Towards a Classification of the Effects of Disorder on Materials Properties

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Many 'interesting' correlated electron materials exhibit an unusual sensitivity of measured properties to external perturbations, and in particular to imperfections in the sample being measured. It is argued that in addition to its inconvenience, this sensitivity may indicate potentially useful properties. A partial classification of causes of such sensitivity is given.

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I. INTRODUCTION

In this brief note I discuss the effects of disorder on correlated electron systems from a perhaps slightly unusual point of view. There is a large, if mainly anecdotal, body of evidence indicating that 'interesting' correlated electron materials are unusually sensitive to disorder. As an example, not quite as frivolous as it may seem at first, I note that in the first few years of investigation of any new class of 'interesting' materials, conferences are dominated by debates concerning which samples exhibit 'intrinsic' behavior and which measurements are meaningless because performed on 'bad' samples. The ubiquity of these discussions suggests that there is a general and possibly interesting phenomenon at work, in other words that one should pose the question:

Why are so many 'interesting' materials so sensitive to (apparently weak) disorder?

The question may be of more than academic interest. A strong effect of disorder on materials properties is simply one of many examples of sensitivity of materials properties to perturbations. This sensitivity may be useful, or inconvenient, or both. A familiar example of a useful sensitivity of properties to perturbations is provided by semiconductors, where in an appropriate device geometry, the resistivity is very sensitive to applied 'gate' voltages and this sensitivity is the basis of the modern electronics industry. Along with this useful sensitivity comes an inconvenient one: the properties of semiconductors are very sensitive to defects, and indeed it took more than two decades of research to learn to control the undesirable sensitivity so that the useful one could be exploited. I suggest that one should view other examples of sensitivity of properties to perturbations in the same light: that a sensitivity of measured properties to sample imperfections may be an indication of some interesting, and potentially useful, properties of the material, so that understanding and controlling this phenomenon are important open issues in materials physics.

In what follows I present a first attempt to address these issues by presenting a 'botany' of materials exhibiting unusual sensitivity to disorder and a partial classification of mechanisms known to be operating in these different cases. I pay special attention to the 'colossal' magnetoresistance (CMR) materials, whose properties seem to indicate a qualitatively new mechanism for sensitivity of properties to perturbations.

This paper is presented in the hope that the participants in the Williamsburg Conference (and especially the muon-spin-rotation community, which has given us so much beautiful information about inhomogeneous structures in correlated materials) will find something of interest.

II. EXAMPLES OF SENSITIVITY OF PROPERTIES TO PERTURBATIONS

A. Overview

The magnitude of the response induced in a material by a perturbation is determined by comparing the size of the perturbation to some property of the material. A large response implies some unusual system property. The cases so far known to the author may be classified as follows:

(a) Small parameter: if some scale in the material is very small, then it is reasonable to assume that even a weak external perturbation may change the system properties dramatically. Two examples of this are the semiconductor (where the small parameter is the electron density) and the 'Kondo disorder' picture of heavy fermion materials (where the small parameter is the Kondo temperature)

(b) (Geometrical) Frustration: in frustrated systems (for example Ising spins on a triangular lattice) a thermodynamically large set of constraints prevents the Hamiltonian from finding a 'natural' ground state, leading (among other things) to a high degeneracy (or near-degeneracy) of low lying states. Disorder, by lifting the frustration, may then rearrange this large number of nearly degenerate states, thus qualitatively changing the observed behavior.

(c) Proximity to second order phase transition (critical or quantum critical point). In this case the divergent sus-
ceptibilities associated with the critical point may couple to disorder, leading to large effects. This may be thought of as a sub-case of (a) with the inverse susceptibility being the small parameter, but requires a separate discussion.

(d) Proximity to a first order transition. Although first order transitions are often considered to be uninteresting, it was shown many years ago by Imry and Wortis that in appropriate circumstances disorder may have a dramatic effect, leading to multiphase coexistence, percolative phenomena and possible changes in the order of phase transitions.

