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Resistivity minima in $Au_{1-x}Ni_x$ alloys ($0.30 \leq x \leq 0.42$)

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To permit the interpretation of the experimentally observed low-temperature resistivity minima in $Au_{1-x}Ni_x$ alloys in the range $0.30 \leq x \leq 0.42$, a model of the dilute spin cluster is proposed. With use of the experimentally determined lattice resistivity, the contribution due to magnetic scattering is separated. It is shown that this magnetic contribution fits with the Kondo description very well.

I. INTRODUCTION

In a previous paper, low-temperature (T) resistivity minima were observed in fast-quenched $Au_{1-x}Ni_x$ alloys in the range of $0.30 \leq x \leq 0.45$.[1] Similar observations have been reported in Cu-Ni alloys of corresponding compositions.[2] This paper is concerned with explaining the resistivity minima in terms of Kondo effect.

The original Kondo model[3] was proposed to understand the phenomenon of resistivity minima in alloy systems with very dilute magnetic impurities (50—1000 ppm range) such as Cu-Fe and Au-Mn.[4] The central concept in the model is the interaction between conduction electrons and localized d electrons associated with the isolated magnetic impurities which leads to spin compensation. As a result, the resistivity contains a term of the form $-\ln T$, which together with the regular phonon contribution are responsible for the observed resistivity minima.

More recently, the Kondo description has been extended to systems of dense rare-earth ions,[5-8] in particular, the intermetallic compounds of Ce.[9-15] Credible theories have also been developed to interpret the experimental results.[16-18] The extension of the Kondo model is based on the assumption that the spin compensation is efficient such that the local magnetic moments are "isolated." Hence each localized spin scatters conduction electrons independently.

The situation with Au-Ni system is somewhat different. The content of Ni is not dilute in the normal sense. The magnetic moments involved are not as highly localized as those on Ce ions. However, in the following, reasons will be presented to justify the use of Kondo model in explaining the resistivity data. The recent theoretical development for systems with more than a single spin[19,20] should be helpful in understanding the present result.

Details of specimen preparation and resistivity measurements were reported previously.[1] For the purpose of comparison two parallel series of alloys were prepared, one each for the Au-Ni and Au-Cu systems in the concentration range of concern. Starting materials were ultrapure elements with minimum purity of 99.999% supplied by American Smelting and Refining Corporation (Au and Cu) and Johnson Matthey and Co. (Ni). Alloys of each composition were first prepared in 3—5 g ingots by arc-melting. The final alloy foils, 30—75 μm thick by $\sim$25 mm in diameter, were obtained using the technique of quenching from the liquid state which effectively suppressed the miscibility gap in the Au-Ni alloys and the order-disorder transformation in the Au-Cu alloys. Prior to the resistivity measurements, all foils were examined by x-ray diffraction to make sure of the single-phase randomly substitutional face-centered-cubic lattice. In fact, our earlier analysis indicates that the Au-Ni solid solution, after being thus quenched, has the Ni atoms distributed nearly at the statistical level.[21]

The resistivity specimens, $\sim$15 mm long and $\sim$2 mm wide, were cut from the quenched foils. A standard four-lead arrangement was used in the measurements with an ac of 1 mA and a fixed frequency of 100 cps, between 1.5 and 300 K.

II. EXPERIMENTAL DATA AND ANALYSIS

The overall resistivity of Au-Ni alloys with different compositions as functions of temperature, $\rho(T)$, was reported earlier.[1] The portions of resistivity minima are shown in more detail in Fig. 1. Listed in Table I are the resistivity values and the temperatures at the minima, $\rho_{\min}$ and $T_{\min}$, respectively, together with the residual resistivity values ρ_r (extrapolated to $T=0$). It is quite evident that both the depths of the minimum, $\rho_r - \rho_{\min}$ and $T_{\min}$, increase with Ni concentration. On the other hand, the resistivity of Au-Cu alloys behaves in a normal manner as expected.

