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# Mössbauer-effect study of $^{57}$Co-doped Ni-Au alloys

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We have carried out Mössbauer-effect studies on $^{57}$Co-doped $Ni_{1-x}Au_x$ alloys in the concentration range $0 \leq x \leq 0.6$. On quenching from 880°C, alloys up to 20-at.% Au are retained in their atomically disordered states, whereas between 30- and 60-at.% Au there is a precipitation into nickel-rich and gold-rich clusters. The cobalt impurity atoms tend to go preferentially to nickel-rich clusters and not to gold-rich clusters. The average hyperfine field at the $^{57}$Fe site does not change with Au concentration up to 30-at.% Au in contrast to the average magnetization which reduces rapidly with increasing Au concentration. The isomer shift increases smoothly as a function of Au concentration.

## I. INTRODUCTION

The nickel-gold system is interesting from the viewpoint of its magnetic as well as metallurgical properties. The addition of a noble metal like gold or copper to nickel results in a reduction of average magnetization which is faster than what is expected from a simple dilution law.[1,2] From a value of $0.6\mu_B$ in pure nickel the average magnetization reduces almost linearly to zero near 60-at.% Au or Cu. The Ni-Cu system has been investigated extensively by neutron diffraction,[3] specific heat,[4] resistivity,[5] and Mössbauer-effect[6] studies. Clinton *et al.*[7] have carried out electrical-resistivity and magnetization measurements on splat-quenched Ni-Au alloys and compared their results with those on Ni-Cu alloys. It is found that the two systems behave differently in the concentration range 35–55-at.% Ni. For the Ni-Cu alloys, resistance anomalies were observed which could not be correlated with bulk Curie temperatures.[8] These anomalies were associated with the presence of clustering effects.[9] For the Ni-Au alloys, however, the resistance maxima could be correlated with Curie temperature and it was thus concluded that the splat-quenched Ni-Au alloys were obtained as random solid solutions.

The phase diagram of the Ni-Au alloy system[10] shows that above 840 °C there exists a single face-centered cubic phase for all alloy compositions. Beyond 8-at.% Ni in Au there is a precipitation into gold-rich ($\alpha_1$) and nickel-rich ($\alpha_2$) phases below 800 °C. The thermodynamic properties of this system have been summarized by Averbach *et al.*[11,12] The heat of mixing is found to be positive and according to quasichemical theory,[13] an atomic configuration with like-nearest-neighbors is preferred. This results in a precipitation into gold-rich and nickel-rich clusters upon cooling. The boundaries of the precipitation region have been determined by Mössbauer[14] and x-ray diffraction studies.[15]

We have carried out Mössbauer-effect studies on $^{57}$Co-doped $Ni_{1-x}Au_x$ alloys in the concentration range $0 \leq x \leq 0.6$. The variation of hyperfine field and isomer shift has been studied as a function of alloy composition and the precipitation behavior of the alloys is examined for various heat treatments.

## II. SAMPLE PREPARATION

Alloy samples were prepared by melting requisite quantities of 99.99%-purity gold and nickel sponge in a high-vacuum resistance furnace. The weight after melting was found to be within 2% of the initial weight for each of the samples. Alloys were made of the composition $Ni_{1-x}Au_x$ for $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6. The samples were homogenized in vacuum at a temperature of 960 °C for a period of 60 h. The homogenized pellets were then pressed and rolled into foils of about 60–80-$\mu$m thickness.

$^{57}$Co activity was deposited on 1-cm$^2$ platelets of the samples as follows: A small region of about 2-mm diam at the center of the plates was roughened by grinding with emery paper. After washing with dilute HCl to remove surface contamination with grease, etc., about 0.5 mCi of carrier-free $^{57}CoCl_2$ activity was placed in the roughened area and evaporated to dryness under an infrared lamp. The chloride was reduced to metallic cobalt with dry hydrogen gas at 850 °C. The activity was subsequently diffused into the samples by annealing at 850 °C under an hydrogen atmosphere for 4 h. Dry and oxygen-free hydrogen was kept continuously flowing in order to ensure proper reduction of the chloride and to prevent oxidation of the samples.

Mössbauer spectra were recorded after subjecting the alloy samples to various heat treatments. These are referred to by (a), (b), (c), (d), (e) and are described: (a) This refers to the spectra taken immediately after the $^{57}$Co activity was diffused at 850 °C and the samples were cooled to room temperature. (b) The samples were disordered by heating at 880 °C for 1 h and then quenched into liquid nitrogen (cf. phase diagram, Ref. 10). (c) The samples were aged at 200 °C for 60 h and furnace cooled. (d) The samples were annealed in the two-phase region at 350 °C for 60 h and cooled. (e) The samples were annealed at 500 °C for 5 days and furnace cooled.

All heat treatments were carried out in a vacuum furnace where the pressure was maintained at $10^{-5}$ Torr and the temperature maintained to within ±5 °C using a commercial temperature controller.[16] The spectra were obtained using a $^{57}$Fe-enriched stainless-steel absorber in transmission geometry.

## III. EXPERIMENTAL RESULTS

### A. Mössbauer spectra of quenched alloys

Figure 1 shows the room-temperature Mössbauer spectra for the slowly cooled samples [heat treatment (a)]. We see that the hyperfine field is only weakly dependent on composition in the 0–50-at. % Au concentration range. As we shall see later, this heat treatment corresponds to extensive clustering and the hyperfine field observed is not due to the random distribution of components but due to clustering of nickel-rich regions.

