What can spin glass theory and analogies tell us about ferroic glasses?

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Abstract  As well as several different kinds of periodically ordered ferroic phases, there are now recognized several different examples of ferroic glassiness, although not always described as such and in material fields of study that have mostly been developed separately. In this chapter an attempt is made to indicate common conceptual origins and features, observed or anticipated. Throughout, this aim is pursued through the use of simple models, in an attempt to determine probable fundamental origins within a larger picture of greater complication, and analogies between systems in different areas, both experimental and theoretical, in the light of significant progress in spin glass understanding.

1 Introduction

The existence of macroscopic magnetism has been known since ancient times, with appreciation of its possible spontaneous microscopic origins coming from the mean-field theories of Weiss (1907) and Stoner (1938), respectively for local-moment and itinerant ferromagnets. The electrical analogue, ferroelectricity, was discovered experimentally in 1920. The subsequent recognition of antiferromagnetic and ferrimagnetic orderings is due to Néel. In these conventional phases, as well as in many other subsequently discovered ferroic phases, the order is macroscopically periodic, as well as of lower symmetry than the corresponding higher temperature para-phases, which lack long range ferroic order.

The recognition of the existence of different dipolar-glassy behaviour in certain alloys, quasi-frozen locally but without periodic ferroic order, dates back some half a century in both magnetic and electrical scenarios. Initially it was thought ‘just’ to represent slowing down of dynamics with reduced temperature as experienced in conventional glasses, but interest in the magnetic ‘glasses’ became more focussed with the observation, at the beginning of the 70s, of sharp but non-divergent low-field magnetic susceptibility peaks as a function of temperature in AuFe alloys, suggesting a conceptually new type of phase transition. In combination with evi-
dence of local spin freezing through Mössbauer experiments and of lack of periodicity through neutron diffraction experiments, the new state became known as ‘spin glass’. Attempting to understand these observations led to theoretical modelling and novel theoretical, experimental and computational methodologies [6, 7, 8, 9] that exposed subtle new concepts and useful applications, not only in many material systems but also in many physically very different complex systems/problems, such as neural networks, hard optimization, protein-folding and also probability theory. At a model level the underlying physical origins of the behaviour are reasonably understood, although some controversies remain, and many material examples are now known; see e.g. [10, 11, 12, 13, 14, 15, 16].

Independently, a potentially related observation was made already in the 50s and 60s in ferroelectric alloys [17, 18], in the form of peaks in the a.c. electrical susceptibility of the perovskite alloy \( \text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 \) (PMN), with significant frequency-dependence, no ferroelectricity and no change of global symmetry, at temperatures much below those of the relatively frequency-independent ferroelectric transition in the related non-disordered compound \( \text{PbTiO}_3 \) (PT). This new behaviour was named ‘relaxor’.

The discovery of the relaxor behaviour in ferroelectric alloys also sparked much interest and practical application, but its fundamental origin has remained uncertain and contested.

A third type of ferroic glass can be found in martensitic alloys, given the name ‘strain glass’ [19], but this was a more recent discovery, despite the fact that practical interest in martensites goes back to the nineteenth century.

In this chapter I shall try to relate these different types of ferroic glasses under a common conceptual umbrella, including both well-defined local moments and induced moments, within minimal modelling.

2 Experimental indications

Before giving a theoretical discussion, it is suggestive to note some further similarities in experimental observations of different systems.

In Fig 1 are shown a.c. susceptibilities (electrical or magnetic, as appropriate), of the original (heterovalent) relaxor PMN, the spin glass \( \text{Pt}_{1-x}\text{Mn}_x \) at \( x = 0.025 \), and the more recently discovered homovalent relaxor \( \text{BaZr}_{1-x}\text{Ti}_x\text{O}_3 \) (BZT) at \( x = 0.65 \). They are clearly very similar, with peaks indicative of transitions or strong crossovers, with strong frequency dependence, slow to respond and glassy, suggesting that similar physics is at play in these experiments. Yet they are rather different in several other aspects of their physical make-ups; both PMN and BZT are ceramic (insulating) substitutional alloys with the basic average perovskite structure \( \text{ABO}_3 \), where A is an ion of charge 2+, B is an ion of charge 4+ and O has charge 2-, but with random substitution on the B sites; however, in BZT the replacement B ions also have charge 4+, hence the labelling as ‘homovalent’, while in PMN the

\[ \text{We use the expression ‘ferroelectric alloy’ to refer to alloys which exhibit ferroelectricity (or antiferroelectricity) at appropriate concentrations and low enough temperatures.} \]
replacement B ions have charges 2+ for Mg and 5+ for Nb, in ratio 1:2 to maintain the average charge, hence the description as ‘heterovalent’; PtMn is a face centred cubic metallic alloy with magnetic moments only on the Mn. It is thus natural to look for conceptual common links beyond normal material appearances.

For comparison/contrast, Fig 2(a) shows the corresponding susceptibilities of BZT at a concentration at which the alloy is ferroelectric, demonstrating no significant frequency dependence and hence no glassy slow response. Fig 2(b) shows the effects of even small applied fields in AuFe, rounding the transition but also suggesting that it is sharp in the limit of zero applied field. One can also note that although the (normal) susceptibility diverges at a second-order ferromagnetic or ferroelectric transition, it does not diverge at spin glass or relaxor transitions, indicating that the global moment is not a primary order parameter for a spin glass or relaxor.

In Fig 3 are shown for comparison examples of the of field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities for the heterovalent relaxor PMN and the spin glass CuMn, along with results of computer simulation of analogous measures for a model of the homovalent relaxor BZT. Again there are clear similarities as the temperature is reduced through that associated with the low-frequency a.c. susceptibility peak, of the continuous separation of the two kinds of susceptibility measure, cooling in the probe field (FC) and cooling without the field and
then applying the field to measure (ZFC), respectively understood as probing all thermodynamic states (FC) and probing only accessible states (ZFC), the separation indicating the onset of a hierarchy of barriers.

Fig. 3 Field-cooled (FC) and zero-field-cooled (ZFC) static susceptibility measurements; PMN \[22\] ©APS (1998), spin glass CuMn \[23\] ©APS (1979), BZT(50:50) simulation \[24\] ©APS (2012)

3 Spin Glasses

The canonical spin glasses, such as AuFe and CuMn, involve non-magnetic hosts, Au and Cu, and a finite concentration of local-moment-bearing substitutions, Fe and Mn. Paramagnetic at high temperatures, they exhibit spin glass behaviour beneath critical temperatures at lower (but finite) concentrations of magnetic ions. A similar behaviour is also found in many other systems, both metals and insulators; see e.g. Fig 4.

Fig. 4 Spin glass phase diagrams; (a) metal: AuFe \[25\] ©Taylor and Francis (1978), (b) semiconductor:Eu\(_{x}\)Sr\(_{1-x}\)S, \[26\] ©APS (1979), (c) SK model with mean and variance of exchange distribution both scaling with concentration \(x\). \[27\] ©Springer (2012)

To model the cooperative magnetic behaviour one typically expresses the Hamiltonian as
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\[ H_{CSG} = - \sum_{(ij) \in \text{Mag}} J(R_{ij}) S_i S_j \]  

(1)

where the \( S_i \) are localized spins, of fixed length but variable direction, located on the magnetic ions, \( J(R) \) is a translationally-invariant but spatially-frustrated ‘exchange interaction’ and the sum is over pairs of sites occupied by magnetic atoms.

