LOCAL MAGNETIC MOMENTS AND THE MOSSBAUER EFFECT

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INTRODUCTION

In this brief paper we will describe the use of the Mossbauer effect to study the behavior of the magnetic properties of impurities in metals. This problem has been named the "localized moment problem" and in recent years has been studied quite thoroughly both theoretically and experimentally.¹ At the beginning of the last decade, it was believed that significant theoretical and experimental progress had been made. Based on earlier concepts of Friedel,² both Anderson³ and Wolff⁴ presented a sound theoretical model for studying the magnetic behavior of a single impurity in a host metal. At about the same time systematic studies of low concentration impurities in alloys of the 4d transition metals had revealed rules for the occurrence and definition of a magnetic impurity.⁵ At this point in the study of the localized moment problem most researchers felt that significant progress had been made and ultimately a first principle understanding of the occurrence of elemental magnetism would soon be presented. This optimism was based on the historical belief that after solving the single impurity problem one could go on to the two impurity problem and then the many impurity problem. Ultimately it was felt that a magnetic metal like Fe could be considered as consisting of magnetic impurities at each lattice site. Unfortunately even the single impurity problem has turned out to be more difficult than first realized and a multitude of magnetic behaviors has been associated within even the single impur-

ity limit depending upon the nature of both the impurity and the host.

Several experimental techniques can be used to study the behavior of a localized magnetic moment at the impurity site itself and with the surrounding conduction electrons, nuclei and other impurities. Both local and long range effects can be studied by microscopic and macroscopic measurements. All the interpretations are based on the fact that both the core electron spin polarization at the impurity site and the extended conduction electron spin polarization around the impurity are proportional to the magnetization of the localized moment associated with the impurity. A listing of both the microscopic and macroscopic experimental techniques for observing the local and long range effects of magnetic impurities has been given in detail by Jaccarino.⁶

The hyperfine interaction at the impurity nucleus allows the study of the localized moment itself. For transition metal impurities such as Fe, there are several contributions to the hyperfine field all of which are proportional to the impurity magnetization $\langle S_z \rangle$. If the impurity behaves like an isolated magnetic moment, then the magnetic field and temperature dependence of the hyperfine field should simply be a Brillouin function

$$H_{\text{hyp}} = H_{\text{sat}} B_S \left(\frac{g \mu_B H_0}{k_B T} \right)$$

where H_{sat} is the saturation hyperfine field for $B_S = 1$ and is proportional to the total impurity moment $\langle S \rangle$ and includes contributions from the polarized s-conduction band via the Fermi contact term, H_0 is the applied external field and T the temperature. The Brillouin behavior is correct as long as the impurity is in thermal equilibrium in a time which is short compared to the Larmor precession time. If, however, the electronic relaxation time becomes longer than the Larmor precession time (e.g., at very low T), then the total hyperfine field no longer follows a Brillouin function although H_{sat} is still proportional to the magnitude of the impurity moment. Although some systems seem to show a Brillouin behavior for the magnetization of the local impurity, under more careful experimentation very few systems are ideal. The susceptibility, the NMR linewidth and the impurity hyperfine field usually display anomalous low temperature

behavior. This is especially true for impurities which do not display a Curie susceptibility at low temperature and in alloys with anomalous resistive behavior such as a resistance minimum.

In a recent paper⁷ a short review of the localized moment problem was presented and in this paper we will concentrate on describing some of the recent theoretical and experimental developments. In particular we will discuss the use of the Mossbauer effect to study the microscopic effects associated with the Kondo effect on the magnetic behavior of Fe in Cu at low temperature. The FeCu alloy system is now considered the classical Kondo system and is the one studied most extensively.¹ We will contrast the behavior of the Mossbauer spectrum of Fe in Rh with the one of Fe in Cu. FeRh alloys unlike FeCu alloys do not show the usual resistance minimum associated with the Kondo effect effect, however, its magnetic susceptibility as well as its Mossbauer hyperfine field indicate an unusual magnetic moment behavior associated with the Fe impurities. The last part of this paper will deal with recent experimental attempts to distinguish between two models for the occurrence of a local magnetic moment. The continuous appearance of a localized moment is usually associated with the Friedel-Anderson-Wolff picture whereas the discontinuous appearance of a moment depending upon the local environment of the impurity is usually associated with a model due to Jaccarino and Walker.⁸ The microscopic Mossbauer probe is an excellent tool for studying and differentiating these two models. Studies on Fe in $\text{Nb}_{1-x}\text{Mo}_x$ alloys, in which a moment seems to appear when $x = 0.4$, indicate the Jaccarino-Walker picture to be appropriate however, even in this case additional complications associated with the Kondo effect seem to be present.