Looking at the resistivity variations of Au-Ni alloys

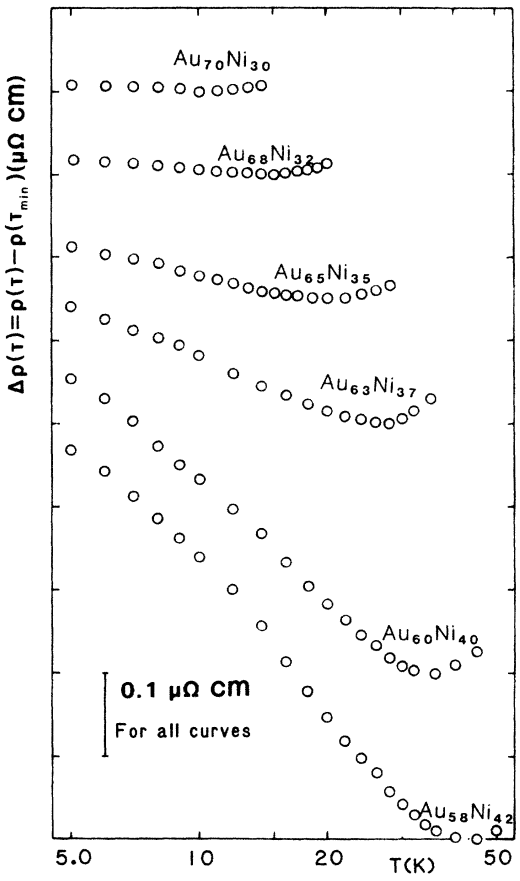

FIG. 1. Resistivity minima in $Au_{1-x}Ni_x$ alloys ($x=0.30$–0.42). Note that the temperature is expressed in logarithmic scale.

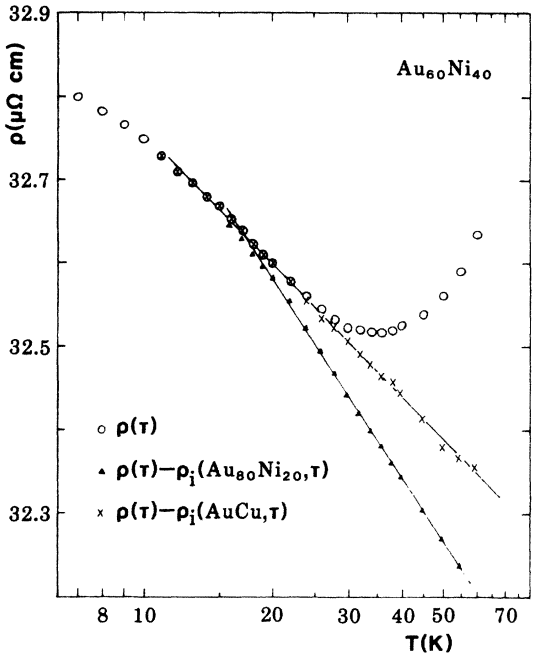

FIG. 2. Temperature dependence of the resistivity of $Au_{60}Ni_{40}$ near the region of the minimum.

systematically, the composition range in which resistivity minima occurs in sandwiched between two distinct regions:[1,22] (1) low Ni concentration ($x \leqq 0.25$) where the magnetic properties of the alloys are characterized by the temperature-independent spin susceptibility which is gradually enhanced by the addition of Ni and (2) higher Ni content ($x \geqq 0.42$) where long-range magnetic ordering sets in. The Curie temperature increases rapidly with increasing Ni concentration. Thus there is no question that the occurrence of resistivity minima is of magnetic origin and is associated with d electrons.

To analyze the resistivity data, the Matthiessen's rule is assumed:

$$\rho(T)=\rho_r+\rho_i(T)+\rho_M(T) \tag{1}$$

where ρ_i and ρ_M are the contributions from the lattice and magnetic scattering, respectively. The function $\rho_i(T)$ has to be determined in order to calculate $\rho_M(T)$.

