Hence, $\sigma_x(H_x, H_y, H_z)$ yields $(H_x, -H_y, -H_z)$, for example, in contrast to an arbitrary normal vector $\sigma_x(A_x, A_y, A_z) = (-A_x, A_y, A_z)$. One can see the effect of these external fields with a brief example: without a magnetic field, for instance, one sees

$$F_{xy} = C_{4z}F_{xy} = -F_{yx},$$
$$F_{xy} = -F_{yx},$$
$$\sigma_{x=y}F_{xy} = \sigma_{x=y}(-F_{yx}) = -F_{xy},$$
$$F_{xy} = -F_{xy} = 0, \tag{3}$$

i.e., χ_{xy} (and, by similar symmetries, all χ_{ij} terms for $i \neq j$) is constrained to be 0. However, introducing a magnetic-field dependency to these terms yields

$$C_{4z}F_{xy}(H_z) = -F_{yx}(H_z),$$
$$\sigma_{x=y}[-F_{yx}(H_z)] = -F_{xy}(-H_z),$$
$$\sigma_{x=y}C_{4z}F_{xy}(H_z) = F_{xy}(H_z) = -F_{xy}(-H_z). \tag{4}$$

Thus, F_{xy} is no longer constrained to be zero, but merely constrained to be odd in H_z, the external field that breaks the symmetry ($\sigma_{x=y}$) that constrained it to be zero. Terms constrained to be equal in the absence of perturbative fields can have dependencies in fields with a slight variation in sign and ordering, but they will maintain identical sets of coefficients; for example, while $F_{xy} = F_{yz}$ without field, $F_{yz}(H_x)$ need not be identical to $F_{xy}(H_x)$, but it must instead be identical to $F_{xy}(H_z)$ (via $C_{3(111)}$), leaving the two terms with identical, if differently ordered, sets of coefficients. Similarly, using the above example, $F_{xy}(H_z) = -F_{yx}(H_z)$, implying F_{xy} and F_{yx} will have the same linear H_z coefficients, but with opposite sign. These symmetry principles will be used in Sec. III to determine allowed terms in several higher rank tensors. Complete descriptions of how these symmetries apply to the various tensors examined in the text can be found in Appendix B.

B. The Γ_3 doublet

While strong spin-orbit coupling among local $4f$ electrons often makes J a good quantum number, the crystalline electric field (CEF) splitting in $4f$ materials can substantially reduce the number of available states within a given J multiplet, at least in a low-temperature regime. One of these CEF eigenstates, the Γ_3 doublet, is generally present in cubic systems, but is rarely the ground state, meaning it cannot often be experimentally isolated. However, calculations have shown that in the special case $J = 4$, associated with the Pr^{3+} ion (with the $4f^2$ orbital) [14], the doublet is a potential ground state [15].

The Pr^{3+} ions in the most prominent octupole case exist on a diamond lattice [11], so the symmetry of the CEF eigenstates is determined by the T_d point group, as this is the local symmetry an individual ion experiences. The Γ_3 doublet, with

basis states (in $J = 4$), is then given by

$$\Gamma_3^{(1)} = \frac{1}{2}\left(\sqrt{\frac{7}{6}}|4\rangle - \sqrt{\frac{5}{3}}|0\rangle + \sqrt{\frac{7}{6}}|-4\rangle\right),$$

$$\Gamma_3^{(2)} = \frac{1}{\sqrt{(2)}}(|2\rangle + |-2\rangle). \qquad (5)$$

As a two-state space, this can be treated as a pseudospin [6], and analogously three operators can potentially split the doublet and create a finite order parameter. Group theory decomposition of the doublet in T_d suggests the symmetry of the allowed operators:

$$\Gamma_3 \otimes \Gamma_3 = \Gamma_3 \oplus \Gamma_2 \oplus \Gamma_1. \qquad (6)$$

Thus, of the three operators that would act as Pauli matrices in this pseudo-half-spin two-state space, two have the symmetry of Γ_3 (E) and one has Γ_2 (A_2) symmetry. One might thus expect one of these operators to break time-reversal symmetry analogously to the Pauli S_y matrix, and indeed the lowest-order multipole of Γ_2 symmetry is then time-reversal odd. Thus, from the angular-momentum operators J_x, J_y, J_z and their various products (the Stevens operators), the allowed order parameters are represented by two time-reversal-even quadrupole operators of Γ_3 symmetry

$$O_2^2 = \frac{\sqrt{3}}{2}(J_x^2 - J_y^2),$$

$$O_2^0 = \frac{1}{2}(2J_z^2 - J_x^2 - J_y^2), \qquad (7)$$

and one time-reversal-odd octupole operator of A_2 symmetry

$$\tau_{xyz} = \frac{\sqrt{15}}{6}\overline{J_x J_y J_z}, \qquad (8)$$

where $\overline{J_x J_y J_z}$ denotes all permutations of the indices x, y, z, i.e., a six-term object. In typical pseudospin fashion, one can note the eigenstates of the three operators in the aforementioned basis: $\Gamma_3^{(1)}$ and $\Gamma_3^{(2)}$ for O_2^0, $\Gamma_3^{(1)} \pm \Gamma_3^{(2)}$ for O_2^2, and $\Gamma_3^{(1)} \pm i\Gamma_3^{(2)}$ for τ_{xyz}. It can then be noted that none of these three operators represents and/or commutes with a magnetic dipole operator. Indeed, in T_d and other cubic point groups, magnetic dipoles belong to a triply degenerate Γ_4 (T_1) irreducible representation, an object that, as seen in the group theory decomposition, one cannot construct from the two Γ_3 (E) basis states. More intuitively, this can be explained by the Γ_3 doublet basis states $\Gamma_3^{(1)}$ and $\Gamma_3^{(2)}$ both having three (primary-axis) C_2 rotational symmetries, which are universally broken by a dipole order parameter. Thus, cubic praseodymium compounds are of particular interest in the study of higher-order multipoles, as they provide the opportunity to directly probe time-reversal-odd octupolar signatures without (magnetic) dipole signatures; dipole moments are forbidden, to the extent that the energy separation between the Γ_3 CEF ground state and any triplet excited states is large relative to the temperature and/or magnetic field.

C. Defining an octupole susceptibility

Given the presence of a potential octupolar moment, the natural question is how best to access it experimentally. As

was noted by Patri *et al.* [6], an octupolar susceptibility can easily be defined for a variety of potential order parameters. Here we choose to focus on a $q = 0$ order parameter, as this presents the most experimentally accessible possibility. It is also, however, of interest for a broader set of potential order parameters; analogously to the magnetic case, finite-q octupole order parameters would likely appear via a sharp feature of some kind in the $q = 0$ octupole susceptibility at or near the relevant ordering temperature.

