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MAGNETISM IN AMORPHOUS SOLIDS

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These lectures aim to provide an overview of collective magnetism in non-crystalline solids. They are predominantly experimental and descriptive in outlook, and they will try to relate amorphous magnetism to well-established ideas of magnetism in crystalline solids, stressing the points where something new emerges because of the lack of a crystal lattice. For example, there are many amorphous ferromagnets yet no amorphous antiferromagnets are known to exist. Why not? In the area of amorphous and disordered solids, magnetism continues to play its traditional role of introducing concepts and posing problems which can be formalised in terms of simplified yet not completely unrealistic models, whose applicability extends far beyond explaining magnetic properties of solids. Past examples of this sort have been in the areas of phase transitions, elementary excitations, two-level systems, physics in one and two dimensions and others. Another important facet is the practical usefulness of amorphous magnets, which provides a ready justification for working in the field. The scope for applications of amorphous magnets will be discussed, and some specific examples presented to lend perspective in this direction. However, the bulk of the lectures will be devoted to a discussion of magnetic order in amorphous solids, and the influence of a non-periodic lattice on its ingredients. Besides the magnetic ground states themselves, points of interest are defects, excitations and the eventual disappearance of magnetic order at a phase transition.

MAGNETISM IN A NON-CRYSTALLINE LATTICE

a) Types of Disorder

Conceptually, it is possible to distinguish three types of disorder in a solid. These distinctions are illustrated in figure 1 for two dimensional networks. By distorting a perfect crystal (figure 1a) in such a fashion as to

introduce bonds of different lengths making different angles with each other it is possible to destroy the periodic structure (figure 1b). This bond disorder is perhaps the simplest variety, as the bond-disordered network remains topologically equivalent to the crystal. Note that some bond disorder is present even in a real crystal at finite temperatures due to thermal displacements of the atoms from their equilibrium lattice sites. These thermal displacements do not destroy the underlying periodicity because there remains in the hot crystal a large probability of finding the atoms close to their lattice sites.

A much stronger type of disorder is the topological disorder shown in figure 1c). The network there includes four, five, seven and eight membered rings distributed at random among the six-membered ones. Topological disorder also results when the number of bonds at each atom deviates from three. It necessarily includes bond disorder, but a topologically disordered netowrk cannot be distorted back into a crystal. Some degree of topological disorder may be essential for forming any amorhpous solid.

Figure 1d) shows the structure of an ordered binary AB alloy. It may be disordered while retaining its crystallinity, figure 1g) and this chemical disorder is of fundamental impotance in metallurgy. In a perfectly random solid solution $A_x B_{1-x}$, the probabillity of an A atom being surrounded by Z B atoms on the N nearest-neighbour sites is

$$P_N(Z) = \frac{N!}{Z!(N-Z)!} (1-x)^{N-Z} x^Z \qquad (1.1)$$

If the disorder is incomplete, the average number of B neighbours will be different from (1-x) N, and a short-range order parameter can be defined. A special case, when $x \to 0$, is the dilute crystalline alloy. The positions of A atoms there are like those of atoms in a gas and, in a sense, they are more disordered than either 1b) or 1c), where each atom in the solid or liquid has a certain number of nearest-neighbours within a narrow range of interatomic distances. Bond disorder may be imposed on chemically ordered or disordered lattices (fig. 1e) or h)). In e) each A atom is surrounded by three B nearest neighbours, but the chemical order is absent in g) h) and i). Finally, when topological disorder is imposed on a binary network, chemical order may be retained (f) or destroyed (i). Metallic magnetic glasses are almost invariably multicomponent alloys, of type h) or i). They involve bond disorder, some chemical disorder, and probably topological disorder as well. Amorphous transition metals are of type c). In amorphous binary compounds, the number of bonds formed by each component ~~may~~ be constant, yet topological disorder can result from a distribution of even-membered rings (f). The magnetic lattice, however, is of type (c) when only one component carries a moment.

Bond and chemical disorder in a magnetic material introduce a distribution in the magnetic moments and exchange coupling between interacting pairs of atoms. In the case when the B atom in an A_xB_{1-x} alloy is non-magnetic, chemical disorder leads us to the idea of <u>percolation</u>. At a certain critical concentration x_p, there appear infinite continuous paths joining atoms, and many of the A atoms belong to the bulk cluster. The rest belong to small, isolated clusters. Any sort of magnetic long-range order is only possible for $x>x_p$, because all the atoms belong to isolated clusters when $x<x_p$. x_p depends critically on the range of the interaction, but for nearest-neighbour coupling it is of order 2/N. Percolation has been extensively studied on crystalline lattices of type g), and the fraction of A atoms in the bulk cluster falls to zero at x_p in a manner perfectly analogous to the order parameter at T_c for second-order phase transition $P_\infty \sim (x-x_p)^\beta$. Provided the bond interaction in a magnetic model is always ferromagnetic, regardless of bond length, bond

disorder will not influence the percolation concentration. x_p depends on the degree of chemical and topological disorder. The disordered A-B alloy with magnetic A atoms is an example of the <u>site</u> percolation problem. Alternatively, one might imagine breaking <u>bonds</u> at random, and the percolation threshold will occur for a fraction y_p of broken bonds. Quite generally, $y_p>x_p$. In magnetic systems it may be useful to think of bond percolation when the interaction strength depends critically on bond length.

b) Effects of Disorder

The basic requirements for magnetic order in a solid are (i) the existence of magnetic moments associated with unpaired electrons on the atoms, and (ii) an interaction to couple them together. The electrostatic fields acting at the atomic sites also have a profound effect, influencing the orientation of the atomic moments through spin-orbit coupling, thereby creating magnetic anisotropy. The various types of disorder modify each of these three key factors, which will now be considered in turn.

i) Magnetic moments: A magnetic moment exists on a free atom whenever the atom has unpaired electrons. Any atom with an odd number of electrons must carry one. However, these electrons in solids are usually employed in the formation of covalent bonds or enter broad bands where their strong paramagnetism is destroyed. Exceptions are the atoms of the transition series where the unpaired electrons reside in an inner shell, and therefore cannot participate fully in the bonding.

A satisfactory theory exists for the magnetic moments of transition ions (including the rare earths) when an integral number of electrons are localized on the ion core. This theory is applicable to many insulating and semiconducting compounds of the 3d series and practically all 4f materials except a few metals involving elements such as Ce which can have two different charge states in their compounds.

The theory of localized magnetism of non-interacting transition ions treats the Hamiltonian

$$H = H^c + H^{so} + H^{ef} \qquad (1.2)$$

where H^c represents the Coulomb interactions among d or f electrons which are responsible for strong electron-electron correlation resulting in coupling of spin and orbital angular momenta of the individual electrons according to Hund's rules to give resultants S and L. H^{so} and H^{ef} represent the much weaker spin-orbit and electrostatic field interactions, whose relative magnitudes are inverted for the 3d and 4f series. The electrostatic field is generally referred to as the 'crystal field', but this terminology is evidently inappropriate in non-crystalline solids. For the rare-earths, the spin-orbit coupling obtained from

$$H^{so} = -\lambda L.S \qquad (1.3)$$

is of order 10^4 K, and L and S couple according to Hund's rules to give a resultant J which is a good quantum number for the 4f series. A perturbation of order 100 K is caused by the interaction of the electrostatic field due to the atom's environment with the asymmetric charge distribution in the unfilled f shell. Its main effect is to introduce local magnetic anisotropy but the atomic magnetic moment at low temperatures may also be reduced from its free-ion value. The electrostatic field interaction is of order 10^4K in the 3d transition series because, unlike the 4f shell, the 3d shell is not an inner shell, well shielded by outer valence electrons from the electrostatic field created by neighbouring ions. Its effect is to quench partially or completely, the orbital angular momentum. Spin-orbit coupling, of order 10^2-10^3 K, then serves to mix the electrostatic energy levels slightly and give a Lande g

factor a little different from the spin-only value of 2. It also beings about local magnetic anisotropy. In crystals, where the local anisotropy is the same for each atom, the contributions add to give magnetocrystalline anisotropy, but in an amorphous solid they add in a random way.

In reality the wave functions of transition metal orbitals containing the unpaired electrons in compounds will be partially mixed with those of the ligands to form molecular orbitals. This covalency reduces the unpaired 3d or 4f occupancy below the purely ionic value, to an extent which depends on the metal-ligand overlap integrals and the energies of the atomic orbitals. The effect of non-crystallinity in an ionic solid will be to replace the fixed crystal field and overlap integrals of the crystal with a distribution of electrostatic field which will be of such low symmetry as to remove all orbital degeneracy, except Kramers degeneracy, and a distribution of overlap integrals which results in slightly different population of the magnetic orbitals from one site to the next. These effects modify the orbital and spin moments of the ion respectively. The latter effect may be examined in S state ions such as Mn^{2+}, Fe^{3+}, Eu^{2+} or Gd^{3+}. It will be unimportant for rare earth ions because the 4f shell is so small and well shielded by outer electrons that the overlap integrals are negligible.