(e) CMR materials: first order energy landscape, ‘martensitic’ accommodation strain, and the importance of nonlinear response. The recent extensive study of the ‘colossal’ magnetoresistance’ (CMR) materials has revealed that the eponymous CMR is but one manifestation of a greatly enhanced sensitivity of properties to perturbations, whose origins involve both a sort of frustration and proximity to a first order phase transition.

In the rest of this section a more detailed discussion of examples (a)-(e) is presented.

B. Small parameter

As noted above, a very familiar example of sensitivity of properties to perturbations is the semiconductor. Here the small parameter is the carrier density, $n$. The low carrier density means that relatively modest changes in external parameters such as a gate voltage can modulate this density and therefore the conductivity of the device. It also means that the device is very sensitive to disorder. In particular, it took many years of materials work before the density of ‘traps’ (sites which capture an electron or hole) could be reduced below the carrier density, so that intrinsic behavior could be observed.

A different example the combination of weak disorder and a small energy scale occurs in the ‘Kondo disorder’ model of non-fermi liquid effects in heavy fermion compounds. This picture was deduced by Bernal and co-workers from their NMR data and was studied theoretically in some detail by Dobrosavljevic and collaborators. The physics at issue is the ‘non-fermi-liquid’ (i.e. weakly divergent) magnetic susceptibility and specific heat exhibited by a range of ‘heavy electron’ materials. The basic physics is this: heavy electron metals involve local moments which are coupled via an exchange coupling $J$ to an electronic conduction band characterized by a fermi energy $E_F$. Both $E_F$ and $J$ are of a reasonable (eV) order of magnitude, although typically $J$ is smaller than $E_F$ by a reasonable numerical factor. In this situation a lattice version of the Kondo effect causes the local moments to dissolve into the conduction band, leading to a ‘heavy fermi liquid’ characterized by an energy scale conventionally denoted $T_K$. For example the specific heat coefficient $\gamma = \lim_{T\to 0} C/T \sim 1/T_K$. The basic scale $T_K$ is given in terms of electronic parameters by $T_K \sim E_F e^{-E_F/J}$. Thus a ratio $E_F/J$ which is not too much larger than unity can lead to an extremely small Kondo temperature. As suggested by Bernal et al and convincingly demonstrated by Dobrosavljevic et al modest disorder can lead to a modest variation in $J$ which, because it is amplified by the exponential factor can lead to very broad distribution of $T_K$ and thus to a dramatic effect on low temperature properties. It is important to note that this ‘Kondo disorder’ is not the only source of non-fermi-liquid physics in heavy fermion materials. Novel single-impurity physics and proximity to quantum critical points are believed also to play some role (for reviews see e.g. but I believe that the existence of the ‘Kondo disorder’ effect is not now in doubt.

C. Frustration

In ‘frustrated’ systems, constraints (often geometrical in nature) prevent the system from achieving a gound state in which all interactions are satisfied. For reviews see . A classic example involves spins located at the vertices of the ‘pyrochlore’ lattice shown in Fig. 1a and interacting mainly by nearest-neighbor antiferromagnetic interactions. In this situation, it is not possible to fully satisfy all bonds, but the many ways to partially satisfy most of the interactions leads to a very large degeneracy of low-lying states, leading e.g. to the large in the spin wave spectrum shown in Fig. 1b. It is natural to expect that lattice distortions, either spontaneously induced or caused by disorder, will lift the frustration and therefore couple to the large density of low-lying states. In non-disordered systems this leads to the interesting ‘spin-Teller’ effect introduced by Yamada and Ueda and by Tschernyshev and co-workers. A similarly large effect from disorder may be anticipated.