Based on the symmetry properties of the τ_{xyz} octupole, one can quickly note that a time-reversal-odd conjugate field would be necessary to couple to it. Utilizing two experimentally common external fields, strain and magnetic field, it can couple bilinearly to two objects, $H_x \epsilon_{yz} + H_y \epsilon_{zx} + H_z \epsilon_{xy}$ and $H_x H_y H_z$ [16] (here these are considered uniform, but a finite-q order parameter could be coupled to via similar but staggered fields). Choosing to focus on the former for the moment, one might then expect that application of this field

$$H\epsilon \equiv H_x \epsilon_{yz} + H_y \epsilon_{zx} + H_z \epsilon_{xy} \qquad (9)$$

could induce a finite octupolar moment in an originally unordered state,

$$O \equiv \langle \tau_{xyz} \rangle, \qquad (10)$$

and one could thus define a susceptibility

$$\chi_O \equiv \frac{\partial O}{\partial (H\epsilon)}. \qquad (11)$$

Here it is worth noting that the octupole has thus far been examined in the T_d point group corresponding to the local symmetry of the $4f$ ion, while discussion on material properties has centered on the O_h point group of the specific material (wherein the Pr sites sit on a diamond lattice [11]), which defines the symmetries of the material's tensor properties. Given that the chosen coupling field will only induce a ferro-octupolar order parameter, one can note that, while an individual octupole has Γ_2 symmetry in T_d, a pair of aligned octupoles on the two independent ion sites in the greater O_h unit cell correspond to a Γ_2^+ symmetry [17]. Thus, for O_h and for a susceptibility as has been described, the order parameter and conjugate field can be more specifically defined as being Γ_2^+. More broadly, it can be seen that, given the basis states are invariant under inversion (to within an overall phase), and all three operators are similarly invariant, any ferroaligned Γ_3 order parameter in T_d will couple as Γ_3^+ in the larger O_h unit cell [18] (Γ_3^- objects can couple bilinearly only to nonferro-aligned Γ_3 order parameters, which break the inversion symmetry of the larger O_h cell).

D. Basic Landau theory

With this $H\epsilon$-type conjugate field, a motivational, simplified model can be established by looking purely at a potential octupolar order parameter. This choice of longitudinal field does leave the aforementioned issues: strain, a second-rank tensor, can couple to a quadrupole moment, while a magnetic field can couple to a magnetic dipole, leaving any octupole interactions potentially masked. Here we again take advantage of the Γ_3 doublet: the two Γ_3 quadrupole moments couple bilinearly only to the two Γ_3 strains, $\epsilon_{xx} - \epsilon_{yy}$ and

$2\epsilon_{zz} - \epsilon_{xx} - \epsilon_{yy}$, while the ϵ_{ij} strains present in the octupole conjugate field are of Γ_5^+ type; they can couple to quadrupoles, but only to the Γ_5^+-type quadrupoles, which are, like the aforementioned magnetic dipoles, forbidden to the extent that the CEF gap is large relative to temperature and strain. Thus, no CEF-allowed multipoles will couple with any of the objects within the octupole conjugate field, allowing one to safely write a lowest-order free energy for just the octupole moment without ignoring any cross-coupling terms not already "forbidden" by the CEF splitting:

$$F = \frac{a}{2}O^2 - \lambda(H\epsilon)O + \frac{C_{44}^0}{2}\left(\epsilon_{xy}^2 + \epsilon_{yz}^2 + \epsilon_{zx}^2\right), \quad (12)$$

where a is then assumed to be of the standard form $a_0(T - \theta)$, so as to allow for a continuous octupole phase transition, and C_{44}^0 is the unrenormalized elastic stiffness.

Assuming the case of a controlled conjugate field [19], one can then note that minimizing free energy requires a finite order parameter,

$$O = \frac{\lambda H\epsilon}{a}, \quad (13)$$

thus allowing one to solve for the octupole susceptibility

$$\chi_O \equiv \left.\frac{dO}{d(H\epsilon)}\right|_{H\epsilon=0} = \frac{\lambda}{a_0(T - \theta)}. \quad (14)$$

Presuming a temperature-independent coupling of the moment and the field λ, the octupole susceptibility may then follow a simple Curie-Weiss functional form, particularly in systems with a tendency toward an explicit octupole ordering. More generally (i.e., beyond just Γ_3 doublet cases), this can be taken as the primary proof-of-existence of a measurable octupole susceptibility: more complicated temperature dependencies will naturally arise from higher-order terms, but they can do so both in systems with and without an independent octupole, given other allowed terms invoking other (biquadratic) multipole couplings. Any free-energy term of the form $H^2\epsilon^2$ (after minimization with respect to the various order parameters) must either invoke the octupole or a product of order parameters (a biquadratic dipole-quadrupole coupling, for instance), and thus will have a more complicated lowest-order temperature dependence, except for coincidental cancellations. The Γ_3 case is, of course, already simplified by the necessary components of such a composite term, the three magnetic dipoles and the $xy/yz/zx$ quadrupoles, requiring excited CEF states. A simple $1/(T - \theta)$ dependence in the relevant free-energy term is then a reliable indicator of an independent octupolar order parameter, or one with a tendency to order in the absence of competing phases.

One can then note that the octupole susceptibility, to within some proportionality constant, can be extracted by taking appropriate derivatives of the free energy:

$$\left.\frac{\partial^2 F}{\partial(H\epsilon)^2}\right|_{H\epsilon \to 0} = -\frac{\lambda^2}{a}. \quad (15)$$

This presents the octupolar susceptibility as being proportional to a term in a sixth-rank magnetoelastic tensor. Of course, simpler and similar quantities also present themselves; one can quickly note that a similar quantity (off by a factor of 2) could be found by taking the derivatives separately, and that $\frac{\partial^2 F}{\partial\epsilon^2}$ corresponds to the elastic stiffness tensor, while $\frac{\partial^2 F}{\partial H^2}$ corresponds to a magnetic susceptibility. We therefore propose measuring the relevant sixth-rank tensor term, and thus the ($q = 0$) octupole susceptibility, via field and/or strain derivatives of more commonly measured tensor quantities; in doing so, the more complicated sixth-rank tensor term can be accessed by well-established and understood experimental methods designed for various second- and fourth-rank tensor quantities.

III. THERMODYNAMIC TENSORS

Thermodynamic quantities, i.e., quantities explicitly representative of derivatives of the free energy, are the most direct potential measurements to capture the octupolar susceptibility. Thus, the most obvious tensor quantities involving strain and magnetic field, elastic stiffness, and magnetic susceptibility are herein enumerated.

It should be noted that all tensors herein are general for the O_h point group; while a given term within a tensor may be of specific interest for the octupole here, the allowed and disallowed terms, and their equalities, are a function solely of the point group (and the definitions of the tensors), and not the details of any given system. The symmetric constraints which allow and/or disallow various terms are detailed in Appendix B. Additionally, it should be noted that none of the coefficients are implied to be equal across tensors, with the exception of a handful of identically labeled coefficients between the elastic stiffness and (strain-dependent) magnetic susceptibility tensors.