For the canonical metallic systems such as \( \text{AuFe} \) and \( \text{CuMn} \), the effective interaction between the magnetic ions is carried by the conduction electrons via the s-d coupling, resulting in the RKKY form

\[ J(R_{ij}) = J^2 \chi_{ij} \]  

(2)

where \( J \) is the coupling strength between the conduction electron spin \( (s_i) \) and the local moment spin \( (S_i) \) and \( \chi_{ij} \) is the conduction band susceptibility between sites \( i \) and \( j \). \( \chi_{ij} \) oscillates in sign with separation \( R_{ij} \), with wavevector \( 2k_F \) where \( k_F \) is the Fermi wavevector, and (in 3 dimensions) also decays in magnitude as \( R^{-3} \). The oscillation in sign results in a competition in ordering tendencies of the spins, now known as ‘frustration’ [28], while the randomness of occupation of lattice sites by magnetic ions provides quenched disorder and inhomogeneity of local environments.

The RKKY interacting metal systems are, however, just one experimental example of the combination of frustration and disorder leading to spin glass behaviour. In the second example of Fig 4 the material is semiconducting, the spins are on the Eu and their interaction arises from shorter-range superexchange, with frustration due to competition between nearest-neighbour and antiferromagnetic next-neighbour interactions.

It is now well-established that the combination of frustration and quenched disorder are the key ingredients for spin glass behaviour. This realisation by Edwards and Anderson (EA) [6] led them to to suggest in 1975 an alternative model for potentially easier but conceptually equivalent theoretical study, along with further new conceptualization and methods of analysis that ignited theoretical excitement. In their model every site is occupied by a magnetic spin but their interactions are chosen randomly and quenched:

\[ H_{EA} = - \sum_{(ij)} J_{ij} S_i S_j \]  

(3)

where the \( J_{ij} \) are chosen randomly from a symmetric distribution of mean zero, ensuring that no conventional periodic order is possible.

Through novel and innovative analysis EA demonstrated the existence of a new phase with random spin-freezing. They noted that a relevant order parameter to test for spin freezing, independent of overall periodic order, is

\[ q_{EA} = \lim_{\tau \to \infty} \overline{S_i(t) S_i(t + \tau)} \]  

(4)

where the overbar refers to an average over sites \( i \) and times \( t \), or, equivalently
where the $\langle \rangle$ brackets refer to a thermodynamic average and the overbar to a site/disorder average. Thus, ‘amorphous’ spin freezing without ferromagnetism is signalled by non-zero $q_{EA}$ but zero overall magnetization $m$, as given by

$$m = \langle S_i \rangle_i.$$  

The EA model has become an important paradigm in further theoretical study. It is normally considered as having only nearest neighbour interactions on a simple cubic (or hypercubic) lattice. Computer simulations have demonstrated that it captures key features of real systems. An extension to allow for competition of the spin glass phase with ferromagnetism by allowing a finite mean $J_0$ to the interaction distribution, of standard deviation $J$, by Sherrington and Southern (SS) \[29\], showed that when $J_0/J$ is large enough the low temperature state is a ferromagnet, while for smaller $J_0/J$, beneath a critical value, the low temperature state is spin glass.

The EA model with finite interaction range is not exactly soluble. However, an extension in which the distribution from which the interactions are drawn is the same for all pairs of sites, independently of their separation, the Sherrington-Kirkpatrick (SK) model \[7\], is soluble, although its solution is very subtle, requiring a description beyond that of a single simple order parameter \[8\], and has exposed several unexpected but interesting features and concepts \[9\]. Its solution clearly demonstrates the existence of phase transition to a glassy phase, even in an applied field, and also that its spin glass phase has a complex structure with a hierarchy of metastable states and chaotic evolution under change of global controls (such as temperature). It has stimulated much further study in many other range-free random problem scenarios. However, there remains controversy about whether all the conceptual results of the SK model studies apply to finite-ranged systems, especially those related to so-called replica-symmetry-breaking \[8\] and to whether a phase transition still persists in an applied field.

### 3.1 Simulations

Computer simulations of model systems have played an important role in determining whether true phase transitions exist also in systems with range-dependent interactions, using their ability to measure directly observables which are not readily accessible to conventional experimentation, such as the spin glass order parameter $q_{EA}$ and a related spin glass susceptibility, as well as the more conventional measures such as the ferromagnetic order parameter $m$.

The existence of true phase transitions can be tested through sophisticated simulation studies, especially through the use of finite-size scaling and Binder plots\[30\]. These studies have provided clear demonstrations of spin glass phase transitions in several interesting situations, \textit{e.g.} as illustrated in Fig \[5\] for three examples; (i)
spin-glass correlations in the SK model with zero mean exchange \cite{31}, (ii) a nearest neighbour Ising EA model in dimensions 3 (again with zero mean exchange) \cite{32} and (iii) a longer-range dipolar model emulating LiHo$_x$Y$_{1-x}$F$_4$ at $x = 0.001$, a concentration at which the system is a spin glass \cite{33}. Corresponding plots for ordinary magnetic correlations in these systems do not show crossings, indicating the absence of a ferromagnetic transition. The combination of these two results, crossing of the size-normalized spin glass correlation lengths together with the lack of crossing of the normal magnetic correlation lengths, lead to the deduction of a true spin glass phase transition at the crossing temperature.

![Graph](image1.png)

**Fig. 5** Spin glass correlation plots for different sample sizes, with crossovers at phase transition temperatures, for (a) SK model \cite{31} @APS (1984), (b) three-dimensional Ising EA \cite{32} @APS 2006 and (c) LiHo$_x$Y$_{1-x}$F$_4$ at $x = 0.001$ \cite{33}

### 3.2 Soft spins

In analytic studies of spin glasses the Hamiltonian is often re-expressed using continuously-valued 'spin fields' \{\phi\} in place of the fixed length spins \{S\}. Within a simplification to one-dimensional (Ising) spins $H_{EA}$ becomes

$$H_{EA_{\text{cont}}} = \sum_i (r_i \phi_i^2 + u_i \phi_i^4) - \sum_{(ij)} J_{ij} \phi_i \phi_j,$$

while the analogue for site-disorder is

$$H_{CSG_{\text{cont}}} = \sum_i (r_i \phi_i^2 + u_i \phi_i^4) - \sum_{(ij)} J(R_{ij}) \phi_i \phi_j.$$  

The full hard-spin Ising case ($S = \pm 1$) results from taking the limits

$$r \to -\infty, u \to \infty, r/2u \to -1.$$  

\footnote{The phase transitions are demonstrated by the crossing of appropriate correlation measures for systems of different sizes, with scaling plots providing further confirmations and exponents.}
The sums are taken over only magnetic sites or, equivalently, the non-magnetic sites can be emulated by taking \( r_i \to \infty \) on those sites. Note, however, that if some \( r_i \) are negative but finite then for those sites to displace there needs to be a sufficient binding energy from the interaction term to overcome the local quadratic penalty for displacements, otherwise the ground state would have \( \phi = 0 \). Such bootstrapping is referred to as ‘induced moment’. Note that the resultant order will depend on the character of the interactions and can be either globally periodic, including ferromagnetic, or spin glass in a system with sufficient disorder and frustration.

