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Geometric frustration in Rare Earth antiferromagnetic compounds

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Abstract

An overview is given of the magnetic phases that emerge or could be expected from the geometric frustration of antiferromagnetic interactions, without strictly adhering to the compounds containing a Rare Earth element. An emphasis is put on the actively searched spin liquid or topological glassy phases and on the mixed phases, characterised by the co-existence of magnetic and non magnetic of otherwise crystallographically equivalent atomic centres, discovered in itinerant antiferromagnets and found out recently to set up also in Kondo lattice compounds and in non Kramers ion based compounds. © 1998 Elsevier Science S.A.

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1. Introduction

Any set of spins with mutual interactions which competes in such a way that no spin configuration can minimise all of the interactions simultaneously is, by definition, frustrated. Originally discovered [1] as a basic ingredient of the spin glass properties [2] of amorphous materials with a random-looking mixture of positive and negative exchange interactions, this phenomenon of frustration can occur in crystalline materials as well, where it can give rise to unusual magnetic behaviour. A distinction is then customary made between the exchange frustration, associated with competing exchange pathways, and the geometric frustration of antiferromagnetic interactions, intrinsic to odd-numbered loops of spins, although both often combine in real crystalline materials.

An exchange frustration can come out in any network of spins with long range exchange interactions. Complicated compromise configurations of spins are then obtained which are unique up to global spin rotations except for specific exchange pathways and magnitudes. An illustrative example is provided by the so-called 3D-ANNNI model whose phase diagram shows numerous long period spin configurations called devil's steps [3,4]. Generally a number of other spin configurations exist also at energies very close to the lowest value which can therefore be stabilised by secondary, even weak, interactions e.g. the combined crystalline electric field and spin-orbit interactions or else the magnetoelastic interactions, involving the orbital degrees of freedom of the magnetic centres. Consequently the spin configurations of real crystalline materials in the magnetically Néel ordered phases do often change, showing a variety of local and/or global spin processes as the temperature is decreased or a magnetic field is applied [5].

A geometric frustration is, in contrast, inherent to the geometry of the network of spins and can come out with nearest neighbour antiferromagnetic interactions. An appropriate geometry is e.g. in two dimension that of the triangular lattice (made of triangles joined by sharing an edge) or that of the kagomé lattice (made of triangles joined by sharing a vertex) and in three dimension that of the face-centre cubic lattice (made of tetrahedra joined by sharing an edge) or that of the pyrochlore lattice (made of tetrahedra joined by sharing a vertex). The nearest neighbours of any spin in these lattices are themselves nearest neighbours of each other, which makes it intrinsically impossible to build a consistent antiferromagnetic configuration of collinear spins. A subset of spins always exists for which there is no way to fix an orientation, which leads to infinitely degenerate manifolds of spin configurations differing from each other by local spin transformations. Selections of spin configurations can result from secondary interactions and/or entropic effects [6–8] and a long range Néel order can form, but this is not always the case. Other non trivial magnetic phases can be induced by more subtle mechanisms [9]. We shall briefly recall a few of these geometric frustration effects where the nature of the magnetic degrees of freedom involved is solely angular.

Considering now the itinerant electron antiferromagnets, the amplitudes of the magnetic moments cease to be sharp quantum numbers and can change, sometimes discontinu-

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ously, with respect to external parameters (temperature, pressure, magnetic field,...). A sudden onset or a collapse of the moments can even occur, defining then a magnetic–non magnetic instability. Associated with this new degree of freedom, further new magnetic phases can be induced by the geometric frustration, in particular mixed phases where magnetic and non magnetic centres co-exist [10–12]. Analogous phases can also occur in Kondo compounds where the spins of the localised electrons centres can be Kondo screened by that of the itinerant electrons [13–15], and even in ionic antiferromagnets when, due to the crystalline electric field, the ionic centres are in a singlet ground state separated from the magnetic excited levels by an energy lower than the exchange energy. We shall discuss a few experimental systems illustrating these different cases where the mixed phase was or could be observed.

2. Geometric frustration with spins of invariant amplitude

A wealth of magnetic phases can already be expected from the geometric frustration of antiferromagnetic interactions between magnetic moments whose amplitudes are frozen to the same identical value, depending on a number of factors.

