

LONG-RANGE CONDUCTION-ELECTRON POLARIZATION IN Pd-BASED Fe-Pd ALLOYS*

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Recently experimental evidence has appeared for the existence of short-range oscillatory terms contributing to the hyperfine magnetic field at Fe in Fe-based Al-Fe and Si-Fe alloys,^{1,2} and in V-Fe alloys.^{1,3} In these experiments the hyperfine magnetic field acting at Fe nuclei could be understood as a sum of contributions (with appropriate sign) from Fe neighbors at various distances from a given site. Neighboring sites occupied by Al, Si, or V atoms appeared to behave as holes in the magnetic structure and did not contribute to the resultant hyperfine field. Analysis of the data led to the conclusion that the exchange field oscillates in sign spatially in a manner similar to that of the Ruderman-Kittel-Yosida type of interaction.

In this Letter we report studies of the variation with composition of the hyperfine magnetic field at Fe sites in a series of ferromagnetic Fe-Pd alloys. In each sample of this random substitutional alloy the hyperfine field at low temperatures was found to be identical at every Fe site, despite the fact that the hyperfine field is a sharply varying function of sample composition. The hyperfine field varies from -295 kOe for Fe in pure Pd to -335 kOe at Fe sites in $\text{Fe}_{43}\text{Pd}_{57}$. The initial variation of hyperfine field with Fe concentration is linear, and is -4.80 kOe per % Fe. These results indicate that the conduction-electron polarization changes only very slowly over extremely long ranges, and furthermore that the exchange interaction does not oscillate in sign spatially. A model is proposed which predicts the variation of the hyperfine field with composition.

At concentrations below 25 at. %, Fe forms a continuous series of solid solutions in Pd, entering the fcc Pd lattice as a random substitutional impurity. The alloy series is ferromagnetic with Curie temperatures decreasing monotonically with decreasing Fe. The related Co-Fe series is known to remain ferromagnetic to Co concentrations as low as 0.1%.⁴ The magnetic moment per Fe increases in the Fe-Pd system from $2.2\mu_{\text{B}}$ (Bohr magnetons) in pure Fe to $12\mu_{\text{B}}$ in highly dilute alloys.^{5,6} Neutron diffraction studies⁷ show the moment on

Fe in FePd_3 to be $2.86\mu_{\text{B}}$. Neutron diffraction studies by Low⁸ of the spatial distribution of spin density at 0.25% Fe concentration have shown that the moment associated with the Fe impurities extends to distances exceeding 10 \AA . The moment associated with each Fe is about $3\mu_{\text{B}}$, while the moment on the Pd has a maximum value of only about $0.06\mu_{\text{B}}$ per Pd.

A series of Mössbauer absorbers were prepared in the composition range $\text{Fe}_4\text{Pd}_{96}$ to $\text{Fe}_{43}\text{Pd}_{57}$. Measurements of the Fe hyperfine field were made in zero external field at liquid-helium temperatures (sufficiently below the sample Curie temperatures that saturation values of the hyperfine fields were observed). In each sample the hyperfine field was found to be unique, in the sense that a six-line hyperfine spectrum was obtained, the lines were approximately Lorentzian in shape, no component line was broadened over the linewidth observed above the Curie temperature (0.4-mm/sec velocity full width at half-maximum for Fe concentrations below 10% Fe and about 0.7 mm/sec near 10% Fe), and no structure was observed in any component line (in contrast to the Fe-Al, Fe-Si, and Fe-V systems).^{1,3} Figure 1 presents the observed hyperfine fields as a function of composition (the point at zero Fe concentration is taken from the paramagnetic studies of reference 6). For Fe concentrations below about 12% the variation of the hyperfine field is rapid. At higher concentrations the field approaches a constant value of about -335 kOe, and thereafter remains almost constant to pure Fe (-338 kOe) despite a phase change to bcc structure.

Uniqueness of hyperfine fields over a range of compositions has been observed previously at low Fe concentrations in the Co-Pd system⁹ and in the Fe-Ni and Fe-Co systems.¹⁰ In those cases there was no variation of hyperfine field with composition, and hence no conclusions could be drawn as to the range of the conduction-electron polarization. In the present case the observation of a unique hyperfine field at each sample composition combined with the rapid variation of hyperfine field as the composition is varied indicates that the conduction-electron polarization remains spatially constant

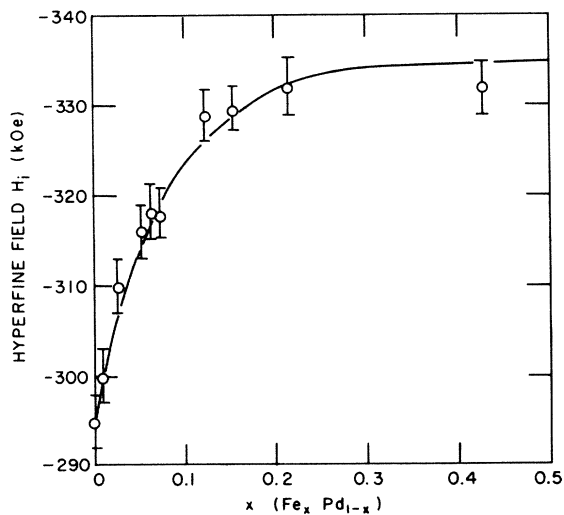


FIG. 1. Hyperfine magnetic fields in a series of Fe in Pd alloys. The curve through the data is based on a semitheoretical model. Agreement of the model with experiment is indicative of long-range conduction-electron polarization which results from the high density of states in these alloys and is in contrast to the Ruderman-Kittel-Yosida type of interaction.

