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The Effect of Hyperfine Coupling on the Electrical Resistivity of Au(Yb) Alloys at Ultralow Temperatures

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# THE EFFECT OF HYPERFINE COUPLING IN THE ELECTRICAL RESISTIVITY OF AU (Yb) ALLOYS AT ULTRALOW TEMPERATURES

By

Vernon Othmar Heinen

## A DISSERTATION

# Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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# AN ABSTRACT OF A DISSERTATION

# THE EFFECT OF HYPERFINE COUPLING IN THE ELECTRICAL RESISTIVITY OF AU(Yb) ALLOYS AT ULTRALOW TEMPERATURES

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Vernon Othmar Heinen

We present the results of a study of the effect of hyperfine coupling on Au(Yb). In order that the main contribution to the temperature dependent resistivity of the samples is due to Yb, the Fe impurity level in the samples must be as low as possible. We have produced samples which, while not Fe-free, had Fe levels low enough that the Yb contribution to the electrical resistivity was larger than that due to Fe. The electrical resistivity of our alloys of  $Au(^{174}Yb)$  and Au (<sup>171</sup>Yb) behaved as predicted down to the lowest temperature we reached, 12.5mK. From the electrical resistivity of  $Au(^{171}Yb)$  we were able to estimate the value of  $T_1$ , the only adjustable parameter in the theory. The electrical resistivity of our alloys of  $Au(^{173}Yb)$  behave as predidicted down to a temperature of 40mK, below which the theory predicted values of resistivity lower than the measured values. The magnetic susceptibility of the alloy  $Au(^{174}Yb)$  behaved as predicted to a temperature of approximately 30mK, below which there appeared to be a departure of the data from the theory. The magnetic slight susceptibility of the alloy  $Au(^{173}Yb)$  followed its predicted behavior

down to 80mK, below which the theory predicted values of  $T^2(\partial \chi/\partial T)$  lower than measured. The disagreements between theory and experiment for the resistivity and the susceptibility for Au( $^{173}$ Yb) may have a common origin. Both disagreements could be interpreted that the theoretical value of  $\langle S_{eff}^2 \rangle$  is too small at the lowest temperature.

We failed to see the effect of hyperfine coupling on the thermoelectric ratio of Au(Yb) except for one sample. The most likely explanation for this is that G due to the residual Fe in the sample is much larger than G due to Yb in the sample.

We have also discovered the presence of superconductivity in Au(Yb) at low temperature. At the present time we do not know what material is causing the superconductivity, and we do not completely understand the coonditions necessary for producing superconductivity. TO MY WIFE, CINDY,

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FOR HER PATIENCE AND UNDERSTANDING

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#### Introduction

This thesis concerns the effect of hyperfine coupling on the electrical resistivity and thermoelectric ratio of a Kondo alloy. In a Kondo alloy the coupling between the magnetic moment of an impurity and the conduction electrons of the nonmagnetic host metal cause the alloy to exhibit anomalous transport properties at low temperatures. For example, the electrical resistance is observed to increase with decreasing temperature, while a decrease in resistance with decreasing temperature is the normal behavior for a metal. The hyperfine coupling between the electronic moment of the magnetic impurity and its nucleus will cause the transport properties of this alloy to deviate from the behavior expected for the case of no hyperfine coupling.

There are several reasons for studying the effects of hyperfine coupling in a Kondo alloy. At the present time dilution refrigerators can operate at temperatures of a few milliKelvin. With adiabatic demagnetization, temperatures of tens of microKelvin can be reached. In the future, even lower temperatures should be attainable by the improvement of present techniques. At these low temperatures hyperfine coupling will become important in more materials, and the effect of this coupling on the transport properties of alloys will need to be well understood. In this thesis we will study a model system, one for which the hyperfine coupling is known accurately and is large enough so that the major effects on the transport properties are observable in the accesible temperature range above 10mK. In this way we will be able to

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test the theoretical predictions concerning the effects of hyperfine coupling on the transport properties.

The Kondo alloy we studied is Au (Yb). Yb has several stable isotopes with different nuclear spins, I. They are: <sup>174</sup>Yb. with I=0, <sup>173</sup>Yb, with I=5/2, and <sup>171</sup>Yb, with I=1/2. Enriched isotopes of Yb can be readily purchased. Data from samples of Au  $(^{174}Yb)$  and Au  $(^{171}Yb)$ were published by Hebral, et al. during the early stages of our study. They measured the electrical resistivity of only two samples, and these samples had a high level of Fe impurities, which made their analysis of the Yb contribution to the resistivity rather uncertain. We were of the opinion that we could produce samples with much lower Fe impurity levels, so that the contribution of the Yb to the resistivity of our samples would be better understood. Also, the facilities at MSU enable us to make resistivity measurements of much greater precision (a few ppm) than Hebral et al. This higher precision would allow us to better determine the physical processes affecting the resistivity of these alloys. We also wanted to produce samples of  $Au(^{173}Yb)$  and see the effect of a nuclear spin of 5/2 on the resisitivity. We believe we have successfully attained these goals, for we have produced several samples in which the effects of hyperfine coupling on the electrical resistivity are very apparent.

We were also enthusiastic about the satisfying intellectual pursuit of significantly modifying the low temperature transport properties of an alloy by changing only the nucleus of the magnetic impurity. The rather different properties of liquid  ${}^{3}$ He and  ${}^{4}$ He is another example of the significant effects of changing a nucleus. We also had hoped to see the effect of hyperfine coupling on the thermoelectric ratio. However, except for one sample, the residual Fe in our samples appears to overwhelm the thermoelectric ratio due to Yb. In addition, we have measured the magnetic susceptibility of Au(Yb) alloys which contained two different isotopes, and as expected, we found differences between the susceptibilities of these alloys. Finally, we have also discovered an apparent superconducting transition in the Au(Yb) system. At the present time we do not know what material is causing the superconductivity, and we do not, as yet, completely understand the conditions necessary for producing the superconductivity.

The first chapter of the thesis discusses the theoretical predictions of hyperfine coupling's effect on the properties we studied. The second chapter explains the sample preparation methods and the measurement procedures. Chapter three presents and discusses the data we took. Chapter four states the conclusions we have reached concerning this study. The appendix discusses the superconductivity seen in some of our samples.

#### CHAPTER 1

# THEORETICAL CONSIDERATIONS

### 1.1 <u>Resistivity</u>

When an electric field is applied to a metal, a current proportional to the electric field will flow.

$$\overrightarrow{J} = \sigma E$$
(1.1)

The electrical conductivity  $\sigma$ , is a tensor, but for a metal with cubic symmetry it reduces to a diagonal tensor in which all the elements along the diagonal are equal. Because of this reduction,  $\sigma$  can be represented as a scalar. The electrical resistivity,  $\rho$ , is the inverse of the conductivity,  $\sigma^{-1}$ . For a simple metal<sup>2</sup>

$$\rho = (m^{*}/ne^{2}) \tau^{-1}$$
(1.2)

where  $m^*$  is the electron effective mass, n is the number of electrons per unit volume, e is the electronic charge, and  $\tau$  is the relaxation time. All of the temperature dependence of  $\rho$  is in the relaxation time, and in metals  $\tau^{-1}$  is proportional to the probability of electron scattering. If there is more than one independent scattering mechanism, then according to Matthiessen's rule<sup>3</sup> the resistivity can be written as a sum of terms; that is

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$$\rho_{\text{total}} = \rho_1 + \rho_2 + \rho_3 + \cdots$$
 (1.3)

where  $\rho_{\mbox{i}}$  is due to the i th scattering mechanism. In the present case, we have

$$\rho^{(T)} = \rho_0^+ \rho_{spin}^{(T)+} \rho_{other}^{(T)},$$
 (1.4)

where  $\rho_0$  is the residual resistivity which is independent of T,  $\rho_{spin}(T)$ is the temperature dependent resistivity caused by the scattering of electrons off localized magnetic moments in which the z component of the conduction electron's spin is changed (spin-flip scattering), and  $\rho_{other}(T)$  is the resistivity caused by other scattering processes, mainly electron-electron and electron-phonon scattering. The term of interest here is  $\rho_{spin}(T)$ , so  $\rho_{other}(T)$  will be ignored. This is allowable because electron-phonon scattering is almost completely frozen out for temperatures below 1K, where most of the measurements included in this thesis were made, and because electron-electron scattering makes a contribution to the resistivity that is much smaller than  $\rho_{spin}(T)$ .

### 1.2 Kondo Effect

In a normal metal the electrical resistivity will decrease monatonically as the temperature is reduced. In an alloy which consists of a nonmagnetic metal and a very dilute concentration of a magnetic impurity, the resistivity will drop, pass through a minimum, and then begin rising again as the temperature is lowered. This low temperature rise in follows approximately a ln(T) behavior. Examples of these alloys are copper, silver, and gold hosts with chromium, manganese, and Figure 1.1 shows the electrical resistivity of gold iron impurties. containing about 3 ppm iron. This resistance minimum effect was known for a long time, but it was not understood until J. Kondo<sup>4</sup> demonstrated that it is necessary to go beyond the first Born approximation to correctly describe the scattering of conduction electrons by the magnetic impurities.

We present here an oversimplified treatment of the problem, following the method used by Dugdale,<sup>5</sup> which shows the physical processes involved and the origin of the logarithmic temperature dependence.

The hamiltonian for a Kondo system is

The first term causes the normal potential scattering which does not make a contribution to the temperature dependent resistivity, and therefore it will be ignored from now on. The second term couples the spin of the conduction electron, s, to the spin of the magnetic ion,  $\mathbf{S}$ ,

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Figure 1.1 Resistivity of Au(Fe)

with the strength J. According to the second Born approximation, the probability that a conduction electron will scatter from state a to state b is

$$P_{a \to b} \sim H_{ab} H_{ba} + \sum_{\neq a} H_{ab} H_{bc} H_{ac} / (E_a - E_c) + c.c.$$
(1.6)

where  $H_{ab} = \langle a | H | b \rangle$  and  $E_{a}$  and  $E_{c}$  are the energies of the states a and c, respectively.

The first term in equation 1.6 does not produce a temperature dependence in  $\rho$  and can be ignored. The second term involves second order scattering in which the conduction electron scatters from state a to state b via an intermediate state c. One form of second order scattering, direct scattering, takes place when the electron scatters into an intermediate state,  $(\vec{R} \rightarrow \vec{q})$ , and then scatters into a final state,  $(\vec{q} \rightarrow \vec{k})$ . Consider the case where the electron undergoes the scattering  $\vec{k} \rightarrow \vec{q} \rightarrow \vec{k}' \rightarrow$ . (The vertical arrows represent the direction of the conduction electron spins.) To conserve the z component of spin, the magnetic ion will simultaneously undergo the transition m  $\rightarrow$ m+l  $\rightarrow$ m where m is the z component of the ion's spin.

The probability for this transition is

$$P_{\vec{k}^{\uparrow}\rightarrow\vec{k}} \stackrel{\sum}{} Jm \text{ (Prob. q is empty) } P(m \rightarrow m+1) P(m+1 \rightarrow m) / (\varepsilon_k - \varepsilon_q).$$

$$k^{\uparrow} \rightarrow k^{\downarrow} \stackrel{\sum}{} q Jm (Prob. q is empty) = (m \rightarrow m+1) P(m+1 \rightarrow m) / (\varepsilon_k - \varepsilon_q).$$
(1.7)

The probability of q being empty is 1-f(q) where f(q) is the fermi function. P(m++1) is the probability of the ion making the transition m++1, etc. In terms of raising and lowering operators this term is proportional to  $J^{3}S_{z}S_{+}S_{-}$ . P(m++1)P(m+++m) results from the operators  $J^{2}S_{+}S_{-}$  and Jm comes from the operator  $JS_{z}$ . We have

$$P_{m+1} = P(m \rightarrow m+1)P(m+1 \rightarrow m) = J^{2}[(S-m)(S+m+1)].$$
(1.8)

Then this probability is

$$P \sim \begin{cases} JmP_{m+1} (1-f(q)) / (\varepsilon_{k} - \varepsilon_{q}) \end{cases}$$
(1.9)

Another form of second order scattering, exchange scattering, occurs when an occupied intermediate state scatters into a final state, and an electron scatters into the intermediate state,  $\vec{q}_{\downarrow\rightarrow}\vec{k}^{\dagger}_{\uparrow}$ ;  $\vec{k}_{\uparrow\rightarrow}\vec{q}_{\downarrow}$ . In this case, the ion undergoes the transition m→m-1→m. The probability of this scattering occuring is

$$P \sim \sum_{\mathbf{q}} Jmf(\mathbf{q}) P_{\mathbf{m}-1} / (\varepsilon_{\mathbf{q}}^{-} \varepsilon_{\mathbf{k}'})$$
(1.10)

where

$$P_{m-1} = P(m \rightarrow m-1)P(m-1 \rightarrow m) = J^{2}[(S-m+1)(S+m)].$$
(1.11)