Figure 2 shows the room-temperature Mössbauer spectra of $Ni_{0.50}Au_{0.50}$ alloy sample which was quenched from 880 °C after various periods of time. This was done in order to determine the

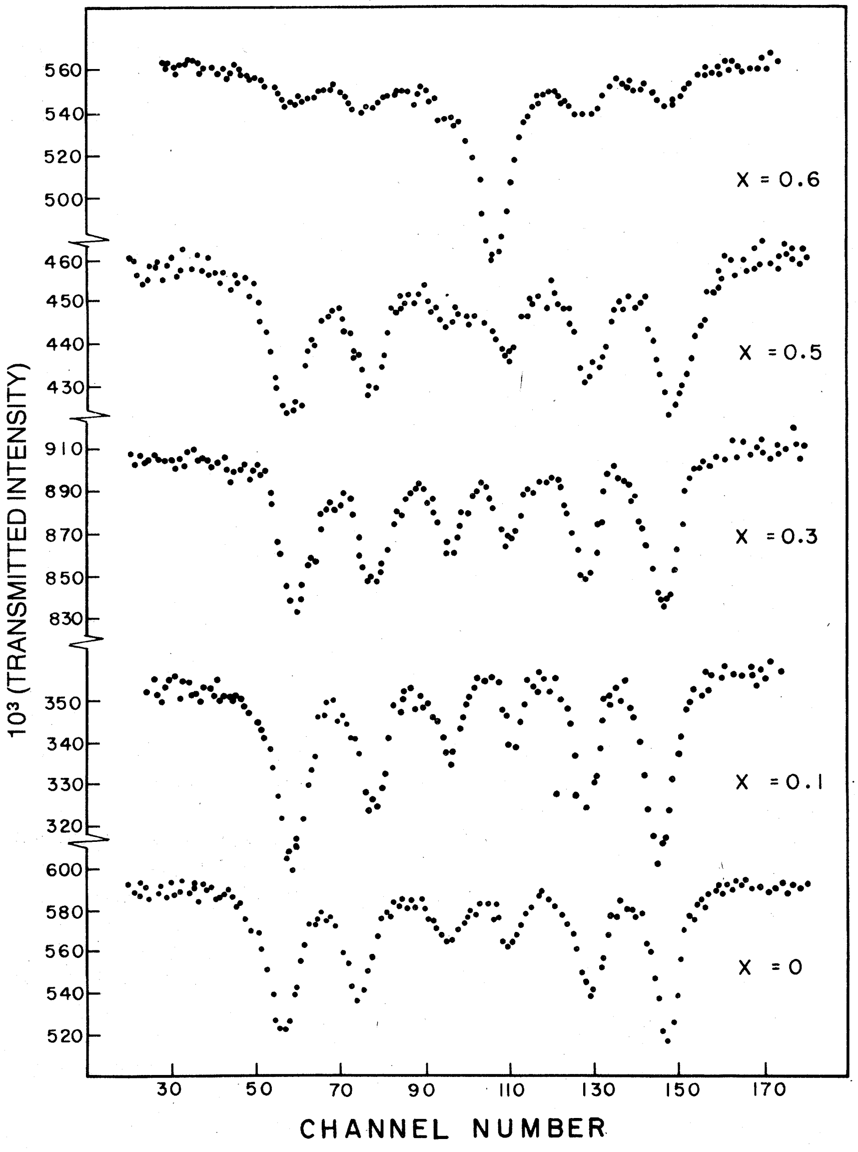

FIG. 1. Mössbauer spectra of $^{57}$Co-doped $Ni_{1-x}Au_x$ alloys furnace cooled from 850 °C after source preparation.

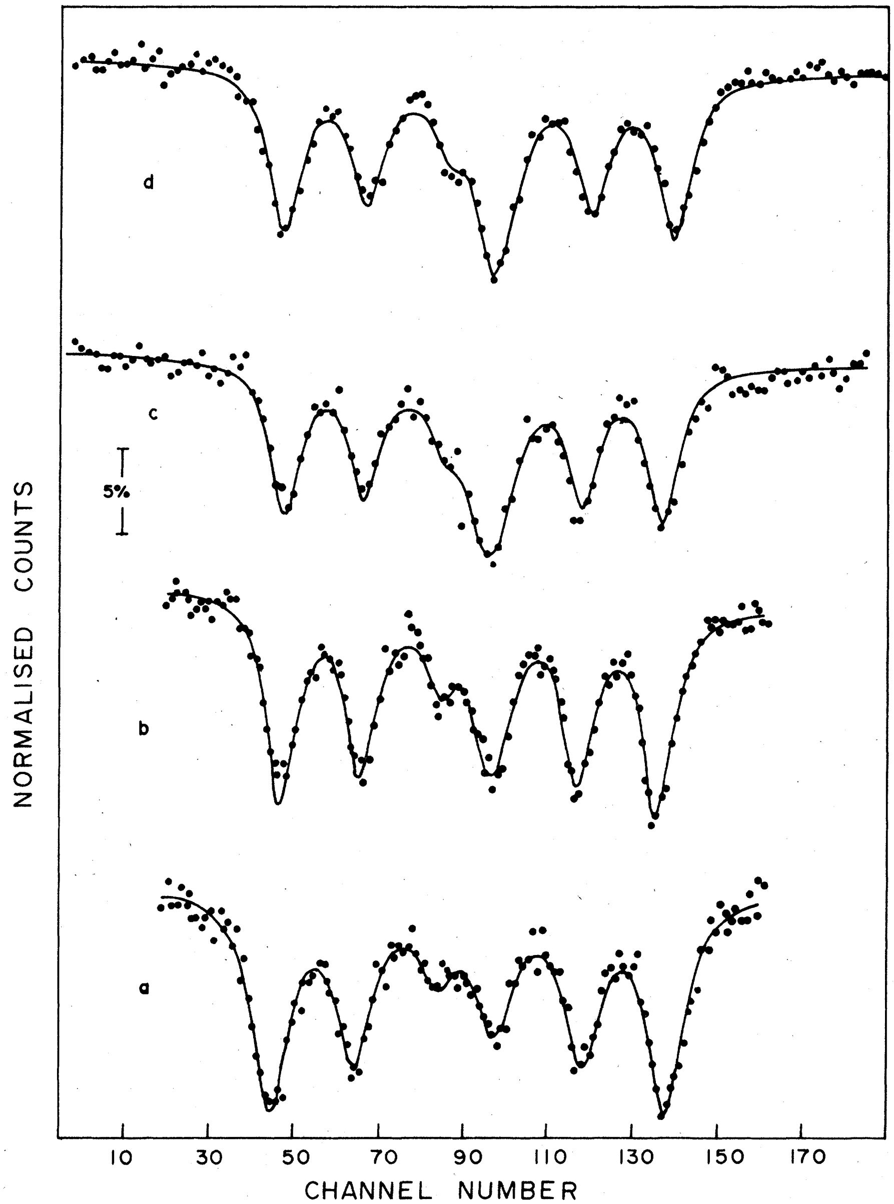

FIG. 2. Mössbauer spectra for $Ni_{0.5}Au_{0.5}$ alloy quenched from 880 °C after various periods of time: (a) furnace cooled; (b) quenched after 30 min; (c) quenched after 60 min; (d) quenched after 75 min.