Figure 2 shows the distributions of hyperfine fields for different types of magnetic glasses. The hyperfine field is roughly proportional to the magnetic moment, so the curves reflect the moment distributions. Data were taken at T ~ 0 so thermal effects are absent. The hyperfine field distribution is extremely narrow for the rare earth Dy, with a relative width of only 1%. It is moderately broad, ~10%, for the insulating ferric compound due to variations in the Fe-O bond length.

Inevitably, direct overlap of 3d or 4f wavefunctions will lead to formation of narrow bands in any solid. In a one-electron picture the bands will conduct electricity if partially filled, but in fact electron-electron interactions may be so strong as to open up a correlation gap in the effective density of states. Many transition-metal compounds, which should be narrow-band metals according to classical band theory, are really Mott insulators because of correlation. As the overlap increases, the 'Mott-Hubbard' sub-bands broaden and the moment is reduced. Ultimately the bands cross at the metal-insulator transition where the greatly reduced localised moment becomes itinerant. As the bands broaden further, the moments are entirely destroyed and the metal ultimately becomes a Pauli paramagnet when they are broad enough for correlations to be neglected entirely. The simplest possible Hamiltonian for a metal which will show magnetic effects is that of Hubbard

$$H = H^T + H^c \qquad (1.4)$$

where $H^T = \sum_{ij\sigma} t_{ij} C_{i\sigma}{}^{+} C_{j\sigma}$ is the term allowing electron transfer from one site to the next which gives the one-electron bond structure. t_{ij} is related to Δ the one-electron bandwidth in the tight-binding approximation by $\Delta = Zt_{ij}$. H^c is the coulomb correlation interaction, written most simply for a single, non-degenerate half filled s-band as $\sum_i U\, n_{i\uparrow}\, n_{i\downarrow}$ where $U = \langle \frac{e^2}{r_2} \rangle$ represents the average intra-atomic Coulomb interaction of two electrons on the same site. The band structure and magnetic moment at $T = 0$ for the Hubbard model as a function of Δ/U are illustrated schematically in figure 3. The ground state for the half-filled s band is antiferromagnetic.

Magnetism in real 3d metals is greatly complicated by the degeneracy of the d bands and their overlap with the 4s band. In the solid, d orbitals of different symmetry will overlap to varying extents, giving bands of different widths. The magnetism of iron, for example, has a partly localised and partly itinerant character which has so far defied accurate calculation.

Early attempts to explain the non-integral magnetic moments in transition metals were based on the concept of a spin-polarized 3d band, overlapping with the 4s band, as shown in figure 4. The occupancy of the $\uparrow$ and $\downarrow$ d bands determines the moment, and this will depend on the total number of 3d/4s electrons which changes by one on passing from one 3d element to the next in the periodic table, or on alloying different elements. The moments of alloys predicted by filling the rigid bands of this model are in fairly good agreement with observation. Even moments of alloys with non-magnetic metals can be explained within the rigid band model by invoking charge transfer. However there is little direct experimental evidence in favour of the required large splitting of $\uparrow$ and $\downarrow$ bands, ~ 1 eV, and photoemission experiments on alloys do not usually support a rigid band picture.

In any case, the 3d metals are near the limit for the appearance of magnetism, and their moments are all quite sensitive to changes in the overlap integrals as shown in figure 3c). Even iron, which has the best-developed moment of them all, can be rendered non-magnetic by alloying with elements which broaden the 3d density of states sufficiently. There will generally be a much greater spread of magnetic moments in amorphous metal due to the variability of nearest neighbour distances than is found in amorphous insulators. This fact was illustrated for amorphous Co_4P in figure 2. In some cases the spread can be large enough to permit coexistence of magnetic and non-magnetic atoms of the same element on different sits of an amorphous metal.

Magnetic and non-magnetic atoms of the same element may co-exist on different sites of crystalline solid solutions, as was first suggested for iron impurities in $Nb_{1-x}Mo_x$, by Jaccarino and Walker. Iron in these alloys is non-magnetic when surrounded by less than seven molybdenum nearest-neighbours. Mixing of the iron d electrons with the conduction electrons of the niobium neighbours broadens the local density of states. If there are enough of them, the broadening is such that the transition element can no longer sustain a moment.

The fate of a single impurity in a broad band metal is particularly instructive. The result of mixing the impurity wave functions with the conduction band is to produce a local density of states $N_i(E)$ for each of the two spin states, separated by the energy U when there is no overlap. This is shown in figure 5. The number of unpaired impurity electrons $n = n_\uparrow - n_\downarrow$ is given by

$$n = \nu(E_F + {}^1/_2 nU) - \nu(E_F - {}^1/_2 nU) \qquad (1.5)$$

where $\nu(E) = \int_0^E N_i(E)dE$. Expanding (1.5) as a power series for small n, we find that

$$n = nUN_i(E_F) + {}^1/_{24}(nU)^3 N_i(E_F) + \dots\dots\dots\dots$$

so that $n = \left[24\{UN_i(E_F)-1\}/1N_i(E_F)\ U^3\right]^{1/2}$ (1.6)

Thus a moment will form provided

$$U > 1/N_i(E_F) \qquad (1.7)$$

$No(E_F)$ is proportional to $1/\Delta_i$ the width of the local density of states, and this depends in turn on the overlap energy integral between the impurity electrons and the conduction band. If $N_i(E_F)$ were to vary smoothly with some parameter such as concentration, then the magnetic moment on the impurity, just below the critical concentration x_c where the moment disappears, would vary as $(x-x_c)^{1/2}$.

ii) Exchange interactions: The appearance of a magnetically ordered

structure such as ferromagnetism requires an interaction to couple the magnetic moments together. It has been found that exchange interactions between two spins usually tend to align them parallel or antiparallel. This tendency is represented phenomenologically by the isotropic Heisenberg interaction for localized moments $g\mu_B S$.

$$H_{ij} = -J_{ij}\ S_i \cdot S_j \qquad (1.8)$$

J_{ij} is the exchange constant between spins at site i and site j. It is positive for ferromagnetic coupling and negative for antiferromagnetic coupling. Typical values for the interaction between two spins lie in the range 1-100 K. Other interactions exist which favour a perpendicular configuration for the pair. These may be represented by the Dzyloshinskii-Moriya (DM) term $D_{ij}\ S_i x S_j$, but they are weak by comparison with the Heisenberg interaction. The DM interaction is zero by symmetry for certain spin configurations in crystals, but no such restraints apply in amorphous solids.

The origin of exchange coupling lies in the electrostatic interaction between electrons of different spins on different sites. Various exchange mechanisms exist - direct exchange, superexchange via ligands, indirect exchange via conduction electrons (RKKY interaction) - but all depend sensitively on the distance between the interacting electrons. Attempts to calculate the exchange constant between localised spins in equation (1.8) from first principles have led to values which are much too small, but nonetheless J_{ij} can be accepted as a phenomenological parameter depending on r_{ij}, and in the case of superexchange on the bond angle. Though J_{ij} or D_{ij} usually assumed to be isotropic, this is a gross simplification. For the 4f series, S in (1.8) is replaced by J, whereas an effective value is obtained for 3d metals by equating the atomic moment to $g\mu_B S$.

The direct exchange mechanism is most important in transition metals. The diagram Slater-Neel in figure 6 indicates roughly how the exchange varies with distance between magnetic shells in the 3d metals. J changes sign for γFe at 2.55 A. It is clear that the distribution of interatomic separations in a non-crystalline solid can lead to a distribution of exchange interactions which may sometimes include interactions of both signs. The same is true of the other exchange mechanisms as well. Superexchange is negative for a 180° metal-ligand-metal bond, but a weaker positive interaction occurs for bond angles near 90°. The Ruderman-Kittel-Kasuya-Yoshida interaction oscillates in sign as a function of r, as shown in figure 7. It arises from polarization of the conduction band by localised spins. Assuming a free-electron model for the conduction electrons, calculation gives

$$J(r) \propto \frac{-18\pi Z^2 J_{sf}^{\,2}}{E_F} \left\{ \frac{x \cos x - \sin x}{x^4} \right\} \qquad (1.9)$$

where $x = 2\,k_F r$. J_{sf} is the interaction between the localised spins and the conduction electrons. E_F and k_F are the Fermi energy and wave vector respectively and Z is the charge of the ion core.

The probability of finding an exchange interaction of a given magnitude and sign may be represented on a P(J) diagram. For a crystal the diagram consists of one or more delta functions, but the disorder in an amorphous solid will broaden the peaks, even to the extent that interactions of both signs may be included in the distribution, as indicated on figure 8.

