Materials Physics and Spin Glasses ‡

David Sherrington

Rudolf Peierls Centre for Theoretical Physics, Clarendon Laboratory, Parks Rd., Oxford OX1 3PU, UK
Santa Fe Institute, 1304 Hyde Park Rd., Santa Fe, NM 87501, USA

E-mail: david.sherrington@physics.ox.ac.uk

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Abstract.

Comparisons and analogies are drawn between materials ferroic glasses and conventional spin glasses, in terms of both experiment and theoretical modelling, with inter-system conceptual transfers leading to suggestions of further issues to investigate.

1. Introduction

The original physical systems that led to the designation 'spin glass' were substitutional alloys of non-magnetic and magnetic metals, such as **Au**Fe and **Cu**Mn, which exhibited unusual features at low temperatures [1].

The challenge to understand them led to the recognition of a need for and the formulation of new statistical physics, new concepts and new methodology, particularly driven by the concept of replica symmetry breaking and its sophisticated formulation and physical understanding by Giorgio Parisi [2, 3]. This theoretical study, in turn, has stimulated extensions of conceptualization, mathematical formulation and practical application in many other areas of many body physics, probablity theory, computer science, biology and econophysics [4, 5], typically characterized by frustrated interactions and quenched (or slower evolving) disorder. It continues to lead to new advances, often in areas which were not anticipated when the original materials were studied and typically in situations where the systems and their interacting microscopic actors are physically different from those in the original metallic alloys. These theoretical extensions and extrapolations have had both fundamental and practical importance.

However, the original spin glass materials themselves have their onset phase transitions at rather low temperatures and have not had practical application. The purpose of this brief paper is to highlight some other material systems, some of which were discovered decades ago to have interesting and applicable characteristics yet lack a

‡ This paper is dedicated to Giorgio Parisi in celebration of his 70th birthday, in appreciation of his enormously innovative and influential contributions to science and its leadership and in gratitude for his friendship.

generally agreed understanding, and to argue that they are essentially soft pseudo-spin glasses [6] that also pose some conceptual issues for statistical physics theory.

2. Relaxors

The first class of systems that I wish to note are the so-called 'relaxors', site-disordered displacive ferroelectrics [7, 8] which experimentally exhibit peaks in their measured dielectric susceptibilities with significant frequency-dependence, very reminiscent of the behaviour of the magnetic susceptibility of conventional spin glasses near their transition temperatures; illustrated in Fig 1. Also like in spin glasses, in the absence of driving fields there is no global polarization. In consequence of these similarities, it is natural to look for similar conceptual origins [13, 14]. I shall argue that there are indeed such similarities but also that their consideration poses further issues and questions for statistical physics.

In fact, however, studies of relaxors and of spin glasses have evolved independently and have largely remained so. The observations illustrated in Fig 1(i) date from the 1950s [10], long before the observation of the sharpening of a cusp-like peak in the low-field susceptibility of **Au**Fe by Cannella and Mydosh [15] sparked the theoretical explosion of interest in spin glasses.

Spin glasses have received much study, both experimental and theoretical and are considered largely understood, albeit with some remaining controversies concerning issues such as the existence or otherwise of 'replica-symmetry-breaking' and of true spin-glass phase transitions in external fields and in systems of finite dimensions; the case of spin glasses with range-free interactions [16] is considered solved [4, 17]. It is generally recognised that the key ingredients for spin glass behaviour are frustrated interactions and effectively quenched disorder. However, the mechanism and essential ingredients for relaxor behaviour remain incompletely understood and disputed (*e.g.*[18]).

The topic of relaxors has been pursued mainly by experimentalists, including considerations of applicable materials design, and a smaller number of theorists mainly concerned with understanding and demonstrating experimental observations via (classical) computer simulations of the finite-temperature behaviour, involving many parameters calculated using realistically full (quantum) first-principles evaluation of model parameters. In contrast, in spin glasses the theoretical interest has been more in studying minimal models to understand the basic physics of the spin glass state, the character and implications of its unconventional features, the fundamental conditions for the existence of true spin glass transitions, and generalizations and applications of the discovered subtle concepts and novel mathematical methods, mostly in topics far beyond the materials that first stimulated their study. Here my intent is to consider displacive relaxors from a similar minimal conceptual viewpoint and to relate to issues of possible potential interest to spin glass theorists, through observations and analogies rather than detailed calculations.