Allowing the non collinearity of the moments does generally not lead to a unique compromise configuration with the lowest exchange energy, except for a few geometries, either because no energy is gained at already the level of the basic building block of the geometry, as for the tetrahedra, or owing to the network connectivity. A triangle of spins interacting antiferromagnetically is of minimum exchange energy if the spin of each corner makes an angle of $2\pi/3$ with the spins of the two other corners. Choosing now such a $2\pi/3$-configuration for that triangle, any other triangle sharing an edge with it can accommodate only one among all the $2\pi/3$-configurations while an infinite number of possibilities exist for a triangle sharing a vertex. Up to global spin rotations, a unique spin configuration of lowest energy is thus obtained for the triangular lattice but not for the kagomé lattice which still shows an infinitely degenerate manifold of spin configurations. Actually, in spite of that uniqueness, the tendency for a Néel ordering in the triangular lattice is inhibited if the quantum fluctuations of the spins which favour collinear spin configurations are taken into account and/or if a uniaxial magnetocrystalline or an exchange anisotropy exist. A Resonating Valence Bond (RVB) phase, consisting in quantum coherent combinations of spin singlet bond configurations on the lattice, was earlier anticipated for the extreme quantum limit of spins 1/2 [16].

Secondary interactions can come into play to lift the degeneracies and either combine or compete to generate a wide variety of Néel orders. With next neighbour interactions non collinear Néel orders are often stabilised. Another possibility is that uncoupled subsets of collinearly coupled spins get coupled by these interactions, which sometimes leads to incommensurate Néel orders. With magnetoelastic interactions, multi-Q Néel orders can emerge, as a sharp compromise between the gain in exchange energy that the induced lattice distortion allows (exchange strengthening on the unfrustrated bonds and exchange weakening on the frustrated bonds) and the gain in magnetoelastic energy associated with the strong magnon–phonon hybridisation that the non collinearity of spins promotes. An illustrative example is the type I antiferromagnetism of the face-centre cubic lattice which can be stabilised as collinear single-Q by tetragonal distortion or tetrahedral triple-Q by magnon–phonon hybridisation or else face-diagonal double-Q, and more generally non collinear unequally Q-populated, as the best compromise [17].

A less obvious mechanism of degeneracy breaking, termed ‘order by disorder’, is that due to the interactions of the fluctuations of neighbouring spins, which tends to select the states whose excitations are the softest in energy [6–8]. A Néel order can then set up but this is not a necessary result: in the kagomé lattice the mechanism operates only to select the coplanar spin configurations with respect to the non-coplanar ones, which is clearly not restrictive enough. A spin parity effect can furthermore be expected: with integer spins the quantum tunnelling between the different spin configurations will compete against the order by disorder effect and tend to drive the system towards a superposition of states favouring disorder, while with half-integer spins that quantum tunnelling should be suppressed by the destructive interference of the Berry phases associated with the different tunnelling paths connecting the spin configurations [18,19].

When the different degeneracy breaking effects are absent or not efficient enough, so that an entropy of discrete ground state degeneracy scaling with the number of spins persists, novel magnetic phases can be induced as outcomes of the interplay between the enhanced short wavelength spin fluctuations, the formation of local spin singlets, partial order by disorder effect, quantum tunnelling induced disorder and the interaction of cooperative spin defects (i.e. local deformations of the spin configurations allowed by the degeneracy) which can create energy barriers separating the spin configurations. A number of possibilities are foreseen: spin liquid phases generalising the RVB phase with spin singlet bond amplitudes depending on the spatial separation between the spin pairs forming the singlets, dimer phases describing frozen spin singlet bond configurations that break the translational invariance of the lattice (when the spin amplitude equals half the coordination number of the lattice a uniform valence bond state is obtained otherwise excess bonds per spin centre exist that lie in an orientation of minimum energy leading to specific states: spin smectic, spin dis-

cotic, etc.), multi-spin orders associated with the breaking of solely space rotational invariance (nematic spin liquid) or with the breaking of solely time reversal and parity invariance (chiral spin liquid), etc., all of which describe a spin 'rigidity' with strong short-range spin correlation but zero spin average on each centre. Also expected are topological glassy phases associated with the binding of topological defects belonging to a non-Abelian homotropy group and whose low temperature magnetic irreversibilities would correspond to the different ways and orders in which the crossings and interactions of the topological defects can take place [9].