In a solid, it is useful to replace the sum of (1.8) over all pairs of sites i,j by a sum over sites i, assuming that the interaction of any atom with all its neighbours may be replaced by an effective field - the molecular field approximation. The moment associated with the spin S_i is $g\mu_B S_i$, and its interaction with a magnetic field H_{eff} is

$$H_i = -g\mu_B\, S_i \cdot H_{eff} \qquad (1.10)$$

H_{eff} is defined by

$$H_{eff} = \frac{1}{g\mu_B} \sum_j J_{ij} \langle S_j \rangle \qquad (1.11)$$

The molecular field approximation therefore consists of replacing $\sum_{ij} J_{ij}\, S_i \cdot S_j$ by $\sum_i (\sum_j J_i \langle S_j \rangle) \cdot S_i$. It is an extremely useful approximation and forms the basis of much of the theory of collective magnetism. In amorphous magnets, the effective field will certainly have a probability distribution of magnitude, and in all cases except ferromagnets where P(J) is predominantly or exclusively positive it will have a probability distribution in direction as well.

Exchange interactions are not the only ones which can be magnetic moments. The classical dipolar interaction

$$H_{ij}^{dip} = \frac{\mu_i \cdot \mu_j}{r_{ij}^{\,3}} - \frac{3(\mu_i \cdot r_{ij})(\mu_j \cdot r_{ij})}{r_{ij}^{\,5}} \qquad (1.12)$$

tends to align the two moments μ_i and μ_j parallel, along the line joining their sites, r_{ij}. Like the RKKY interaction, the dipolar interaction varies as $^1/r^3$, but it is much weaker than exchange in most materials, except for some insulating compounds of the rare earths. Dipolar interactions between two moments are of order 1 K and are quite anisotropic since they depend on the orientation of the moments relative to r_{ij}. The net dipolar field is identically zero at sites in a lattice having cubic symmetry. In non-crystalline solids it will be distributed both in magnitude and direction.

iii) Anisotropy: The electrostatic field created by the surroundings at an atomic site in a crystal has the point symmetry of the site. Its interaction with 3d electrons is stronger than either spin-orbit coupling or exchange, and it acts to remove some or all of the orbital degeneracy of the free ion. Cetain preferred directions are then imposed on the ionic moment in the ground state by spin-orbit coupling, and this is the microscopic origin of magnetocrystalline anisotropy. For the 4f electrons, spin-orbit coupling is much greater than the electrostatic field interaction, so magnetocrystalline anisotropy is created by the latter directly. The interaction can be epxressed by the single ion Hamiltonian

$$H^{ef} = \sum_{n=0}^{n'} \sum_{m=-n}^{n} \langle J \| \theta_n \| J \rangle \langle r^n \rangle (1-\sigma_n) \; K_n^m A_n^m O_n^m \qquad (1.13)$$

where n is even and $n > |m|$. Terms up to $n = 4$ are required for d ions and terms up to $n = 6$ for f ions. The number of terms in equation (1.13) is greatly reduced by symmetry in crystals, with an appropriate choice of axes. For instance there are no second order ($n = 2$) terms on sites of cubic symmetry. The A_n^m's are known as crystal field parameters. They involve sums over the surrounding ionic charge distribution and a conduction electron contribution when necesary. O_n^m are Stevens operator equivalent which are combinations of the angular momentum operators $\langle J \| \theta_n \| J \rangle$ are reduced matrix elements, and K_n^m are constants tabulated by Hutchings $(1-\sigma_n)$ is a shielding factor and $\langle r^n \rangle$ is the average over the 3d or 4f wave functions.

No simplification of (1.13) by symmetry will occur in a non-crystalline solid. The electrostatic interaction may be imagined to give a complicated three-dimensional energy contour, according to the direction of the orbital moment, with no particular symmetry except an inversion centre. Reversing the direction of the orbital motion does not change the energy. One axis however must be lower in energy than all the rest, and this is the justification of the model of Harris, Plishke and Zuckermann who represent the electrostatic field interction in non-crystalline solids by the single ion Hamiltonian

$$H^{ef}{}_i = -D_i S_{zi}{}^{i2} \qquad (1.14)$$

where D_i has a distribution in magnitude and defines easy axes z_i which are different in direction at every site. Figure 9 summarizes the effects of disorder, comparing the ingredients of magnetism in a perfect crystal and an amorphous solid.

c) Collective Magnetic Order.

i) Ferromagnetic and antiferromagnetic interactions: Ferromagnetic order requires the presence of magnetic moments, and a positive exchange interaction to couple them together. It is not incompatible with a noncrystalline structure provided the concentration of magnetic atoms exceeds the percolation threshold, the distribution of exchange is essentially positive, and random anisotropy is negligible with exchange coupling. Ferromagnetism has been well-known in chemically disordered crystals for a long time, but it was not until 1960 that Gubanov pointed explicitly to the possibility of amorphous ferromagnetism, and extensive experimental study of amorphous ferromagnets has been going on since about 1970. Chemical and bond disorder may modify the magnitude of the atomic moments and bond disorder will bring about a distribution of exchange interactions, but neither effect will destroy the ferromagnetic ground state provided J remains positive and $X > X_p$. There are no fundamental differences in principle between crystalline and amorphous ferromagnets. In certain circumstances the phase transition at the Curie point may be smeared out by disorder, and magnetic and non-magnetic atoms can sometimes coexist in the ferromagnetically ordered phase. These effects, like many others in amorphous magnetism, are also found in chemically disordered crystals.

Nevertheless, there are often large differences in the values of the magnetic parameters compared with crystals of the same composition. For example, crystalline YCo_3 has its Curie point at 300 K whereas the amorphous form would become paramagnetic only above 500 K. The Curie point of the amorphous phase cannot actually be attained because it recrystallizes first. In other cases such as Fe_2B, the amorphous form has the lower ordering temperature. Other features of amorphous ferromagnets are that the M(T) curves tend to be flatter than for crystals, and the Block $T^{3/2}$ law for the low-temperature variation of the magnetization due to spin waves applies over a wider range of reduced temperature, Bulk anisotropy may be much less than in corresponding crystalline phases.

In contrast to ferromagnetism, where disorder does not necessarily induces much change in the phenomenon itself, antiferromagnetic interactions on a disordered lattice can produce results which are quite different to those in crystals. The concept of frustration is not entirely unfamiliar in crystals. It is present to a limited degree on the fcc lattice, and on the two dimensional triangular lattice. Frustration arises with antiferromagnetic interactions whenever the geometry of the lattice is such that the neighbours of a given atom are themselves neighbours of each other. It is therefore impossible to find a configuration for the spins where all the interactions are simultaneously satisfied. The idea is most simply presented by considering the three, four and five-membered rings of figure 10. With Ising spins, $S_z = \pm 1$, the lowest energy configurations have energy -0.33 J, -J and -0.4 J per bond for antiferromagnetic pair interactions, but all have the lowest possible energy, -J per bond, with ferromagnetic coupling. Frustration occurs with antiferromagnetic interactions on odd-membered rings. A related feature is the degeneracy of the lowest energy state, 6, 2 and 10 for the three rings with negative J, but 2 for all three when J is positive. Increased degeneracy (or near-degeneracy when the bond interactions are unequal) accompanies

frustration. The classical limit is also quite instructive. Bond energies for classical spins are higher than for Ising spins, -0.5 J, -J and 0.81 J for the three rings respectively, but frustration is still present in the odd-membered ones, and it leads to non-collinear lowest energy states as shown in the figure.

Frustration also arises on even lattices, such as the square lattice, when positive and negative exchange bonds are distributed at random. A square or 'plaquette' is frustrated if there is an odd number of antiferromagnetic interactions (1 or 3). The degree of frustration depends on the relative proportion of the two signs of interaction.

No frustration is introduced by chemical disorder alone in an unfrustrated crystal with antiferromagnetic nearest-neighbour exchange interactions, but but the interaction is longer range and at least partly antiferromagnetic (e.g. RKKY), the lattice will be frustrated. Bond disorder of the unfrsutrated crystalline lattice wil introduce frustration if the change in length of some of the bonds is sufficient to change of J from negative to positive. Topological disorder is always prone to frustration when it involves odd-membered rings. In any case, whenever frustration is present it will be accompanied by degeneracy or near-degeneracy of the ground state. Many different configurations of the spin system are close in energy although to pass from one of these states to another involves going through intermediate higher-energy states, so they are separated by energy barriers. The free energy surface in spin configuration space is corrugated and pitted with many local minima.

ii) Ideal magnetic structure: From the considerations in the preceeding paragraph, it is plausible that frustration in a random lattice will result in random non-collinear magnetic structures. Frustration introduced by competing interactions in crystals sometimes results in helimagnetic order, but long-range helimagnetism is unlikely in a non-crystalline solid. One approach would be to consider the random non-collinear structures in amorphous solids as superpositions of spirals of variable phase and propagation direction. Frustration arises in non-crystalline solids from anti-ferromagnetic interactions on lattices with particular topological disorder (odd-membered rings), and also when competing exchange interactions of both signs are present on any disordered lattice. In a broader sense, we can also consider that amorphous solids with significant single-ion anisotropy are also frustrated. It is impossible to fully satisfy the exchange and single-ion interactions at each site because they favour different orientations of the spins. The energy of the compromise ground state wil be higher than that given by the sum of the interactions, and a number of alternative configurations will exist which have almost the same energy, but are separated by energy barriers of different heights. Competition between single-ion anisotropy and exchange in a non-crystalline solid will lead to some sort of a random non-collinear structure even if J is everywhere positive. Competition between exchange and anisotropy also produces spiral or periodically modulated spin arrangements in some crystals, including certain rare-earth metals.

