PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 5, NO. 12 15 JUNE 1972

Matrix and Impurity-Cluster Polarization in Ni-Pt and Ni-Pd Alloys*

W. A. Ferrando† and R. Segnan
American University, Washington, D. C. 20016
and
A. I. Schindler
Naval Research Laboratory, Washington, D. C. 20390

(Received 14 October 1971)

A study of hyperfine magnetic fields at nuclei of ^{57}Fe diffused as impurities in the transition-metal alloys Ni-Pt and Ni-Pd and at nuclei of ^{61}Ni in the Ni-Pt system has been carried out using the Mössbauer-effect technique. The fields were measured as a function of composition and temperature on the atomically disordered alloys. The experimentally determined Curie temperatures T_C and saturation hyperfine fields are presented for the entire composition range of each system. Analysis of the Mössbauer spectra of specific samples for various diffusion times of the ^{57}Fe traces gives clear indication of iron impurity clustering within the Ni-Pd and Ni-Pt alloy matrices. A simple phenomenological theory is presented in an attempt to explain the T_C vs concentration dependence in these alloys.

I. INTRODUCTION

Magnetization studies of Pd and Pt alloyed with the 3*d* transition elements (Fe, Co, Ni) have been of interest[1-3] for a number of years. These studies were made by conventional methods and revealed average polarization effects. Recently, investigations have also been carried out using neutron-diffraction techniques[4] which have revealed details of the magnetic-moment distribution and the variation of this distribution with composition. In addition, Mössbauer investigations have been made in the Fe-Pd[5] and Ni-Pd[6-8] systems which have yielded information not only of the matrix polarization, but also of the clustering of the ^{57}Fe nuclei which are employed as magnetic probes. In the case of the Ni-Pd system a rather different behavior has been observed in the concentration dependence of the hyperfine field as measured at ^{57}Fe and at ^{61}Ni nuclei.[6,8]

Mössbauer measurements in the Ni-Pt system using either ^{57}Fe or ^{61}Ni nuclei as probes are of interest for the following reasons. (i) The results can yield further information on both impurity-clustering and matrix-polarization effects in such magnetic alloys. (ii) The discrepancy in the concentration dependence of the hyperfine fields in Ni-Pd can be further examined in the Ni-Pt system.

For the reasons enumerated, Mössbauer measurements were made as a function of composition for the Ni-Pt system at temperatures ranging from 4 to 630 K. In this paper we present (a) saturation-hyperfine-magnetic-field data for Pt-Ni both at Fe nuclei diffused as probes in the Pt-Ni matrix, and at ^{61}Ni nuclei present as constituents of the matrix, (b) data of Curie temperature vs Ni concentration of the Pt-Ni system, and (c) a simple phenomenological theory of the composition dependence of the Curie temperature applicable to these alloy systems. Finally, these data will be compared to previous work[6,8] on the Pd-Ni alloy system.

II. EXPERIMENTAL PROCEDURE

Alloy samples were prepared from 99.999% Pt and 99.999% Ni by induction melting in a high vacuum several times to ensure uniformity. The samples were then cold rolled to about 0.1-mm thickness. Small pieces to be used as sources were cut from these foils, the remainder being retained for later use as absorbers in the ^{61}Ni measurements. X-ray diffraction and chemical analysis confirmed concentration values to ±0.5 at.%. Sources for the ^{57}Fe measurements were prepared by placing a few drops of radioactive ^{57}Co (which decays to ^{57}Fe) in an HCl solution on the alloys's surfaces, followed by drying and diffusing for several days at 1000 °C in an H_2 atmosphere. The atmosphere was switched to He for the final $\frac{1}{2}$ h and the samples were allowed to furnace cool to room temperature (~ minutes). ^{57}Co concentrations produced in the alloys during the diffusion process were 20–100 ppm by weight. The length of diffusion time was sufficient to produce an essentially uniform distribution of ^{57}Co. Shorter diffusion times were employed on specific samples for reasons indicated in Sec. III.

It should be emphasized here that we could not, without risking invalidating the experiment, diffuse large quantities of ^{57}Fe into the alloys. The sources, therefore, were generally quite weak. This led necessarily to some compromise on statistics due to time limitations in data accumulation.

No heat treatment was performed on the foils to be used in the ^{61}Ni-site measurements subsequent to the cold rolling. Enrichment of the ^{61}Ni isotope in these foils was not necessary as the natural abundance, ~2% (hereafter, alloy compositions of X at.% will be written X%), was sufficient for observation of the ^{61}Ni resonance at the lowest Ni concentrations attempted (45%). The source used in the ^{61}Ni measurements was a vacuum-melted ^{62}Ni–17%-Cr disk, which was determined to be paramagnetic at 4 K. This disk was irradiated by bremsstrahlung from a LINAC target using a beam energy of about 60 MeV. The reaction is $^{62}\mathrm{Ni}(\gamma, p)\,^{61}\mathrm{Co}$, where ^{61}Co decays by β^- emission 100% through the 67-KeV ^{61}Ni Mössbauer level. Measurements on the ^{61}Ni sites were performed with both source and absorber at 4.2 K.

