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Disorder and Frustration in Heavy-Fermion Systems - Revisited

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Heavy-fermion (strongly correlated electron) materials possess unconventional ground states that are related to quantum phase transitions and non-Fermi liquid behavior. These phenomena are particularly sensitive to crystallographic disorder and geometric magnetic frustration. In this bried review I shall examine the latest developments in studies of the magnetic properties of four heavy-fermion systems based upon the presence or absence of disorder and frustration. All four materials (URu_2Si_2, UNi_4B, $CePd_2Al_3$ and URh_2Ge_2) exhibit unusual and not fully understood behavior that are surprising for stoichiometric single-crystal intermetallic compounds.

KEYWORDS: disorder, frustration, heavy-fermion

§1. Introduction

Heavy-fermion or strongly correlated electron compounds offer a variety of intriguing ground states.[1] These include unusual magnetic ordering, unconventional superconductivity and quadrupolar or structural transitions. Also coexistences among the different ground states are possible leading to multiple and coupled order parameters. With the great present-day interest in quantum ($T = 0$) phase transitions and non-Fermi liquid behavior,[2] our correlated compounds are of particular importance for here quantum effects play a significant role, especially as $T \rightarrow 0$. When disorder and frustaration are incorporated into the problem, new and surprising features occur, some of which are predicted theoretically, that have not been fully examined experimentally. The disorder and frustration produce novel forms of quantum magnetism such as spin liquids, Kondo-disorder, quantum spin glasses, spin and charge separation, etc. So it is imperative that the disorder and (geometric) frustration are well characterized in the given sample. This usually required elaborate metallurgical investigations and exotic local probe methods, e.g., XAFS,[3] which take us far beyond the usual X-ray diffraction adn electron-probe micro analysis. Up until recently detailed studies of the specific samples with respect to their defects, impurity, randomness, polycrystallinity, etc. have been sadly lacking. Bad samples give bad physics.

In this brief review we focus upon four strongly correlated, heavy-fermion intermetallic compounds all fabricated in single-crystal form. Here we compare the differences in behavior when disorder and frustration are added to the compound. The four systems (URu_2Si_2, UNi_4B, $CePd_2Al_3$ and URh_2Ge_2) are given in Fig. 1 which exemplifies the possible magnetic ground states created by the inclusion of disorder, frustration or both. Usually this classification has been applied to insulating magnetic materials[4] but in what follows we show that it also pertains to our metallic heavy fermions. Although these systems have been reviewed in previously articles,[5] there are various new developments and fresh unsolved issues that keep such materials as a topical problem area.

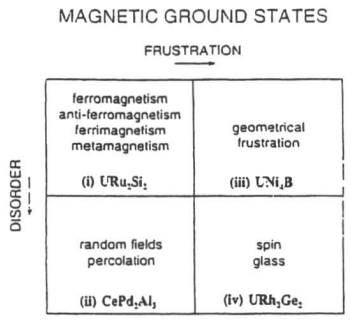

Fig. 1. Possible magnetic ground states obtainable from the perspective of site disorder and frustration.

§2. URu_2Si_2

For almost 15 years now the dramatic bulk phase transiton at 17.5 K has remained a mystery. All the basic properties (resistivity, specific heat, magnetization, thermal expansion) of URu_2Si_2 exhibit a clear mean-field-like transition at a robust $T_0 = 17.5$ K independent of sample quality and in contrast to the lower superconducting T_c. Yet the neutron-determined tiny magnetic moments disappear at a magnetic field where the bulk transitions are unaffected. So what is the order parameter ? It can not be simply magnetic.

Recently theory[6] has considered the possibility of a "hidden" primary order parameter ψ with a secondary order parameter being the staggered magnetic moment m. Depending upon the occurrence or lack of time-reversal-symmetry breaking, the field behavior of $\psi(H)$ and $m(H)$ have been predicted along with the $H - T$ phase diagram. Here we do have the end points from experiments : $H_c = 40$ T (a rather large field which just lately has become available for specific-heat measurements) and $T_0 = 17.5$ K. Despite all these efforts we still do not know what ψ is so we can not track it as a function of field and temperature.