CLASSICAL BEHAVIOR

In the simplest theory, the localized moment problem can be separated into two parts: 1) If a localized moment exists in a metal, what is its behavior right at the impurity site and its immediate environment? 2) What conditions both for the impurity and the host metal are necessary in order to have a localized moment form? These two questions presume that the formation of the localized moment and its interaction with the surroundings can be separated. However, in more realistic models, the conditions for the formation

of the moment and its interaction with the host are linked in a quite complicated feedback system of equations.

The classical answer to question 1 can be obtained using s-d Hamiltonian proposed by Zener⁹ to study the magnetism of the transition metals. Zener proposed a model in which d electrons were assumed to be localized and the s conduction electrons itinerant. The interaction can be written in the form

$$H_{s-d} = - \sum_i J(r - R_i) \sigma(r) \cdot S_i$$

where $J(r - R_i)$ is the s-d exchange coupling integral, $\sigma(r)$ is the spin density of the conduction electrons and S_i is the localized spin at the i th lattice sites.

An early attempt to quantify microscopically the conditions under which a local moment would form on an impurity (question 2) was presented by Friedel² and later developed by Anderson³ and Wolff.⁴ These models all include the following terms: 1) the kinetic energy of the conduction electrons; 2) the local energy E_d of the impurity state, 3) the s-d admixture element V_{sd} which acts to broaden the localized state leading to a width $\Delta = \pi N_c(0) V_{sd}^2$ where $N_c(0)$ is the host metal density of states at the Fermi surface. Within the Hartree-Fock approximation the local susceptibility of the impurity using the Anderson Hamiltonian is

$$\chi_{imp} = \frac{2\mu_B^2 N_d(0)}{1 - N_d(0)U}$$

where $N_d(0)$ is the density of states of the impurity d level at the Fermi surface and for one electron per impurity is given by $N_d(0) = 1/(\pi\Delta)$. Thus the criteria for the formation of a local moment is the divergence of χ_{imp} leading to the condition $1 - N_d(0)U \leq 0$ which is equivalent to $[U/(\pi\Delta)] > 1$. This simple formula was used to interpret the classical susceptibility measurements by Clogston et al.⁸ on the magnetic behavior of 1% Fe in binary alloys of neighboring 4d transition metals. In a rigid band model for the density of states of the 4d band electrons, the impurity width and thus $\Delta = V_{sd}^2 N_{4d}(0)$ varies dramatically while U remains virtually the same as one changes the d band occupation from 0 to 10 electrons. When $N_d(0)$ is large near the ends of the 4d band, Δ is narrow and $N_d(0)U$ is expected to

be large satisfying the condition for the divergence of the local moment susceptibility. Thus one observes the appearance and disappearance of a localized moment with alloying depending upon the value of $N_d(O)U$.

Higher order many body effects have been shown to suppress the divergence of the susceptibility and thus a more rigorous treatment can be used even for a single impurity. The correlations can be included in the calculation of the dynamic frequency dependent susceptibility $\chi(\omega)$ in which the spin moment decays with a characteristic lifetime τ_{sf} called the spin fluctuation lifetime. τ_{sf} increases with U but never becomes infinite even when $(U/\pi\Delta) > 1$. Thus in this more rigorous theory the observation of a spin moment will depend upon whether the fluctuations of the spin are sufficiently slow compared with the time scale of the experimental probe.

