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Experimental Investigation on Exchange Interaction in Platinum-Iron Alloys*

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Measurements of the temperature dependence of the hyperfine magnetic field H_i at Fe nuclei and the concentration dependence of the transition temperature T_c in platinum-iron alloys have been carried out by using the Mössbauer-effect technique. These experiments have been done in a series of dilute alloys ranging between 1 and 15 at.% of iron concentration. We find that at low temperatures ($T \ll T_c$), H_i is nearly the same at each Fe nucleus. As the temperature is increased, a broadening of the absorption lines of the Mössbauer spectra is observed. Such broadening may be due to the presence of a rather wide distribution of fields H_i, although relaxation effects cannot be completely ruled out. The concentration dependence of the transition temperature T_c can be related to a short-range interaction (not necessarily first nearest neighbors) between magnetic atoms (for Fe concentrations between about 2 and 8 at.%), and to a longer-range weaker interaction (below 1 at.% Fe) between magnetic impurities via the enhanced conduction-electron polarization of the platinum matrix.

INTRODUCTION

RECENTLY the problem of ferromagnetism in alloys of the iron-series elements with the platinum-group elements has been studied extensively. In particular, susceptibility, magnetization, and hyperfine field measurements on Fe–Pd and Co–Pd alloys[1–5] indicate that the magnetic moment associated with each cobalt or iron atom increases from $1.8\mu_B$ and $2.2\mu_B$ in pure cobalt or iron to about $10\mu_B$ at very small iron or cobalt concentrations (less than 1 at.%). Moreover, ferromagnetism has been detected in all these alloys down to iron or cobalt concentration of less than 1 at.%, indicating long-range ferromagnetic interactions. Neutron-diffraction measurements in dilute ferromagnetic Fe–Pd alloys performed by Low[6] *et al.* indicate that the magnetic-moment density on Pd atoms surrounding an iron atom falls off rather gradually with distance from the iron atom, decreasing to one-half of its value at about 5 Å from the iron. The large moments and the long-range interaction imply a long-range spin polarization in the host metal. Measurements[7] of the temperature dependence of the hyperfine field at the Fe nuclei in a dilute ($Fe_{2.65}Pd_{97.35}$) alloy indicate that the variation of the hyperfine fields in the ferromagnetic region follows the bulk magnetization for the whole temperature range up to the Curie point.

Studies of the magnetic hyperfine field of iron–platinum-group alloys can therefore be expected to enhance our knowledge regarding the problem of ferromagnetism in metals and in particular the electron spin polarization in strongly paramagnetic host lattices with dilute magnetic impurities.

The present work reports measurements of the hyperfine field H_i at the Fe nuclei in iron–platinum alloys using the Mössbauer-effect technique. A careful study of these fields as a function of temperature and concentration in the Fe–Pt system and a comparison with the corresponding values in Fe–Pd alloys is important, since, in contrast to the Fe–Pd system, which is magnetically similar to the Fe–Pt system, the hyperfine fields in the Fe–Pt alloys can also be studied at the nuclei of the host atoms using the Mössbauer line in Pt^{195}. Thus, one can gain additional information on the mechanism of the magnetic interactions in these systems.

EXPERIMENTAL PROCEDURE

Alloys

A series of Fe–Pt alloys was prepared ranging from 1 to 15 at.% in iron concentration. The alloys were prepared by melting, in an argon arc furnace, pure (99.99%) platinum and spectroscopically pure iron (99.99%) in the desired proportions. The iron content of the samples was determined by chemical analysis to an accuracy of at least 0.05 at.%. Spectrographic analysis indicated the absence of any impurity in relevant quantity.

Traces of radioactive Co^{57} were diffused into ≈0.001-in.-thick foils of the alloys by heating in hydrogen at 900°C for 2 h. Each sample was then annealed for 24 h in a vacuum ($\approx 3\times10^{-6}$ mm). The $Fe_{13.1}Pt_{86.9}$ sample was annealed in vacuum at 800°C for 6 days. These foils were used as sources in the Mössbauer measurement. The absorber was a $K_4Fe(CN)_6\cdot10H_2O$ disk, with 75 at.% Fe^{57} enrichment which gave a linewidth of 0.30 mm/sec with a natural linewidth Co^{57} in the copper source.

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Measurements

The measurements were performed by using a standard Mössbauer arrangement: sinusoidal or parabolic absorber motion, linear velocity to pulse-height conversion, and data accumulation in a multichannel analyzer.

The temperature-control system employed was based on the one described by Sommers.[8] The temperature of the alloys was kept constant within a tenth of a degree for several days by enclosing the samples, the heater element, the thermometer resistor, and the thermocouple in a styrofoam capsule which was sealed off with epoxy resin, which provided a tight seal even when immersed in liquid helium.

