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Conduction Electron Scattering in Alloys*

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Abstract

The aim of this review is to present a simple physical picture which shows how the electrical resistivity of a system depends upon the spatial extent and lifetime of the scattering disturbance measured in relation to the conduction electron mean free path and relaxation time. The contribution from spin fluctuations associated with isolated magnetic impurities is discussed on the basis of this model and it is shown that at temperatures below the characteristic spin fluctuation temperature the impurity acts as though it were nonmagnetic. Some results are given for both 'Kondo' (Anderson) and exchange enhanced (Wolff) systems. Spin glasses are also discussed and the resistivity behaviour is shown to result from a competition between the RKKY interaction and spin fluctuation effects. Ordered magnetic clusters are shown to be static for periods comparable with the conduction electron relaxation time, so that there is no resistivity anomaly expected at the superparamagnetic blocking temperature. The observed temperature dependence of the resistivity then follows simply from the change in magnetic correlations within the cluster.

1. Introduction

It is a fairly simple matter to determine the electrical resistivity ρ of a material. If a specimen of uniform cross sectional area A is available, one simple passes a known current I through the specimen and measures the voltage drop V that occurs over some distance l. This arrangement is shown in Fig. 1 and one finds that

$$V = I\rho l/A. \tag{1}$$

However, such a description suggests that the measurement is quite 'static'. While this may well be true on the time scale of laboratory measurements it is certainly not so on the characteristic time scale of the conduction electrons concerned. In order to understand such behaviour we need to consider the actual scattering processes concerned and, in particular, we need to identify the characteristic scattering times and volumes. The aim of this review is to facilitate a simple conceptual understanding of the physical processes concerned, a more complicated and often quite subtle theoretical analysis being required to obtain solutions and quantitative data. As such it is hoped that the presentation will be digestible by 'non-experts' and will provide some insight into this fascinating field of study.

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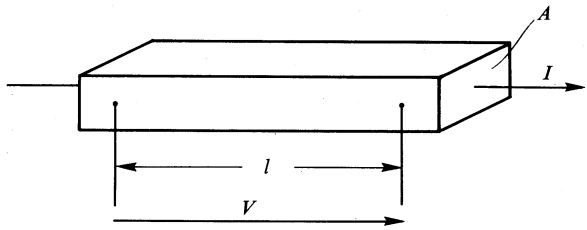

Fig. 1. Simple experimental arrangement for determining the resistivity of a conducting bar: A is the cross-sectional area, l the distance between contacts, I the current flowing and V the resultant potential drop.

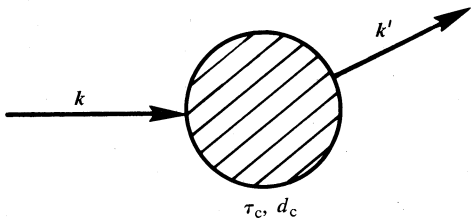

Fig. 2. Schematic picture of scattering of a conduction electron by a region of disorder characterised by a lifetime τ_c and a dimension d_c.

The scattering process may be represented by the simple scheme shown in Fig. 2. This represents an electron with a wavevector k being scattered by some deviation from perfect periodicity (described by some characteristic lifetime τ_c and size d_c) into a state characterised by a new wavevector k'. However, if we denote the average distance between scattering events (i.e. the conduction electron mean free path) by Λ, the deviation from perfect periodicity is determined only over a volume $\sim\Lambda^3$. Furthermore, it must exist for a time at least as long as the average time between scattering events τ_e. If we overlook for the moment arguments which seek to relate such a parameter to particular changes in the electron distribution via the Boltzmann or Kubo–Greenwood equations, we can simply regard τ_e as the conduction electron relaxation time. The parameters τ_e and Λ are of course related to each other and to the resistivity, the free electron relationships being the most transparent:

$$\Lambda = \tau_e v_F, \qquad \rho = m/ne^2\tau_e, \tag{2,3}$$

where n, m, e and v_F are the free electron density, mass, charge and velocity respectively. More realistic models which take into account electron band-structure effects and scattering anisotropy lead to similar functional dependences. We can now see that our 'static' picture of a resistivity measurement is based on the assumption that the lifetime of the scattering centre τ_c is greater than the conduction electron relaxation time τ_e and that we are only sampling deviations from true periodicity on a scale $\sim\Lambda$. This latter point has been discussed in detail elsewhere (see Hillel and Rossiter 1981; Rossiter 1986, and references therein) and so we will concentrate here mainly on the lifetime effects. For typical metals and alloys, τ_e lies in the range 10^{-12}–10^{-16} s. Such periods are very much shorter than the time of fluctuation characteristic of any atomic defects which will cause conduction electron scattering. However, there is another form of readily available 'defect' that is much more fleet of foot. This is associated with the spin of an electron resident in an unfilled inner

orbital or narrow band and which is responsible for the dominant magnetic behaviour. Such a spin will interact with the conduction electrons via the short range Heisenberg exchange and/or Coulomb interactions. Conduction electrons will thus be scattered from those spins and a nonzero resistivity will result if the spatial distribution of the spins is not perfect (at least on a scale $\sim \Lambda$). Let us now consider the dynamics of these spins in relation to the conduction electron scattering process.