The drive system employed uses the multichannel-analyzer analog address voltage to produce the drive signal in constant acceleration mode. Coupled with appropriate feedback this produced a linewidth of 0.35 mm/sec using $K_4Fe(CN)_6$ 76%-enrichment absorber against a ^{57}Co-in-Cu source.

III. EXPERIMENTAL RESULTS

A. Evidence for Fe-Co Clustering in Ni-Pt System

The hyperfine field vs temperature behavior was studied in detail in three samples: $Pt_{10}Ni_{90}$, $Pt_{29}Ni_{71}$, and $Pt_{50}Ni_{50}$. In each sample the Co-Fe impurities were diffused for two different periods of time. First, Co-Fe atoms were diffused in the Pt-Ni alloys for a 30-min period, followed by a second diffusion period of 3 h or longer. Figure 1 shows the result of a series of measurements of the hyperfine field temperature dependence for $Pt_{10}Ni_{90}$ following a 30-min diffusion. We observe a behavior similar to that previously noted in the Ni-Pd system,[6] i.e., two distinguishable hyperfine field patterns just below the Curie temperature. We attribute the split pattern to iron-cobalt clustering coupled indirectly through the Ni-Pt matrix. This splitting corresponds to a field which varies between 75 and 80% of the pure-iron hyperfine field at this temperature. The central pattern indicates the Ni-Pt matrix polarization. We can clearly see such behavior by examining the spectra at 558 and at 563 K in Fig. 1. We notice further that the splitting which we attribute to the clusters displays a small residual effect above the Curie temperature of the matrix. For instance, the matrix Curie temperature of the $Ni_{90}Pt_{10}$ sample is about 565 K. We see that the broad central spectrum at 563 K narrows very abruptly as the temperature is increased; at the same time the (cluster) wing peaks decrease in intensity noticeably but not completely. We do not have an explanation of the persistence of the cluster peaks above the Curie temperatures of the matrix. A theory of the Co-Fe clustering in the Ni-Pd matrix has been given by Rubenstein.[7] Rubenstein's model is based on superparamagnetism in which a molecular-field theory for the temperature dependence of matrix and cluster polarization is used to explain the existence of

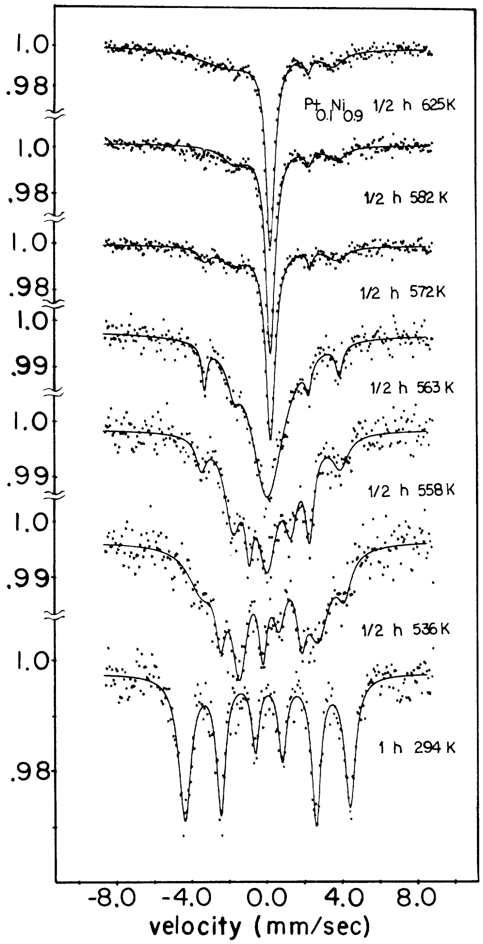

FIG. 1. Mössbauer absorption spectra for $Pt_{10}Ni_{90}$ after a 30-min diffusion of ^{57}Co-^{57}Fe probes. h = hours.

superparamagnetic iron clusters embedded in a ferromagnetic nickel-palladium matrix. The superparamagnetic iron clusters are ferromagnetically ordered through the nickel-palladium-matrix exchange interaction which in this case performs a similar role to an externally applied field.

In Fig. 2 is shown the series of spectra for a $Pt_{29}Ni_{71}$ sample which was annealed for 3 h. We notice a single hyperfine field pattern, corresponding to the Ni-Pt-matrix polarizations. Long-term annealing, 3 h or more, produced a single Mössbauer pattern indicating homogenization of the Co-Fe atoms and consequent dissociation of the clusters. Apparently a shorter annealing time is required for disassociating the clusters in the Ni-Pt system (of the order of 1 h) than was required for the Ni-Pd system (of the order of 10 h). It is clear that the annealing times are critical to the extent that for a long annealing period the cluster splitting disappears completely. We point out that in the cases noted the cluster splitting disappears at temperatures above T_C of the alloy but well below that of pure Fe.