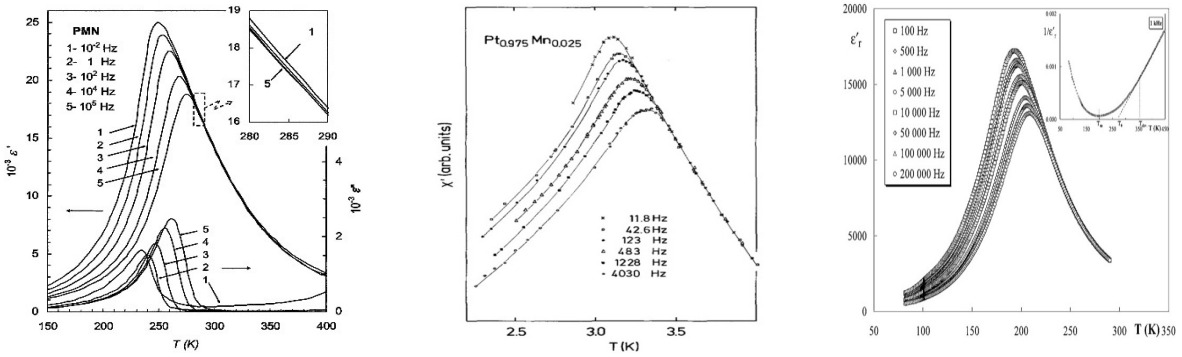

Figure 1: AC susceptibilities;(i) heterovalent relaxor $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) [9] ©Springer (2006) [10], (ii) spin glass **Pt**Mn [11] ©Springer (1983), (iii) homovalent relaxor $BaZr_{0.35}Ti_{0.65}O_3$ (BZT) [12] ©IOPP (2004) .

2.1. Displacive ferroelectrics

Displacive ferroelectrics are ionic crystals which undergo ion-displacive phase transitions from higher-temperature high-symmetry structures without any global electric moments to lower-temperature phases of lower-symmetry with different intracell displacements of ions of opposite signs, leading to overall electric dipolar moments. This is illustrated in Fig 2(left) for $PbTiO_3$, which at higher temperature has the classic (cubic) perovskite structure and formula ABO_3 with nominal charges A^{++}, B^{++++} and O^{--}, distorting as temperature is lowered beneath a critical temperature to a tetragonal structure with the ions also internally displaced relatively to one another so as to yield a ferroelectric moment, as further illustrated in Fig 2(right) for $PbTiO_3$ [19] and $BaTiO_3$ [20].

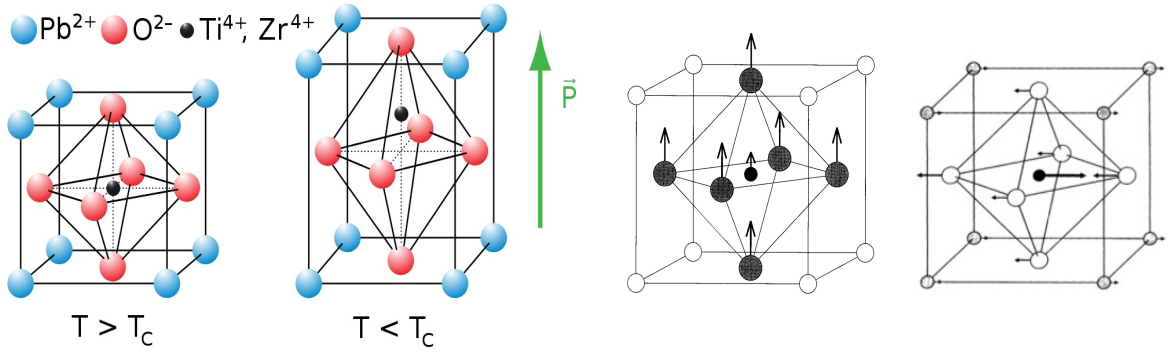

Figure 2: Left half: Unit cell structure of $PbTiO_3$ above and below the ferroelectric transition temperature. Right half: Relative ionic displacements in tetragonal (left) $PbTiO_3$ [19] and (right) $BaTiO_3$ [20].

Modelling involves taking account of both cellular strain and intra-cell relative displacements of the different ions [21, 22].

2.2. Displacive relaxors

All three examples of Fig 1 involve the combination of (i) pairwise interactions that involve mutual frustration/competition but are essentially lattice-periodic and (ii) quenched atomic-type disorder that works against a simple compromise of periodic magnetic or displacive order. In the spin glass of Fig 1(ii) the relevant microscopic variables are the orientations of local moments/fixed-length spins (on the **Mn**), subject to long-range oscillatory/frustrated Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions, $J\cos(2k_F R)/R^3$. In the two relaxor examples the relevant microscopic entities are continuously-valued and oriented displacements of ions from their positions in an ideal perovskite structure, essentially soft *pseudo*-spins, interacting via a combination of shortish-range quantum mechanical effects and long-range Coulomb/dipolar interactions. In all the examples the quenched disorder arises from the different types of atoms/ions occupying the nominal lattice sites.

Just as spin glasses have no overall global magnetization, displacive relaxors have no global lattice structure change, remaining cubic as the temperture is reduced through the transition from paraelectric.