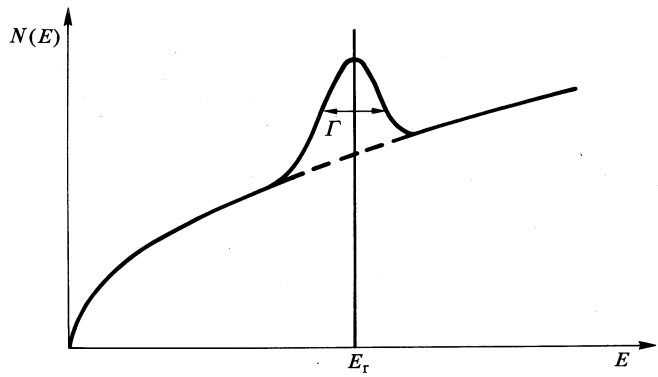

Fig. 3. Change in the density of states $N(E)$ due to an impurity having a resonant energy E_r and width of resonance Γ.

2. Isolated Spins

In order to understand the dynamics of an isolated spin we need to know where the spin and its associated magnetic moment comes from. From the static Hartree–Fock model (Stoner 1947, 1951) it was known that impurity atoms of Cr, Mn or Fe in Cu or Au hosts should carry a magnetic moment, but not isolated single impurity atoms of Co or Ni. It was later discovered in bulk magnetic studies that pairs of Co impurity atoms or groups of eight Ni impurity atoms appear to acquire a moment, and a variety of rather empirical models have been proposed to explain this dependence upon environment (Jaccarino and Walker 1965; Kouvel 1969; Perrier *et al.* 1970). We now understand that the presence or absence of a moment is tied up with the concept of virtual bound states introduced by Friedel (1958). Let us consider an impurity which has a strong attractive interaction with the conduction electrons. Electrons attracted to the impurity will be spatially localised in the potential well, i.e. 'bound' states will form at energies somewhere below the Fermi level. If the potential of the impurity is such that this localised level lies within the conduction band, conduction electrons will be scattered into it and leak back out into the conduction band. This means that the lifetime of the state τ_Γ is limited leading, to first order, to a broadening of the impurity level. The formation of such a 'virtual' bound state leads to a locally increased density of states as shown schematically in Fig. 3. For s and p states the broadening is usually so large that the concept of a virtual bound state is meaningless. In the case of d states, however, the broadening is not so large and a well-localised virtual bound state can form. Whether or not such a state can support a magnetic moment is determined by the electronic Coulomb interaction between the electrons occupying that state. That this interaction can have the effect of supporting a magnetic moment can be seen from the simple model of Anderson (1961). Let us

assume that there is a single localised energy level which can be occupied by only two electrons, one having a spin up and the other a spin down. The interaction U between these electrons causes a splitting of the level and if the higher state then lies above E_F this leads to a significant net spin polarisation. If we neglect the effects of thermal fluctuations, a Hartree–Fock calculation shows that a localised moment will exist if $UN_d(E_F) > 1$, where $N_d(E_F)$ is now the local density of d states at the impurity. This leads to the predictions shown in Table 1. But what happens if $UN_d(E_F)$ is just too small? In such cases there will be large fluctuations into the spin polarised state, the mean lifetime of these spin fluctuations τ_{sf} being given by

$$\tau_{sf} = \pi N_d(E_F)/\{1 - UN_d(E_F)\}\,. \tag{4}$$

(Note that this is not the same as the lifetime of the virtual bound state τ_Γ which must be greater.) We can then define a characteristic spin-fluctuation temperature T_{sf}:

$$T_{sf} = \hbar/k_B\tau_{sf}\,. \tag{5}$$

Table 1. Presence or absence of localised moments of transition metals dissolved in nonmagnetic hosts on the basis of the Hartee–Fock criterion

Presence is indicated by 'Yes', while a question mark indicates uncertainty (from Heeger 1969)

Impurity	Host			
	Au	Cu	Ag	Al
Ti	No	—	—	No
V	?	—	—	No
Cr	Yes	Yes	Yes	No
Mn	Yes	Yes	Yes	?
Fe	Yes	Yes	—	No
Co	?	?	—	No
Ni	No	No	—	No

Table 2. Approximate characteristic temperatures (in K) for magnetic impurities in some nonmagnetic hosts in the dilute limit

Impurity	Host							
	Au	Cu	Ag	Al	Zn	Pt	Ir	Rh
V	290[A]							
Cr	3[C]	3[E]		1200[B]		200[A]		
Mn	1[E]	1[E]	1[E]	530[A]	1[A]			
Fe	5[E]	12[A]	10[E]		80[A]		225[C]	12[D]
Co	100[E]							

[A] Rizzuto *et al.* (1973). [B] Caplin and Rizzuto (1968). [C] Sarachick (1968).
[D] Rusby (1974). [E] See Daybell and Steyert (1968).

At temperatures below T_{sf} rapid temporal spin fluctuations occur, but above T_{sf} the spin polarisation exists for a time that is long compared with the spatial thermal fluctuation of the moment. That is, for temperatures *above* T_{sf}, the impurity acts as

though it had a well-defined thermally fluctuating moment but this vanishes below T_{sf} as the polarisation begins to fluctuate more rapidly. Some values for T_{sf} are given in Table 2 and comparison with Table 1 shows that a 'No' in the Hartree–Fock sense really just implies a high T_{sf}. The concept of localised spin fluctuations thus replaces the artificially sharp boundary between magnetic and nonmagnetic impurities of the Hartree–Fock model with a smooth transition between slow and fast localised spin-fluctuation regimes. A single Co atom in a Cu host probably has a spin-fluctuation temperature around 500 K. From equation (5) this gives a mean spin lifetime of $\sim 2\times 10^{-14}$ s, quite long enough for the moment to scatter a conduction electron. Thus, while a bulk magnetic property study would pronounce a dilute random Co–Cu alloy nonmagnetic, a resistivity study would indicate a scattering component due to isolated magnetic moments. Such a component has a calculated temperature dependence as shown in Fig. 4 (see e.g. Rivier and Zlatic 1972*a*). Some experimental data are shown for comparison in Fig. 5. At very low temperatures, the conduction electrons being scattered are those which have already formed the resonant virtual bound state and thus have already experienced the resonant phase shift of $\pi/2$ (i.e. they are at the 'unitary limit'). The additional scattering resultant from the thermal excitations of the long lived spin fluctuation at $T > T_{sf}$ drives them off resonance and the resistivity decreases as the temperature increases. This behaviour leads to the ubiquitous 'Kondo' minimum when it is added to the conventional temperature dependent phonon scattering term, as shown for example in Fig. 6.