Results

Figs. 1–3 show the usual Mössbauer spectra as a function of absorber velocity over a wide range of temperature for three Fe–Pt alloys of different concentration. The alloys show the same general behavior. Since the experimental linewidths observed in our alloys well above the transition temperature T_c (up to room temperature) and at 4°K are about the same, it can be deduced that the hyperfine fields are nearly unique at low temperatures. As the temperature is raised, however, the linewidth increases in a qualitatively similar manner for each concentration and could be attributed to a wider distribution of fields.

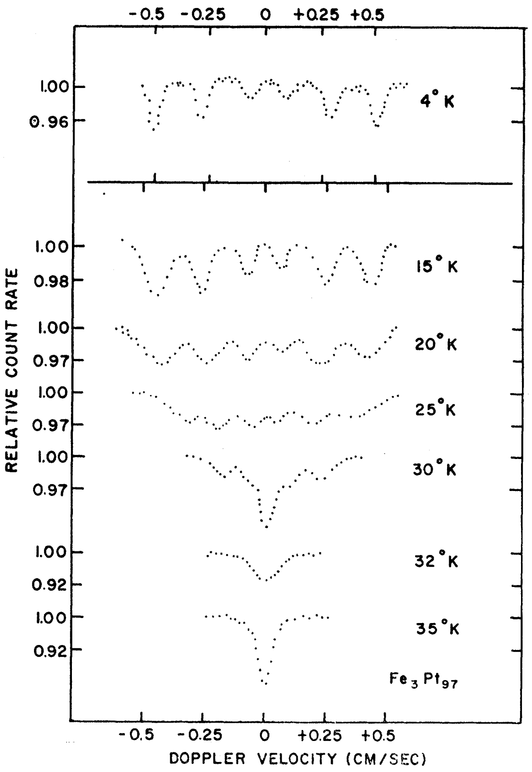

FIG. 1. The Mössbauer absorption spectra for Fe_3Pt_{97}.

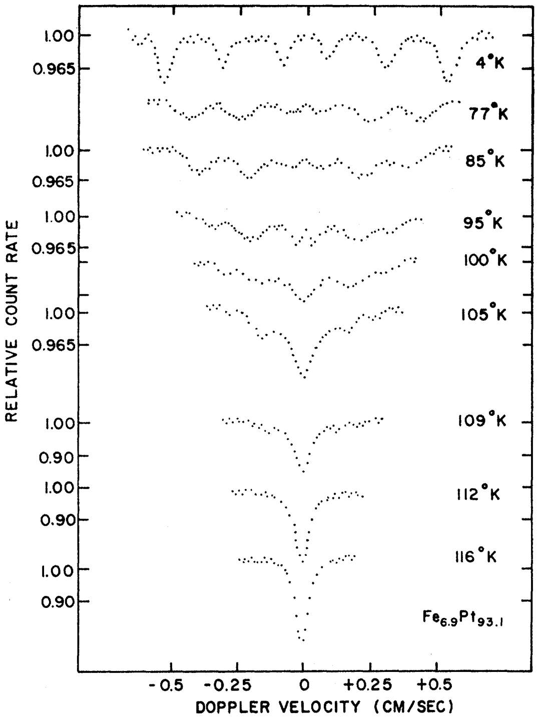

FIG. 2. The Mössbauer absorption spectra for $Fe_{6.9}Pt_{93.1}$.

The Curie temperatures T_c were determined as a function of composition for several alloys (Fig. 4). Determinations of the Curie temperatures from bulk magnetization measurements[4] are also included in the figure. The agreement between the two sets of data is remarkably good. The Curie temperature was determined from measurements of (1) the linewidth and (2) the intensity of the Mössbauer line near T_c as a function of temperature. In the first method T_c is determined by measuring the onset of a constant linewidth, in the second method by measuring the height in the absorption spectrum. Apart from the purely experimental uncertainties in this determination, the Curie temperatures determined by these methods may be somewhat larger than the correct ones if the distribution of hyperfine fields at the Fe sites varies markedly near the transition region. We estimate however that our Curie-point values are accurate to within at least ±2°K. The observed flattening out of the T_c-versus-Fe-concentration curve which starts above about 8 at.% Fe concentration might be associated with the formation of a superlattice structure near the $FePt_3$ composition. On the other hand, the flattening could be attributed to saturation effects, i.e., there is a limitation on the polarization that can be induced on a Pt atom since the magnetic atoms, being now present in great enough number, start to compete with each