A few of the above non trivial magnetic phases seem to have been materialised in several materials. We shall quote the semiconductor $R_2M_2O_7$ series, which crystallises in the cubic space group Fd3m, with R, a trivalent rare earth ion (Y^{3+} or Tb^{3+}), and M, a tetravalent transition metal ion (Mn^{4+} or Mo^{4+}), forming interpenetrating pyrochlore lattices. Magnetisation measurements performed on these compounds are well interpreted in terms of a spin-glass freezing, although no structural disorder is detected to the best experimental accuracy [20,21]. Neutron scattering measurements show diffuse elastic signals, corresponding to spin–spin correlation extending to the nearest neighbours of a tetrahedron only, which increase in intensity but not in width as the temperature is decreased. A quasi-elastic signal, that also increases as the temperature is decreased, dominates the inelastic scattering. No anomaly is detected at the freezing temperature deduced from the magnetisation measurements [22,23]. All of these properties suggest that the low temperature glassy phase sets up through a dynamical transition which transposes to a slowing down of short-range correlations that becomes static on the time scale of the respective measurements, but the irreversibilities at low temperature indicate that the transition is not an equilibrium process. Worthwhile to quote even though not containing a Rare Earth element is also the insulator $CsXYF_6$ family, which crystallise in the cubic Fd3m space group, with X, a divalent transition metal ion (Fe^{2+}, Ni^{2+} or Mn^{2+}), and Y, a trivalent transition metal ion (Fe^{3+}, Cr^{3+} or V^{3+}), randomly distributed at the corners of a pyrochlore lattice: $CsNiCrF_6$ shows a dynamical spin freezing analogous to that in the $R_2M_2O_7$ series. Single crystal neutron scattering measurements on this compound reveal a magnetic elastic scattering similar to the liquid structure factor, with an inelastic contribution extending in energy beyond that corresponding to the freezing temperature, indicating that the mechanism of spin glassiness in this compound is somewhat different from that of the conventional spin-glasses [24–26]. A few experimental prototypes for the two dimensional kagomé lattice of antiferromagnetically coupled spins were also discovered: ^{3}He adsorbed on graphite [27–29] and $Cu_6F_2(cpa)_6.xH_2O$ [30] as spin-1/2 models, the organic radical (*m*-*N*-methylpyridinium-α-nitronyl nitroxyde).X^- compound [31] as a spin-1 model, $SrCr_xGa_{12-x}O_{19}$-SCGO(*x*) as a spin-3/2 model (although the network of magnetic centres in this oxide formed by the Cr^{3+} ions should rather be described in terms of three-layer pyrochlore-like slabs) [32–34] and the family of Jarosite minerals $AM_3(SO_4)_2(OH)_6$ (where A=Na^+, K^+, Rb^+, Ag^+, Tl^+, NH_4^+, H_3O^+, $1/2Pb^{2+}$ or $1/2Hg^{2+}$ and M=V^{3+}, Cr^{3+}, Fe^{3+}, In^{3+}or Ga^{3+}) which provide prototypes with different spin values: S = 1 (V^{3+}), 3/2 (Cr^{3+}), 5/2 (Fe^{3+}) [35]. Unfortunately most of these systems are either controversial, still not investigated in depth or prone to nonstoichiometry, although exceptions can now be found as within the Jarosites family [36]. A prototype containing a Rare Earth element is $Gd_3Ga_5O_{12}$ (Gadolinium Gallium Garnet or GGG) which is structurally well-ordered and where the lattice of the magnetic Gd^{3+} ions, although not planar, shows the same connectivity as that of the kagomé lattice provided the exchange interactions are purely first neighbours (which is practically the case). Careful magnetisation and ac susceptibility measurements performed on high quality single crystals suggest a spin glass transition in this compound with nevertheless unusual thermal behaviour of the imaginary component χ'' of the ac linear susceptibility as well of the static nonlinear susceptibility χ_3, both showing two maxima at low temperature [37]. Orbital degrees of freedom can inhibit or promote the non trivial magnetic phases: in the $NaTiO_2$ insulator, where the Ti^{3+} ions form a triangular lattice of spins 1/2, a Néel order forms while an RVB phase was expected [16]. At the transition a structural distortion occurs and the entropy change exceeds the value expected from the sole spin degrees of freedom suggesting an orbital ordering that makes the exchange interactions non uniform [38]. On the other hand, in the $LiNiO_2$ insulator, where the Ni^{3+} ions form a face-centred cubic lattice of spins 1/2 (single e_g electron), a spin-orbital liquid seems to be stabilised by the orbital degeneracy that tends to increase the spin quantum fluctuations. Conditions for that phase to set up appear to be weak orbital and weak electron–phonon couplings compared to the spin coupling, which in $LiNiO_2$ could be due to a strong delocalisation of the Ni e_g electron over the Ni and surrounding O ions [39].