The total probability of these two scattering paths being followed is

$$P_{\sim} \sum_{q} Jm(1-f(q)) P_{m+1} / (\varepsilon_{k} - \varepsilon_{q}) - \sum_{q} Jmf(q) P_{m-1} / (\varepsilon_{q} - \varepsilon_{k}^{+})$$
(1.12)

The minus sign comes from the fact that direct and exchange amplitudes for fermions are to be added with minus signs.<sup>6</sup> In these scattering processes energy is conserved, so  $\varepsilon_{\vec{k}} = \varepsilon_{\vec{k}}$ , and thus we have

$$P \sim \sum_{q} JmP_{m+1} / (\varepsilon_{k}^{+} - \varepsilon_{q}^{+}) - \sum_{q} Jmf(q) (P_{m+1} - P_{m-1}) / (\varepsilon_{k}^{+} - \varepsilon_{q}^{+}).$$
(1.13)

The first term is temperature independent and will be ignored. We note that  $P_{m+1} - P_{m-1} = -2J^2m$ ., Thus we obtain

$$P \sim \frac{\sum_{q} m^2 J^3 f(q) / (\varepsilon \rightarrow \varepsilon \rightarrow) .}{k q}$$
(1.14)

When the temperature is equal to zero, we note that f(q)=1 for  $q < q_0$  and f(q)=0 for  $q > q_0$ , where  $q_0$  is the fermi momentum. Changing the previous equation from a sum to an integral and substituting  $\epsilon \rightarrow \frac{1}{q}h^2q^2/2m$ , we obtain

$$P \sim m^{2} J^{3} \int_{0}^{1} q^{2} dq / (k^{2} - q^{2}) m^{2} J^{3} [1 + k/2q_{0} \ln j (k - q)_{0} / (k + q)_{0}]. \qquad (1.15)$$

When T is not zero, but still much less than the fermi energy, we have  $|k-q_0| \sim k_B T q_0 / E_f$  and  $|k+q_0| \sim 2q_0$ . Then the temperature dependent part of the scattering probability becomes

$$P \sim m^2 J^3 \ln (kT/2E_f)$$
. (1.16)

For temperatures much larger than any possible energy splitting of the spin levels of the magnetic moment, m can take on any value. The average value of  $m^2$  is<sup>7</sup>

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$$(m^2)_{ave} = (\sum_{m=-S}^{5} m^2) / (2S+1) = S(S+1) / 3.$$
 (1.17)

Considering all other possible scattering processes,  $(\vec{k}_{+}\rightarrow\vec{k}'_{+}, \vec{k}_{+}\rightarrow\vec{k}'_{+}, \vec{k}_{+}\rightarrow\vec{k}'_{+}\rightarrow\vec{k}'_{+}, \vec{k}_{+}\rightarrow\vec{k}'_{+}\rightarrow\vec$ 

$$\rho = m^{*}/ne^{2} \tau^{-1} = \rho + \rho_{A} J^{3} S(S+1) \ln T$$
(1.18)

where  $\rho_A$  is a constant. For an increase in resistivity as the temperature is decreased, the coupling constant, J, between the conduction electron and the local magnetic moment must be negative. The lnT term results from the fact that  $P_{m+1}\neq P_{m-1}$ . For a more rigorous derivation of the resistivity it is necessary to use a more accurate approximation of the fermi-function for T $\neq$ 0 in equation 1.14, but the simple assumptions used here show the origin of the lnT term.

So far in this discussion we have not taken into account the possibility of there being significant energy splittings ( $\Delta$ ) for the magnetic ion. The application of a magnetic field would produce such splittings, for example. For the Kondo effect, such energy splittings will manifest themselves when one has  $k_B^{T\sim\Delta}$ . We now explore the consequences of such splittings

When one has  $k_B^{T} \sim \Delta$ , both the lnT term and S(S+1) will be modified. The modification of the lnT term comes from the need to include the energy splitting  $\Delta$  in the denominator of equation 1.13, as required by equation 1.6. The integral in equation 1.14 becomes, approximately,

$$P^{\circ} = m^{2} J^{3} \int q^{2} dq / (k^{2} - q^{2} + \Delta') = m^{2} J^{3} \int q^{2} dq / (k'^{2} - q^{2})$$

$$\sim m^{2} J^{3} [1 + k/2q_{0} \ln (k' - q_{0}) / (k' + q_{0})] \qquad (1.19)$$

where  $\Delta' = q_0 (\Delta/E_F)$  and  $k'^2 = k^2 + {\Delta'}^2$ . As  $T \to 0$ , the lnT divergence in this equation will be cut off at an approximate value of  $\ln(\Delta/k_B)$ . The modification of S(S+1) comes about because for  $k_B T \Delta$ ,  $(m^2)_{ave}$  must be

calculated with the proper thermal weighting, with the result that  ${m^2 \choose ave} < S(S+1)$ . Thus one expects such energy splittings to diminish the Kondo effect at low temperatures since the lnT divergence will be cut off and  ${m^2 \choose ave}$  will be smaller.

At higher temperatures, electron-phonon scattering becomes important.<sup>8</sup> This term is proportional to  $T^4$  for Au, and will eventually overcome the -lnT term, resulting in a resistance minimum. For gold iron this minimum occurs at about 4K. At low temperatures the rate of spin-flip scattering by conduction electrons will approach the unitarity limit with the result that the resistivity will depart from its -lnT behavior and eventually become temperature independent at very low The temperature halfway between the resistivity minimum temperatures. and the temperature where the resistivity becomes temperature independent is experimentally defined as the Kondo temperature,  $T_{\mu}$ . For gold iron,  $T_{\kappa}$   $\infty$ .4K, see Figure 1.1.

## 1.3 Hyperfine Coupling

The fact that spin-flip scattering results in a lnT dependence in the resistivity shows that it is a very weak effect, and one that can be easily interfered with. As we have shown, the logarithmic temperature dependence of the resistivity can be changed significantly if we increase  $\Delta$  sufficiently. As we have already suggested, one way of increasing  $\Delta$  is to put the ion in a magnetic field. Another way of creating a significant energy splitting is to increase the concentration of the magnetic impurity so that there is an appreciable interaction between the spins. Thus the exact behavior of the resistivity will depend on the concentration.<sup>9</sup> Of main interest here is the production of significant energy splittings due to a large hyperfine coupling between the magnetic moment of the impurity and its own nucleus. With hyperfine coupling the hamiltonian becomes

$$H = nV - 2J\vec{S} + A\vec{S} + A\vec{S} + \vec{I} - 2J'\vec{I} \cdot \vec{S}$$
(1.20)

where  $\vec{T}$  is the nuclear spin, A is the strength of the hyperfine coupling, and J' is the strength of the coupling between the nuclear spin and the spin of the conduction electron. We assume J' << J, A, so that the last term in the hamiltonian can be ignored. This hamiltonian couples the nuclear magnetic moment with the electronic magnetic moment of the ion. This coupling interferes with the Kondo effect. The reason for replacing the ionic spin,  $\vec{s}$ , with  $\vec{s}_{eff}$  will be explained below. For this study the alloy gold-ytterbium (AuYb) was used. Dissolved in Au, Yb is trivalent with the configuration  $46^{13}$ . The ground state is a j=7/2 multiplet which is well separated from a j=5/2 multiplet by spin-orbit coupling. The j=7/2 multiplet is split by the cubic crystal field into a  $\Gamma_{\gamma}$  doublet and two excited levels, a  $\Gamma_{g}$  quartet and a  $^{\Gamma}_{6}$  doublet. The  $^{\Gamma}_{8}$  and  $^{\Gamma}_{6}$  states are both approximately 90K above the ground state.<sup>10</sup> Because of this large splitting the Yb has an effective spin of 1/2 at low temperatures. ESR measurements have shown that Au(Yb) has a Kondo temperature of  $T_{K}^{-1}$  10 $\mu$ K.<sup>11</sup> The effective spin of 1/2 gives us the simplest case of the Kondo effect, and the low Kondo temperature means that all of our measurements will be at temperatures (T>10mK) where the Kondo resistivity should have a strictly InT behavior.

Ytterbium has several stable isotopes with different nuclear spins and hyperfine coupling constants. The isotopes used are  $^{171}$ Yb,  $^{173}$ Yb, and  $^{174}$ Yb. Their nuclear spins and coupling constants are listed in table 1.1.<sup>12</sup> These measurements of A were made in a cubic insulator. However the value of A differs from the value found for  $^{171}$ Yb in Au by an insignificant amount.<sup>13</sup> Thus the value of A for  $^{173}$ Yb in a metal is also expected to be very close to A for  $^{173}$ Yb in an insulator. The isotope  $^{174}$ Yb presents the simplest case. Here the nuclear spin is zero, and thus there is no hyperfine coupling. Hence the resistivity should keep rising logarithmically down to well below lmK.

In the cases of nonzero nuclear spin a qualitative picture of the expected behavior of the resistivity is easily deduced. For Au( $^{171}$ Yb), the hyperfine coupling is "antiferromagnetic" which produces an energy splitting of 127mK. At temperatures well above 127mK, the nuclear and ionic moments are essentially uncoupled, and the conduction electrons will scatter off the local moment of the ion as if the nuclear spin were zero. In this region of temperature the resistivity should rise logarithmically with decreasing temperature. Because both the nuclear and ionic moment are spin 1/2, the ground state is an electro-nuclear

Table 1.1 Coupling Constants and Nuclear Spins of the Ytterbium Isotopes

lsotope	1	Α
171	1/2	0.127K
173	5/2	-0.035K
174	0	-

singlet state with an effective spin of zero. At temperatures well below 127mK, only this ground state singlet will be populated. Thus the conduction electrons will no longer be able to spin-flip scatter off the ytterbium ions, and the resistivity will drop to the value it would have if the ytterbium were a non-magnetic impurity.

For Au( $^{173}$ Yb) the coupling is "ferromagnetic" with an energy splitting of 105 mK. In this case the ground state is a septuplet, and the excited state is a quintuplet. For high temperatures, as in the case for Au( $^{171}$ Yb), the resistivity should rise logarithmically with decreasing temperature. During the scattering process, the Yb ions can make transitions within the septuplet and quintuplet as well as between the two states. At temperatures well below 105mK, only the septuplet state will be populated. The Yb ion can then make transitions within the septuplet state. The ytterbium will still have a non-zero effective spin, and a logarithmic divergence in the resistivity will still exist, but with a smaller multiplicative coefficient than occurs at temperatures that are much higher than 105mK.

To make a quantitative prediction for the temperature dependence of the resistivity is very difficult for  $^{173}$ Yb. In contrast, for the case of Au( $^{171}$ Yb), the theoretical predictions of Matho and Beal-Monod<sup>14</sup> can be used. They solved the problem of interacting pairs of magnetic ions. The hamiltonian they used is

$$H = (n_1 + n_2) V - 2J(\vec{s}_1 \cdot \vec{s}_1 + \vec{s}_2 \cdot \vec{s}_2) - W\vec{s}_1 \cdot \vec{s}_2$$
(1.21)

where  $\vec{s}_1$  and  $\vec{s}_2$  are the spins of two magnetic ions, W is the strength of the coupling between the ions, and  $\vec{s}_1$  and  $\vec{s}_2$  are the spins of conduction

electrons. The first term in the equation causes the potential scattering of conduction electrons off the two ions. The second term causes the spin-flip scattering of the electrons off the magnetic ions. The spins of two conduction electrons must be included because of the physical separation of the magnetic ions. In the case of Au ( $^{171}$ Yb), the two spins are at the same site and one of the spins does not couple to the conduction electrons, so this term reduces to  $-2JT \vec{s} -2J\vec{s}_{eff} \vec{s}$ , with J' << J. The last term in the hamiltonian corresponds to the hyperfine coupling in Au(Yb). The theory of Matho and Beal-Monod requires that  $\vec{s}_1 = \vec{s}_2$ , which is the case for Au<sup>171</sup>Yb where  $\vec{T} = \vec{s}_{eff} = 1/2$ . Their result for the electrical resistivity of antiferromagnetically coupled ions can then be directly transformed into the equation:<sup>1</sup>

$$\rho = \rho_{V} - \frac{4}{3} \rho_{K} S_{eff}^{2} (-A/k_{B}T) \log ((T^{2} + (0.77A)^{2})^{1/2}/T_{1}), \qquad (1.22)$$

with

$$S_{eff}^{2}(x) = 3/2 (1+x/(exp(x)-1))/(exp(-x)+3),$$
 (1.23)

where  $\rho_V$  is the resistivity due to potential scattering,  $\rho_K$  is a constant which equals  $-d\rho/d(\ln T)$  at high temperatures, and  $T_1$  is an adjustable parameter. In terms of our discussion at the end of section 1.2, we have that  $\langle S_{eff}^2 \rangle = (m^2)_{ave}$  which has high and low temperature values of S(S+1)=3/4 and 0, respectively. The numerator of the log term in  $\rho$  contains a term added to the temperature which removes the low temperature divergence of the resistivity as predicted by equation 1.19. The behavior of the resistivity versus temperature for Au( $^{171}$ Yb) is shown in Figure 1.2. This figure shows that  $T_1$  adjusts the size of the



Figure 1.2 Resistivity of Au(<sup>171</sup>Yb)

resistivity decrease below the maximum, but has very little effect on the position of the maximum or on the overall shape of the curve.