Another form of behaviour can occur if the host is nearly magnetic (e.g. Pt, Pd or Rh). These materials already have a large spin enhancement and the presence of an impurity which causes a local increase in $UN_d(E_F)$ (such as Ni or Fe) will further increase the amplitude of these fluctuations into the magnetic state (see e.g. Lederer and Mills 1968). Thus, even though there is no impurity scattering resonance in the band structure, there can still be large localised spin fluctuations. If the temperature is above the characteristic spin-fluctuation temperature T_{sf}, the conduction electrons are again scattered by the thermal fluctuation of the localised spin. However, in this case the conduction electron is simply scattered by the sum of the impurity potential and the scattering interaction with the localised spin fluctuation. This is in contrast to the case described previously in which the conduction electron has to first scatter into the extra localised state before seeing the spin fluctuation. The high temperature resistivity is thus characteristic of the scattering by a disordered array of spins and reaches a plateau at the spin-disorder limit as shown in Fig. 7 (Rivier and Zlatic 1972*b*). At low temperatures the spin-fluctuation scattering rate approaches zero as the fluctuation lifetime τ_{sf} becomes much shorter than τ_e. Note that this behaviour is the complement of that shown in Fig. 4.

The nature of the localised spin fluctuations are the same in the 'Kondo' or exchange-enhanced alloys. Whether the resistivity increases or decreases with increasing temperature depends upon their electronic structures and in particular whether the host conduction states are orthogonal to the impurity states. If they are, the conduction electron must first scatter into the extra impurity orbital to see the localised spin fluctuation and the behaviour is given by the Anderson (1961) model. If they are not (i.e. the extra 'orbital' is simply a linear combination of host d states without additional orbitals), then the fluctuations are seen by the conduction electrons in the conduction band and the Wolff (1961) model applies. The change in the orthogonality is illustrated by the series of Cr, Mn, Fe, Co impurities in Pd, Pt

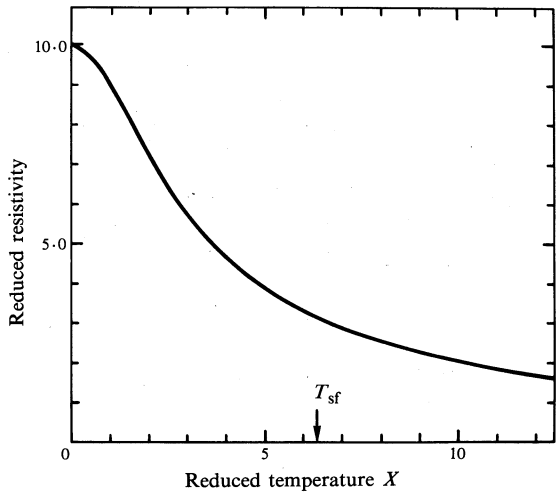

Fig. 4. Reduced resistivity as a function of reduced temperature $X = 2\pi UN_d(E_F)T/T_{sf}$. The position of T_{sf} for $UN_d(E_F) \approx 1$ is indicated. [From Rivier and Zlatic (1972*a*).]

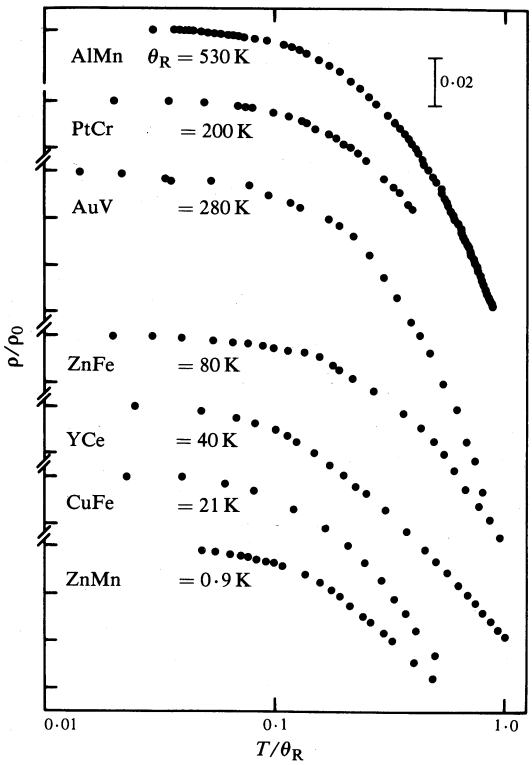

Fig. 5. Normalised resistivity ρ/ρ_0 as a function of normalised temperature T/θ (θ_R is related to T_{sf} by a simple numerical factor). The experimental points for each system were obtained from a number of specimens having a range of compositions. [From Rizzuto *et al.* (1973).]

or Rh hosts. The orthogonality decreases from Cr to Co. Thus dilute alloys of Pd, Pt or Rh with Cr impurities act as 'Anderson' alloys and exhibit resistivity minima at low temperature, whereas the impurity states of Mn, Fe, Co in Pd, Pt or Rh

are sufficiently non-orthogonal for them to act progressively (from Mn to Co) more like 'Wolff' alloys, with a resistivity that increases monotonically with temperature. The effects of this orthogonality have been discussed in detail by Rivier and Zitkova (1971). A summary of the type of behaviour found in a variety of alloys is given in Table 3.