Early experimental indications of induced moment spin glass behaviour were found in the alloys \( YTb \) and \( SCb \), in which crystal field effects lead to a singlet ground state for isolated Tb ions. For Tb concentrations less than a small but finite percentage the ground state is non-magnetic, in contrast to the corresponding alloys with non-singlet ground state Gd in place of Tb, in which the spin glass state continues to the lowest finite concentrations.

A simple extension of the EA model exhibiting induced moment spin glass behaviour was introduced in 1977 by Ghatak and Sherrington (GS) [35];

\[
H_{GS} = -\sum_i DS_i^2 - \sum_{ij} J_{ij} S_i S_j \tag{10}
\]

with the \( S \) taking values \( S = 0, \pm 1 \) and the \( \{ J \} \) again drawn randomly from a distribution of mean zero. For \( D \) less than a critical (negative) value \( D_c \) there is only a paramagnetic phase, while above there is an induced-moment spin glass phase.

### 4 Polar glasses and relaxors

Ferroelectric systems are often categorized as being of polar/‘order-disorder’ type or ‘displacive’ type.

In the former one envisages local electric dipolar moments well formed (but not cooperatively ordered) already in the paraelectric phase above the macroscopic ordering transition to ferroelectricity (or, if energetically preferable, to another periodic phase), in close analogy with local moment magnetism. Correspondingly, alloys with sufficient dilution of local moment units by neutral ones, together with frustrated interactions, can lead to close analogies of conventional local moment spin glasses [36] [37]. Extensions of spin glass modelling and analysis have also been developed for systems characterised by the interaction of higher-order local moments [38] [39] [40].

By contrast, in displacive ferroelectrics there are no long-lived electric moments above the transition to ferroelectricity and the charged ions fluctuate around a mean lattice structure with no overall electric moment. Rather, in such ferroelectrics, as the temperature is lowered beneath the transition temperature the time-averaged positions of charged ions displace collectively in such a manner as to yield overall ferroelectricity. The transition to ferroelectric is typically accompanied by a change
in global symmetry but the ferroelectricity itself is caused by a relative distortion of positively and negatively charged ions within the unit cells, yielding electric moments. Unless preempted by a first order transition, the susceptibility diverges at the transition. However, not all candidate systems with the same ionic charges and higher temperature structures do exhibit cooperative ordering; for example $\text{BaTiO}_3$ (BT) is a displacive ferroelectric while $\text{BaZrO}_3$ (BZ) is not. An energetic advantage of distortion is needed.

Displacive ferroelectrics can be modelled by considering the displacements of the ions as variables governed by Hamiltonians including local costs, the (non-local) effects of interactions between displacements at different sites and the effects of charges on different sites, with coefficients calculable by first-principles methods, followed by computer simulations at finite temperatures.

A detailed first-principles theoretical/computational study of $\text{BaTiO}_3$ was given in [41] and demonstrated the ferroelectric transition; see also [42]. However, the conceptual principles can be seen already from a simplified model allowing only for one-dimensional displacements of the most polarizable ions:

$$H_R = \sum_i \left\{ \kappa u_i^2 + \lambda u_i^4 \right\} + \sum_{ij} J_{ij} u_i u_j$$

where the $u_i$ are the displacements of the ions at sites $\{i\}$, the first (single-site) term describes the local energy costs of displacements and the last term represents the interaction energy. Clearly, this has a similar form to Eqn. (7) and can yield an induced moment (displaced $u \neq 0$) ground state if the energy minimising gain from the interaction term can overcome the local cost from the $\kappa$ term, with a corresponding transition at a higher temperature. For $\kappa$ close to zero one expects features of both displacive and order-disorder behaviour, reducing $\kappa$ making it more order-disorder-like.

Fig. 6 Unit cell structure of $\text{PbTiO}_3$ above and below the ferroelectric transition temperature. $\text{BaTiO}_3$ is similar, but with smaller tetrahedral stretching.

Here, however, the main interest is in alloys. In particular, we shall concentrate on alloys of underlying perovskite structure $\text{ABO}_3$ with substitutional disorder on the B sites. This disorder can be either homovalent, for which the ions on the B-sites all have the same 4+ charge as the template, or heterovalent, for which the B-ions have different charges but with the average charge of 4+.
4.1 Homovalent relaxors

The homovalent alloy Ba(Zr$_{1-x}$Ti$_x$)O$_3$ (BZT) exhibits ferroelectricity at higher $x > x_{c1}$, only paraelectricity for $x < x_{c2}$, with relaxor behaviour in between [43]. The present author has argued that the relaxor state of BZT is essentially an induced moment spin glass [44]. The susceptibility measured in BZT in a relaxor region of the concentration $x$ is shown in Fig 1.

Here we shall use only a simplified model to illustrate the probable origin of the relaxor behaviour observed in BZT at intermediate concentrations [45]. We note that at the para- to ferro-electric transition, while the overall lattice structure stretches from cubic to tetrahedral, the B-site ions displace from the symmetric lattice positions; see Fig 6, yielding ferroelectricity. Also, it is observed that in the relaxor state the overall average lattice structure remains cubic. Hence, while all the ion locations are, in principle, variable, we shall initially ignore any A and O site displacements, coupling to global strain and change in global lattice structure and concentrate on the deviations of the B-site ions from their locations on the pure perovskite ABO$_3$ lattice, using

$$H_R = \sum_i \{ \kappa_i |u_i|^2 + \lambda_i |u_i|^4 + \gamma_i (u_i^2u_{i'}^2 + u_i^2u_{i''}^2 + u_{i'}^2u_{i''}^2) \} + \sum_{(ij)} \sum_{\alpha\beta} J_{ij}^{\alpha\beta} u_{i\alpha}u_{j\beta}$$

(12)

where the $\{u_i\}$ are the displacements of the ions at B-sites $\{i\}$, the first (single-site) term describes the local energy costs of displacements, with the $\kappa$, $\lambda$ and $\gamma$ coefficients depending upon the types of atoms at those sites, and the last term represents the interaction energy, involving a short-range contribution due to (quantum mechanical) electronic interference of neighbouring pairs of B ions, long-range Coulomb interactions and effective interactions via the ions on A and O sites. This is immediately recognisable as a vector analogue of Eqn. (7), also allowing for anisotropy.