B. Atomic-Ordering Effects in $Ni_{50}Pt_{50}$

The Ni-Pt system forms a superlattice structure at the $Ni_{50}Pt_{50}$ composition.[9] It has the tetragonal CuAu ($L1_0$) type of structure with a c/a of 0.939 and an atomic-ordering temperature of about 645 °C. The effect of atomic ordering on the magnetic behavior is illustrated in Fig. 3. The two top spectra were taken at 60 and 4.2 K, respectively, with the sample still in the atomically disordered state. (The Co-Fe probes were diffused into the Ni-Pt matrix at 1273 K, well above the atomic-ordering temperature.) The single six-finger Mössbauer pattern indicates a magnetically ordered state with a Curie temperature of 100 K (see Table I).

The two center spectra display the results of measurements at 28 and 4.2 K, respectively, after 2 days of atomic ordering at ~900 K. The spectrum at 28 K consists of a single narrow peak with a linewidth similar to the paramagnetic room-temperature linewidth. At 4.2 K, however, the spectrum displays a split structure indicating a broad distribution of hyperfine fields with a prominent paramagnetic central peak. The Curie temperature, therefore, has been depressed below 28 K.

Results after an additional day's anneal at 900 K are shown in the two lower spectra of Fig. 3. At both 18 and 4.2 K a single paramagnetic peak is evident with perhaps a remnant of additional structure at 4.2 K. The Curie temperature has been further reduced to below 4.2 K.

The experimental data of Fig. 3, as well as those of Figs. 1 and 2, were fit using an unconstrained-least-squares program. This program linearizes the assumed Lorentzian peaks and iteratively performs the least-squares analysis. Two parameters for each peak (peak position and width at half-maximum) are initially entered as first guess. Due to computer-time limitations, in some cases only the most prominent peaks were fit. In no case does this choice jeopardize the interpretation of the experimental results.

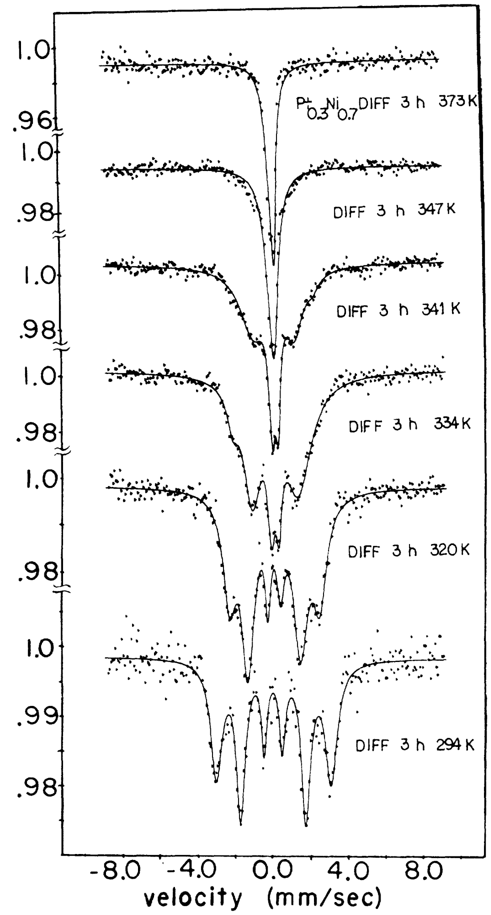

FIG. 2. Mössbauer absorption spectra for $Pt_{29}Ni_{71}$ after a 3-h diffusion of ^{57}Co-^{57}Fe probes. DIFF = diffused; h = hour.

We call attention to the unusual intensity ratios and asymmetries of the spectra of Fig. 3. These features can be attributed to partial domain polarization in the foil-source samples (easily magnetized in their planes), coupled with small quadrupole-interaction distributions at various sites.

Microscopically, one might picture the sample as divided into regions of varying amounts of order; the degree of local order increases with longer annealing time near the ordering temperature. ^{57}Fe probes which find themselves in fully ordered regions see an essentially zero hyperfine field while those in disordered regions sense various fields depending on the degree of local disorder. That is, the amount of local order can be related to the