time necessary to equilibrate the high-temperature state before quenching. The Curie temperature for an alloy of this composition is much below room temperature[7] and the atomically disordered state corresponding to this composition should give rise to a paramagnetic single line at room temperature. As seen in Fig. 2 the slowly cooled sample [heat treatment (a)] shows only 7% absorption in the paramagnetic phase. When quenched after keeping at 880 °C for 30 min the absorption in the central line increases to 12%. After 60 min this remains the same. Thus it was determined that the time necessary to equilibrate the high temperature state is 60 min and all the subsequent alloys were quenched from 880 °C after maintaining them at this temperature for a period of 60 min.

Figure 3 shows the 300-K spectra for quenched alloys [heat treatment (b)] corresponding to Au concentrations of 0, 10 and 20 at.%. There is a single-phase hyperfine-field-split spectrum for the three concentrations. These have been fitted to a six-line pattern resulting from a single field value. The widths of all six lines have been constrained to be equal and the line intensities constrained to $1{:}X{:}3$. The hyperfine-field and isomer-shift values are obtained from these fits.

Mössbauer spectra of quenched $Ni_{1-x}Au_x$ alloys

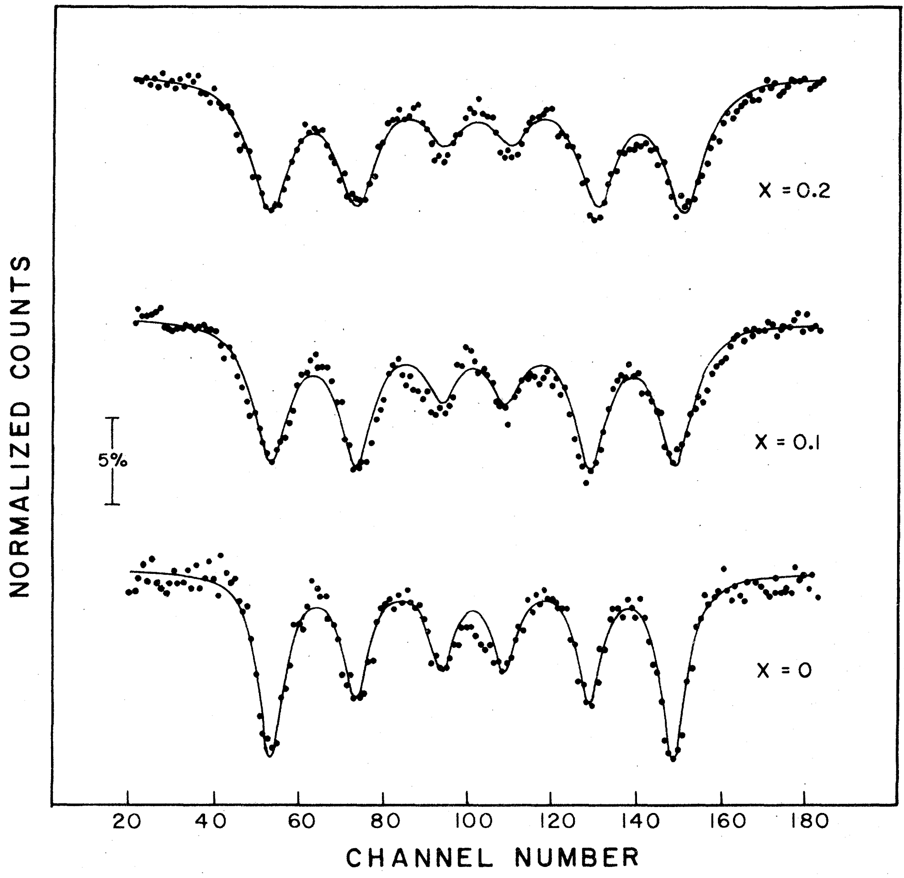

FIG. 3. 300-K Mössbauer spectra of quenched $Ni_{1-x}Au_x$ alloys [heat treatment (b)] for $x=0$, 0.1, and 0.2 alloy compositions. The spectra are fitted to a hyperfine-field-split six-line pattern.

for $x=0.3$, 0.4, 0.5, and 0.6 at 300 K are shown in Fig. 4. All spectra in this concentration range show a paramagnetic line near zero velocity together with a hyperfine-split six-line pattern. The Curie temperature for these alloys[7] lies below 300 K and therefore one should observe a single-line spectrum at room temperature. The presence of high-field components which correspond to $^{57}$Fe hyperfine field in nickel metal shows that it has not been possible to retain the disordered phase on quenching from 880 °C. The equilibrium temperature corresponding to the atomic configuration which is retained in the system by this quenching thus lies in the two-phase region of the phase diagram. It is not possible to quench from a still higher temperature because there is a "safe" range of only about 100 °C between the liquidus (temperature above which melting starts) and the miscibility curve (temperature below which precipitation starts). Raising the sample temperature to 1000 °C before quenching (which was tried for one sample) resulted in diffusion of the $^{57}$Co activity deep inside the sample.

To compute the ratio of the two phases, the spectra were fitted to two sets of lines:

(i) A six-line pattern was fitted to the high-field component. The widths of all the six lines were constrained to be equal and the intensity ratios constrained to 3 : 2 : 1 :: 1 : 2 : 3. Later the intensity ratios were also permitted to be variable.

