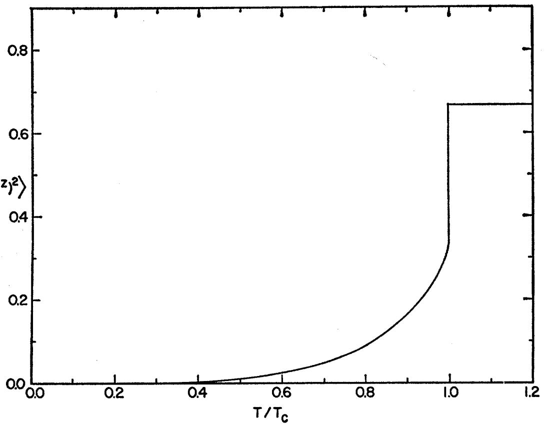

FIG. 1. The average value $\langle (J^z)^2 \rangle$ as a function of temperature.

Equation (34) implies that the $M_J = \pm 1$ states must contribute equally, i.e., that they correspond to a twofold degenerate level in the internal-field approximation. The relation (36), specifying $\langle (J^z)^2 \rangle$ as a function of temperature, is the same as the one obtained by the more conventional internal-field approximation, based on the minimization of the free energy.[1,12] In that treatment it was found[1] that the model undergoes a first-order orientational transition at a temperature given by $kT_c = 19\Gamma/(4\ \ln 2)$. Figure 1 shows $\langle (J^z)^2 \rangle$ as a function of temperature. At $T=0$ there is an ordered phase with $\langle (J^z)^2 \rangle = 0$. At $T=T_c$, we see that $\langle (J^z)^2 \rangle$ abruptly assumes the value $\frac{2}{3}$, characteristic of the orientationally disordered phase, which is stable at all higher T. A complete discussion of this transition is given elsewhere.[1,2]

In order to obtain a higher-order treatment (than the internal-field approximation) of the orientational order-disorder transition in fcc (or hcp) solid ortho-H_2, it is of course necessary to consider the more general Hamiltonian, given by Eqs. (1) and (2).

ACKNOWLEDGMENT

The authors wish to acknowledge the hospitality of the Summer Institute of Theoretical Physics at Brandeis University, where this work was initiated.

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[12] See Eq. (6) of S. Strässler and C. Kittel [Phys. Rev. **139**, A758 (1965)], with $g_0/g_1 = \frac{1}{2}$.

PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

Ferromagnetic Transitions in Dilute Solutions of Cobalt in Palladium*

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(Received 6 July 1966; revised manuscript received 8 December 1966)

Ferromagnetic transitions have been observed in dilute random solutions of Co in Pd having Co concentrations between 0.07 and 4.5 at.%. The transition regions near T_c have been explored by using the Mössbauer effect of Fe^{57} present as a very dilute impurity in the alloys. The hyperfine fields have been measured by the standard Doppler technique at low temperatures and by a thermal scanning method near the transition temperatures. Data have been interpreted as showing the effects of statistical fluctuations in the concentration of the alloys, and have been analyzed to yield values for the mean Curie temperature and the mean-square deviation in Curie temperature as a function of concentration. These values have been related to the spatial dependence of the exchange interaction through a molecular-field calculation. It is found that if one assumes the interaction is given by a Gaussian $J(r) = \exp(-r^2/4\sigma^2)$, in correspondence with neutron diffraction results in Co-Pd alloys, then the values deduced from this study are $\sigma = 11.5 \pm 1.2$ Å and $J_0/k = 0.02$°K. However, comparison of the effective range obtained in the present study with the neutron data and the total localized moment suggest that the Gaussian form factor is incorrect at large distances and that the interaction has a more slowly varying and weak tail.

INTRODUCTION

IN certain solid solutions of magnetic ions in a nonmagnetic material, the variation of Curie temperature with concentration may provide information on the range of the magnetic interaction. It has been shown[1,2] that, within the Bethe-Peierls-Weiss approximation with nearest-neighbor interactions, such a solid solution will not support long-range magnetic order if the concentration is less than a critical value c_0, where

$$c_0 = 1/(z-1). \tag{1}$$

Here z is the number of nearest-neighbor sites. If the interaction is assumed to be constant over a larger number of sites N in the magnetic cluster, then z in Eq. (1) is replaced by N. If in some alloy system one observes a concentration below which the Curie temperature is zero, then the inverse of this concentration gives the approximate number of sites enclosed by the interaction.

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* Work supported in part by the U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-594-64.