A. Elastic stiffness tensor

The elastic stiffness tensor, defined by $C_{ij,kl} \equiv \frac{\partial^2 F}{\partial\epsilon_{ij}\partial\epsilon_{kl}}$, represents the stress (i.e., force) necessary to produce a given set of strains in a material. It inherits several symmetries from its definition and that of the strain tensor, $\epsilon_{ij} \equiv \frac{\partial\mu_i}{\partial x_j} + \frac{\partial\mu_j}{\partial x_i}$. Namely, the definition of the strain tensor requires that ϵ_{ij}, and thus $C_{ij,kl}$, is invariant under exchange of i and j (or k and l), while the definition of $C_{ij,kl}$ requires it to be invariant under exchange of ij and kl. These taken together motivate the use of compactified Voigt notation rather than a full 9×9 matrix, as many terms are exactly identical to their neighbors in such a full construct (e.g., $C_{xy,xy} = C_{xy,yx} = C_{yx,xy} = C_{yx,yx}$).

Taking two field derivatives then reconstructs the desired $\chi_O \equiv \frac{\partial O}{\partial(H\epsilon)} \propto \frac{\partial^2 F}{\partial(H\epsilon)^2}$, and thus the field dependence of the tensor is the primary point of interest. The aforementioned inherent symmetries combined with those of the point group leave three independent nonzero terms in the absence of a magnetic field, with arbitrary magnetic fields breaking the point-group symmetries and allowing 10 additional independent coefficients (to second order in field), as can be seen in Table II. The A_5 (yellow, diagonal boxes) and D_3 (blue, off-diagonal boxes) coefficients would then represent the desired direct probe of octupolar

TABLE II. The full elastic stiffness tensor in O_h, in compactified Voigt notation and to second order in magnetic field, color-coded to indicate which terms are identical.

	xx	yy	zz	yz	zx	xy
xx	$C_{11}^{(0)} + A_1 H_x^2 + A_2(H_y^2 + H_z^2)$	$C_{12}^{(0)} + A_4 H_z^2 + A_3(H_x^2 + H_y^2)$	$C_{12}^{(0)} + A_4 H_y^2 + A_3(H_x^2 + H_z^2)$	$+D_1 H_y H_z$	$B_1 H_y + D_2 H_z H_x$	$-B_1 H_z + D_2 H_x H_y$
yy	$C_{12}^{(0)} + A_4 H_z^2 + A_3(H_y^2 + H_x^2)$	$C_{11}^{(0)} + A_1 H_y^2 + A_2(H_z^2 + H_x^2)$	$C_{12}^{(0)} + A_4 H_x^2 + A_3(H_y^2 + H_z^2)$	$-B_1 H_x + D_2 H_y H_z$	$+D_1 H_z H_x$	$B_1 H_z + D_2 H_x H_y$
zz	$C_{12}^{(0)} + A_4 H_y^2 + A_3(H_z^2 + H_x^2)$	$C_{12}^{(0)} + A_4 H_x^2 + A_3(H_z^2 + H_y^2)$	$C_{11}^{(0)} + A_1 H_z^2 + A_2(H_x^2 + H_y^2)$	$B_1 H_x + D_2 H_y H_z$	$-B_1 H_y + D_2 H_z H_x$	$+D_1 H_x H_y$
yz	$+D_1 H_y H_z$	$-B_1 H_x + D_2 H_y H_z$	$B_1 H_x + D_2 H_y H_z$	$C_{44}^{(0)} + A_5 H_x^2 + A_6(H_y^2 + H_z^2)$	$+D_3 H_x H_y$	$+D_3 H_z H_x$
zx	$B_1 H_y + D_2 H_z H_x$	$+D_1 H_z H_x$	$-B_1 H_y + D_2 H_z H_x$	$+D_3 H_x H_y$	$C_{44}^{(0)} + A_5 H_y^2 + A_6(H_z^2 + H_x^2)$	$+D_3 H_y H_z$
xy	$-B_1 H_z + D_2 H_x H_y$	$B_1 H_z + D_2 H_x H_y$	$+D_1 H_x H_y$	$+D_3 H_z H_x$	$+D_3 H_y H_z$	$C_{44}^{(0)} + A_5 H_z^2 + A_6(H_x^2 + H_y^2)$

susceptibility:

$$A_5 = \frac{\partial^2 F}{\partial^2 (H_i \epsilon_{jk})} \propto \chi_O, \qquad (16)$$

$$D_3 = \frac{\partial^2 F}{\partial(H_i \epsilon_{jk})\partial(H_j \epsilon_{ki})} \propto \chi_O. \qquad (17)$$

Practical considerations

A number of considerations present themselves in potential measurements of the relevant coefficients. First, it should be noted that while A_5 is unconstrained in its sign by symmetry, the octupole contribution to A_5 would necessarily be negative, or correspond to a softening of the lattice:

$$F = -\frac{\lambda^2 (H\epsilon)^2}{2a} + \frac{C_{44}^0}{2}\left(\epsilon_{xy}^2 + \epsilon_{yz}^2 + \epsilon_{zx}^2\right),$$

$$C_{44} = \frac{\partial^2 F}{\partial \epsilon_{ij}^2} = C_{44}^0 - \frac{\lambda^2 H_k^2}{a}. \qquad (18)$$

In short, a finite field allows a finite octupole moment, and thus a finite shear strain, to reduce the free energy, reducing the energy cost associated with strain via the C_{44}^0 term and thus making the lattice more susceptible to said strain, or softer.

As far as conducting the measurement, a [111]-oriented field could be used to measure a combination of A_5 and D_3 via intermixing the nine terms in the lower-right quadrant. The A_6 coefficient would be induced, but is likely small, as it corresponds to the lowest-order interaction of CEF-forbidden octupoles, or a higher-order interaction invoking CEF-forbidden quadrupoles and dipoles. Alternatively, a [001] aligned magnetic field could be used for measuring a specific elastic constant for the orthogonal shear plane. This, however, would break the degeneracy typical of these three coefficients, inducing the A_5 term within only one (C_{xyxy} for H_z), meaning the measurement may need to distinguish a newly differentiated C_{ijij} from the still-equal C_{jkjk} and C_{ikik}.

Generally, associated changes in sound velocities/resonant frequencies would likely invoke nearly all C and D coefficients from Table II. However, assuming a [111]-oriented magnetic field, all (field-dependent) contributions associated with the allowed Γ_3 quadrupoles would cancel (the allowed couplings to field would be to $H_x^2 - H_y^2$ and $2H_z^2 - H_x^2 - H_y^2$). Thus, the remaining coefficients would correspond to CEF-forbidden multipoles, and would likely be small. In contrast, a field aligned along a single principal axis would have a symmetry-allowed coupling to an allowed quadrupole, though the coupling of this quadrupole and the field to shear strains specifically would be higher order and not likely to be significant. Field-independent effects from the Γ_3 quadrupoles would naturally remain, which would manifest via $C_{11} - C_{12}$, or $C_{11}^{(0)} - C_{12}^{(0)}$ using coefficients from Table II.

Lastly, it should be noted that the B_1 coefficients are constrained to be time-reversal odd/imaginary, and thus linear contaminants would likely be either absent or out-of-phase (and thus easily filtered).