The original and most famous displacive relaxor of Fig 1(i) is the heterovalent alloy $PbMg_{1/3}Nb_{2/3}O_3$, commonly known as PMN, in which the Ti^{++++} ions of $PbTiO_3$ (coloured black in Fig 2) are replaced randomly and heterovalently by Mg^{++} and Nb^{+++++} in the ratio 1:2, thereby introducing disorder in the site occupation, the local restoring forces and the effective interactions driving correlations between the displacements at different sites, along with effective random fields.

2.3. Homovalent relaxor alloys

In considering the modelling of relaxors it is, however, easier (from a spin glass theory perspective) to start with the (more recently discovered [23] homovalent alloy $BaZr_xTi_{1-x}O_3$ (BZT), an alloy of $BaTiO_3$ and $BaZrO_3$ in which Ti^{++++} and Zr^{++++} ions are randomly placed on the B-sites of the ABO_3 structure; Fig 1(iii) refers to an example with $x = 0.35$.

Because the Ti and Zr ions are of the same charge (4+), to a first approximation there are no consequential extra charges or fields and the intersite Coulomb interactions are relatively unaltered. However, there is still important site disorder, with the Ti and Zr ions having different local displacement-energy coefficients. That for the term quadratic in the displacement of Ti ions is positive but small enough that energy reduction due to interaction bootstrapping is sufficient so that $BaTiO_3$ is a ferroelectric at low enough temperature, with coherent spontaneous ionic displacements from pure perovskite. In contrast, the local harmonic restoring coefficient of Zr ions is too great for $BaZrO_3$ to be able to bootstrap ferroelectricity via interaction gains. Hence, in BZT the Zr ions are essentially analogues of the non-magnetic constituents in normal spin glass alloys, with relaxor (or ferroelectric) behaviour arising from the Ti.

Because experiment has shown that relaxors do not exhibit average cell strain, it

is reasonable to ignore the strain terms and express the Hamiltonian for a homovalent relaxor alloy in terms only of the local displacements of ions from their positions in the perfect perovskite, as

$$H = \sum_i \{\kappa_i |\boldsymbol{u}_i|^2 + \lambda_i |\boldsymbol{u}_i|^4 + \gamma_i (u_{ix}^2 u_{iy}^2 + u_{iy}^2 u_{iz}^2 + u_{iz}^2 u_{ix}^2)\} - \sum_{(ij)} \sum_{\alpha\beta} J^{\alpha\beta}(R_{ij}) u_{i\alpha} u_{j\beta}, \quad (1)$$

where the $\{\boldsymbol{u}_i\}$ are the displacements and the coefficients $\{\kappa_i$, λ_i and $\gamma_i\}$ depend on the types of ions at the corresponding sites $\{i\}$. The interaction term is frustrated, with both short-range exchange and long-range frustrated Coulomb/dipole contributions, the latter going as

$$H_{dip} = \sum_{(ij)} (Z_i Z_j/\epsilon)[\mathbf{u}_i.\mathbf{u}_j - 3(\hat{\mathbf{R}}_{ij}.\mathbf{u}_i)(\hat{\mathbf{R}}_{ij}.\mathbf{u}_j)]/|\mathbf{R}_{ij}|^3. \quad (2)$$

There is an immediately apparent analogy with a continuous spin-length (soft) version of the Hamiltonian for a conventional classical Heisenberg spin-glass

$$H = \sum_{occupied\, sites} \{\kappa |\boldsymbol{\phi}|_i^2 + \lambda |\boldsymbol{\phi}_i|^4\} - \sum_{ij} J(R_{ij}) \boldsymbol{\phi}_i.\boldsymbol{\phi}_j, \quad (3)$$

where the usual hard-spin S limit results from

$$\kappa \to -\infty, \lambda \to \infty, \kappa/2\lambda \to -S^2. \quad (4)$$

However, by contrast, in the displacive perovskites of interest the κ are positive, so an isolated ion $i = 0$ in an otherwise pinned structure $\{\phi_{j\neq 0} = 0\}$ would not displace (no local moment). For macroscopic ferroic order at sites with positive κ the bootstrapped energy gain from interactions needs to be sufficient to overcome the local displacement cost, resulting in *'induced moments'* on the relevant sites. In the case of $BaTiO_3$, the $\kappa_{\rm Ti}$ is smaller than the critical (maximum) value for spontaneous coherent ferroelectric order, while for $BaZrO_3$ $\kappa_{\rm Zr}$ is too great and there is no ferroic order. In consequence one can deduce that any order on B-sites in BZT is driven by the Ti ions. Also, in $BaTiO_3$ it is observed that of the positive ion displacements those of the Ti are dominant. Hence, in minimalist modelling, it is natural to concentrate on the Ti ions.