In the case of Au<sup>173</sup>Yb ightarrow 
ighta

$$\rho = \rho_V - \rho_K \log (T/T_1)$$
(1.24)

where  $T_1$  is a constant. We will rewrite this as

$$\rho = \rho_V - \frac{4}{3} \rho_K S_{eff}^{2} \log(T/T_1). \qquad (1.25)$$

This is done because at high temperatures one has  $<S_{eff}^{2}>=S(S+1)=3/4$  and  $\rho_{K}=-d\rho/d(1nT)$ , a parameter often used to quantify the size of the logarithmic divergence. At temperatures large in comparison to the hyperfine coupling energy the magnetic susceptibility of Au(Yb) will follow a Curie law, see section 1.5. In that section will we derive the magnetic susceptibility,  $\chi$ , for Au( $^{173}$ Yb). The temperature multiplied by the susceptibility, TX, is equal to the Curie constant, C, which is proportional to S(S+1). If we normalize T $\chi$  so that at high temperatures T $\chi=3/4$ , then T $\chi$  will be the effective spin squared, T $\chi=<S_{eff}^{2}>$ . At very low temperatures  $<S_{eff}^{2}>[=(m^{2})_{ave}]$  must be evaluated in a 1/2+5/2 manifold where  $S_{eff}=(\vec{S}\cdot\vec{J})\cdot\vec{J}/j(j+1)$  and  $j=|\vec{T}+\vec{S}|=3$  or 2. For the ground state septuplet (j=3) we have  $\vec{S}_{eff}^{=3}/6$ , so  $<S_{eff}^{2}>=j(j+1)/36=1/3$ . In Figure 1.3 we show  $<S_{eff}^{2}>$  versus T for Au( $^{173}$ Yb). At low temperatures 1/3 as expected.



Figure 1.3 
$$of \frac{173}{Yb}$$

The energy splitting between the septuplet ground state and the quintuplet excited state should also remove some, but not all, of the low-temperature logarithmic divergence in  $\rho$ . The calculation by Matho and Beal-Monod can also be applied to this "ferromagnetic" coupling but only for  $\vec{S} = \vec{l}$ , see equation 1.21. This theory predicts the following change in the logarithmic term:

$$\log(T/T_{1}) \rightarrow 1/2[\log(T/T_{1}) + \log((T^{2} + T_{W}^{2})^{1/2}/T_{1})]$$
(1.26)

with  $T_W=0.77 \ ^{\Delta'}/k_B$ , where  $^{\Delta'}$  is the energy splitting between the ground state and the highest excited state. As one can see, the divergence is not eliminated since the ground state is degenerate and thus there are still available elastic spin-flip channels at very low temperatures. The second term in equation 1.26 represents the inelastic channels. For Au ( $^{173}$ Yb), where the coupled spins are unequal, a diminished logarithmic divergence should also persist at the lowest temperatures. Here only the elastic spin-flip channels within the septuplet ground state will contribute to the divergence.

For the unequal spin case, the two terms in equation 1.26 should not necessarily have equal weight. If we arbitrarily allow for unequal weighting, the logarithmically diverging term will be

$$1/2[a \log(T/T_1) + b \log((T^2+T_W^2)^{1/2}/T_1)].$$
 (1.27)

If we let a=2 and b=0, the logarithmic divergence will be undiminished at the lowest temperatures, and thus would overestimate the size of the divergence. The resistivity calculated using these values of a and b is an upper bound to the resistivity expected for Au( $^{173}$ Yb). If we let a=0 and b=2, the logarithmic divergence will be completely eliminated. The resistivity calculated using these values of a and b will be a lower bound on the resistivity of Au( $^{173}$ Yb). In Figure 1.4 we show the upper and lower bounds for the resistivity of Au( $^{173}$ Yb) where equation 1.27 has been substituted into equation 1.25. The overall shape of the two curves is very similar. The greatest differences between the two curves occurs at the lowest temperature because the upper bound on the resistivity continues diverging as T→0, while the lower bound approaches a constant.

# 1.4 Thermoelectric Ratio

When there is a temperature difference across a sample, usually a voltage will appear across the sample. The thermopower (S) is this voltage divided by the temperature difference. For normal metals at low temperatures the thermopower is in general small, negative, and proportional to T. $^{15}$ 

Instead of measuring the thermopower, we measured the thermoelectric ratio, G. G is measured by running thermal  $(\dot{Q})$  and electrical (I) currents through the sample and adjusting the electrical current until the voltage across the sample is zero. The thermoelectric ratio is defined as

$$G=I/\dot{Q}\Big|_{E=0}$$
(1.28)

Most theoretical work has been carried out for the thermopower. Fortunately, S and G are easily related by <sup>15</sup>



Figure 1.4 Upper and Lower Bounds of the Resistivity of Au(173Yb)

where L is the Lorenz ratio. For temperatures of 4.2K and below L is almost constant and equal  $L_0=2.44\times10^{-8}V^2/K^2$ . If S is proportional to T, then G will be a constant at low temperatures.

In a Kondo alloy the thermopower is larger in magnitude and is roughly constant for  $T>T_K$ ,<sup>5</sup> so the thermoelectric ratio should diverge as  $T^{-1}$ , while  $T \rightarrow T_K$ . In Figure 1.5 we show the thermoelectric ratio of a sample of Au(Fe). To explain this behavior it is necessary to consider scattering processes that are higher than second order. For Kondo alloys that also have hyperfine coupling, the theory of Matho and Beal-Monod<sup>16</sup> predicts that the behavior of S should be significantly modified when the temperature is of the order of the hyperfine coupling energy. Indeed for the case of "antiferromagnetic" coupling, S, and therefore G, should change sign at these temperatures

# 1.5 Magnetic Susceptibility

The magnetic susceptibility of these alloys is also affected by the hyperfine coupling. The magnetic susceptibility of a Kondo alloy should follow approximately a Curie-Weiss law of the form: <sup>17</sup>

$$\chi = g^2 \mu_B^2 S(S+1) / 3k_B(T+T_K). \qquad (1.30)$$

For Au(Yb) we have  $T_{K}^{\sim 10\mu K}$ . Thus for T>10mK the  $T_{K}$  in the denominator can be ignored, and the susceptibility will follow a Curie law so long as T is much larger than any hyperfine coupling energies. The ground


Figure 1.5 Thermoelectric Ratio of Au(Fe)

state of ytterbium in gold is a doublet with several other states 90K above the ground state,<sup>10</sup> so for temperatures well below 90K the alloy will have an effective spin of 1/2 with g=3.4.<sup>18</sup> Because the susceptibility is proportional to  $N_0$ , the number of Yb atoms, the susceptibility of a Au(Yb) sample in a temperature range where C is a constant can be used to determine its Yb concentration. When the temperature is reduced to temperatures where the hyperfine coupling becomes important, the Curie constant is expected to reduce. In the case of Au(<sup>171</sup>Yb) the ground state has spin zero, so the Curie constant should go to zero, which is what has already been observed experimentally.<sup>18</sup>

The case of  $Au^{173}$ Yb is more complicated. The hamiltonian for an atom with hyperfine coupling in a magnetic field, H, is

$$H = g \mu_{B} \vec{S} \cdot \vec{H} + A (\vec{S} \cdot \vec{I})$$
(1.31)

which for 1=5/2 and S=1/2 yields the following energy levels:

$$E_{m} = -A/4 \pm 3A/2 (1+2mx/9+x^{2}/9)^{1/2}$$
(1.32)

where  $x=g\mu_BH/A$ . For the plus sign m can be any integer from -3 to 3, while for the minus sign m can range from -2 to 2. If we let

$$z(m) = 3A/2 (1+2mx/9+x^2/9)^{1/2},$$
 (1.33)

then the free energy is

$$F = -k_{B}T \ln \left[ \sum_{n} exp(-E_{n}/k_{B}T) \right]$$

$$= -k_{B}Tln[e^{A/4k}B^{T}\{e_{2}^{-z(-3)/k}B^{T} + e^{-z(3)/k}B^{T} + 2\sum_{m=-2}^{2} \cosh(z(m)/k_{B}^{T})\}]$$
(1.34)

The magnetization is M=- $\frac{\partial r}{\partial H}$  and the susceptibility is  $\chi = M/H$ . The quantity we measured was  $\frac{\partial \chi}{\partial T}$ . The magnetization is easily obtained in closed form by analytically differentiating the free energy. To differentiate the magnetization analytically is very messy, so  $\frac{\partial \chi}{\partial T}$  was computed by twice numerically differentiating the magnetization, first with respect to the magnetic field and then with respect of the temperature. In terms of  $\chi=C/T$ , one has

$$T^{2} \partial \chi / \partial T = -C + T \partial C / \partial T.$$
 (1.35)

If Curie's law is obeyed, then C will be a constant, and the left-hand side of this equation will be independent of temperature. In Figure 1.6  $T^2 \partial_X / \partial T$  is plotted for Au( $^{173}$ Yb). At high temperatures the Yb has an effective spin of 1/2, so S(S+1)=3/4. At low temperatures the ground state has a spin of 3 in a 5/2+1/2 manifold, so S(S+1)=1/3 as discussed in Section 1.3. At the lowest temperatures the Curie constant will drop to  $4/9^{\text{th's}}$  its value at high temperature.

The behavior of the electrical resistivity, thermoelectric ratio, and the magnetic susceptibility of Au(Yb) at temperatures below approximately 100mK will be modified by the nuclear spins of the Yb ions.

The theories developed in this chapter predict that the behavior of several properties of Au(Yb) will be different depending on the nuclear spin of the isotope of Yb used to make the alloy. The properties of



Figure 1.6  $T^2(\partial\chi/\partial T)$  Normalized to 1 at High Temperature

interest here are the electrical resistivity, the thermoelectric ratio, and the magnetic susceptibility.

#### CHAPTER 2

#### EXPERIMENTAL PROCEDURE

### 2.1 Chlorine Annealing

As described in the previous chapter, the Kondo effect seen in Au (Yb) is caused by the f electrons of the ytterbium. In Au (Fe) it is caused by d electrons. The f electrons in ytterbium are inner electrons, and they are screened by the outer d electrons. This makes the coupling of the magnetic moments of conduction electrons to the moment of an Yb ion much weaker than that for iron. In fact the slope of the logarithmic term of the resistivity is 800 n $\Omega$ cm/at%logT for AuFe<sup>19</sup> while it is only 2.79 to 3.58 n $\Omega$ cm/at%logT for AuYb.<sup>1,20,21</sup> Thus on a per-impurity basis, Fe makes a contribution to P which is about 250 times larger than for Yb. The samples will be made with a few hundred ppm of Yb, so the Fe level in the samples must be much less than 1 ppm for the Yb contribution to predominate.

Iron is the fourth most abundant element (5%) in the Earth's crust,<sup>22</sup> so it is a major impurity in almost everything. There is a method, first proposed by C. Walker,<sup>23</sup> for removing iron impurities from gold by annealing in a chlorine atmosphere at elevated temperatures. At temperatures above  $300-350^{\circ}$ C gold chlorides are unstable, but iron chlorides do form and are volatile. In a hot chlorine atmosphere any Fe atoms on the surface of gold will form these volatile chlorides which will be carried away from the gold and condense onto the cold parts of the system. Iron in the interior of the gold will eventually diffuse to

the surface of the gold and be removed, reducing the overall iron concentration in the gold. In practice the annealing is done at about  $850^{\circ}$ C to speed the diffusion of the iron through the gold.

During the chlorine anneal, the gold was in the shape of foils about  $0.005^{\prime\prime}$  thick. According to Shewman,<sup>24</sup> the average iron concentration left in foils of thickness h after a time t (except for small t) should be

$$c = c_0 8 / \pi^2 \exp(-\pi^2 D t / h^2)$$
 (2.1)

where  $c_0$  is the initial concentration, and D=5.66x10<sup>-10</sup> cm<sup>2</sup>/sec, the diffusion constant of iron in gold at 850°C.<sup>23</sup> For t=24 hours,  $c/c_0=0.04$ . The gold we used contains initially approximately 0.2 ppm iron, so after a 24 hour chlorine anneal the iron impurity level should be 0.008 ppm, a level low enough for our purposes.

# 2.2 Sample Preparation

The most difficult part of this project was the sample preparation. Several methods of sample preparation were tried. We will describe first the method found to work the best followed by some of the other methods that were tried and found unsatisfactory.

