Dilute Magnetic Alloys

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Abstract

A survey is given of the major strands in the development of the study of the magnetic behaviour and related properties in dilute alloys of elements capable of possessing magnetic moments in appropriate hosts. While the main emphasis is on the growth of the experimental information and the theoretical concepts needed for adequate explanations, indications will be given of significant recent developments. Specific topics include the Kondo effect, superconductivity in dilute alloys, spin glasses and the onset of long-range magnetic order.

1 Introduction

This is a topic (one with which I was first concerned 44 years ago) that has had an impact in a number of areas of metal physics and one to which Allan Mackintosh and his coworkers made significant contributions. It has been argued that theoretical work in this area provided important insights for more general areas of metallic magnetism, and a review of the topic (Morandi et al., 1981) has even used its history as a model system for the examination of aspects of the sociology of science.

The present paper will trace the main lines of development in this field and indicate some recent developments where new concepts have emerged or old ones revived.

2 The early roots

I have in other places (Coles, 1984, 1985) given some historical musings on the origins of later intensive studies of the results of interactions between magnetic moments in dilute alloys (the spin glass problem), but this followed a period where these interactions were seen as complications in efforts to understand the single impurity problem (Rizzuto, 1974). The earliest manifestation of interesting effects in the electronic properties of dilute alloys were found in the electrical resistivity at low temperatures, but it was not immediately clear that these were associated only with impurities of magnetic character, since it seemed that that the resistivity minimum found in gold containing some impurities (see van den Berg, 1964, 1965) could be produced by additions of elements like tin to copper that did not have such a minimum. However, that effect was explained when it was realized (Gold et al., 1960) that in alloying the tin could reduce particles of iron oxide to introduce Fe into solid solution. Theoreticians (Korringa and Gerritsen, 1953) had early suggested a role for magnetic impurities and resonant scattering, but it was a little while before it became clear that the resistivity minimum in dilute alloys of 3*d* elements in Cu or Au was a single impurity effect while the resistivity maximum below it found at only slightly larger concentrations was the result of long-range interactions between moment-bearing impurities through the conduction electrons. During the period that then elapsed (∼1954 to 1964), before the basic theory of the minimum was enunciated by Kondo (1964) and baptized into the church of physics with his name, important developments had taken place in our understanding of the basic question "under what circumstances does a 3*d* atom possess or fail to possess a magnetic moment in solid solution in another metal ?" In most such work the criterion for the existence of a moment was the manifestation of a Curie–Weiss susceptibility and it was not at first recognized that in some systems that criterion could give different answers at high and low temperatures. The first significant breakthrough was by Friedel (1956), who came to the problem via his concern with the scattering produced by transition metal solutes in various hosts, especially Cu and Al, introducing the concept of the virtual bound state produced by 3*d*-conduction electron mixing. He recognized the possibility that this, like the 3*d* band of a pure transition metal, could be magnetic or non-magnetic depending on whether a criterion like the Stoner criterion was satisfied. This at once explained why some alloys (e.g. **Au**Fe) could behave like a dilute magnetic salt (e.g. (**Zn**,**Mn**)SO_4) while others like **Al**Fe had temperature-independent susceptibilities, although the 3*d* shell was clearly not full. At the end of the 3*d* series it seemed possible that the collective band model successful for **Ni**Cu (Wohlfarth, 1949) might be applied to **Cu**Ni with Ni filling its 3*d* shell as Pd does in Ag, but it became clear (Coles, 1952) that at the Cu-rich end also empty Ni(3*d*) states existed without Curie–Weiss susceptibilities, and the approach of Friedel solved this problem. A little later the intuition of Matthias (Matthias et al., 1960), that the different effects of Fe on the superconductivity of host metals were associated with whether or not it carried a moment, directly stimulated the important work of Anderson (1961) who put the 3*d*–conduction electron hybridization on a firm theoretical basis with the Hamiltonian that bears his name. I was pleased, with Matthias's encouragement, to be able to show (Coles, 1963) that Fe produced a resistance minimum in Mo but not in Nb. That, incidentally, led to the serendipitous discovery of the strange resistivity behaviour of **Rh**Fe which became a useful low temperature thermometer. During the same period a very important study was made by Owen et al. (1957) of the "good" moment system **Cu**Mn, a system later shown (Hirshkoff et al., 1971) to maintain, in the dilute limit, a good Curie–Weiss behaviour down to 10 mK, in contrast to **Cu**Fe where it is lost below about 10 K. The **Cu**Mn study was important for two reasons. First the good spin-resonance behaviour showed that Mn carried into the alloy the intra-atomic correlations that made it possible to speak of it as essentially $3d^5$, $S = \frac{5}{2}$, $g = 2$ and the importance of on-site Hund's rule correlations was later emphasized in the work of Hirst (1970). (The importance of these "ionic" aspects was even greater in later work on the rare earth solutes, where additional structure in the resonant levels is due to crystalline electric field effects, normally assumed to be strong enough in $3d$ materials to quench orbital contributions to the moments). Second, the observation of susceptibility maxima in quite dilute alloys was reminiscent of antiferromagnetism and showed clearly that interactions between these moments were important. At about the same time a number of people were demonstrating large extra contributions to the specific heat in such alloys at low temperatures (see Coles, 1984), effects which led to the concept of a distribution of effective fields seen by the solute moments. Blandin in his thesis (1961) (see Blandin and Friedel, 1959) seems to have been the first to recognize that the origin of this distribution had its roots in the very on-site mixing of the $3d$ and conduction electron states that had created the virtual bound states, but an intriguing suggestion was that of Overhauser (1959) that the local moments stabilized a spin-density wave in the conduction electrons of Cu, a situation later found to hold for dilute solutions of heavy rare earths in yttrium (Sarkissian and Coles, 1976).