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Alloys of Co in Pd have been previously investigated[3] for concentrations ranging from 10 to 0.1% Co by conventional magnetization measurements. All alloys were found to be ferromagnetic, the 0.1% alloy having a relatively high Curie temperature of 7°K. For these fcc alloys, where $z=12$, Eq. (1) would give a critical concentration of about 8%. Ferromagnetic transitions in these alloys therefore imply that the magnetic interaction extends over many times the distance between nearest neighbors. Similar results have been observed in other alloys of transition metals in hosts of $4d$ transition metals.[4]

The present paper presents a report on a study which overlaps some of the previously studied concentrations of Co-Pd alloys and extends that work to lower concentrations. In the present study, Curie temperatures are measured by utilizing the Mössbauer effect of Fe^{57} present as a dilute impurity in the Co-Pd samples.[5] As the Mössbauer effect measures a local magnetization, it is not subject to the problems of domain alignment which complicate the bulk-magnetization measurements. The Mössbauer effect provides a measurement of the Curie temperature which is more directly obtained from the data, and is not subject to uncertainties arising from extrapolations to zero applied magnetic field.

The Fe-Pd system, which has magnetic properties very similar to the Co-Pd system, has been previously studied by the Mössbauer method. Paramagnetic samples containing Fe^{57} in a Pd host have been investigated in the presence of an external field H_0.[6] It was found that the magnetic hyperfine field H_i is given by the relation

$$H_i = H_{\text{sat}} B_s(g\mu_0 S H_0/kT), \quad T > T_c \tag{2}$$

where B_s is the Brillouin function, $S=13/2$ and $gS=12.6$, thus indicating the presence of a large magnetic moment localized on the Fe atoms which is independent of temperature and applied field. This value for the moment is in agreement with that obtained from susceptibility measurements.[7]

In ferromagnetic materials, however, the temperature dependence of the hyperfine field may be quite complicated.[8,9] Within the molecular-field model this dependence is given by

$$H_i(T) = H_{\text{sat}} B_s(g\mu_0 S\lambda M_s/kT), \tag{3}$$

where M_s is the host magnetization,

$$M_s = M_0 B_J(g'\mu_0 J\lambda' M_s/kT). \tag{4}$$

In the above, $g\mu_0 S$ is the moment localized on the impurity atom, $g'\mu_0 J$ is the moment of a host atom, λ is a gauge of the host-impurity interaction, and λ' is a gauge of the host-host interaction. For a pure homogeneous material, (3) and (4) combine to give

$$\frac{H_i}{H_{\text{sat}}} = \frac{M_S(T)}{M_0} = B_S\left(\frac{3S}{S+1}\,\frac{M_S/\mathrm{M}_0}{T/T_c}\right), \tag{5}$$

where T_c is the Curie temperature. However, for the case of an impurity with a localized moment or molecular-field constant significantly different from the host, the hyperfine field may be either larger or smaller than the magnetization, depending on whether the argument of the Brillouin function in Eq. (3) is larger or smaller than that in Eq. (4). Behavior of this kind has been seen for Mn^{55} in[10] Fe and for Fe^{57} in Ni.[11]

The temperature dependence of the hyperfine field of Fe^{57} in a ferromagnetic $Fe_{2.65}Pd_{97.35}$ alloy has been compared to the alloy magnetization.[12] In zero external field, Eq. (5) was found to apply, with $S=1$. With an external field present, the behavior was in disagreement with molecular-field expectations; however, in all cases the hyperfine field was found to be proportional to the bulk magnetization.

There is some question as to the validity of extending low-temperature dependences into the critical region. Brout[13] has discussed the possible effect of short-range order in the vicinity of the Curie temperature. If short-range order is present it will affect both magnetization measurements and Mössbauer spectra. In addition, if the electron-spin-relaxation time is not short enough, anomalous splittings and line shapes can occur in magnetic hyperfine spectra.[14–16] In a study of Fe^{57} in Ni,[17] Doppler spectra were obtained at temperatures $T/T_c \leq 0.999$ and these spectra showed no appreciable changes from normal behavior. A nuclear magnetic resonance investigation on[18] EuS showed that the temperature dependence of the hyperfine field was described by a $\beta=\frac{1}{3}$ power law over a range of temperatures extending to $T=0.99T_c$.

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[4] J. Crangle and W. R. Scott, J. Appl. Phys. **36**, 921 (1965).

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White and Clogston[19] have discussed the temperature dependence of the magnitude of a localized moment in the ferromagnetic region, based on Anderson's theory of localized states.[20] If such dependence exists, it has not yet been seen either in hyperfine-field measurements or in bulk-magnetization measurements.

EXPERIMENTAL

Sample Preparation

Samples were prepared from 99.999% Co rod and 99.999% Pd sponge, both obtained from United Mineral and Chemical Corporation. Preparation of the dilute alloys has been done by initially preparing a master alloy (about 11% Co) which was sequentially diluted with Pd. In this way the amount of material used at each step was sufficiently large to allow weighing to an accuracy of one part in 10^3. For each alloy the component materials were initially pumped and baked at a low temperature in a quartz capsule which was then sealed. The alloys were then melted in a graphite crucible in an induction furnace. In all cases after melting the samples showed no sign of chemical reaction with the quartz, and had a bright metallic surface in which crystalline faces could be seen. The homogeneity of the alloys is shown by the fact that different samples taken from the same melt showed the same Curie temperature.