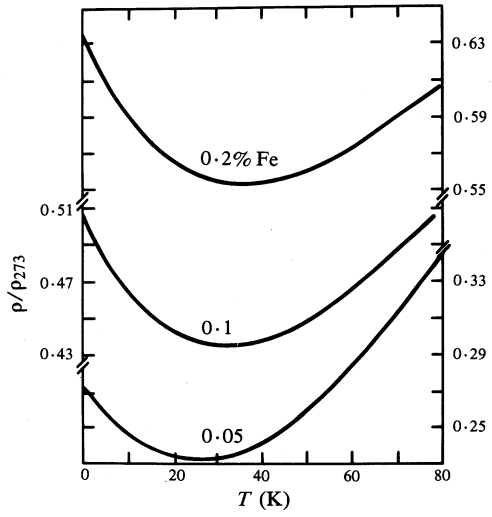

Fig. 6. Electrical resistivity of some dilute Cu–Fe alloys as a function of temperature indicating the ubiquitous Kondo minimum. [From Franck *et al.* (1961).]

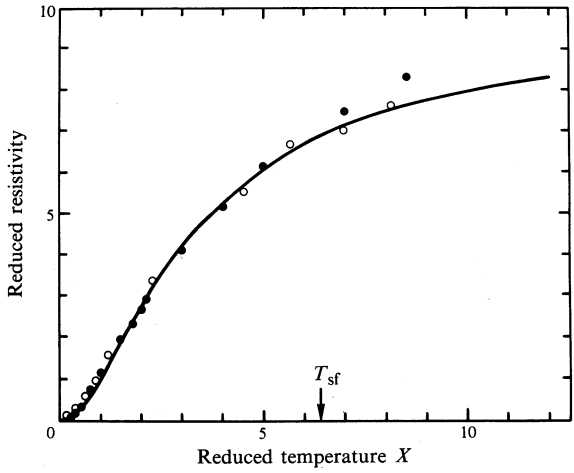

Fig. 7. Reduced resistivity as a function of reduced temperature $X = 2\pi T/T_{sf}$. The solid circles indicate the experimental data for Rh–Fe (<0·1% Fe, $T_{sf} = 12$ K) and the open circles indicate the results for In–Fe ($T_{sf} = 225$ K). The spin-fluctuation temperature T_{sf} is indicated. [From Rivier and Zlatic (1972*b*).]

The above results are based on the assumptions of a single conduction band, that the virtual bound state (determined by the impurity potential scattering) lies at E_F and consists of a single orbital in the Anderson model, and of zero atomic scattering potential in the Wolff model. It appears that these assumptions are not trivial. For

Table 3. Nature of impurity states in a number of alloy systems (from Rossiter 1986)

Solvent	Solute		Solvent	Solute		Solvent	Solute	
	Anderson	Wolff		Anderson	Wolff		Anderson	Wolff
Al	Cr		Rh	Cr	Mn	Pt	Cr	Mn
	Mn				Fe			Fe
					Co			Co
Zn	Mn				Ni			Ni
	Fe							
			Pd	V	Mn?	Au	Ti	
Cu	Ti			Cr	Fe		V	
	V?			Mo	Co		Cr	
	Cr			Ru	Ni		Mn	
	Mn			Rh			Fe	
	Fe			Ag^A			Co	
	Co			Pt^A			Ni	
	Ni^A			Au^A				
				U				
				Np				

[A] Concentrated.

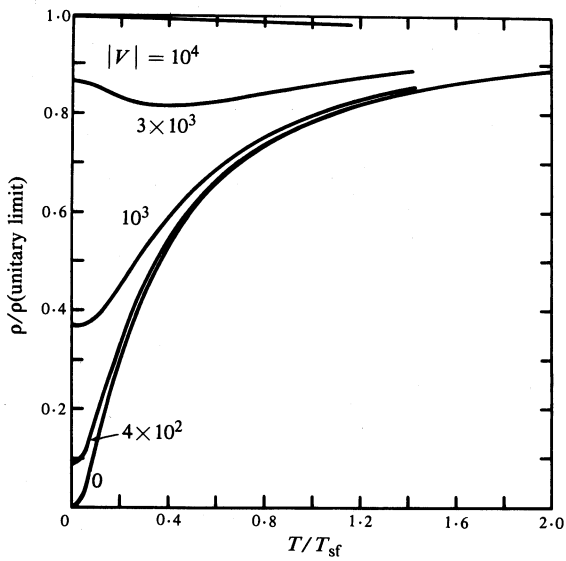

Fig. 8. Normalised resistivity due to localised spin fluctuations as a function of reduced temperature for different atomic scattering strengths (measured in terms of the shift V of the resonance with respect to the Fermi surface in units of $k_B T$). [From Fischer (1974).]

example, Fischer (1974) has shown that in alloys with a small enhancement of the host susceptibility, the resistivity due to the localised spin fluctuation in the Wolff model is modified by the host scattering potential (measured in terms of the shift V of the resonance with respect to the Fermi surface) as shown in Fig. 8. These results show that both the magnitude and sign of the T^2 coefficient found at low temperatures are dependent upon the degree of atomic scattering. In fact for very