(ii) The paramagnetic phase near zero velocity was fitted to a single line with position, width, and intensity kept as free parameters. From the fitted width and intensities the areas under the absorption curves for the two components were calculated. The relative fraction of the two phases was then obtained after applying $f$-factor corrections as discussed in Sec. IV.

Figure 5 shows the 80-K spectra for the quenched 30-60-at. % Au alloys. The $Ni_{0.7}Au_{0.3}$ spectrum splits into a six-line pattern whereas the paramagnetic phase of $Ni_{0.6}Au_{0.4}$ still remains a single line but slightly broadened compared to that at 300 K. The Curie temperatures of the 50- and 60-at. % Au alloys are below 80 K and the paramagnetic line neither broadens nor splits at 80 K.

### B. Temperature dependence of Mössbauer spectra

The temperature dependence of Mössbauer spectra for clustered $Ni_{0.7}Au_{0.3}$ alloy [heat treatment (a)] was investigated in the temperature range

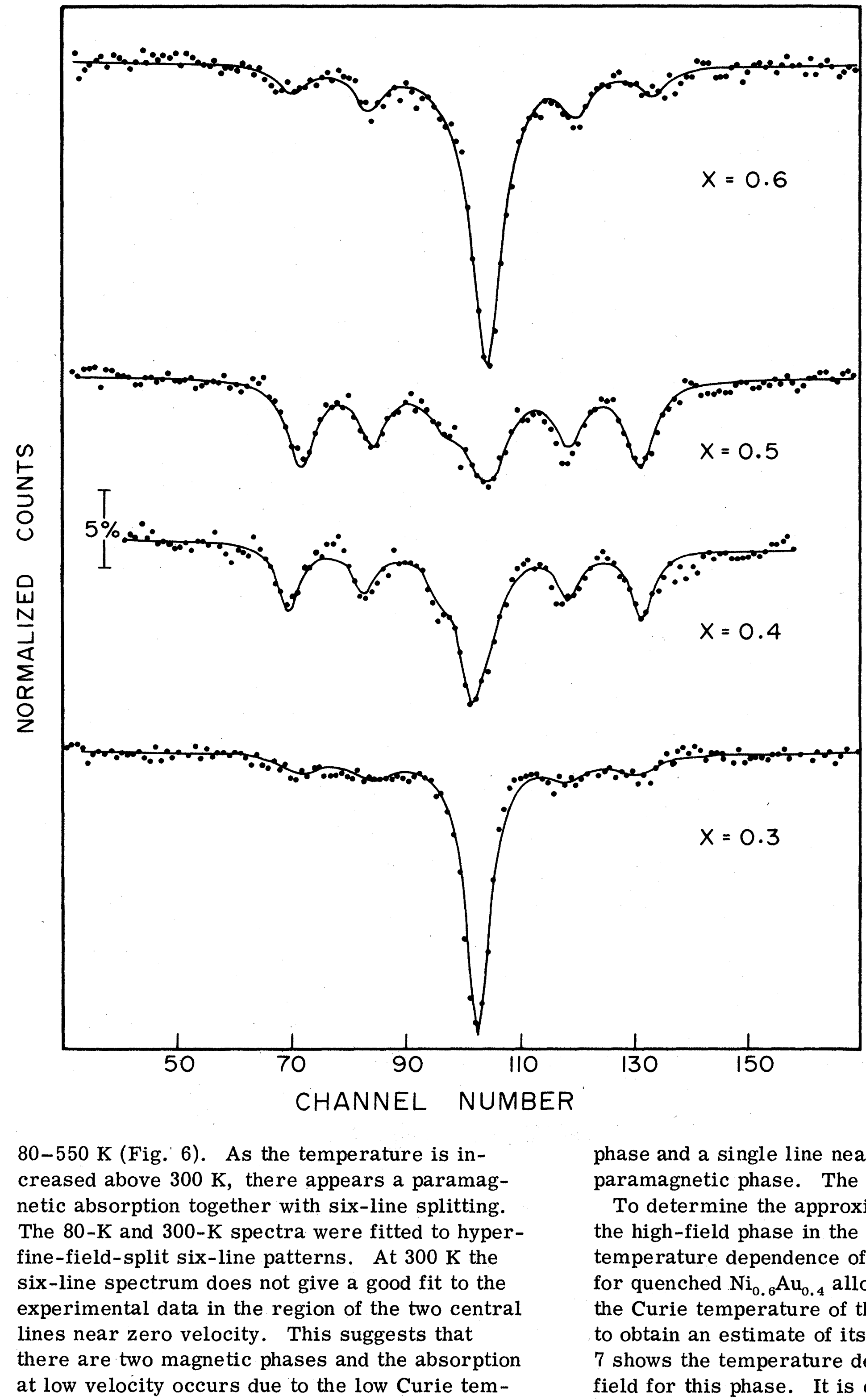

FIG. 4. Mössbauer spectra of quenched $Ni_{1-x}Au_x$ alloys [heat treatment (b)] at 300 K.

80–550 K (Fig. 6). As the temperature is increased above 300 K, there appears a paramagnetic absorption together with six-line splitting. The 80-K and 300-K spectra were fitted to hyperfine-field-split six-line patterns. At 300 K the six-line spectrum does not give a good fit to the experimental data in the region of the two central lines near zero velocity. This suggests that there are two magnetic phases and the absorption at low velocity occurs due to the low Curie temperature phase approaching it Curie point. The spectra above 300 K were fitted to two components, viz., a six-line pattern for the ferromagnetic phase and a single line near zero velocity for the paramagnetic phase. The fits are shown in Fig. 6.