The samples were made from 6-9 gold shot purchased from Cominco American Incorporated<sup>25</sup> and isotopically enriched ytterbium purchased from Oak Ridge National Laboratory.<sup>26</sup> The isotopic abundances are listed in Table 2.1. The iron impurity level in the Yb is less than 200 ppm for all the isotopes, a level low enough for our purpose. Approximately 2.5 grams of gold shot were rolled on CuBe rollers into

Table 2.1.	Isotopic	Concentration	of	Ytterbium	(%)
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Isotope	171 <sub>Yb</sub>	173 <sub>Yb</sub>	<sup>174</sup> чь
168	<0.01	<0.02	<0.01
170	0.38	0.05	<0.02
171	95.07	0.3	0.08
172	2.61	1.41	0.20
173	0.74	95.0	0.52
174	0.99	2.89	98.97
176	. 0.21	0.34	0.22

foils about 0.005" thick in order to shorten the chlorine annealing The gold was then washed in aqua regia and rinsed several times time. in distilled water to remove any contaminants. It was then put into nested quartz tubes, see Figure 2.1. These quartz tubes were used because they provided an easy means of sealing the tubes for later melting of the Au, and they reduced the volume inside the tube which limited the amount of ytterbium that became a vapor. At 850°C the vapor pressure of Yb is approximately 0.5 atmospheres, 27 so the volume in which the AuYb mixture is melted was made as small as possible. The nested quartz tubes containing the gold were then put into the chlorine annealing system, see Figure 2.2. The annealing system consisted of a quartz tube 1" in diameter and about 2.5' long which was sealed at one end and had a balljoint with an O-ring seal at the other end. This tube attached to a pyrex manifold that had pyrex valves with O-ring sealed teflon valve stems to permit the evacuation and admittance of necessary A pyrex bottle containing chlorine gas was attached to the gases. manifold by a balljoint with an O-ring seal. All the joints and valves were greased with Fluorolube Grease GR-90.<sup>28</sup> The manifold was on a



Figure 2.1 Quartz Tubes

.



Figure 2.2 Chlorine Annealing System

cart with wheels to slide the quartz tube into and out of a tube furnace.

The guartz tube was pumped out and then slid into the furnace which had been heated to  $850^{\circ}$ C. The tube was pumped on for at least 12 hours to outgas the quartz tubes and the Au. The pressure inside the quartz tube was less than  $10^{-4}$  microns Hg during this time. In order to reduce iron oxides in the Au a mixture of 10% hydrogen and 90% argon gas was then introduced, and the anneal continued for 10 to 24 hours at a gas pressure of 1000 to 2000 microns Hg. At the end of the annealing time, the hydrogen argon mixture was pumped out to a pressure less than  $10^{-4}$  microns Hg. Chlorine gas was added to a pressure of about 300 microns Hg, and the Au was annealed for about 24 hours. At the end of this time, the chlorine gas was removed by cryopumping the gas back into the bottle and then pumping with a diffusion pump until the pressure was less than  $10^{-4}$  microns Hg. The hydrogen argon mixture was reintroduced at a pressure of 1000 to 2000 microns Hg, and the anneal continued for another 12 hours. This reintroduction was done as a precaution so that any chlorine which had diffused into the gold would be removed. Then the tube was slid out of the furnace, and it was left to cool to room temperature.

The nested quartz tubes containing the Au were removed from the chlorine annealing system and put into a glove-bag that was taped to the side of a balance. The glove-bag prevented any dust from getting onto the gold. The inner quartz tube was removed from the outer one. A sample of ytterbium was massed on the balance and put into the outer quartz tube with the gold. Not all of the Yb would go into solution in the Au, so the amount of Yb added was approximately 30% more than the

amount that was wanted in solution in the gold. There appeared to be some reaction between the Yb and the quartz, so this is probably what happened to the "lost" Yb. The inner quartz tube was then reinserted into the outer tube, and the nested tubes were removed from the The nested tubes were evacuated to a pressure of less than glove-bag.  $10^{-4}$  microns Hq. These tubes were next filled with a 1/4 atmosphere of the hydrogen argon mixture, and the tubes were sealed as close to the bottom of the inner tube as possible. The hydrogen argon gas was used to reduce any ytterbium oxides that might be present. The gold-ytterbium (AuYb) mixture was melted in an induction furnace for 1 hour at 1125 °C. The tubes were in a graphite holder, and the melting was done inside an evacuated guartz tube to prevent any oxygen from diffusing through the quartz tubes and oxidizing the Yb. At the end of the melting, the evacuated quartz tube was vented to the atmosphere and removed from the induction furnace. The tubes containing the AuYb were removed from the graphite holder and quickly immersed in water while the gold was still molten. The time necessary to cool the AuYb from the molten state to a temperature of about  $600^{\circ}$ C (judged from the glowing of the AuYb) was approximately 5 seconds. This quenching seemed necessary to prevent an onset of superconductivity which appeared in some samples. This problem will be discussed further in the Appendix. When the tubes were cool, the AuYb sample was removed, washed in aqua regia, and rinsed in distilled water several times. Then it was rolled into the shape of a wire of about 1.5 mm diameter on a copper-beryllium roller. Any iron added while rolling out the sample should be in an oxide form; and because the gold is never annealed from this point on, the iron should not go into solution in the gold. Therefore this iron contamination

should not make a significant contribution to the resistivity at low temperatures.

A piece of the wire about 3/4 cm long was cut off so that it could be used later to determine the ytterbium concentration of the sample. Another piece about 2 cm long was cut off and rolled into a foil 5 to 7 cm long, 1/2 to 3/4 cm wide, and 0.1 mm thick. This piece was used for resistivity measurements. A slit 1.3 cm long was spark cut about 2 mm from and parallel to one side, see Figure 2.3. A cut was made into the piece formed by the slit, and the pieces were bent up and used for potential leads. These pieces were then tinned with Rose's alloy. The bottom end of the foil and a strip across the foil about 3 cm from the bottom were also tinned with Rose's alloy. The current leads were attached to the sample at these two places. Electrical connections to the sample were made via 0.05 mm Niomax CN wire.<sup>29</sup> Niomax CN wire is a multifilament niobium-titanium superconducting wire in a copper-nickel For physical support, the sample was spotwelded to a silver matrix. foil of approximately the same size and thickness as the sample. Care was taken so that the sample would not heat up during spotwelding. The silver foil had been previously spotwelded to a silver tab for mounting on the dilution refrigerator. The silver foil was covered with cigarette paper and wrapped with thread to prevent electrical or thermal contact between the silver and gold foils except at the spotweld. A heater was soldered onto the bottom of the sample for thermopower 4k measurements.

The remainder of the AuYb wire (3 to 5 cm) was used for making low temperature susceptibility measurements.



Figure 2.3 Sample Geometry

Before this method of making samples was developed several other methods were tried and found to not work. Initially the addition of the Yb to the Au was not done inside a glove bag. The samples made this way appeared to have large amounts of iron in solution in them. When the Yb was added to the Au, it is possible that various surfaces might become contaminated with Fe. A 5 minute chlorine anneal was done after the Yb was added in order to remove this surface contaminant. Initially this short anneal was done at 850°C, but unfortunately all the Yb evaporated. This was tried again with an annealing temperature of  $550^{\circ}$ C. The Yb didn't evaporate, but the amount of Yb in solution in the Au was not reproducible from sample to sample. The Yb concentration varied from 0 to 50% of the expected concentration. Furthermore, the amount of Fe in solution was not significantly reduced from previous attempts. Another method tried was to make a master alloy of Au with 2-5% Yb. A piece of the master alloy was then added to the chlorine annealed Au foils, and this was chlorine annealed for 5 minutes at  $850^{\circ}$ C. Again the amount of Yb in solution in the Au varied widely from sample to sample, and the amount of Fe in solution was not significantly reduced. These samples were made by rolling the AuYb into a wire and then spotwelding on pure Au wires as potential leads. It may have been the spotwelding that drove the Fe into solution. After this the samples were in the form of foils as described above.

In an effort to reduce the time it took to make a sample, a chlorine annealing was attempted in an induction furnace with the Au in a molten state at  $1150^{\circ}$ C. In this case the iron concentration in the Au should drop by several orders of magnitude after a 1 hour anneal.<sup>30</sup>

Samples made with Au that had been annealed in this manner had low Fe levels, but they often had low temperature resistivities that were very highly current dependent, which is perhaps related to the onset of superconductivity mentioned earlier.

The problem of making samples with low Fe levels was the most time consuming, difficult, and frustrating aspect of this project. A study of AuYb done by Hebral *et al.*<sup>1</sup> also suffered Fe contamination problems. In their samples the effect on the resistivity due to Fe was at least four times larger than the effect due to Yb. Using the first method described we were able to get samples with an iron concentration low enough that the main influence on the behavior of the resistivity was due to Yb.

#### 2.3 Dilution Refrigerator

The data presented in this thesis were obtained on a dilution refrigerator made by J. Imes, and W. Pratt.<sup>31,32</sup> For a general description of the operation of a dilution refrigerator see Lounasma.<sup>33</sup> For these experiments, a new mixing chamber (MC) was constructed and attached to the refrigerator, see Figure 2.4. With this new MC the refrigerator could reach approximately 0.0125K.

The upper part of the MC, the copper flange and stainless steel tube were taken from an earlier MC. See references 31 and 32 for details. The new MC was attached to the stainless steel tube, and it was made of Epibond-100A epoxy.<sup>34</sup> The parts were glued together with Stycast 1266 epoxy.<sup>35</sup> The MC has a rectangular base, approximately 1 cm wide by 4 cm long and is 3 cm high. The 3-mm-diameter return line runs up the side of the MC and then runs back inside near the top.



Figure 2.4 Mixing Chamber

Inside the MC are 4 sintered silver disks which consist of a silver foil 0.1 mm thick by 1.5 cm high by 4 cm long to which a 1-mm-diameter silver wire had been spotwelded. Sintered onto each side of the silver foil were 0.5-mm-thick sintered silver wafers made from 700Å silver powder. These sintered disks were made in much the same manner as those described by Frossati,<sup>36</sup> and their high surface area provides good thermal contact to the  ${}^{3}$ He- ${}^{4}$ He mixture. The silver wires come out of the bottom of the MC and are spotwelded to 2 silver mounting pieces which have holes threaded for 8-32 screws. Two Ag wires are spotwelded to each mounting piece. In the figure, only one mounting piece is These mounting pieces are designed to provide good thermal shown. contact between any two metallic samples and the refrigerator. These mounting pieces are electrically isolated from each other even though they provide good thermal contact to the refrigerator.

Attached to each of these silver mounts are separate mounts for the samples, heaters, thermometers, etc, see Figure 2.5. Two silver pieces are soldered to a 1/8" diameter stainless steel tube about 2 cm long. The top piece has 2 holes drilled in it, one for the 1/8" stainless steel tube and the other for attaching the piece to the refrigerator mount with an 8-32 screw. The bottom has several holes drilled into it for attaching thermometers and samples. Between the top and bottom silver pieces is spotwelded a 2 cm long Ag (0.1%Au) wire which has a resistance of about 50  $\mu\Omega$ . Heaters are attached to the top and bottom silver pieces so that a temperature gradient can be established at will across the gold-silver wire without significant changes in the temperature of the MC. With this setup (1/ $\rho$ ) (d $\rho$ /dT) can be measured.<sup>37</sup> For my samples p was not measured in this fashion, but this



Figure 2.5 Sample Mounts on the Mixing Chamber

temperature-modulation method was necessary for measurements of the sample susceptibilities .

#### 2.4 Thermometry

The main thermometers used in the dilution refrigerator were two germanium resistance thermometers and one cerrous magnesium nitrate (CMN) thermometer. The germanium resistance thermometers were mounted in the holes on the bottom pieces of the sample mounts using Apiezon N grease $^{38}$  for thermal contact.

For temperatures above approximately 1.5K, R6, a Lakeshore Cryotronics<sup>39</sup> resistor was used. This was calibrated as follows: the susceptibility of a sample of CMN was measured at 6 temperatures from 0.099K to 3.41K as determined by Superconducting Fixed Point Devices, SRM767 and SRM768 from the National Bureau of Standards.<sup>40</sup> The sample consisted of a right circular cylinder (height=diameter=2.2cm) of a mixture of powdered CMN and Apiezon J Oil filled with a brush of Cu wires for thermal contact to the refrigerator. The susceptibility of CMN is proportional to  $T^{-1}$  over the temperatures of interest here, so temperatures different from the fixed points are easily determined from the susceptibility of the CMN. Using a least squares fit, the resistance of R6 was fit to the temperature as given by the CMN for temperatures between 1K and 4.2K using the equations

$$LogT = \sum_{n=0}^{N} a_{n} (LogR)^{n}$$
(2.2)

and

$$LogR = \int_{n=0}^{N} b_{n} (LogT)^{n}$$
(2.3)

with N=7. With these fits, the temperature given by R6 is estimated to be within 0.3% of the absolute temperature.

