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Spin Glasses

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ABSTRACT. During the last decade the term 'spin glass' has become prominent in the literature on magnetism. It refers to magnetic alloys where the spins on the impurities become locked or frozen into random orientations below a characteristic temperature T_0. In this article the properties of spin glasses are described with particular reference to the two archetypal examples *Au*Fe and *Cu*Mn. Interest in spin glasses was mainly stimulated by some a.c. susceptibility measurements which showed sharp, cusp-like peaks, accurately defining T_0 and suggesting that some type of phase transition was occurring. The Mössbauer effect and the anomalous Hall effect also showed clear features at T_0 supporting this viewpoint. But measurements of the electrical resistivity and 'specific heat', here usually meaning the molar heat capacity, also the remanence, magnetic hysteresis and time-dependent effects observed in spin glasses were difficult to reconcile with a phase transition approach. This article discusses the results obtained from the very wide variety of experimental techniques which have been used to investigate spin glasses, and also deals with some of the important theoretical concepts which have arisen out of these studies. Then follows a short account of the many systems which have been found to exhibit spin glass behaviour and which suggest that it is a widespread magnetic state of matter. Lastly, an example is given which shows that some of the ideas of spin glasses are applicable to problems outside the sphere of magnetic alloys.

1. Introduction

Although magnetism in the form of the lodestone was known to the ancient Greeks, ir understanding of it is still very incomplete. One reason for this is that magnetism .ppears in many different forms such as diamagnetism, paramagnetism and ferromagnetism and there is no unified theory. Over the last decade another distinct magnetic state known as the spin glass or mictomagnet† has been recognized. The term spin glass is due to B.R. Coles of Imperial College, London and derives from certain similarities which these materials have with real glasses, whereas the word mictomagnet was coined by P. A. Beck of Urbana, Illinois and comes from the Greek prefix meaning mixed.

Spin glass behaviour was first observed in fairly concentrated alloys (about 1 to 10 at.% of impurities) of iron in gold (*Au*Fe) and manganese in copper (*Cu*Mn). The first of the two metals, as *Au* in the alloy (*Au*Fe) is the host, and the second, as Fe, the impurity. The explosion of interest in this subject arose from some fascinating and important measurements by Cannella and Mydosh (1972, 1973) who observed a cusp-like peak in the a.c. susceptibility of *Au*Fe alloys at a well defined temperature T_0, known as the spin glass freezing temperature. Their work will be discussed fully in the next section. Far from being confined to just a few alloys, such behaviour has been found in many systems. It is this ubiquitous nature of the spin glass which has proved to

† Spin glass is the much more widely used term. Nowadays mictomagnet generally refers to concentrated alloys where the behaviour is dominated by large clusters (see Section 4).

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be such a fruitful field of study for many research groups and has led to the belief that is a fundamental magnetic state of matter. A complete picture has yet to emerge. There is still a great deal of controversy over whether a phase transition is in fact occurring at T_0.

The behaviour of the 3d transition elements in the noble metals copper, silver and gold and also in metals such as aluminium and zinc has been a topic of interest for many years. The criteria for magnetism in these alloys was worked out mainly by J. Friedel and coworkers and also by P. W. Anderson in the 1950s and 60s. In the 1930s a resistance minimum occurring around 10–20 K was found in nominally pure copper and gold. This was attributed to the presence of magnetic impurities. The major breakthrough in the understanding of the resistance minimum effect was the calculation by J. Kondo in 1964 which led to an enormous amount of theoretical and experimental work on what became known as the Kondo problem (see Bell and Caplin (1975)). An essential feature of the Kondo problem is that it assumes that the impurities are isolated from each other, that is, there are no interactions between impurities. It became apparent that in real alloys this situation is often realized only at extreme dilution (sometimes with as little as a few p.p.m. of impurities) and it is this which made it very difficult to study the Kondo problem experimentally. Impurity spins are able to interact with each other by polarizing the conduction electrons and this is known as the RKKY (Ruderman–Kittel–Kasuya–Yosida) interaction. Its form is shown in fig. 1 where it can be seen that the interaction, $J(r)$, is oscillating and dies away rather slowly as the inverse cube at large distances from a given spin ($J(r) \sim \cos 2k_F r/(k_F r)^3$ as $r \to \infty$, where k_F is the Fermi wave-vector). This oscillatory RKKY interaction is important for understanding spin glass behaviour. From fig. 1 it can be seen that the coupling between the magnetic moments of two impurity spins can be either ferromagnetic or antiferromagnetic depending upon their separation. Because of the random positions of the impurity spins within the crystal, the magnetic interactions are also randomly distributed. This gives rise to the term spin glass in analogy with a real glass or an amorphous solid where the atomic sites are without order or regular structure.

As the concentration of impurities increases, there is a tendency just on statistical grounds to form pairs, triplets and eventually clusters of impurities. A spin glass with 10 at.% of impurities is represented schematically in fig. 2. Clearly one has a very complicated situation where a given impurity is influenced by many others. It was the unexpected discovery of a sharp transition in the a.c. susceptibility which focused attention on these alloys. This will now be discussed.

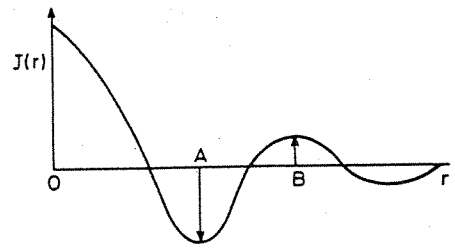


Fig. 1. The RKKY interaction $J(r)$ between two magnetic impurities in a metal as a function of their separation r. If one magnetic moment is fixed at the origin O, then a second impurity situated at a distance $r = OA$ will be coupled *antiferromagnetically* with it. A second impurity at a distance $r = OB$ then will be coupled *ferromagnetically* but less strongly than that at distance OA.

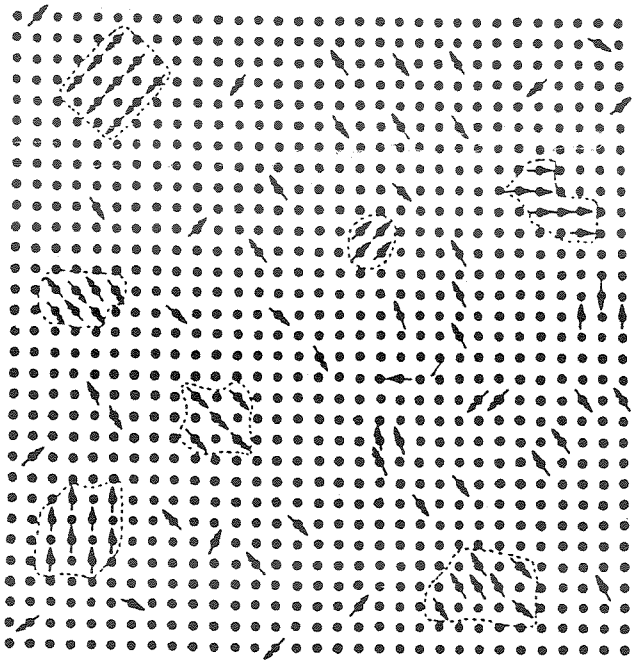


Fig. 2. Representation of a spin glass with about 10 at.% of impurities showing mictomagnetic clusters (After Mydosh 1975).

Since c.g.s. electromagnetic units are still to be found in published work, and the distinction between magnetic field strength H (now in $A\,m^{-1}$) and magnetic flux density B (now in $T = V\,s\,m^{-2}$) is often not made clear and could possibly be irrelevant for the purpose of this article, units and numerical values will not be introduced unnecessarily. For many graphs where variation or trend is the chief interest, the axes will be labelled as for 'arbitrary units', while B and H will mostly follow the original workers.

As most usually defined, magnetization M and magnetic field strength H are measured in the same units, so the magnetic susceptibility $\chi_M = M/H$ is dimensionless. Mass susceptibility χ_M/ρ has the same units in any system as $1/\rho$, where ρ is the density of the material.

2. Alternating-current susceptibility

Cannella and Mydosh (1972, 1973) measured the a.c. susceptibility of several $AuFe$ alloys and observed a sharp, cusp-like peak at a well defined temperature which was called the freezing temperature T_0. Such measurements provide the most accurate method to date of determining T_0. Some of their results are shown in figs. 3 and 4. Their apparatus consisted of a very sensitive, low audio frequency (around 150 Hz) mutual inductance bridge which needed a driving field of about 0·5 mT. No dependence of the peak on frequency was observed but application of small external fields of 10 to 20 mT produced a rounding of the peak similar to that observed earlier with d.c. techniques (see fig. 4). It was also found that T_0 increased with the impurity concentration, c, roughly as $c^{2/3}$, although a more nearly linear dependence on c was found below 1 at.%. Below T_0 the impurity spins are no longer able to fluctuate rapidly with time but instead are locked or frozen into random orientations. As the temperature approaches the

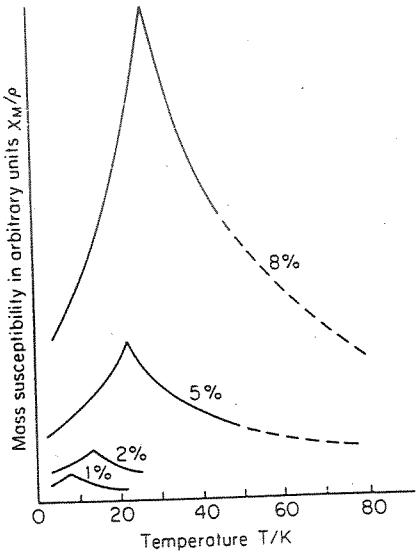


Fig. 3. Low-field susceptibility $\chi_M(T)$ for four *Au*Fe alloys (After Cannella and Mydosh 1972).