Monte Carlo simulations [24] of a model of $BaZr_xTi_{1-x}O_3$ at $x = 0.5$, allowing for explicitly different local coefficients κ for Ti and Zr but only averaged interactions $J(R)$, have demonstrated a 'critical' temperature marking a peak in the quasi-ZFC susceptibility, evaluated from correlations using the fluctuation-dissipation relationship, together with the onset of a separation from the directly measured FC susceptibility, reminiscent of the corresponding behaviour in conventional spin glasses. Later molecular dynamics simulations [25] have yielded frequency-dependent susceptibility peaks similar to those measured experimentally and displayed in Fig 1(iii).

To the best knowledge of the present author, sophisticated studies of critical transitions via finite-size scaling of spin-glass correlation lengths, now-standard in spin glass simulations, have not yet been published for homovalent relaxors [26], although the conceptually analogous (but spin-length-discretized) Ghatak-Sherrington model [27]

$$H = \sum_i D S_i^2 - \sum_{(ij)} J_{ij} S_i S_j; \; S = 0, \pm 1; \; \text{quenched random } \{J_{ij}\} \quad (5)$$

has been studied by such methods [28], demonstrating the induced moment spin-glass phase for small positive D (the analogue of small positive κ) .

2.4. Heterovalent relaxor alloys

Turning to the heterogenous case of PMN ($PbMg_{1/3}Nb_{2/3}O_3$), one way of modelling, through extension from the spin glass perpective of homovalent relaxors discussed above, is to consider it as a fictitious alloy $PbMg^*_{1/3}Nb^*_{2/3}O_3$, where Mg* and Nb* are fictitious ions with charges +4 but with all other model-relevant properties the same as those for Mg^{++} and Nb^{+++++}, along with extra charges -2 at Mg positions and +1 at Nb positions [29]. Noting that the ionic radius of Mg^{++} (86 pm.) is the same as that of Zr^{++++} (86 pm.) and the ionic radius of Nb^{+++++} (78 pm.) is close to that of Ti^{++++} (74.5 pm.) [30], one might expect that $PbMg^*_{1/3}Nb^*_{2/3}O_3$ should behave like PZT ($PbZr_xTi_{1-x}O_3$) with $x = 1/3$.

Given that BZT is a relaxor one might further naïvely anticipate that PZT might also be a relaxor, but this has not been observed, probably because Pb is much softer than Ba, as is observed in differences between the magnitudes of their displacements in the ferromagnetic phases of $PbTiO_3$ and $BaTiO_3$ [31, 32] and as suggested by the differences in the ionic radii of Pb^{++} (133 pm.) and Ba^{++} (149 pm.).

Hence, one may deduce that $PbMg^*_{1/3}Nb^*_{2/3}O_3$ alone would probably not have a relaxor phase. So that leaves the likelihood that the random fields due the extra charges -2 (on Mg sites) and +1 (on the Nb sites) are also needed to explain the relaxor behaviour of PMN, as was proposed in [33]. Given that there is a common belief in the spin glass community that fields destroy spin glass transitions, this qualitative comparison already indicates an intriguing situation for statistical physics.

PMN has also been simulated [34], using a model with the dominant displacements on the Pb ions [35] and a simply-averaged virtual-crystal interaction function, both (i) without and (ii) with random fields due to the different extra effective charges on the Mg^{++} and Nb^{+++++} B-ions. In case (i) this demonstrated the sharp susceptibility peak expected of a ferroelectric, while case (ii) exhibited instead a more rounded peak at a lower temperature, interpreted as a relaxor peak and suggesting that random fields alone, without interaction disorder, might be capable of driving relaxor behaviour in a system with frustrated interactions, although a more sophisticated simulational study would be required to be convincing of a true transition.

2.5. Hard or soft (pseudo)spins.

As noted above, these relaxor ferroelectrics have positive (and usually small) values of κ. Hence they can be considered as having 'soft' (pseudo) spins, that require cooperative behaviour to become significant, in contrast to most systems conventionally studied in statistical physics, where the spins are normally considered as 'hard', so their phase transitions differ analagously to those of BCS (soft) and BEC (hard) Bose condensation,

while both are type II in the notation of [36]. There exist other hard dipolar and higher-moment analogues of hard-spin spin glasses (*e.g.* [37]), but they are not pursued here.

3. Strain Glass

Another set of material systems relevant to spin glass/random field conceptualization are quenched disordered variants of the 'shape-memory alloy' Nitonol (NiTi), such as $Ni_{0.5+x}Ti_{0.5-x}$ and $Ti_{0.5}Ni_{0.5-x}Fe_x$, which have recently been observed to exhibit distortive pseudo-spin glass behaviour for sufficient x [38, 39]. Pure NiTi itself is a metallic compound which at higher temperature is of simple cubic rocksalt (NaCl) structure, known as austenite, but which, as temperature is lowered, undergoes a first-order distortive transition to a twinned phase of stripes of local cells of differently oriented tetragonal symmetry, known as martensite. Martensite can be thought of as the elastic analogue of periodic ferro- or antiferro-magnetic order in magnetic systems, arising as a best compromise in a system with periodic but frustrated interactions but no quenched disorder. Disorderly alloying, for example randomly replacing some Ti with extra Ni or of some Ni by Fe, can lead to the above-mentioned pseudo-spin-glass, now known as *'strain glass'* [38, 39, 40].