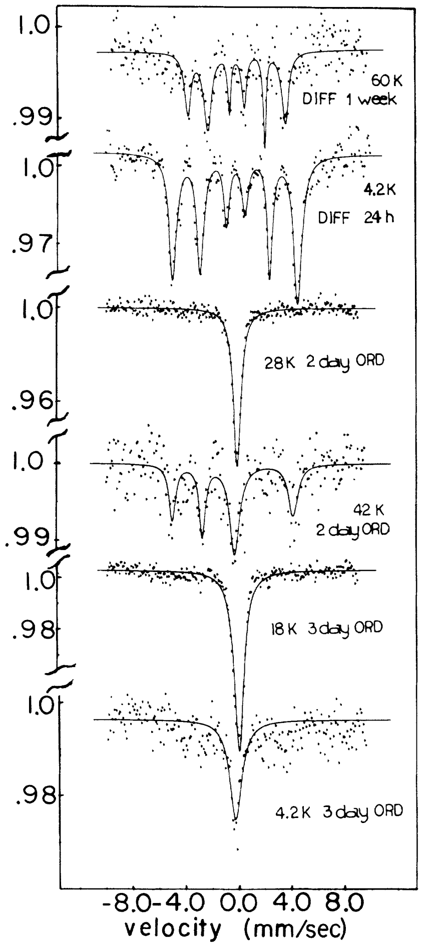

FIG. 3. Mössbauer absorption spectra for the superlattice structure $Pt_{50}N_{50}$. DIFF = diffused; ORD = ordered; h = hours (see text for explanation). We were unable to fit properly the first, fourth, and sixth spectra on account of source weakness in conjunction with the great distributions of hyperfine fields occurring at these temperatures and states of partial atomic order. An additional contribution to the small percent effect evident in many of our spectra might have arisen from a low Debye-Waller factor of the diffused sources. Also, absorber thickness could have been optimized for effect intensity.

observed Curie temperature. Recent susceptibility measurements[10] on a similar $Ni_{50}Pt_{50}$ sample are in agreement with these results. In that investigation a substantially ordered paramagnetic behavior was observed after several days anneal near the ordering temperature.

C. T_C vs Ni Composition in the Ni-Pt and Ni-Pd Systems

Data on Curie temperature of disordered Ni-Pt alloys are presented in Table I and plotted in Fig. 4. Included here also for comparison are the Ni-Pd data from Ref. 6. Figure 5 displays Curie temperatures of the low-concentration-Ni region of the Ni-Pd curve with results for several other alloy systems[11] for further comparison. These data show clearly the finite Ni concentration required for the onset of ferromagnetism. Furthermore, it is clear from the data that, contrary to the results of simple magnetic dilution, the Curie temperatures of both the Ni-Pd and the Ni-Pt alloys increase nonlinearly with Ni concentrations. A simple model (originally suggested by Daniel) in which a uniform exchange enhancement is assumed and in which the short-range intra-atomic Coulomb repulsion between *d* electrons is the same everywhere throughout the solid, seems to account reasonably well for the observed experimental results. Such a model should be appropriate for Ni-Pt alloys since the critical concentration for the occurrence of ferromagnetism is found to be near the 50-50 composition. Sufficient compositional averaging should be present so that a uniform-enhancement model is probably appropriate. However, such a model may not be appropriate for the Ni-Pd alloys when only 2% Ni is required for the onset of ferromagnetism. For such alloys a "local-enhancement" model is clearly more appropriate in which the short-range Coulomb repulsion between *d* electrons associated with the Ni impurity atoms should be stronger than that associated with the host Pd matrix. Nonetheless, the results of the uniform-enhancement model appears to fit both the Ni-Pt and the Ni-Pd data equally well.

The calculation relating the Curie temperatures to the alloy composition is based on a shielded Cou-

TABLE I. Curie temperature and saturation hyperfine field at ^{57}Fe sites for Pd-Ni and Pt-Ni alloys.

Ni composition (at. %)	T_C (K)	H_{sat} (kG)[a]
	(a) Pd-Ni	
1.95	2	
2.25	27 ± 5	290 ± 3
3.6	···	292 ± 3
6.1	82 ± 5	297 ± 3
17	208 ± 5	308 ± 3
44.5	439 ± 5	310 ± 3
65	···	299 ± 3
73.2	575 ± 5	296 ± 3
88.5	589 ± 5	290 ± 3
100	638 ± 5	285 ± 5[b]
	(b) Pt-Ni	
46	18 ± 5	285 ± 5
50	100 ± 5	292 ± 3
60	···	295 ± 3
71	349 ± 5	296 ± 3
80	460 ± 5	291 ± 3
90	562.5 ± 5	288 ± 3

[a] Although the sign of the hyperfine field was not measured in this work, all values given in this table are assumed to be negative.

[b] C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, Proc. Phys. Soc. (London) 81, 1079 (1963).