For $\kappa$ positive the ground state will have $u = 0$ if the interaction strength is insufficient to overcome it. This appears to be the case for Zr in BaZrO$_3$, which is everywhere paraelectric, while for Ti $\kappa$ is smaller and BaTiO$_3$ is ferroelectric. Empirically, for a pure system at finite temperature, one can consider Eqn (12) to represent instead an effective Landau free energy with temperature-dependent coefficients,

$$\kappa = \kappa_c + a(T - T_c) + \mathcal{O}(T - T_c)^2$$

(13)

where $\kappa_c > 0$ is the critical value at which the energy cost from the local harmonic term equals the maximum energy gain from the interaction and $T_c$ is the transition temperature.

For alloys such as BZT one can model as in Eqn. (12) but with different $\kappa$, $\lambda$ and $\gamma$ on Zr and Ti sites. Given that $\kappa^{Zr}$ is too great to allow order in BZ, the situation is analogous to that in Eqn. (8), albeit without the extremes of coefficients and with $r$ rather positive on Zr sites, reminiscent of the non-magnetic sites in conventional spin glasses but allowing for some paraelectric induction.
Dipolar interactions are frustrated, as well as long-ranged, well-known to lead to several different magnetic phases in different structures and in combination with different extra shorter-range interactions [46]; e.g. a simple cubic Ising dipolar system has an antiferromagnetic ground state, while the tetragonal LiHoF₄ is ferromagnetic at low temperature. It is also known from experiment and from computational studies of hard-spin dipolar models that site-dilution of dipolar sites can lead to spin glass phases in such systems; see the first two sub-figures of Fig 7 [47] [48].

Hence it seems reasonable to anticipate a corresponding soft pseudo-spin glass phase in homovalently-diluted frustrated ferroelectrics in appropriate parameter regions and for the observed relaxor state in BZT to be a manifestation of such a phase, the pseudo-spins being the local dipoles induced by displacement of the charged B-ions. Computer simulations of Ba(Zr₀.₅Ti₀.₅)O₃ (50:50 BZT) [24] demonstrate such behaviour; see Fig 3.

Note, however, that for any ordered phase the binding energy from the interaction term must be sufficient to overcome the cost of any positive $\kappa$. Hence the phase diagram for soft-spin versions of the models of [47] [48] would be expected to correspond to lowering the phase transition lines shown in the first two sub-figures of Fig 7 by an amount of order $\kappa$Ti, thereby yielding a phase diagram as indicated schematically in the third sub-figure[3] in qualitative accord with observations [21] [43] [45].

In the model considerations above we have ignored any possible change in the basic cubic lattice structure. This is in accord with observations for relaxors. However, in para- to ferro-electric transitions there are normally observed changes in the global average lattice structure, for example in BaTiO₃ and PbTiO₃ to a tetragonal structure. This is a consequence of inclusion of global strain coupling which we have not included explicitly; see [41]. It will affect the relative energetic preferences for the ferroelectricity and relaxor and hence transition compositions at phase boundaries separating them, but the present author believes it does not affect the conceptual principles given above for the existence of pseudo spin glasses and ex-

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Conceptually, at the simplest level, the Zr ions are analogues of the non-magnetic atoms in conventional local moment spin glasses (e.g. Cu or Au in CuMn and AuFe), although in fact they should be paraelectrically displaced a small amount by interaction with the displaced Ti ions.
experiment shows no change in global symmetry at the relaxor transition. We have also not considered the other constituent elements explicitly, only assumed inclusion of their contributions implicitly via the effective interactions between B-ions. Such extra effective interaction contributions will depend upon the ions on the A sites and is presumably at least part of the reason why BaZr$_{1-x}$Ti$_x$O$_3$ (BZT) has a relaxor phase but PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) appears not to have one; while the direct B-B interactions should be similar in both alloys, the indirect interaction via the A ions will be different, with that for A=Pb more strongly ferroelectric than that for A=Ba. In fact, both experiment [49][50] and theoretical calculations [42] show that while the Ti displacements in BaTiO$_3$ are much greater than those of the Ba ions, in PbTiO$_3$ the situation is almost inverted, the Pb displacements being greater than those of the Ti ions. Hence, in the Pb-based systems ideally one should include the Pb (and O) displacements explicitly in the Hamiltonian. However, the combination of frustration and disorder should continue to allow for the possibility of a spin-glass-like relaxor state, albeit that it may not be a preferred one in PZT.

4.2 Heterovalent relaxors

The original classic relaxor PMN is heterovalent, the B-site 4+ ions of the ABO$_3$ template being replaced by Mg 2+ ions and Nb 5+ ions in the ratio 1:2. Below we attempt to move conceptually towards a possible understanding in the light of the observations above, albeit in a discussion that is at some variance with convention.

Let us first consider in terms of the basic Hamiltonian of Eqn (12) but now with account needing to be taken of the fact that the B-ions are of different charges and hence that $J_{ij}$ depends on the particular ions at $i$ and $j$ and not simply on their separation. Allowing also for different types of A ions we shall refer to this Hamiltonian as $H^1_{AMN}$. Let us also introduce a corresponding Hamiltonian $H^1_{AM*N*}$ for a fictitious material AM*N* in which the Mg++ and Nb+++++ of AMN are replaced by fictitious ions Mg*++++ and Nb*++++ which have the same properties as Mg++ and Nb+++++ except for their charges, which are ++++ as in the standard ABO$_3$ template. We next note that Mg++ has an ionic radius similar to that of Zr++++ and hence can be expected to have a similar large $\kappa$, while Nb+++++ and Ti++++ also have similar but smaller ionic radii, suggesting similar $\kappa$ and likelihood to displace. We shall assume that the B-ion replacement is random. Consequently, one might initially expect that AM*N* would have a similar phase structure to AZT at the same relative concentrations of 1:2. This would suggest that BM*N* would be a relaxor, or close to a boundary between ferroelectric and relaxor, while PM*N* would be a ferroelectric.

Hence the observation that PMN appears to show the same sort of relaxor behaviour as BZT indicates that the difference between $H^1_{PMN}$ and $H^1_{PM*N*}$ is important in stabilising the relaxor phase in PMN. This difference is given by

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4 The absence of a global strain in the relaxor state can be attributed to the lack of an overall global moment.
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\[ H^1_{PMN} = H^1_{PM^*N^*} + V_{\text{Coulomb}}(Z_i, Z_j, R_{ij}) - V_{\text{Coulomb}}(Z^0_i, Z^0_j, R_{ij}) \]  

where \( V_{\text{Coulomb}}(Z_i, Z_j, R_{ij}) \) is the Coulomb energy associated with charges \( Z_i \) and \( Z_j \) separated by a distance \( R_{ij} \), the \( \{ Z_i \} \) are the actual charges at sites \( \{ i \} \) while \( Z^0_i \) is the charge at site \( i \) accounted for in PM\(^*\)N\(^*\) (i.e. for B-sites, \( Z^0 = 4+ \), for A-sites \( Z^0 = 2+ \) and for O-sites \( Z^0 = 2- \)), and

\[ R_{ij} = |R^0_i + u_i - R^0_j - u_j|. \]

Expanding, the perturbation component compared with PM\(^*\)N\(^*\) includes terms both linear and bilinear in the displacements [51]. The coefficients of the linear terms can be viewed as effective fields and the bilinear terms as effective extra interactions. The effective fields at any site \( i \) depend upon the types of ions on all sites \( j \neq i \). Given that the B-site interactions are (quasi-)random, so are the effective fields.