For temperatures between approximately 0.040K and 1.5K, R7, a  $Cryocal^{41}$  CR50 resistor was used. This resistor had been calibrated earlier,<sup>31</sup> but for all the data presented here a new calibration was used. The method of calibration was very similar to that used for R6, except that the susceptibility of an irregular single crystal of 10% CMN and 90% lanthanum magnesium nitrate (LMN) was used for interpolating between the fixed points. The resistance of R7 was fit to the temperature given by the susceptibility of the CMN-LMN using the equations above with N=9. The temperature as established by R7 is estimated to be within 0.7% of the absolute temperature.

The CMN thermometer was used for temperatures below approximately 0.060K, and it consisted of a susceptometer (to be described in the following section) and a CMN pill. The CMN pill was a 50:50 volume mixture of CMN and Ag powder pressed onto a 0.012" diameter Ag(0.4%Au) wire. The pill was a right circular cylinder (height=diameter=1/8") containing approximately 18mg of CMN and 95 mg of Ag. The Ag-Au alloy wire was used to reduce any possible eddy currents caused by the 17 Hz magnetic field used to measure the susceptibility. The eddy currents could produce fields which would effect the measured susceptibility and could also cause heating of the CMN pill. This wire was approximately 1" long and was spotwelded to a pure silver wire which in turn was spotwelded to the bottom silver piece of Figure 2.5 to which the sample

is attached.

The CMN thermometer was calibrated on each run against the SRM768, the low temperature standard. A linear least squares fit was done to the 99, 160, and 204mK points assuming a Curie law behavior for the susceptibility of the CMN. The temperatures determined by the CMN at the fixed points are listed in Table 2.2. The 15.5mK point was not used, because not including it gave a better fit at the higher temperatures while still disagreeing with the 15.5mK point by less than 0.3%. The 22mK point was not used because this superconducting transition was in complete disagreement with the other fixed points.

The superconducting transition temperatures can be affected by the ambient magnetic field. To reduce the ambient field a mu metal can 10" in diameter by 5' long was put placed over dewar. From the supercooling of the W transition temperature the ambient magnetic field was estimated to be less than 35mGauss.<sup>42</sup> A field of 35mGauss would lower the transition temperature of W by 0.3mK. There is some disagreement over the transition temperature of W, and it may be as high as 15.7mK. The ambient magnetic field would lower the transition temperature to about 15.4mK, bringing it in close agreement with  $T_{CMN}$ .

Table 2.2 CMN Temperature Calibration

Material	T <sub>CMN</sub> (mK)	T <sub>NBS</sub> (mk)	(T <sub>CMN</sub> -T <sub>NBS</sub> )/T <sub>NBS</sub> X100
W	15:46	15:50	<u>-0.25</u>
Be	21.29	22.92	-7.10
lr	99.08	99.13	-0.05
AuAl	160.50	160.43	0.04
Auln <sub>2</sub>	204.42	204.36	0.03

# 2.5 <u>Susceptometer</u>

The method of measuring the susceptibility is based on the sample's magnetization changing the mutual inductance between a primary and two secondary coils. The primary coil is used to produce a magnetic field. The almost identical secondary coils are coaxial with the primary, but they are wound in opposition. With no sample in the susceptometer, the mutual inductance to first order is zero. With a sample present, the mutual inductance is no longer zero, but it is proportional to the sample's total magnetic susceptibility.

The primary coil was wound onto a hollow tube made from copper coil-foil and Stycast 1266 epoxy. Coil-foil consists of fine copper wires bonded parallel to each other to form flat sheets. It has good thermal conductivity along the wires and reduces any possible eddy currents. The tube has a 1/8" diameter and is 3 1/4" long, see Figure The primary coil was 1.5" long consisting of 395 turns of 0.003" 2.6. diameter pure niobium wire. The primary coil was calibrated by measuring the reduction in the superconducting transition temperature of indium for a given current in the primary coil. The calibration showed that the primary coil provided a magnetic field of 120 gauss/amp. The leads were connected to a superconducting persistent switch in order to trap a constant field in the primary coil. Onto the primary coil were wound the secondary coils. These were two oppositely wound coils (3/4")apart), each consisting of 12 turns of 0.05 mm Niomax CN wire. These were connected to the leads of a Superconducting Quantum Interference Device (SQUID) mounted on the dilution refrigerator. The ends of the Niomax wire were prepared in a manner so as to make superconducting



Figure 2.6 Susceptometer

joints with the SQUID leads.<sup>43</sup> The secondary coils and the SQUID formed an entirely superconducting circuit. A SQUID is an ultrasensitive current detector, in which the room temperature electronic controls produces a voltage proportional to current through the superconducting sensing coils of the SQUID. The primary and secondary coils were surrounded by a 1/2" diameter by 2 3/8" long niobium tube with niobium end caps through which the coil-foil tube extended. To cool the niobium tube it was wrapped with a copper wire held in place with Stycast 1266 epoxy. This copper wire and the coil-foil were spotwelded to a silver mounting tab.

The susceptometer was mounted on one side of the dilution refrigerator. The samples were in the form of wires and were inserted into the coil-foil tube, extending into one of the secondary coils. The other end of the sample was spotwelded to a Ag wire which was attached to the other side of the refrigerator.

Measurements were made by trapping a field in the primary coil (usually 6 gauss). The temperature of the susceptometer was kept fixed, and the temperature of the sample was varied in the same manner as was done to measure  $(1/\rho) (d\rho/dT)$ .<sup>37</sup> When the susceptibility of the sample changes, it induces a change in the current in the secondary coils. The change is detected by the SQUID and results in a change in the output voltage of the SQUID electronics. The SQUID voltage change divided by the temperature change is proportional to  $d_X/dT$ . The temperature of the susceptometer was fixed at a new temperature, and the measurement repeated for a different sample temperature. Making the measurements in this fashion eliminated any errors caused by a temperature dependence of the mutual inductance between the primary and secondary coils due to the

ever present paramagnetic impurities in the structural materials.

The susceptometer for the CMN thermometer is of essentially the same design, except that the primary coil was wound with 0.05 mm Niomax CN wire. This was used because a steady field was not trapped in the primary coil. Instead, the ac susceptibility was measured using an AC mutual inductance bridge described by Giffard, Webb, and Wheatley<sup>44</sup> operating at 17 Hz.

# 2.6 Resistivity and Thermoelectric Ratio Measurement Procedures

The method used to measure resistivity is well described elsewhere,  $^{37}$  and 1 will only describe it briefly. The circuit used is shown in Figure 2.7. Current is run through two resistors and the ratio of the two currents is adjusted until the potentials across both resistors are equal. This balance is indicated by a null reading on the SQUID. A superconducting 50µH inductor is placed in series with the SQUID which makes the low temperature circuit into a low-pass filter that filters out noise primarily due to electromagnetic interference.

When the potentials across the two resistors are equal, one has

$$R_1 = I_2 R_2 / I_1 = c R_2.$$
 (2.4)

The geometric factor (A/l=cross-sectional area/length) is determined by measuring the resistance at room temperature and assuming the resistivity is the same as for pure gold (2.44  $\mu\Omega$ cm). Then, we have

$$\rho = cR_2^{A/1}$$
(2.5)

where  $R_2$  is made from a Au(13%Ag) wire whose low temperature resistance



Figure 2.7 Resistivity Measurement Circuit

is  $90.6\,\mu\Omega$  and has a negligible temperature dependence. The ratio c is measured to a precision of about 5 ppm which is more than necessary for this experiment.

The thermoelectric ratio was measured by first turning on a heater  $(\dot{Q})$  which is attached to the bottom of the sample, causing a temperature gradient to appear across the sample. If the sample has a nonzero thermopower, this gradient produces a voltage across the sample which causes a current to flow through the SQUID. Then a current, I, is run through the sample to bring the potential across the sample back to zero as determined by the SQUID. The thermoelectric ratio is defined as

$$G = 1/\tilde{Q}.$$
 (2.6)

# 2.7 Determination of Ytterbium Concentration

To perform an accurate analysis of the data, the concentration of ytterbium in solution in gold must be determined. There are several methods of doing this, but there are serious problems with most of them. Trying to determine the concentration from the resistivity rise with lowering temperature is not very accurate because any iron remaining in the sample may make a significant contribution to this rise. One way of estimating impurities in metals is by measuring the residual resistivity  $\rho_0$ . This is not a good estimate in this case because the contribution to  $\rho_0$  of dislocations, which are introduced into the samples by rolling them into foils, overwhelm contribution due to the ytterbium. There was no correlation between  $\rho_0$  and the determined Yb concentrations of the samples. Chemical analysis could be done; but the samples would be

destroyed in the process and a significant time delay in obtaining the results would occur since we did not have local facilities for these measurements. Instead we chose to determine the concentration by measuring the magnetic susceptibility of the samples. This method had the advantages that the measurements were done locally, and the samples were not destroyed. The susceptibility will be proportional to the concentration of ytterbium in solution in the sample (see Chapter 1).

The susceptibility was measured on a S.H.E. Corp.<sup>45</sup> model VTS-801 magnetometer from 2K to 20K in a magnetic field of 1000 gauss. The magnetometer had a superconducting magnet capable of reaching fields of 10 kgauss. The secondary coils were two astatically wound coils with a geometry similar to that of the susceptometers described above. The sample was raised or lowered through both secondary coils, and the total change in the SQUID voltage was measured. The magnetometer was calibrated by S.H.E. to an accuracy of 1%, and it displayed a number which when divided by the applied field was equal to the total susceptibility of the sample. The susceptibility per unit mass was calculated, and this quantity is proportional to the ytterbium concentration in the gold.

### CHAPTER 3

#### RESULTS

Most of the samples which we made had iron impurity levels so high that the contribution to the resistivity due to Yb was less than that due to Fe. After trying many unsuccessful methods of sample preparation, we developed the method of sample preparation described in Section 2.2. We produced 5 samples in which the major contribution to the resistivity was due to Yb. These samples had Fe impurity levels much lower than the samples of Hebral et al. <sup>1</sup> The concentration of Yb in our samples was determined to an accuracy of about 5% from the magnetic susceptibilities of the samples from as measured on the S.H.E. Magnetometer from 3 to 20K. In this chapter we will discuss and interpret the data we obtained from these best samples.

# 3.1 Electrical Resistivity

In this section we will discuss qualitatively the resistivity data of our best Au(Yb) alloys, data which include the contribution from Fe contamination. Then we will explain the procedure used to correct the total resistivity of each sample for this contamination. The corrected resistivity should be affected primarily by the Yb, which will allow a comparison with the theory developed in Section 1.3.

Two of these 5 samples were alloys of  $Au(^{174}Yb)$ . They had Yb concentrations of 180 ppm, (sample 174-9), and 1000 ppm, (sample 174-7). The uncorrected electrical resistivities of these samples are shown in



Figure 3.1 Resistivity of Sample 174-9 (180 ppm Yb)



Figure 3.2 Resistivity of Sample 174-7 (1000 ppm Yb)

Figure 3.1 and Figure 3.2, respectively. The resistivity of sample 174-9 does follow the expected logarithmic divergence between 1K and 0.1K. However, below 0.1K there is a significant negative departure from this logarithmic divergence. This deviation is due primarily to residual iron in the sample. The uncorrected resistivity of sample 174-7 exhibits a maximum near 30mK. This maximum is caused by the high concentration of Yb ions in this sample. We have already pointed out in Section 1.2 that significant interactions between the magnetic moments of the ions will cause a maximum in  $\rho$  to occur.

Only one sample of relatively uncontaminated Au( $^{171}$ Yb) was produced (sample 171-2). The Yb concentration in this sample was 1500 ppm. The resistivity exhibits a maximum near 150mK, and a very large decrease at lower temperatures, see Figure 3.3. Near 10mK the  $^{173}$ Yb ions will be in their electro-nuclear singlet ground states, and this large decrease in  $\rho$  below 150mK is due primarily to the preferred population of this singlet state, as shown theoretically in Figure 1.2. Below 15mK the resistivity approaches a constant indicating that almost all of the Yb ions are in their singlet ground state, and therefore the conduction electrons can no longer spin-flip scatter off these ions.

Because of the high Yb concentration of this sample (1500 ppm), we expect to see an effect on the resistivity caused by interactions between the Yb ions, but the decrease in the resistivity of this sample is too large to be attributed entirely to interaction effects. Sample 174-7 had an Yb concentration of 1000 ppm, and the resistivity exhibited a relatively small decrease at temperatures below that of the maximum. For an Yb concentration of 1500 ppm one would expect the decrease to be larger, but not as large as the decrease seen in the resistivity of



Figure 3.3 Resistivity of Sample 171-2 (1500 ppm Yb)

sample 171-2. Also, at low temperatures the Yb ions will be in their singlet states, and to first order the magnetic moment of these ions will be zero. (They may still have an induced moment, but it will be small.) Therefore, at the lowest temperatures the interaction effects will have negligible effect on  $\rho$ .