Some typical initial magnetization curves for a selection of amorphous magnets are shown in figure 11. These curves are all taken at a temperature of 4.2 or 1.6 K, close to T = 0, and they show the reduced magnetization M/M_o, where M_o is the value corresponding to parallel alignment of all atomic moments. The maximum field, 150 kOe, is large by laboratory standards but much less than the dominant interactions (exchange for YCo_3, YFe_3 and FeF_3, single-ion anisotropy for $DyNi_3$). These materials each contain only one

magnetic species and so there is a single magnetic subnetwork. (Nickel in $DyNi_3$ does not bear a moment). The applied field is corrected for demagnetizing effects. YCo_3 saturates very easily, like a typical ferromagnet. It obviously has a simple colliner structure and any antiferromagnetic interactions or random anisotropy introduce neglibable perturbations of the ferromagnetic order. The field induces only very weak magnetization in FeF_3, with a susceptibility which is essentially independent of field. Apart from a tiny remanence, $M_r/M_o \sim 10^{-3}$, the magnetization curve of amorphous FeF_3 resembles that of a crystalline antiferromagnet. By contrast, for $DyNi_3$ and YFe_3 the field quite easily induces a large moment approximately one half of the saturation magnetization, but the approach to saturation in higher fields is slow, and it would be necessary to apply fields of order 10^6Oe to align the spins completely. Both materials show remanence at low temperatures such that $M_r/M_o > 10^{-1}$. Clearly, in the magnetized state at least, they have a magnetic structure with a large net magnetization which nevertheless falls far short of the ferromagnetic saturation value.

As an aid to discussing magnetism in non-crystalline solids we define some category of magnetic order which are encountered in amorphous materials. The definitions for materials with one magnetic subnetwork are illustrated in figure 12 a) and b) represent collinear structures having respectively the maximum and zero net moment, corresponding to ferromagnetic and antiferromagnetic order. c) and d) represent random non-collinear structures, one with substantial net magnetization, the other with none. We will refer to them as asperomagnetic and speromagnetic respectively. In the speromagnetic structure, the moment are distributed at random in direction with no preferred orientation. The formal definition $S_iS_j = 0$, $\langle S_i(o).S_j(r)\rangle = 0$ for $r_{ij} > a$. S represents the time average of the moment, which may have spin and orbital contribution and $\langle\rangle$ is the average over all pairs with separation r_{ij}. a is the interatomic separation. The definition admits the possibility of very short range averaged correlation at the level of the first or second neighbour shells, such as may exist when the nearest neighbour interactions are antiferromagnetic, but there are no correlations on average at longer distances. By contrast there is some long-range preferred orientation of the moments in an asperomagnet, such that $S_z^2 > \langle S_i(o).S_j(r)\rangle > 0$ for $r_{ij} > a$, $S_z^2 = \langle S_i(o).S_j(r)\rangle$. Any definition of a magnetically-ordered structure is only valid within a domain, so some consideration has to be given to the length scale over which the definition may be applied. An iron bar usually has no net magnetization if no field is applied, so $\langle S_j(o).S_j(r)\rangle = 0$ for r_{ij} much greater than the ferromagnetic domain size. The definition of ferromagnetic order therefore applies only within a domain, whose size is usually at least one micron. The concept of a domain size has no obvious meaning for a speromagnet, but for an asperomagnet it can be defined as the distance beyond which $\langle S_i(o).S_j(r) \simeq 0$. The definition is useful provided that distance is much greater than the interatomic spacing, although the physical explanation of domain formation may not necessarily be the same as in a ferromagnet, where the reason for the domain structure is the need to minimize the energy of the sample in its own dipolar field.

Of the four structures in figure 12 there is direct experimental evidence of all except the amorphous antiferromagnet. These structures are for materials with one magnetic subnetwork, a subnetwork being a chemical sublattice, defined as the ensemble of atoms which carry a magnetic moment and have similar magnetic interactions. For the example in figure 11 the subnetworks are composed of the cobalt, iron or dysprosium atoms in YCo_3, FeF_3

or $DyNi_3$. Amorphous materials also exist with two magnetic subnetworks. All those that are known are alloys of rare-earth and transition metals where each chemical subnetwork is composed of atoms of one sort or the other. It is doubtful whether one can ever distinguish two magnetic subnetworks on a geometrical rather than a chemical basis in non-crystalline solids. In crystals this is possible. The spinel structure for example, has two sublattices formed by cation sites with tetrahedral (A) and octahedral (b) oxygen coordination, and the principal magnetic interaction is A-B coupling because the neigbouring cations of an atom on one sublattice all belong to the other. While it is surely possible to conceive of a non-crystalline structure with the property (a spinel with bond disorder would do), it is unlikely that examples they really exist.

Several classes of two-subnetwork structure may be distinguished. Possible collinear structures are ferromagnetic or ferrimagnetic, according to whether the subnetworks are coupled parallel or antiparallel. If one or both subnetworks possess a random, non-collinear structure but nevertheless have a net magnetization the structure will be termed sperimagnetic. If both possess random non-collinear structures with no net moment, the structure is speromagnetic. Figure 13 illustrates the definitions.

Compared with regular crystals, the novel feature of magnetism in amorphous solids is the possibility of finding 'ordered' magnetic structures where the atomic moments are fixed in directions which are essentially random. Order in this sense means that there are no significant fluctuations in the average moment directions on an experimental timescale. Temporal but not spatial fluctuations are supressed as the spins 'freeze' on cooling the sample sufficiently, but there is little evidence that this occurs at a well-defined phase transition. In contrast, a phase transition quite analogous to that in crystals is found in many amorphous ferromagnets and ferrimagnets. The random, non-collinear magnets, speromagnetic, asperomagnetic and sperimagnetic have magnetic excitation spectra which may be quite different compared with those of collinear and crystalline magnets.

iii) Spin glasses: In the broadest sense of the term, all the random, non-collinear amorphous magnets might be described as 'spin-glasses'. They do not exhibit the normal sort of magnetic phase transition, the magnetic order is random to some degree, and there are indications that the ground state is not unique. Originally applied by Coles to dilute crystalline alloys such as Au Fe or Cu Mn containing about 1% of magnetic impurities, the term spin glass no longer has any precise generally-accepted significance as it has been applied by various authors to materials which are magnetically dilute or concentrated, metallic or insulating, crystalline or amorphous but possess at least one magnetic characteristic in common with the canonical examples. It also denotes a class of theoretical models which may have some relevance in explaining these characteristics. Sometimes 'spin glass' is used in the sense of an ideal magnetic structure, similar to speromagnetism, except that not even short-range correlations are allowed; $S_i(o).S_{ij}(r) = 0$; $\langle S_i(o).S_j(r)\rangle = 0$ for all r.

The canonical spin glasses, dilute alloys of transition metals in noble metal hosts whose disorder has more in common with a gas than a liquid, showed the following characteristic magnetic properties.

- A sharp peak appears in the low field (~1 Oe) ac susceptibility at a temperature T_f which increases with increasing measuring frequency.
- The peak becomes rounded in higher ac or dc fields.
- Near T_f, irreversile behaviour including remanence and coercivity appear.

- The remanence, or order a few percent of the collinear saturation magnetization at T = 0, decays with time, varying almost linearly as a function of ℓn t.
- The magnetic entropy at T_f is less than half of the total magnetic entropy of disorder.
- The paramagnetic Curie temperature θ_p, extrapolated from susceptibility data taken well above T_f, is close to zero.
- Various magnetic properties including spin freezing temperature and magnitude of the remanence scale with the concentration of magnetic impurities.

Together this behaviour constitutes the spin glass syndrome. Some of the properties, like ℓn t decay of the remanence, $\theta_p \approx 0$, or field dependence of the susceptibility peak, occur also for other sorts of magnetism, so in practice it is necessary to observe several of these characteristics before classifying any material as a spin glass. There is no consensus as to just which ones are essential, and which are incidental.

The first theoretical models of spin glasses were based on the idea that the magnetic interaction in chemically disordered dilute alloys must be of the oscillatory RKKY type, so that the P(J) distribution was taken as a gaussian, centred at J = 0. Treated in the molecular field approximation, this leads to a phase transition, but the transition is absent in more exact treatments. The spin freeze progresively into random directions as the temperature is lowered, and there is no net magnetization.

In these lectures we will adopt the term 'spin glass' to denote disordered magnets, whether crystalline or amorphous, whose magnetic properties are due to a broad distribution of exchange interactions of both signs, with $\langle J\rangle \sim 0$.

We will now go on to consider in more detail the behaviour of amorphous magnetic materials where the exchange interactions are predominantly of one sign or the other, when random anisotropy can be neglected.