B. Magnetic susceptibility tensor

Magnetic susceptibility, herein defined (in slight contrast to convention, and for para-/diamagnetic states) via

$$\chi_{ij} \equiv \frac{\partial^2 F}{\partial H_i \partial H_j}\bigg|_{H \to 0} \propto -\frac{\partial M_i}{\partial H_j} = -\frac{\partial M_j}{\partial H_i}, \qquad (19)$$

is a frequently measured quantity, characterizing the linear response of induced magnetic moment to external magnetic field. While the octupole would not produce the simple dipole response typically dominant in susceptibility, the dependence of magnetic susceptibility (quadratically) on strain would give an effective $H\epsilon$ conjugate field and recover $\chi_O \equiv \frac{\partial O}{\partial (H\epsilon)} \propto \frac{\partial^2 F}{\partial (H\epsilon)^2}$, similarly to the aforementioned tensors.

For O_h symmetry, there is a single independent (nonzero) term in the susceptibility tensor in the absence of strain, χ_{ii}^0. Externally induced strains introduce 12 additional independent coefficients (to second order in strain). Thus, for $i \neq j$,

$$\chi_{ii} = \chi_{ii}^{(0)} + E\epsilon_{ii} + F(\epsilon_{jj} + \epsilon_{kk}) + A_1 \epsilon_{ii}^2$$
$$+ A_2\left(\epsilon_{jj}^2 + \epsilon_{kk}^2\right) + A_3 \epsilon_{ii}(\epsilon_{jj} + \epsilon_{kk})$$
$$+ A_4 \epsilon_{jj}\epsilon_{kk} + A_6\left(\epsilon_{ij}^2 + \epsilon_{ik}^2\right) + A_5 \epsilon_{jk}^2, \qquad (20)$$

$$\chi_{ij} = G\epsilon_{ij} + D_3 \epsilon_{ik}\epsilon_{jk} + D_1 \epsilon_{ij}\epsilon_{kk} + D_2 \epsilon_{ij}(\epsilon_{ii} + \epsilon_{jj}), \qquad (21)$$

where A_5 and D_3 again represent the desired coefficients proportional to the octupole susceptibility, $\frac{\partial^2 F}{\partial (H_i \epsilon_{jk})^2}$ and $\frac{\partial^2 F}{\partial (H_i \epsilon_{jk}) \partial (H_j \epsilon_{ik})}$, respectively. As implied by the labeling, many coefficients here are constrained by the definition of the tensors (as derivatives of free energy) to be identical to counterparts in the elastic stiffness tensor.

Practical considerations

Two experimental configurations are suggested. First, to recover the A_5 coefficient, susceptibility could be measured along any principal axis, while a shear strain is applied in a plane perpendicular to said axis. The likely application of a net compressive or tensile strain, as opposed to pure shear strain, would induce several other coefficients. The E and F coefficients, in particular, would correspond to allowed bilinear couplings of the Γ_3 quadrupoles, but they are easily experimentally distinguished by their representing linear strain dependencies (as opposed to quadratic). The rest are unlikely to be large, given that they do not represent the lowest-order allowed coupling to either allowed quadrupole.

Alternatively, the D_3 coefficient could potentially be measured by applying two simultaneous shear strains, and measuring the transverse susceptibility using the two axes perpendicular to said shear strains. In practice, a simpler method would be to use a [111]-aligned magnetic field and a [111] uniaxial stress, inducing all three shear strains simultaneously to measure a combination of A_5 and D_3. Unfortunately, this would likely induce all the coefficients simultaneously, but again they would likely be small compared to A_5 and D_3 given their connection to no multipoles and/or CEF-forbidden multipoles (excepting potentially E and F, which would again distinguish themselves from the terms of interest by their linearity in strain).

Many common measurements for magnetic susceptibility involve centering a sample in a detection solenoid and varying field (ac), or setting a field and moving a sample through a detection solenoid (dc), to measure its moment via the response in said solenoid. In either case, unexpected sample movement relative to the detector would generate a spurious signal. Thus, the use of dc strains is motivated, as effects of ac strains would be very difficult to decouple from the effects of sample movements (relative to a detector) that most strain-applying techniques are likely to produce. Unfortunately, this means the susceptibility would have to be measured as a function of strain, with the zero-strain term presenting itself as a constant background; measuring only the strain-dependent term, rather than its sum with the zero-strain susceptibility, would require ac strains. However, with the Γ_3 doublet being nonmagnetic, the strain-independent term should be both generally small and not strongly enhanced by low temperatures, potentially allowing easily realized strains to drive the octupolar contribution to dominance over any background. An experimental apparatus capable of measuring magnetic moments while compensating for the effects of sample movement, via careful strain application or a detector with significant positional tolerance (perhaps an optical probe or a detector mounted on the strain cell, for instance), may then further apply ac strain and ac magnetic field; an octupole susceptibility could then be isolated from much of the background by measuring the component of the magnetic moment varying with the sum or difference frequency of the strain and magnetic field frequencies.

Lastly, it should be noted that controlling strain would be a potential difficulty, as a measurable octupole susceptibility would lead to a softening of the shear mode with field. Thus, application of constant stress would lead to increasing strain with increasing field. Careful and direct measurement of strain, or the use of a fairly small ac magnetic field for susceptibility measurements, could help mitigate this softening.

C. Nonlinear magnetic susceptibility

While not the primary focus of this paper, the aforementioned $H\epsilon$ product is not the unique lowest-order object the octupole can couple to within the limits of strain and magnetic field; an object of identical symmetry can be constructed simply with a cubic magnetic field term, $H_x H_y H_z$ [20]. Thus, higher-order magnetization effects can often capture the same information as strain dependencies. Using the same susceptibility definition (albeit without the $H \to 0$ limit), but expanding in magnetic field rather than in strain, five new independent terms to fourth order are introduced for $i \neq j$,

$$\chi_{ii}^{(0)} + AH_i^2 + B\left(H_j^2 + H_k^2\right) + CH_i^4 + D\left(H_j^4 + H_k^4\right)$$
$$+ 6DH_i^2\left(H_j^2 + H_k^2\right) + EH_j^2 H_k^2, \tag{22}$$

$$\chi_{ij} = 2BH_i H_j + 2EH_i H_j H_k^2 + 4DH_i H_j \left(H_i^2 + H_j^2\right), \tag{23}$$

where the E coefficient represents the desired $\frac{\partial^2 F}{\partial (H_x H_y H_z)^2}$. None of these coefficients are implied by symmetry to be identical to any from the previous tensors.

Practical considerations

Experimentally, the obvious complication is that the high fields potentially necessary to accurately fit a quartic or higher function could render the higher CEF states relevant to the result. Magnetic energy would become comparable to the gap for fields of $\sim$15–30 T depending on the material (likely $\sim$0.42 T/K for a given CEF gap, which is in the 40–60 K range [8]).

Two methods present themselves: a simple magnetization-versus-field measurement for a [111]-aligned field and thus [111]-aligned magnetization, and a simple [100] susceptibility measurement with a secondary transverse field along an [011]-type axis. In the [111] case, magnetization would be expected to be $\propto H^5$, or $\frac{dM}{dH} \propto H^4$. Thus, magnetization would have to be sensitively plotted against a fairly wide field range, with a background from the simple dipolar susceptibility being present (but again, likely small for appropriately low field strengths and temperatures, given the CEF splitting). Alternatively, this method would also potentially lend itself to an ac measurement scheme; an ac magnetic field could be applied, and the magnetization measured at the fifth harmonic, potentially providing a dramatic improvement in signal-to-background ratio for the octupolar signal.