Let us concentrate now on the possible effects of including the random fields, which have been considered as driving forces for relaxor behaviour in PMN, particularly since the work of [52]; for more recent discussion see [53] [54].

Microscopically random magnetic fields are difficult to produce so there is little experiment to compare directly with in magnetic systems; rather, diluted antiferromagnets have been studied in uniform fields, emulating ferromagnets in random uniaxial \( \pm h \) fields; in the context of relaxor analogies see [55].

The problem of the statistical physics of a system controlled by the Hamiltonian of Eqn. (14) is not soluble exactly and raises many questions. One relates to whether a system with a spin-glass transition in the absence of applied fields should continue to exhibit a sharp transition in the presence of such field(s). It is accepted that the range-free SK model (with spins of any dimension) has an ergodic-non-ergodic spin glass transition even in the presence of uniform or randomly chosen local fields [56] [57] [58] [59]. On the other hand, there remains controversy about the effects of fields in short-range spin glasses, with many authors arguing that they destroy sharp spin glass transitions, on the basis of both theoretical arguments and computer simulations, but still without a clear accepted answer [60] [61] [62] [63]. Most computer simulations have been performed on Ising EA-like model systems with interactions drawn randomly from symmetric (zero-mean) distributions, whereas in the relaxor systems there are biases in the overall effective interactions, as demonstrated by the existence of ferroelectric phases in appropriate concentration regimes. Most of the simulated models have also had short-range nearest neighbour interactions or are on one-dimensional structures employed to emulate short-range systems in different dimensions.

It is generally accepted that random fields have a detrimental effect on tendencies for ferromagnetism and that for sufficient strength they suppress ferromagnetism. Thus, the effective random fields in PMN can be expected to act to reduce the ferroelectric tendency anticipated above in PM\(^*\)N\(^*\). An approximate Ising analogue of interactions in PMN has, in fact, been studied in computer simulations of Ising spins based on magnetic (Ho) sites of the diluted alloy LiHo\(_x\)Y\(_{1-x}\)F\(_4\) [64] and of an EA model with non-zero mean exchange [65], each in the presence of random fields; see
These simulations also indicate what their authors call a ‘quasi-spin-glass’ in not-too-large random fields, including the existence of parameter regions where the quasi-spin-glass is preferred to the ferromagnet in sufficient finite random fields, even though at lower random fields the opposite is the case and for higher fields the system is paramagnetic. It is tempting to wonder whether PMN might lie in such a region, hence relaxor. However, more study is needed, particularly of the transition/crossover from paramagnet to (quasi-)spin glass; currently there is no computational study indicating a sharp transition from paraelectric to relaxor, as suggested by extrapolation to zero frequency of the a.c. susceptibility observed experimentally in PMN.

![Phase diagrams](image)

Fig. 8 Phase diagrams: Computer simulations of (a) diluted Ising model based on $\text{LiHo}_x\text{Y}_{(1-x)}\text{F}_4$ plus Gaussian distributed quenched random fields of standard deviation $h$ [64] ©APS (2013) (b) n.n. EA/SS Ising model with finite mean $J_0 = 1$ and variance $J$ with Gaussian-distributed random fields of standard deviation $H_r$. [65].

We also note that computer simulational study of an Ising dipolar system on a simple cubic lattice has indicated that the sharp spin glass transition seen in zero applied field is removed in a uniform field [66]. Note, however, that random ±$h$ fields cannot be simply gauged away into a uniform field $h$ in systems with non-zero mean exchange, as they can in the usually-studied models with zero mean. Furthermore, the magnitudes of effective fields in PMN are also randomly multivalued.

It should also be recalled that the displacements in real relaxor systems are not one-dimensional, but are 3-vector. It was realised long ago that vector spin versions of the SK model in a uniform field would exhibit a spin glass transition in a transverse direction as the temperature is lowered [58], but with only weak non-ergodicity in the longitudinal direction until a lower crossover temperature [59]. It seems probable that the first of these transition temperatures will persist even for short-range interactions. It has also been observed experimentally [67]. It is also of probable relevance that the effective dipolar interaction in displacive systems is not anisotropic as in the Ising cases of Refs. [64] and [65], in which the dipoles are

5 via a study of the size dependence of the spin glass correlation length, showing no Binder crossover.
constrained to lie in the z-direction. Rather it has the more general isotropic form
\[ u_i u_j - 3 \langle \hat{R}_{ij} u_i \rangle \langle \hat{R}_{ij} u_j \rangle / |\hat{R}_{ij}|^3. \]

As already noted, others have claimed that the relaxor peak observed in PMN is driven dominantly by the random fields. A recent simulational study inspired by PMN has also indicated in favour of this, using a model similar to Eqn. with the only disorder attributed to the random field terms; i.e. with \( H_{PMN}^1 \) calculated with parameters averaged over the M and N and ignoring the extra site-interaction terms. Fig 9 shows the results obtained for the susceptibility both with and without inclusion of the random fields. Taken in combination these results are suggestive that relaxor/glass-like behaviour might be possible in the combination of frustrated interactions and disorder of either dilution or random fields. However, as yet, there is no convincing finite-size scaling demonstration of a true thermodynamic transition in the case of purely random field disorder, even when the non-disordered system has a ferro transition. There remains also uncertainty in the statistical mechanics community as to whether there can be a frozen spin glass phase driven purely by random fields without exchange frustration, although it has been proven not to be a thermodynamically stable state in a system of one-dimensional spins with only ferromagnetic (or zero) exchange interactions.

### 4.3 Polar nanoregions

Another observed feature of displacive relaxors is that of the appearance of polar nanoregions (PNRs) already at temperatures higher than those of the susceptibility peaks, beneath a higher so-called ‘Burns temperature’ characterised by the onset of deviations from Curie behaviour. A commonly expressed conceptualization is that relaxor behaviour is a consequence of interaction of such PNRs, but specific details are not clarified. Here we indicate how such PNRs and both ferroelectric and relaxor phase transitions can be expected as a consequence of a

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6 See also [54]
simple extension of the modelling above. The initial discussion will be restricted to a simple mean field consideration and, for simplicity, within a picture allowing only for one-dimensional deviations, but allowing for spatial inhomogeneity.

We start with the homovalent case. Thus we consider minimization of a Landau-type free energy

$$F_R = \sum_i \{ \tilde{\kappa}(T) u_i^2 + \tilde{\lambda}(T) u_i^4 \} - \sum_{i,j} \tilde{J}(R_{ij}, T) u_i u_j.$$  \hspace{1cm} (16)

where the coefficients are now temperature-dependent, the \( \{ u \} \) at minimum are now the mean-field values and allowance is made for different \( u \) at different sites \( i \).