ANOMALOUS IMPURITY MOMENT BEHAVIOR

The simplicity of the Friedel-Anderson-Wolff model plus its physical appeal and the experiments by Clogston et al. gave hope that the single impurity problem was relatively solved. In 1964, however Kondo¹⁰ showed that the resistance minimum seen in such alloys as Fe in Cu could be interpreted as being due to a higher order scattering between the magnetic Fe impurity and the Cu conduction electrons. Kondo showed that this higher order scattering increased the resistivity as $\log T$ at low temperature and was the result of a strong correlation between the magnetic impurity and the conduction electron. Kondo started with the Zener s-d Hamiltonian and showed that the resistance due to magnetic impurities to 2nd order in the Born approximation is given by

$$\rho_T(T) = AT^5 + c\rho_m [1 - N(O)J \ln(T/D)]$$

where AT^5 is the temperature dependence of the resistance associated with phonon scattering, c the concentration of impurities, ρ_m the 1st Born approximation scattering resistance per impurity, J the s-d coupling constant, and D a measure of the width of the conduction band. $\rho_T(T)$ shows a minimum which is weakly dependent upon concentration, $T_{min} \propto c^{1/5}$. The expansion must break down when the high order term $-N(O)J \ln(T/D) \approx 1$ giving rise to the Kondo

temperature $T_K = D_{\text{exp}} [-1/N(O)J]$. Much below this characteristic temperature very strong correlations exist between the d spin electrons localized on the impurity site and the conduction electrons. These spin correlations considerably modify the low temperature spin behavior both on the impurity site and on the host metal electrons and ions in the neighborhood of the impurity. In other words, the arbitrary separation of the problem into two parts posed above breaks down. The Mossbauer effect being a microscopic probe is an ideal tool to study the formation and effects of these low temperature correlations. In what follows we will contrast the susceptibility, resistivity and Mossbauer measurements for FeCu with that of FeRh.

Besides the resistivity, the Kondo effect is believed to affect the magnetization of the impurity which can be seen in the measurement of the susceptibility. Below the Kondo temperature low temperature resistivity measurements indicate that the $\log T$ divergence levels off approaching a saturation value corresponding to the unitarity limit of scattering per impurity. The unitarity limit is expected when the scattering potential becomes so strong that it actually binds the electrons. Although the theory and experiments have advanced considerably and are quite sophisticated it is easiest to appreciate some of the physical difficulties by relying first on some earlier simpler interpretations. The unitarity limit in the resistivity seems to be the result of a complicated singlet spin coupling between the conduction electron spin and the impurity spin. This coupling of the impurity and conduction electron spins leads to an effective cancellation of the moment associated with the impurity. Thus at low temperature the susceptibility no longer follows a Curie law but seems to vary as

$\chi(T) \propto C/T + T_K$ and no longer diverges as $T \rightarrow 0$. Examples of the low temperature resistivity and susceptibility behaviors of Fe in Cu are given in Figs. 1a and 2a. Thus, it seems that associated with the Kondo effect is a characteristic energy $k_B T_K$ which represents the effective correlation energy between the impurity and the conduction electron spin. In addition because of the singlet nature of the coupling, the effective spin moment of the impurity seems quenched and equal to zero at low temperature. First, this quenching of the spin moment should be observable using the microscopic Mossbauer probe at the impurity site and second, this quenching of the impurity moment should be capable of being destroyed by the application of a magnetic field such that

Fig. 1. The anomalous resistivity per impurity of Fe in Cu and the total resistivity of 1% Fe in Rh.

Fig. 2. The low temperature susceptibility per impurity of Fe in Cu and Fe in Rh.

$$\mu_B H_0 \approx k_B T_K.$$

The Kondo temperature of Fe in Cu is believed to be on the order of 10 K which is ideal experimentally since it can conveniently be studied at temperature T both above and below T_K and a magnetic field of about 100 kG is expected to have a strong destructive effect with respect to the formation of the spin correlated state. The hyperfine field at the Fe nucleus is primarily due to the core-polarization produced by the moment on the Fe and the conduction electron spin polarization associated with the moment. Thus any changes in the behavior of the measured hyperfine field reflect the local nature of the correlations associated with the formation of the low temperature Kondo spin compensated state.