3. Geometric frustration in itinerant electron antiferromagnets

As with spins of invariant amplitude the geometric frustration in itinerant electron antiferromagnets leads most often to complicated Néel orders (non collinear, incommensurate with uncoupling effects, multi-Q,...) due to secondary interactions of similar nature (next neighbour exchange interactions, magnetoelastic interactions,...). Occurrences of the non trivial magnetic phases are however not unlikely and can also be expected when the different degeneracy breaking effects are not efficient enough:

itinerant electron equivalents of multi-spin orders in localised systems were anticipated in terms of Pomeranchuk instabilities of the Fermi liquid or electron–hole condensations near nested Fermi surfaces (if the electronic spectrum shows appropriate nesting properties). A difference with localised electrons systems is that the order parameter is then no more a multiple-spin average but distortions of the Fermi surface or wavefunctions of electron–hole condensate showing the symmetry breaking of a multi-spin order [40].

Actually all the magnetic variables of itinerant magnets, e.g. magnetic moments, exchange interactions, etc. have that distinctive feature to emerge from quantum mechanical averages over collective states involving all the atomic centres of a crystal, which phenomenologically should be understood as averages over the fast electronic hopping processes. A variable gets a finite value and/or fluctuates at time scales slower than that of an electron hop solely when the statistical weight of the occupied collective states leads to a non zero statistical sum of the corresponding quantum mechanical averages, which of course will depend on the nature of the low-lying excited collective states. So does in particular the amplitude of the magnetic moment at an atomic centre, which is then no more restricted to have specific quantified values as for ionic spins and can even change discontinuously with respect to the temperature, the pressure and an applied magnetic or exchange field. Combined with the geometric frustration that magnetic–non magnetic instability can lead to mixed phases where only a fraction of otherwise crystallographically equivalent atomic centres shows a finite magnetic moment.

Geometric frustration induced fractional vanishing of moments was first discovered in the RMn_2 intermetallics. According to the Rare Earth element R, these compounds crystallise in either the C14 hexagonal (for R=Sc, Pr, Nd, Sm, Ho, Er, Tm, Lu or Th) or the C15 cubic (for R=Y, Sm, Gd, Tb, Dy or Ho) Laves phases. Within these crystal structures the Mn atoms are distributed at the corners of regular tetrahedra stacked in a base to base and summit to summit sequence along the six fold axis in the hexagonal phase and in a corner sharing way i.e. forming a pyrochlore lattice in the cubic phase, both giving rise to a geometric frustration of the dominant Mn–Mn antiferromagnetic exchange interactions. Additionally the Mn itinerant magnetism shows a magnetic–non magnetic instability that appears to depend on the Mn–Mn interatomic spacing: with Sc and the heaviest Rare Earth, i.e. Ho, Er, Tm and Lu, the Mn centres are non magnetic while with Y and lighter Rare Earth, i.e. Pr, Nd, Sm, Gd and Tb, a magnetic moment with a large amplitude ($\approx 2.6\mu_B$) is stabilised on the Mn centres [41,42]. Complicated Néel orders are then stabilised at low temperature as revealed by neutron elastic scattering [43–46]: a double-Q magnetic structure is found in YMn_2, with long wavelength helical components that are strongly distorted due to the Mn magnetocrystalline anisotropy, while in $PrMn_2$ and in $NdMn_2$ the Mn magnetic moments are shared out on two magnetic sublattices with different propagation vectors, coupled solely via the R–Mn exchange interactions. A spin reorientation process occurs at low temperature in the magnetically ordered phase of $NdMn_2$. Associated with the crystalline electric field effects on the Nd^{3+} ions, it leaves one of the two sublattices of Mn magnetic moments unchanged, suggesting that the R–Mn exchange interactions are weak not only as compared to the Mn–Mn exchange interactions but also to the Mn magnetocrystalline anisotropy of the centres that have the same local crystal symmetry as in YMn_2. In $GdMn_2$ and $TbMn_2$, the exact magnetic moment arrangements are so complicated that they remain still unsolved, despite many experimental efforts (perhaps neutron spherical polarimetry could help). All of these Néel orders set up through a first order transition with a large volume discontinuity (amounting up to $\Delta V/V \approx 5\%$ in YMn_2) which is accounted by a substantial jump of the Mn moment at the ordering. A large magnetic contribution to the thermal lattice expansion is then measured in the paramagnetic phase [41,42]. The mixed phases set up, through a second order transition, in $ThMn_2$ [43–46], with 3/4 Mn centres being magnetic and 1/4 Mn centres being non magnetic but belonging to distinct crystallographic sites, and in $DyMn_2$, where even though all the Mn centres are in a single crystallographic site only 1/4 of the Mn centres bear a magnetic moment [47,48]. A mixed phase similar to that in $DyMn_2$ was also found by substituting a small amount of Sc (3%) for Tb in $TbMn_2$. Actually, it also occurs in $TbMn_2$ within a small temperature range ($\Delta T \approx 5$ K) below the paramagnetic phase. At decreasing the temperature below this range ($T < 40$ K) the magnetic configuration tips up then towards a Néel phase through a first order transition. The mixed phase can again be generated through a first order transition from that low temperature Néel phase by applying either a magnetic field or hydrostatic pressure [49,50].