The alternative [100] case may represent a simpler measurement with a more complicated apparatus. If a strong field

could be applied along the [011] axis, a traditional magnetic susceptibility measurement could then be performed along the [100] axis, with the results plotted against H_{011} and fit to a quartic function. Using an ac technique for the [100] susceptibility measurement would eliminate much of the contamination from field misalignment, though background susceptibility from nonoctupolar sources would remain a potential issue; in particular, a quadratic dependence on field could potentially arise from a coupling to the O_2^2 quadrupole, forbidden with the previous alignment scheme but potentially induced here.

IV. RESISTIVITY

Resistivity is not a thermodynamic quantity, but terms in the resistivity tensor can nevertheless contain information about the onset of order parameters. Appropriate derivatives of resistivity tensor elements can then sometimes capture information similar to that in derivatives of the free energy, i.e., thermodynamic probes [12]. In particular, perturbations that break symmetries of the crystallographic point group can induce changes in resistivity tensor terms, should the perturbation(s) or some product thereof belong to the same irreducible representation as a given resistivity tensor term. Should the applied perturbation also then match the irreducible representation of the order parameter, a term in the change in resistivity will then be linearly proportional to the order parameter, allowing the change in the resistivity to reflect the associated susceptibility to within some proportionality constant.

Thus, higher rank tensors describing derivatives of resistivity often contain information regarding susceptibility toward symmetry-breaking instabilities, to within some coupling constant. This constant can potentially depend on temperature, or allow certain order parameters to more strongly influence resistivity than others. These complications are generally not insurmountable in extracting the dependence of the underlying order parameter on strain/field. This, combined with the fact that resistivity is, generally, more easily accessed experimentally than many thermodynamic quantities, particularly when trying to measure in a symmetry-selective way, motivates a thorough evaluation.

In the specific context of the τ_{xyz} octupole allowed in the Γ_3 doublet, the cyclic permutations of $H_z \epsilon_{xy}$ can couple bilinearly to the octupole, but both of these objects are of Γ_2^+ symmetry in O_h, a symmetry that cannot be constructed purely via elements of the resistivity tensor (Γ_2^+ has no quadratic basis functions in O_h). However, expanding a Γ_5-type term in the resistivity tensor ρ_{xy}, one can note that two objects already present, H_z and τ_{xyz}, together form an object of appropriate Γ_5 symmetry. The symmetry-allowed dependency is therefore

$$\Delta\rho_{xy}(H_z, \epsilon_{xy}) \propto H_z \tau_{xyz},$$
$$\Delta\rho_{xy}(H_z, \epsilon_{xy}) \propto H_z^2 \epsilon_{xy} \chi_O, \quad (24)$$

and thus the object of relevance is a first derivative with respect to strain and a second derivative with respect to magnetic field of a resistivity tensor term, i.e., a term in a sixth-rank tensor. This object is most easily approached by considering either the second field derivative of the fourth-rank elastoresistivity tensor, or the first strain derivative of the fourth-rank

second-order magnetoresistance tensor. We focus here primarily on the former.

A. Elastoresistivity tensor

Elastoresistivity is defined via [12]

$$m_{ij,kl} \equiv \frac{\partial\left(\frac{\Delta\rho}{\rho}\right)_{ij}}{\partial\epsilon_{kl}}. \quad (25)$$

Herein the normalized resistivity tensor is defined in a manifestly symmetric manner for convenience, $(\frac{\Delta\rho}{\rho}) = \rho^{-1/2}(\Delta\rho)\rho^{-1/2}$ [12], enabling the use of the symmetry $(\frac{\Delta\rho}{\rho})_{ij}(H) = (\frac{\Delta\rho}{\rho})_{ji}(-H)$. Thus, the overall tensor is similar, but not identical to, the elastic stiffness tensor; for example, it is not symmetric under exchange of ij and kl, and purely dynamic contaminants such as the simple Hall effect appear in several terms. The full tensor is shown in Table III, to second order in magnetic field; there are only three allowed unique field-independent terms, with an additional 15 being induced by applied field. The use of compactified Voigt notation is motivated by this high level of symmetry; excluded terms have identical coefficients to those included in the table, but they may have some sign differences, which can be calculated trivially via the symmetries of ρ_{ij} (switching coefficients adds a sign change to each H term) and ϵ_{ij} (switching coefficients changes nothing); e.g., via the symmetry of ρ_{ij}, m_{zyyy} would be $-B_2 H_x + D_2 H_y H_z$, in slight contrast to $m_{yzyy} = +B_2 H_x + D_2 H_y H_z$. The A_6 (yellow boxes) and D_5 (blue boxes) coefficients then represent the desired susceptibility:

$$A_6 = \frac{\partial^2 m_{ij,ij}}{\partial H_k^2} \propto \chi_O, \quad (26)$$

$$D_5 = \frac{\partial^2 m_{ij,jk}}{\partial H_k \partial H_i} \propto \chi_O. \quad (27)$$

It should be further noted that similar notation to previous tensors was chosen for convenience, but that none of these coefficients are constrained by symmetry to have any relationship with those in any of the thermodynamic tensors.

Practical considerations

The tensor presents several obvious experimental opportunities and challenges. First, inspection of the yellow boxes in Table III makes it clear that the m_{xyxy} elastoresistivity coefficient is even in H_z, and hence that measurement of the A_6 coefficient is possible without a linear-in-field contaminant, meaning that it could potentially be extracted as the sole fit parameter of elastoresistivity versus field data. This, in turn, would mean that the coefficient could potentially be extracted with a fairly limited field range, limiting issues arising from high fields (i.e., non-negligible mixing of CEF states).

Most experimental methods of probing elastoresistivity, however, do not apply pure shear strains, but they also induce normal strains ϵ_{xx}, ϵ_{yy}, and ϵ_{zz}. The associated symmetry-preserving strain component couples directly to a simple Hall effect via changing the carrier density; with small strains, charge carrier count would remain constant against an increasing/decreasing volume. Thus, even without a linear-in-field term in the desired m_{ijij} elastoresistivity term, a

TABLE III. The full elastoresistivity tensor in O_h in compactified Voigt notation, color-coded to indicate which terms have identical or differing coefficients.