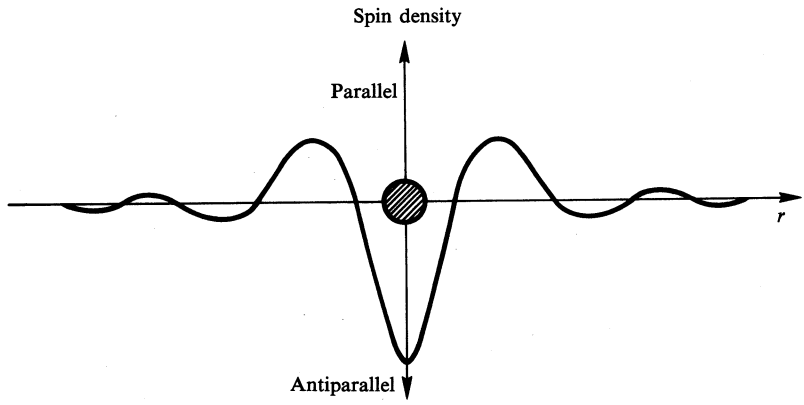

Fig. 9. Schematic representation of conduction electron spin density around an isolated magnetic impurity.

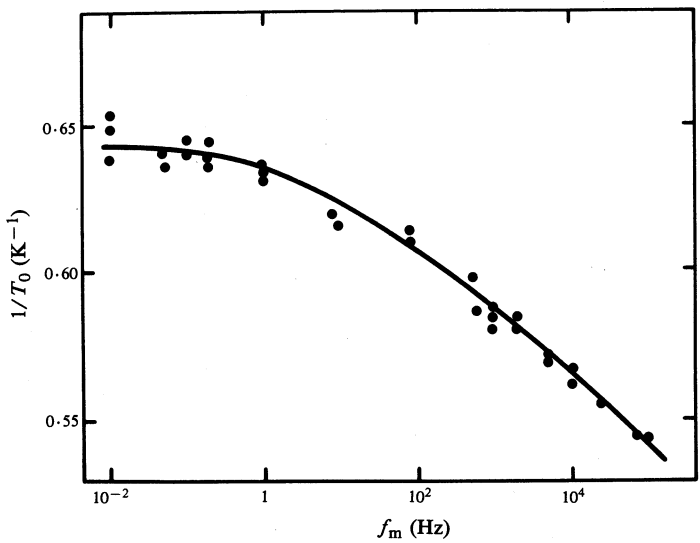

Fig. 10. Reciprocal of the apparent spin-glass freezing temperature T_0 as a function of the characteristic frequency of measurement f_m. [From Maletta (1981).]

large V one obtains the mirror image of the curve for $V = 0$. This corresponds to the Anderson model with $V = 0$ and reflects the changes expected with differing degrees of orthogonality between the host and impurity states described above.

We can also now understand why small groups of Co or Ni impurities appear to suddenly acquire a magnetic moment in a bulk magnetic property study. The effect of impurities in close proximity is to change the local Coulomb interaction U by some amount δU, thus leading to a change in the spin-fluctuation temperature (or lifetime):

$$T_{sf}(P) = \frac{\hbar}{k_B} \frac{1-(U+P\,\delta U)N_d(E_F)}{\pi N_d(E_F)}, \tag{6}$$

where P is the number of impurity nearest neighbours. This effectively lowers the temperature of the onset of magnetic behaviour or, in terms of the fluctuations, it increases the spin-fluctuation lifetime.

3. Spin Glasses

Let us now increase the concentration of impurities so that they can start to interact via the comparatively long range RKKY type of interaction. The usual static picture of this interaction is as follows. A localised moment induces a local spin density polarisation of the conduction electrons which oscillates and decays with distance from the impurity, as shown schematically in Fig. 9. Randomly distributed individual moments will interact indirectly via these spin density polarisation fluctuations with a random sign of interaction and so will freeze into a spin glass below some characteristic spin-glass freezing temperature T_0. However, the physical properties of a spin glass are determined by the dynamic spin–spin correlations. At very high temperatures the spins will behave paramagnetically, although there may be some short range spin–spin correlations. As the temperature is reduced, spin clusters emerge from these short range correlations, their size and shape being determined by the distribution of other spins in the immediate neighbourhood (see e.g. Levin *et al.* 1979). Furthermore, the coupling within and between the clusters depends upon the spatial distribution of the spins according to the RKKY interaction. At this stage an experiment would encounter a wide distribution of relaxation times varying from that of the single paramagnetic isolated spin to those of some much larger more slowly responding clusters associated with favourable concentration fluctuations. As the temperature is further lowered towards T_0, the size and density of the clusters increases until finally at T_0 an 'infinite' glassy cluster of frozen spins forms. However, there will still be many free smaller clusters that are not part of this large cluster and which can respond to external fields maintaining a distribution of relaxation times. As T is lowered well below T_0, more and more of those clusters join the 'infinite' cluster or become blocked due to a lack of thermal activation energy (see the next section). The wide spectrum of relaxation times characteristic of excitations over a wide range of energy barriers can make analysis of spin-glass behaviour confusing. Again the value of a measured property will depend upon the frequency (or characteristic time) of measurement. This aspect is graphically demonstrated in Fig. 10 where the reciprocal of the apparent freezing temperature T_0 of a spin glass is plotted as a function of the characteristic frequency of measurement (Maletta 1981).

The magnetic excitations of the spin glass at low temperatures may be regarded as diffusive spin waves, the damping resulting from the lack of translational periodicity. These will give rise to a $T^{3/2}$ resistivity behaviour if scattering from long wavelength spin waves is allowed, or a T^2 behaviour if the rate of scattering by other imperfections is significant, this effectively excluding coherent scattering from the long wavelength spin waves by the effects of a finite conduction electron mean free path. Some experimental data are shown fitted to a $T^{3/2}$ power law in Fig. 11.