To determine the approximate composition of the high-field phase in the quenched alloys, the temperature dependence of Mössbauer spectra for quenched $Ni_{0.6}Au_{0.4}$ alloy was studied. From the Curie temperature of this phase it is possible to obtain an estimate of its composition. Figure 7 shows the temperature dependence of hyperfine field for this phase. It is compared with the temperature dependence of hyperfine field at $^{57}$Fe in a nickel matrix. At 600 ± 10 K the field reduces to zero as compared to 630 K for pure nickel. From

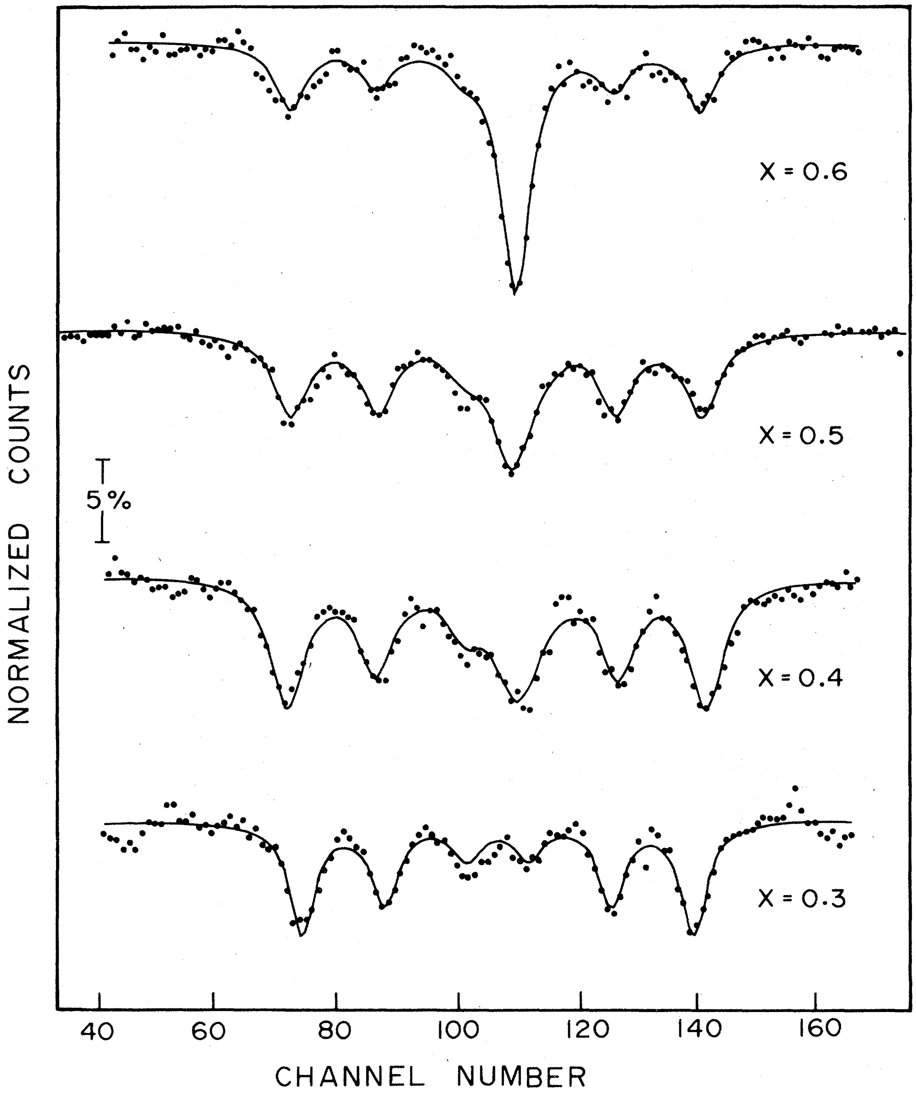

FIG. 5. Mössbauer spectra for quenched $Ni_{1-x}Au_x$ alloys at 80 K. The spectra for $x = 0.4$, 0.5, and 0.6 alloy compositions have been fitted to two sets of lines: a hyperfine-field-split six-line pattern and a single paramagnetic line.

magnetization studies of Clinton *et al.*[7] this value of $T_c$ corresponds to a 96–98-at.% Ni-Au alloy. It can thus be concluded that this phase is comprised of nickel-rich clusters.

In the discussion that follows we will associate the central paramagnetic line near zero velocity with the atomically disordered phase ($0.3 \leq x \leq 0.6$) and the six-line splitting with nickel-rich clusters. One would expect that precipitation of nickel-rich regions should also give rise to gold-rich regions and there should be absorption in the central paramagnetic line due to gold-rich clusters. The isomer-shift data of Howard *et al.*[14] (Fig. 9) show that gold-rich clusters would give rise to a paramagnetic absorption near 0.64 mm/sec. However, the isomer shifts for the paramagnetic lines of our spectra vary from 0.08 to 0.47 mm/sec.

## IV. DISCUSSION

The hyperfine field at $^{57}Fe$ in $Ni_{1-x}Au_x$ as a function of Au concentration ($x$) is shown in Fig. 8. The average magnetization data of Clinton *et al.*[7] are also shown after multiplying by an arbitrary constant, such that the magnetic moment of pure nickel corresponds to the observed hyperfine field at $^{57}Fe$ in Ni. The change in hyperfine field is small compared to the change in average magnetic moment. A similar result is obtained in studies on other nickel-based alloy systems like Ni-Mn,[17,18] Ni-Cu,[19] and Ni-Pt.[20]

Figure 9 shows the isomer-shift behavior. A comparison is made with the earlier data of Howard *et al.*[14] and the two sets of data agree well with each other. The observed behavior is also