Two acceptable samples of Au ( $^{173}$ Yb) were produced. These samples had Yb concentrations of 258 ppm, (sample 173-10), and 1000 ppm, (sample 173-9). The resistivity of sample 173-10 has a maximum near 70mK, with a relatively small decrease in the resistivity as the temperature is lowered further, see Figure 3.4. The resistivity of sample 173-9 has a maximum near 90mK with a much larger decrease in the resistivity below 90mK, see Figure 3.5. Interaction effects due to the higher Yb concentration in sample 173-9 is most likely the cause of this larger decrease in  $\rho$  and the shifting of the maximum from 70 to 90mK. Note that sample 174-7, which had the same Yb concentration as 173-9 exhibited a maximum in  $\rho$  due to the interaction effects.

# 3.2 Procedure to Correct for Fe Impurities.

To do a quantitative study of the resistivity of these samples, the contribution to the resistivity due to the Fe contamination must be subtracted out. If we assume that only Fe and Yb contribute to the logT behavior of the resistivity, then we have

$$X_{\text{Tot}} = X_{\text{Yb}} + X_{\text{Fe}}$$
(3.1)

where  $X_{Tot} = -d\rho/d(\log T)$ , the total logarithmic slope of the resistivity, and  $X_{Yb}$  and  $X_{Fe}$  are the contributions to this slope due to Yb and Fe,



Figure 3.4 Resistivity of Sample 173-10 (258 ppm Yb)


Figure 3.5 Resistivity of Sample 173-9 (1000 ppm Yb)

respectively. If the concentration of Yb in the samples is known, then  $X_{Yb} = c_{Yb} \frac{\rho}{K}$ , where  $\rho_{K}^{Yb}$  is the known logarithmic slope due to 1 ppm Yb, and  $c_{Yb}$  is the Yb concentration in ppm. Given that  $X_{Fe} = c_{Fe} \rho_{K}^{Fe}$ , where  $\rho_{K}^{Fe}$  is the known logarithmic slope in the resistivity due to Fe, then

$$c_{Fe} = (X_{Tot} - c_{Yb} \rho_{K}^{Yb}) / \rho_{K}^{Fe}.$$
(3.2)

From other work, the value of  $\rho_{\rm K}^{\rm Yb}$  is estimated to be in the range  $^{1,20,21}$  2.79 to  $3.58 \times 10^{-4} n\Omega cm/(ppm-LogT)$  and for  $\rho_{\rm K}^{\rm Fe}$  the value is estimated to be  $^{19}$  0.08n $\Omega$ cm/(ppm-LogT). Notice that only 1 ppm of Fe contamination produces the same value of X as approximately 200 ppm of Yb. Table 3.1 lists  $X_{\rm Tot}$ ,  $X_{\rm Yb}$ ,  $X_{\rm Fe}$ , and  $c_{\rm Fe}$  of our samples estimated using this method. The range of the values of  $X_{\rm Yb}$ ,  $X_{\rm Fe}$ , and  $c_{\rm Fe}$  is due to the range in the estimated value of  $\rho_{\rm K}^{\rm Yb}$ . All except one of our samples had Fe impurity levels less than 1 ppm. The exception had an Fe impurity level of less than 1.5 ppm. The isotopically enriched Yb used to produce the samples contained less than 200 ppm Fe. A sample containing 1000 ppm Yb for which the Yb contained 200 ppm Fe would have an Fe level of less than 0.2 ppm. This indicates that we have produced

Table 3.1 Contributions to the Resistivity due to Yb and Fe

SAMPLE	с <sub>vь</sub>	X <sub>Tot</sub>	Xvh	X <sub>F</sub>	C <sub>E</sub>
	ppm	nΩcm/LŏğT	nΩcm/LŏgT	nΩcm/LõgT	ppm
174-9	180	0.124	0.050-0.064	0.060-0.074	0.75-0.92
174-7	1000	0.396	0.279-0.358	0.038-0.117	0.48-1.46
171-2	1500	0.412	0.419-0.537	0	0
173-10	258	0.095	0.072-0.092	0.003-0.023	0.04-0.25
173-9	1000	0.299	0.279-0.358	0-0.020	0-0.25

Au (Yb) samples with fe concentrations as low as would be expected considering the upper bound for the Fe impurity level in the Yb. Hebral et al. estimated the Fe impurity levels of their two samples to be 1.8 and 3.9 ppm, which is much higher than for our samples. A comparison of  $X_{Yb}$  and  $X_{Fe}$  for our samples shows that, except for sample 174-9, the contribution to the resistivity due to Yb is much larger than that due The samples of Hebral et al. had Yb concentrations of to Fe. approximately 400 ppm. The values listed for  $\rho_{\rm K}^{\rm Yb}$  and  $\rho_{\rm K}^{\rm Fe}$  indicate that for their better sample  $X_{Fe} \sim X_{Yb}$  and for their other sample  $X_{Fe} \sim 2X_{Vb}$ . Note that  $X_{Tot}$  for samples 171-2 and 173-9 is approximately equal to the lower limit of  $X_{vb}$  for the respective sample. This the more appropriate choice of  $\rho_{\kappa}^{\ Yb}$  is indicates that 2.79X10<sup>-4</sup>n $\Omega$ cm/(ppmLogT). In adopting this value of  $\rho_{K}^{Yb}$ , we are chosing Table 3.1. the larger values of c<sub>Fe</sub> in Using  $\rho_{\rm K}^{\rm Yb}$ =3.58X10<sup>-4</sup>n<sub>Ω</sub>cm/(ppmLogT) does not significantly alter the discussion which follows, or the conclusions.

Below we describe the method used to subtract the contribution to the resistivity due to Fe. We used the data shown in Figure 1.1 as the model behavior of Au(Fe). The resistivity of this sample we call ρ<sub>Fe</sub>(T). Below 20mK  $ho_{Fe}$  (T) is taken to be constant. We estimate that the  $\rho_{FF}$  (10mK) is less than 0.003 n cm larger than  $\rho_{Fe}$  (20mK). Ignoring this increase will have a negligible effect on our analysis of the data. To eliminate the contribution to the resistivity due to the electron-phonon interaction, we will only consider the resistivity for temperatures below 1K. Also, since we are only interested in the logarithmic slope of the resistivity and not the total resistivity, we define a new resistivity  $\rho'(T)$  for which  $\rho'(1K)=0$ , arbitrarily. We have then  ${}^{\rho'}Tot^{(T)=\rho}Tot^{(T)-\rho}Tot^{(1K)}$  and  ${}^{\rho'}Fe^{(T)=\rho}Fe^{(T)-\rho}Fe^{(1K)}$ . For each sample we now define a new resistivity  ${}^{\rho''}Fe^{(T)=B\rho'}Fe^{(T)}$  with B chosen so that  $-d{}^{\rho''}Fe^{(T)}/d(LogT)=X_{Fe}$  for the sample as listed in table 3.1. The contribution to the resistivity due to Yb is then

$$\rho' Y b^{(T)} = \rho' T o t^{(T)} - \rho'' F e^{(T)}$$
 (3.3)

For noninteracting Yb moments, the quantity  $\rho'_{Yb}/c_{Yb}$  should be independent of  $c_{Yb}$ , which will allow direct comparison between samples which have different Yb concentrations. In the following sections we will present and discuss  $\rho'_{Yb}/c_{Yb}$  for each of our samples. In order to demonstrate the improvements that we have made upon the work of Hebral *et al.*, in Figure 3.6 we show the resistivity of their Au(Yb) samples. There is a large amount of scatter in their data due to the fact that they measured  $\rho$  to a lower precision than we did and they had to make a large correction due to Fe impurities in their samples.

The isotopically enriched Yb used to produce our samples contained isotopes of Yb other than the one desired, see Table 2.1. The adjustment to the theory necessary to account for these other isotopes is negligible, and therefore will be ignored.



Figure 3.6 Resistivity of Au(Yb) measured by Hebral et al.

# 3.3 The Resistivity of Au(<sup>171</sup>Yb) as Corrected for Fe Impurities

In Figure 3.7 we show  $\rho'_{Yb}/c_{Yb}$  for the sample 171-2 and the prediction of equation 1.22. For the theoretical curve we have chosen  $T_1$ =125K so that the decrease in the resistivity predicted by the theory equals the decrease seen in the data. As we have seen in Figure 1.2, adjusting  $T_1$  changes the size of the decrease in the resistivity as temperatures below that of the maximum, but it has very little effect on the temperature of the maximum, or on the overall shape of the curve. We made the theory and data agree at low temperatures because in this limit the effects of interactions between the magnetic moments of the Yb ions are reduced at these temperatures for the reasons discussed in Section 3.1. Note that even with only one adjustable parameter there is very good agreement between the theoretical predictions and the resistivity measured.

It is important to note that only the data of the Au( $^{171}$ Yb) alloy can establish the proper "zero" for the Kondo effect's contribution to  $\rho$ . At the lowest temperatures, only the electronuclear singlet state of  $^{171}$ Yb is populated. Thus the Kondo effect makes no contribution to at these lowest temperatures. The setting of T<sub>1</sub> at 125K amounts to properly taking account of this true zero, and this value of T<sub>1</sub> will be used for the other Yb isotopes.

A comparison of our data with the data of Hebral *et al.*, see Figure 3.1, shows that we have much less scatter in our data. From our data we can make a better estimate of the value of  $T_1$ . The three curves shown for the data of Hebral *et al.* in Figure 3.6 correspond to  $T_1 = 30$ , 80, and 100K. Our estimated value of  $T_1$  is in rough agreement with the



Figure 3.7  $\rho'_{Yb}/c_{Yb}$  of Sample 171-2 (1500 ppm Yb)

values estimated by Hebral et al.

# 3.4 The Resistivity of $Au(^{174}Yb)$ as Corrected for Fe Impurities

In Figure 3.8 we show  $\rho'_{Yb}/c_{Yb}$  for samples 174-9 and 174-7. The solid line is the theoretical behavior of  $\rho'_{Yb}/c_{Yb}$  for Au( $^{174}$ Yb) in which the interaction between the Yb magnetic moments has been ignored. The resistivity of sample 174-7 (1000 ppm Yb) exhibits a large deviation from LogT behavior. There is a maximum in the resistivity near 35mK. This deviation is caused by the above mentioned interaction effects. Because of the high Yb concentration, the magnetic moments of the Yb ions are coupled which reduces  $<S_{eff}^2>$ . Therefore the resistivity departs from LogT behavior. The resistivity of sample 174-9 (180 ppm Yb) follows the expected LogT behavior to the lowest temperature measured. However this lower concentration sample does exhibit some negative curvature on this graph. It is not clear at the present time whether this deviation is due to residual interactions between the Yb moments or is due to our method of correcting for the Fe contamination.

As a model for the coupling between the Yb moments we use the RKKY interaction.  $^{46}$  For the RKKY interaction, magnetic ions with spin S at sites i and j are coupled according to the hamiltonian

$$H = -W \hat{S}_{i} \cdot \hat{S}_{j} \qquad (3.4)$$

with

$$W = - (3z)^{2}/2 (2J_{eff})^{2}/E_{F} \cos(2k_{F}R) / (2k_{F}R)^{3}$$
(3.5)

where z=1 is the valence of Au,  $k_r$  is the Fermi wave vector, R is the





distance between sites i and j, and J<sub>eff</sub> is the effective coupling between S and the conduction electrons. Equation 3.5 is actually the asymptotic form of the RKKY interaction for which one must have  $2k_FR>>1$ . For Au we have a nearest neighbor distance of 2.9Å and  $k_F=1.2$  (Å)<sup>-1</sup>. Hence we have  $2k_FR=7.0$ , which satisfies the requirement. Let us place the i<sup>th</sup> moment at the origin of our coordinate system. The number of sites within a distance R of the origin is N(R)= $4\pi R^3/(3v_o)$  where  $v_o$  is the atomic volume. Substituting this into equation 3.5, we have

$$W = -B \cos(2k_F R) / N(R)$$
(3.6)

with

$$B = 3(\pi z J_{eff})^{2} / (v_{o} E_{f} k_{f}^{3})$$
$$= J_{eff}^{2} / E_{f}$$
(3.7)

using  $v_0 k_F^{3=3\pi^2}$ . As R is increased, the coupling between the moment at the origin and a moment a distance R from the origin will oscillate between approximately  $\pm B/N(R)$ . We shall arbitrarily divide these interactions with the moment at the origin into two categories, where the dividing line between them is defined by  $R_T$  such that  $B/N(R_T)=k_BT$ . For one category the coupling between the magnetic moment at the origin and a moment at R is less than the temperature:  $B/N(R) < k_BT$ , with  $R > R_T$ . For these interactions we will assign the coupling between the moments to be zero. For  $R > R_T$ , the moment at the origin will contribute to the Kondo resistivity in the normal way,  $\rho'_w = -\rho'_K Log(T/T_1)$ , where  $\rho'_K$  is the resistivity due to a single spin.