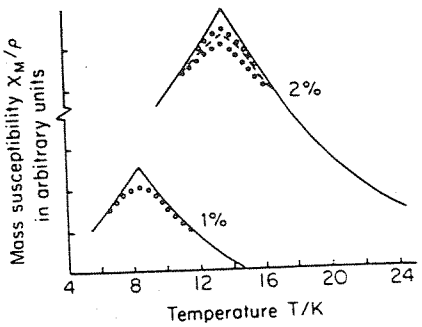


Fig. 4. Low-field susceptibility $\chi_M(T)$ for two *Au*Fe alloys showing the effect of increasing the external field. The full line represents the zero field limit (After Cannella and Mydosh 1972). Flux density ○ ○ ○ 10 m T; ---20 m T; ● ● ● 30 m T.

absolute zero, χ_M extrapolates to a finite value $\chi_M(0)$ and the ratio $\chi_M(0)/\chi_M(T_0)$ has a nearly constant value of about 0·6 for impurity concentration between 0·1 and 5 at.%. Above T_0 the susceptibility could be fitted to a modified Curie–Weiss law. The observation by Cannella and Mydosh of these sharp, cusp-like peaks in the a.c. susceptibility has provoked widespread interest and controversy. They suggest that some type of phase transition is occurring at T_0 and much of the early theoretical work on spin glasses was centred around understanding the peaks. For many years the behaviour of such dilute magnetic alloys had been interpreted in terms of a random molecular field model having a distribution of internal fields which had been developed by Marshall (1960) and Klein and Brout (1963). According to Cannella (1973) such a model would predict: (1) broad, rounded maxima in $\chi_M(T)$. (2) The peaks should not be dependent upon field for low fields. (3) For low concentrations the magnitude of the peaks should be concentration-independent. (4) The temperature of the maximum

should be directly proportional to the concentration. The measurements of Cannella and Mydosh were in clear conflict with such a model and pointed to a new effect. They were a significant experimental observation giving rise to the topic of spin glasses and producing a whole body of fascinating experimental and theoretical research.

One early criticism of the measurements of Cannella and Mydosh was that the sharp peaks were an artefact arising from the use of an a.c. susceptibility technique. However the elegant measurements of Guy (1975, 1977a, b, 1978) who used a refined Faraday balance requiring fields of only about 2 mT to make the measurements, showed that this was not the case. With this static susceptibility technique he also observed sharp peaks very similar to those of Cannella and Mydosh under short time conditions. Guy also observed some very important time-dependent magnetization effects which will be discussed in the next section.

A second important controversy, which has still not been fully resolved, is over the frequency dependence of the susceptibility maximum. The question is an important one. If there is a phase transition at T_0, then the singularity in the a.c. susceptibility should not depend on the frequency. If, however, the spin glass is some sort of metastable state, then a frequency dependence should be expected. This latter situation occurs when very large magnetic clusters are present which freeze out around T_0 and it has been observed experimentally by Zibold (1978) for some concentrated *Au*Fe alloys. Although Cannella and Mydosh (1972, 1973) observed no frequency dependence in the a.c. susceptibility, Guy (1977a) found a pronounced frequency dependence below $0{\cdot}6T_0$ and also observed a shoulder in the low field susceptibility at this temperature. The a.c. susceptibility measurements of Löhneysen *et al.* (1978) on dilute $(La_{1-x}\ Gd_x)Al_2$ showed a series of strongly frequency-dependent susceptibility maxima. By contrast a similar investigation for dilute *Ag*Mn alloys by Dahlberg *et al.* (1979) showed no frequency dependence over a range of five decades. An attempt to reconcile the apparently conflicting observations of Löhneysen *et al.* and Dahlberg *et al.* has been made by Murani (1980a) who has considered the different relaxation rates of 4*f* and 3*d* magnetic impurities in non-magnetic hosts.

3. Remanence, hysteresis and time-dependent effects

In the previous section the a.c. response of a spin glass was described. In this section the d.c. response is discussed and it will be seen that important additional features are observed which must be taken into consideration for any comprehensive description of spin glasses. In the last section it was stated that very low d.c. fields (less than 2 mT) produce sharp susceptibility peaks at T_0 which are similar to the a.c. results. High d.c. fields completely smear out the transition at T_0 and also produce striking remanence and hysteresis effects below T_0. The existence of such effects in alloys of *Au*Fe, *Cu*Mn and *Ag*Mn has been known for many years, well before spin glasses became a fashionable research topic. However it is only fairly recently that the remanence behaviour has come under careful scrutiny particularly by the Grenoble group (Souletie and Tournier 1969, Tholence and Tournier 1974, 1977) and by Guy (1977a, b). In discussing the remanence one has to distinguish between two experimental situations. These are the isothermal remanent magnetization (I.R.M.), which is a field cycling effect and the thermoremanent magnetization (T.R.M.) which is a field cooling effect. In the I.R.M. situation a specimen is cooled to below T_0 in zero field whereupon a field H is applied which is then slowly reduced to zero. In the T.R.M. case the specimen is measured in zero field after cooling the sample from above to below T_0 in a field H. Tholence and Tourner (1974) have studied the two types of remanence behaviour in

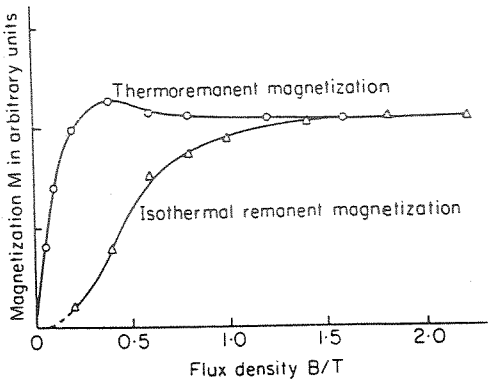


Fig. 5. Field dependences of the thermoremanent magnetization and the isothermal remanent magnetization for a *Au*Fe alloy at $T \ll T_0$ (After Tholence and Tournier 1974).

*Au*Fe and these are shown in Fig. 5. It can be seen that the I.R.M. and T.R.M. both saturate at the same value although the T.R.M. does so at a lower field.

Tholence and Tournier (1974) have shown that the total susceptibility χ_{tot} of a spin glass has both a reversible and an irreversible part. The reversible part χ_{rev}, defined by $\chi_{rev}=(M(H)/H)_{H-0}$, is measured either with the a.c. technique (Cqnnella and Mydosh 1972, 1973) or with a very low d.c. field (Guy 1975, 1977 a, b). Above a certain critical d.c. field, H_{crit}, this reversible behaviour no longer occurs. Tholence and Tournier (1974) have found that for *Au*Fe, $H_{crit} \sim 100c$ mT, where c is the concentration of the impurities. However Guy (1977 a) has argued that remanent behaviour is seen at much lower fields and has suggested that perhaps there is no lower limit for the onset of irreversible behaviour in a spin glass. The irreversible part of the susceptibility, χ_{irrev}, is obtained from the thermoremanent magnetization data, likewise written:

$$\chi_{irrev}=(\mathrm{TR}\, M(H)/H)_{H-0}$$

The total susceptibility χ_{tot} is the sum of the reversible and irreversible parts

$$\chi_{tot}=\chi_{rev}+\chi_{irrev}$$

Tholence and Tournier (1974) have shown that the total susceptibility of spin glasses remains independent of temperature below T_0.

The properties of the remanent magnetization of a spin glass have been extensively investigated and several important features have emerged from these studies. Firstly remanence and hysteresis behaviour are only observable below T_0. Secondly, as seen in fig. 5, both the I.R.M. and the T.R.M. have the same saturation value σ at a given temperature T. Souletie and Tournier (1969) have pointed out that in the concentration range between about 0·1 and 1 at.%, quantities such as the magnetization M c. saturation remanence σ/c and molar heat capacity C_M/c follow universal functions of the reduced variables H/c and T/c. This scaling approach is based on the RKKY interaction and arises from its $1/r^3$ dependence at large distances which leaves cr^3 concentration-independent. This scaling breaks down at higher concentration because of the increasing importance of short range correlations. A final important feature of the remanent magnetization is the time-dependent behaviour of both the I.R.M. and the T.R.M. This has had a very important bearing on our understanding of spin glasses and is discussed later in this section.

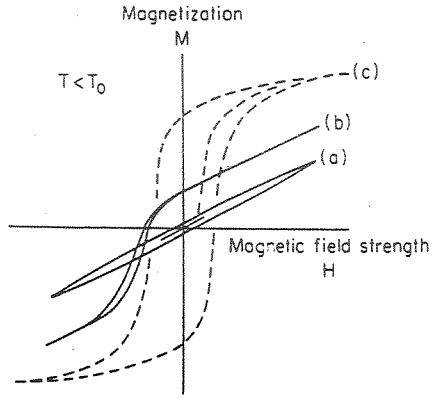


Fig. 6. Illustrating hysteresis loops of magnetization M against magnetic field strength H for (*a*) spin glass cooled in zero field (*b*) spin glass cooled in magnetic field and (*c*) ferromagnet (After Mydosh 1975).