D. Proximity to a phase transition

A second order phase transition involves a diverging length scale $\xi$ and diverging susceptibilities. Disorder which couples to these divergences can have very large effects, which have been extensively studied. It is conventional to represent the critical degrees of freedom by an order parameter field $\phi$ and to model the static part of the energy via a Landau Free energy for a system in an applied field $h_0$ which couples to the uniform component of the order parameter:

$$F = \xi^{-2} \dot{\phi}^2 + (\nabla \phi)^2 + u \phi^4 + (h_0 + h_{ran}(x)) \phi(x) + m_{ran}(x) \phi^2(x) + \ldots \quad (1)$$

It is useful to distinguish between random fields (such as $h_{ran}$) above, which couple linearly to the order parameter and thus locally ‘tell it which way to point’ and a random mass which couples to the square of the order parameter, and may be thought of as changing the local value
FIG. 1: Panel a: Left side: section of pyrochlore lattice, highlighting tetrahedra of frustrated spins (from $^5$). Right side: example of spin arrangement partially satisfying nearest neighbor antiferromagnetic bonds (from $^5$). Panel b: Theoretically expected spin wave spectrum in two cases: Solid line: undistorted lattice. Note the sharp peak at $\omega = 0$. Dashed line: distorted lattice–note peak is shifted to much higher energies by distortion. Inset: spin excitation giving rise to sharp peak. From $^8$.

of the transition temperature. Random field and random mass effects have been extensively studied, and may in appropriate circumstances be very large. For example, in a system with Ising symmetry at $h_0 = 0$ an arbitrarily weak random field $h_{\text{ran}}$ will destroy the long range ordered state in spatial dimension $d \leq 2$ while an arbitrarily weak ‘random mass’ will be a relevant perturbation (thus changing e.g. the critical exponents characterizing the phase transition) if the product of the pure system correlation length exponent $\nu$ and the spatial dimensionality $d$ is less than 2 (for a discussion and references in the context of quantum ($T = 0$) phase transitions see e.g. $^{10}$).

In both random field and random mass cases, when the randomness is important (either because its strength is sufficiently large or because the dimensionality is sufficiently low) the main effect is to produce ‘droplets’ of one phase inside a region which is on average composed of the other, and to change the character of the phase transition (if any) to a percolative one in which, as a parameter is varied, droplets of one phase increase in size and gradually connect, leading to a long ranged order.

Recently, Morr, Schmalian and the author studied perhaps the simplest example of a ‘droplet’–namely that nucleated by a single, localized random mass defect. For a system sufficiently near a quantum critical point a surprisingly ‘universal’ behavior of the space dependent droplet amplitude was found (see Fig 2). Also, perhaps not very surprisingly, in three dimensional systems line and plane defects (produced e.g. by screw dislocations or stacking faults) are much more effective at nucleating droplets than are point defects. It is tempting to speculate that such defects (which have been argued to exist $^{12}$) are responsible for some of the weak magnetism observed $^{13}$ e.g. in heavy fermion materials such as $UPt_3$.

FIG. 2: Form of ‘droplet’ induced in metallic quantum critical system by local defect. Here the ‘core size’ $r_0$ depends on the defect strength and on the relative dimensionality $D$ between the defect and the host material, while $\kappa$ is the inverse correlation length of the host system. From $^{11}$.

1. Random fields and first order phase transitions

The behavior of the Ising model in $d > 1$ at very low temperatures and in an applied field $h_0$ constitutes a very interesting example of this phenomenon. If $h_{\text{ran}} = 0$ then the model exhibits a first order phase transition as $h_0$ is varied through $h_0 = 0$. (In the ground state, all of the spins point parallel to $h_0$ and therefore change direction when $h_0$ goes through 0). In the presence of an arbitrarily weak random field in $d = 2$ or a sufficiently strong random field in $d = 3$, the situation is changed: for very large $h_0$ all the spins follow $h_0$, but as $h_0$ is reduced towards 0, more and more of the spins follow the random field and so domains of misoriented spins ap-
pear and as $h_0$ goes through zero the mean polarization vanishes. Thus the random field has turned a first order transition into a second order one. This observation was generalized by Imry and Wortis\textsuperscript{14}, who noted among other things that one could map a generic system undergoing a first order phase transition onto the random-field Ising model, by identifying the two different phases with the ‘spin up’ and ‘spin down’ phases of the Ising model and noting that any randomness coupling to the energy density would favor one phase more than the other and would therefore behave as a random field.