Following melting the samples were rolled into 1-mil foils. These foils were used as cathode material to prepare alloy films of approximately 0.5-mil thickness by sputtering in purified argon. The sputterer used is of an asymmetrical ac design such that during one half-cycle the current is forward, depositing material onto the anode. During the next half-cycle the current is reversed at a much lower value so that weakly bound gas atoms and impurities on the sputtered surface are removed in preference to alloy atoms. This method has been previously used to obtain very pure foils of strongly gettering materials such as Pd and Ta.[21]

By comparing the Curie temperatures of both rolled and sputtered foils it was determined that the alloy concentration did not change in the sputtering process. However, we have observed that the magnetic transitions of the rolled alloys extend over a wider temperature range than for those of the sputtered alloys of the same concentration. This seems to indicate an increased homogeneity in the sputtered alloys, presumably due to the removal of dislocations formed when rolling and/or an increased randomization of the component elements during the sputtering process.

The sputtered foils were then doped with ≤ 0.1 mCi radioactive Co^{57}. This was obtained by spreading a requisite amount of $Co^{57}Cl_2$–0.1 N HCl solution in small drops over the face of the sample, after which the chloride was reduced in purified H_2 and the Co^{57} diffused into the foil. Since H_2 is known to seriously alter the magnetic properties of Pd and Pd alloys,[22] the H_2 was subsequently removed by pumping and flushing with pure helium at 1000°C.

The uniformity of the activity on the face of the samples was checked by counting the radiation from different parts of the sample through a pinhole lead mask, and by autoradiographs. It was determined that the activity was generally spread over one-third to one-half of the sample area and that the local concentration did not vary by more than a factor of 5. The uniformity of the activity through the thickness of the foil was checked by placing the sample at an angle α to the detector and then counting the intensity as α was varied, thus causing the radiation to pass through varying thicknesses of material. Assuming that the diffusion process distributes the activity through the thickness of the material exponentially, it is estimated that the concentration of the Co^{57} does not vary by more than 20% from front to back. On the basis of all these considerations it is estimated that the amount of activity used does not change the local concentration of Co by more than 0.01 at.%. This constitutes the largest impurity in the sample.

Experimental Technique

Obtaining hyperfine spectra near the Curie point in ferromagnetic materials is difficult because the six lines of the magnetic spectra overlap, making resolution poor. In addition, the magnitude of the hyperfine field changes rapidly with temperature, so that one requires very high-temperature stability over the several hours required to accumulate a spectrum. In the present case there is an additional complication because the active Co must be kept to a low level in order to avoid affecting the alloy concentration, thus requiring extremely long counting times to accumulate a complete Doppler spectrum.

In order to avoid these complications, the method of "thermal scanning" has been used.[5,17] In this method an absorber is chosen such that the absorption spectrum overlaps the paramagnetic line of the Co-Pd source. Both source and absorber are held stationary, and the intensity transmitted through the absorber is counted as a function of source temperature. When the source becomes magnetic, the hyperfine spectrum splits away from the absorption spectrum and the transmitted intensity increases. The detailed temperature dependence of the intensity $I(T)$ depends on the relative isomer shift between source and absorber, the shape of the spectrum, the relative intensities of the lines comprising the magnetic spectrum, and the temperature dependence of the hyperfine field $H_i(T)$. With the assumption that line shapes, relative splittings, and relative intensities of the hyperfine components near T_c remain un-

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[19] J. A. White and A. M. Clogston, J. Appl. Phys. 34, 1187 (1963).

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[22] J. Burger, Ann. Phys. (Paris) **9**, 345 (1964).

changed from their values measured at lower temperatures, the transmitted intensities can be analyzed to determine $H_i(T)$ near the Curie temperature. The details of the method and the analysis are given elsewhere.[23]

DATA AND ANALYSIS

Data

Five samples have been investigated, having concentrations of 4.5, 1.91, 0.49, 0.19, and 0.07 at.% Co. At very low temperatures the alloys show resolved magnetic hyperfine spectra with relative line intensities of 3:4:1 as expected for thin films. The saturation hyperfine field is found to be $H_{\text{sat}}=300\pm10$ kOe independent of concentration, in agreement with previous work.[24] All alloys have about the same isomer shift, 0.17±0.03 mm/sec with respect to metallic Fe. The absorber used for the thermal-scanning measurements was lithium fluoroferrate, whose absorption spectrum taken with the 1.91% paramagnetic source is shown in Fig. 1. This relatively wide absorption line is more useful for thermal scanning than more commonly used narrower lines since it remains sensitive to changes in the splitting of the source over a broader range of temperatures below T_c. The fact that the source line lies near one side of the bottom of the absorber is also convenient because small splittings will produce significant changes in transmitted intensity.