The remanence and irreversible behaviour of spin glasses can also be seen in their hysteresis loops. These were first studied in rather concentrated *Ag*Mn and *Cu*Mn alloys ($c \sim 10$ at.%) in the late 1950s and early 60s (see for example Kouvel 1961, 1963.) Figure 6 is a picture of typical hysteresis loops. Part (*a*) is the zero-field cooled M–H characteristic. The inner portion is reversible until the critical field, H_{crit}, is exceeded when a small hysteresis and I.R.M. develop corresponding to the outer loop of part (*a*). Part (*b*) represents a field-cooled spin glass which has a striking displaced hysteresis loop. This was explained by Kouvel (1963) in terms of a model involving the unidirectional exchange interaction. This model considers the interfacial interactions between ferromagnetic and antiferromagnetic domains resulting from concentration fluctuations in the alloy. It 'remembers' that it has been cooled in a large field and attempts to keep this frozen-in memory. A much smaller oppositely directed (negative) field is able to cause an abrupt reversal of the magnetization . When the magnitude of this negative field is again reduced the alloy still possesses its remembrance of the field cooling and flips back to a positive magnetization. The unusual behaviour of a field-cooled spin glass can be compared with that of a typical ferromagnetic loop shown in (*c*).

The first observation that the saturated remanent magnetization of *Au*Fe alloys decreases as the logarithm of time was made by Tournier in the mid-60s. Since then, time dependent effects in spin glasses have been studied in some detail particularly by the Grenoble group and also by C. N. Guy. Figure 7 shows some typical data due to Guy (1978) for the time decay of the T.R.M. for a 2 at.% *Au*Fe alloy. For times greater than about 10 s the time decay of both the I.R.M. and the T.R.M. can be written in the form

$$M = M_0 - S \ln t$$

where M_0 is the initial value of the remanence and S is a constant which can depend on the field, temperature and material. Guy (1978) found that for both the I.R.M. and T.R.M., S had a maximum at $0{\cdot}6\,T_0$. He also found from plots of S/M_0 against T that one could define two distinct regions which occurred above and below $0{\cdot}8\,T_0$.

The a.c. susceptibility data described in the previous section strongly suggested that some type of phase transition was occurring at T_0. Much of the early theoretical work on spin glasses, which is described in Section 6, centred around trying to understand

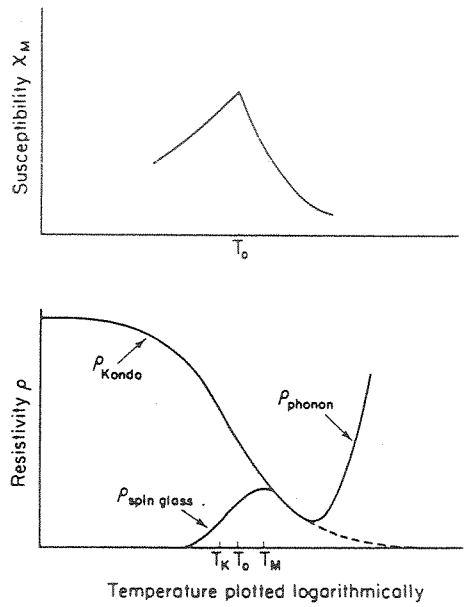


Fig. 8. Variation with temperature T/K of the susceptibility of a spin glass and the Kondo and spin glass resistivities (After Schilling *et al.* 1976).

concentration (Ford *et al.* 1977). In this latter case Δ_c increases with concentration whereas T_K remains unaltered.

A low temperature resistance maximum in *Au*Fe and *Cu*Mn alloys occurs up to a concentration of about 0·5 at.%. In this region both T_M and T_0 are increasing linearly with concentration and the scaling laws due to Souletie and Tournier (1969), discussed in the previous section, are applicable. This concentration is therefore sometimes referred to as the scaling spin glass regime.

Figure 9 due to Mydosh *et al.* (1974) shows the overall temperature variation up to 300 K of the impurity resistivity $\Delta\rho$ ($\Delta\rho = \rho_{alloy} - \rho_{pure\ metal}$) for some *Au*Fe alloys. Similar features have been observed for *Cu*Mn, *Au*Mn, *Ag*Mn and *Au*Cr alloys (Ford and Mydosh 1976). The low temperature behaviour of the resistivity has been the subject of considerable interest. The above authors found that the resistivity obeyed the relation

$$\Delta\rho(T,c) = c\Delta\rho_0 + A(c)T^{3/2}$$

the coefficient of $A(c)$ varying slowly with concentration. The value of the impurity resistivity $\Delta\rho$ arises partly from the spin-split virtual bound state of the 3d impurities (see Bell and Caplin 1975) and also from the disorder scattering of the randomly frozen spins. At extremely low temperatures, less than 0·3 K, Laborde and Radhakrishna (1973) have observed a T^2 dependence. The low temperature resistivity, particularly the $T^{3/2}$ region, has been ascribed by Rivier and Adkins (1975) to long wavelength elementary excitations which are diffusive in character. The excitations are highly damped, independent, localized spin fluctuations which scatter the conduction electrons. A more recent theory due to Fischer (1979), which considers different diffusive modes from those used by Rivier and Adkins, has emphasized the T^2 region. Around T_0 the resistivity is varying roughly linearly with temperature. At higher temperatures a resistance maximum is observed. This is rather broad for *Au*Fe alloys

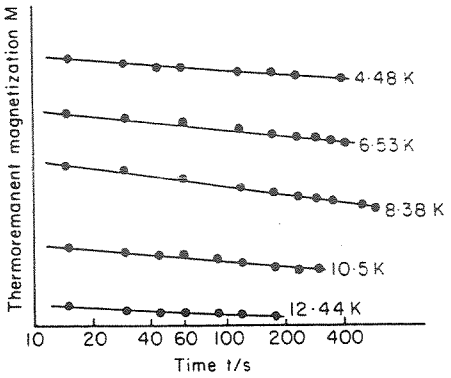


Fig. 7. Time decay. Thermoremanent magnetization plotted against time t for a 2 at.% *Au*Fe alloy which had been field cooled in 12·8 mT (After Guy 1978).

such a phase transition. By contrast, the remanence, hysteresis and time-dependent effects described in this section cannot readily be understood within such a framework. However, such features are seen in a very different branch of magnetism, namely, that of rock magnetism. Wohlfarth (1977) has very explicitly pointed out the similarity between the properties of rock magnets and many aspects of spin glasses. Many magnetic rocks also have a sharp peak in their susceptibility, which is called the Hopkinson peak, a fact which has been known since the end of the last century. An alternative description of spin glasses, not involving a phase transition, but invoking some of the concepts used to describe rock magnetism has become very prominent and will also be discussed in Section 6.

4. Electrical resistivity

The electrical resistivity of *Au*Fe and *Cu*Mn has been studied with impurity concentrations varying from less than 1 p.p.m. to more than 50 at.%—a range of well over five decades. As the concentration increases, so different effects dominate and this is illustrated nicely by variations in the behaviour of the electrical resistivity. Figure 8 shows variations of the resistivity and also the a.c. susceptibility of dilute alloys. At extreme dilution one has the isolated impurity Kondo behaviour mentioned in the introduction. For rather larger concentrations, the RKKY interaction between the impurities suppresses the spin flip scattering responsible for the Kondo effect and this results in the appearance of a rounded maximum at a well defined temperature T_M.

Larsen (1976) has derived an expression for T_M as a function of T_K, the Kondo temperature, and Δ_c, the average RKKY interaction. He finds that in the limit $\Delta_c \gg T_K$, which is the spin glass region, $T_M \sim \Delta_c \ln(\Delta_c/T_K)$. In the same limit $T_0 \sim \Delta_c$ and hence T_M is greater than T_0 as can be seen in fig. 8. The theory of Larsen can be used to explain the measurements of Schilling *et al.* (1976) who studied the effect of applied pressure on T_M for alloys of *Au*Mn, *Cu*Mn and *Au*Fe. Applying pressure increased T_M for *Au*Mn, had little effect on *Cu*Mn and decreased T_M for *Au*Fe. The effect of pressure is to increase J, the s–d exchange interaction, and this has a dramatic effect on T_K, through its exponential dependence on J, but a much smaller effect on Δ_c through its $|J|^2$ dependence. Hence the direction in which T_M changes depends on the relative magnitudes of T_K and Δ_c. Pressure has proved to be a useful tool in the study of spin glasses and this has been comprehensively reviewed by Schilling (1979). The effect of pressure on T_M complements the study of the variation of T_M with increasing impurity

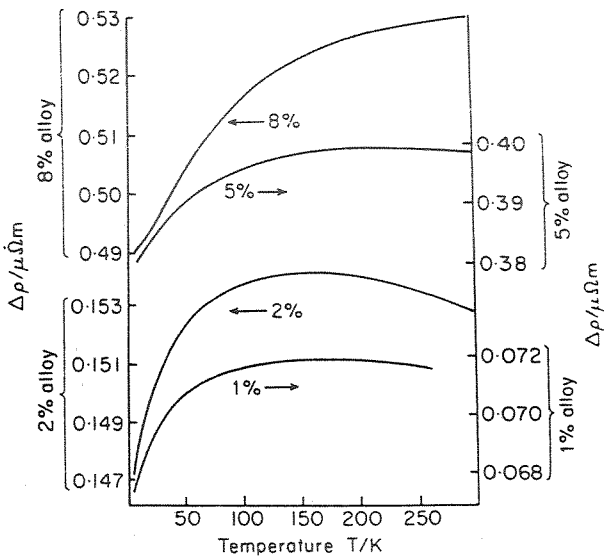


Fig. 9. Temperature dependence of the impurity resistivity $\Delta\rho$ for four *Au*Fe alloys. (After Mydosh *et al.* 1974).

but is much sharper for *Cu*Mn, *Ag*,Mn, *Au*Mn and *Au*Cr (Ford and Mydosh 1976). In these latter cases a continuous fall-off of the resistivity occurs as room temperature is approached. It appears probable that above the resistance maximum thermal disorder is gradually breaking up the interactions between the impurities to give rise to a modified Kondo scattering. It is very difficult to analyse the high temperature data with any certainty because of contributions due to other effect such as deviations from Matthiessen's rule.