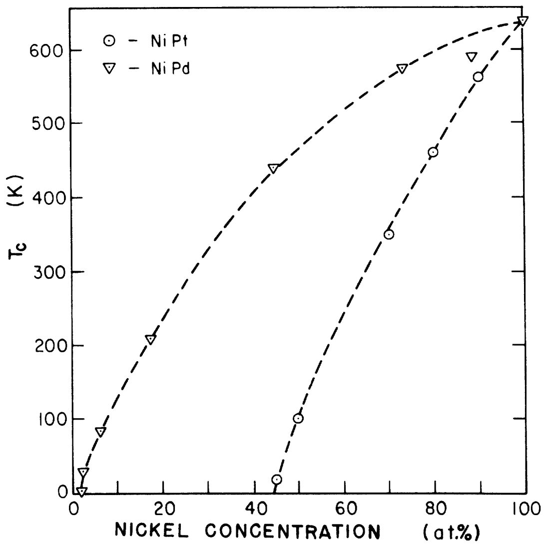

FIG. 4. Plot of the Curie temperature vs Ni concentration for the Pd-Ni and Pt-Ni systems. Estimated errors in the measurements are given in Table I.

lomb repulsion term in the Hamiltonian which can be written as a function of the fraction of Ni in either the Pd or Pt matrix:

$$H_0 = T + (U + c\Delta)\sum_j n_{j\uparrow} n_{j\downarrow} \;, \tag{1}$$

where T is the kinetic energy of the d electrons, U is the intra-atomic Coulomb repulsion term between electrons of opposite spin state appropriate to either pure Pd or pure Pt, c is the Ni concentration, and Δ is the increase in the Coulomb repulsion interaction resulting from the Ni impurities. In this extremely simple model, we assume that the Coulomb interaction is uniform throughout the matrix and increases linearly with Ni concentration. Following Izuyama, Kim, and Kubo[12] it can be shown that the static magnetic susceptibility for such an alloy system is

$$\chi = \chi_0/[1 - \chi_0 (U + c\Delta)] \;, \tag{2}$$

where χ_0 is the unenhanced Pauli susceptibility, and χ is the exchange-enhanced susceptibility. At the critical composition $c = c_0$, the denominator diverges and

$$1 - \chi_0 (U + c_0\Delta) = 0 .$$

To obtain the composition dependence of the Curie temperatures, we must calculate the dependence of χ_0 on temperature up to order T^2. For temperatures not too large,

$$\chi_0 = 2\mu_B^2 N(\mathcal{E}_F^0)\left(1 + \frac{\pi^2}{6}(kT)^2 \left.\frac{d^2 \ln N(\mathcal{E})}{d\mathcal{E}^2}\right|_{\mathcal{E}=\mathcal{E}_F^0}\right) \;, \tag{3}$$

where μ_B is the value of the Bohr magneton, and $N(\mathcal{E}_F^0)$ is the single-spin-state density of states of the d band evaluated at the Fermi energy at $T = 0$. Retaining terms only up to order T^2 in χ is justified for all these alloys since for the maximum Curie temperature (T_C for Ni is ~ 600 K) the thermal energy is small (~ 1/20 eV) compared to the separation of the Fermi level from the top of the d band (~ several tenths of eV).

Performing the logarithmic derivative and expanding χ_0^{-1}, we obtain

$$\chi_0^{-1} \approx A + BT^2, \tag{4}$$

where

$$A = [2\mu_B^2 N(\mathcal{E}_F^0)]^{-1} \;,$$

$$B = \frac{\pi^2 k^2}{12\mu_B^2 N(\mathcal{E}_F^0)}\left[\left(\frac{N'(\mathcal{E}_F^0)}{N(\mathcal{E}_F^0)}\right)^2 - \frac{N''(\mathcal{E}_F^0)}{N(\mathcal{E}_F^0)}\right] \;.$$

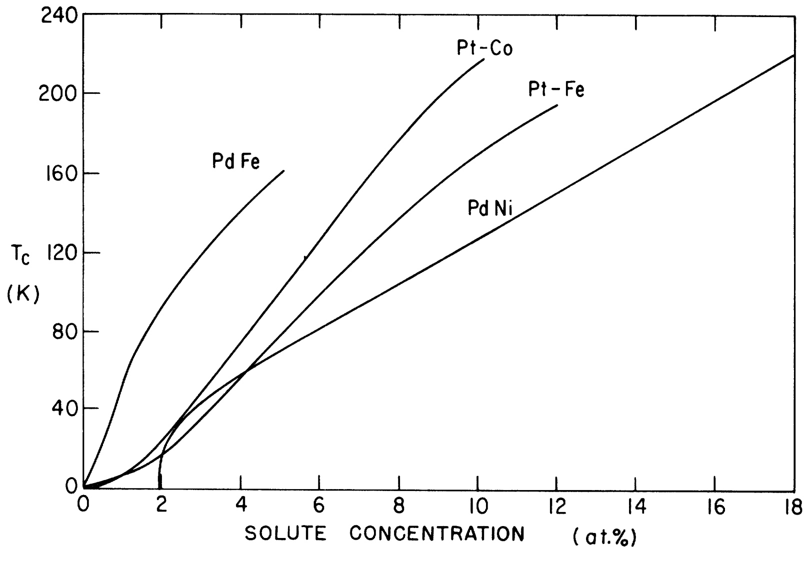

FIG. 5. Curie temperatures in the low-nickel-concentration region for various alloy systems.