Minimizing with respect to the \( \{ u_i \} \) yields the self-consistency relation

$$\tilde{\kappa}(T) u_i - \sum_j \tilde{J}(R_{ij}) u_j = -2\tilde{\lambda} u_i^3.$$  \hspace{1cm} (17)

Of particular interest are non-zero solutions and phase transitions as a consequence of reducing the \( \tilde{\kappa}(T) \) with reducing \( T \). This equation (17) always allows solutions \( \{ u = 0 \} \), corresponding to undisplaced paraelectricity, but interest is in possible solutions \( \{ u \neq 0 \} \). These only occur for small enough \( \tilde{\kappa} \).

For a pure ferroelectric all the \( u_i \) have the same value, given by

$$u = \left\{ \sum_j \tilde{J}(R_{ij}) - \tilde{\kappa}(T) / \tilde{\lambda}(T) \right\}^{1/2},$$  \hspace{1cm} (18)

from which we see that there is a critical temperature \( T_c \) given by

$$\tilde{\kappa}(T_c) = \sum_j \tilde{J}(R_{ij}, T_c).$$  \hspace{1cm} (19)

For \( T < T_c \) the system is ferroelectric whereas for \( T > T_c \) it is paraelectric.

In a general alloy, however, the solutions \( u_i \) for different sites \( i \) will vary. Eqn.(17) must have a (real) solution at each site \( i \) and, in principle, can be either localized or extended/percolating. Localized solutions would represent internally ordered nanoregions, while the onset of extended solutions would signify a phase transition. A suggestive conceptual guide to the character of such solutions can be visualized by comparing with the (linear) Anderson localization equation \[73\]

$$\varepsilon_i \psi_i + \sum_j t_{ij} \psi_j = E \psi_i.$$  \hspace{1cm} (20)

with the identifications

$$\{ \varepsilon_i \} = \{ \tilde{\kappa}_i \}; \quad \{ t_{ij} \} = -\{ \tilde{J}_{ij} \}.$$  \hspace{1cm} (21)

Fig[10] shows a schematic density of states \( \rho(E) \) for the Anderson model in a situation where the lower band edge is positive. Correspondingly the only solution to Eqn.(17) is \( u = 0 \). However, if the temperature is reduced so the mean \( \varepsilon \) is decreased
sufficiently for the lower band edge to reduce below zero, then solutions of Eqn. (17) with \( u \neq 0 \) exist. For a pure system with no \( \varepsilon \)-disorder, all the states of Eqn. (20) are extended, with the lower band edge state having the highest symmetry, resulting in a phase transition to a state of similar symmetry for Eqn. (19). This corresponds to the ferroelectric transition as found in BT, whereas in BZ, \( \kappa^{EF} \) is never small enough for $\rho(E)$ to reach $E = 0$.

However, if the Anderson model coefficients, such as the \( \varepsilon \), are disordered then states at the outer regions of $\rho(E)$ are localized, with the mapping leading to internally-correlated but not cooperatively-frozen clusters, identifiable as the observed PNRs, while for a true thermodynamic phase transition an extended state solution is required. Hence it is (crudely) suggestive that the temperature must be lowered further until the lower mobility edge, separating localized and extended states, crosses $E = 0$. This consideration suggests that lowering $T$ in the model system of Eqn. (12) will lead first to finite internally ordered nanoregions, growing in number and size as $T$ is lowered, followed by a true thermodynamic transition at a lower temperature. The onset of PNRs is expected at a temperature region close to the phase transition of the pure ferroelectric host. The cooperatively ordering phase transition is expected to be to ferroelectric at higher concentrations of ferroelectric B-ions, passing to relaxor/pseudo-spin-glass at intermediate concentrations, and failing to reach cooperative order at too low concentrations. This is illustrated schematically in Fig. 11, where the solid lines indicate phase transitions but the dotted and dashed lines are heuristic indications of onset and visibility of PNRs.

This conceptually one can view the situation in a substitutional alloy as follows: (i) quenched statistical fluctuations in the locations of the ions on the underlying lattice will lead to a range of clusterings of the more potentially displacable ions (Ti in BZT), with regions both denser and less dense than the average concentration; (ii) For clusters to displace-order internally the energy lowering gained through interaction must overcome the local free energy penalties; (iii) such internal correlation will first occur on clusters that are close in structure to the pure ferroelectric one (BT for BZT); (iv) this can always occur in principle at a temperature close to that of the pure ferroelectric, but will become rarer as the concentration of potentially ferroelectric ions reduces; (v) as the temperature is lowered the decrease in the effective $\kappa(T)$ will lead to the internal mean-field stabilization of larger clusters, until eventually there will be clusters that percolate throughout the whole system; (vi) the character of the final low temperature macroscopically cooperative state...
prediction including PNRs is in qualitative accord with experimental observations [43].

**Fig. 11**  Schematic ‘phase diagram’ for BZT expected in the light of heuristic considerations. Solid lines denote true phase transitions. The dotted line indicates the onset of PNRs in the picture discussed. The dashed line is a speculative illustration of crossover for the onset of significant visibility of PRNs.

For heterovalent alloys it is necessary also to take account of the effective random field terms in the Hamiltonian, which yield corresponding linear contributions to the mean-field free energy of Eqn. (16) and consequently terms of zero-order in the \( \{ u \} \) in Eqn. (17) and hence induced displacements even at higher temperatures; e.g. even without any interaction terms the presence of the extra charges on Mg++ and Nb+++++ ions randomly-distributed on B-sites of PMN would lead to a corresponding quasi-spherical distribution of Pb deviations from their mean-lattice positions, as discussed in [74], in qualitative accord with observations [75]. Statistical clusterings of effective fields of similar orientations can be expected to lead to nucleation of polar nanoregions, even without frustration in the site-to-site interactions. Although the suggestive quasi-mapping to the Anderson equation suggested above will no longer be applicable, the concept of relating the ‘transition’ to an ‘edge’ separating localized and extended solutions should remain qualitatively valid.

In principle one could also change description further by considering the PNR as ‘superspins’ with effective interactions between them, with eventually a percolating coherence between them marking the relaxor transition. This conceptualization was used in the context of itinerant spin glasses in the early 70’s [76] and has become popular in considerations of relaxors; for a recent discussions see e.g. [53] [77] [78] [54].

Of course, to be fully representative of even the soft-Ising-like model of Eq. (12) for a homovalent alloy, one needs to go beyond the simple mean-field form used above.

will be determined by minimizing the free energy, which in a disordered and frustrated system can be either globally periodic or spin glass-like.
5 Itinerant spin glasses

In fact, some of the suggestions above in section 4 were conceptually pre-empted many decades ago by theoretical considerations of itinerant spin glasses, in which the magnetism resides with conduction electrons [76] [79] [80]. These studies were not pursued but are probably worthy of resurrection here in the light of [44]. Again, we follow the philosophy of using a simple model and approximations for illustration.