In a neutrong scattering experiment performed under

high pressure up to 3GPa,[7,8] we have been able to transform URu_2Si_2 into a good magnetic system. As the pressure increases, so does the magnetic moment $m(P)$, see Fig. 2, from $0.02\mu_B$ at $P = 0.1$ MPa to $0.2\mu_B$ at $P = 1.3$ GPa. For higher pressures a sudden first-order crystal structure transformation occurs with a sharp step in the pressure dependence of the lattice constant a and m jumps to $0.4\mu_B$. Now the staggered magnetization or order parameter $m(T)$ for $T < T_m = 23$ K follows a sharp onset, Ising-like T-dependence compared to the smeared $m(T)$ behavior for $P < 1.3$ GPa. Note in Fig. 2 that T_m increases only to 23 K from its original $T_0 = 17.5$ K. This is an increase of ca. 30% compared to the 20-fold increase of the magnetic moment. These exciting results (usually pressure decreases the magnetism) indicate that the order parameter m switches from secondary at low pressures to primary at $P > 1.3$ GPa. However, we still do not know the "hidden" primary order parameter of the low pressure phase. Nevertheless, there are experimental evidences for either an anti-parallel quadrupolar ordering or a charge density wave (CDW) formation which takes place below 17.5 K and which represents the primary order parameter. Presently, the key and difficult task of the experimentalist is to determine the exact nature of the "hidden" order parameter. Unfortunately neutron scattering is not directly sensitive to quadrupoles or CDW's (periodic latttice distortions) so an X-ray/synchrotron scattering technique would be more appropriate.

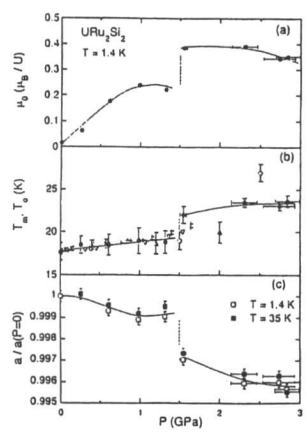

Fig. 2. Pressure dependence of the staggered magnetic moments, m, (represented by μ_0), the ordering temperatures, T_0 and T_m, and the lattice constant, a, for URu_2Si_2. From Amitsuka *et al.*[7]

§3. UNi_4B

Recalling that UNi_4B is a geometrically frustrated, partially ordered antiferromagnet[9] by virtue of its hexagonal crystal structure, little or no disorder, antiferromagnetic coupling in plane (where the U-moments are oriented), and feromagnetic coupling along the c-axis. At $T_N = 20$ K a well-defined second-order transition occurs. Bulk and neutron scattering clearly detect the long-range magnetic ordering and the resulting magnetic structure is given in Fig. 3. Note that only 2/3 of the U-moments participate in the magnetic transition. The U-atoms at sites (1) and (2) remain paramagnetic or frustrated below T_N. What happens when we reduce the temperature into the millikelvin range?

Very recently specific heat measurements were performed with fields up to 9 T down to 100 mK.[10] From C/T vs T plots we notice a large increase in γ $(= C/T)$ below 5 K something highly unusual for a conventional antiferromagnet and its spin waves ($C/T \propto T^{1/2}$ or T). γ reaches heavy-fermion values 550 mJ/mole.K^2. Then at $T^* = 300$ mK a peak appears and γ continues to decrease until the specific heat finally sees a hyperfine or nuclear contribution. Does this signify the magnetic ordering of the missing 1/3 U-moments? When an entropy analysis is carried out, the entropy value at T^*, the peak temperature, is 40 times less than that recovered at 25 K (above T_N). If the above specific heat behavior represents a second magnetic transition of the remaining U-spins, then we must account for its very low transition (T^* is 60 times less than T_N) and the tiny entropy involved in the transitions.

There are two mechanisms at work which rusult in a reduced T^* and limited entropy peak in C/T at the pase transition. (i) Frustration affects both the low (T^*) and high (T_N) temperature ordering transitions. When coupled with the weak AF exchange (J_2 in Fig. 3 since $J_1 \approx 0$) and the new renormalized trianglar lattice below T_N, the 1/3 paramagnetic spin remain frustrated with strongly reduced ordering temperature. (ii) Kondo-screening (suggested theoretically[11]) and development of the heavy-fermion state are present with characteristic temperature $T_K \approx 9$ K. Such screening with this value of T_K would be expected to greatly reduce the nonordered U-spins at T^*, thereby absorbing most of the spin entropy into γ and effectively weakening the exchange interaction between the 1/3 paramagnetic spins. Hence, due to frustration and the Kondo effect T^* is much smaller than T_N and most of the entropy associated with the paramagnetic spins is liberated well above T^*, resulting in a small specific-heat feature at T^*. In order to confirm this interpretation of the specific-heat measurements neutron diffraction must be performed at such low temperatures. Currently these experiments are being carried out at NIST.[12]