FIG. 1

Types of Disorder

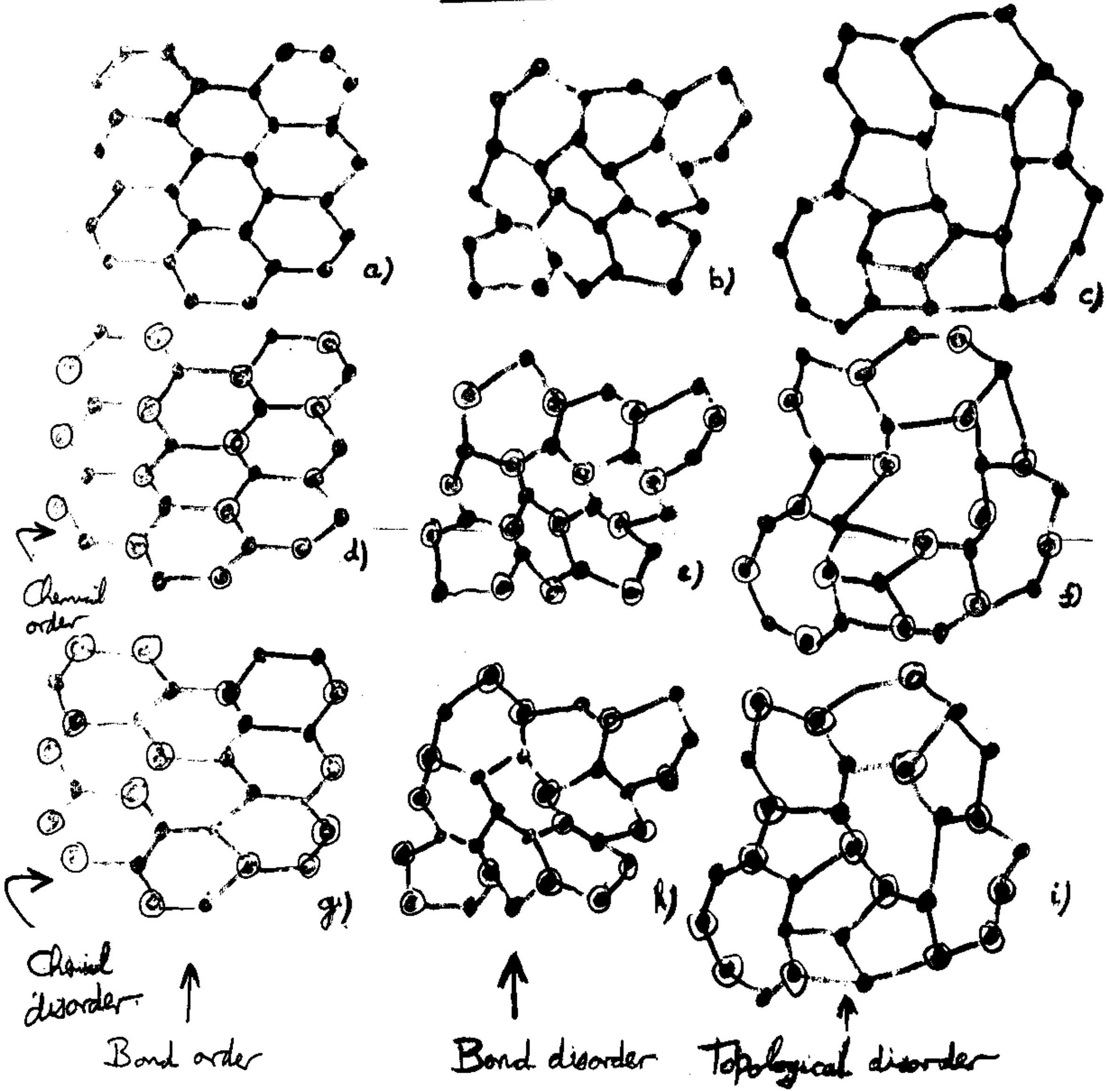


fig 1

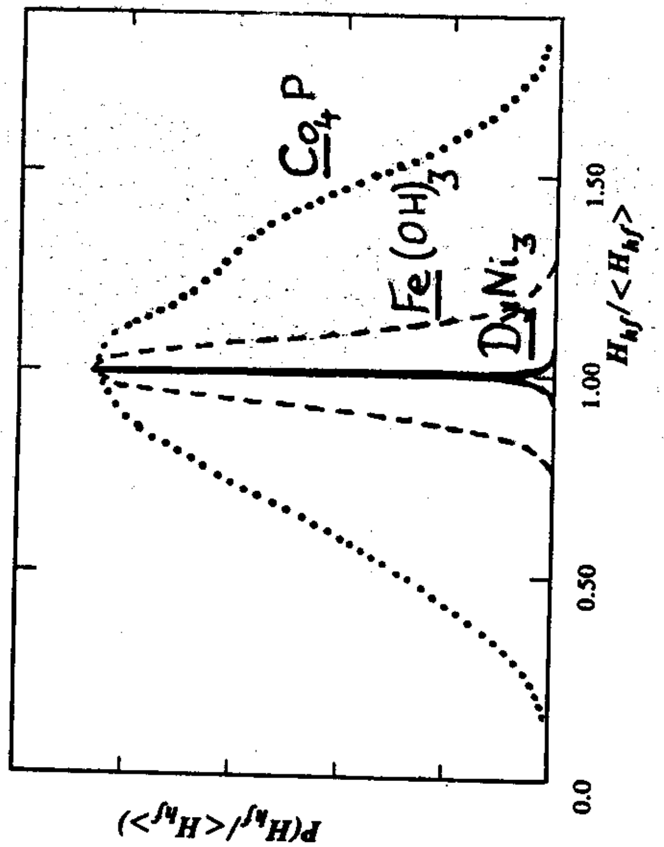

$P(H_{hf}/<H_{hf}>)$
$H_{hf}/<H_{hf}>$
0.0
0.50
1.00
1.50
$\underline{Co}_4P$
$\underline{Fe}(OH)_3$
$\underline{Dy}Ni_3$

fig 2

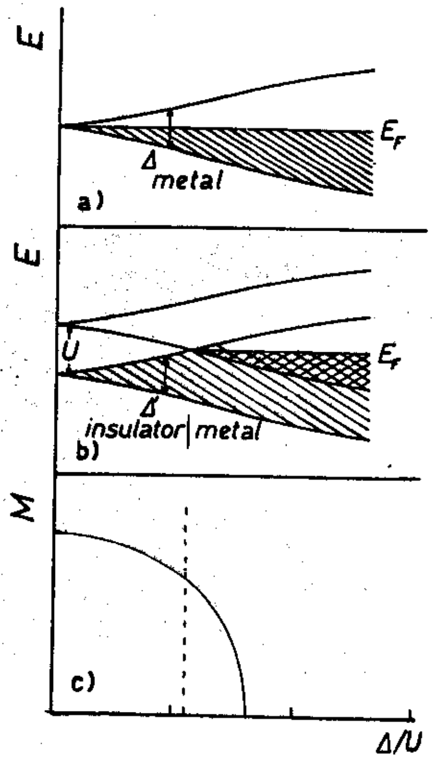

E
E_F
Δ
metal
a)
E
U
E_F
Δ
insulator | metal
b)
M
c)
Δ/U

fig 3

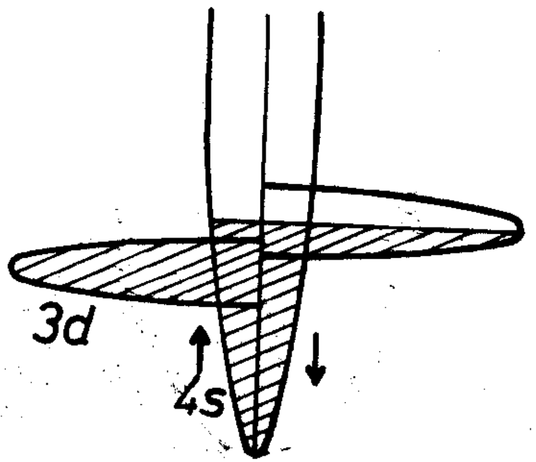
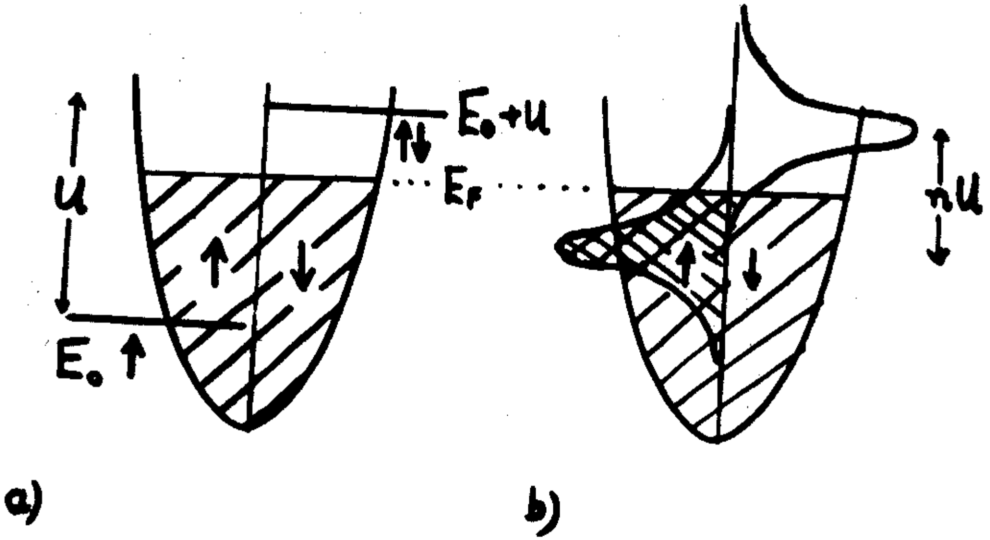