A relationship with spin glass conceptualization is easily visualized by using simple Ginzburg-Landau phenomenological modelling in terms of deviatoric strains. For illustrative simplicity we consider a two-dimensional model where the local transition is from square to rectangle, characterized by the deviatoric strain $\phi = (\epsilon_{11} - \epsilon_{22})$, the $\epsilon_{\alpha\beta}$ being normal strain tensors. The local contribution to the free energy can then be modelled as

$$F_L = \sum_i [A_i(T){\phi_i}^2 + B_i(T){\phi_i}^4 + C_i(T){\phi_i}^4], \tag{6}$$

where the {i} label local cells. There are also effective site-to-site interactions

$$F_I = -\sum_{(ij)} J(\mathbf{R}_{ij})\phi_i\phi_j \tag{7}$$

where $J(\mathbf{R})$ includes both the usual short-range ferro contribution and a long-range term arising from the application of St. Venants constraints on the strains [41], of the form

$$J_{SV}(\mathbf{R}_{ij}) \sim f(\cos 4\theta_{ij})/|\mathbf{R}_{ij}|^2 \tag{8}$$

where θ_{ij} is the angle subtended by $\mathbf{R}_{ij}$ in the Cartesian coordinate frame of the lattice. This interaction is frustrated, with both positive and negative contributions as a function of $\cos 4\theta$.

In a pure system, such as NiTi itself, there is no disorder among the local coefficients and the transition between austenite and martensite occurs when the temperature is lowered until A(T) is reduced (from a positive value) sufficiently until the lowest free energy occurs at a finite $|\phi|$. However, in the case of local disorder in the A_i, combined

with (even periodic) frustration in the interactions, there arises the possibility of a spin-glass-like distortion in preference to the normal martensitic stripes [42].

Noting that the austenite-martensite transition is observed as first order, it follows that B in eqn.(6) must be negative, C positive. It is thus natural to simplify further to a discrete formulation

$$F = \sum_i D_i(T) S_i^2 - \sum_{(ij)} J(\mathbf{R}_{ij}) S_i S_j; \;\; S = 0, \pm 1, \tag{9}$$

where $S = 0$ corresponds to a locally cubic cell and $S = \pm 1$ correspond to the two possible orthogonal rectangular cells. With quenched disorder in the $\{D_i\}$ this yields a random site variant of the GS model (5) and so can be expected to exhibit a spin glass phase for sufficient disorder as the mean D is reduced [43].

In the real alloys, one can anticipate that changes in chemical enviroments and point defects would introduce also random local terms linear in ϕ (or S), alias random fields. Indeed, in the context of the earlier discussion of relaxors, it is interesting to note that phase-field computer simulations of a model martensitic alloy including disorder purely of random field character, but not random A, have been performed and argued to show the same sequence of phase transitions, austenite-martensite to austenite-strain glass as the quenched disorder is increased [44], as is expected from the case of purely random A. Thus, this appears to suggest again that random field disorder, in combination with long-range frustrated interactions but without site dilution or interaction disorder, may also be able to lead to a quasi-spin glass.

4. Coulomb Glass

Another situation where spin glass-like behaviour driven by random field disorder has been proposed is in the Coulomb Glass problem [45],

$$H = \frac{e^2}{4\pi\epsilon_0} \sum_{(ij)} (n_i - \nu) \frac{1}{|\mathbf{r}_{ij}|} (n_j - \nu) + \sum_i n_i \varepsilon_i, \tag{10}$$

where the $\{n_i = 0, 1\}$ are electron site occupations, ν is the filling factor and the $\{\varepsilon_i\}$ are quenched random local site energies, which for half-filling can be expressed in pseudo-spin notation as an Ising model with long-range pairwise antiferromagnetic Coulomb interactions, dependent only on the separation, along with quenched random local fields [46];

$$H = A \sum_{(ij)} \sigma_i \sigma_j / |\mathbf{r}_{ij}| + \sum_i h_i \sigma_i; \;\; \sigma = \pm 1; \;\; P(h) = P(-h). \tag{11}$$

Analytic studies have demonstrated mean-field similarity to the SK spin glass and predicted a sharp phase transition to a spin-glass like phase above a critical disorder [47, 46]. A recent computer simulation of this case [48] using modern sophisticated scaling tests has demonstrated a sharp transition from plasma/paramagnet to a Coulomb Glass state as temperature is reduced, beyond a sufficient strength of quenched randomness.