Intensity transmitted through this absorber from the 0.19% alloy, taken as a function of the alloy temperature, is shown in Fig. 2. For comparison, the intensity that would be obtained if the hyperfine field followed a simple Brillouin-function dependence as in Eq. (5) is shown by the dashed line. It is clear that the transition takes place over a much wider temperature range than would be appropriate if the sample were behaving as a simple ferromagnet. This discrepancy cannot be resolved with any single value of the parameters of Eq. (5). Similar discrepancies are observed for all alloys investigated, but the transitions are seen to approach the normal shape monotonically as the concentration increases.

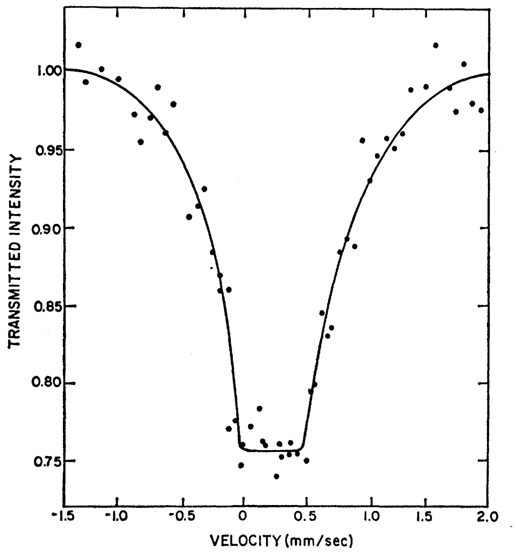

FIG. 1. Lithium-fluoroferrate absorption spectrum, for a paramagnetic source of 1.91% Co in Pd alloy.

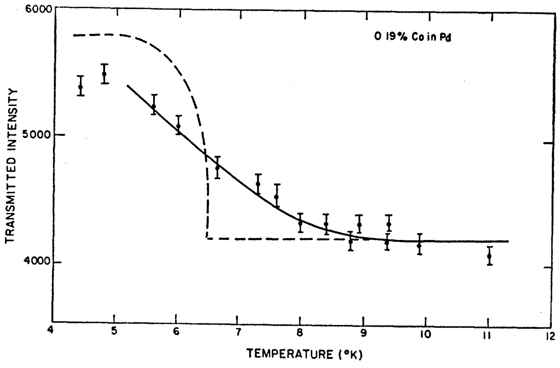

FIG. 2. Thermal-scanning data for the 0.19% Co-Pd alloy. The dashed line shows the anticipated intensity for a simple Brillouin-function dependence of the hyperfine field.

Analysis

We have interpreted our results in terms of a cell model in which the cell magnetization reflects the local concentration of Co and the equilibrium temperature of the entire sample. The concentration is assumed to vary throughout the sample according to a random Gaussian distribution. Within each cell, the magnetization follows a single molecular-field equation according to the Curie temperature of the concentration of the cell, while the spin S and the saturation field H_{sat} are independent of concentration. The cell volume is a parameter to be determined primarily by the analysis of the widths of the transitions. The statistical basis of our analysis is similar to that of Marshall[25] and of Klein and Brout,[26] who treated the specific heat and susceptibility of antiferromagnetic dilute alloys of copper manganese in terms of a Ruderman-Kittel interaction.

We consider the magnetic interaction to extend around each Co atom over a volume including the nearest N sites, where N is assumed to be the same for each Co atom and is assumed to be temperature-independent. Each Co atom interacts with the n Co atoms in the surrounding N sites. For random alloys n varies throughout the material, with the probability of finding n Co atoms in N sites being given, for dilute alloys with $n \gtrsim 5$, by

$$P(n)=\frac{1}{(2\pi\bar{n})^{1/2}}\exp\left(-\frac{(\bar{n}-n)^2}{2\bar{n}}\right), \tag{6}$$

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[23] B. D. Dunlap, Ph.D. thesis, University of Washington, Seattle, Washington, 1966 (unpublished).

[24] D. E. Nagle, P. P. Craig, P. Barrett, D. R. F. Cochran, C. E. Olsen, and R. D. Taylor, Phys. Rev. **125**, 490 (1962).

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where $\bar{n}=cN$ is the average value of n, and c is the bulk concentration of Co atoms in the material.

Each cell has a local Curie temperature θ determined by the number of atoms n within the cell. If the dependence of θ on n does not have an excessively high curvature, then we can write

$$\theta(n)=\theta(\bar{n})+(d\theta/dn)_{\bar{n}}(n-\bar{n})\,, \tag{7}$$

or

$$\theta(n)=T_c+a(n-\bar{n})\,, \tag{8}$$

where $\theta(\bar{n})=T_c$ is the average Curie temperature and

$$a=(d\theta/dn)_{\bar{n}}\,. \tag{9}$$

Combining Eqs. (6) and (8) we obtain the probability that a cell has the Curie temperature θ:

$$P(\theta)=\frac{1}{t(2\pi)^{1/2}}\exp\left(-\frac{(\theta-T_c)^2}{2t^2}\right), \tag{10}$$