There are two ways to closely approximate $\rho_i(T)$. In the Au-Ni alloy system, the alloy with ~ 20 at. % Ni is the composition which contains the highest content of Ni, and yet its resistivity does not show any strong deviation from that of a normal nonmagnetic metal. Thus it is safe to assume $\rho_M(T)=0$ in $Au_{80}Ni_{20}$ and to use its $\rho_i(T)$ as the phonon contribution in all other alloys with higher Ni concentrations. This practice is acceptable when the Ni content is not too much greater than 20 at. %, otherwise substantial error could result in the final analysis. Another reasonable approach is to compare the resistivities of two parallel alloy sequences of Au-Ni and Au-Cu with identical Au contents, and to assume the corresponding $\rho_i(T)$ to be similar. The rationale for such a proceeding is rather obvious. Ni and Cu are neighboring elements in

TABLE I. Summary of experimental results related to Kondo effect.

x	T_{min} (K)	ρ_r ($\mu\Omega$ cm)	ρ_{min} ($\mu\Omega$ cm)	$\rho_r-\rho_{min}$ ($\mu\Omega$ cm)	$\log_{10}T$ range (K)
0.30	10	22.15	22.12	0.03	2–10
0.32	15	25.78	25.74	0.04	1.5–15
0.35	19	28.09	27.99	0.10	5–19
0.37	28	31.12	30.90	0.22	5–25
0.40	36	33.00	32.56	0.44	11–60
0.42	45	33.82	33.21	0.61	12–50

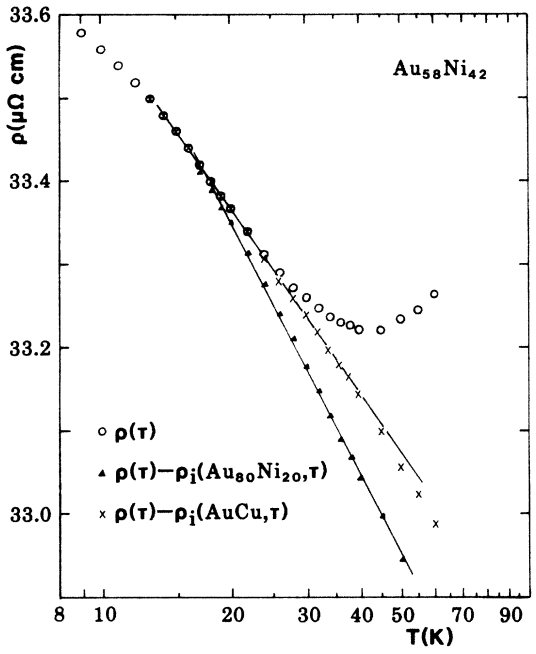

FIG. 3. Temperature dependence of the resistivity of $Au_{58}Ni_{42}$ near the region of the minimum.

the Periodic Table. When phase segregation and order-disorder transformations are suppressed, both of them form continuous random solid solutions with Au. A major distinction between the two alloy systems exists however. When electronic structures are considered, Cu can be viewed as a simple metal while Ni is characterized by its nearly filled d band. Consequently, s-d scattering is expected to be important in the electron transport in Au-Ni alloys and only s-s scattering can exist in Au-Cu alloys.

Both methods of approximating $\rho_i(T)$ have been tested and the results are as expected. For alloys with $\leqq 32$ at.% Ni, $\rho_i(T)$ of $Au_{80}Ni_{20}$ is a good approximation. At higher Ni concentration, $\rho_i(T)$ of corresponding Au-Cu alloys proves to be superior. In the typical analysis, Eq. (1) was used. The magnetic contribution $\rho_M(T)$ was obtained by subtracting ρ_r and $\rho_i(T)$ (of either $Au_{80}Ni_{20}$ or the corresponding Au-Cu alloy) from the experimental data $\rho(T)$. Examples are shown in Figs. 2 and 3. Clearly, $\rho_M(T)$ thus calculated reveals $-\log_{10}T$ dependence quite well, which serves as a strong indication that the Kondo effect is important for the case under consideration.