However, we must also consider the fluctuations of the individual spins. From the discussions above, it is clear that spin-glass behaviour is only possible at temperatures above T_{sf}. It appears that in many cases the RKKY interaction below T_0 may be sufficiently strong to destroy the resonant spin-fluctuation state. Well below T_0 the $T^{3/2}$ or T^2 behaviour should thus be observed. However, as the temperature

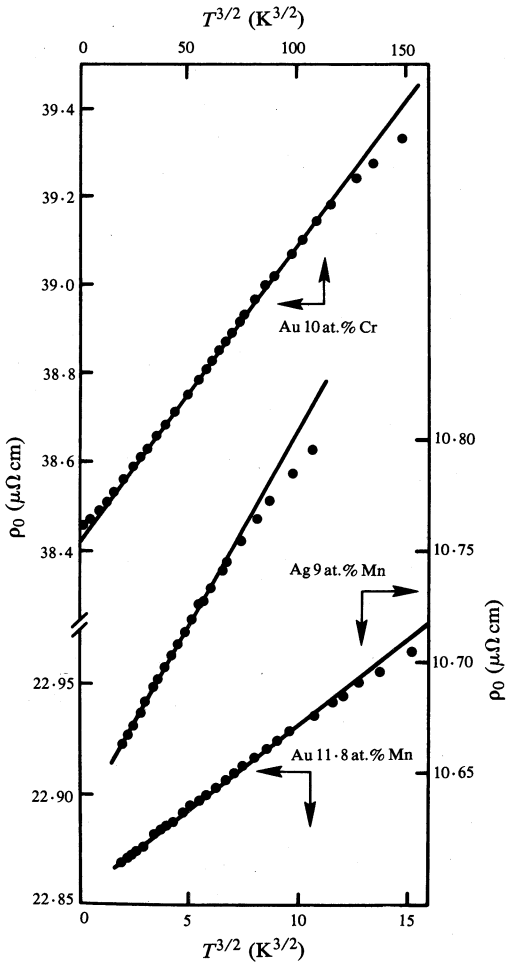

Fig. 11. Resistivity (corrected for the phonon scattering) as a function of $T^{3/2}$ for Au–Cr, Ag–Mn and Au–Mn. [From Ford and Mydosh (1974).]

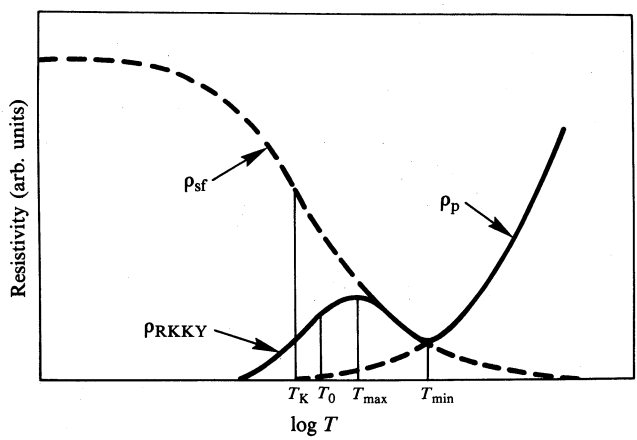

Fig. 12. Schematic representation of the resistivity due to isolated impurities ρ_{sf}, interacting impurities ρ_{RKKY} and phonons ρ_p as a function of log T. The combined effect is shown as the solid curve.

approaches T_0 the thermal breakdown of the RKKY interaction allows the resonant state to be established leading to a decrease in the resistivity with increasing temperature. This behaviour is shown schematically in Fig. 12, and it is clear that a maximum in the resistivity at T_{max} can result from a competition between the RKKY interaction and the spin-fluctuation effects. Such a maximum is characteristic of many spin glasses based on noble metals as shown for example in Fig. 13. Note that there is no obvious resistivity anomaly at T_0 (indicated by ↑) since on the characteristic time scale of a resistivity measurement ($\sim 10^{-14}$ s) the spin-glass structure has already formed at much higher temperatures.

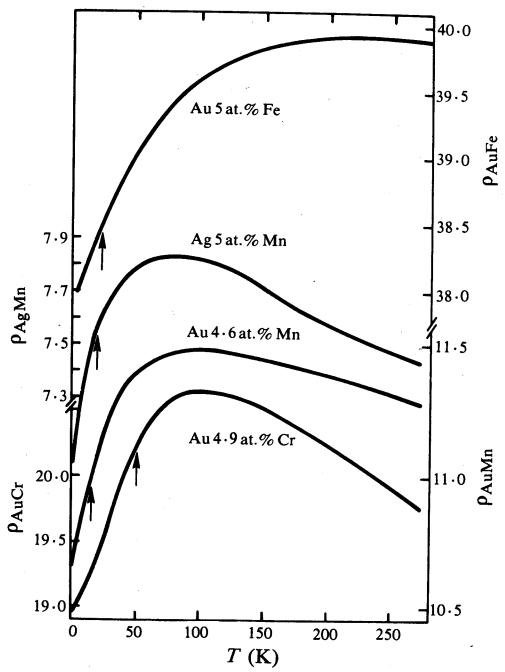

Fig. 13. Temperature dependence of the resistivity (in $\mu\Omega$ cm and corrected for the phonon contribution) of Au–Cr, Au–Mn, Ag–Mn and Au–Fe. The static spin-glass freezing temperatures T_0 are indicated by the arrows on each curve. [From Ford and Mydosh (1974).]

Spin-glass behaviour is also observed in alloys with exchange enhanced hosts (such as Pd or Rh), again characterised by a $T^{3/2}$ law at low temperatures. However, in these cases the coefficient of the $T^{3/2}$ term may be negative if the magnitude of the atomic scattering potential is sufficiently large (Rivier 1974; Rivier and Adkins 1975), the resistivity then exhibiting a minimum at low temperatures. The inversion in slope with increased atomic scattering is of the same nature as discussed in the previous section.