An interpretation of the mixed phases in the RMn_2 series was obtained within a pseudo-moment model derived from the Hubbard model for itinerant electrons close to a magnetic–non magnetic instability i.e. for intra-atomic Coulomb energy U of the order of the electronic band structure width W [10–12]. Use was then made of the functional integral technique for the partition function, but a more phenomenological approach can be worked out. Assuming that the effect of the electron correlations can be represented by an effective field $\vec{H}_i = U\vec{m}_i/2\mu_B^2$ at each centre i, where $\vec{m}_i$ is a magnetic moment and μ_B the Bohr magneton, defining $\chi^0_{\vec{k}}$ and $\chi_{\vec{k}}$ as the $\vec{k}$-Fourier components of the magnetic susceptibility of the itinerant electron without and with electron correlations and applying a spatially periodic magnetic field of single Fourier component $\vec{H}^0_{\vec{k}}$ we can write: $\chi_{\vec{k}}\vec{H}^0_{\vec{k}} = \chi^0_{\vec{k}}(\vec{H}^0_{\vec{k}} + \vec{H}_{\vec{k}})$, where $H_{\vec{k}} = Um_{\vec{k}}/2\mu_B^2$ with $\vec{m}_{\vec{k}}$ the $\vec{k}$-Fourier component of the

distribution of the magnetic moments $\vec{m}_i$. Assuming further that the coupling between the $\vec{m}_{\vec{k}}$ is negligible, i.e. performing a random phase approximation (which will be valid all the more as the amplitudes of the $\vec{m}_i$ are small enough), the overall magnetic energy of the itinerant electrons is given as $E=(1/2)\Sigma_{\vec{k}}\vec{m}^2_{\vec{k}}/\chi_{\vec{k}}$, which in real space leads then to:

$$E=(1/2N)\Delta\sum_i \vec{m}_i^{\,2}-(1/N)\sum_{i,j<i}J_{i,j}\vec{m}_i\cdot\vec{m}_j$$

where

$$\Delta=(1/2N)\sum_{\vec{k}}(1/\chi^0_{\vec{k}}-U/2\mu_B^2)\quad\text{and}\quad J_{i,j}$$
$$=-(1/N)\sum_{\vec{k}}\exp[i\vec{k}\cdot(\vec{R}_i-\vec{R}_j)]/\chi^0_{\vec{k}}$$