	xx	yy	zz	yz	zx	xy
xx	$m_{11}^{(0)} + A_1 H_x^2 + A_2(H_y^2 + H_z^2)$	$m_{12}^{(0)} + A_3 H_z^2 + A_4 H_x^2 + A_5 H_y^2$	$m_{12}^{(0)} + A_3 H_y^2 + A_4 H_x^2 + A_5 H_z^2$	$D_1 H_y H_z$	$D_2 H_z H_x$	$D_2 H_x H_y$
yy	$m_{12}^{(0)} + A_3 H_z^2 + A_4 H_y^2 + A_5 H_x^2$	$m_{11}^{(0)} + A_1 H_y^2 + A_2(H_z^2 + H_x^2)$	$m_{12}^{(0)} + A_3 H_x^2 + A_4 H_y^2 + A_5 H_z^2$	$D_2 H_y H_z$	$D_1 H_z H_x$	$D_2 H_x H_y$
zz	$m_{12}^{(0)} + A_3 H_y^2 + A_4 H_z^2 + A_5 H_x^2$	$m_{12}^{(0)} + A_3 H_x^2 + A_4 H_z^2 + A_5 H_y^2$	$m_{11}^{(0)} + A_1 H_z^2 + A_2(H_x^2 + H_y^2)$	$D_2 H_y H_z$	$D_2 H_z H_x$	$D_1 H_x H_y$
yz	$B_1 H_x + D_3 H_y H_z$	$B_2 H_x + D_4 H_y H_z$	$B_2 H_x + D_4 H_y H_z$	$m_{44}^{(0)} + A_6 H_x^2 + A_7(H_y^2 + H_z^2)$	$B_3 H_z + D_5 H_x H_y$	$B_3 H_y + D_5 H_z H_x$
zx	$B_2 H_y + D_4 H_z H_x$	$B_1 H_y + D_3 H_z H_x$	$B_2 H_y + D_4 H_z H_x$	$B_3 H_z + D_5 H_x H_y$	$m_{44}^{(0)} + A_6 H_y^2 + A_7(H_z^2 + H_x^2)$	$B_3 H_x + D_5 H_y H_z$
xy	$B_2 H_z + D_4 H_x H_y$	$B_2 H_z + D_4 H_x H_y$	$B_1 H_z + D_3 H_x H_y$	$B_3 H_y + D_5 H_z H_x$	$B_3 H_x + D_5 H_y H_z$	$m_{44}^{(0)} + A_6 H_z^2 + A_7(H_x^2 + H_y^2)$

successful measurement would likely still show a strain-dependent Hall effect that would need to be accounted for via the traditional methods (this would correspond to an admixture of the B_1 and B_2 coefficients in the table). For fields aligned precisely along one of the crystal axes k, measurement of ρ_{ij} in positive and negative fields would, in principle, allow cancellation of this linear contaminant. Contact misalignment, which can result in admixture of ρ_{ii} in an attempt to measure ρ_{ij}, can be subtracted using ideas developed earlier in Ref. [21].

Perhaps more importantly, elastoresistivity requires controlling/measuring the strain experienced by a crystal. If an experiment failed to hold strain constant as a function of field, the octupole susceptibility would not be faithfully measured. An example would be the case where stress is held fixed, i.e., a piezoresistance measurement. Given that the octupole susceptibility can manifest in the elastic stiffness (see Sec. III A), the very application of field would change the stiffness independently of temperature, thus changing the strain under conditions of constant stress. Such an effect can be minimized via the use of a strain-applying apparatus that is very stiff relative to the sample, or nearly eliminated by directly measuring and controlling for strain. An appropriate experimental apparatus for such a task has been developed [22].

It should be further noted that Table III represents a general compilation of terms allowed in an expansion of resistivity in terms of strain and magnetic field (to first order in strain, second order in field); the order of derivatives is not particularly relevant, and thus strain dependencies of the magnetoresistance would draw from the same set of allowed terms, though high fields (or high strains) would potentially render relevant higher terms than those contemplated here.

V. CONCLUSION

The Γ_3 doublet ground state for local $4f$ orbitals in a cubic point symmetry was motivated as an ideal system to study octupole order parameters and their associated susceptibility, given the allowed τ_{xyz} octupole and the energetic disfavoring of magnetic dipoles. Considering the allowed couplings of

such an order parameter, several commonly measured tensor quantities in which it might appear were discussed. These were fully elucidated in the O_h point group, the point group of experimental realizations of an octupolar order parameter [8,11]. Specific terms within external-field-dependent elastic stiffness, elastoresistivity, and magnetic susceptibility tensors which would be linearly proportional to a potential τ_{xyz} octupole susceptibility were identified. Potential measurements, and complications arising from contaminant terms, were discussed for each individual tensor, with several octupole-isolating experiments ultimately proposed.

More broadly, similar ideas could be used to isolate contributions of a variety of higher-order local multipoles and in any number of material systems. The chosen system was convenient for both being relatively simple (a doublet ground state) and having no overlap in conjugate fields (the strain component of the octupole conjugate field coupled to no other order parameters allowed by the CEF ground state). Nonetheless, the core idea of isolating specific multipolar contributions to potentially rich phase diagrams via higher-rank tensor properties is broadly applicable to a variety of localized $4f$ systems.

APPENDIX A: CHARACTER TABLE

See Table IV. For convenience, a series of symmetrized cubic rotation products have been added. These have the same spatial symmetries as the magnetic octupole, and thus indicate

TABLE IV. O_h character table.

O_h		E	$8C_3$	$6C_2$	$6C_4$	$3(C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Linear functions and rotations	Quadratic functions	Cubic functions and cubic rotation products
Γ_1^+	A_{1g}	+1	+1	+1	+1	+1	+1	+1	+1	+1	+1		$x^2+y^2+z^2$	
Γ_2^+	A_{2g}	+1	+1	−1	−1	+1	+1	−1	+1	+1	−1			$\overline{R_x R_y R_z}$
Γ_3^+	E_g	+2	−1	0	0	+2	+2	0	−1	+2	0		$(2z^2-x^2-y^2,$ $x^2-y^2)$	
Γ_4^+	T_{1g}	+3	0	−1	+1	−1	+3	−1	0	−1	−1	(R_x, R_y, R_z)		(R_x^3, R_y^3, R_z^3) $(\overline{R_x R_z^2}+\overline{R_x R_y^2}, \overline{R_y R_x^2}+\overline{R_y R_z^2},$ $\overline{R_z R_y^2}+\overline{R_z R_x^2})$
Γ_5^+	T_{2g}	+3	0	+1	−1	−1	+3	−1	0	−1	+1		(yz, zx, xy)	$(\overline{R_x R_z^2}-\overline{R_x R_y^2}, \overline{R_y R_x^2}-\overline{R_y R_z^2},$ $\overline{R_z R_y^2}-\overline{R_z R_x^2})$
Γ_1^-	A_{1u}	+1	+1	+1	+1	+1	−1	−1	−1	−1	−1			
Γ_2^-	A_{2u}	+1	+1	−1	−1	+1	−1	+1	−1	−1	+1			xyz
Γ_3^-	E_u	+2	−1	0	0	+2	−2	0	+1	−2	0			
Γ_4^-	T_{1u}	+3	0	−1	+1	−1	−3	−1	0	+1	+1	(x, y, z)		(x^3, y^3, z^3) $(xz^2+xy^2, yx^2+yz^2, zy^2+zx^2)$
Γ_5^-	T_{2u}	+3	0	+1	−1	−1	−3	+1	0	+1	−1			$(xz^2-xy^2, yx^2-yz^2, zy^2-zx^2)$

the irreducible representations of the various possible magnetic octupole moments.