Unlike the a.c. susceptibility, a direct measurement of the electrical resistivity does not yield a value for the freezing temperature T_0. Measurement of the temperature dependence of $\mathrm{d}(\Delta\rho)/\mathrm{d}T$ (Mydosh *et al.* 1974, Ford and Mydosh 1976) gives a clear maximum which is generally at a lower temperature than T_0, although the agreement is quite good in the case of *Au*Fe. The method is not a reliable one for determining T_0 in spin glasses in contrast to materials which have a long range order where a maximum or sometimes a divergence is observed at the ordering temperature.

The spin glass region in *Au*Fe alloys occurs from about 0·5 to 10 at.% of impurities. Above this concentration there is an increasing statistical probability of one impurity having another as a first or second nearest neighbour. There is therefore a tendency to form magnetic clusters due to concentration fluctuations in the alloy and this region is known as the mictomagnetic or cluster spin glass. It is a difficult region to study experimentally since many of the results depend strongly on the metallurgical state of the sample. Different heat treatments and plastic deformations can greatly affect the cluster formation. The effects of different metallurgy, particularly on the magnetic properties of concentrated *Cu*Mn alloys, have been studied extensively by Beck and coworkers and are summarized in his review article (Beck 1978).

At a certain concentration, which depends on the type of crystal structure, each impurity will have at least one impurity as a nearest neighbour. The whole alloy is thereby linked from one end to the other by a chain of impurities and it is said to have reached the percolation limit. Percolation problems occur in a wide variety of studies

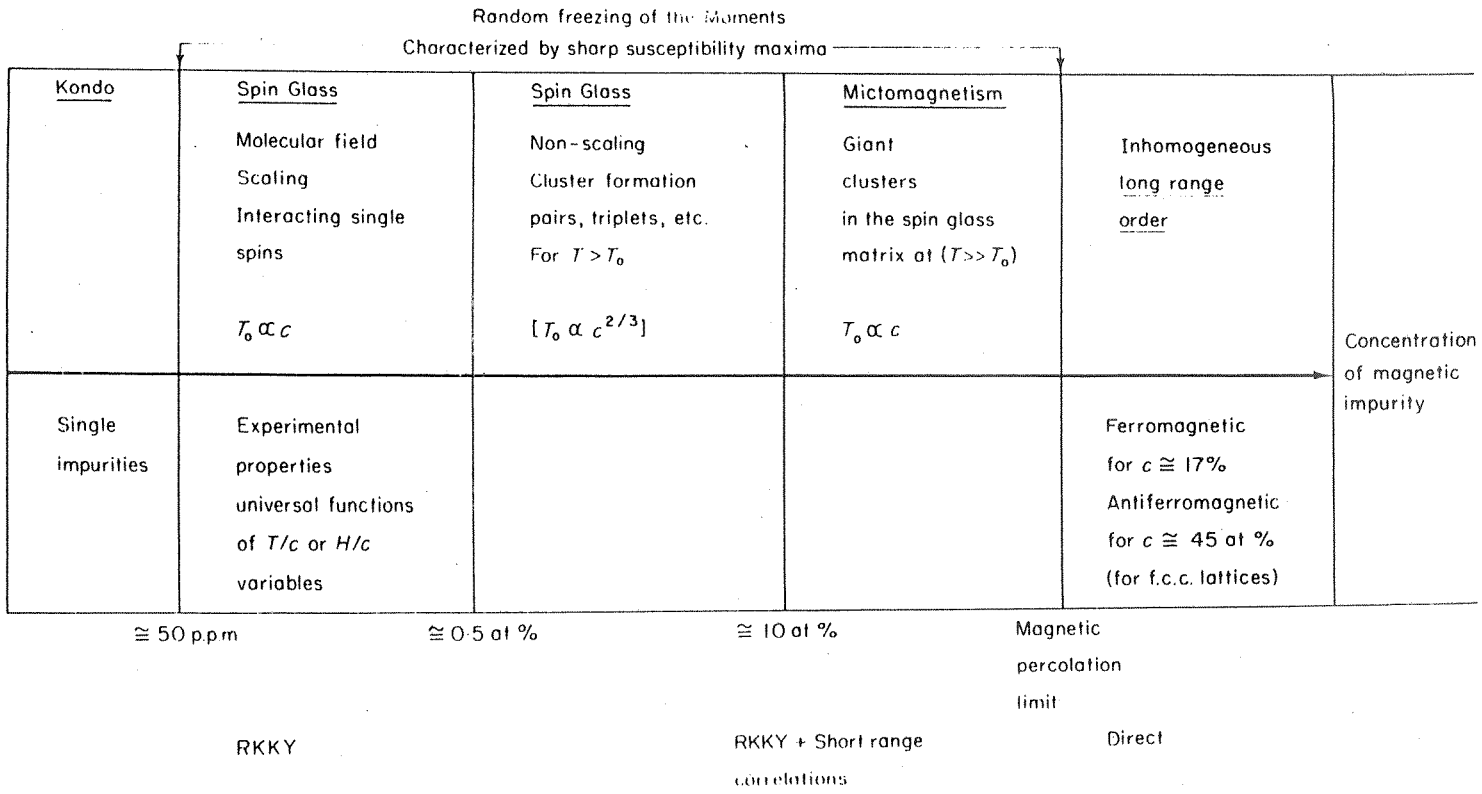


Fig. 10. The various concentration regimes for a magnetic alloy showing the different types of magnetic behaviour which can occur (After Mydosh 1978).

(see for example Domb *et al.* 1980). The magnetic consequence of the percolation limit is to give rise to a long-range but very inhomogeneous magnetic order. In the case of *Au*Fe, which is an f.c.c. lattice, an inhomogeneous ferromagnetism occurs above about 17 at.% Fe. The effect of this magnetic order can be seen as a characteristic knee in the behaviour of the resistivity as a function of temperature (Mydosh *et al.* 1974). For *Cu*Mn, which is also an f.c.c. lattice, inhomogeneous antiferromagnetism occurs above a percolation limit of 45 at.% Mn.

The different concentration regions which have been discussed in this section are summarized in fig. 10. Two points should be emphasized. Firstly, there is no universal agreement on the various spin glass terms mentioned here and some research groups use these terms in a rather different context to that given here. Secondly, the electrical resistivity in particular shows a gradual change in behaviour and the different regions which have been mentioned merge into each other rather than being sharply divided.

5. Further measurements

Spin glasses have been examined by a wide variety of experimental techniques which have yielded a considerable amount of information. A comprehensive account has been given in the review article by Mydosh and Nieuwenhuys (1980). At one time it seemed possible to divide the experimental measurements into those which showed a sharp effect at T_0, giving a clear indication of the freezing temperature, and those which exhibited a broad change in their behaviour over a large temperature range. For example the a.c. susceptibility belonged to the former category and the electrical resistivity to the latter. A discussion of the various measurements on spin glasses based on this approach has been given by Mydosh (1977). Since that time some of the measurements have been refined and others have come under closer scrutiny and it is less easy nowadays to make such a distinction. There is considerable controversy surrounding the interpretation of some of the data and a generally accepted picture has yet to emerge. Two excellent critical discussions of experiments on spin glasses have been given by Murani (1977 a, 1978 a). In this section the first four measurements which are described are macroscopic properties of spin glasses and the remainder are microscopic properties.

5.1. *Hall effect*

McAlister and Hurd (1976 a, b) have pointed out that measurement of the anomalous Hall effect is a sensitive method for studying spin glasses. A simple metal has a very small Hall effect due to the classical Lorentz force. When magnetic impurities are present there is an additional large component due to the spin–orbit coupling between the conduction electrons and the localized moments. This coupling results in an asymmetric or skew scattering for those moments which have been aligned by a magnetic field applied perpendicular to the current flow. This produces an additional contribution to the transverse electric field which is known as the skew component and which is a measure of the degree of alignment in the magnetic field. A more detailed explanation is given in the article by Hurd (1975). For a random arrangement of moments there is no average skew component and thus at high temperatures the skew scattering is small due to the effect of thermal disorder. The skew component is very sensitive to the rearrangement of the moments which occurs around the freezing temperature and this gives rise to a clear maximum at T_0 as can be seen in fig. 11. Again there is a sharp reduction in the skew component below T_0 due to the random freezing of the moments. The data of fig. 11 has similarities with the a.c. susceptibility

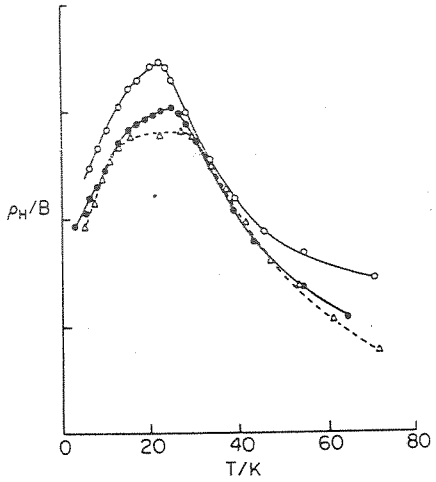


Fig. 11. Temperature dependence of ρ_H/B (where ρ_H is the Hall resistivity and B the magnetic flux density) for 8 at.% *Au*Fe alloy: ○, 20 mT; ●, 50 mT; △, 100 mT. (After McAlister and Hurd 1976a).

measurements shown in figs. 3 and 4. In both cases there is a substantial rounding of the peak as the external field is increased. Guy (1978) has also drawn attention to the fact that both the low field susceptibility and the anomalous Hall effect have a shoulder at 0·6 T_0.