A simple Hubbard model for a transition metal alloy is given by the Hamiltonian

$$H_{\text{HA}} = \sum_{i,j;\sigma=\uparrow,\downarrow} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \sum_{i;\sigma=\uparrow,\downarrow} V_i a_{i\sigma}^\dagger a_{i\sigma} + \sum_{i} U_i \hat{n}_i \hat{m}_i$$

(22)

where the $a,a^\dagger$ are site-labelled d-electron annihilation and creation operators, $\hat{n}_i = a_{i\sigma}^\dagger a_{i\sigma}$ and, in general, the $t_{ij}$, $V_i$ and $U_i$ depend upon the type of atoms at sites $i,j$. We are concerned with cases in which the electron density is such that the conduction band is only partially filled and the alloys are metallic.

This can be transformed into a form analogous to that of Eqn. (12) with the variables local magnetization and charge fluctuations.

We first re-write $\hat{n}_i \hat{m}_i$ in terms of complete squares using the identity

$$\hat{n}_i \hat{m}_i = \frac{1}{4} \{ \hat{n}_i^2 - \hat{m}_i^2 \}$$

(23)

where

$$\hat{n}_i = \hat{n}_i^\uparrow + \hat{n}_i^\downarrow; \quad \hat{m}_i = \hat{n}_i^\uparrow - \hat{n}_i^\downarrow.$$  

(24)

For easier conceptualization of the possible magnetic consequences, with minimal more peripheral distractions, we further simplify by assuming that the charge fluctuations are of lesser importance and take their contribution to be absorbed into the $V_i$ and furthermore set all these $V_i$ equal and hence ignorable. Further re-writing in a symmetric notation, we are left with

$$H = \sum_{i,j,\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} - \frac{1}{4} \sum_{i} U_i \hat{S}_i \hat{S}_i$$

(25)

where

$$\hat{S}_i = a_{i\sigma}^\dagger \sigma_{s,s'} a_{i\sigma'}.$$  

(26)

The quadratic form of the $\hat{S}$-term in Eqn. (25) enables the use of an ‘inverse completion of a square’ procedure [81] [82] [83] [84] [85] [86] to effectively ‘linearize’ the Hamiltonian in $a_{i\sigma}^\dagger a_{i\sigma'}$ through the introduction of an auxiliary magnetization field variable $\hat{m}$, conjugate to $\hat{S}$.

One can then further ‘integrate out’ the original electron operators in favour a description in terms purely of magnetization variables [86]. Further taking the static approximation yields an effective Hamiltonian in local magnetisation variables to

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8 Note that here the $\hat{m}$ are auxiliary field variables, not the actual equilibrium magnetizations.
fourth order,

\[ H_m = \sum_i (1 - U_i \chi_{ii}) |\hat{m}_i|^2 - \sum_{ij;i \neq j} U_i^{1/2} U_j^{1/2} \chi_{ij} \hat{m}_i \hat{m}_j - \sum_{ijkl;\alpha\beta\gamma\delta} \Pi_{ijkl}^{\alpha\beta\gamma\delta} \hat{m}_i^\alpha \hat{m}_j^\beta \hat{m}_k^\gamma \hat{m}_l^\delta, \]  

(27)

where \( \chi \) is the static band susceptibility function of the bare system (with only the \( t \) term), \( \Pi \) is a corresponding bare 4-point function and we have dropped the higher order contributions.

A further change of variables

\[ \hat{M}_i = \hat{m}_i \]  

(28)

immediately brings this to a form reminiscent of Eqn.(12): 

\[ H_M = \sum_i (U_i^{-1} - \chi_{ii}) |\hat{M}_i|^2 - \sum_{ij;i \neq j} \chi_{ij} \hat{M}_i \hat{M}_j - \sum_{ijkl;\alpha\beta\gamma\delta} \Pi_{ijkl}^{\alpha\beta\gamma\delta} \hat{M}_i^\alpha \hat{M}_j^\beta \hat{M}_k^\gamma \hat{M}_l^\delta, \]  

(29)

with local self-energy weight \((U_i^{-1} - \chi_{ii})\) the analogue of \( \kappa \) in Eqn.(12). Minimization of \( H_m \) or \( H_M \) gives the equation for the the magnetizations \( \{m\} \) in mean field approximation, the itinerant magnetic analogue of the relaxor Eqn.(17).

A simple consideration of a system with two components A and B with \( U_A = 0 \) but \( U_B > 0 \) immediately demonstrates the following well-known mean field results: (i) pure A is only paramagnetic; (ii) pure B is ferromagnetic only if \((1 - U_B \sum_j \chi_{ij}) \equiv (1 - U_B \chi(q = 0)) < 0\), the Stoner criterion [2], otherwise paramagnetic, (iii) a single B substituted in an A-host will only carry a mean-field moment if \((1 - U_B \chi_{ii}) \equiv (1 - U_B \int_q \chi(q)) < 0\), the Anderson condition [87].

For metallic systems \( \chi_{ij} \) oscillates in sign as a function of separation, so there is frustration in the effective interactions of Eqn. (29). Hence, a more concentrated alloy with a sufficient finite non-zero density of B atoms can, in principle, exhibit either ferromagnetism or another periodic order, while, beneath a critical concentration \( x_c \) and with sufficient frustration, it can exhibit spin-glass order.

If the Anderson local moment criterion is satisfied at B-sites, then the situation is essentially the same as in the conventional hard spin case discussed in Section 3.

However, if the Anderson criterion is not satisfied (equivalent to \( \kappa > 0 \)) then a sufficiently strong potential energy lowering due to coherently-acting mutual magnetization fluctuation freezing at different sites is needed to bootstrap a macroscopic magnetically ordered phase, overcoming the \((1 - U_B \chi_{ii}) |\hat{m}_i|^2\) local fluctuation penalties on a percolating network, otherwise the system would be paramagnetic. For the case of a high concentration of B this phase is still essentially Stoner’s itinerant ferromagnetism. But for an intermediate concentration of B the spontaneous cooperative phase can be a spin glass, bounded by a lower critical concentration separating it from the (Pauli-type) paramagnet and an upper critical concen-
Spin glass theory and ferroic glasses

Furthermore, the same considerations concerning the formation of PNRs as discussed for displacive ferroelectric alloys should apply to the formation of bootstrapped super-spin nano-clusters due to quenched statistical fluctuations in the locations of the B atoms, in such itinerant magnetic alloys, even above a transition temperature for spin glass or ferromagnet \[76\] \[79\]. Their ‘visibility’ would however depend on their effective dynamical lifetimes, not discussed here but surely much shorter than those for ferroelectric PNRs.

The sequence paramagnet/spin glass/ferromagnet was already observed in the early days of experimental spin glass physics; e.g. in RhCo alloys \[88\]. It seems highly probable that a similar phenomenological explanation should apply in other metallic spin glass alloys, especially those labelled as ‘cluster glasses’, and it could prove interesting to review them in this light. A full theoretical treatment would require going beyond the simple mean-field theory presented above, as well as beyond the other simplifying assumptions employed above, but hopefully it could already provide a useful starting perspective complementary to those currently employed.

6 Strain glass

In this section we consider another analogue of spin glasses, of glassy strain distortions in martensitic alloys \[19\] \[89\] \[27\] \[90\] and given the name ‘strain glass’.