III. DISCUSSION

A. Spin clusters in Au-Ni alloys

To interpret the resistivity data of Au-Ni alloys in the composition range 30—45 at.% Ni, the concept of spin cluster has to be considered. In an earlier article, the magnetizations of $Au_{1-x}Ni_x$ alloys ($x=0.30$—0.60) were reported.[21] The measured magnetic moments are in good agreement with the average moments calculated from a nearest-neighbor model.[23] The main result of this simple model is that, in the Au or Cu matrix, a Ni atom develops its full magnetic moment of $0.606\mu_B$ if surrounded by at least 8 Ni nearest neighbors and possesses no moment otherwise. For the present liquid-quenched Au-Ni alloys, the distribution of Au and Ni atoms is at a nearly completely random state. According to the model, the atomic fraction of magnetic Ni atoms in an alloy $Au_{1-x}Ni_x$ is $x\sum_{z=8}^{12}f(z)$, where z is the number of nearest-neighbor Ni atoms and $f(z)=C_z^{12}x^z(1-x)^{12-z}$ is the binary distribution function. The calculated values of $x\sum_8^{12}f(z)$ listed in Table II are very low, ranging from 0.28% for $x=0.30$ to 3.2% for $x=0.42$.

As to the interaction between neighboring magnetic Ni atoms, the d-d exchange constant J^{dd} can be estimated.[24] Assuming the exchange to be the same as in pure Ni with a spin of $s=\frac{1}{2}$, and using the molecular-field theory,

$$\frac{J^{dd}}{k_B}=\frac{3}{2z}\frac{T_c^{\mathrm{Ni}}}{s(s+1)}\simeq 105\ \mathrm{K}\ ,$$

where T_c^{Ni} is the Curie temperature of pure Ni, k_B is the Boltzman constant, and $z=12$ is the nearest-neighbor coordination number. For $Au_{1-x}Ni_x$ alloys in which resistivity minimum occurred ($x=0.30$—0.42), $T_{\min}$ is always much lower than J^{dd}/k_B. Thus the spins of neighboring magnetic Ni atoms are ferromagnetically correlated, which leads to the formation of spin clusters. Furthermore, because of the low concentration of magnetic Ni atoms in Au-Ni alloys with $x=0.30$—0.42, spin clusters are reasonably well isolated from each other.

TABLE II. Parameters related to spin-cluster calculation and values of the exchange constant J^{sd}. [All symbols are defined in the text. J^{sd} is calculated for a typical case: $S_{\mathrm{cl}}=10$, $S_{\mathrm{cl}}(S_{\mathrm{cl}}+1)=110$, and $m^*/m_0=10$.]

x	N (10^{23} cm^{-3})	$x\sum_{z=8}^{12}f(z)$	n ($c=10$)	N_{cl} (10^{19} cm^{-3})	n_s	J^{sd} (eV)
0.30	0.6530	0.002 80	0.000 280	1.80	0.702	−0.267
0.32	0.6580	0.004 62	0.000 462	3.04	0.683	−0.250
0.35	0.6651	0.008 93	0.000 893	5.94	0.655	−0.297
0.37	0.6702	0.013 30	0.001 330	8.91	0.638	−0.327
0.40	0.6785	0.022 92	0.002 292	15.55	0.614	−0.374
0.42	0.6837	0.031 93	0.003 193	21.83	0.599	−0.384

B. The model for Kondo effect

The preceding analysis indicates that spin clusters are "dilute" and are reasonably well separated from each other for Au-Ni alloys in the composition range where resistivity minimum occurs. It is then possible to treat the spin clusters in these Au-Ni alloys as isolated magnetic "ions," leading to a resistivity contribution from Kondo scattering. The following model is appropriate for such an alloy system in the paramagnetic state.