The Hall effect appears to be the only transport property where there is a rather clear anomaly at T_0. This is probably because the normal component of the Hall effect is very small whereas in the case of the electrical resistivity and the thermopower there are large additional components which can mask any small effect occurring at T_0.

A good review of the anomalous Hall effect in spin glasses has been given by McAlister (1978).

5.2. *Thermoelectric power*

The thermoelectric power is extremely sensitive to very small amounts of magnetic impurities which can give rise to the giant thermopowers seen in the Kondo problem (see Bell and Caplin 1975). Figure 12 shows experimental results due to Cooper *et al.* (1980) for the thermoelectric power of spin glasses containing approximately 5 at.% of transition metal impurities. The data have some interesting features. Firstly in contrast to measurements of the a.c. susceptibility (Cannella 1973) and the electrical resistivity (Ford and Mydosh 1976) of these alloys, the thermopower data are not even qualitatively similar. Secondly there is no clear indication of a freezing temperature from the raw data shown in fig. 12. Foiles (1978) has suggested that the temperature at which the thermoelectric power changes sign corresponds to the freezing temperature. A considerable difficulty in analysing thermopower data is that several contributions are involved such as those arising from phonon, potential and magnetic scattering. An attempt to extract the magnetic contribution has been made by Cooper *et al.* (1980). They found that the temperature at which this reversed sign was in reasonable agreement with T_0 for *Au*Cr, *Au*Mn and *Ag*Mn alloys. However *Au*Fe alloys show no signs of reversal over a very wide range of concentration and do not seem to fit in with this scheme.

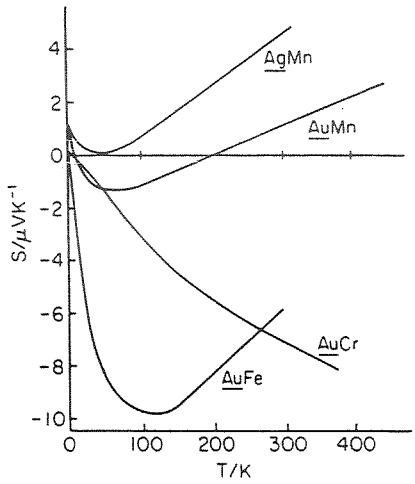


Fig. 12. Variation with temperature of the thermopower S of several spin glasses, each with approximately 5 at.% transition metal impurity. (After Cooper *et al.* 1980).

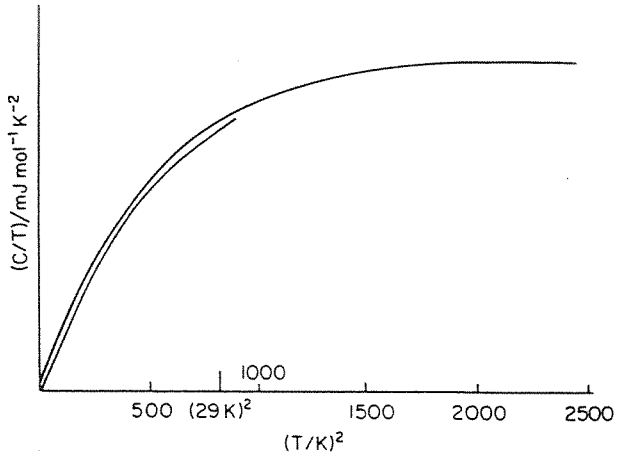


Fig. 13. Temperature dependence of the *total* molar heat capacity for 8 at.% *Au*Fe alloy (T_0 = 29 K) expressed as a plot of C/T against T^2. The lower curve is the calculated non-magnetic contibution. (After Wenger and Keesom 1975).

5.3. *Heat capacity*

Considerable interest has centred around the 'specific heat' (molar heat capacity) of spin glasses. If a phase transition is occurring, which is similar to that found in normal ferromagnets, then an anomaly at T_0 would be expected. Wenger and Keesom (1975, 1976) have examined the molar heat capacity of some *Au*Fe and *Cu*Mn alloys. Their measurements of the molar heat capacity for a *Au*Fe alloy are shown in fig. 13. The data were taken particularly carefully around T_0, but Wenger and Keesom found no anomaly, although the characteristic cusp in the a.c. susceptibility was observed on a portion of the same sample. A rather broad peak occurs at a temperature which is well above the freezing temperature and there is no correlation between the two. At low temperatures the molar heat capacity is varying linearly with temperature and is independent of concentration. Similar behaviour has been found in ordinary glasses and this is a further reason for the use of the term spin glass.

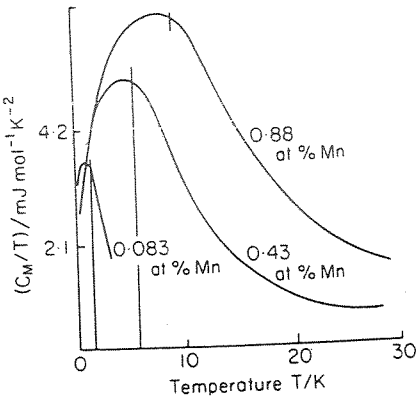


Fig. 14. Variation of C_M/T, where C_M is the magnetic contribution to C, with temperature for three CuMn alloys. The vertical lines show the freezing temperature for each concentration (After Martin 1980a).

More recently some very precise measurements down to 0·35 K have been made by Martin (1979, 1980a, b) on CuMn and AuFe alloys with concentrations of 1 at.% and less. He found no anomaly at T_0 in the magnetic part of the molar heat capacity, C_M as a function of temperature T. However, a plot of C_M/T versus T showed a pronounced 'knee' at the freezing temperature. This is illustrated in fig. 14 for some CuMn alloys. The area under the curve corresponds to the entropy and the data therefore show that above T_0 the rate of increase of the entropy begins to decrease rapidly. The magnetic entropy up to T_0 is given by

$$S_M = \int_0^{T_0} \frac{C_M(T)\,dT}{T}$$

A comparison with the total entropy per mole of Mn, corresponding to $R \ln(2S+1)$, where S is the impurity spin, suggests that less than half the total spin glass entropy is taken up in heating from the absolute zero to T_0. This implies the presence of considerable amounts of short range magnetic order above T_0.

The measurements of Martin are the first time that a clear feature in the heat capacity has been observed at the freezing temperature. His work suggested that the 'knee' became less pronounced as the impurity concentration increased and might therefore have not been observable in the alloys examined by Wenger and Keesom (1975, 1976).

Recently Thomson and Thompson (1981) have analysed various published data on the low temperature specific heat capacity and magnetization of CuMn, AuMn and AgMn alloys. They have concluded that in both cases the dominant excitations at low temperatures lead to a $T^{3/2}$ temperature dependence in a similar manner to that observed for the electrical resistivity (Ford and Mydosh 1976).

5.4. *Ultrasonic measurements*

Ultrasonic measurements are a very sensitive method for examining magnetic phase transitions. With the pulse echo overlap technique it is possible to detect velocity changes as small as one part in 10^7. For long range magnetic order a sharp maximum in the ultrasonic attenuation and a clear minimum in the ultrasonic velocity have been observed at the transition temperature. There are thermodynamic relations between the temperature dependence of the sound propagation and the value of C. Hence any

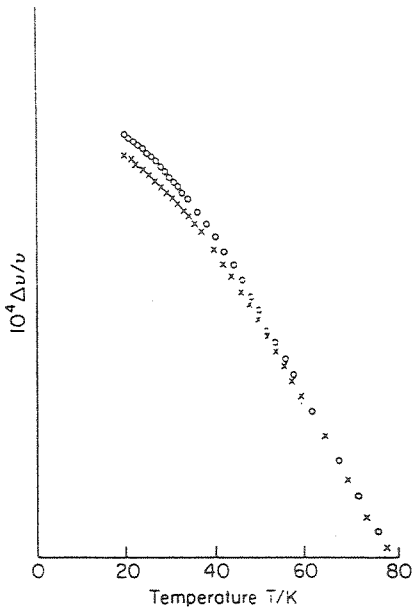


Fig. 15. Temperature dependence of the 30 MHz longitudinal wave sound velocity v for 8 at.% *Au*Fe alloy (×) and for pure gold (○) (After Hawkins *et al.* 1976).

anomaly which is observable in the value of C should also be clearly visible in the ultrasonic velocity. Several typical spin glasses have been examined with the ultrasonic technique by Hawkins and coworkers (Hawkins *et al.* 1976, 1977, Hawkins and Thomas 1978). Longitudinal wave sound velocity measurements at 30 MHz were made on part of the *Au*Fe alloy used by Wenger and Keesom (1975) for their specific heat measurements. These are shown in fig. 15 where it can be seen that there is no anomaly at T_0. Similar results were obtained for *Au*Mn and *Cu*Mn. However for *Au*Cr alloys rounded minima in the sound velocity were observed which correlated quite well with the freezing temperature obtained by other techniques. Hawkins and Thomas (1978) studied in *Cu*Mn alloys the change in sound velocity at a given temperature due to applying a 1·1 T transverse magnetic field. They found positive deviations above T_0, negative deviations below T_0 and no change in the sound velocity at T_0.