The expression for B is valid only where $N(\mathcal{E})$ varies smoothly over energies of the order of kT (the derivatives then have meaning). In Ni, even though numerous peaks occur near the Fermi energy, the constant B is known experimentally to be > 0.

Now, the condition for ferromagnetism is

$$1-\chi_0(U+c\Delta)=0=1-(U+\Delta)\chi_0-(c-1)\Delta\chi_0. \qquad (5)$$

Using Eq. (4), we then have

$$1-\frac{U+\Delta}{A+BT_C^2}-\frac{\Delta(c-1)}{A+BT_C^2}=0. \qquad (6)$$

It is then easy to show that

$$T_C=T_{\rm Ni}\left(\frac{c-c_0}{1-c_0}\right)^{1/2}, \qquad (7)$$

where $T_{\rm Ni}$ is the Curie temperature of Ni (the limit of T_C for $c=1$) and c_0 is the critical composition of Ni required for the onset of ferromagnetism, i.e., ~2% for Pd-Ni and ~40% for Pt-Ni.

This calculated variation of T_C with composition is in reasonable agreement with the experimental results of Fig. 4. Near the composition c_0, the Curie temperature increases extremely rapidly with composition; Eq. (7) suggests an infinite slope of T_C vs composition at $c=c_0$. Furthermore a clearly nonlinear variation of T_C with c is observed for both Ni-Pt and the Ni-Pd alloy systems. However, the data for neither alloy system vary exactly as $c^{1/2}$. Because of all the simplifying assumptions made in the calculations, one would not expect exact agreement. In particular one would not expect χ_0 to be composition independent, since this would require the band structures of Pd, Pt, and Ni to be identical. Furthermore χ_0 should also reflect the readjustment of the spin-up and spin-down bands as the alloy system became ferromagnetic. The above calculation ignores these subtleties as well as interatomic Coulomb repulsion and local-enhancement considerations.

It is interesting to point out that if one assumes a local-moment behavior and a Curie-law susceptibility $\chi_0 \sim 1/T$ for the unenhanced susceptibility, then one finds

$$T_C=T_{\rm Ni}\left[1-\left(\frac{c-1}{c_0-1}\right)\right]. \qquad (8)$$

A linear variation of T_C with composition is then predicted for Curie-law behavior. The curvature observed in T_C vs c for both the Ni-Pd and the Ni-Pt alloy systems favors the concept of itinerant-electron ferromagnetism in both systems.

D. Saturation Hyperfine Field Dependence in Pt-Ni

Dependences of the saturation hyperfine fields ($H_{\rm sat}$) on Ni concentration at the diffused ^{57}Fe sites in Pt-Ni and in previously published Pd-Ni are given in Table I and plotted in Fig. 6. Behavior of the saturation field is qualitatively the same in each case. The rise in saturation hyperfine field at low Ni concentration may be explained within the framework of the rigid-band model assuming a statistical distribution of Ni-atom neighbors surrounding the ^{57}Fe impurity. If the full complement of such neighbors provides some maximum hyperfine field, then at low Ni concentrations their statistical distribution will contribute some smaller average hyperfine field causing a drop in the measured saturation field.

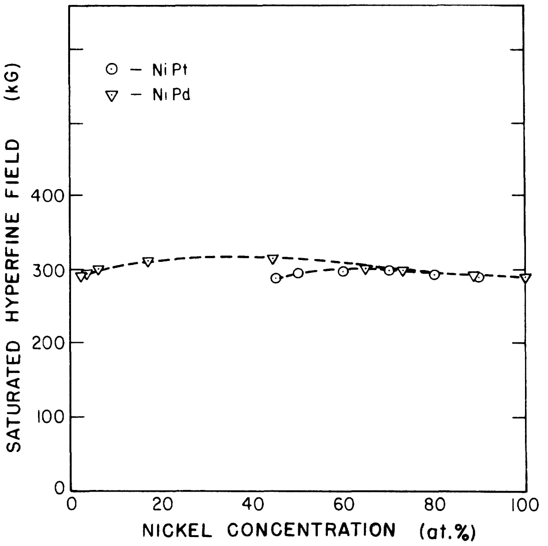

FIG. 6. Saturation hyperfine fields at the diffused ^{57}Fe sites as a function of Ni concentration in Pt-Ni and Pd-Ni alloys. Pumped He (2 °K) runs were taken on the low-concentration samples of each series, 4.2 °K runs were used for the remainder. Error estimates are indicated in Table I.

The statistical rigid-band model predicts a constant saturation hyperfine field at high Ni concentration. We can offer a possible explanation for the drop in this region by employing the results of recent neutron-diffraction measurements of Cable and Childs.[4] They find that the magnetic moments of the Ni atoms increase from the pure-Ni value of $0.6\mu_B$ to $\sim 1.2\mu_B$ at 90% Pd as Pd is added to the system due to electron redistribution. Assuming that contributions to $H_{\rm sat}$ are proportional to the magnitude of neighbor-Ni moments at a given concentration, $H_{\rm sat}$ will increase as Pd is alloyed with pure Ni. This increase combined with the tendency toward a statistical decrease in $H_{\rm sat}$ at higher Pd content produces the observed maximum in $H_{\rm sat}$.