§4. $CePd_2Al_3$

Hexagonal $CePd_2Al_3$ posesses a strange type of "unintentional" disorder in its Al sub-lattice. Since the magnetic exchange is ferromagnetic in the triangular plane and antiferromagnetic along the c-axis, there can be no frustration.[13] NMR/NQR studies[14] have shown that in single crystals (as-grown) of $CePd_2Al_3$ the Al-atoms can occupy two different sites in the interstitial Al-plane with a random distribution among these sites. Through annealing or in polycrystalline samples there is a reduction in this ramdom site duality and an antiferromagnetic phase transition occurs at $T_N = 2.7$ K. The thermodynamic properties of single crystal $CePd_2Al_3$ resemble those of a non-fermi liquid, i.e., C/T and χ trace a weak upturn with decreasing temperature, a monotonic behavior down to 1.5 K with no signs of maxima.

Accordingly, some intriguing questions arise: Now that we know what the disorder is, can we control it,

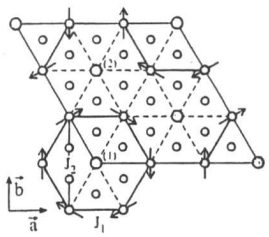

Fig. 3. Magnetic structure of hexagonal UNi_4B in the basal plane. The magnetic layers are stacked ferromagnetically along the c-direction. Note the presence of the "frustrated" U-spins indicated by (1) and (2) with two inequivalent magnetic environments. The nearest and next nearest neighbor magnetic exchange couplings are denoted by J_1 and J_2. From Menting *et al.*[9]

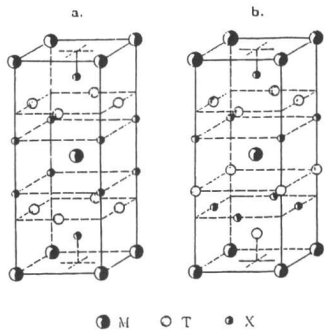

Fig. 4. Possible crystal structures of URh_2Ge_2. Left: $ThCr_2Si_2$; right: $CaBe_2Ge_2$. M denotes U, T represents Ru and X is Ge.

and thereby change the low-T magnetic properties? Does the randomness cause short-range magnetic order (long-range order is definitely prevented) that mimics or even creates the non-Fermi liquid behavior? Both questions seem difficult to answer at present. For it appears that in the single-crystal growth process of $CePd_2Al_3$ various degrees of disorder can occur and this greatly complicates the thermodynamic T-dependences.[15] So we must return to the metallurgy and develop sensitive detection schemes (beyond EPMA) for the measurement of this ligand (non-magnetic site) disorder that can play a major role in governing the magnetic behavior and ground state properties. Just because you have a "perfect" single-crystal, on-stoichiometry, sigle-phase, ternary intermetallic compound does not mean the absence of randomness or disorder. Site exchange or displacements among the ligand still could be present and such is very difficult to detect.

§5. URh_2Ge_2

As our final system we consider URh_2Ge_2 where the unintentional randomness caused by the Rh and Ge site interchange is so severe that both lattice disorder and magnetic frustration are produced leading to a heavy-fermion, spin-glass ground state. Now what is the exact cause of the disorder in this body-centered tetragonal (bct) compound - see Fig. 4? After extensive metallurgical, and neutron and X-ray diffraction measurements[16] we conclude: (i) There is a mixture of the two possible bct-crystal structures, $ThCr_2Si_2$ and $CaBe_2Ge_2$ as shown in Fig. 4. (ii) A rondom exchange of Rh and Ge sites occurs. (iii) A distribution of the free positional z-parameter of Rh and Ge takes place. And (iv) a small amount of vacancies exists on these ligand sites.

Note the magnetic U-sites are perfectly ordered (single crystal) and the stoichiometry of the 122-compound is retained. Only the local environments are affected by the Rh and Ge randomness. Quantitatively, we still do not know how much site exchange of Rh and Ge has occurred, nor the local symmetry or exact positions of the ligands. Inorder to ascertain the above, we have begun a series of XAFS measurements[17] which can determine the local occupancies and their surrounding environments. Such experiments have been very helpful in establishing the Kondo disorder in $UPdCu_4$.[3] When the randomness in URh_2Ge_2 is combined with predominantly ferromagnetic interactions in the basal plane and antiferromagnetic couplings along the c-axis, we have the competing exchanges to create magnetic frustration, and therefore a 3D, Ising-like, random-bond, metallic spin glass ($T_f = 9$ K) results.[16] All of the bulk properties exhibit the behaviors of an archetypal spin glass, e.g. CuMn (see Fig. 5). The electrical resistivity if the sole exception here and it is the subject of further investigation.[18]

Suppose we anneal our spin glass sample of URh_2Ge_2.[18] Fig. 5 shows the change in behavior of the field-cooled (FC) and zero-field-cooled (ZFC) magnetizations. Note the system has been transformed from a spin glass to a long-range order antiferromagnet. The "cusp" at $T_N = 13.5$ K has a totally different character and no irreversibilities. Neutron diffraction has confirmed the long-range nature and established the antiferromagnetism as alternating, along the c-axis, ferromagnetic planes.