fig4

fig5



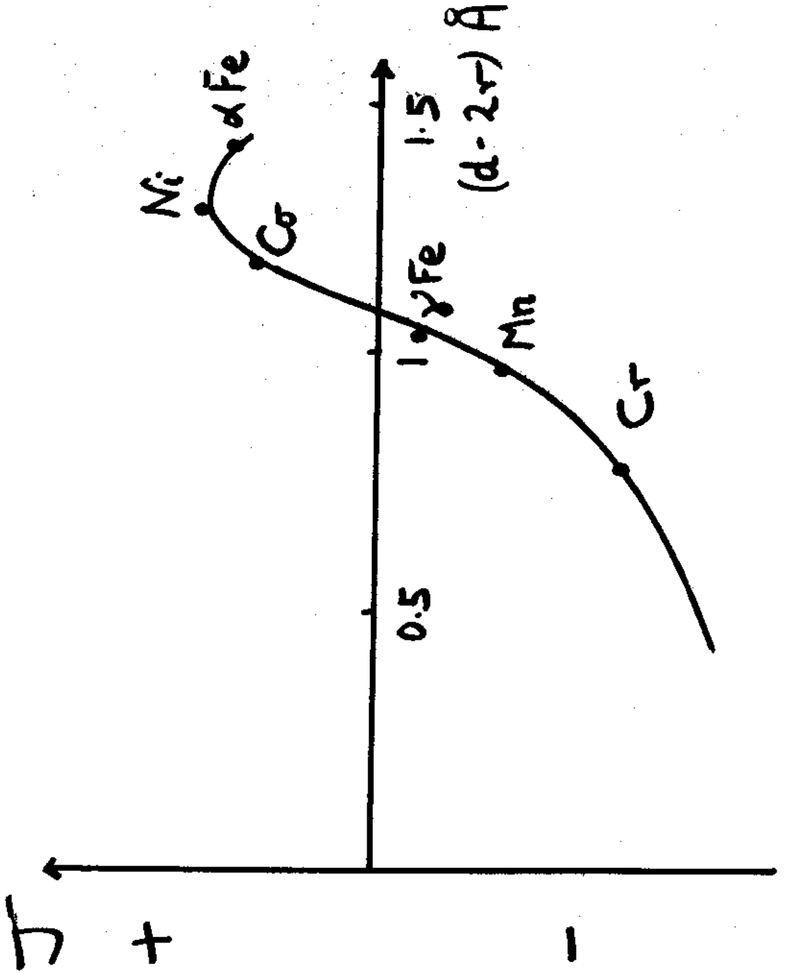


fig 6

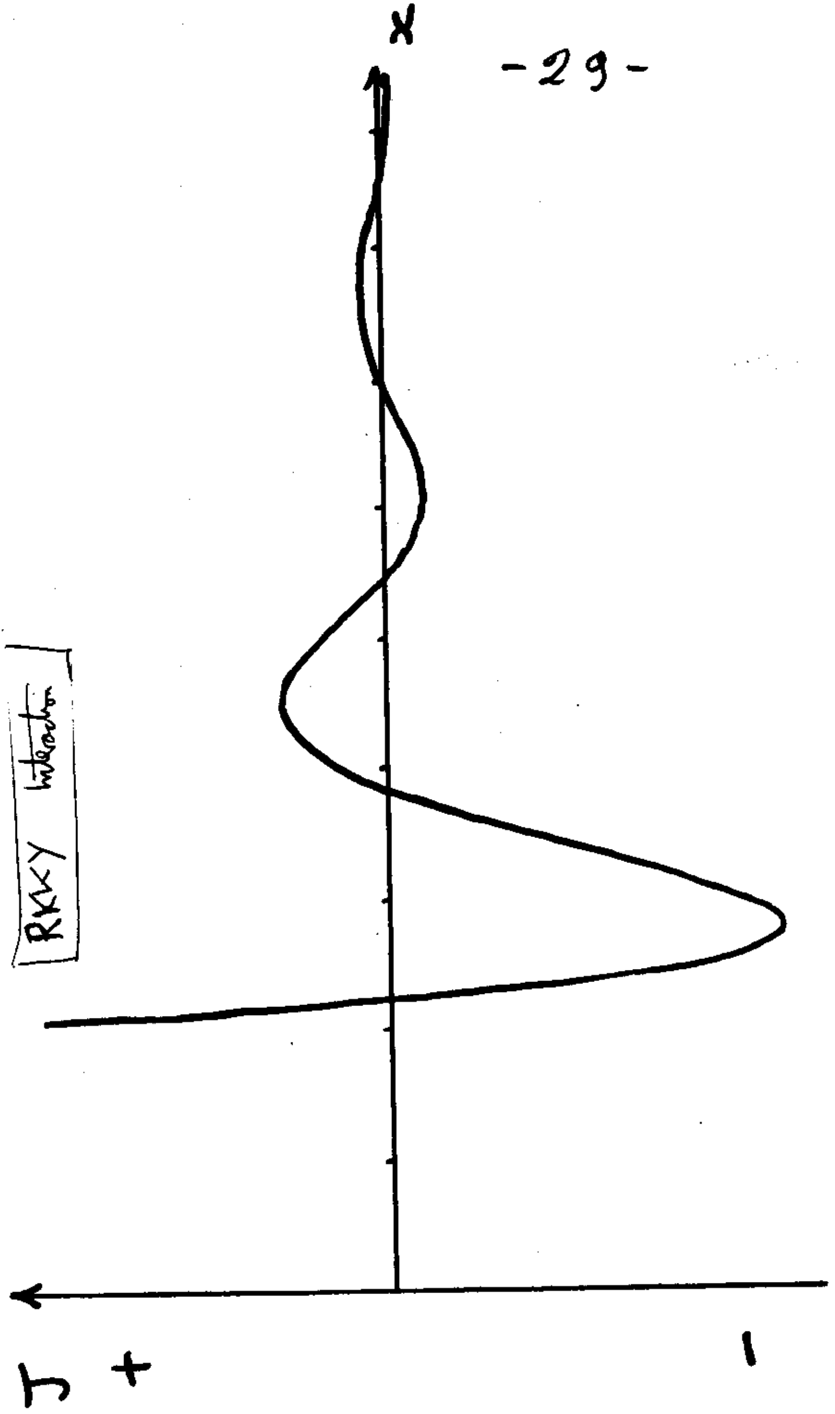


fig 7

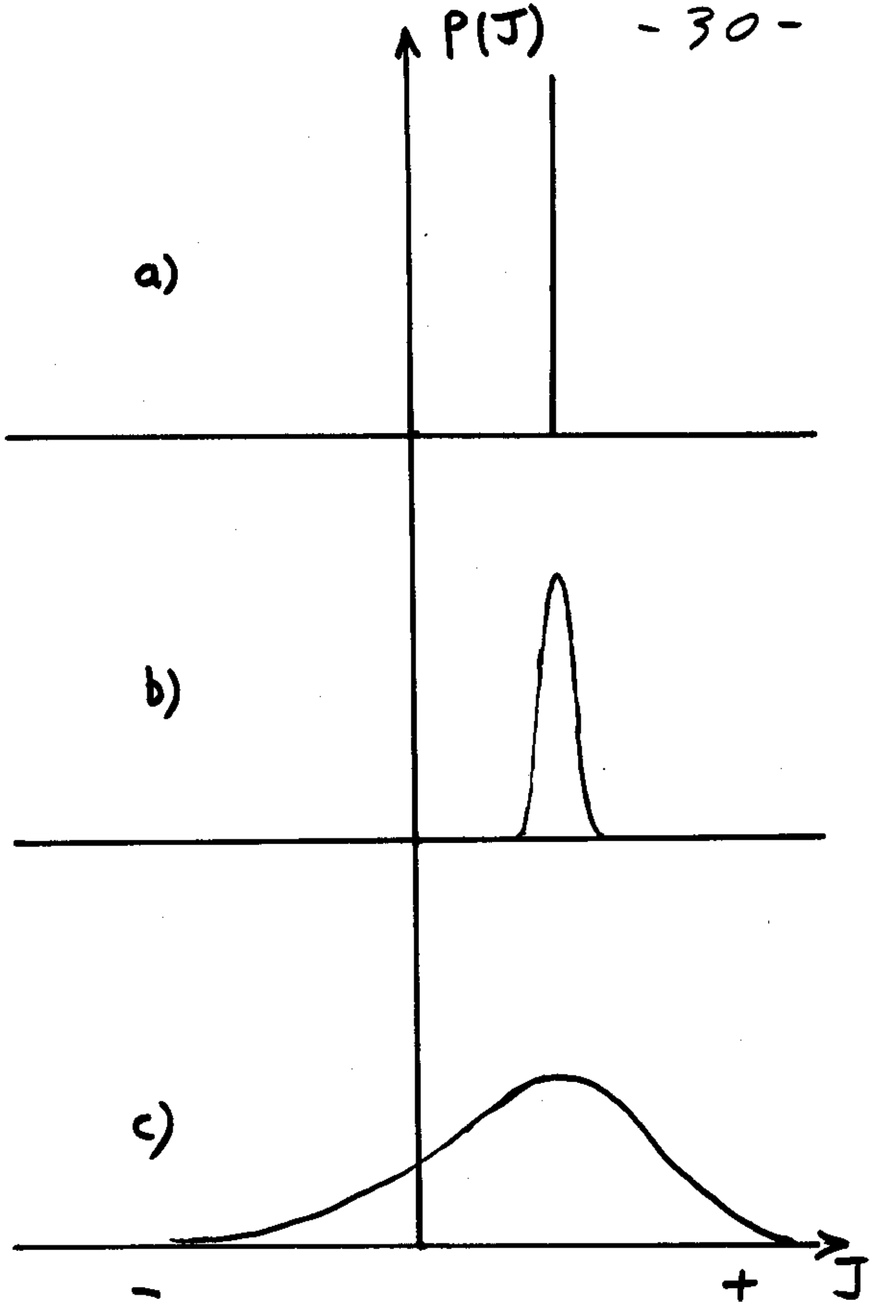
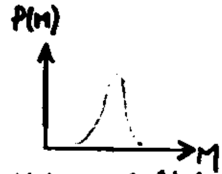
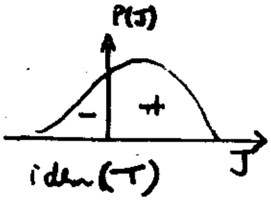


fig 8



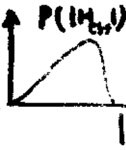
Hyperfine field distributions
(ME, NMR)