where the mean-square deviation t^2 in Curie temperatures is given by

$$t^2=a^2\bar{n}=a^2cN\,. \tag{11}$$

We assume that the hyperfine fields of the Fe^{57} atoms in each cell follow the magnetization of the cell, each cell contributing an intensity $I(T/\theta)$ similar to the dashed line in Fig. 2, but each corresponding to the Curie temperature of the cell. The total intensity transmitted at a given temperature is determined by adding up the intensity contributions at that temperature arising from the distribution of Curie temperatures, each contribution being appropriately weighted by the Gaussian. Thus, the total intensity is

$$I(T)=\int_0^\infty I(T/\theta)P(\theta)d\theta\,. \tag{12}$$

In order to calculate $I(T/\theta)$ we have assumed that the hyperfine field on an Fe nucleus is proportional to the host magnetization. The justification for this approximation is based on the following reasons:

(1) The magnetic properties of Fe in Pd and of Co in Pd are very similar for dilute concentrations. It is then reasonable to expect Fe in Co-Pd to behave similarly to Co in Co-Pd.

(2) If the hyperfine field is not strictly proportional to the magnetization according to Eqs. (3) and (4), they become nearly proportional near T_c, as one may verify by expanding the Brillouin functions in terms of T/T_c.[27]

(3) Small deviations from the molecular-field approximation will not strongly affect the analysis because the curves calculated from Eq. (12) are strongly influenced by the Gaussian distribution and are much less sensitive to the temperature dependence of $H_i(T)$ near T_c. Therefore, we have taken

$$\frac{H_i(T)}{H_{\text{sat}}}=B_S\left(\frac{3S}{S+1}\,\frac{H_i/H_{\text{sat}}}{T/\theta}\right). \tag{13}$$

The value of S has been taken to agree with that obtained for Fe in Pd,[6] $S=13/2$, for all samples. Our results are very insensitive to this choice. Near the Curie temperature, there are no large differences between the Brillouin functions for S values varying over a considerable range, and because of the third reason stated above the particular choice of S has very little effect. Intensity curves calculated from Eq. (11) using both $S=13/2$ and $S=1$ show no important differences.

Using Eq. (12) with $S=13/2$ and the observed line shape, one can calculate the form of $I(T/\theta)$. Using this intensity distribution along with Eq. (10) in Eq. (12), we have calculated a family of curves parametrized by different values of t/T_c. These results have been compared to the data, thus providing empirical values of T_c and t/T_c for each concentration. In Fig. 3 the calculated intensities are compared to the data.

Data have also been taken for the case in which a small external field H_0 is applied to the sample. In this case the temperature dependence in each region of the material should be, within the molecular-field approximation,

$$H_i(T/\theta)=H_{\text{sat}}B_S\left(\frac{3S}{S+1}\,\frac{H_i/H_{\text{sat}}}{T/\theta}+\frac{g\mu_0SH_0}{kT}\right). \tag{14}$$

For a given sample one determines the value of T_c and of t/T_c from the $H_0=0$ data. Using these results in Eq. (10), the calculation is repeated for $H_0\neq0$, adjusting the value of $g\mu_0S$ to best fit the data. Results for the case of the 0.19% sample in an external field of 1.6 kOe are compared with a calculated curve in Fig. 3. The calculated curve corresponds to $g\mu_0S=14\pm2\mu_0$, in agreement with the assumption of the values $S=13/2$, $g\cong2$.

According to Eq. (8), if the quantity a^2N is independent of concentration, then the root-mean-square deviation in Curie temperatures t should vary as the square root of the concentration. This behavior is shown in Fig. 4. As a test of the statistical homogeneity of the lowest-concentration alloy, the values of t for other samples have been extrapolated to give the value shown by the open circle at $c=0.07\%$. This value has then been used for the calculated curve of the 0.07% alloy in Fig. 3.

The results for all alloys are given in Table I. The errors in T_c arise from the combined uncertainties in the data and in fitting the theoretical curves to the data. The uncertainties in t represent the range of values which describe the data at each concentration.

DISCUSSION OF RESULTS

We now present a simple calculation which relates the mean Curie temperature and the mean-square de-

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[27] K. P. Belov, *Magnetic Transitions* (Consultants Bureau Enterprises, Inc., New York, 1961), p. 18 ff.