(1) In the alloy system $Au_{1-x}Ni_x$ with a total of N atoms per unit volume, the fraction of magnetic Ni atoms is $x\sum_8^{12} f(z)$. Assume there are in the average c magnetic atoms in each cluster, the number of spin clusters expressed in terms of magnetic atoms is $n=(x/c)\sum_8^{12} f(z)$. Then

$$N_{\rm cl}=Nn=N\frac{x}{c}\sum_8^{12} f(z)$$

is the number of spin clusters per unit volume. For simplicity, $c=10$–20 is chosen for model calculation. The values of these parameters are tabulated in Table II.

(2) The intracluster exchange interaction J^{dd} is strong, causing the c spins within a cluster ferromagnetically correlated and producing a cluster spin $S_{\rm cl}$. Clusters of Ni atoms below the threshold of eight Ni neighbors carry no moment.

(3) Because of the dilute nature, spin clusters are assumed to be isolated for each other. Hence there is no exchange interaction among them and the alloy behaves paramagnetically. However, s-d interaction exists between cluster spins and conduction electrons.

(4) Referring to the original, Kondo's derivation,[3] the Kondo resistivity is given by

$$\rho_K=n\rho_0-n\rho_1\log_{10}T\ , \tag{2}$$

where ρ_0 is temperature independent, and hence the term $n\rho_0$ is a part of ρ_r

$$\rho_1=\rho_a\frac{3n_sJ^{sd}}{E_F}$$

and

$$\rho_a=\frac{3\pi m(J^{sd})^2S_{\rm cl}(S_{\rm cl}+1)}{2e^2E_FN\hbar}\ .$$

In these expressions, the symbols are defined in the usual manner. J^{sd} is the s-d exchange constant between spin cluster and conduction electrons, n_s is the average number of conduction electrons per atom, E_F, e, m^*, and $\hbar$ are the Fermi energy, the electronic charge, the effective mass of electrons, and the Planck constant, respectively. Thus Eq. (1) becomes

$$\rho(T)=\rho_r'+\rho_i(T)-n\rho_1\log_{10}T\ . \tag{3}$$

C. Numerical calculation of Kondo resistivity

1. The determination of ρ_0 and ρ_1

As stated previously, the lattice resistivity of either $Au_{80}Ni_{20}$ or a Au-Cu alloy with corresponding composition is used as the appropriate $\rho_i(T)$ of a $Au_{1-x}Ni_x$ alloy with $0.30\leq x\leq 0.42$. The experimental data of $\rho(T)-\rho_i(T)$ exhibits $-\log_{10}T$ behavior over a wide temperature range, indicated in Table I. From Eq. (3), ρ_r' and ρ_1 can be conveniently determined, shown in Table III. The values of $n\rho_0$ can be established from an analysis of ρ_r.

TABLE III. Parameters related to the Kondo resistivity.

x	ρ_r' ($\mu\Omega$ cm)	$n\rho_1$ ($\mu\Omega$ cm)	ρ_1 ($\mu\Omega$ cm)
0.30	22.128	0.0269	96.07
0.32	25.776	0.0354	76.62
0.35	28.110	0.1089	121.95
0.37	31.180	0.2078	156.24
0.40	33.268	0.5121	223.43
0.42	34.340	0.7454	233.45

2. The value of J^{sd}

To estimate the exchange constant J^{sd}, reasonable numbers have to be assigned to the parameters n_s, E_F, $S_{\rm cl}$, and m^*. The average size of the magnetic clusters in Au-Ni alloys is believed to be rather small because of the technique of quenching directly from the liquid state. For simplicity, the number of magnetic atoms in each spin cluster is assumed to be the same and $c=10$–20 is a proper choice. Again assuming each magnetic Ni atom has a spin of $\frac{1}{2}$, $S_{\rm cl}=5$–10. The number of conduction electrons per atom is ~ 1 for Au and is usually taken to be 0.6 for Ni.[25] The calculated values of n_s for Au-Ni alloys using the expression

$$n_s=(1-x)+0.6x\sum_{z=8}^{12} f(z)$$

are listed in Table II.