neutrons?

magnetization
neutrons
M.E.



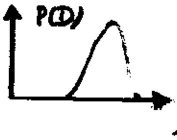
i dem (T)
χ ~

M(H) curves
neutrons



Distribution in magnitude (direction)

Specific heat
neutrons

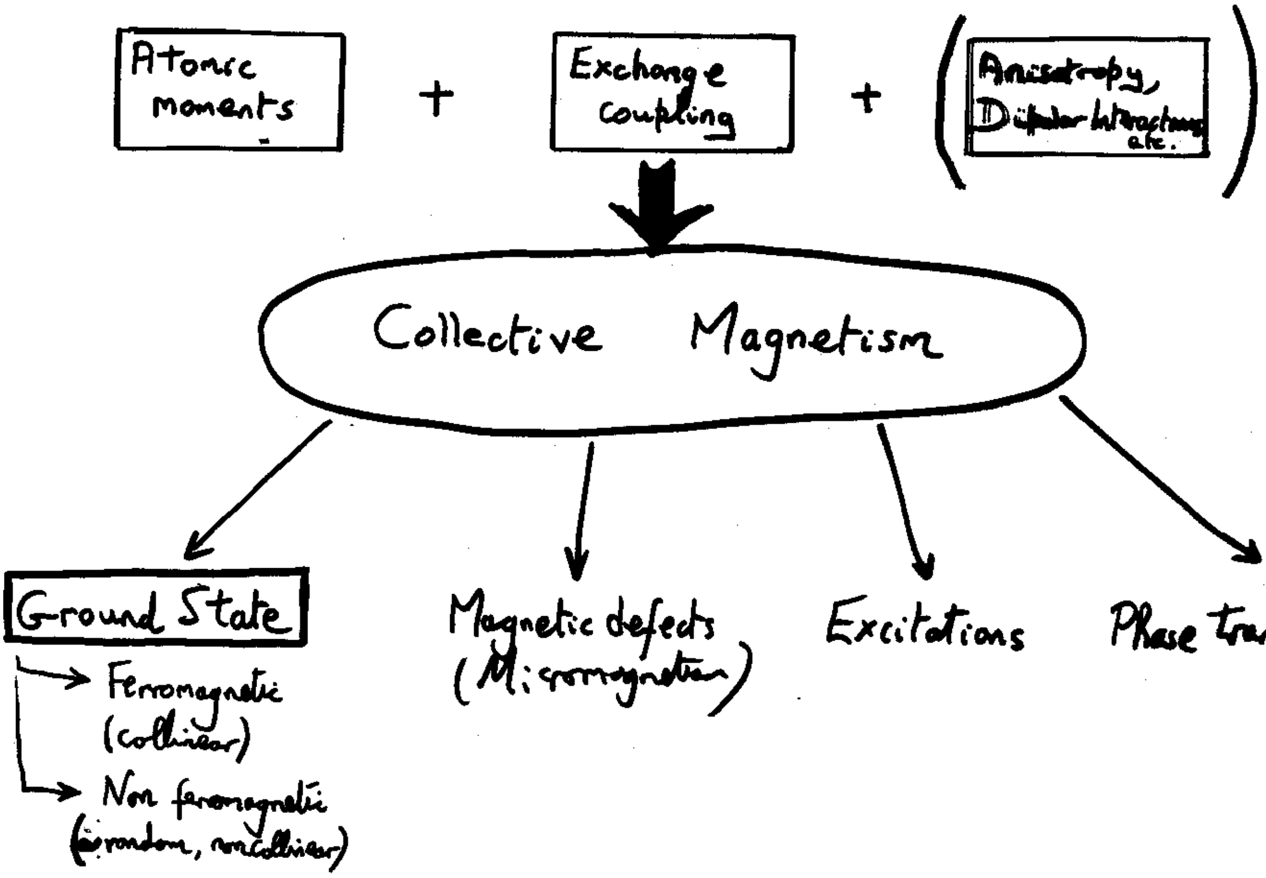


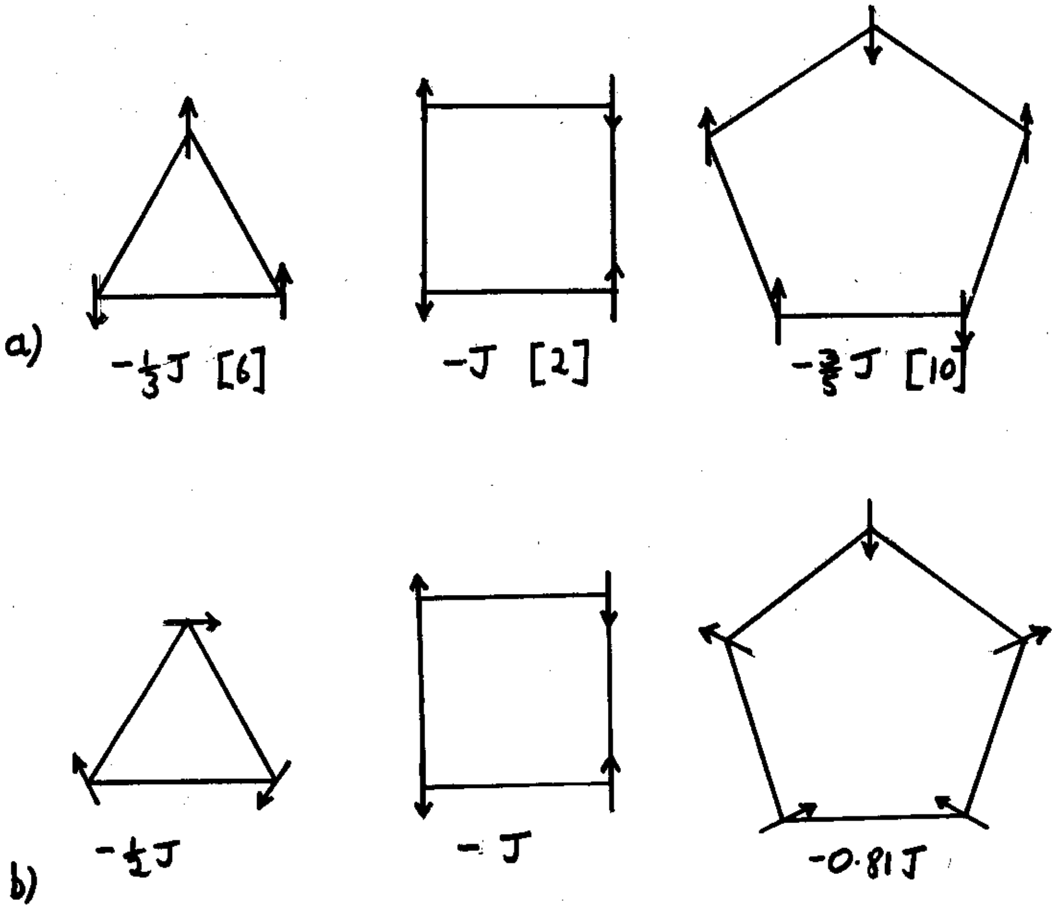
Distribution of ~~dipolar fie~~
~~randomly~~
~~oriented~~