For the other category the coupling between the moment at the origin and a moment at R is greater than the temperature:  $B/N(R) > k_BT$ , with  $R < R_T$ . For these interactions we will treat them as if they were in the strong coupling limit,  $B/N(R) >> k_BT$ . The theory for this strong coupling limit was worked out by Matho and Beal-Monod.<sup>14</sup> For  $|\vec{S}_i| = |\vec{S}_j| = 1/2$ , the contribution to the resistivity due to two spins strongly coupled "antiferromagnetically is zero because  $< S_{eff}^2 >= 0$  at low temperatures. For strong "ferromagnetic" coupling  $< S_{eff}^2 >$  is reduced from 3/4 at high temperature to 1/2 at low temperature, so the contribution to the resistivity due to this sign coupling, while not zero, is still reduced. For a preliminary analysis, we shall assume that the "ferromagnetically" coupled spins make no contribution to the resistivity in the strong coupling limit.

The resistivity due to a single impurity is then

$$\rho' = \rho' \mathbf{w}^{\mathbf{n}} \mathbf{w} \tag{3.8}$$

where  $n_W$  is the probability that a site  $R>R_T$  will be occupied, which represents "weak" coupling with the moment at the origin. This probability is equal to  $n_W=1-n_s$ , where  $n_s$  is the probability that a site  $R<R_T$  will be occupied, which is the "strong" coupling case. The number of strongly coupled sites is  $N^*(T)=N(R_T)=B/(k_BT)=T_s/T$ . The mean occupation of these sites is  $n_s^{\gamma} c N^*(T) = cT_s/T$ , where c is the concentration of magnetic ions. The resistivity per impurity is then

$$p'(T) = -p'_{K} Log(T/T_{1})(1-n_{s})$$
  
=  $-p'_{K} Log(T/T_{1})(1-cT_{s}/T)$ 

In Figure 3.9 we show equation 3.9 compared with the data of sample 174-7. The value of  $cT_s=2.5mK$  was chosen in order to have the best overall agreement between equation 3.9 and the data. For sample 174-7, c=1000 ppm, thus  $T_s=B/k_B=2.5K$ . Figure 3.9 also shows equation 3.9 with  $T_s=2.5K$  and c=180 ppm compared with the data of sample 174-9. There is a large disagreement between our data and the behavior of the resistivity predicted by our theory, but this method allows us to make a crude estimate of the value of B.

The hamiltonian for dipole-dipole coupling for Yb at the nearest neighbor distance for Au is approximately

$$H \sim g^{2} \mu_{B}^{2} / R_{nn}^{3} \vec{s}_{1} \cdot \vec{s}_{2}$$
  
=  $(4\pi g^{2} \mu_{B}^{2}) / (3\nu_{o}) \vec{s}_{1} \cdot \vec{s}_{2} / N (R)$   
=  $B' \vec{s}_{1} \cdot \vec{s}_{2} / N (R)$ . (3.10)

For Yb in Au we have g=3.4 and  $v_0 = 1.7 \times 10^{-24} \text{ cm}^3$  and thus B'/k<sub>B</sub>=1.8K. The value of B from equation 3.6 we estimated to be 2.5K, approximately the same value as the dipole-dipole interaction. Equation 3.7 relates B to  $J_{eff}$ , the effective coupling between the Yb ions and the conduction electrons by

$$J_{eff} = (BE_{F})^{1/2}.$$
 (3.11)

For Au,  $E_F/k_B = 6.4 \times 10^4 K$ . Evaluating equation 3.11 we have  $J_{eff} = -400 K$  or  $J_{eff} = -0.034 eV$ . The fact that  $d^{0}/d(\log T) < 0$  for Au(Yb) indicates that



Figure 3.9  $\rho'_{Yb}/c_{Yb}$  of Samples 174-9 (180 ppm Yb) and 174-7 (1000 ppm Yb) Compared with Theory

.

 $J_{eff}$  <0. We can estimate  $J_{eff}$  from the Kondo temperature by <sup>11</sup>

$$T_{K} = D \exp(d/(2J_{eff}N(E_{F})))$$
(3.12)

where d=3 is the degeneracy factor and  $N(E_F)=3/(4E_F)$  the density of states at the Fermi energy. D is a temperature of the same order of magnitude as the Fermi temperature. According to Matho and Beal-Monod, <sup>14</sup> D=0.77E\_F=5X10<sup>4</sup>K. The Kondo temperature of Au(Yb) is estimated to be<sup>11</sup>~10 K. From this we estimate  $J_{eff}$  -6X10<sup>3</sup>K or  $J_{eff}$ =-0.5eV. We have a large disagreement between the value of  $J_{eff}$  we estimate from the interaction effects in our samples and the value of  $J_{eff}$  as estimated from the Kondo Temperature. Even though the method we used to account for the interaction effects is very crude, the disagreement between the values of  $J_{eff}$  estimated using these two methods should not be as large as it is.

# 3.5 The Resistivity of $Au(^{173}Yb)$ as Corrected for Fe Impurities.

In Figure 3.10 we show  $\rho'_{Yb}/c_{Yb}$  for samples 173-9 and 173-10. For the theoretical curve we have used  $T_1$ =125K as determined in the previous section. For temperatures as low as 40mK,  $\rho'_{Yb}/c_{Yb}$  of sample 173-10 follows the upper bound of the resistivity as predicted by Equation 1.25 with the substitution of Equation 1.27. Note, in particular, that the maximum occurs at the temperature predicted by the theory. Below 40mK  $\rho'_{Yb}/c_{Yb}$  is larger than the values predicted by our theory. The value of  $\rho'_{Yb}/c_{Yb}$  of sample 173-9 is within the upper and lower bounds of the values predicted by theory. This sample has an Yb concentration of 1000 ppm. The behavior of  $\rho'_{Yb}/c_{Yb}$  for sample 174-7 indicates, see Figure





3.8, that at this 1000 ppm concentration there is an appreciable interaction between the magnetic moments of the Yb ions. Hence, it is not surprising that the maximum in the data of sample 173-9 occurs at a higher temperature than for 173-10, and below this temperature the data fall below those of sample 173-10. Note that at the lowest temperatures the difference in  $\rho'_{Yb}$ /  $c_{Yb}$  samples 173-10 and 173-9 is smaller than this difference for samples 174-9 and 174-7. For  $^{173}$ Yb at the lowest temperatures, the hyperfine coupling to the I=5/2 nucleus lowers the effective electronic moment, see Figure 1.6. Thus it is plausible that the resistivity of the  $^{173}$ Yb alloys might exhibit a smaller effect due to interactions between the Yb ions than for  $^{174}$ Yb alloys of the same concentration. We conclude that the expected hyperfine coupling effect has been seen for  $^{173}$ Yb. However, at low temperature there is a disagreement between the approximate theory we developed and the data.

### 3.6 Thermoelectric Ratio

There is a large difference between the resistivities of Au(Yb) samples made with different isotopes of Yb. This indicates that we are seeing the effects caused by the hyperfine coupling. Unfortunately, the effects of hyperfine coupling on the thermoelectric ratios, G, of the samples are not so clear. The values of G for samples 173-9, 173-10, 174-7, and 174-9 are shown in Figure 3.11. The behavior of G for these samples is very similar to the behavior of G for Au(Fe), see Figure 1.5. As can be seen in Figure 1.5, for Au(Fe) the values of G are very large in magnitude and negative, while for Au(Yb) G is expected to be much smaller.<sup>47</sup> Near 20mK, the magnitude of G for our sample with the highest Fe concentration, 174-7, is relatively small, while for one of our most



Figure 3.11 G of Samples 173-9, 173-10, 174-7 and 174-9

Fe-free samples, 173-9, the magnitude of G is about 4 times larger. This confusing situation makes it impossible to draw any conclusions about the effect of hyperfine coupling on G.

On the other hand, for sample 171-2, G changes sign near 30mK, see Figure 3.12. The theory of Matho and Beal-Monod<sup>16</sup> predicts this sign change in G for the case of "antiferromagnetic" electro-nuclear coupling, and this sign change should occur at approximately the observed temperature. We note that this sample appears to have negligible Fe contamination. From the behavior of G for these samples, it appears that in order to see clearly the effect of hyperfine coupling on G, the Fe impurity level must be reduced to even lower levels than we have so far acheived.

Even though G does not show the effect of the hyperfine coupling for the samples other than 171-2, it can be used as another check on the estimated Fe concentration of the samples by using the Gorter-Nordheim relation.<sup>15</sup> Here the thermopower and the resistivity due to an impurity, i, is related to the total thermopower by

$$S = S^{j} + \rho_{i} / \rho_{i} (S^{i} - S^{j})$$
 (3.13)

where S is the total thermopower, S<sup>i</sup> is the thermopower due to the impurity i, S<sup>j</sup> is the thermopower due to other impurities (j),  $\rho$  is the total resistivity, and  $\rho_i$  is the resistivity due to impurity i. Because G is proportional to S, this relation can be rewritten as:

$$G = G^{j} + \rho_{i} / \rho (G^{i} - G^{j}).$$
 (3.14)

Let impurity i be Fe, and we expect  $G_{Fe} >> G_i$ . We then have



Figure 3.12 G of SAmple 171-2

$$G \sim \rho_{Fe}^{\rho} G_{Fe} + G_{j}$$
 (3.15)

We will also assume that  $G >> G_{j}$ ; that is, the Fe impurities will make the major contribution to G. Rewriting this equation we have

$${}^{\mathbf{G}}\mathbf{Fe} \stackrel{\sim}{}^{\rho}\mathbf{Fe}^{/\rho} \quad \mathbf{G}. \tag{3.16}$$

The value of  $G_{Fe}$  was estimated using the resistivity and thermoelectric ratio data of three Au(Fe) samples we had measured. The value of  $\rho_{Fe}$  was taken to be  $-d\rho/d$  (LogT) between 0.2 and 1K. We estimate  $G_{Fe}$  to be  $6X10^{-4}V^{-1}$  +50% at 20mK. Because G of Au(Fe) is large, see Figure 1.5, and G of Au(Yb) is much smaller, <sup>47</sup> we will assume that G of our samples is due entirely to the iron impurity. We can then estimate the resistivity due to Fe in our samples to be

$${}^{\rho}Fe = {}^{\rho} (G/G_{Fe})$$
(3.17)

where G is the value of the thermoelectric ratio of our Au(Yb) samples. On Table 3.2 are presented the estimates of  $c_{Fe}$  obtained from G. The values of G that were used in these computations are also tabulated. Because we attributed G for our samples to be due entirely to Fe, this method will overestimate the Fe concentration in our samples. Even though these estimates are very crude, the values of  $c_{Fe}$  are in rough agreement with the values presented in Table 3.1. The one exception is sample 173-9, where  $c_{Fe}$  as estimated by the Gorter-Nordheim relation is much larger than its value in Table 3.1. The cause of this discrepancy is not understood. Table 3.2 Estimates of c<sub>Fe</sub> Using the Gorter-Norderheim Relation.

SAMPLE	<sup>с</sup> ғе	G (20mK)
	ppm	v <sup>-1</sup>
174-9	0.43	-10
174-7	0.78	- 6
173-10	0.38	-13
173-9	1.41	-20

## 3.7 <u>Magnetic</u> Susceptibility

The derivative of the magnetic susceptibility,  $\partial \chi/\partial T$ , of three samples, 173-10, 174-9 and 174-7 was measured at low temperature.  $T^2\left(\partial\chi/\partial T\right)$  for these samples and the theoretical predictions for  $T^{2}(\partial \chi/\partial T)$  for Au(<sup>173</sup>Yb) and Au(<sup>174</sup>Yb) are shown in Figure 3.13. The data and the theoretical curves are normalized to have the value 1 at high temperature.  $T^2(\partial_{\chi}/\partial T)$  for Au(<sup>174</sup>Yb) is expected to be constant to temperatures well below 10mK. The data obtained from samples 174-9 and 174-7 are nearly constant down to approximately 30mK, with slight deviations in the data occuring at lower temperatures. One might expect deviation to occur for sample 174-7 because of the high Yb а concentration of that sample. The departure of the resistivity data for this sample from LogT behavior indicated the presence of interactions between the Yb ions in the sample. This interaction would also show up as a deviation in  $T^2(\partial \chi/\partial T)$  at low temperature. The deviation for the data of sample 174-9 at low temperatures is much smaller. This would indicate the possible presence of smaller interaction effects between the Yb ions in this sample.



Figure 3.13 T<sup>2</sup>( $\partial_X/\partial T$ ) of Samples 173-10, 174-9, and 174-7 Normalized to 1 at High Temperature

The data obtained from sample 173-10 follows the expected behavior down to approximately 80mK. Below this temperature the data depart significantly from the theoretical values. As mentioned in Section 1.5, if Curie's law is obeyed then  $T^2(\partial \chi/\partial T)=C$ . C is proportional to  $<S_{eff}^2>$ of the magnetic impurity.  $T^2(\partial \chi/\partial T)$  for sample 173-10 is significantly larger than the predicted value, indicating that the value of  $\langle S_{aff}^2 \rangle$  is larger than the theoretical prediction. The isotopically enriched 173Yb used to make this sample contained 95% 173Yb. The remaining 5% consists almost entirely of isotopes which have a nuclear spin of 0. The behavior of  $T^2(\partial\chi/\partial T)$  for these isotopes is identical to that of <sup>174</sup>Yb. Including the contribution of these even isotopes will raise the T=10mK intercept of the theoretical curve from 0.44 to 0.47, an amount too small to bring the theory into agreement with the data. Similar corrections for  $Au(^{174}Yb)$  are also negligible. We conclude that we have seen the effect of hyperfine coupling in  $Au(^{173}Yb)$ , but at low temperature there is a disagreement between the theory and the data.