Interestingly, while theoretical arguments strongly suggest that two and three dimensional systems should behave very differently, experimental evidence suggests that the behavior of a the classic random field system in $d = 3$ is quite similar to that expected theoretically for systems in $d = 2\textsuperscript{15}$.  

2. One dimensional physics

One dimensional (or quasi one dimensional) materials are in a certain sense critical systems—the generic low temperature and low energy behavior involves power law correlations with novel exponents, and it is not surprising that one dimensional systems are unusually sensitive to disorder. A large theoretical literature exists on this question which will not be summarized here. One very interesting example however should be noted. The material $CuGeO_3$ is an insulator. The $Cu$ site is magnetic (each $Cu$ has a $S = 1/2$ magnetic moment) and the magnetic couplings are such that the material should be thought of as a collection of spin chains. and is most strongly coupled to two but at low temperatures a non-magnetic state is formed, evidently because of a spin-Peierls distortion, and one consequency of the disruption that it clearly demonstrates that the observed large sensitivity is not due to a large linear response. The initial slope of the $\rho$ vs $T$ curve is consistent with conventional, ‘unitarity-limit’ expectations. The large effects only occur when the concentration exceeds a small, material-dependent threshold, above which the properties change dramatically. Note in particular the $x$-dependence of the threshold concentration. In the undoped (no $Al$) material, $x \approx 0.18$ marks the boundary between a larger $x$ ferromagnetic metal phase and a smaller $x$ charge and orbitally ordered insulating phase. The systematic $x$ dependence of the $Al$ doping effects investigations reported in the condensed matter physics literature\textsuperscript{16} and have been the subject of a great resurgence of interest (for reviews see, e.g.\textsuperscript{17} since Jin and co-workers\textsuperscript{18} showed that in appropriately designed materials the magnetoresistance (dependence of resistivity on magnetic field) could be made extremely large (‘colossal’). Fig 3a shows an example of the eponymous magnetoresistance, from the early work of Schiffer et. al.\textsuperscript{19}.

![FIG. 3: Left side–middle panel: resistivity as function of temperature for a 'CMR material, demonstrating large change of resistivity with magnetic field. Upper panel: magnetization vs temperature for a 'CMR material, demonstrating large change of resistivity with magnetic field.](image)

![FIG. 3: Right side: Resistivity as function of aluminum doping, from\textsuperscript{20}](image)

The interesting point which has emerged from subsequent study is that the very large magnetoresistance is but one example of a generically extreme sensitivity of properties to perturbations. The right hand side of Fig. 3 shows a very interesting second example of this phenomenon: a sharp sensitivity of electrical resistivity to changes in chemical composition (in this case, doping $Al$ into the electrically active $Mn$ site) observed by Sawaki and co-workers\textsuperscript{21}. In the author’s view the great conceptual importance of the result shown in the panel is that it clearly demonstrates that the observed large sensitivity is not due to a large linear response. The initial slope of the $\rho$ vs $Al$—concentration curve is consistent with conventional, ‘unitarity-limit’ expectations. The large effects only occur when the concentration exceeds a small, material-dependent threshold, above which the properties change dramatically. Note in particular the $x$-dependence of the threshold concentration. In the undoped (no $Al$) material, $x \approx 0.18$ marks the boundary between a larger $x$ ferromagnetic metal phase and a smaller $x$ charge and orbitally ordered insulating phase. The systematic $x$ dependence of the $Al$ doping effects

III. ‘COLOSSAL’ MAGNETORESISTANCE MANGANITES

The ‘colossal’ magnetoresistance (CMR) manganites, which are pseudocubic perovskites of the form $Re_{1-x}A_xMnO_3$ with $Re$ a rare earth and $A$ a divalent alkali (examples also exist in the closely related Ruddlesden-Popper structures) offer a surprising new paradigm for strong effects of weak disorder. These materials have been known for a long time (and indeed were the subject of one of the first neutron scattering
strongly suggest that, when the \((x - \text{dependent})\) threshold is exceeded the effect of Al substitution is transform the material into the insulating phase.