In Fig. 3 we show the hyperfine field measurements of Fe^{57} in Cu as a function H_0/T .¹¹ The three solid line curves represent the observed hyperfine field at constant magnetic field and decreasing temperature. Note the hyperfine field does not follow a Brillouin function and that the saturation hyperfine field as $T \rightarrow 0$ is not a constant but depends upon the applied field. The growth observed in H_{sat} with H_0 can be interpreted as the breaking up of the spin compensated state and the growth of the moment on the iron impurity. From a plot of $H_{\text{sat}}(H)$ vs H_0 as given in Fig. 4a an order of magnitude value for T_K can be obtained. The high temperature and therefore Brillouin behavior of the hyperfine field can be used to obtain H_{sat} which represents the saturation hyperfine field which would have been obtained for $H_0/T \rightarrow \infty$ had not the spin compensated state formed at low temperature. The value for $\mu_B H_K$ gives a value for $k_B T_K$ on the order of the Kondo energy. The actual approach to saturation of the moment as a function of H_0 for $T < T_K$ has been studied theoretically by Nam and Woo¹² and by Ishii.¹³ They find that the moment starts off increasing linearly with field and eventually curves over and saturates at high field. This region where $\mu_B H \gg k_B T_K$ has recently been investigated by Maley and Taylor¹⁴ in Fe in Mo which has a $T_K \sim 0.25$ K. In Fe in Cu for low applied field H_0 , $H_{\text{sat}}(0)/H_{\text{sat}} \ll 1$ confirming in part the singlet nature of the spin compensated state for $T < T_K$. More details of the experiment are given by Frankel et al.¹¹ and a review of Mossbauer and NMR as well as other studies on the Kondo effect are given in the review paper by Heeger.¹

Fig. 3. The hyperfine field for Fe^{57} in Cu as a function of H_0/T for three values of the external field.

In addition to Fe in Cu the low temperature high field Mossbauer measurements have been performed in other alloys including Fe in Rh.^{15,16,17} Fe in Rh is a very interesting dilute alloy system. In Figs. 1b and 2b we plot the resistivity and susceptibility of Fe in Rh and contrast its behavior with that of Fe in Cu. The resistance decreases with temperature and does not show any resistance minimum, however, the susceptibility of Fe in Rh except for a scaling factor looks very much like that of Fe in Cu. One can therefore ask, since the magnetic susceptibility of FeRh is essentially similar to that of FeCu , what are the microscopic details of the magnetic behavior of the Fe impurity? If the localized magnetic behavior is the same, then why is the resistivity of FeCu and FeRh so different?

High field and low temperature Mossbauer measurements have been performed on Fe in Rh and the hyperfine field as a function of applied field shows a behavior similar to that of Fe in Cu. The saturation hyperfine field $H_{\text{sat}}(H_0)$ vs H_0 is shown in Fig. 4b and seems to grow linearly with applied field. The limiting saturation hyperfine field yields a Kondo field $H_K \approx 300$ kG and represents a compensation energy $\mu_B H_K \approx k_B T_K \approx 30$ K which agrees well with the compensation temperature obtained from the fit to susceptibility data.

Fig. 4. The saturation value of the magnetic hyperfine field at low temperature as a function of applied magnetic field for Fe in Cu and Fe in Rh.

The interpretation of the growth of the low temperature moment in terms of the breaking up of the spin compensated state is among one of the models used to explain the Mossbauer data. Another approach is to use the spin fluctuation model in which the characteristic spin fluctuation energy $\hbar\omega_{sf} \approx k_B T_K$ such that for $T > T_K$ there appears to be a moment and for $T < T_K$ there is no moment because the spin moment fluctuates too fast leading to no net moment. There are various theories to explain the unusual resistivity behavior shown in Fig. 1b. In one model due to Knapp,¹⁸ the Rh host is believed to be composed of both d electrons and s electrons. The d electrons partake in the spin compensation of the Fe impurity moment and the s conduction electrons carry the current and scatter off of the compensated state. Since the resistivity is proportional to the square of the Fe impurity moment, one expects the resistivity as a function of T to be proportional to the square of the effective temperature dependent moment or equivalent $\rho(T) \propto T \chi(T) \propto \mu_{eff}^2(T)$. This simple two-band model seems to give a good fit to the resistivity and susceptibility data. Another model making use of the spin fluctuation theory has recently been worked out in detail by Doniach.¹⁹ Very low temperature resistivity measurements by Foner et al.²⁰

seem to indicate some difficulty in obtaining a unique characteristic spin fluctuation temperature. High field magnetoresistance measurements by Foner²⁰ on FeCu and FeRh also confirm the anomalous magnetic behavior of FeRh .