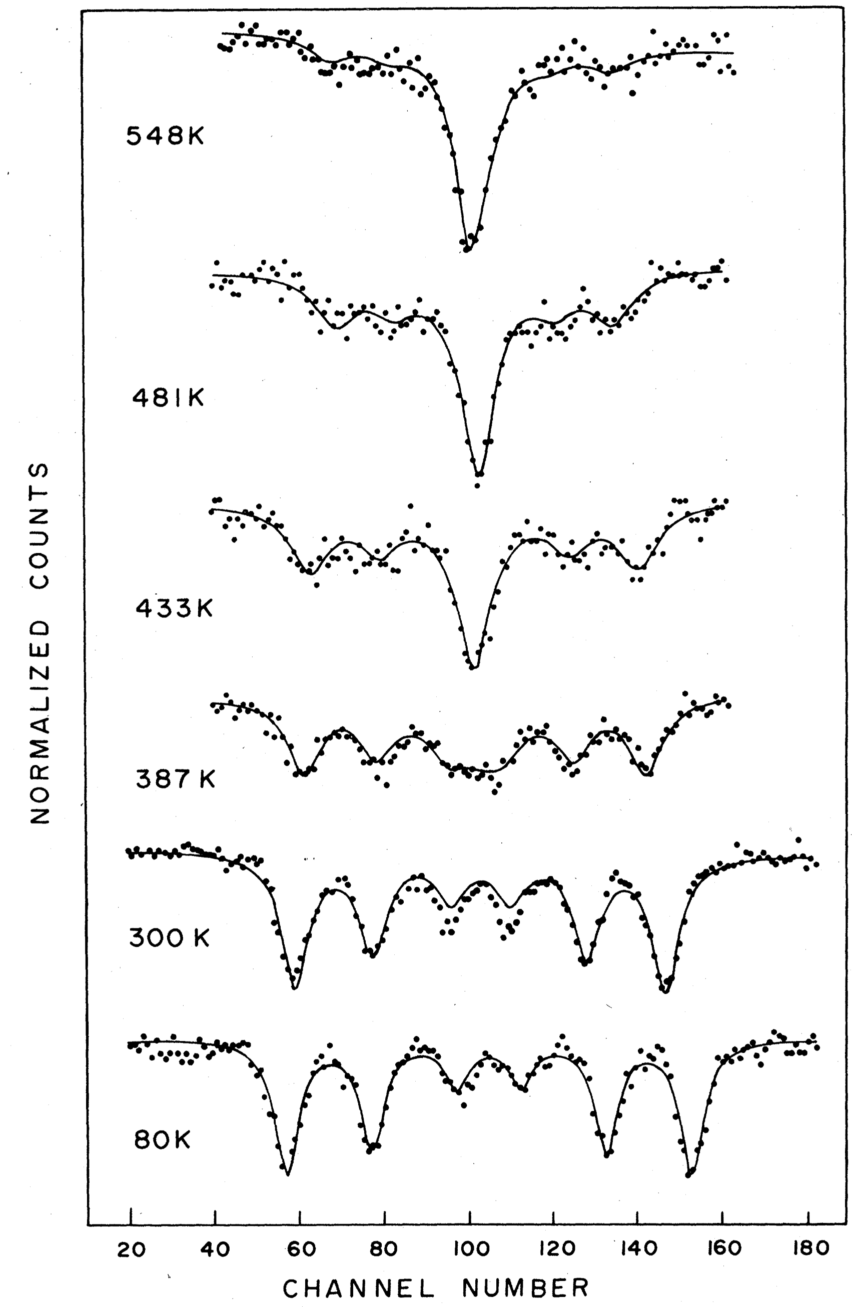

FIG. 6. Temperature dependence of Mössbauer spectra for $Ni_{0.7}Au_{0.3}$ alloy [heat treatment (a)]. The 80- and 300-K spectra have been fitted to a hyperfine-field-split six-line pattern. Beyond 300 K a zero field phase giving rise to a paramagnetic absorption line is also introduced in the fits.

qualitatively similar to that of $^{57}$Fe in the Ni-Cu system.[6]

A quantitative understanding of the precipitation behavior of the alloy system can be obtained from the Mössbauer spectra if due account is taken of the fact that the recoil-free fractions of the precipitated phases could be appreciably different. The relative concentration of the nickel-rich phase is given by[21]

$$r=\frac{A_1}{A_1+A_2 f_1/f_2},$$

where $A_1$, $f_1$ denote the area under the absorption curve and recoil-free fraction of the nickel-rich phase and $A_2$, $f_2$, the respective quantities for the nickel-poor phase. The $f$ factors are calculated in the Debye approximation,[22] where the Debye temperatures used are extrapolated from data on Debye temperatures available in the higher Au concentration region.[23] An additional correction arising due to the difference in host-host and host-impurity coupling constants[24] has not been considered. Within these approximations the calcu-

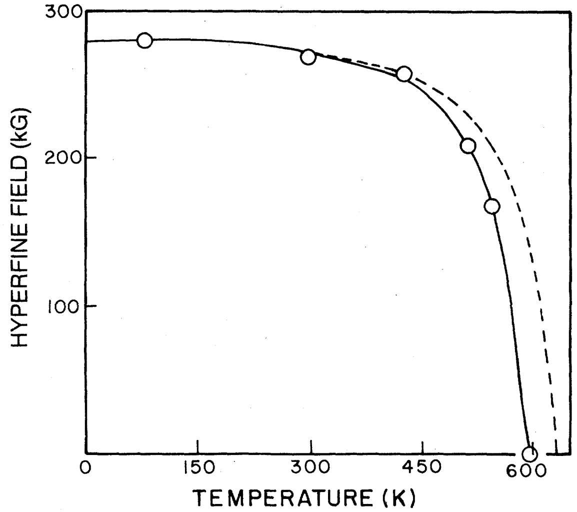

FIG. 7. Temperature dependence of hyperfine field for the high-field phase of the quenched $Ni_{0.6}Au_{0.4}$ alloy. The dashed line shows the hyperfine-field temperature dependence for $^{57}Fe$ in nickel (Ref. 28).