## CHAPTER 4

### CONCLUSIONS

The goals of this study were to explore the effects of hyperfine coupling on a Kondo alloy, Au(Yb). The most difficult problem we had to overcome was the high Fe impurity level in our samples. After much trial and error, we were able to produce samples which, while not iron free, had iron levels low enough that the Yb contribution to the electrical resistivity was larger than that due to Fe. The level of Fe contamination in our samples was significantly lower than in the samples of Hebral et al. The electrical resistivity of our alloys of Au(<sup>174</sup>Yb) and Au(<sup>171</sup>Yb) behaved as predicted down to the lowest temperature we reached, 12.5mK. From the electrical resistivity of  $Au(^{171}Yb)$  we were able to estimate the value of  $T_1$ , the only adjustable parameter in the The electrical resistivity of our alloys of  $Au(^{173}Yb)$  behaved theory. as predicted down to a temperature of 40mK, below which the theory predicted values of resistivity lower than the measured values. The magnetic susceptibility of the alloy  $Au(^{174}Yb)$  behaved as predicted to a temperature of approximately 30mK, below which there appeared to be a slight negative departure of the data from the theory. The magnetic susceptibility of the alloy  $Au(^{173}Yb)$  followed its predicted behavior down to 80mK, below which the theory predicted values of  $T^2(\partial x/\partial T)$  lower than measured. Perhaps the disagreements between theory and experiment in  $\rho$  and  $\chi$  for <sup>173</sup>Yb have a common origin. Both disagreements could be interpreted as indicating that the theoretical value of  $< S_{eff}^2$  is too

small at the lowest temperatures.

We failed to see the effect of hyperfine coupling on the thermoelectric ratio of Au(Yb) except for one sample. The most likely reason for this is that G due to the residual iron in the samples is much larger than G due to Yb in the sample. In order to see the effect of hyperfine coupling on G, the residual Fe level must be reduced below the level we reached for most of our samples.

We have discovered the presence of superconductivity in Au(Yb) at low temperatures. At the present time we do not know what material is causing the superconductivity, and we do not completely understand the conditions necessary for producing superconductivity. The scanning transmission electron microscope recently acquired by MSU would be useful in determining the material causing the superconductivity. A study of the effects of annealing Au(Yb) at different temperatures would aid in determining the conditions necessary for producing superconductivity.

Extending the temperature of our measurements to below 10mK would allow a better investigation into the discrepancy between the data and the theory for Au( $^{173}$ Yb) and perhaps make possible an estimate of the weighting factors to the logarithmically diverging and nondiverging terms of equation 1.27. The study of Au( $^{174}$ Yb) at lower temperatures and higher Yb concentrations would make possible a better estimate of  $J_{eff}$  for Yb in Au.

APPENDIX

### APPENDIX

### Superconductivity in Au(Yb)

Besides the problem of iron contamination in our samples, which we had anticipated, we encountered what appeared to be a superconducting transition in some of our samples. The appearance of superconductivity in the samples made the investigation of the Yb-isotopic effect impossible, so certain methods of sample preparation were developed in order to try to avoid this superconductivity. Neither Au or Yb separately are known to be superconducting above our minimum temperature of 12.5mK. However, Au is expected to have a superconductivity has been seen.<sup>48</sup> The possibility of superconductivity in a combination of these two elements is unexpected and very interesting. This appendix details the work done so far and indicates a possible direction for future work.

The superconductivity first appeared in a AuYb sample we tried to make by diffusing Yb directly into a Au foil. A small amount of Yb and a 0.005" thick foil of chlorine-annealed Au were sealed under vacuum in a quartz tube so there was no physical contact between the Yb and the Au. This tube was placed in a furnace, and the Au-Yb was annealed at  $850^{\circ}$ C for 48 hours. At  $850^{\circ}$ C, Yb has a vapor pressure of 0.5 atmospheres. During this anneal the Yb vapor should diffuse into the Au foil. After the anneal, the inside of the quartz tube appeared to be coated with a black material, and the Au foil was discolored, partially melted, and brittle, indicating a high Yb concentration in the foil.

The resistivity of the sample exhibited a current dependence at temperatures below 1K. At 150mK the resistivity increased by more than 25% when the current was increased from 50 to  $100\mu$ A. At temperatures below approximately 80mK the resistivity of the sample appeared to drop to zero for currents less than  $1\mu$ A. The behavior of the potential across the sample versus the current through the sample is similar to the behavior seen in granular superconductors.<sup>49</sup>

All other samples were made by sealing the Yb and the Au in quartz tubes and melting them in an induction furnace following the method described in Section 2.2, except that initially we did not quench the samples. Instead we admitted Ar gas into the quartz tube containing the graphite holder and allowed the sample to cool to room temperature by thermal radiation and by thermal conduction through the Ar gas. The graphite holder (and presumably the Au-Yb mixture) cooled from 1150°C to approximately 600°C (estimated from the glow of the graphite holder) in about 1 minute. Approximately 10 samples were made that were not quenched, of which l exhibited superconductivity. For the samples made after this we used the method of quenching described in Section 2.2 in an attempt to avoid the superconductivity. Approximately 10 samples were made using the quenching method, of which 1 exhibited superconductivity. From these results it is not clear whether or not quenching has an effect on the presence of superconductivity in samples made in this manner. Three samples were made using the method described in Section 2.2 except that the Au had been chlorine annealed in a liquid state at 1150°C while sitting at the bottom of a quartz tube. All three of these samples exhibited superconductivity.

In Figure A.1 we show the resistivity of a sample in which there was an onset of superconductivity. As the temperature of the sample is reduced, the resistivity increases slightly down to a temperature of approximately 150mK, below which the resistivity begins decreasing rapidly. This sample contained 140 ppm of 173Yb and was made with Au that had been chlorine annealed in a liquid state. The resistivity below 350mK is current dependent with a maximum in the resistivity occurring at a temperature dependent on the the current used to measure the resistivity, see Figure A.2. With two exceptions (which will be discussed below) the behavior of the resistivity of all other samples in which we saw superconductivity was very similar to that discussed above. Each one of these samples had a resistivity maximum in the temperature range from 0.2 to 1K with a sharp decrease in the restivity as the temperature was reduced below the temperature of the maximum. For two samples we measured the potential drop across the sample as a function of current through the sample at temperatures less than 100mK. In both cases the potential drop across the sample was 0 for currents less than 1 A, indicating that there was a completely superconducting path through the sample. Also the resistivity was highly current dependent for temperatures near and below the temperature of the resistivity maximum.

We thought silicon from the quartz tube in which the Au and Yb were sealed could play some role in the superconductivity. The quartz tube in which the Au and Yb were sealed was always partially discolored after the melting of the Au and Yb had taken place. This discoloration did not occur when pure Au was melted in quartz, indicating that the discoloration was caused by a reaction between the Yb and the quartz.



Figure A.1 Resistivity of Au(Yb) with a Superconducting

Transition



Figure A.2 Current Dependence of the Resistivity of the Superconducting Sample of Figure A.1

Also Au and Si have a very low eutectic temperature<sup>50</sup>  $(370^{\circ}C)$ , and in fact Si is very mobile in Au at temperatures as low as  $150^{\circ}C$ .<sup>51</sup> A sample of "pure" Au was made using Au that had been chlorine annealed in a liquid state while in contact with quartz. Unlike the three superconducting Au (Yb) samples that had been made using Au that had been chlorine annealed in a liquid state, this sample did not exhibit supeconductivity. It would seem that the presence of Yb is necessary for the superconductivity to occur. The resistivity of this sample deviated from logarithmic behavior near 0.8K, see Figure A.3. The cause of these deviations is not understood, but perhaps it might be related to the presence of Si. To explore the role Si could play in causing superconductivity, the samples described below were melted in a graphite crucible which had been placed inside a quartz tube to prevent the Au-Yb from contacting the walls of the quartz tube.

Two samples were made with the graphite crucible having a loose fit inside the quartz tube. These samples exhibited superconductivity and are the exceptions alluded to above. One sample had a nominal Yb concentration of 10%, Au(10%Yb)-1. In this sample the resistivity decreased by about 90% over a temperature interval of less than 100mK, see Figure A.4. This sample was melted and quenched as discussed above. Because of the loose fit of the graphite crucible inside the quartz tube, the quenching time was probably longer, although from the glow of the crucible it is not possble to say with certainty that the quenching time had been longer. After the AuYb mixture was quenched, it was removed from the graphite crucible, was sealed inside another quartz tube containing a quarter atmosphere of  $10\%H_2-90\%Ar$  gas, and then annealed at  $500^{\circ}C$  for 60 hours. X-ray analysis of this sample indicated



Figure A.3 Resistivity of Au(Fe) Which had been Chlorine Annealed in a Molten State



Figure A.4 Resistance of Samples Au(10%Yb)-1 and Au(5%Yb)

the presence of another crystalline material, but the lines did not correspond to the expected lines of any of the known Au-Yb intermetallics.<sup>52</sup> A preliminary study of this sample with a scanning electron microscope revealed regions of high Yb concentration of approximately 5 microns diameter. No significant concentration of Si was detected in the sample. The other sample had a nominal Yb concentration of 5% Au(5%Yb) and was prepared in the same manner as sample Au(10%Yb)-1 except that it was annealed at  $560^{\circ}$ C for 6 days. The decrease in the resistivity of this sample was not as dramatic as for the previous sample, but the decrease started at the same temperature as in the 10% Yb sample, see figure A.2

An alloy of Au with a nominal Yb concentration of 10%, Au(10%Yb)-2, was made using the same method that was used for sample Au(10%Yb)-1, except that the outer quartz tube had been collapsed onto the graphite crucible in order try to decrease the time it took to quench the sample after it had been melted. However, visual observation of the quench indicated no significant change in the cooling rate. This alloy was then cut into several samples. One sample was made from the alloy as quenched, one was annealed in  $H_2$ -Ar gas at 600°C for 8 days in contact with quartz, and another annealed in the  $H_2$ -Ar gas at 600°C for 5 days in contact with graphite. There were no significant differences between the behaviors of the resistivity of these three samples, see Figure A.5.

A study of Yb in Au, Ag, and Au-Ag alloys by Talmor and Sierro<sup>53</sup> saw large resistivity decreases at temperatures below approximately 3Kin samples that had been annealed at  $560^{\circ}$ C, but none in samples annealed at  $850^{\circ}$ C. They attributed these decreases to antiferromagnetic ordering in their samples. X-ray analysis of their samples indicated the



Temperature (K)

Figure A.5 Resistance of Samples of Au(10%Yb)-2. The Symbols at the top of the graph indicate which scale corresponds to each set of data.
presence of an intermetallic compound,  $(YbAu_3)$ . They made two intermetallic samples, one containing  $YbAu_3$  and  $YbAu_4$ , and the other containing YbAu and YbAu<sub>2</sub>. Each of the samples had a decrease in the resistivity at temperatures below approximately 5K that was larger than in their other samples. The lowest temperatures of their measurements was greater than 1.5K. The temperature dependence of the resistivity of their samples was very similar to the temperature dependence in our samples, so if their measurements had been extended to sufficiently low temperatures their samples might have shown superconductivity.

The study by Talmor and Sierro suggests that the superconductivity is produced by the Au-Yb intermetallics. Annealing at  $600^{\circ}$ C causes precipitation of Yb in AgAu(Yb) alloys.<sup>54</sup> Anneals of Au(Yb) near this temperature may cause the formation of Au-Yb intermetallics. If this is the case, the annealing temperature is very critical. Sample Au(10%Yb)-1 was annealed at  $500^{\circ}$ C and had a very sudden superconducting transition. Sample Au(5%Yb) was annealed at  $560^{\circ}$ C, and the transition occurred over a much larger temperature range. Samples made from Au(10%Yb)-2 were either not annealed, or annealed at  $600^{\circ}$ C. These samples had no superconducting transition.

The results of the electron-microscope study of sample Au(10%Yb)-1along with the fact that there were no differences in the behavior of the resistivity of the samples Au(10%Yb)-2 suggest that silicon does not play a role in the occurance of superconductivity. On the other hand, the superconductivity of the three samples that were made with Au that had been chlorine annealed in a liquid state suggest that if Si does play a role in the superconductivity, Yb must also be present for superconductivity to occur. The most promising directions for future study are: (1) a thorough study of the effects of different annealing temperatures on the resistivity, especially anneals between 500 and  $600^{\circ}$ C. and (2) the study of the resistivity of Au-Yb intermetallics.

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