3 The Kondo effect

At this point it seems appropriate to look at the developments in our understanding of the single magnetic impurity before returning to the treatment of the interactions between them. Kondo's (1964, 1969) breakthrough work on the origin of the resistivity minimum opened the floodgates to theoretical work on the nature of the ground state of a system consisting of a local moment coupled by exchange interaction to the conduction electrons. (This $J_{\rm sd}$ term is often called the Kondo exchange Hamiltonian but it had been used earlier by workers in USSR, USA and Japan). The irony was that to produce the resistivity minimum J had to be negative and it was fortunate that earlier he (Kondo, 1962), de Gennes (1962) and Anderson and Clogston (1961) had shown that the local state-conduction electron mixing led to an effective (not classical) exchange that was negative.

Not only was there, in the description of the ground state, a fascinating and difficult problem but it was one on which the condensed matter theorists could exercise their recently developed many-body muscles. As it became clear that the ground state became non-magnetic by the compensation of hybrid up-spins with hybrid down-spins (not a simple antiferromagnetic coupling of a local spin with a conduction electron spin) the range above T_K and the range $0 < T \ll T_K$ could be treated with reasonable approximations, but no treatment was available to take the system through T_K until the breakthrough provided by Wilson's (1975) use of renormalization group methods. (It may be noted that although the binding energy $k_B T_K$ was similar in form – $D \exp(1/N(0)J)$ – to that for the BCS superconductor there could be no phase transition in this essentially zero-dimensional system.) More recently analytical treatments founded on a Bethe ansatz have underpinned this approach (Andrei, 1980; Wiegman, 1980; Wiegman and Tsvelik, 1983), and it is possible in principle to calculate T_K for different systems. Few such calculations have been made and I suspect that it would be very difficult to justify the very low T_K in **Cu**Mn without carefully taking into account the hybridization that has already taken place in the $l = 2$ channel in pure Cu. Similarly the "good" moment Fe shows in Mo (where $n(E_F)$ is larger than that of Al, although small for a transition metal, and with dominately d character) seems difficult to reconcile on any simple approach with the absence of such a moment for Fe in Al. The full story of the developments of the theory of the Kondo effect and our present state of understanding of it have been presented in a recent book by Hewson (1994).