$1/\chi^0_{\vec{k}}$ depends on the electronic band structure and is essentially proportional to the bandwidth *W*, so that according to whether U/W is larger or smaller than a critical value, Δ can be positive, in which case a magnetic moment is self stabilised at each centre and a Néel order can set up due to the exchange interactions $J_{i,j}$, or negative, in which case a magnetic moment will exist at a centre solely when the exchange interactions with its surroundings are large enough and a fractional vanishing of moments can be expected. As such the model does, however, not lead to a mixed phase even though considered within a network giving rise to a geometric frustration. A sufficiently large magnetocrystalline anisotropy should exist, as is precisely the case for Mn in the RMn_2 series. Monte Carlo simulations as well as analytical calculations were performed to investigate the phase diagram of the model on the triangular lattice with exchange interactions extending up to the third nearest neighbours. A number of Néel and mixed ordered phases as well as a wealth of thermal behaviour and applied magnetic field effects were found: mixed phases setting up through either a first or a second order transition, multiple transitions in temperature or magnetic field-induced transitions mimicking the behaviour observed in $TbMn_2$, magnetic field-induced mixed phase with ferromagnetic alignment of the non zero magnetic moments, etc. [10–12]. Investigations of the model on the pyrochlore and kagomé lattices were also performed. Shown on Fig. 1 is the phase diagram obtained for Ising spins on the kagomé lattice with antiferromagnetic first nearest neighbour exchange interactions ($J_1<0$). With ferromagnetic second nearest neighbour exchange interactions ($J_2>0$), we get a Néel phase for $\Delta<2J_2$, a mixed phase for $2J_2<\Delta<2J_2-J_1$ and a fully non magnetic state for $\Delta>2J_2-J_1$. With antiferromagnetic second nearest neighbour exchange interactions ($J_2<0$), we get the non magnetic state for $\Delta>-(J_2+J_1)$, another mixed phase $0<\Delta<-(J_2+J_1)$, and a state with fluctuating finite moments but no magnetic orders for $\Delta>0$ (in effect this is the region of the phase diagram where the non trivial spin liquid or spin glass phases can be expected). When the magnetocristalline anisotropy is not large enough, a mixed phase can also be stabilised with the help of magnetoelastic interactions, which in the RMn_2 series are large as evidenced by the spontaneous magnetovolume and anisotropic strains at the magnetic ordering as well as the magnetostriction effects under applied magnetic fields [41,42]. As an example, in the triangular lattice with only first nearest neighbour exchange interactions and no magnetocristalline anisotropy, if the exchange interaction parameter (J_1) happens to be dependent on the distance between the atomic centres it suffices that $(\partial_{\vec{t}}J_1)^2>(16/3)C_{\vec{t}}(J_1/2-\Delta/3)$ for mixed phases to form, where $C_{\vec{t}}$ is the elastic constant conjugate to the strain along the $\vec{t}$ direction. Other magnetoelastic interactions involving the on-centre parameter Δ can work as well.

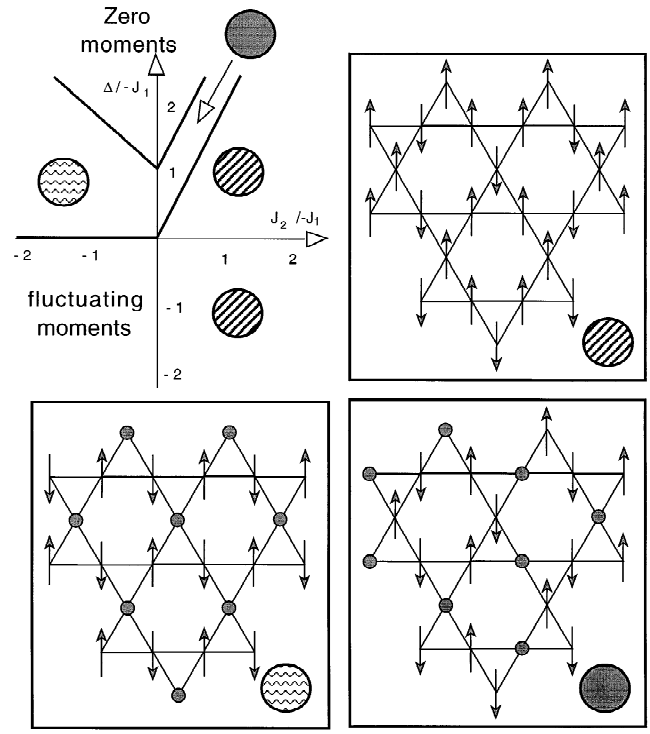

Fig. 1. Example of magnetic phase diagram of the pseudo-moment model on the Kagomé lattice