Given that the antiferromagnetic Coulomb interaction is frustrated, as are the interactions in the perovskite ferroelectrics above (eqn.(2)) and the martensitic alloys (eqn.(7)), this observation gives extra weight to a speculation that in a system with appropriate frustrated (but not necessarily random) interactions the addition of quenched disorder through sufficiently potent local random fields alone could induce a spin-glass/relaxor phase. What is 'appropriate' is less clear; however, all these examples have interactions that have no cut-off and decay only as powers of $1/R$.

Beneath the critical disorder strength the low temperature phase of the Coulomb Glass problem is a periodic one, known as 'charge-ordered' in reference to its character in the original electron occupation basis. It has its analogue in the perovskite displacement problem in the ferroelectric phase found at levels of quenched disorder beneath a critical value; albeit that strain coupling and global lattice change also contribute to the free energy, while for $\kappa > 0$ sufficient potential binding energy is also needed to bootstrap moments at all.

5. Polar nanoregions, tweed and cluster glasses

5.1. Relaxors

A concept regularly employed in discussions on relaxor ferroelectrics is of so-called polar nanoregions (PNRs), clusters of short-range correlated dipolar moments, onsetting well above the temperature of the relaxor susceptibility peaks and growing as temperature is lowered towards the transition [7, 49]. Conceptually these can be expected as arising from statistical clusterings of ion placements in the nominal lattice, leading to a distribution of local displacement correlation strengths, with stronger regions visible to probes of appropriate timescales, as long as their temperature-dependant lifetimes are sufficient.

A proper modelling of PNRs should involve a dynamical treatment, but as a simple guide/illustration one might consider a crude (but inhomogeneous) mean-field free-energy analogue of the homovalent BZT model introduced above, eqn.(1), for simplicity considering only one-dimentional displacements:

$$F(T) = \sum_i \{\kappa(T) < u_i >^2 + \lambda_i(T) < u_i >^4\} - \sum_{(ij)} J(R_{ij}, T) < u_i >< u_j >, \quad (12)$$

where the $\{< u_i >\}$ represent effective local-moment averages of the $\{u_i\}$. Minimising with respect to the $\{< u_i >\}$ yields the self-consistency equation

$$\kappa_i(T) < u_i > - \sum_{j \neq i} J(R_{ij}, T) < u_j >= -2\lambda_i(T) < u_i >^3 . \quad (13)$$

Clearly, there are always solutions $\{< u >= 0\}$. However, for the $\{\lambda\}$ positive, comparison with the eigenequation

$$\kappa_i(T) v_i - \sum_{j \neq i} J(R_{ij}, T) v_j = E v_i \quad (14)$$

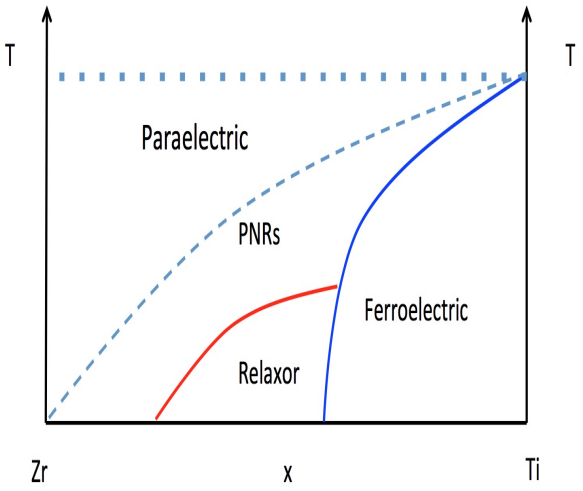

Figure 3: Schematic 'phase diagram' for BZT expected in the light of heuristic considerations; from [50]. Solid lines denote true phase transitions. The dotted line indicates the onset of PNRs in the picture discussed. The dashed line is a speculative illustration of crossover for the onset of significant visibility of PRNs.

suggests that solutions of eqn.(13) with $< u > \neq 0$ require that $A_{ij} \equiv \{\kappa_i(T)\delta_{ij} - J(R_{ij}, T)\}$ has negative eigenvalues. The most relevant T-dependence is anticipated for the $\{\kappa(T)\}$ which are expected to increase as T increases, so that at high temperature the system is paraelectric, but with temperature reduction allowing for a lower value yielding an ordered phase if sufficient.

For the pure case (all κ equal) all these eigenfunctions are extended, with the ferroelectric phase transition signalled by the band edge reaching $E = 0$ as T is reduced. However, for a system with quenched disorder it can be anticipated that the solutions of eqn. (14) near the band edge will have finite lifetimes, unstable against fluctuations and effectively localized, with the true phase transition delayed until a lower temperature, depending on the degree of quenched disorder (*c.f.* localization edge).

Note that this argument for finite-lifetime short-range correlated clusters above a true phase transition extends to (disordered) alloys with either spin-glass-like or quasi-periodic ordered phases, with the upper temperature limit of PNRs of the order of the ferroelectric transition of the more ferroelectric pure state (*c.f.* Griffiths phases [51]). Thus for homovalent alloys one might expect a phase diagram of the schematic form of Fig.3.