APPENDIX B: TABLE SYMMETRIES

Herein, terms are defined by "types," where a given type is defined by having a unique index composition (i.e., ii, ii versus ii, jj), and $i \neq j \neq k$ holds for all types. A type then constitutes a term, and all terms that can be generated from that (arbitrary) original term by various symmetries, which can be simplified to include only the symmetries of a given tensor, the threefold rotational symmetry, and the various fourfold rotations. For example, type II for the elastic stiffness tensor, $C_{ii,jj}$, includes $C_{xx,yy}$, $C_{yy,xx}$ (due to the symmetry of the tensor; see the relevant section below), $C_{yy,zz}$, etc. The wording "sign change" is used to indicate the operation $(x) \rightarrow (-x)$ for a given variable a tensor depends on, such as magnetic field.

1. Elastic stiffness

Here the C symmetry is defined as that which exchanges the two subsets of indices (i.e., $C_{ab,cd} \rightarrow C_{cd,ab}$), while the ϵ symmetry is defined as that which switches indices within a subset ($C_{ab,cd} \rightarrow C_{ba,cd}$).

Type I: $C_{ii,ii}$ (red boxes in Table II)

1. Invariant under simultaneous sign change of any two field components ($\sigma_i/\sigma_j/\sigma_k$)

2. Invariant under simultaneous exchange of H_j and H_k and sign change of H_i ($\sigma_{j=k}$)

Final form: $C_{11}^0 + A_1 H_i^2 + A_2(H_j^2 + H_k^2)$

Type II: $C_{ii,jj}$ (green boxes in Table II)

1. Invariant under simultaneous sign change of any two field components ($\sigma_i/\sigma_j/\sigma_k$)

2. Invariant under simultaneous exchange of H_i and H_j and sign change of H_k ($\sigma_{i=j}$, C)

Final form: $C_{12}^0 + A_3(H_i^2 + H_j^2) + A_4(H_k^2)$

Type III: $C_{ij,ij}$ (yellow boxes in Table II)

1. Invariant under simultaneous sign change of any two field components ($\sigma_i/\sigma_j/\sigma_k$)

2. Invariant under simultaneous exchange of H_i and H_j and sign change of H_k ($\sigma_{i=j}$, ϵ)

Final form: $C_{44}^0 + A_6(H_i^2 + H_j^2) + A_5(H_k^2)$

Type IV: $C_{ii,ij}$ (orange boxes in Table II)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Antisymmetric under simultaneous sign change of H_k and H_j/H_i (σ_i/σ_j)

Final form: $B_1 H_k + D_2 H_i H_j$

Type V: $C_{ij,kk}$ (purple boxes in Table II)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Invariant under simultaneous exchange of H_i and H_j and sign change of H_k ($\sigma_{j=k}$, ϵ)

3. Antisymmetric under exchange of H_i and H_j followed by sign change of H_i (C_{4k}, ϵ)

Final form: $D_1 H_i H_k$

Type VI: $C_{ij,jk}$ (blue boxes in Table II)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_k)

2. Invariant under simultaneous exchange of H_i and H_k and sign change of H_j ($\sigma_{i=k}$, C, ϵ)

3. Antisymmetric under exchange of H_i and H_k followed by sign change of H_i (C_{4j}, C)

Final form: $D_3 H_i H_k$

2. Strain-dependent magnetic susceptibility

The magnetic susceptibility tensor, again defined by

$$\chi_{ij} \equiv \left. \frac{\partial^2 F}{\partial H_i \partial H_j} \right|_{H \to 0} \propto -\frac{\partial M_i}{\partial H_j} = -\frac{\partial M_j}{\partial H_i}, \qquad \text{(B1)}$$

has one obvious symmetry. This symmetry, herein defined as "χ" symmetry, implies invariance under simple exchange of indices, i.e., $\chi_{ij} \rightarrow \chi_{ji}$.

Type I: χ_{ii}

1. Invariant under sign-change of $i/j/k$ indices ($\sigma_i/\sigma_j/\sigma_k$)

2. Symmetric under exchange of j and k indices ($\sigma_{j=-k}$)

Final form: $\chi_{ii} = \chi_{ii}^{(0)} + A\epsilon_{ii} + B(\epsilon_{jj} + \epsilon_{kk}) + C\epsilon_{ii}^2 + D(\epsilon_{jj}^2 + \epsilon_{kk}^2) + E\epsilon_{ii}(\epsilon_{jj} + \epsilon_{kk}) + F\epsilon_{jj}\epsilon_{kk} + G(\epsilon_{ij}^2 + \epsilon_{ik}^2) + L\epsilon_{jk}^2$

Type II: χ_{ij}

1. Zero in the absence of symmetry-breaking field, strain or otherwise (σ_i or σ_j)

2. Antisymmetric under sign change of i/j (σ_i/σ_j)

3. Invariant under exchange of i and j coefficients ($\sigma_{i=-j}. \chi$)

Final form: $M\epsilon_{ij} + N\epsilon_{ik}\epsilon_{jk} + O\epsilon_{ij}\epsilon_{kk} + P\epsilon_{ij}(\epsilon_{ii} + \epsilon_{jj})$

It can then be noted that, given the definition of C and the definition of χ, each of these terms corresponds to some allowed term in the free energy, and the terms which give rise to many of the C tensor terms are identical to many that give rise to the strain-dependent χ tensor terms. Thus, the terms can be rewritten as

Final form: $\chi_{ii} = \chi_{ii}^{(0)} + E\epsilon_{ii} + F(\epsilon_{jj} + \epsilon_{kk}) + A_1\epsilon_{ii}^2 + A_2(\epsilon_{jj}^2 + \epsilon_{kk}^2) + A_3\epsilon_{ii}(\epsilon_{jj} + \epsilon_{kk}) + A_4\epsilon_{jj}\epsilon_{kk} + A_6(\epsilon_{ij}^2 + \epsilon_{ik}^2) + A_5\epsilon_{jk}^2$

Final form: $G\epsilon_{ij} + D_3\epsilon_{ik}\epsilon_{jk} + D_1\epsilon_{ij}\epsilon_{kk} + D_2\epsilon_{ij}(\epsilon_{ii} + \epsilon_{jj})$

3. Nonlinear magnetic susceptibility

The inherent symmetry of the tensor here remains $\chi_{ij} \rightarrow \chi_{ji}$, as in the previous case.

Type I: χ_{ii}

1. Invariant under simultaneous sign change of any two field components ($\sigma_i/\sigma_j/\sigma_k$)

2. Invariant under simultaneous exchange of H_j, H_k and sign change of H_i ($\sigma_{j=-k}$)

Final form: $\chi_{ii}^{(0)} + AH_i^2 + B(H_j^2 + H_k^2) + CH_i^4 + D(H_j^4 + H_k^4) + EH_i^2(H_j^2 + H_k^2) + FH_j^2H_k^2$

Type II: χ_{ij}

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Invariant under simultaneous sign change of H_i, H_j (σ_k)

2. Antisymmetric under simultaneous sign change of $H_j, H_k/H_k, H_i$ (σ_i/σ_j)

3. Invariant under simultaneous exchange of H_i, H_j and sign change of H_k ($\sigma_{i=-j}, \chi$)

Final form: $\chi_{ij} = GH_iH_j + LH_iH_jH_k^2 + NH_iH_j(H_i^2 + H_j^2) + OH_k(H_i^2 - H_j^2)$

Furthermore, moving beyond Neumann's principle, it can be noted that the aforementioned definition of magnetic susceptibility implies each term derives from a corresponding term in the free energy. Some of these χ tensor terms are then implied to derive from the same allowed term within the free energy, and are thus constrained to be equal, to within a numerical factor (given different derivative orders). Additionally, one term allowed by Neumann's principle in χ_{ij}, $OH_k(H_i^2 - H_j^2)$, implies a term in χ_{ii}, $H_iH_jH_k$, that is forbidden, and is thus not allowed (alternatively, the free-energy term implied by $OH_k(H_i^2 - H_j^2)$ is found to cancel if the equivalent free-energy terms from χ_{ij}, χ_{jk}, and χ_{ki} are added together, yielding $H_iH_jH_k(H_i^2 - H_j^2 + H_j^2 - H_k^2 + H_k^2 - H_i^2)$).