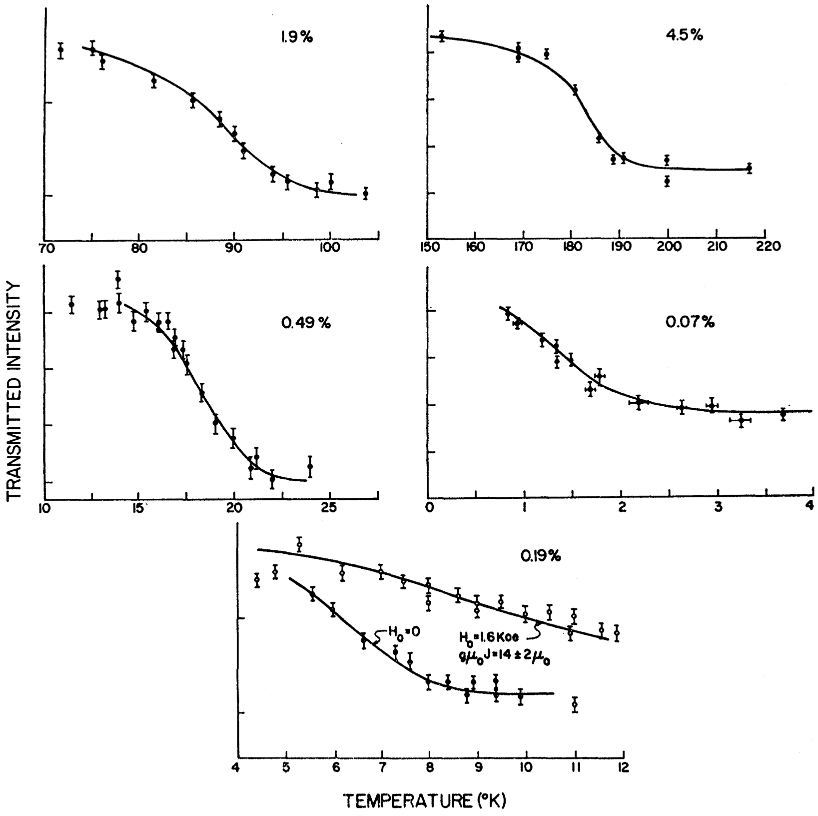

FIG. 3. Thermal-scanning data for Co-Pd alloys. The solid lines are calculated as described in the text.

viation in Curie temperatures to the spatial dependence of the magnetic interaction. In the nearest-neighbor molecular-field approximation, the local Curie temperature θ is given by

$$\theta=[2S(S+1)/3k]Jn\equiv\gamma Jn, \qquad (15)$$

where J is the nearest-neighbor exchange integral and n is the number of magnetic nearest neighbors. If the interaction has a longer range, then the formal extension of the above is

$$\theta=\gamma\sum J_i n_i, \qquad (16)$$

where J_i is the assumed isotropic exchange interaction on the ith neighboring shell and N_i is the number of magnetic atoms in the ith shell. In a random alloy, the average Curie temperature is then

$$T_c=\theta(\bar{n})=\gamma\sum J_i\bar{n}_i=\gamma c\sum J_i N_i, \qquad (17)$$

TABLE I. Concentration dependence of the mean Curie temperature T_c and the root-mean-square deviation in Curie temperatures t.

c (at.%)	T_c(°K)	t/T_c	t(°K)
4.5	186 ±1	0.03±0.005	5.58±0.99
1.91	90 ±1	0.06±0.01	5.40±0.92
0.49	18.8 ±3	0.10±0.01	1.88±0.30
0.19	6.5 ±0.5	0.20±0.05	1.30±0.37
0.07	1.55±0.1	0.48	0.75(extrapolated)

where c is the bulk concentration of magnetic atoms and N_i is the number of sites in the ith shell. The mean-square deviation in Curie temperatures throughout the material is given by

$$t^2=\langle\theta^2\rangle_{\text{av}}-(\bar{\theta})^2=\gamma^2\sum J_i^2[\langle n_i^2\rangle_{\text{av}}-(\bar{n}_i)^2]. \qquad (18)$$

For dilute alloys one has

$$\langle n_i^2\rangle_{\text{av}}-(\bar{n}_i)^2=c(1-c)N_i\cong cN_i, \qquad (19)$$

and therefore

$$t^2=\gamma^2 c\sum J_i^2 N_i. \qquad (20)$$

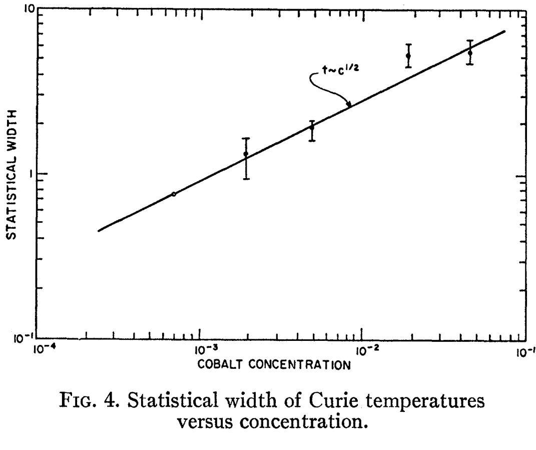

FIG. 4. Statistical width of Curie temperatures versus concentration.