The E_F of pure Au is 5.51 eV, calculated from the free-electron model.[26] Due to the difference in potential used in the calculation, two values of E_F were obtained for Ni: 5.06 and 7.21 eV.[27] In a recent electronic-structure calculation E_F was given as ~ 7 eV for all Au-rich Au-Ni alloys.[28] In the present study $E_F=5.51$ eV is chosen, not so much because the E_F value of pure Au is favored, but rather it is a reasonable intermediate number when all factors are taken into consideration. Because of the proximity between the Fermi level and the d-band edge,[28] electrons involved in the s-d scattering are expected to have strong d admixture. Consequently, the electronic mass must be substantially different from the rest-mass value m_0, and $m^*/m_0=5$–10 is not deemed unreasonable.

Using the numbers outlined above, the J^{sd} values are calculated. Judging from the numbers, the case of $S_{\rm cl}=10$ and $m^*/m_0=10$ appears to be acceptable (see Table II). The result points to a trend that the J^{sd} value would be more reasonable when the average cluster spin is even larger.

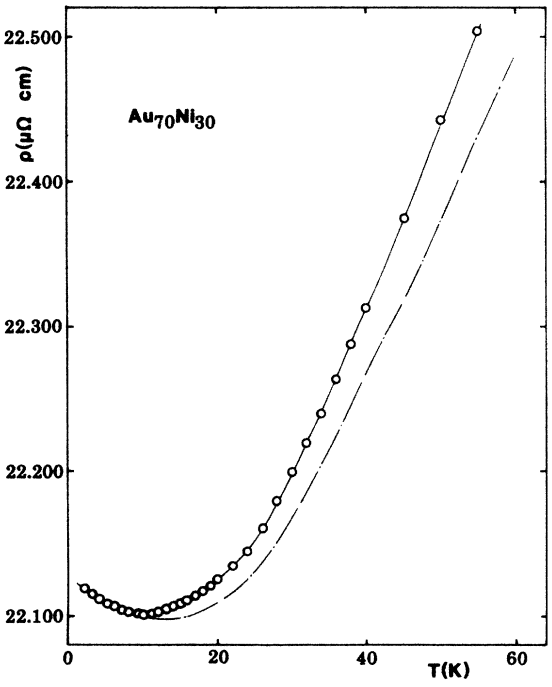

FIG. 4. Electrical resistivity of $Au_{70}Ni_{30}$. The open circles are experimental points. The dashed-dotted curve is calculated in terms of $\rho_i(T)=\rho_i(Au_{80}Ni_{20},T)$. The fitting using $\rho_i(T)=\rho_i(\text{Au-Cu},T)$ is very poor.

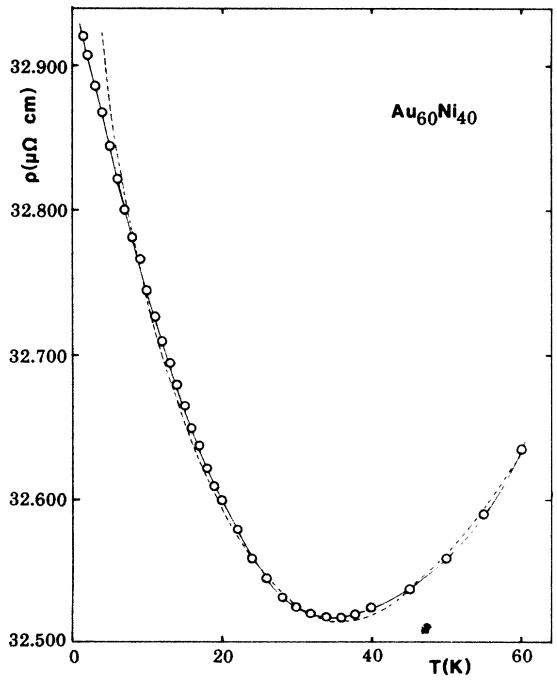

FIG. 5. Electrical resistivity of $Au_{60}Ni_{40}$. The open circles are experimental points. The dashed curve is calculated in terms of $\rho_i(T)=\rho_i(\text{Au-Cu},T)$.