4. Magnetic Clusters

At higher concentrations of a magnetic impurity, the direct interactions between the spins may become strong enough to condense small regions into a magnetically aligned state. Such regions will usually be associated with composition fluctuations which increase the local concentration of magnetic species. Here there are two separate situations that should be identified. If the magnetic clusters develop from a spin-glass state they will interact with the (isolated) spins in the surrounding spin-glass matrix, giving the so-called mictomagnetic structure (Beck 1972). Below

the spin-glass freezing temperature T_0 these clusters will be locked into directions determined by the local frozen spin alignment. Above T_0 they will act as giant paramagnetic (i.e. superparamagnetic) units and at still higher temperatures (i.e. at the Curie temperature of clusters) the magnetic alignment within the clusters will be destroyed. An alternative situation applies to systems in which the impurity atoms only acquire a magnetic moment if they are present in sufficient concentration, for example Co or Ni in a Cu matrix (although, as in the case of isolated moments discussed above, it should be remembered that whether or not a cluster is deemed to have a magnetic moment depends upon the rate of spin fluctuation of the cluster in relation to the coherence time of the probe being used). If the particle concentration is small they will act as independent entities in a nonmagnetic matrix. However, if the density of clusters is sufficiently large, the RKKY intercluster interaction may be sufficiently strong to promote freezing of the cluster moments into a cluster glass below some particular temperature. Evidence for this type of behaviour has been found at compositions near the ferromagnetic transition in systems such as Au–Fe (Coles *et al.* 1978; Sarkissian 1981), Cu–Ni (Aitken *et al.* 1981) and Pd–Ni (Cheung and Kouvel 1983). In the case of an alloy system with a nearly magnetic matrix there is also the interesting possibility of polarisation fluctuations in the matrix being enhanced by the particle moments.

Table 4. Superparamagnetic relaxation time as a function of $\Delta E/k_B T$

$\Delta E/k_B T$	τ (s)
50	$5{\cdot}2\times10^{12}$
25	$7{\cdot}2\times10$
25·3	10^2
10	$2{\cdot}2\times10^{-5}$
1	$2{\cdot}7\times10^{-9}$

Whatever the situation, there will in general always be some local magnetic anisotropy described by an anisotropy constant K. If the volume of each particle is V then the energy barrier that must be overcome before a particle can change its direction of magnetisation is $\Delta E = KV$. The rate of change of magnetisation is given approximately by (see e.g. Cullity 1972)

$$-\frac{dM}{dt} = \frac{M}{\tau_{sp}} = 10^9 M \exp(-\Delta E/k_B T), \tag{7}$$

where the rate of change dM/dt has been written as M/τ_{sp} for a single relaxation time process. This equation allows definition of the superparamagnetic freezing or blocking temperature T_B which gives a relaxation time τ_{sp} of $\sim 10^2$ s, a typical period of observation in a bulk magnetic experiment. Application of a field H causes a decrease in the height of the energy barrier to

$$\Delta E = KV(1 - HM_s/2K), \tag{8}$$

where M_s is the magnetic moment per atom within the cluster. Thus the bulk magnetic behaviour will depend upon time, temperature, field and particle size. The variation of τ_{sp} with $KV/k_B T$ (for small H) is given in Table 4 and shows that

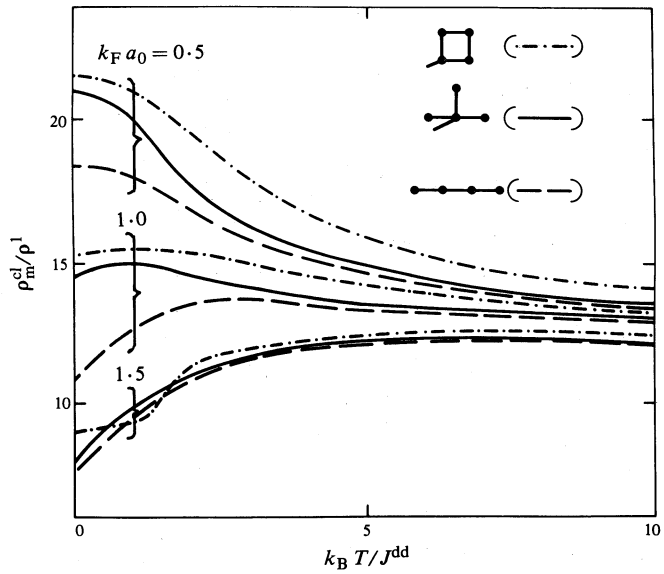

Fig. 14. Magnetic contribution of the resistivity of a cluster of four atoms as a function of reduced temperature $k_B T/J^{dd}$ for three different atomic configurations and three values of $k_F a_0$ as indicated. The resistivity has been normalised to that of a single isolated spin ρ^1. [From Levin and Mills (1974).]