Neutron-diffraction measurements have not yet been performed on the Pt-Ni system. The similar behavior of $H_{\rm sat}$ for Pt-Ni, however, suggests that such measurements on the atomically disordered phase of this system should reveal an increase in

TABLE II. Hyperfine field at ^{61}Ni site for Pt-Ni alloys.

Ni composition (at.%)	H_{hf} at 4.2 K[a] (kG)
50	35.6 ± 19.9[b]
55	48.2 ± 16.6
60	64.8 ± 20
71	93.0 ± 19.6
80	91.4 ± 9.2
90	90.2 ± 6
100	75.1 ± 10 75 ± 3

[a] The measured hyperfine fields given above are assumed to be negative, although we did not determine the sign in this experiment.

[b] Errors estimated from uncertainties in peak positions and half-widths.

the Ni moment as Pt is added. This increase will probably be less than that reported for Pd-Ni.

E. Hyperfine Fields at ^{61}Ni Sites in Pt-Ni

Hyperfine field measurements taken on the same set of Pt-Ni alloys at 4.2 K on ^{61}Ni sites are given in Table II and plotted in Fig. 7. The hyperfine field ($H_{4.2}$) at 4.2 K for these sites shows the same general trend as H_{sat} for the diffused ^{57}Fe sites. The maximum in $H_{4.2}$ of about 93 kG is observed again near 70% Ni. The drop of $H_{4.2}$ at lower Ni concentration is more pronounced than in H_{sat} at the ^{57}Fe sites. This could be due to the fact that measurements were taken at 4.2 K rather than at $T = 0$ K. Since $T_C = 100$ K for the 50%-Ni sample, the difference from H_{sat} in this worst case should be no larger than several percent. Another possibility is that if the samples were not totally disordered, the measured hyperfine field of the alloys around 50% Ni would be lowered along with T_C as indicated in Sec. II. This effect would be difficult to estimate.

The large error bars in Fig. 7 are due essentially to the difficulty in properly fitting the ^{61}Ni spectra. The computer program available was unable to resolve the 12 closely spaced absorption peaks. In order that some uniformity in analysis prevail, each spectrum was fit to two Lorentzians. The hyperfine fields were then calculated by adding the separation of these peaks to the sum of their half-widths. This admittedly arbitrary procedure produced reasonably good fits to the data and gave consistent results for the hyperfine fields. Error bars were determined by adding the positional uncertainties of the two peaks.

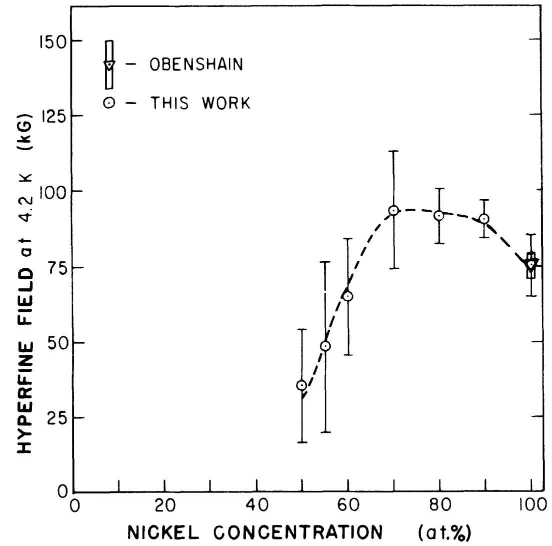

FIG. 7. Hyperfine fields at ^{61}Ni sites as a function of Ni concentration in the Pt-Ni system.

Our results here should be compared to recent ^{61}Ni Mössbauer studies on the Pd-Ni system by Obenshain *et al.*[8] They find a distribution of hyperfine fields at every Ni concentration. H_{hf}, the net hyperfine field (at 4.2 K) has a minimum of about 30 kG near 50% Pd and a maximum of about 90 kG near 90% Pd. They have interpreted their data by assuming the hyperfine field at the ^{61}Ni sites is determined by the distribution of Ni and Pd atoms on neighboring sites. The Pd atoms give a strong positive contribution to H_{hf} in their model.

By contrast, our hyperfine field data on the Pt-Ni system at both ^{61}Ni and diffused ^{57}Fe nuclei exhibit a broad maximum centered around 75-at.% nickel. As stated previously, we explain this behavior by assuming that the principal contribution to H_{sat} at any Ni or Fe site is due to Ni neighbors with small residual contributions from neighboring Pt atoms.