Later in the dilute alloy story interesting effects of Kondo-related character were found for some alloys containing Ce and Yb, elements known to have unstable valencies, and these were of particular interest when the host was superconducting, see Sect. 4. These effects also proved to be important in the heavy fermion industry since compounds of these elements were the early players, and a sort of taxonomy has developed where Kondo lattices are distinguished from homogeneous mixed valence compounds rather as one distinguishes "good" moment solutes with Kondo effect from non-magnetic virtual bound states with local spin fluctuations in the dilute alloy story.

Little work has been done on dilute alloys containing U, although these should be of interest, partly because of the large number of heavy fermion compounds of U and partly because the radial extent of the $5f$ wave functions for U and Pu can be expected to be intermediate between that of the $3d$ states of Fe and that of the $4f$ states of Ce. Correspondingly the behaviour of U varies greatly with the character of the host in its dilute alloys. Thus in Au it shows a "good" moment and a resistivity minimum (Hillebrecht et al., 1989), in Th strong local spin fluctuation character (Maple et al., 1970) where the superconducting behaviour is of interest, but in Nb and Mo non-magnetic virtual bound state character (Coles et al., to be published). Interestingly there is no indication of the marked contrast for these two hosts that they show for Fe as solute; certainly U has little effect on the superconductivity of Nb, but meaningful measurements on the superconductivity of **Mo**U await the availability of high purity iron-free Mo.

4 Superconductivity in dilute magnetic alloys

This also is a topic that has been reviewed in a number of places (see especially Maple, 1973) and reference has been made above to the role of Matthias's intuition in stimulating both experimental and theoretical work on the dilute alloy problem. Quite early in this era, when the topic was escaping from the pejorative "dirty superconductors" label, Anderson (1959) made clear the reason for the sharp difference between the effects of simple and moment-bearing solutes on superconducting transition temperatures: although in the former k and $-k$ are no longer strictly good quantum numbers because of scattering there is no objection to pairing a scattered state with its time reversed conjugate; but when spin dependent scattering occurs time reversal symmetry is broken and pair-breaking takes place. The consequences for systems like **La**Gd were calculated by Abrikosov and Gor'kov (1961), and for rare earth systems free from intermediate valence tendencies the situation is fairly well understood, although consideration of crystal field effects is required. These and the modifications for solutes with finite Kondo temperatures or spin-fluctuation temperatures are discussed in detail by Maple (1973). That crystal field split levels could be clearly defined enough and weakly enough coupled to the conduction electrons was demonstrated by the observation of non-S-state paramagnetic resonances. These levels and their role in the magnetic, electrical and thermal properties of dilute alloys of the heavy rare earths are now fairly well understood, especially following the work of the Danish groups (Høg and Touborg, 1974; Rathmann et al., 1974) which was greatly aided by Allan Mackintosh's deep understanding of the rare earths.

5 Spin glasses

Although the term spin glass has been applied to a wide range of systems without long-range magnetic order, the concept had its roots in the dilute alloy problem. When it was recognized that interactions between solute atoms were taking place at quite low concentrations unless frustrated by Kondo, general arguments such as those of Blandin (1961) and the character of the specific heat made it clear that no straightforward antiferromagnetic transition was taking place. (I have referred elsewhere to the ironies that the negative θ-values that led Néel to his great theory of antiferromagnetism never took him back to explore the low temperature properties of the alloys manifesting them, and that Kittel failed initially to invoke for **Cu**Mn his own RKKY interaction).

The experimental situation for spin glasses in dilute alloys is now fairly clear and has been set out by Mydosh (1993), whose demonstration (Cannella and Mydosh, 1972) of sharp peaks in the ac susceptibility had played a major role in attracting the attention of theorists, and led to an explosion of sessions on the topic at magnetism conferences. (On a personal note I find it interesting that my own suggestion of an analogy between such spin glasses and conventional "atomic position" glasses was developed in the context of dilute alloys with by-no-means good moments in the systems **Au**Co and **Rh**Fe). The competition in dilute alloys between a Kondo or Friedel–Anderson spin compensation and spin glass freezing has a close relationship to the delicate balance between magnetic and non-magnetic ground states for atomically ordered heavy fermion compounds; the problem of this balance was first addressed by Doniach (1977).