χ, efg
D
neutrons

Specific heat
Computer experiments

COLLECTIVE MAGNETISM in AMORPHOUS METALS





Lowest-energy configurations for rings of 3 4 and 5 Ising spins (a) and classical spins (b). Energy per bond in units of J and degeneracy (for Ising spins) are shown under each ring

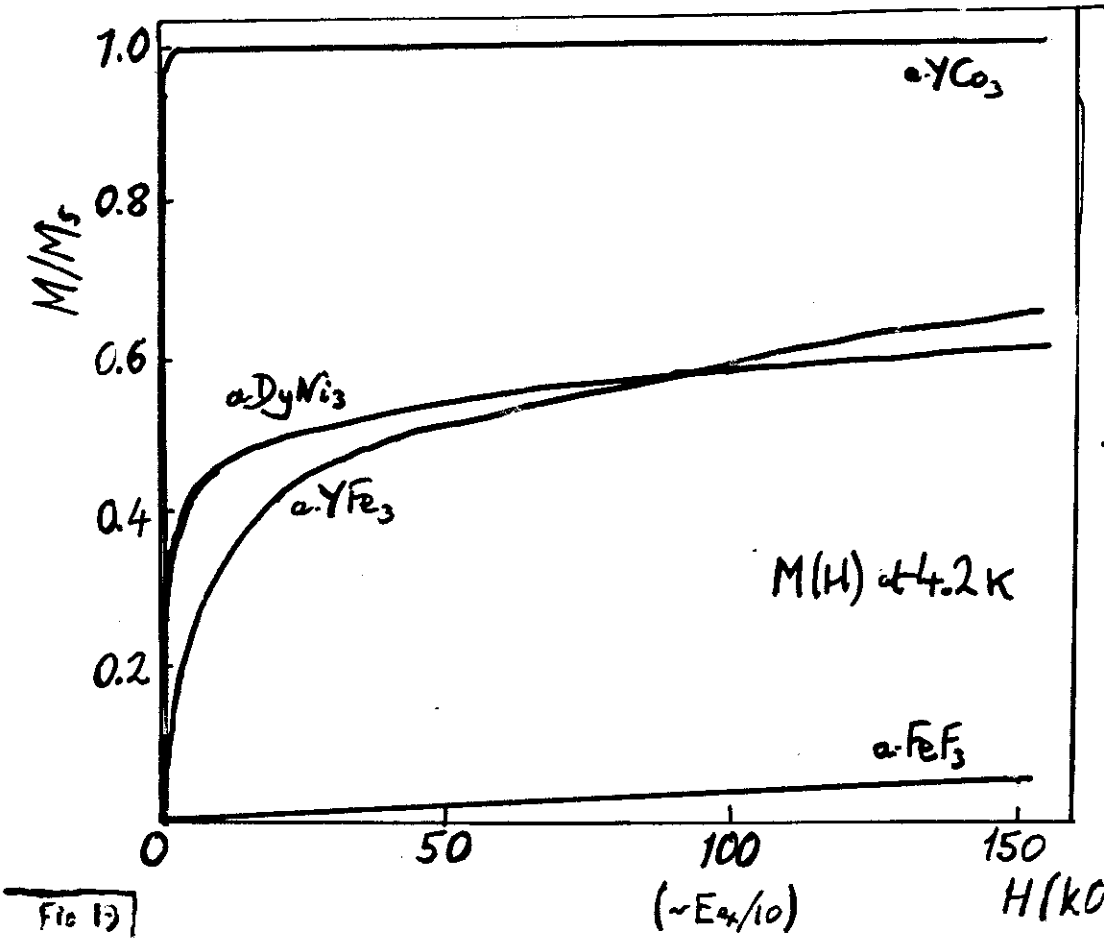
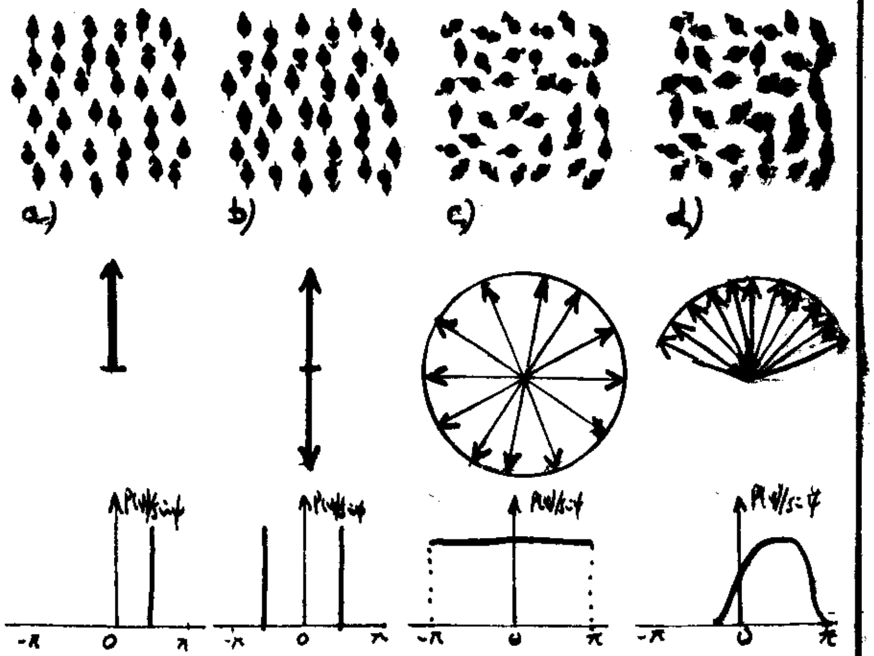


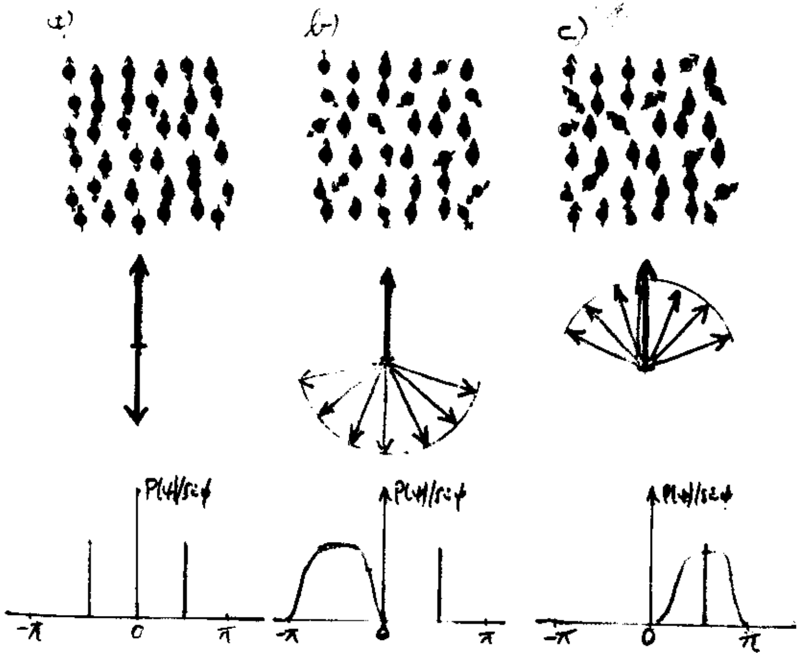
Fig 17

III One Subnetwork Magnetic Structures



$\bar{S}_{iz} \neq 0$	$\bar{S}_{iz} \neq 0$	$\bar{S}_{iz} \neq 0$	$\bar{S}_{iz}^2 \neq 0$
$\bar{S}_i \cdot \bar{S}_j = \bar{S}_i^2$	$\bar{S}_i \cdot \bar{S}_j = \pm \bar{S}_i^2$	$-\bar{S}_i^2 \leq \bar{S}_i \cdot \bar{S}_j \leq +\bar{S}_i^2$	$-\bar{S}_i^2 \leq \bar{S}_i \cdot \bar{S}_j \leq \bar{S}_i^2$
$\langle \bar{S}_i \cdot \bar{S}_j \rangle = \bar{S}_i^2$	$\langle \bar{S}_i \cdot \bar{S}_j \rangle_{r_{ij} > a} = 0$	$\langle \bar{S}_i \cdot \bar{S}_j \rangle_{r_{ij} > a} = 0$	$0 < \langle \bar{S}_i \cdot \bar{S}_j \rangle < \bar{S}_i^2$
Ferromagnet	Antiferromagnet	Speromagnet	Asperomagnet

Two Subnetwork Magnetic Structures



Ferrimagnet	Sperimagnets	
$GdCo_2$	$DyCo_2$	$NdCo_2$