PHYSICAL REVIEW B VOLUME 26, NUMBER 8 15 OCTOBER 1982

Electrical resistivity of Au-Ni alloys

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(Received 6 April 1982)

Electrical resistivities were measured for Au-Ni alloys containing 0–60 at. % Ni in the range of 1.5–300 K. Anomalous behaviors in the forms of low-temperature minima and "saturation" at higher temperature were observed. The current theories are not adequate to explain these anomalies satisfactorily.

I. INTRODUCTION

Owing to the well-established metallurgical similarities between the Cu-Ni and Au-Ni alloys systems,[1] the nearly identical behavior in their physical properties at corresponding compositions is no surprise. The electrical and magnetic properties of Cu-Ni alloys have been extensively investigated,[2] but except for our earlier work,[3–5] information concerning Au-Ni alloys has been rather sketchy.

As part of our continuous effort in the systematic study of Au-Ni alloys, we will report here on the experimental results of electrical resistivities of this alloy system. Similar to those of the Cu-Ni alloys, the temperature dependence of resisitivity appears to be anomalous.

II. EXPERIMENTAL PROCEDURES

The details of alloy preparation have been reported earlier.[4] High-purity starting material of Au (99.999% American Smelting and Refining Corporation) and Ni (99.999% Johnson, Matthey and Co.) were arc-melted in an ultrapure argon atmosphere. Alloy foils 30–75 μm thick and $\sim$25 mm in diameter were obtained using the piston-and-anvil arrangement for quick quenching from the liquid state. This technique was adopted not only for the purpose of effectively suppressing the miscibility gap in the Au-Ni alloy system, but also to produce random solid solutions with Ni atoms distributed nearly at the statistical level. Such expectation was confirmed in our earlier results that the average size of magnetic clusters was much smaller in Au-Ni alloys than that in Cu-Ni alloys of the corresponding Ni content.[5]

Resistivity specimens were cut from the quenched foils with typical dimensions of 15 mm length and 2 mm width. Throughout the specimen preparation, special care was taken to avoid any possible contamination of Fe, the level of which was extremely low ($\sim$3 ppm) in the meticulously chosen starting material.

All alloy compositions reported are nominal but should be accurate within 0.1%. Prior to resistivity measurements, all specimens were examined with the use of x-ray diffraction to ensure the alloy specimens being of single-phase material. The measured lattice constants also served as an independent check of the alloy compositions.

The resistivity measurements were made with a standard four-probe arrangement and an ac current source at a fixed frequency of 100 cps. The temperature range of the experiments was between 1.5 and 300 K. Two thermometers were used for temperature monitoring: a germanium sensor for the range 1.5–75 K and a platinum resistor for above 60 K. Because of the metastable nature of the solid solution retained by quenching no attempt was made to extend the resistivity measurements beyond room temperature. To determine the relative stability of the metastable solid solution, the temperature dependence of the resistivities of several representative specimens were remeasured after these specimens were kept at room temperature for 12–18 months. No detectable change was observed.

The amplitude of specimen current was of the order of 1 mA. The voltage reading had a precision of about 5×10^{-10} V. The single most important factor which affected the accuracy of the measurements was the determination of the specimen dimensions, in particular the thickness. The

widths of the specimens and the separations between the spring-loaded voltage contacts were determined with an optical microscope and were accurate within 0.1%. However, the thickness of the specimens was not completely uniform. In determining the resistivity, an average thickness calculated from values of a number of measurements across the specimen was used. The overall accuracy of the measurements was estimated to be within 1%.

III. EXPERIMENTAL RESULTS

The complete data of resistivity as a function of temperature $\rho(T)$ are plotted in Figs. 1—3. It is clear that, with increasing Ni content, $\rho(T)$ varies quite systematically.