Geometric frustration in the RMn_2 series leads also to quite unusual behaviour in the paramagnetic phase: in $TbMn_2$ magnetic correlations extending up to 10 Å and involving both the Mn and the Tb magnetic moments are detected by powder elastic neutron scattering in a wide range of temperature above the magnetic ordering, in YMn_2 the paramagnetic susceptibility increases with increasing temperature, in $(Y_{0.97}Sc_{0.03})Mn_2$ where the substitution of 3% of Sc for Y suppresses the Néel order, a low temperature behaviour typical of a heavy fermion system is observed with a linear contribution γT to the specific and a quadratic contribution AT^2 to the resistivity whose coefficients γ ($\approx$160–200 mJ K^{-2} mol^{-1}) and A ($\approx$0.25 $\mu\Omega$ cm K^{-2}) are strongly enhanced up to values

quite unexpected for nearly antiferromagnetic metallic systems ($A/\gamma^2 \approx 10^{-5}$ $\mu\Omega$ cm (K mol mJ^{-1})^2) [41,42]. A single crystal inelastic neutron scattering investigation of $(Y_{0.97}Sc_{0.03})Mn_2$ showed that the spin fluctuation spectrum in this compound is broad in energy with no significant dispersion and no gap (up to the best energy resolution (150 μeV) of recent experiments using cold neutrons) and is extended in wavevector along the directions of the Brillouin zone boundary. No magnetic scattering is observed in the Brillouin zone around the origin and certain reciprocal lattice vectors implying that the self-time correlation of the magnetic moments within each Mn tetrahedron is zero and suggesting the formation of 4-centres collective spin singlets [51]. Whether these unusual properties can be considered as that of an itinerant electron spin liquid is a matter of debates owing mainly to the absence of a spin fluctuation energy gap (analytical perturbation calculations of the density operator and exact diagonalisation performed on finite systems shows nevertheless that in the pyrochlore lattice of quantum spins 1/2 with first nearest neighbour exchange interactions, the spin–spin correlations fall off exponentially with a correlation length of the order of the separation between two neighbouring spins and the spin gap vanishes to zero thus leading to an unconventional spin liquid [52]). A physical analogy exists anyway with the phenomenology of the 4f and 5f heavy fermion materials: (i) that the magnetic scattering is extended along certain reciprocal directions is interpreted as degeneracies associated with the geometric frustration but reminds us also of the fact that the Kondo fluctuations are localised in real space and leads to a flat dynamical susceptibility in the reciprocal space (ii) the exchange interactions give rise to one energy scale but the existence of the 4-centres collective spin singlets transposes to strong intratetrahedral and weak intertetrahedral spin–spin correlations that, even though induced by pure geometrical effects, reminds us now of the two energy scales of a heavy fermion compound i.e. the Kondo temperature below which a spin singlet tends to form on each centre and the RKKY exchange interactions that favour a magnetic order.

4. Geometric frustration and Kondo instabilities

Usually the f electrons in various materials do not show any magnetic–non magnetic instability, except in intermetallic compounds with Ce, Eu, Yb or Actinide elements where the hybridisation of the localised f electrons with itinerant electrons induce a wealth of qualitatively different behaviours. Although not rigorously sharp the distinction is then generally made between two main sets of compounds according to the energy difference between the f electrons and the Fermi level of the itinerant electrons as compared to the electrostatic energy associated with the hybridisation. When that difference is small the dHvA measurements detect f electrons at the Fermi surface and one gets an intermediate valence compound, which with regards to the magnetic properties smoothly connect to that of an itinerant magnet should the f electron transfer become further appreciable. Otherwise no f electrons are detected at the Fermi surface and one gets a Kondo lattice compound whose magnetic properties can be captured in terms of a network of localised spins interacting with itinerant electrons spin through an effective exchange interaction (Schrieffer–Wolff transformation of the periodic Anderson model). Although that simplified the full understanding of the Kondo lattice compounds is however far from being complete. Complex heavy fermions behaviours are observed either with or without magnetic ordering as well as unusual superconducting behaviours.