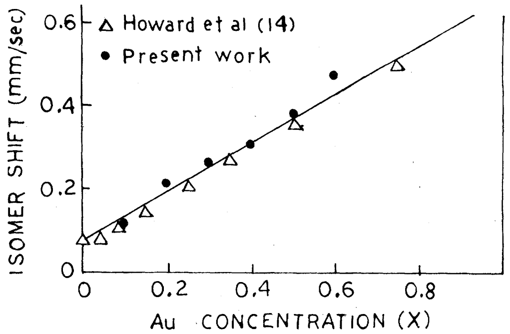

FIG. 9. Variation of isomer shift with Au concentration ($x$). The data of Howard *et al.* (Ref. 14) are also shown for comparison.

lated values of $r$ from the spectra of samples with heat treatment (b) are shown in Fig. 10. One finds a maximum precipitation is the nearly equiatomic region which is consistent with other thermodynamic properties of the system,[10-12] mainly positive heat of mixing which is maximum in the region of the 50-50 alloy composition.

For systems with a positive heat of mixing the two types of precipitation processes, viz., homogeneous nucleation and growth process and the spinodal decomposition process would give rise to different behaviors of Mössbauer spectra. In the first process the Mössbauer absorption due to the final equilibrium precipitate (or near to the final) would exist very early in the process and then increase in amount at the expense of the matrix when sufficient activation energy is provided. In spinodal decomposition, on the other hand, the composition continually changes and the Mössbauer spectra should show a gradual change in isomer shift and hyperfine field.[25] In the Au-Ni alloys the critical temperature for spinodal decomposition is well below the chemical decomposition temperature. Woodilla and Averbach[26] determined the maximum in the spinodal curve at 45-at.% Ni and 220 °C by observing satellite lines near the fundamental peaks in electron diffraction photographs. The time required to observe these modulated structures varied between 1 and 17 h, depending upon annealing temperatures and compo-

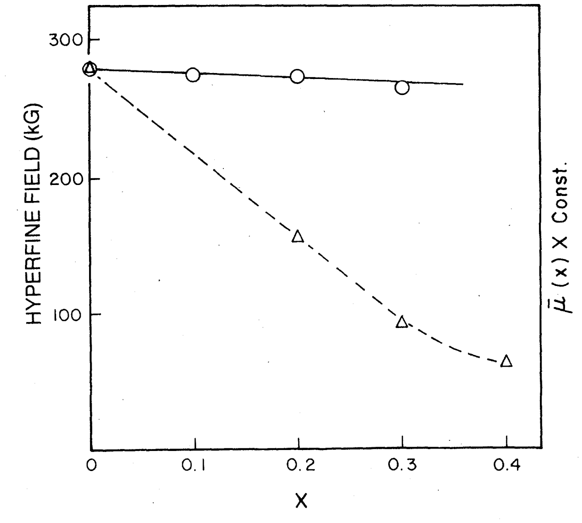

FIG. 8. Average hyperfine field at $^{57}Fe$ in $Ni_{1-x}Au_x$ alloys as a function of alloy concentration (circular data points). Average magnetization data (Ref. 7) is shown after multiplying with an arbitrary constant (triangular points).

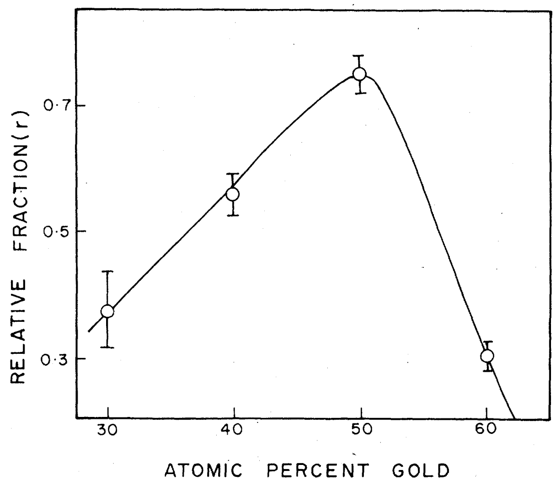

FIG. 10. Relative fraction of the nickel-rich phase ($r$) for $Ni_{1-x}Au_x$ alloys ($0.3 \leq x \leq 0.6$) quenched from 880 °C.