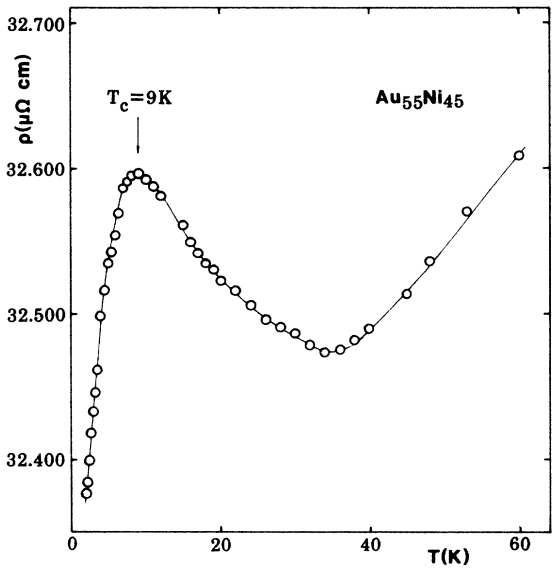

FIG. 6. Electrical resistivity of $Au_{55}Ni_{45}$. The arrow indicates the magnetically determined Curie temperature which is very close to the resistivity maximum at 9.0 K. This is the only case in the present study in which long-range ferromagnetic ordering and Kondo effect "coexisted."

3. *The "theoretical" curves of* $\rho(T)$

Using Eq. (3), the experimentally determined values of ρ_r' and ρ_1 and the $\rho_i(T)$ of either $Au_{80}Ni_{20}$ or a Au-Cu alloy with the appropriate composition, $\rho(T)$ can be calculated for all temperatures. However, because Kondo effect is basically a low-temperature phenomenon and the approximations are involved in writing Eq. (3), its validity is not expected much above $T_{\min}$. This is indeed the case. As shown in Figs. 4 and 5, the calculated $\rho(T)$ fit the experimental data very well up to ~ 60 K.

D. Competition between interactions

In the spin-cluster model for Au-Ni alloys, there are two fundamental electron-electron interactions: (1) the *s-d* interaction between localized *d* electrons in a spin cluster and the conduction electrons and (2) the *d-d* exchange among clusters. The effect of the *s-d* interaction on resistivity is predominantly at low temperature and is always overwhelmed by phonon scattering at moderate temperature. Its strength is not expected to change drastically as Ni content increases. On the other hand, the intercluster *d-d* exchange (DD) strongly depends on the Ni concentration. For $Au_{1-x}Ni_x$ with $0.30 \leq x \leq 0.42$, DD is weak and the clusters are allowed to behave independently. When the Ni content increases, the average size of spin clusters becomes larger and the distance separating them become shorter. When a critical composition is reached, the strength of DD increases to the level that neighboring clusters begin to align together, which leads to long-range ferromagnetic ordering. Very near the critical composition, the Curie point (T_c) is very low and the Kondo ef-

fect can exist at higher temperature. Figure 6 gives such an example in $Au_{55}Ni_{45}$. At still higher Ni concentration, T_c increases rapidly and the concept of "spin clusters" no longer is valid. Consequently, the Kondo effect is expected to disappear, and instead, the spin-disorder scattering becomes important in the paramagnetic state.

IV. CONCLUSION

The $\rho_i(T)$ of Au-Ni alloys can be reasonably approximated by either $\rho_i(T)$ of $Au_{80}Ni_{20}$ or that of a Au-Cu alloy with the corresponding composition. When this $\rho_i(T)$ is subtracted from the total $\rho(T)$, $\rho_M(T)$ is determined and is found to reveal $\log_{10}T$ dependence over a wide temperature range.

The observed resistivity minima in Au-Ni alloys with 30—42 at. % Ni can be understood through the Kondo *s-d* scattering mechanism. But instead of single isolated spins as in the original Kondo description, a model of dilute spin clusters is proposed. A similar analysis should be applicable in the understanding of resistivity minima in Cu-Ni alloys,[2] provided a suitable $\rho_i(T)$ can be approximated for Cu alloys.

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