5.5. *Mössbauer effect*

The Mössbauer effect has found wide applications in both nuclear and solid state physics as well as in chemistry, biology and other disciplines. Some of the basic principles are described in the article by Dale (1975). The Mössbauer effect in *Au*Fe alloys was studied by several groups during the 1960s (see for example Violet and Borg 1966, 1967). It was found that a rather sharp transition took place from a single paramagnetic line to a six-fingered spectrum. A typical spectrum is shown in fig. 16. The transition temperatures which were determined for *Au*Fe were in good agreement with those found later by the more accurate a.c. susceptibility technique. The onset of a hyperfine field, which is assumed to be proportional to the local spontaneous magnetization, is generally associated with some type of magnetic ordering. However a careful analysis of the intensity ratios of the six lines, both with and without an external magnetic field, indicated that there was in fact a random alignment of the spins. Murani (1977 a, 1978 a) has argued that the transition temperature observed in the Mössbauer

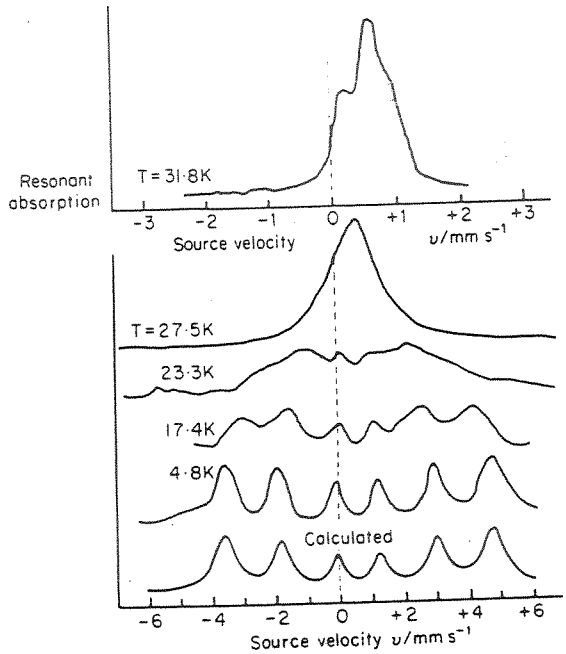


Fig. 16. Mössbauer absorption spectra of a 6·7 at.% *Au*Fe alloy at different temperatures obtained at the Lawrence Livermore National Laboratory, University of California in a project supported by the U.S. Department of Energy. The lowest curve is the calculated low temperature spectrum (After Violet and Borg 1966).

effect is not as sharp as is generally supposed and that a measurable hyperfine field still exists at temperatures well above the freezing temperature. This suggests that there is still a certain amount of short-range order above the transition temperature. Although the freezing temperatures obtained from the Mössbauer and a.c. susceptibility techniques are in close agreement for *Au*Fe, this does not seem to be the case for all systems. Murani (1977 a, 1978 a) has cited the case of *Rh*Fe and also *Cu*Mn where the freezing temperatures obtained from Mössbauer measurements are systematically higher than those obtained from susceptibility measurements.

6. *Muon spin depolarization*

A recent technique which has been finding increasing applications in solid state physics involves the use of polarized muons. A good account of the principles of the technique has been given by Schenk (1978). A. T. Fiory and coworkers (Murnick *et al.* 1976, Fiory 1976) have fired positive muons into *Au*Fe and *Cu*Mn alloys which had been cooled to below 20 K in an applied field. The muons enter the alloy and take up random sites precessing about both the applied field and the internal field. The muons decay with the following scheme

$$\mu^+ \rightarrow e^+ + \nu + \bar{\nu} \quad \tau = 2{\cdot}2\,\mu s.$$

The oscillation of the emitted positron intensity at a fixed angle is a sensitive measure of the local magnetic field. The results are shown schematically in fig. 17. Above T_0 the muons see on average only the external applied field since the internal fields are fluctuating on a far shorter time scale than a muon precession time. As a result the

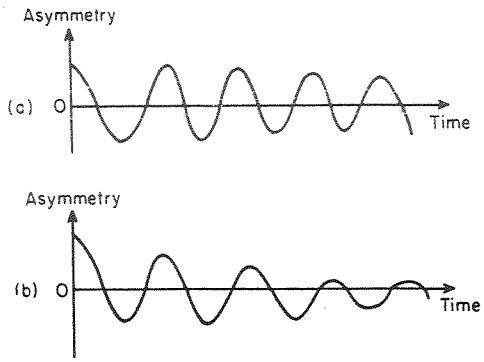


Fig. 17. Variation of the asymmetry of positron detection with time (*a*) just above the freezing temperature, (*b*) just below the freezing temperature.

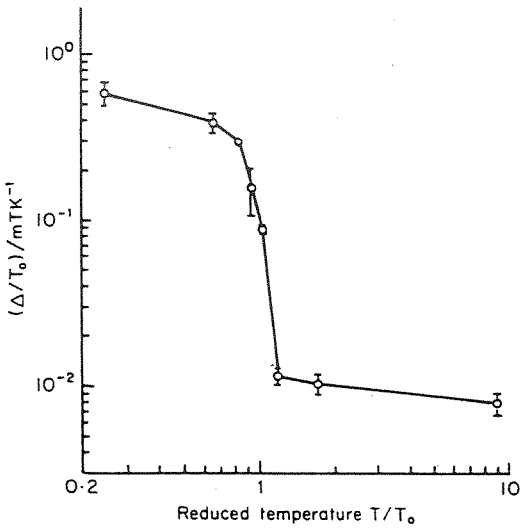
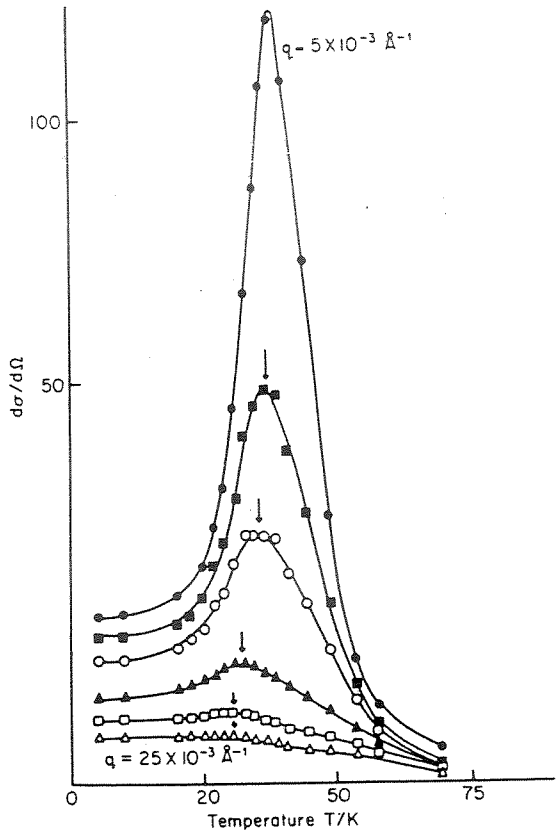


Fig. 18. Variation of the muon depolarization rate (expressed as a linewidth Δ measured in millitesla divided by the freezing temperature) with the value of the reduced temperature (T/T_0) for a 0·7 at.% *Au*Fe alloy (After Fiory 1976).

muons precess together and give rise to the steady oscillations shown in (*a*). Below T_0 the impurity spins are frozen into random orientation and the internal fields in the alloy become fixed in time. Each muon therefore precesses at a different rate and after a very few cycles they no longer precess together and the amplitude of the positron signal dies away rapidly as shown in (*b*). Some of the data obtained by Fiory (1976) on a *Au*Fe alloy is shown in fig. 18. The muon depolarization time t_2^* is expressed as an effective linewidth $\Delta=(\gamma_\mu t_2^*)^{-1}$, where γ_μ is the muon's gyromagnetic ratio. As can be seen from fig. 18, the appearance of local fields at the freezing temperature causes a rather abrupt change in Δ due to the additional depolarization.

5.7. *Neutron scattering*

Neutron scattering studies on spin glasses have produced very interesting results. The majority of these have been obtained by A. P. Murani and coworkers using the I.L.L. high flux reactor at Grenoble. The availability of such high flux reactors has enabled the problem of neutron absorption in the noble metals to be overcome



..19. Small angle neutron scattering cross section (the ordinate units are barn st^{-1} at^{-1}) per alloy atom versus temperature for 10 at.% *Au*Fe alloy. These are for a series of values of the wave vector q, ranging from 5×10^{-3} Å^{-1} to 25×10^{-3} Å^{-1}. (After Murani 1977 b).

allowing the best known spin glasses *Au*Fe and *Cu*Mn to be examined. In a useful review article Murani (1978 b) has summarized some of the basic equations and definitions used in the analysis of neutron scattering data on spin glasses. An investigation of the small-angle neutron scattering on *Au*Fe alloys containing 10 and [illegible]% Fe has been made by Murani (1976, 1977 b). Some of the data for the temperature variation of the small angle scattering cross-section per alloy atom for different values of the wave-vector q is shown in fig. 19. The scattering cross section is proportional to $\chi(q, T)T$, where $\chi(q, T)$ is the wave-vector dependent susceptibility. Figure 19 shows maxima in $\chi(q, T)$ which are particularly pronounced for the lowest q values. The data are similar to the critical scattering peaks observed in normal ferromagnetic systems, although they differ in one important respect, namely that, instead of showing a single unique temperature for the maxima of the peaks, there are a series of q-dependent maxima. Murani has argued that this is strong evidence for a series of freezing temperatures in spin glasses rather than a single sharp phase transition. They support the model alluded to in Section 3, and discussed more fully in the next section, that the spin system can be thought of as subdivided into magnetic clusters of various sizes which freeze out at different temperatures.