$T_B \approx KV/25k_B$. A comparison of τ_{sp} with the conduction electron relaxation time ($\sim 10^{-14}$ s) shows that over all temperatures up to the Curie temperature of the particle, the superparamagnetic particles will appear to be stationary (frozen or blocked) in a resistivity study, a clear example of the caution suggested in the Introduction. While the freezing processes involving a glassy phase are fundamentally different to superparamagnetic blocking in a nonmagnetic matrix [it has been argued that the former process is the result of a cooperative process involving all of the particles of the system (see e.g. Edwards and Anderson 1975) whereas the latter is an independent particle effect], in both cases the Curie temperature of the cluster or particle will be relatively independent of particle size (Kneller 1958), although it could of course depend upon the chemical composition of the cluster. A determination of the resistivity due to magnetic scattering from a cluster $\rho_m^{cl}(T)$ thus requires some model calculation of the spin–spin correlation function within the cluster as a function of temperature. To this end Levin and Mills (1974) have employed the Heisenberg Hamiltonian to treat the interaction between spins within the same cluster and the molecular field approximation for interactions between clusters if the alloy is ferromagnetic. Their result for the temperature dependence of $\rho_m^{cl}(T)$ for a cluster of four spins in different configurations within a simple cubic lattice is shown in Fig. 14 for three different values of the parameter $k_F a_0$ (corresponding to three different values of n), where k_F is the Fermi wavevector and a_0 the lattice parameter. These results were obtained using the first Born approximation, and inclusion of the next higher terms in the perturbation expansion can lead to a Kondo effect at low temperatures.

There are two main features that we want to point out. Firstly, the general form of the behaviour is not particularly sensitive to the cluster topology, and secondly, whether the cluster causes an increase or decrease in ρ compared with the high temperature (spin-disordered) value $\rho_m^{cl}(\infty)$ depends upon $k_F a_0$ (i.e. n). It might also be noted that the cluster resistivity does not reach the high temperature value until temperatures well above $5J^{dd}/k_B$. Increasing the size of the cluster was found to increase the magnitude of the deviation in $\rho_m^{cl}(0)$ from the high temperature value.

The behaviour shown in Fig. 14 effectively assumes that the cluster size d is smaller than Λ. If $d > \Lambda$ the cluster resistivity $\rho_m^{cl}(0)$ should always lie below the high temperature value $\rho_m^{cl}(\infty)$ since the electron in the cluster is then effectively inside a body with long range magnetic order. The magnetic contribution to the resistivity will thus pass through a maximum with increasing cluster size at $d \sim \Lambda$, provided that $k_F a_0$ (or n) is such that the cluster initially causes an increase in ρ_m. However, there is the additional complication that the magnitude of the mean magnetic moment per atom may depend upon the number of other magnetic atoms and degree of atomic correlation within the cluster. This effect is probably due to a change in the spin-fluctuation rate as discussed above, although it must be admitted that specific details of the effect on a time scale of $\sim 10^{-14}$ s are not really known.

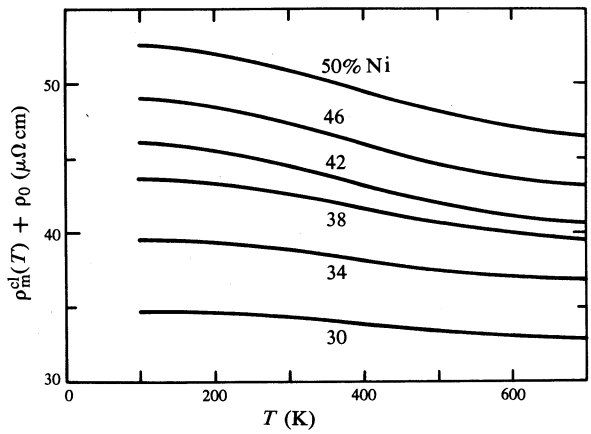

Fig. 15. Sum of the magnetic cluster resistivity $\rho_m^{cl}(T)$ and the atomic disorder resistivity ρ_0 of Cu–Ni as a function of temperature. The Ni concentrations are indicated. [From Rossiter (1981).]

Unfortunately, there are few systems that permit an experimental verification of this behaviour. One requires that the alloy can be prepared in an initially fairly random state, that the magnetic clusters associated with composition fluctuations can be formed by suitable heat-treatment and that the temperature dependence of the resistivity can be determined over a temperature range at least up to $\sim J^{dd}/k_B$ without introducing changes to the atomic configuration. Many potentially suitable alloys involving a nonmagnetic host such as Au or Cu with Fe, Co or Ni solutes have been investigated. The precipitate formed is usually fairly pure Fe, Co or Ni and so J^{dd}/k_B is given roughly by their bulk Curie temperatures which are 770°C, 1131°C and 358°C respectively (see Cullity 1972, Appendix 5). This effectively rules out systems containing Fe or Co precipitates, as significant atomic diffusion will

occur before the variation of ρ_m^{cl} with temperature due to magnetic disordering can be determined. The Au–Ni decomposes at quite low temperatures into a finely divided two phase modulated structure and so is not a suitable candidate. However, the rate of atomic diffusion in Cu–Ni alloys is quite low up to 200–300°C. The magnetic contribution to the resistivity of these alloys has been investigated over a wide range of compositions and measuring temperatures and does indeed have the form expected from the above discussions as shown in Fig. 15 (see e.g. Rossiter 1981).

5. Conclusions

Any deviation from perfect periodicity will lead to a resistivity contribution which will depend upon the spatial extent and lifetime of the disturbance measured in relation to the conduction electron mean free path and relaxation time. A spin associated with an isolated impurity has a lifetime which depends upon the environment such that at high temperatures the electrons 'see' a long lived thermally fluctuating spin, i.e. a good magnetic moment, whereas at low temperatures the spin-fluctuation lifetime is less than the relaxation time and no moment is registered. However, the dynamics of spin aggregates like spin glasses or superparamagnets are such that they are effectively static over the conduction electron relaxation time so that there is no resistivity anomaly directly associated with the spin-glass freezing temperature or superparamagnetic blocking temperature. In general, the short conduction electron relaxation time means that a resistivity measurement is sampling a structure on a much shorter time scale than many other techniques such as the Mössbauer effect or neutron scattering, a factor which should be borne in mind when analysing any experimental data.

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