Up to 10 at. % Ni, $\rho(T)$ behaves as expected from a common metal in that residual resistivity is clearly exhibited below 10 K, and $\rho(T)$ is practically linear from 80 K up to room temperature. From 20 at. % Ni on, the deviation from such linearity becomes more and more pronounced until a "saturation" is reached at 40—50 at. % Ni. For alloys with 30—45 at. % Ni, the low-temperature $\rho(T)$ is anomalous in the appearance of resistivity minimum. Above 45 at. % Ni, there occurs another type of anomaly in the form of discontinuous $d\rho/dT$, which closely resembles the resistivity characteristic of pure Ni near its Curie point.

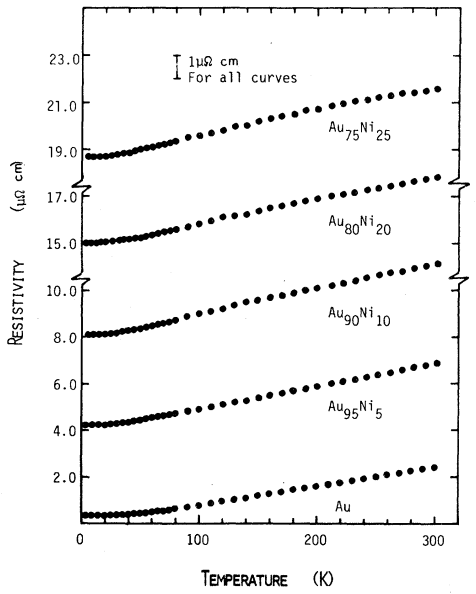

FIG. 1. Resistivity of Au-Ni alloys with less than 25 at. % Ni. The temperature dependence generally behaves like a "normal" metal.

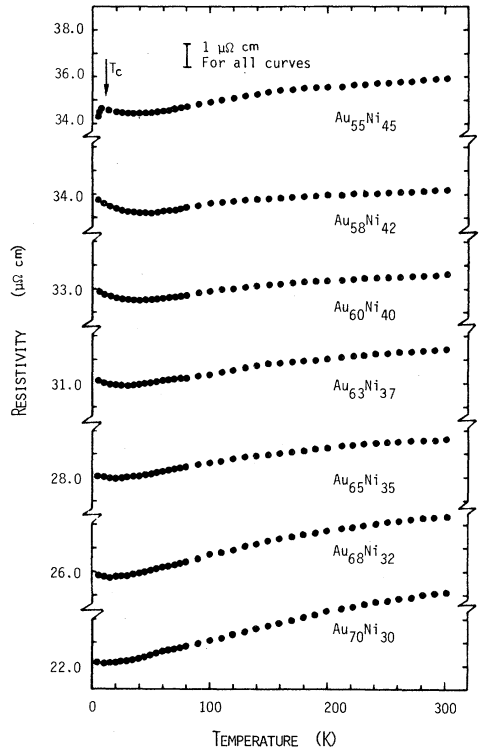

FIG. 2. Resistivity of Au-Ni alloys with 30—45 at. % Ni. Anomalous behaviors gradually appear: Minima exist at low temperatures and resistivity tends to "saturation" at higher temperatures.

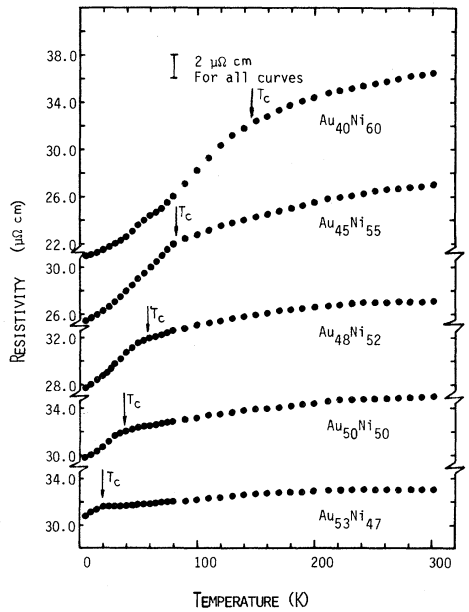

FIG. 3. Resistivity of Au-Ni alloys with 47 at. % Ni and beyond. The general behavior is "Ni-like": A change of slope occurs at or near the magnetically detected Curie temperature indicated by the arrows.