over regions long in comparison to composition fluctuation distances. Thus, if only nearest-neighbor interactions were involved, in the 5% sample over half the Fe atoms would have no Fe nearest neighbors, and would exhibit the hyperfine field of -295 kOe characteristic of infinitely dilute Fe in Pd,⁶ in contrast to the unique field of -317 kOe observed. By considering various numbers of nearest neighbors and compositions we conclude that for the compositions studied the hyperfine field is unique for all Fe atoms separated from other Fe atoms by many times the mean Fe-Fe spacing, in agreement with Low's range of induced polarization of about 10 \AA for 0.25% Fe in Pd.⁸

The presence of long-range polarization of the Pd conduction band suggests a simple mechanism which allows us to explain the concentration dependence of the hyperfine field. We consider the Pd to act as a polarizable matrix. The polarization is taken as a constant over a correlation distance R determined by the Fe impurity concentration x . At low Fe concentrations this range is long,⁸ while at higher concentrations (e.g., pure Fe) it decreases.^{1,3} We assume the hyperfine field at any Fe atom to be the hyperfine field of an isolated Fe atom in Pd (at infinite dilution) plus a concentration-dependent term due to the modification of the

contact interaction arising from polarization of the Pd-band electrons by the N Fe atoms within a volume $V(x) \sim R^3$.^{11,12} The contribution to the conduction-electron polarization from pairs of adjacent Fe impurities differs from that of Fe impurities with no nearest neighbors due to interactions between neighbors.¹³ An essential assumption of our model is that one Fe nearest neighbor is sufficient to saturate this interaction, so the effect of one or of more than one nearest neighbor is identical. Since each Fe impurity produces a contribution to the total polarization within $V(x)$ of order $1/N$, the field at each Fe impurity in $V(x)$ is independent of the number of its Fe neighbors, and depends only upon the total polarization within $V(x)$.

If we denote by $P_0(x)$ the probability that any Fe atom has zero Fe nearest neighbors, then the probability of one or more nearest neighbors is $1 - P_0(x)$. The magnitude of the hyperfine field [unique at all sites within $V(x)$] is proportional to the conduction-electron polarization and may be expressed as the sum of the contribution due to the $NP_0(x)$ Fe atoms with no nearest neighbors plus that from the $N[1 - P_0(x)]$ Fe atoms with one or more Fe nearest neighbors:

$$H_i = a_0 NP_0(x) + a_1 N[1 - P_0(x)], \quad (1)$$

where a_0 and a_1 are constants. For the fcc Pd lattice $P_0(x) = (1-x)^{12}$. We assume R to be determined by mean free path effects limited by the Fe impurities, and hence proportional to the mean Fe spacing: $R = bx^{-1/3}$ where b is concentration independent. Within a volume $V(x) \sim R^3$ the hyperfine field at any Fe impurity is proportional to the sum of the polarization produced by N Fe atoms. Since $N = xV(x)$ and $V(x) \sim R^3 = b^3/x$, the number N of Fe atoms contributing to the polarization at any point is independent of concentration. This assumption is similar to a conclusion of Klein and Brout regarding the correlation range in dilute alloys.^{14,15} The coefficients a_0N and a_1N of Eq. (1) may now be determined using the known hyperfine fields at $x = 0$ (-295 kOe)⁸ and large x (-335 kOe). Therefore, we have

$$H_i = -295 - 40[1 - (1-x)^{12}] \text{ kOe}, \quad (2)$$

which is plotted as the solid curve in Fig. 1 and offers excellent agreement with experiment. Of particular interest is the ability of the mod-

el to predict accurately the initial slope of the hyperfine field with concentration using as input parameters only the limiting hyperfine field values at low and high Fe concentrations.

These results suggest that the exchange mechanism in Pd differs considerably from that in most other systems. The difference is characterized by long-range conduction-electron polarization with little if any oscillatory part over distances long compared to composition fluctuation distances. Insight into the origin of these differences in behavior may be found in the studies of Anderson,¹⁶ Wolff,¹⁷ and Clogston¹⁸ on the occurrence of local moments associated with magnetic impurities. Clogston et al.⁵ have discussed Fe dissolved in transition metals, and have found that the large electronic density of states of Pd leads to giant moments, with the majority of the moment arising from the polarization of the host through the large scattering cross section associated with the formation of virtual levels. These studies showed that an iron impurity in Pd has a local electron density which is strongly peaked near the Fermi energy, the peak superimposed on the normally high density of states of Pd. As the iron concentration increases, the "virtual level" is expected to broaden into an impurity band and to modify the average electron density of states in the alloys. Consideration of this broadening permits us to understand in a more fundamental way the linear portion of the variation of H_i with Fe concentration. We have thus far been unable to carry the model to the point of treating high concentrations where nonlinear behavior sets in, and which is so easily dealt with on the model presented above. Eventual understanding of the effects observed must certainly be in terms of density-of-state arguments. In the meantime, the effect of composition on the density of states may be studied through the electronic specific heats of dilute Fe in Pd alloys. Results similar to those in the Fe-Pd system are also ex-

pected in other high density-of-state alloys such as Fe in Pt.

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