ACKNOWLEDGMENTS

The authors would like to gratefully thank Dr. J. Cullen and Professor E. Daniel for many helpful and stimulating discussions. In addition they would like to thank D. J. Gillespie for invaluable assistance in sample preparation. The authors would also like to thank R. A. Tobin of the Naval Research Laboratory LINAC branch for his cooperation in the Ni^{61} source irradiation.

---

*Supported in part by the National Aeronautics and Space Administration under Grant No. NGR-09-003-014.

†AEC Graduate Laboratory Fellow.

[1] J. Crangle, in *Electronic Structure and Alloy Chemistry of Transition Elements*, edited by P. Beck (Interscience, New York, 1963), p. 51.

[2] C. Chouteau, R. Fourneaux, K. Gobrecht, and R. Tournier, Phys. Rev. Letters 20, 193 (1968).

[3] D. J. Gillespie and A. I. Schindler, in *Proceedings of the Conference on Magnetism and Magnetic Materials, Chicago*, 1971 (AIP, New York, 1972).

[4] J. W. Cable and H. R. Child, Phys. Rev. B 1, 3809 (1970).

[5] W. L. Trousdale, G. Longworth, and T. A. Kitchens, J. Appl. Phys. 38, 922 (1967).

[6] W. A. Ferrando, R. Segnan, and A. I. Schindler, J. Appl. Phys. 41, 1236 (1970).

[7] M. Rubinstein, Solid State Comm. 8, 919 (1970).

[8] F. E. Obenshain, W. A. Glaeser, G. Czjzek, and J. E. Tansil, J. Phys. Paris 32, 783 (1971).

[9] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958), p. 1032.

[10] A. I. Schindler and D. J. Gillespie, in *Proceedings of the Twelfth International Conference on Low Temperature Physics, Kyoto*, 1970, edited by E. Kauda (Academic Press of Japan, Kyoto, Japan, 1971), p. 777.

[11] R. Segnan, Phys. Rev. 160, 404 (1967).

[12] T. Izuyama, D. J. Kim, and R. Kubo, J. Phys. Soc. Japan 18, 1025 (1963).

PHYSICAL REVIEW B VOLUME 5, NUMBER 12 15 JUNE 1972

Pseudopotential for the Calculation of Transition Rates of Atoms Chemisorbed on Metals*

Pradeep Kumar and Harry Suhl
Department of Physics, University of California, San Diego, La Jolla, California 92037

(Received 10 January 1972)

We isolate the part of the interaction responsible for energy transfers between reacting chemicals adsorbed on a solid from the part that gives the potential-energy surface familiar in the description of the bonding of adsorbates.

I. INTRODUCTION

Chemical reactions are generally described by rate equations. If the reaction is of the so-called "adiabatic" kind, these are differential equations for the numbers of the various participating species which, at a given time after the onset of the reaction, find themselves in the various quasistationary energy levels appropriate to the various wells of the energy surface calculated by assigning fixed values to the core coordinates, neglecting the core kinetic energy, and solving the Schrödinger equation for the motion of the outer electrons. The energy so calculated is a function of the core coordinates. It is represented by a hypersurface in the space of these coordinates and acts as potential energy in the next stage of a so-called Born-Oppenheimer calculation of the motion of the cores.

A reaction corresponds to the transfer of the system from one minimum on the hypersurface to another, via a saddlepoint. Quantum mechanically the process can be described by a rate equation describing the occupation numbers of the various (quasistationary) levels in the minima as a function of the time.[1] Its solution generally leads to a reaction-rate formula of the type given by Eyring *et al.*[2]

The general problem of the establishment of rate equations was discussed by Van Hove,[3] who noted that special care is required when the Hamiltonian of the system does not obviously split into an unperturbed part and an extremely small perturbation. Other criteria then determine the decomposition. This question is especially acute in the case of chemical reactions. The same forces that mold the effective potential well in which the reagents find themselves are presumably also the forces responsible for the reaction. We here focus attention on the case in which some or all of the reagents are chemisorbed on the surface of a metal.

This metal substrate is approximated, for simplicity, by a semi-infinite uniform fixed background of positive charge pervaded by conduction electrons. This approximation precludes phonon processes in the reaction and focuses attention on the effects of electron charge and spin fluctuations as the operative dynamic factor in the reactions of chemisorbed species. Generalization to the case in which phonons, too, are operative is not difficult, however.

In searching for a "small" perturbation for use in the calculation of the transition coefficients that occur in the rate equation, one must clearly go beyond the straightforward expression for the interaction of the adatoms with the metal. That interaction is responsible for the very level scheme within which it induces transitions, and is thus hardly to be regarded as perturbation.

The appropriate decomposition of the Hamiltonian into a perturbed and unperturbed part is determined by a physical hypothesis as to which variables in the problem are slowly varying. For example, it is reasonable to suppose, at least in some cases, that the nuclear motion of the adatoms, as governed by the level scheme of the Born-Oppenheimer well, is described by level occupation numbers that change slowly compared with the rate of charge or