However the fundamental character of the spin glass transition has taken a long time to resolve and the theoretical techniques used to address it have become less clear to the experimentalist. The current situation is well reviewed by Fisher and Hertz (1991), and the consensus seems to be that in Ising systems a phase transition does exist in 3 dimensions, although that is below the critical dimensionality for Heisenberg systems, which then require anisotropies to yield a phase transition.

6 The onset of long-range order

In some dilute alloys with good moments it had seemed from Mössbauer and high field magnetization measurements that ferromagnetism occurred at quite dilute concentrations, but it later became apparent (Murani, 1974; Murani et al., 1974; Coles et al., 1978) that **Au**Fe is, in fact, a spin glass with strong ferromagnetic bias to the competing interactions, and that long-range ferromagnetism only sets in above a percolation concentration (∼18% Fe) where nearest neighbour interactions dominate. Just above that concentration, however, the effects of co-existing finite clusters gave rise to a situation often described (not quite accurately) as a re-entrant spin glass (see Roy and Coles, 1993).

Long-range order can set in quite rapidly at quite low solute concentrations when the host is strongly exchange-enhanced and the onset of ferromagnetism has been intensively studied in both **Pd**Ni and **Pd**Fe. In the former the local extra enhancement associated with the Ni atoms (which do not carry a moment in the dilute limit) fairly rapidly leads to ferromagnetism at ∼2.4% (Murani, 1974; Murani et al., 1974) but there is evidence from neutron scattering (Aldred et al., 1970) that close pairs of Ni atoms play a significant role in producing the polarization clouds that over-lap to give long-range, although inhomogeneous, ferromagnetism. In **Pd**Fe the solute does possess a good moment and at very dilute concentrations ($\sim$ 0.01%) giant polarization clouds overlap to give ferromagnetism. In most other $4d$–$3d$ alloys the first magnetic freezing that occurs is clearly of spin glass character, and there are indications that at very low temperatures for very small concentrations **Pd**Fe also has a spin glass regime.

A fascinating, but rather neglected aspect of dilute alloy magnetism is the occurrence of ferromagnetism for small substitutions of Mn for Ge in GeTe (Cochrane et al., 1974) where the small carrier concentration ($\sim 10^{21}$ cm^{-3}) yields a value of the Fermi wave vector so small that up to large distances the RKKY interaction has not crossed zero and no competing interactions exist to give a spin glass. (This is not the case for all magnetic semiconductors however).

7 Recent developments

Two inter-related aspects of the dilute alloy problem that have attracted attention in recent years are the multichannel Kondo effect, originally introduced by Nozières and Blandin (1980) but rather neglected since, and the quadrupolar Kondo effect (Cox, 1988). Much attention has been focussed on substitutions of U for Y in YPd_3 where the effective Kondo temperature changes rapidly with U concentration (an effect sometimes called Fermi level tuning) from values above room temperature to values small enough for antiferromagnetic order to dominate over Kondo above 20% (Dai et al., 1995). This makes it difficult to be sure that the undoubted deviations in the susceptibility, resistivity and specific heat (Seaman et al., 1991) from the expectations of Fermi liquid theory require these new approaches or follow from the decline of characteristic temperatures towards 0 K. (For the resistivity, at least, related deviations are found close to the critical concentration for ferromagnetism in **Pd**Ni and for spin glass formation in **Rh**Fe. The suppression of any T^2 regime to very low temperatures in the latter is what makes it a useful low temperature thermometer).

For dilute U alloys, as emphasized by Coleman (1995), the role of Hund's rule effects have yet to receive a satisfactory treatment, and this makes them more difficult to discuss than those of Ce.

In conclusion it seems clear that, as predicted many years ago, the understanding of the single solute atom behaviour will continue to make important contributions to attempts to provide a sound basis for discussing magnetism in strongly correlated systems, including both heavy fermions and high temperature superconductors.

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