Approximating the sums in Eqs. (17) and (20) by integrals, we obtain

$$T_c=\gamma c\rho\int J(r)d^3r\,, \tag{21}$$

$$t^2=\gamma^2 c\rho\int J^2(r)d^3r\,, \tag{22}$$

where ρ is the number of sites per unit volume. Thus, the magnitude and spatial dependence of the exchange interaction may be related to the quantities measured in the experiment.

A neutron-diffraction examination of a series of dilute ferromagnetic alloys of Co in Pd and Fe in Pd has shown that the density of electron polarization surrounding each magnetic ion decreases very slowly with distance.[28] The distribution of magnetization, at intermediate distances from the magnetic impurity, can be approximated by a Gaussian:

$$m(r)=m_0\exp(-r^2/2\sigma^2)\,. \tag{23}$$

We are able to make use of this form factor by assuming that the exchange integral between magnetic ions is proportional to the overlap of their magnetizations.[29] For two impurities separated by a distance r', this exchange integral is

$$\begin{aligned} J(r')&=\text{const}\int m(r)m(r-r')d^3r \\ &=J_0\exp(-r'^2/4\sigma^2)\,. \end{aligned} \tag{24}$$

We may now obtain T_c and t^2 according to Eqs. (21) and (22):

$$T_c=\gamma\int J(r')d\bar{n}(r')=(4\pi\sigma^2)^{3/2}J_0\gamma\rho c\,,$$

$$t^2=\gamma\int[J(r')]^2d\bar{n}(r')=(2\pi\sigma^2)^{3/2}J_0{}^2\gamma^2\rho c\,. \tag{25}$$

The range parameter σ can be obtained directly from the ratio

$$(T_c/t)^2=8(2\pi\sigma^2)^{3/2}\rho c\,. \tag{26}$$

From the four alloys in the concentration range 0.19% to 4.9%, we obtain the value

$$\sigma=12.7\pm1.1\text{ Å}.$$

The number of atomic sites included in this range is

$$N_\sigma=\tfrac{4}{3}\pi\rho\sigma^3=500\pm140.$$

The exchange constant corresponding to this value of σ is $J_0/k=0.018\pm0.004$°K. Neither σ nor J_0 show any trend with concentration within the experimental range.

We may also estimate the range from the critical concentration for ferromagnetic ordering. The values of T_c obtained experimentally are seen to be proportional to c in agreement with Eq. (25) for concentrations $\gtrsim0.1\%$; however, the value obtained for $c=0.07\%$ falls below the linear relation. This is due to the failure of the molecular field model in the low-concentration region, which predicts T_c proportional to c for all concentrations. For nearest-neighbor interactions and classical spins in a Bethe-Peierls-Weiss (BPW) approximation, it has been shown[1,2] that the Curie temperature should be given as a function of concentration by

$$\mathcal{L}\left[\frac{2s(s+1)J}{kT_c}\right]=\frac{1}{c(z-1)}\,, \tag{27}$$

where $\mathcal{L}(x)$ is the Langevin function, J is the nearest-neighbor interaction, and z is the number of nearest-neighbor sites. If the interaction is constant over N sites and zero beyond that, then Eq. (27) is still true with N replacing z. We note from Eq. (25) that the Curie temperature

$$T_c=6\pi^{1/2}N_\sigma\gamma cJ_0 \tag{28}$$

is equivalent to the BPW Curie temperature due to a constant exchange J_0 acting over $6\pi^{1/2}N_\sigma$ sites. Therefore, we expect that the variation of T_c with c should correspond to the Smart and Lyons dependence, with an effective interaction number $6\pi^{1/2}N_\sigma$. The data are compared with this model in Fig. 5 for several choices of N_σ. The data appear best described by $N_\sigma=180\pm20$, less than one-half of the value deduced from the relative widths of the transitions. The corresponding range $\sigma=10\pm0.4$ Å. Although we feel that the more detailed measurements of the transition curves yield a more reliable value for σ, we find it difficult to make a quantitative weighting of their reliability, and therefore take the average value

$$\sigma=11.5\pm1.2\text{ Å}.$$

The range σ determined from our measurements is considerably greater than that indicated by neutron scattering. For five alloys of 0.3% to 4.0% Co in Pd at helium temperature, the measurements of Low and Holden[28] indicate $4\text{ Å}\leqslant\sigma\leqslant5\text{ Å}$ for distances in the range 3–9 Å. However, as Low and Holden note, the neutron data in this range yield values for the total localized moment of each Co impurity which are at least a factor of 2 lower than the moments directly determined by magnetization studies.[7] The same pattern of disagreement is found for alloys of Fe in Pd. The neutron measurements[28] show a similar shape for the form factor of the distribution of magnetization about the Fe impurities, with $2.8\text{ Å}\leqslant\sigma\leqslant3.2\text{ Å}$, and an integrated total moment less than one-half of the directly measured value.[7] A recent study of Mössbauer spectra

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[28] G. G. Low, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society of London, 1965), p. 133; G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) 89, 119 (1966).