THE LOCAL ENVIRONMENT EFFECT

In the study of the formation of a local moment, macroscopic measurements are unable to determine the microscopic behavior of the local moment uniquely. The interpretation of the magnetic properties of Fe impurities in 4d transition metal binary alloys assumed that when the Fe impurities are magnetic they all have the same net moment. The rigid band uniform model has been challenged by Jaccarino and Walker⁸ who proposed that the magnetic moment on an impurity occurs discontinuously and its appearance depends upon the local environment about the impurity rather than the Anderson $U/(\pi\Delta) > 1$ requirement. The experimental confirmation of this local environment model was observed in interpreting the Co^{59} NMR spectrum in the $\text{Rh}_{1-x}\text{Pd}_x$ alloys. As x increased the Co^{59} signal decreased in intensity but did not shift in frequency from that observed for Co in pure Rh where there is no moment. If all the Co atoms had the same average moment, then as the concentration of Pd increased above that necessary for magnetic behavior no diminution of the signal would have been seen, but rather a gradual shift in the resonance due to the hyperfine field generated by the localized moment formed on the Co.

Jaccarino and Walker were able to account for the results by assuming that a given impurity was limited to having either no moment or its full moment depending on whether or not it has a minimum number of Pd near neighbors. Then the intensity of the Co^{59} NMR resonance and the average moment per impurity could be calculated from a binomial like distribution.

The same behavior has been observed in Fe and Co-doped $\text{Nb}_{1-x}\text{Mo}_x$. Neither Fe or Co are magnetic in Nb metal, but both have moments in Mo. In the Co-doped alloys NMR in Co^{59} by Brog et al.²¹ detect two resonances which change in intensity as a function of x , one of which is due to those nuclei which see only the external field and the other of which is due to those nuclei whose resonance is shifted by a hyperfine interaction due to the presence of a localized moment

on the impurity. The important point is that as x changes, only the relative intensity of the two resonances, not the positions of the resonances changes.

The Fe-doped alloys have been studied by Mossbauer spectroscopy and show similar effects.^{22,23,24} In Fig. 5 we show the Mossbauer spectrum for Fe in pure Nb and pure Mo. In Nb there is no moment so that the low temperature hyperfine field at the nucleus is the same as the applied field 75 kG. In Mo there is a moment and the hyperfine field is -115 kG, which leads to a 40 kG separation of the outer lines in the Mossbauer spectrum. The Mossbauer experiments have been performed on binary alloys of $\text{Nb}_{1-x}\text{Mo}_x$ for $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0. Above $x = 0.4$ the hyperfine field shows two distinct sites indicating the local environment effect of full moment Fe impurity coexisting with Fe impurities with no moment. The temperature and field dependence of the Mossbauer data is actually more complicated due to the appearance of Kondo like spin compensation

Fig. 5. The Mossbauer spectrum at 4.2 K and 75 kG for Fe in pure Nb and pure Mo.

effects at low T.

Recently, the relation between the Jaccarino-Walker effect and the Anderson model was studied by Kim.²⁵ Kim discusses the effect of the self energy of an impurity due to the interaction with other surrounding impurities. The real and imaginary parts of the self energy give rise respectively to the shift and broadening (or narrowing) of the impurity state. The local environment effects of Jaccarino and Walker originate from the fact that the self energy of an impurity, the broadening and the shifting of the impurity level, depends on the distribution of the other impurities in its immediate neighborhood.

CONCLUSION

In spite of the large amount of theoretical and experimental work done on the dilute alloy problem, it remains something of a mystery. The single impurity problem is an especially difficult many body problem as compared to superconductivity. For superconductivity the electron-phonon interaction so dominates the superconducting behavior of metals that normal metal parameters such as density of states and other electron-electron interaction can be neglected in a first order calculation. Essentially, a law of corresponding states exists between all the superconductors with the transition temperature or energy gap being a measure of the correlation effects. This is not true for a single impurity interacting with the host metal. There are many interactions which must be included to discuss the magnetic properties of the impurity and include the s-d overlap interaction, the d-d interaction, and even the s-s exchange interaction. In addition, details of the density of states of the host metal can effect the properties of the impurity state. Thus the very strongly correlated behavior involving V_{sd} , U , E_d and the density of states can lead to a large multitude of behaviors each of which may have little in common with one another. The simple Hartree-Fock treatment first proposed by Anderson becomes extremely complicated when higher order correlations are taken in account even for idealized parabolic host bands and a single orbital. Unfortunately, it may turn out that a general solution of the localized moment problem will not be possible, but subclasses of the general problem can be used to interpret the experimental results. And while we are waiting for the perfect theory,

there are many experimental studies that remain to be done to present even a phenomenological understanding of the problem.

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