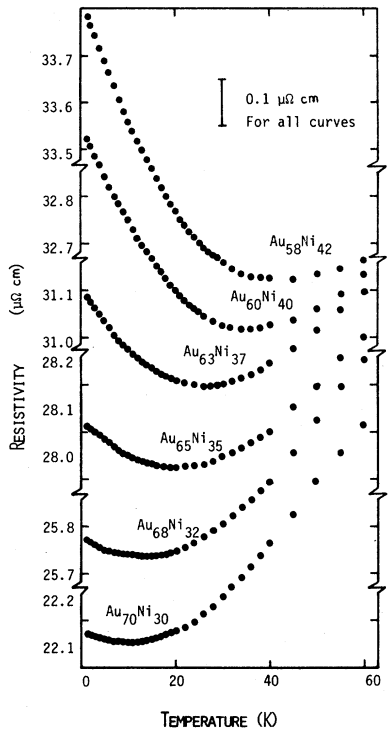

FIG. 4. Expanded view of the resistivity minima in the range of 30–42 at. % Ni.

IV. ANALYSIS AND DISCUSSION

Looking at the overall picture of the present data, the Au-Ni alloys can be divided into several regions. The resistivity in each region has its own distinct features, which can be correlated with the magnetic characteristics of the alloys. Up to 20 at. % Ni, the resistivity data indicate that the alloys behave as a "normal" metal. Above 42–45 at. % Ni, long-range ferromagnetic ordering sets in. The temperatures at which the discontinuities in $d\rho/dT$ occurred were unambiguously identified with the Curie points in our previous work.[3] Between 30 and 42 at. % Ni resistivity minimum appears for all alloys. The temperature ($T_{\min}$) and the depth of the minimum are composition dependent, as clearly depicted in Fig. 4. Since this region is sandwiched between a normal paramagnetic region and a ferromagnetic region, the resistivity minima would have to be of magnetic origin.

In analyzing the present resistivity data, we shall adopt a common practice by taking the Matthiessen rule as a first approximation. Thus the experimentally measured values of resistivity is expressed as the sum of three terms:

$$\rho(T)=\rho_0+\rho_i(T)+\rho_M(T)\ ,$$

where ρ_0 is the residual resistivity, $\rho_i(T)$ is the normal contribution due to phonon scattering, and $\rho_M(T)$ is of the magnetic origin. At low concentrations of Ni, we expect that

$$\rho_M(T)\simeq 0\ .$$

A. The residual resistivity

The part of ρ_0 can easily be separated. The results obtained by extrapolating the experimental data to $T=0$ are listed in Table I. For the purpose of comparison, the ρ_0 values of Au-Ni alloys together with the literature data of Cu-Ni alloys[6–10] and Ag-Pd alloys[10–12] are plotted in Fig. 5 as a function of $x(1-x)$, x being the Ni or Pd concentration. It is clear that for all these systems, the Nordheim rule[13] is obeyed only for alloys with $x<0.1$. Between $x=0.1$ and 0.5, the ρ_0 values are consistently higher than expected from the Nordheim rule, and increase monotonically with increasing Ni or Pd content. The similar behavior of ρ_0 of Au-Ni, Cu-Ni, and Ag-Pd alloys as shown in Fig. 5 simply confirms the fact that the basic physical mechanisms which contribute to ρ_0 are the same for all these alloy systems.