Qualitatively two energy scales seem to govern the magnetic properties of the Kondo lattice compounds, the Kondo temperature T_K which scales as $(\rho J_{eff})^{1/2}$ exp$(1/\rho J_{eff})$ and the RKKY exchange energy I_0 between the localised spins which scales as $(\rho J_{eff})^2$ where J_{eff} is the parameter of the effective exchange between the localised and itinerant electrons and ρ the density of states at the Fermi level. With two localised spins and when I_0 is antiferromagnetic a spin singlet is stabilised on each centre solely if $I_0 < 2\ T_K$, otherwise we get the collective spin singlet formed by the two localised spins. Mixed phases can then naturally be expected in the case of a network of localised spins with geometric frustration, when I_0 is of the order of $2\ T_K$. So far, at least three compounds seem to stabilise that mixed phase: CeSb [53–55], UNi_4B [56–58] and CePdAl [59]. CeSb orders through a first order transition to a square-wave modulated phase magnetic structure that can be described along the propagation vector in terms of parallel ferromagnetic planes of Ce sandwiching non magnetic planes of Ce. With decreasing temperature, it undergoes five further transitions corresponding to different stacking of the magnetic and non magnetic Ce planes. Under an applied field different other transitions are observed, leading to a phase diagram in the (T, H) plane certainly among the most complex ever since determined. An interpretation of the occurrence of the different mixed phases in this compound was provided within a mean field approach [13–15]. UNi_4B and CePdAl order at low temperature through a second order transition to magnetic structures that can be described in terms of ferromagnetic and non magnetic chains. Within the planes perpendicular to the chains the U atoms in UNi_4B form a triangular lattice and the U magnetic moments form a vortex structure with each vortex enclosing a non magnetic U, while the Ce in CePdAl form a network having the kagomé connectivity and show a magnetic configuration, which with regard to the distribution of non magnetic Ce, is similar to the one depicted in Fig. 1 for $0 < \Delta < -(J_2 + J_1)$. An effective energy E can be derived in these two cases by considering in mean field approximation the energy of two neighbouring Kondo chains according to

whether one is magnetic and the other not, none is magnetic, both are magnetic and coupled ferromagnetically or both are magnetic and coupled antiferromagnetically [52]:

$$E = \sum_i \Delta_i \vec{m}_i^{\,2} - \sum_{i,j<i} J_{i,j} \vec{m}_i \cdot \vec{m}_j + \sum_{i,j<i} R_{i,j}(m_0 - |\vec{m}_i|) \cdot (m_0 - |\vec{m}_j|)$$

where the on-centre parameter Δ is now of Kondo origin whilst the exchange interactions are RKKY in nature. An expression similar to that of the pseudo-moment model for itinerant electrons is obtained, except for an additional term of Kondo origin that disfavours non magnetic nearest neighbour centres.

5. Geometric frustration with spins in a singlet ground state

Another instance where mixed phases can emerge with an f electron magnetism is with non Kramers ions when the crystalline electric field interactions at each centre lift the degeneracy of the ground state multiplet into a singlet ground state and magnetic excited states at energy lower than the exchange energy. The amplitude of a magnetic moment at a centre becomes then dependent on the local magnetic moment configurations via the exchange field. The phenomenon is not new and gives rise e.g. to the sine wave modulated magnetic structure observed down to the lowest temperature in the $TbNi_{1-x}Cu_x$ compounds for $0.4 \leq x \leq 0.65$ [60]. A mixed phase can intuitively be expected but requires that the exchange field variation from centre to centre is not smooth and that the singlet ground state and magnetic excited states do cross and not anticross under the exchange field (i.e. the exchange field operator does not mix the ground and excited wavefunctions). A geometric frustration by favouring the uncoupling of the magnetic moments into subsets of collinear moments can help. Experimentally a mixed phase seems to have been observed in $TbRu_2Ge_2$ [61].

6. Conclusion

A number of non Néel magnetic phases can be generated by the geometric frustration of antiferromagnetic interactions among which only a few have recently been discovered in Rare Earth or Actinide based compounds. A topological spin glassy phase seems to have been stabilised in the $R_2 M_2 O_7$ series and in the Gd gallium garnet. An unconventional itinerant electron spin liquid seems to exist in the paramagnetic phase of the RMn_2 series. Mixed phases were discovered within the RMn_2 series associated with itinerant electron instability, in CeSb, UNi_4B and CePdAl associated with Kondo instabilities and in $TbRu_2Ge_2$ associated with the crystal field effects on the Tb^{3+} non Kramers ions. These different mixed phases proceed from microscopic mechanism of different origins but can be mapped into the same pseudo-moment model initially used to describe the itinerant electron magnets.

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