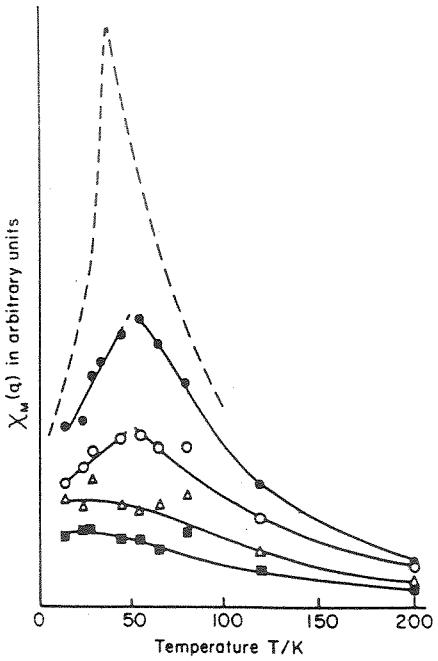


Fig. 20. Wave-vector-dependent susceptibility as a function of temperature for 8 at.% *Cu*Mn alloy, obtained from neutron scattering results. The broken line is an a.c. susceptibility measurement. (After Murani and Tholence 1977.)

Murani's interpretation of his data has been criticised by Soukoulis *et al.* (1978). They have developed a cluster mean-field theory of a spin glass and have used it to compute the frequency-integrated neutron scattering cross-section. They find that the temperature of the maximum is q dependent as observed by Murani but is different from the freezing temperature where there is a cusp in the a.c. susceptibility. They therefore conclude that his data are in fact consistent with a sharp phase transition at a unique temperature. The interpretation of the neutron scattering data does appear to be very difficult and the controversy over it is still not resolved (see Murani (1980 b) and Levin *et al.* (1980)).

A further neutron scattering investigation has been made by Murani and Tholence (1977). They used a time-of-flight spectrometry and were able to evaluate the integrated quasi-elastic, elastic and total cross sections at different temperatures for a 8 at.% *Cu* Mn alloy. They found that the quasi-elastic scattering begins to decrease continuously below about 80 K and this is accompanied by a corresponding build-up of the elastic scattering. These results suggest the formation of magnetic clusters taking place at temperatures well above the freezing temperature. From the data Murani and Tholence have computed the wave-vector dependent susceptibility $\chi(q, T)$ and this is shown in fig. 20 together with the $q=0$, a.c. susceptibility data on the same alloy. The results show the strong q-dependence of $\chi(q, T)$. For large q values, which correspond to very small regions in real space, there is no indication of a freezing process. As q is reduced a maximum begins to appear in $\chi(q, T)$. The temperature of the maximum corresponding to the lowest value of q is 52 ± 3 K. By contrast the a.c. susceptibility, $q=0$, data gives a maximum at 39 ± 1 K. The reason for this temperature difference lies in the different time scales involved for the two measurements. The a.c. susceptibility

measurements use audio frequencies with a time constant of about 10^{-2} s. By contrast the instrumental energy resolution for the neutron-scattering measurements sets a time constant of around 10^{-11} s. Thus neutron scattering is only able to sense the very fast non-interacting spins. Once the spins begin to correlate to form clusters, there is a slowing down of the spin dynamics and this is no longer detectable by the neutron technique. By contrast the a.c. susceptibility technique has a very long measurement time and is particularly able to respond to the largest clusters. On these arguments it follows that the cusp in the a.c. susceptibility corresponds to the freezing out of the largest magnetic clusters whereas the neutron scattering technique is mainly responding to the fastest spins.

6. Theory of spin glasses

There has been an enormous amount of theoretical work on spin glasses using a wide variety of techniques. In this section only a few features will be considered. Further details can be found in review articles such as those due to Fischer (1977), Binder (1977, 1978), Blandin (1978) and De Dominicis (1979). In addition the proceedings of the 1978 Les Houches Summer School, edited by Balian *et al.* (1979) provides an outstanding selection of theoretical and experimental articles on spin glasses and related problems.

It was the a.c. susceptibility measurements of Cannella and Mydosh discussed in Section 2 that focused attention on the spin glass problem. The measurements suggested that some type of phase transition was occurring at the freezing temperature, a fact which was not readily explicable in terms of the accepted ideas at that time on dilute magnetic alloys. Much of the early theoretical work on spin glasses was devoted to trying to understand the a.c. susceptibility data. A calculation that has had a considerable influence in this respect is that due to Edwards and Anderson (1975). The essence of their theory is that, despite the random arrangement of spins, there is nevertheless a certain configuration which minimizes the potential energy of the system and which corresponds to the ground state. As the spins move into this ground state there is a well defined magnetic transition giving rise to a cusp like peak in the a.c. susceptibility. Edwards and Anderson have introduced an order parameter, q, such that if one observes that a spin has a value $S_i^{(1)}$ at time t_1, then, if it is studied a long time later at time t_2, there is a non-vanishing probability that $S_i^{(2)}$ will be pointing in the same direction. Above the freezing temperature T_0 the order parameter q is zero. Below T_0 one can write

$$q = \langle S_i^{(1)} \cdot S_i^{(2)} \rangle \neq 0,$$

and q increases towards unity as the temperature approaches the absolute zero.

The approach adopted by Edwards and Anderson derives much of its inspiration from the problem of gelation in polymer science. When a solution of very long molecules increases in density, at a certain density the mobility of a molecule falls essentially to zero and the system gels. Such a molecule will still appear as a random coil but viewed later it will be *the same* random coil.

The theory of Edwards and Anderson predicted a cusp in the susceptibility although the expected shape of the cusp is somewhat different from that observed experimentally. It also predicted a cusp in the 'specific heat'. The original theory was classical in nature in that it did not consider the quantization of the spins of the impurities. A considerable amount of theoretical work has stemmed from the original

calculation of Edwards and Anderson much of which is discussed in the review articles cited at the beginning of this section.

In Section 3 the remanence, hysteresis and time-dependent effects of spin glasses were discussed. It is very difficult to reconcile these observations as well as others with the theoretical work of Edwards and Anderson and with the idea of a phase transition in a spin glass. However, similar effects have been seen in magnetic rocks and are discussed in terms of the Néel theory of superparamagnetism (see Néel 1955). It is appropriate that the Grenoble group were the first to suggest that some of the concepts of Néel's theory could usefully be applied to the spin glass problem (see Tholence and Tournier 1974, 1977). Many experimental measurements on spin glasses such as the electrical resistivity, specific heat capacity, neutron scattering and susceptibility suggest that to some extent the spins are correlated into magnetic clusters or domains at temperatures well above that of the freezing temperature. These arise from statistical concentration fluctuations in the alloy which means that there are regions where there is a high probability that an impurity will have another as a first-or second-nearest neighbour. For 3d transition metal impurities, the 3d electron wavefunctions have a finite extent and there is an interatomic overlap resulting in a direct magnetic exchange. This adds a short-range interaction which can couple impurities resulting in the formation of a magnetic cluster. This tendency to form clusters is opposed by thermal disorder. As the temperature decreases so the regions of correlated spins become larger and the spin system in the alloy can be thought of as being subdivided into independent magnetic clusters of different size. The freezing process can be understood as resulting from a distribution of temperatures at which the different magnetic clusters are no longer able to overcome an energy barrier and are therefore blocked. If a cluster is blocked for a time which is greater than a typical measurement time, it will appear frozen and will not be sensed by the measuring technique. From the Néel theory of superparamagnetism the relaxation time of a magnetic cluster is given by

$$\tau = \tau_0 \exp\left(\frac{E_a}{kT}\right)$$

where τ_0 is some characteristic relaxation time for the spins and E_a is an anisotropy energy. This expression is sometimes called the Arrhenius equation. The anisotropy energy is largely due to dipolar coupling although there are other contributions such as those due to cluster shape and surface effects. On this model the a.c. susceptibility measurements of Cannella and Mydosh are interpreted as due to the freezing out of the largest clusters. The sharp, cusp-like peak reflects the exponential variation of the relaxation time with $1/T$ and also the fact that the anisotropy energy itself is a strong function of temperature. Guy (1977a, 1978) has given a full account of the applications to spin glasses of Néel's theory of superparamagnetism and models developed from it. He has drawn attention to several experimental features which are observed at $0{\cdot}6\,T_0$ and which can be understood in terms of a peak in the distribution of the energy barriers.

A rather successful cluster mean field theory of a spin glass has been developed by Soukoulis and Levin (1977, 1978; see also Levin *et al.* 1979). This theory combines the effects of magnetic clusters with the approach due to Edwards and Anderson. They have taken into account both the interactions within a cluster (intracluster interactions) and interactions between clusters (intercluster interactions). Because the spins within a cluster are strongly interacting they may be treated exactly while the much weaker intercluster interactions can be approximated using mean field theory. By considering

both types of interaction, Soukoulis and Levin were able to account successfully for the experimental observation of both a sharp cusp-like peak in the a.c. susceptibility at the freezing temperature T_0 and a broad maximum in the specific heat at a somewhat higher temperature. This was an improvement over the theory of Edwards and Anderson and its immediate extensions which predicted cusps at T_0 for both parameters. Soukoulis and Levin found that their expression for the intercluster term was similar to that found by Edwards and Anderson and predicted a cusp in the susceptibility at T_0. By contrast the intracluster contribution had no features at T_0 but instead predicted a rounded maximum in the specific heat at a higher temperature which was dependent upon the size of the exchange interactions within a cluster. As mentioned in Section 5.7, they were also able to account for the small angle neutron scattering data of Murani although there is still considerable controversy over the interpretation of this data.

Finally in this section mention should be made of the important new concept of frustration. This was introduced by Toulouse (1977, 1980) and may prove to be basic not only to the understanding of spin glasses but also to other related condensed matter phases. Because the spins in a spin glass are located at random, there will frequently be a conflict or competition between the way they will order due to different paths connecting the same pair of spins. It is this competition of positive and negative spin alignments which is called frustration and is essential to the formation of a spin glass. It puts the system in a quandary as to how to best minimise its energy. Toulouse (1980) recalls hearing a lecture on spin glasses by P. W. Anderson in 1976 and written on one corner of the blackboard were the words "the name of the game is frustration". This he later remembered when he was looking for a word which would evoke the ideas of contradiction and would also be analogous to the word percolation.