For heterovalent alloys account must also be taken of the random fields, so that extra terms of the form $\sum_i \boldsymbol{h}_i.\boldsymbol{u}_i$ are needed in the Hamiltonian and consequently in an effective mean-field theory. Also, as noted earlier, it appears from experiment that the most important positive ions with regard to displacements in Pb systems are the A-site ions rather than the B-site ones on which the extra charges reside. Even without the interaction effects integral to B-site ion-type disorder of PM*N* the extra random charges on the B-sites of PMN would lead to effective random fields on the Pb ions such as to lead to corresponding thermodynamically weighted random displacements of the Pb ions from their sites in the pure perovskite [29], extending even to high temperatures. Thus, different behaviour can be anticipated for the temperature extent of PNRs in homogeneous and heterogeneous alloys.

It should be noted, however, that there remains disagreement among practitioners on the character and origin of PNRs, in both homovalent and heterovalent relaxor systems.

5.2. Martensitic alloys

In the case of martensitic materials, already for many years a pre-martensitic 'phase' exhibiting intermixed domains of different martensitic orientations and of austenite, known as *'tweed',* was observed for a range of temperatures above the transition to the martensitic striped phase. It has now been interpreted as an analogue of the region of still-para behaviour with PNRs above the phase transition (be it to ferroelectric/martensite or relaxor/strain glass), as discussed above for ferroelectric alloys [52, 53].

5.3. Itinerant cluster glasses

Most statistical physics studies of magnetism consider local moment spins of discrete length. However, it has been known for a long time [54] that one can have itinerant ferromagnetism induced due to collective behaviour of conduction electrons in transition metals [55]. Already in the 1970s, this concept was extended to an itinerant analogue of local moment spin glasses [56, 57, 58], but these papers have not received much further consideration (but see *e.g.* [59]).

Theoretical modelling of disordered transition metal alloy magnetism can be expressed so as to lead to close analogy with the discussion of relaxors presented above [56, 60]. Let us start with a simple random Hubbard model for a transition-metal alloy of two metals, A and B, of different on-site Coulomb repulsion strengths;

$$H_{HA} = \sum_{ij;s=\uparrow,\downarrow} t_{ij} a^{\dagger}_{is} a_{js} + \sum_{i;s=\uparrow,\downarrow} V_i a^{\dagger}_{is} a_{is} + \sum_i U_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}, \tag{15}$$

where the $a, a^{\dagger}$ are site-labelled d-electron annihilation and creation operators, $\hat{n}_{is} = a^{\dagger}_{is} a_{is}$, and in general the t_{ij}, V_i and U_i depend upon the type of atoms at sites *i,j.* Re-writing in terms of complete squares of local magnetization and charge fluctuation operators, concentrating on the spin fluctuations and, for conceptual simplicity, absorbing effects of charge fluctuations approximately into average hopping and local terms, we consider as a minimal electronic model

$$H = \sum_{ij,s=\uparrow,\downarrow} t_{ij} a^{\dagger}_{is} a_{js} - \frac{1}{4} \sum_i U_i \boldsymbol{S}_i . \boldsymbol{S}_i \tag{16}$$

where

$$\boldsymbol{S}_i = \sum_{s=\uparrow,\downarrow} a^{\dagger}_{is} \boldsymbol{\sigma}_{s,s'} a_{is'}. \tag{17}$$

Using a Lagrangian functional integral many-body formulation an 'inverse completion of a square' procedure [61] may be employed to effectively linearize the Hamiltonian in $a^{\dagger}_{is} a_{js'}$ through the introduction of an auxiliary magnetization

field variable $\boldsymbol{m}$, conjugate to $\boldsymbol{S}$ [62]. One can then further 'integrate out' the original electron operators in favour of a description in terms purely of auxiliary magnetization variables. Further taking the static approximation yields an effective free energy functional in local magnetization variables; to fourth order,

$$F_m = \sum_i (1 - U_i\chi_{ii})|\boldsymbol{m}_i|^2 - \sum_{ij;i\neq j} U_i^{1/2}U_j^{1/2}\chi_{ij}\boldsymbol{m}_i.\boldsymbol{m}_j$$
$$- \sum_{ijkl;\alpha\beta\gamma\delta} (U_iU_jU_kU_l)^{1/2}\Pi_{ijkl}^{\alpha\beta\gamma\delta} m_i^\alpha m_j^\beta m_k^\gamma m_l^\delta + \text{higher order terms}, \qquad (18)$$

where χ is the static band-susceptibility function of the bare system and Π is a corresponding bare 4-point function. A further change of variables

$$\boldsymbol{M}_i = U_i\boldsymbol{m}_i \qquad (19)$$

immediately brings this to the form of Eqn.(1):

$$F_M = \sum_i (U_i^{-1} - \chi_{ii})|\boldsymbol{M}_i|^2 - \sum_{ij;i\neq j} \chi_{ij}\boldsymbol{M}_i.\boldsymbol{M}_j$$
$$- \sum_{ijkl;\alpha\beta\gamma\delta} \Pi_{ijkl}^{\alpha\beta\gamma\delta} M_i^\alpha M_j^\beta M_k^\gamma M_l^\delta, \qquad (20)$$

with local self-energy disorder weight $(U_i^{-1} - \chi_{ii})$ the analogue of κ in Eqn.(1) and χ_{ij} the analogue of J_{ij}.