The qualitative phenomena revealed by Al doping, namely a linear response which is not particularly large and an enormous nonlinear response characterized by a low threshold for transforming the material into another phase, seem to characterize all of the other enhanced responses in the CMR materials. In particular, in all CMR materials, the very low field magnetoresistance (the coefficient \(\rho_2\)) is not especially large--in fact it is rather smaller than the \(\rho_2\) found in the 'GMR' multilayer devices used in present-day magnetic read-heads. The truly large effects arise when \(B\) exceeds a low (order \(1\mathrm{T}\)) threshold, above which material properties change qualitatively from insulating to metallic, so the question becomes: why is the threshold so low?

This phenomenon is not yet well understood, but multiphase coexistence due (in some as yet mysterious way) clearly plays a key role. Important early work discussed electronically driven phase segregation into two phases of different electronic density\(^{24}\), and helped introduce the concept of inhomogeneity in the manganite context but it seems to this author that two crucial pieces of the physics and materials science came from experiments. One is due to Fath and collaborators\(^{26}\) and S-W. Cheong and co-workers\(^{26}\) who showed in thin film (Fath) and bulk (thinned for TEM) (Cheong) materials that very large domains of magnetic and non-magnetic material can occur. Cheong and collaborators extended this work, showing convincingly that the CMR materials exhibiting the largest magnetoresistance are tuned to be near a first order transition (in which a putative completely un-disordered material would change ground state from charge ordered insulator to ferromagnetic metal) and exhibit multiphase coexistence (a term I prefer to phase separation), with large (up to micron-scale) domains of ferromagnetic metal interleaved with similar size non-ferromagnetic, charge and orbitally ordered insulator. The large size of the domains guarantees that the phenomenon is not driven by charge inhomogeneity. Subsequent experiments\(^{27}\) showed in detail that the 'colossal' effects were shown to arise from a percolation phenomenon, in which as a parameter (e.g. field) was varied the volume fraction of conducting material grew and eventually percolated. One may follow Imry and Wortis and attempt to model this phenomenon in terms of the low-T behavior of the random-field Ising model in a uniform applied field: (for a discussion and references see e.g. the article of Burgy et. al. in this volume\(^{28}\). However, the real-materials aspects of the energetics have not yet been addressed. In particular, there is to the authors knowledge no understanding of domain wall energies or stiffnesses.

The Cheong group also uncovered a second key aspect of the phenomenon\(^{25}\), namely an essential role of 'martensitic' accommodation strain. The charge and orbitally ordered phase induces a long-ranged strain which, with the absence of constraints, would cause a change in shape of the material as the order is established. Typically, constraints prevent this from occurring, so the strain leads to a long-ranged, frustrating interaction (which gives rise, e.g. to the Tweed pattern observed both in conventional martensites and, recently, in CMR materials). The relation of this physics to the observed sensitivity remains an open problem.

IV. CONCLUSION

This short note has attempted to outline a 'botany' of causes for the (surprisingly widespread) phenomenon of 'non-intrinsic behavior' of, as I prefer to put it, sensitivity of properties to perturbations. The CMR materials were argued to exhibit an unexpected sensitivity phenomenon characterized not by an enhanced linear response to disturbance but by a low threshold to a qualitatively different nonlinear response. I suggest that refining and extending the classification scheme given here is an important task of materials physics and, as shown by the familiar example of semiconductors, may concievably lead to new and useful materials functionalities.

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