A further analysis reveals that ρ_0 values of these alloy systems can be normalized to fit a universal curve (Fig. 6). The normalizing factor is the extrapolated ρ_0 value of the individual alloy system at $x=0.5$ according to the Nordheim rule. This pro-

TABLE I. Residual resistivity of Au-Ni alloys.

x	$x(1-x)$	ρ_0 ($\mu\Omega$ cm)
0	0	0.3585
0.05	0.0475	4.216
0.10	0.09	8.153
0.20	0.16	15.00
0.25	0.1875	18.70
0.30	0.21	22.15
0.32	0.2176	25.78
0.35	0.2275	28.09
0.37	0.2331	31.12
0.40	0.24	33.00
0.42	0.2436	33.82
0.45	0.2475	32.27
0.47	0.2491	30.48
0.50	0.25	29.52
0.52	0.2496	27.65
0.55	0.2475	25.37
0.60	0.24	20.94

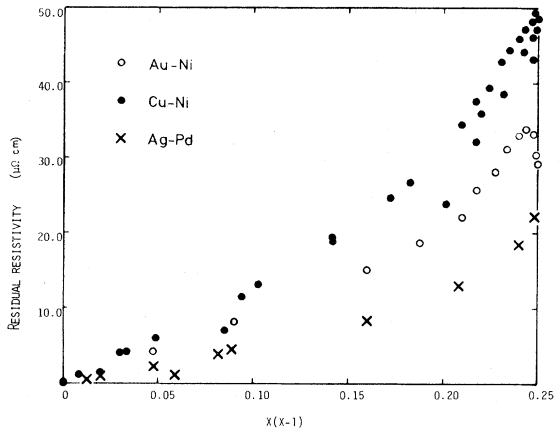

FIG. 5. Residual resistivities of Au-Ni, Cu-Ni (Refs. 6—10), and Ag-Pd (Refs. 10—12) alloys. The data scatter in Cu-Ni alloys is due to the fact that the values were taken from different authors.

cedure demonstrates that the appropriate expression for ρ_0 is

$$\rho_0=\rho_0(0)+Ax(1-x)+\Delta\rho_0 ,$$

in which only the coefficient A is alloy dependent. $\rho_0(0)$ is the residual resistivity of the noble-metal host which is usually very small. The deviation from the Nordheim rule, $\Delta\rho_0$, is the same for all three alloy systems after normalization. Coles and Taylor correctly assumed this condition in their analysis of the Ag-Pd data.[11]

B. Phonon scattering

The phonon contribution to the electrical resistivity of metals as well understood through the Grüneisen-Bloch theory.[14,15] If Ni were a simple metal it is expected that the temperature dependence of resistivity of the alloys would have followed the Grüneisen-Bloch relation closely. However, because of the incomplete d band of Ni, complexities develop in the resistivity of Au-Ni alloys in the form of high residual values, low-temperature minima, and "saturation" at moderate temperatures.

To delineate the phonon contribution from such complex ρ vs T relations appears to be a formidable task, particularly for alloys containing 30—45 at. % Ni. Efforts in estimating the phonon contribution are planned to be described in a forthcoming paper.

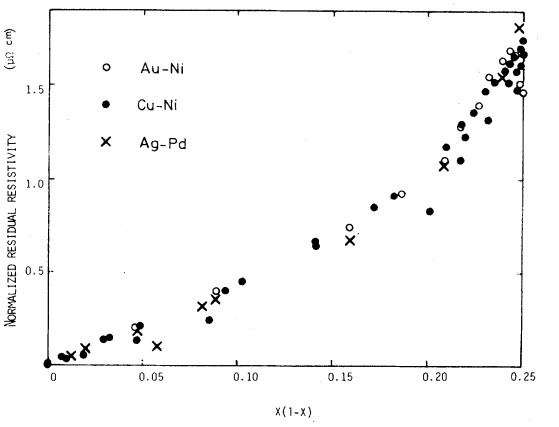

FIG. 6. Normalized residual resistivities of Au-Ni, Cu-Ni, and Ag-Pd alloys.