[29] We are grateful to T. A. Kitchens (private communication) for this point, correcting an error in an earlier version of this paper.

from Fe^{57} in 0.22% to 13% Fe in Pd,[30] when analyzed on the same basis as our assumptions of random local variations of impurity concentration, indicates a longer range $\sigma \simeq 4.2$ Å.[31]

The discrepancies among the three sets of measurements—magnetization, neutron, and Mössbauer effect—seem to indicate a form factor different from the assumed Gaussian dependence. The existence of a slowly varying low tail to the distribution is not ruled out by the existing neutron data. Such a longer-range component would easily raise the integrated form factor to the measured value of the local moment. However, it is clear that the simple addition of a weakly varying tail to a Gaussian having the presently deduced m_0 and σ would not bring all the data into agreement. This is because the range determined by the Mössbauer study of Co alloys, together with the value of m_0 extrapolated from the neutron data, yield a value for the total localized moments considerably larger than that directly measured.[7]

For concentrations greater than 2%, the previously obtained Curie temperatures[3] are in agreement with those obtained in the present work. However, in the very dilute alloys the current measurements give substantially lower values of T_c. For example, Bozorth *et al.* quote a value of 7°K for the Curie temperatures of a 0.1% alloy whereas we find a mean Curie temperature of 2.8°K for the same concentration. Such discrepancies between Mössbauer measurements and conventional magnetization measurements have been observed before for similar alloys. Craig *et al.*[12] used both the Mössbauer technique and magnetization measurements to determine T_c in an alloy of 2.65% Fe in Pd. It was found that conventional extrapolation procedures applied to the magnetization gave a Curie temperature of 107°K while the Mössbauer effect showed the Curie temperature to be 90°K. It was concluded that great caution must be exercised in performing the extrapolation of the magnetization, and that the Mössbauer method provided a more sensitive and more reliable value of T_c.

In very dilute alloys there is another effect which may cause the results obtained by Mössbauer measurements to differ from magnetization results. Magnetization measurements will yield for the Curie point the temperature at which a significant spontaneous magnetization appears. Due to the distribution of Curie temperatures present in the alloy, this temperature can be significantly higher than the average Curie temperature. The precise value of T_c obtained from the magnetization will depend on the extent of the fluctuations as well as on the sensitivity of the experiment. Thus, for concentrations in which the value of t is an appreciable fraction of T_c the results of the methods will differ, and this in fact will be the region of low concentration.

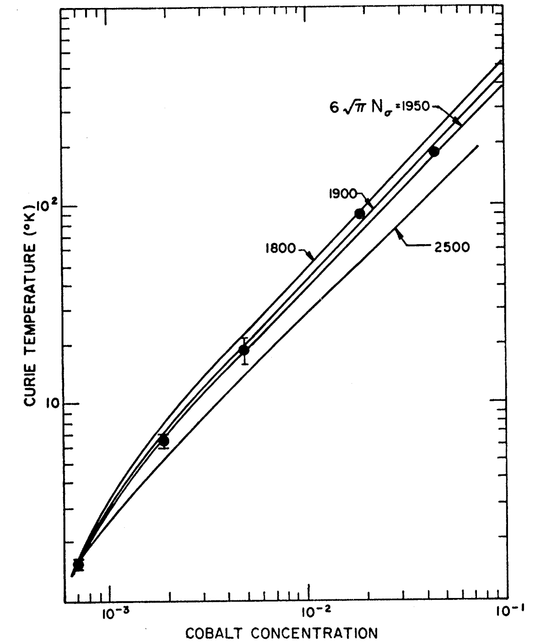

FIG. 5. Mean Curie temperature versus concentration. The solid lines are calculated assuming a sharp-cutoff interaction.

Support for this suggestion comes also from another set of experiments. Specific-heat measurements on a series of Fe-Pd alloys[32] having Fe concentrations between 1.52 and 0.09 at.% show a very broad magnetic anomaly, whose width is attributed by the authors to concentration fluctuations. If this is the case, then we can consider the temperature of the specific-heat maximum to represent the mean Curie temperature. Independent measurements of similar alloys[4] yield Curie temperatures significantly higher than the mean Curie temperatures of the specific-heat anomaly.

ACKNOWLEDGMENTS

We wish to acknowledge the assistance of P. M. Higgs, D. G. Howard, and J. D. Siegwarth throughout the course of this research. We are especially grateful to P. M. Higgs for the design and construction of the sputtering apparatus used in the preparation of the samples. W. D. McCormick was helpful in early discussion of the research.

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[30] W. L. Trousdale, T. A. Kitchens, and G. Longworth (to be published).

[31] The range parameter given by Trousdale *et al.* (Ref. 30) is a factor $\sqrt{2}$ larger due to their use of the Gaussian $\exp(-r^2/\sigma^2)$ for the magnetization in place of our $\exp(-r^2/2\sigma^2)$.

[32] B. W. Veal and J. A. Rayne, Phys. Rev. **135**, A442 (1964).