What makes URh_2Ge_2 particularly interesting are its low T_f and Ising-like character, and thereby, its proximity to a theoretically predicted quantum critical point. Recent theories[19] have calculated a unique temperature versus quantum fluctuation strength, r, phase diagram, as depicted in Fig. 6. Here T_f can be experimentally "tuned" by changing the disorder, applying high pressure or employing a transverse (to Ising axis) magnetic field. Our attempts at varying the disorder have only lessened it, so instead of approaching the quantum critical point at r_c, we move away from r_c upwards toward the antiferromagnet at $T_N = 13.5$ K. Since we do not understand the anomalous zero-pressure dependences of the resistivity, its variation with pressure is not useful. Finally, if we can establish the true Ising nature of URh_2Ge_2, then low-temperature susceptibility experiments in a transverse field $H_\perp$ will be performed. Remember for an Ising magnet $H_\perp$ is a source of quantum fluctuations destabilizing the Ising ordering.

URh_2Ge_2 might also allow a classical Griffiths phase

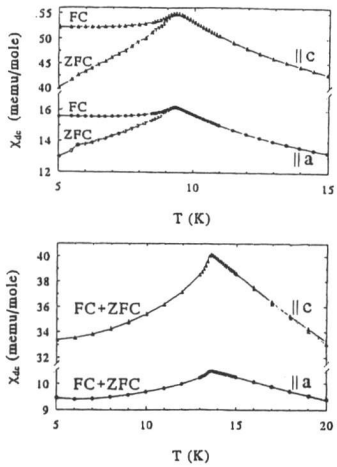

Fig. 5. FC and ZFC magnetization of URh_2Ge_2. Top: single crystal (*as*-grown) in the spin glass state (T_f = 9 K). Bottom: after annealing, the magnetization exhibits antiferromagnetic behavior (T_N = 13.5 K). From Süllow *et al.*[18]

(in contrast to the quantum one[20]) beyond r_c at $T = 0$) to be examined between 13.5 K (T_N) and 9 K (T_f) in the spin glass sample. Because of the few large antiferromagnetic clusters remaining in this T-range, relaxation and time dependent effects should be seen in the magnetization (long time) or the imaginary part of the susceptibility (short time). Also this "ghost" of the antiferromagnetism could be detected in the neutron scattering. So URh_2Ge_2 endures as a very interesting material for future study.

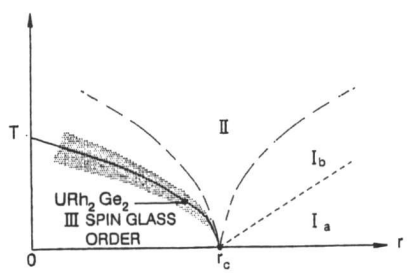

Fig. 6. Theoretical phase diagram for metallic spin glass. For the case of URh_2Ge_2 the tuning parameter "r" can be disorder, pressure or transverse (to the Ising axis) magnetic field. r_c denotes the quantum critical point. Region I is a quantum-disorder phase. Region II is the non-Fermi liquid regime. And Region III represents the spin-glass ordered phase. From Sachdev and Read.[19]

§6. Conclusions

In the preceding sections Ihave illustrated the role of (unintentional) disorder and frustration in determining the magnetic bahavior and ground state properties of heavy-fermion compounds. Novel effects reaching into the realm of quantum magnetism were obbserved with the very latest results being presented in this review. Disorder, even of an unintentional type or in tiny amounts can greatly modify the magnetic character, especially if frustration also exists. Presently it is extremely difficult to control or quantify the disorder. Most of it is accidental and we only have quenching and annealing as uncontrolled ways of affecting the disorder. More direct/local technigues such as XAFS or NQR need to be used in the study of disorder and its control. Until such is accomplished we will have an incomplete understanding of disorder and frustration and their effects in the strongly correlated electron systems.

This article is dedicated to my old and dear friend Professor Yoshi Miyako on the eve of his emeritus from Osaka University. For more than 25 years we have followed similar paths: along the spin glasses, through the heavy fermions, and now into the future. It has been and will be a special delight to continue our collaborations.

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