Martensitic materials, see e.g. \[91\] \[92\], exhibit first-order structural transitions from higher to lower symmetry phases as temperature is lowered. An example is from high temperature cubic austenite to a lower temperature phase of alternating twin planes of complementary tetragonal character, epitomized by TiNi which in its pure higher-temperature state is an ordered compound of rocksalt structure. Our interest here will be particularly in when this compound is atomically disordered, for example by randomly altering the balance of Ti and Ni or by replacing some of these atoms by another element (e.g. Fe).

Although, in principle, it could be modelled microscopically in terms of atomic displacements, as was done for relaxor problem of section 4 or phenomenologically at a Landau-Ginsburg level in terms of continuous-valued deviatoric strains, here we shall simply employ a crude discrete pseudo-spin mean-field modelling for illustration. Furthermore, again for simplicity, we shall consider a two-dimensional version in which the local cell structure is describable in terms of a variable \(S_i\) which takes the values 0, +/-1 corresponding respectively to a square and two orthogonal rectangular structures. The local part of an effective free energy is then given by

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9 Using a different formulation than presented here.
10 These early papers discussed the formation of clusters and anticipated that their interactions would then yield the spin glass state, much as in later considerations of relaxors.
\[ F_L = \sum_i D_i S_i^2 \]  

(30)

where the \( \{i\} \) label cells, so that if \( D_i > 0 \) then minimizing \( F_L \) yields \( S_i = 0 \), while if \( D_i < 0 \) it yields degeneracy \( S_i = \pm 1 \). There are also intercell interaction terms

\[ F_{\text{int}} = -\sum_{ij} S_i V_{ij} S_j \]  

(31)

arising from both short-range neighbouring similarity effects and from longer range St. Venant’s compatibility constraints that give (in 2 dimensions)

\[ V_{ij}^{SVV} \propto -\cos(4\theta(\mathbf{R}_{ij}))/|\mathbf{R}_{ij}|^2 \]  

(32)

where \( \theta(\mathbf{R}) \) is the angle subtended by \( \mathbf{R} \) at a Cartesian axis of the cubic lattice.

Temperature is emulated by taking the \( D \) to be temperature dependent, reducing with reducing temperature. Without the interaction term the \( S \)-values at the minimum of the free energy will change from \( S = 0 \) to \( S = \pm 1 \) when their corresponding \( D \) change from positive to negative. When the interaction is included cooperative bootstrapping will result in \( S = \pm 1 \) at sites where the resultant free energy minimization can overcome the local \( D \), with the favoured state given by the relative signs of the \( \{S_i\} \) that yield the lowest free energy. For a pure system one gets the martensite phase of diagonally alternating stripes of \( S = +1 \) and \( S = -1 \). For a system with quenched randomness of site occupation one can expect a corresponding quenched randomness of the \( \{D_i\} \), along with quenched effective random fields.

Clearly this represents a scenario similar to that discussed above for relaxors and spin glasses, namely that for sufficient quenched disorder the frustration, arising from the antiferroelastic interactions at values of \( \theta \) where the cosine is negative, leads to an expectation of strain glass, as has been observed \cite{94} \cite{95}; see Fig. 12. Both the cases of quenched \( D \) \cite{89} and of the effective random fields \cite{96}, arising from local substitutions, have been proposed separately as the disorders responsible strain glass behaviour. The reality probably includes both.

### 7 Conclusion

In this chapter I have tried to demonstrate similarities in the potential for ferroic glass behaviour in several different types of system, magnetic, ferroelectric and martensitic/ferroelastic alloys, both metallic and insulating, using a combination of simple modelling and analogies, experimental, theoretical/mathematical, computational and conceptual, and with a particular consideration of ‘induced moment’ and continuously displaceable systems.

The key ingredients to permit such glassy behaviour appear to be frustrated interactions and quenched disorder, as has often been expressed before. Probing these

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\[11\] In this case the analogue of the ferromagnet is the martensitic stripe phase.
Spin glass theory and ferroic glasses

Fig. 12 $Ni_{50-x}Ti_{50+x}:$ (a) FC/ZFC evidence for strain glass \[94\] ©APS (2007) (b) Phase diagram \[95\] ©APS (2010)

relationships has provided possible explanations for phenomena such as the onset of non-ergodicity and slow dynamics. Cluster effects such as those known as polar nano-regions (PNR) in displacive relaxors are considered in analogy with localization phenomena.

The simple analogies considered here suggest further conceptual transfers between different ferroic materials and further experimental investigations; for further discussion concerning characteristic experimental aspects of spin glasses see \[97\]; for a complementary recent discussion of relaxors see \[54\].

These comparisons have also highlighted some remaining questions, particularly concerning the issue of the role of quenched random fields. BZT has no quenched random fields but PMN has significant such fields, yet the susceptibility measurements look very similar to one another.

As noted earlier, there is controversy in the spin glass community as to whether a true spin glass phase transition can continue to exist in the presence of an applied field. Even without a non-analyticity it would not necessarily mean that the peak in the pure zero-field susceptibility cannot continue in a finite-field, in a more rounded form, as indeed was clear already in the early important small-field experiments of Cannella and Mydosh \[5\]; see Fig 2(b). There has been much interest in the random field Ising model (RFIM), normally with short-range ferromagnetic interactions, without demonstration of a spin glass, and indeed it has been proven not to be thermodynamically stable for purely ferromagnetic or zero interactions \[69\]. There have been theoretical suggestions that in a system with higher spin dimension there could be a ‘spin glass’ state driven by the random fields \[98\] but there has been no observed evidence of a sharp transition to such a phase in a magnetic system.

Although there have been many experimental demonstrations of spin glass behaviour in frustrated and quench-disordered 3-dimensional systems of 3-dimensional (Heisenberg) spins, there is still some debate about theory \[15\]. There are no simple experimental methods to apply three-dimensional random magnetic fields On the
other hand, the relaxor systems discussed above have displacement variables able to orient in the full 3-dimensional space and in heterovalent relaxor alloys, such as PMN, the effective random fields are also spread throughout the 3-dimensional orientation space and are of significant strength, yet the peaks in the susceptibility are quite sharp. Both the classic spin glass and the relaxor examples have long range interaction frustration.

It is thus tempting to wonder whether the criterion of frustrated interaction and quenched disorder as the key ingredients for spin glass/relaxor/strain glass behaviour might apply independently whether the disorder arises from site-disorder, bond-disorder or random fields, or a combination, preventing simple homogenous and smoothly varying optimal compromises, and also whether one needs to go beyond one-dimensionality of the ‘pseudospins’, but more work is required to help decide.

Finally, let me note that my aim has not been to describe quantitavely or completely the systems that I have discussed, but rather through simple extraction and comparisons, to try to draw links and to expose contrasts and remaining puzzles and uncertainties, in the hope that they might stimulate work that might not have been obvious within the confines of just sub-classes of systems. I should also point out that I am not the first to propose that either relaxors or martensitic alloys might be considered as pseudo-spin glasses (see e.g. [99] [100] [101]), but I hope my small contribution can be stimulating in moving towards a greater understanding.

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