C. Resistivity minima

The occurrence of low-temperature resistivity minima in alloys with 30—45 at. % Ni, both $T_{\min}$ and the depth of the minimum increasing with Ni content (Fig. 4), is very intriguing. Whenever such data are observed, it is tempting and sometimes customary to interpret the results in terms of Kondo-related phenomena. As a matter of fact, the present data can be fitted nicely with a logarithmic dependence of temperature near the minimum. However, since the temperature regions involved are rather narrow, the log$T$ dependence cannot be taken as established. It must also be pointed out that low-temperature specific-heat anomalies observed in the same composition range[4] cannot be coincidental. Any appropriate explanation must account fully the resistivity minima as well as the specific-heat anomalies together.

Among the various theories giving provision of negative $d\rho/dT$, none seems to be adequate to explain satisfactorily the low-temperature resistivity minima of these alloys. On the other hand, since according to the x-ray diffraction patterns all the Au-Ni alloys are well crystallized and the absolute resistivity of the alloys is not nearly as high as amorphous metals, the minima are unlikely to be either of structural origin,[16] or due to a temperature-dependent Debye-Waller factor.[17] Also, according to the recent calculations[18] the contribution due to the mechanism of Fermi surface smearing of effective density of states,[11,19,20] is not sufficient to play an important role.

Viewing the Au-Ni system as a whole, with increasing Ni contents, the region of compositions in which low-temperature resistivity minima are observed is just prior to the onset of long-range ferromagnetic order. The phenomena of such resis-

tivity minima can also be easily interpreted as the precursor of ferromagnetic ordering. However, in view of the fact that, such minima also were observed in Ag-Pd and Au-Pd alloys[19,21] it seems more appropriate to seek a more generalized interpretation to encompass all these systems.

D. Saturation

Beginning with the alloy of 10 at. % Ni, the resistivity shows slight deviation from the linear temperature dependence near 300 K. With increasing Ni content, this deviation becomes more and more pronounced and extends further towards low temperatures, and a trend towards "saturation" can be clearly established. To explain this "saturation," it is tempting to invoke the model of mean free path being reduced to the order of lattice parameter.[22] However, this ultimate limit of mean free path is expected to be reached at rather high temperatures,[23,24] never near room temperature. Furthermore, for pure Au, there is no sign of serious deviation from linearity even near its melting point.[25] Therefore, it would be more appropriate to consider this phenomena again in a more generalized framework, such as *s-d* scattering. This point will be made abundantly clear in the planned forthcoming paper dealing with the phonon scattering.

E. Spin-disorder scattering

For alloys containing more than 45 at. % Ni, long-range ferromagnetic ordering occurs. The Curie temperatures were clearly correlated by the discontinuities in $d\rho/dT$. The rapid decreases of resistivity below T_c demonstrate the well-known mechanism of spin-disorder scattering. According to the established theory,[26,27] the contribution due to spin disorder gives rise to a T^2 dependence. However, such a temperature dependence was not demonstrated in the experimental results. Instead, the present data point to a T^n dependence with $n=1.5-1.7$. Such a temperature dependence may not be totally unexpected if the resistivity data of pure Ni are considered. For pure Ni, it is well established that the temperature dependence is stronger than T^2 in the low-temperature region.[28,29] However, at temperatures below the Curie point (150–600 K), a dependence of $T^{1.73}$ is clearly seen when the data are plotted.[30] Therefore, the possibility arises that the ρ-T relationship below Curie temperature of the ferromagnetic Au-Ni alloys in the present study and of pure Ni follows the same trend.

As a final remark, the resistivities of several representative specimens of Au-Ni alloys were remeasured after being kept at room temperatures for 12–18 months and no detectable change was observed. This observation is in strong contrast with the Cu-Ni alloys.[6] The underlying reason why the quench-retained solid solution in Au-Ni alloys is more stable than the corresponding Cu-Ni alloys at room temperature remains to be explained.

ACKNOWLEDGMENTS

The authors are indebted to Professor W. L. Johnson for the use of fast-quenching facilities in his laboratories. This research was supported by NSF Grant No. DMR-8108421.

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