Frustration can most easily be understood by considering a two-dimensional square lattice with Ising spins (see Toulouse 1977, 1980). In this case the spins S_i are such that $S_i = \pm 1$ and one can consider nearest neighbour interactions J_{ij} such that $|J_{ij}| = 1$. When $J_{ij} = +1$ the ground state is ferromagnetic; if $J_{ij} = -1$ it is antiferromagnetic and if $J_{ij} = \pm 1$ at random then one has a disordered magnet. Figure 21 (*a*) shows a perfect ferromagnetic configuration with $J_{ij} = +1$ throughout. In fig. 21 (*b*) the sign of J_{ij} is reversed on all the bonds around one site. This does not produce a serious amount of disorder and the energy of the spin configuration is the same as that for a perfect ferromagnet. All the bonds are satisfied and one has what is known as an unfrustrated system. However the situation is very different for the case shown in fig. 21 (*c*). Here there is no way of choosing the orientation of the spin sites around the square without causing at least one frustrated or broken bond. It is this frustration effect which can

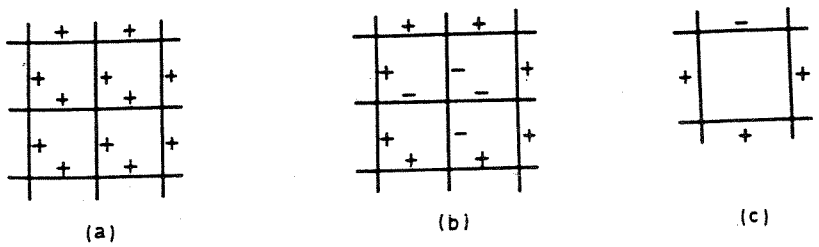


Fig. 21. (*a*) A ferromagnetic configuration of bonds. (*b*) All the bonds around the central site have been made negative. (*c*) A frustrating configuration of bonds (After Toulouse 1977).

cause serious disorder. For example a square lattice of Ising spins orders cooperatively if all the fundamental squares are unfrustrated, but if all are frustrated, the ground state is highly degenerate and there is no cooperatively ordered phase.

The idea of frustration is rather new and its many implications are still being actively studied. It may be basic to our understanding of spin glasses and related physical systems. It also has analogies with gauge theories in electrodynamics and elementary particles. The bond interactions J_{ij} play a role somewhat similar to the electromagnetic potential A.

7. Spin glass systems

So far in this article almost all the experimental measurements which have been discussed were made on *Au*Fe and *Cu*Mn alloys. These must be regarded as the archetypal spin glasses. However one reason for the prominence which has been given to spin glasses is the wide variety of systems where such behaviour has been seen. In this section a brief survey will be given of some of these systems. Further details together with additional references can be obtained from the review articles of Mydosh (1975, 1977, 1978) and Mydosh and Nieuwenhuys (1980).

Ford and Mydosh (1976) suggested two criteria which were necessary in order to most easily study spin glass behaviour in noble metals containing 3*d* impurities. These are, firstly, that the impurities should have a high solubility in the host, at least up to 10 at.%, so as to approximate to the ideal case of a truly random solid solution. Secondly, the alloy should have a low Kondo temperature, less than 1 K, so that one is dealing with good moment systems. Of the variety of combinations which are available only five systems satisfy both requirements. These are *Au*Fe and *Cu*Mn and in addition *Au*Cr, *Au*Mn and *Ag*Mn. All five systems have now been examined fairly extensively using a variety of techniques. The overall features seen in all the systems are similar, although there are interesting variations in detail, such as for example in the thermopower behaviour discussions in Section 5.2.

The article by Mydosh and Nieuwenhuys (1980) gives a table of spin glass combinations for noble metal hosts–3d-transition-metal impurities and also for transition-metal hosts–transition-metal impurities. For the exchange enhanced hosts palladium and platinum with 3d impurities there is a strong tendency to form giant moment systems. However it is possible to reduce or even destroy the exchange enhancement either by alloying with silver or by charging with hydrogen. Under these circumstances the spin glass state can be formed. Without resorting to such methods it is still possible in some instances to form a spin glass by adding a sufficient concentration of impurities. This is particularly so with manganese and chromium.

In Section 2 the frequency dependence of the a.c. susceptibility maximum of the rare earth spin glass $(La_{1-x}Gd_x)Al_2$ was discussed. An increasing number of spin glasses containing rare earth impurities are being found and some of these have been tabulated in the article by Mydosh (1978). The fact that the spin glass behaviour observed for both the 4f and 3d impurities is very similar suggests the general nature of the freezing process. It implies that any system which has local moments could be expected to show spin glass behaviour. Since the 4f electron wavefunctions are highly localized the rare-earth spin glasses demonstrate the importance of the RKKY interaction for coupling the impurities. Rare earth spin glasses have also been very interesting in a different context. For many years there has been controversy over the coexistence of superconductivity and magnetism. Measurements by Davidov *et al.* (1977) on $(Gd_x Th_{1-x})Ru_2$ and $(Gd_x Ce_{1-x})Ru_2$ have shown very conclusively that one can have

coexistence between superconductivity and the spin glass state. The authors also quote three other examples of rare-earth alloys studied earlier where such a coexistence has almost certainly been seen.

Mizoguchi *et al.* (1977) have made some elegant susceptibility measurements on a sputtered film of amorphous $Gd_{0.37}$ $Al_{0.63}$. They used a SQUID technique and observed sharp peaks in the susceptibility which became increasingly more rounded as an external magnetic field was applied. The possibility of studying spin glass behaviour in amorphous or highly disordered materials opens up a potentially exciting new field of research. Such materials can be made by quench condensation of thin films, splat cooling and ion implantation. Some investigations of spin glass behaviour in these disordered materials have been discussed in the article by Mydosh (1978).

There has been considerable controversy over whether insulating random substitutional materials can be regarded as spin glasses since they do not possess RKKY interactions. Much of the debate has centred around the system $(Eu_x Sr_{1-x})S$ which has now been extensively studied by Maletta and Felsch (1979). They have found clear spin glass behaviour for concentrations $0{\cdot}13 \leqslant x \leqslant 0{\cdot}5$. The interaction responsible for this is mainly the competition between ferromagnetic and antiferromagnetic exchange and is predominantely of short range. This seems to produce very similar effects to those observed with the RKKY interaction and leads Maletta and Felsch to conclude that one should not attempt to draw a distinction between different types of spin glasses depending on their metallic or insulating nature. Near the percolation threshold of exchange interactions, $x = 0{\cdot}13$, they observed a transition from spin glass behaviour to superparamagnetism. A rather detailed theoretical study into the possibility of obtaining a wide range of insulating spin glasses has been made by Villain (1979).

Finally an example is given of a very different type of material, namely solid hydrogen, which suggests that some of the ideas of spin glasses have a rather wide spread application. Solid hydrogen is a random alloy of ortho-hydrogen molecules ($J = 1$) and para-hydrogen molecules ($J = 0$, ground state). This latter has the effect of diluting the ortho-molecules whose quadrupolar moments play the same role as the magnetic moments in a spin glass. Interactions between the ortho-molecules is mainly through the electrostatic quadrupole–quadrupole interaction which in contrast to the RKKY interaction is short ranged and anisotropic. Sullivan *et al.* (1978) have examined solid hydrogen at low temperatures and found that for ortho-hydrogen concentrations less than 55% there is an ordered phase in which the quadrupolar moments are frozen at random. They talk of a quadrupolar glass phase in solid hydrogen, which is similar to the spin glass and can be understood within the same basic framework.

8. Conclusions

Although alloys like *Au*Fe and *Cu*Mn containing several at.% of impurities have been studied for many years, it was the a.c. susceptibility measurements of Cannella and Mydosh, made roughly a decade ago, which focused attention on what has now become known as the spin glass problem. Since that time there has been the customary literature explosion on this topic. However, despite this enormous amount of effort, a complete understanding of spin glasses still seems to be a long way off. This is rather evident from the summary made by Mydosh (1980) at the most recent International Conference on Magnetism (Munich 1979). Both from an experimental and a theoretical point of view the question of whether there is in fact a phase transition in a spin glass has still not been resolved, although the evidence is clear that it is certainly not a simple type

of phase transition. On the other hand it appears that the Néel model of superparamagnetism, although very useful, does not provide a complete description of a spin glass. Theoretical work on spin glasses is still very active. From an experimental point of view, P. A. Beck has constantly emphasized the importance of correct metallurgy in studying spin glasses. Different heat treatments and sample preparation can radically affect results, particularly in more concentrated alloys. In addition some of the rather sophisticated techniques which have been used to study spin glasses, such as neutron scattering, require considerable expertise to perform and specialized knowledge to interpret and do not seem to provide unambiguous answers. What does seem to have emerged over the last ten years is the large number and variety of alloys which exhibit spin glass behaviour. It would also appear that some of the ideas of spin glasses are applicable to other problems. Toulouse has emphasized the fundamental nature of the concept of frustration which is applicable to spin glasses and possibly to a vast class of condensed matter phases. It is still too early to tell whether he is correct or not. However, he may very well be, and then perhaps we will realize that when we start playing with spin glasses "the name of the game is frustration".

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Note added in proof

In the period between the completion of this article and its appearance in print interest in spin glasses has been maintained. The output of research papers on this subject continues to be large. Some of the recent trends and developments have been summarized in the latest review article by Mydosh (1982).

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