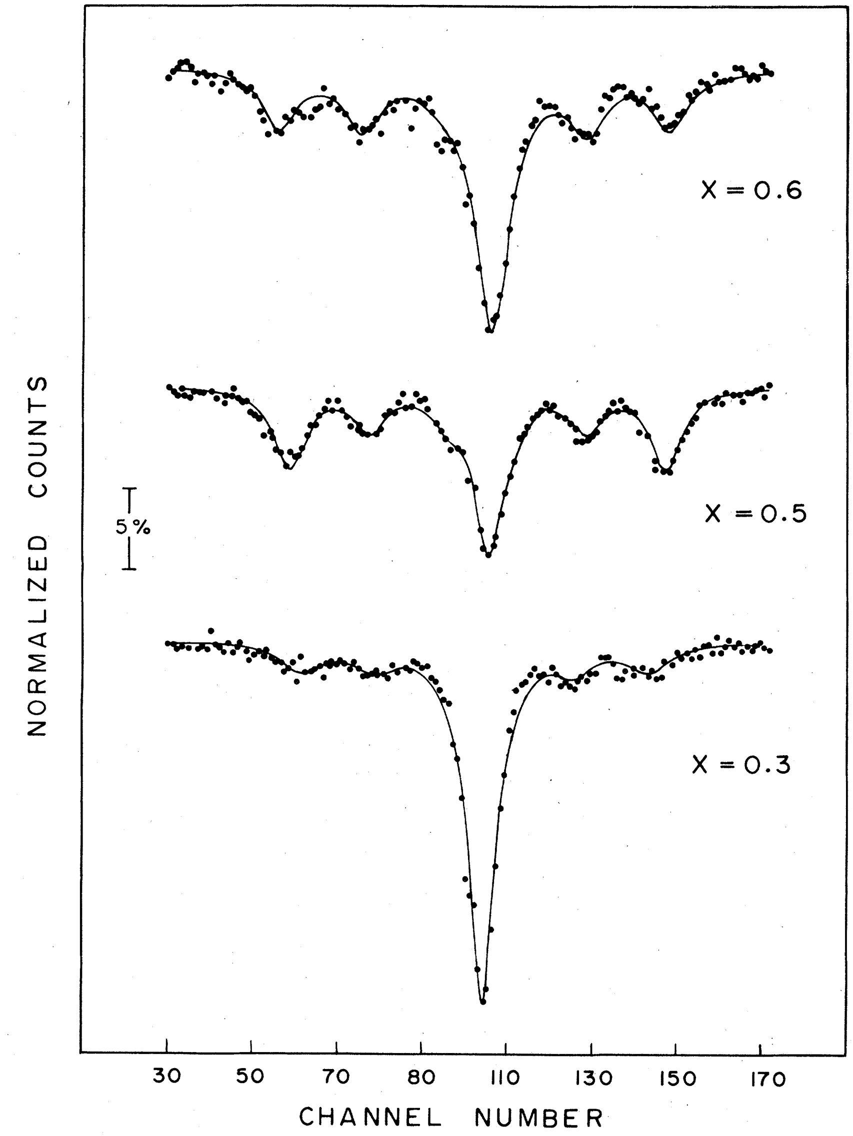

FIG. 11. Room-temperature Mössbauer spectra for 30, 50, and 60 at. % Au alloys aged at 200° C for 60 h [heat treatment (c)].

sition. Our Mössbauer spectra for alloys aged at 200 °C for 60 h (Fig. 11) show no change in the spectra, i.e., no intermediate phases were developed. Also in the Cu-Ni-Fe system Mössbauer studies[25] did not detect any composition fluctuations although x-ray and electron diffraction studies showed strong evidence for modulated structures. This discrepancy is not yet cleared up. However, Butler and Thomas[27] have given evidence of a rapid decomposition during the quench so that even the as-quenched alloys in Mössbauer study may have been well beyond the early stages of the decomposition. We also recorded Mössbauer spectra for $Ni_{0.6}Au_{0.4}$ quenched alloy after aging at room temperature for various periods of time. But after as long as 200 h no observable change in spectra were detected. To observe the precipitation behavior at higher temperature, viz., in the two-phase regions of the phase diagram, the alloys were annealed at 350 °C for 60 h [heat treatment (d)]. This resulted in an appreciable formation of the nickel-rich clusters for 30-, 40-, and 50-at.% Au alloys (Fig. 12). There was no appreciable change for the 60-at.% Au alloy. This sample was annealed at a higher temperature of 550 °C [heat treatment (e)] after which the nickel-rich phase was completely formed.

## V. CONCLUSIONS

From our Mössbauer-effect studies on $^{57}$Co doped $Ni_{1-x}Au_x$ alloys ($0 \leq x \leq 0.6$) presented here we can draw the following conclusions:

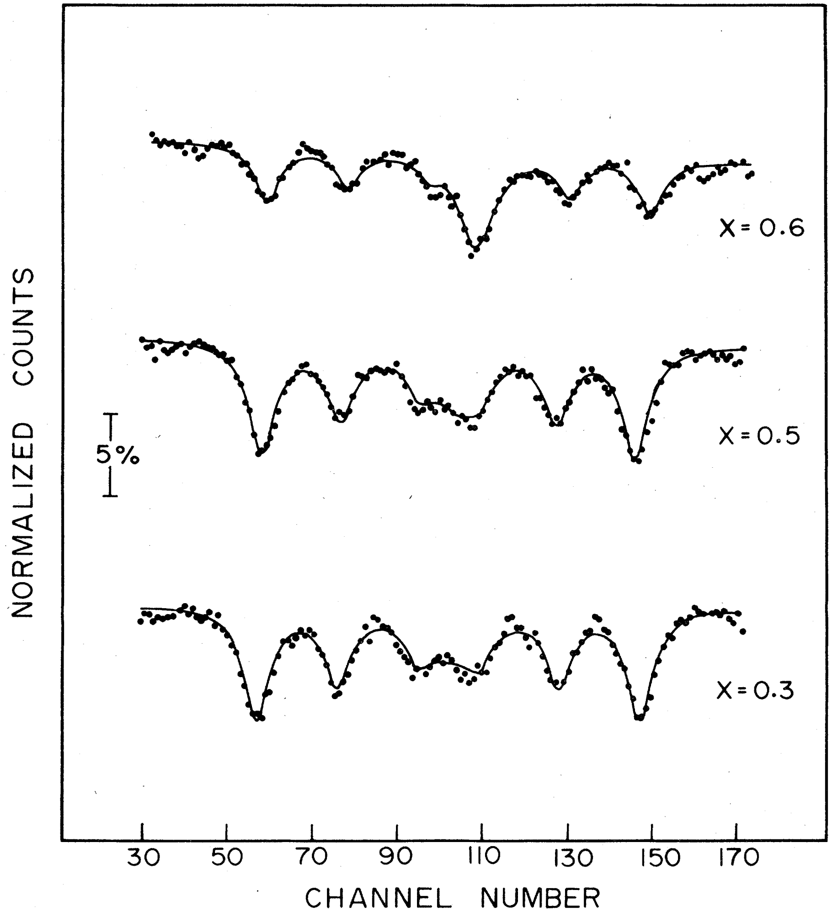

FIG. 12. Mössbauer spectra at 300 K for $Ni_{1-x}Au_x$ alloys annealed at 350 °C for 60 h [heat treatment (d)].

(i) Alloys with Au concentration between 0 and 20 at.% can be retained in their atomically disordered states by quenching from a temperature above 880 °C. Between 30- and 60-at.% Au the alloys precipitate into gold-rich and nickel-rich clusters.

(ii) The average hyperfine field at an $^{57}$Fe site does not change appreciably with alloy concentration in contrast to the average magnetization.

(iii) The average isomer shift increases as a function of gold concentration.

(iv) The Fe impurity atoms show a selective preference for Fe-Ni clustering. This is borne out by the fact that the Mössbauer spectra show the presence of magnetic phases which can be associated with nickel-rich clusters. Even on annealing in the two-phase regions, where the alloys are definitely seen to decompose into gold-rich and nickel-rich phases by electron diffraction studies, the iron impurity atoms go selectively to nickel-rich clusters.

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