Thus, the allowed terms can be further simplified to

$$\chi_{ii}^{(0)} + AH_i^2 + B(H_j^2 + H_k^2) + CH_i^4 + D(H_j^4 + H_k^4)$$
$$+ 6DH_i^2(H_j^2 + H_k^2) + EH_j^2H_k^2\chi_{ij}$$
$$= 2BH_iH_j + 2EH_iH_jH_k^2 + 4DH_iH_j(H_i^2 + H_j^2).$$

4. Elastoresistivity

Elastoresistivity, defined again by

$$m_{ij,kl} \equiv \frac{\partial\left(\frac{\Delta\rho}{\rho}\right)_{ij}}{\partial\epsilon_{kl}}$$

does not admit the exchange of the index pairs, i.e., $m_{ij,kl} \rightarrow m_{kl,ij}$. Thus, the symmetries of the constituent components are the only major symmetries of the tensor itself. First, the inherent "ϵ" symmetry implies invariance under $m_{ij,kl} \rightarrow m_{ij,lk}$. Next, the symmetry of the normalized resistivity tensor, defined here (for the purposes of symmetry[12]) via

$$\left(\frac{\Delta\rho}{\rho}\right) = \rho^{-1/2}(\Delta\rho)\rho^{-1/2}, \tag{B2}$$

implies invariance under the "ρ" symmetry operation, $m_{ij,kl} \rightarrow -m_{ji,kl}$, as noted in the relevant section above.

Type I: $m_{ii,ii}$ (red boxes in Table III)

1. Even in $H_i/H_j/H_k$ ($\sigma_i/\sigma_j/\sigma_k, \rho$)

2. Invariant under exchange of H_j, H_k ($\sigma_{j=k}, \rho$)

Final form: $m_{11}^0 + A_1H_i^2 + A_2(H_j^2 + H_k^2)$

Type II: $m_{ii,jj}$ (green boxes in Table III)

1. Even in $H_i/H_j/H_k$ ($\sigma_i/\sigma_j/\sigma_k, \rho$)

Final form: $m_{12}^0 + A_3H_k^2 + A_4H_i^2 + A_5H_j^2$

Type III: $m_{ij,ij}$ (yellow boxes in Table III)

1. Invariant under simultaneous sign change of any two field components ($\sigma_i/\sigma_j/\sigma_k$)

2. Invariant under exchange of H_i, H_j ($\sigma_{i=-j}, \rho, \epsilon$)

Final form: $m_{44}^0 + A_6H_k^2 + A_7(H_i^2 + H_j^2)$

Type IV: $m_{ii,ij}$ (peach boxes in Table III)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Antisymmetric under simultaneous sign change of $H_j, H_k/H_k, H_i$ (σ_i/σ_j)

3. Invariant under simultaneous sign change of H_i, H_j (σ_k)

4. Invariant under simultaneous sign change of H_i, H_j, H_k (ρ)

Final form: $D_2H_iH_j$

Type V: $m_{ij,jj}$ (orange boxes in Table III)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Antisymmetric under simultaneous sign change of $H_j, H_k/H_k, H_i$ (σ_i/σ_j)

3. Invariant under simultaneous sign change of H_i, H_j (σ_k)

Final form: $B_2H_k + D_4H_iH_j$

Type VI: $m_{ij,kk}$ (purple boxes in Table III)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_j)

2. Antisymmetric under simultaneous sign change of $H_j, H_k/H_k, H_i$ (σ_i/σ_j)

3. Invariant under simultaneous sign change of H_i, H_j (σ_k)

4. Invariant under exchange of H_i, H_j ($\sigma_{x=-y}, \rho$)

Final form: $B_1H_k + D_3H_iH_j$

Type VII: $m_{ii,jk}$ (violet boxes in Table III)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_j or σ_k)

2. Odd in H_j/H_k (σ_j/σ_k, ρ)

3. Even in H_i (σ_i, ρ)

Final form: $D_1 H_j H_k$

Type VIII: $m_{ij,jk}$ (blue boxes in Table III)

1. Zero in the absence of symmetry-breaking field, magnetic or otherwise (σ_i or σ_k)

2. Antisymmetric under simultaneous sign change of $H_j, H_k/H_i, H_j$ (σ_i/σ_k)

3. Invariant under simultaneous sign change of H_i, H_k (σ_j)

Final form: $B_3 H_j + D_5 H_k H_i$

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[7] Neumann's principle essentially states that a crystal's physical properties must be invariant under the symmetry operations of the crystal.

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[13] Herein, all proposed measurements treat strain as an extrinsic property, controllable via application of external force; as such, it is not constrained by Neumann's principle.

[14] Using the Russell-Saunders coupling scheme, U^{4+} ($5f^2$) can also manifest a $J = 4$ state. However, the extended nature of $5f$ orbitals often smears out the CEF eigenstates. Furthermore, in some cases j-j coupling is more appropriate. Hence, Pr^{3+} is the clearest manifestation of a $J = 4$ state.

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[16] Looking to a character table quickly shows these two objects to be of A_2 symmetry in T_d, when H is properly acknowledged as a pseudovector.

[17] The magnetic octupole is itself invariant under inversion symmetry, while inversion swaps the two independent ion sites in the broader O_h unit cell (equivalent to the two diamond sublattices); thus, if the local octupoles are aligned identically on the two sites, i.e., a ferro-octopolar configuration, the system is invariant under inversion symmetry (Γ_2^+ in O_h has the same symmetries as Γ_2 in T_d, plus inversion, due to T_d being a subgroup of O_h).

[18] Analogously to the Γ_2 case, Γ_3^+ in O_h is equivalent to Γ_3 in T_d with added inversion symmetry.

[19] Strain is a thermodynamic quantity, and the material will adapt a value that minimizes the free energy subject to a given set of stresses. However, experimental configurations can be established in which stresses are applied such that given (measured) strains are established. From a thermodynamic perspective, this is equivalent to a Legendre transformation in which strain now becomes a forced (controllable) parameter.

[20] Though microscopics may vary, in pure symmetry terms, ϵ_{ii} and ϵ_{ij} transform equivalently to H_i^2 and $H_i H_j$, respectively; H_i belongs to a T_1 representation, and the product of two different field components $H_i H_j$ creates a T_2 object symmetrically analogous to a shear strain.

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