Before considering finite-concentration alloys, we note that simple consideration of a system with two components A and B with $U_A = 0$ but $U_B > 0$ immediately yields the well-known mean field results: (i) pure A is paramagnetic; (ii) pure B is ferromagnetic if the Stoner criterion $(1 - U_B\sum_j \chi_{ij}) \equiv (1 - U_B\chi(q=0)) < 0$ is satisfied, but otherwise paramagnetic, (iii) an isolated B in an A-host will only carry a moment if $(1 - U_B\chi_{ii}) \equiv (1 - U_B\int_q \chi(q)) < 0$, the Anderson condition [63].

In metals χ_{ij} oscillates in sign as a function of separation, so the effective interactions of Eqn. (20) are frustrated. It also has long-range decay as an inverse power of R. Hence, an $A_{1-x}B_x$ alloy with a sufficient concentration x of B atoms would be expected to exhibit the sequence of behaviours as the concentration of B is increased from 0 to 1, {(Pauli) paramagnet - itinerant spin glass - ferromagnet}, analagously to the corresponding sequence predicted for a homovalent relaxor and depicted qualitatively in Fig 3. This phase structure was already reported in experiments on **Rh**Co in the early 70s [64], but again further studies of this system seem not to have been pursued.

Concerning analogues of PNRs, clearly the same arguments as used above for homovalent relaxors can be applied to the transition metal alloys. In fact, already in 1973 this locally-coherent cluster concept was proposed for alloys like **Rh**Co, formalized using the mapping to the effective magnetization field description of eqn.(20) and its further minimization and comparison with the localization eigenequation (14), along with the further suggestion that residual interactions between the clusters might lead to a spin glass.[56]. The lifetime of isolated clusters in the itinerant magnet case are, however, expected to be much shorter than for the displacive problem.

6. Conclusion

Several materials systems of active interest exhibiting ferroic glassy behaviour have been considered in analogy with spin glasses, with aims both to understand the materials systems and to suggest issues for statistical physics beyond those of conventional spin glass studies. These involve both effective random interactions and random fields.

We have argued for many analogues of spin glasses involving soft induced-moment pseudo-spins, in contrast to the most-studied hard spins of conventional spin glass physics, including extending the concept of itinerant periodic magnetism to intinerant spin glasses.

Examination and comparison of measured properties in materials systems and observations of some computer simulations of theoretical models has led to an apparent conclusion that *either* random dilution *or* random fields have the potential to yield qualitatively similar glassy features in many systems with frustrated long-range interactions, both for systems with good local moments already in their higher temperature para phases and for others in which moments need to be cooperatively induced in ordered phases. Spin glass-like behaviour in the case of random dilution of a system with frustrated interactions is expected and believed to be conceptually similar to that of random bond disorder [65], but the existence of true transitions in short-range disordered and frustrated systems in the presence of fields is still hotly contested, while the conventional (ferromagnetically interacting) random-field Ising model has been argued to not permit a spin glass thermodynamic phase [66]. Thus, questions remain, on the correct vision of some of the materials systems discussed above (*e.g.* whether the observed diffuse susceptibility peaks indeed correspond to true phase transitions in the thermodynamic static limit) and on conditions on interaction forms for the possible existence of spin glass behaviour (i) where the only quenched disorder is of local random fields and (ii) where there are both effective bond disorder and random fields.

Attention has also been drawn to observations of finite-lifetime pseudospin-correlated clusters in several disordered ferroelectric and ferroelastic materials, as well as predicted for some transition metal alloys, and a crude consideration has been presented in terms of a naïve inhomogeneous mean field modelling, but more sophisticated analysis and simulation, including dynamics, would be useful for better understanding. In principle one could imagine mapping to a basis of eigenstates of eqn.(1) with interactions between them, developing with temperature, and attempting to emulate and build on the qualitative conceptualizations that have been expressed, but currently a formal expression of this is missing.

Noting that effective random fields occur naturally in the heterovalent displacive ferroelectric alloys, in contrast to normal magnetic alloys, and they are not collinear, unlike the effective fields in gauge-transformed diluted antiferromagnets [67], it seems possible that some ferroelectric and ferroelastic alloy materials systems could provide experimental testbeds complementary to those available in magnetic systems.

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