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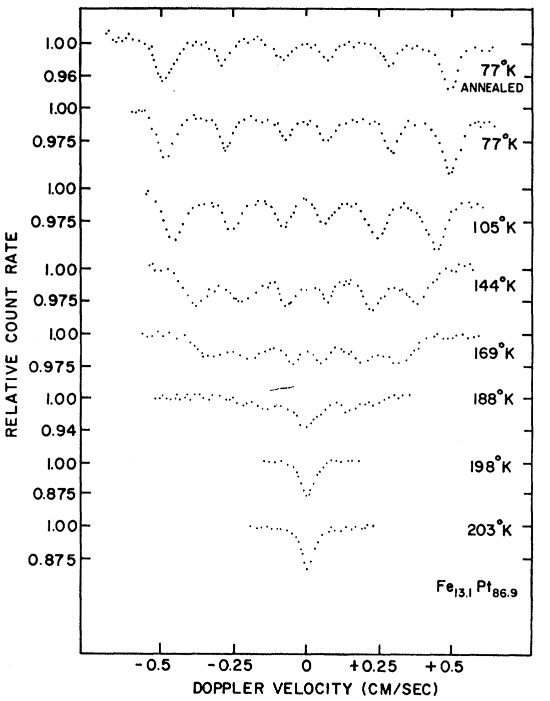

FIG. 3. The Mössbauer absorption spectra for $Fe_{13.1}Pt_{86.9}$.

other for the polarization of the matrix. Measurements by Crangle[9] suggest the existence of antiferromagnetism in the order state of these alloys near the 25 at.% iron concentration. This region is presently being investigated in detail using the Mössbauer-effect technique. In this paper we discuss only the low-Fe-concentration region.

DISCUSSION OF RESULTS

It is apparent from Figs. 1–3 that the temperature dependence of the hyperfine field H_i exhibits a complex behavior. At low temperatures ($T \ll T_c$), H_i is nearly the same at each Fe nucleus. As the temperature is increased the linewidth broadens; this may be due to a rather wide distribution of fields H_i but may also be caused by relaxation effects. If the effect is due to a distribution of fields, then it is tempting to analyze the data in terms of a statistical distribution of magnetic atoms. It should then be possible to extract, from fits of the experimentally determined line shape with molecular-field–type calculations, the strength of the interaction between magnetic atoms and gain some information regarding the range of the interaction. An extensive analysis of this kind was carried out by Trousdale, Kitchens, and Longworth[10] on Fe–Pd alloys. These authors included explicitly in their statistical model up to 126 lattice sites extending to eight orders of nearest neighbors. Magnetic atoms beyond the eighth nearest neighbors were taken into account by considering such lattice sites as being of uniform density in concentric spherical shells. The calculation was cut off when a uniform density of the remaining atoms contributed less than 5% to the average field. By considering an interaction between two iron atoms of the type $J \propto \exp(-r^2/2\sigma^2)$ (where J is the exchange integral and σ is the distance at which the polarization around an iron atom falls to $1/e$ of its maximum value), Trousdale, Kitchens, and Longworth obtain from their analysis a value of about 6.5 Å for the range of the interaction σ. By assuming the same kind of interaction between two iron atoms, we could carry out a similar analysis for the Pt–Fe system obtaining a value for the range constant. Since our results are very similar to those obtained in the Fe–Pd system, it can be deduced that the value of σ in Fe–Pt will be in the same range as in Fe–Pd, although it might be somewhat smaller. We have not carried out the detailed analysis since an accurate value of the range of the interaction and a detailed reliable one-parameter fit was difficult to obtain by this method. In addition, an analysis in terms of relaxation phenomena gave a good fit to the Mössbauer spectra so that at least part of the line broadening may have its origin in this effect. In view of these facts, we feel that it would be difficult to extract from our data any quantitative information about the mechanism of the interaction in these systems without additional experimental and theoretical work.

The existence of local magnetic moments at the Fe atoms has been established in Fe–Pd alloys by means of neutron-diffraction experiments, for example; local moments should also exist in Fe–Pt alloys. The interaction between these local spins proceeds via the conduction electrons and can be described in terms of the well-known Ruderman–Kittel–Kasuya–Yosida (RKKY) theory. However, the original RKKY theory must be modified since the conduction electrons in the present case have considerable d rather than pure s character, and we should also consider the mutual

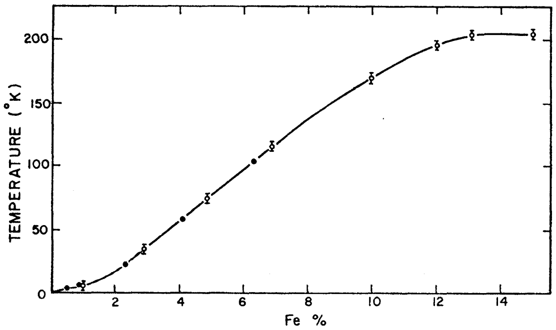

FIG. 4. The transition temperature of the Fe–Pt system as a function of the Fe concentration in at.%. The black dots represent bulk-magentization data taken from Ref. 4, the open circles represent data obtained in this work.

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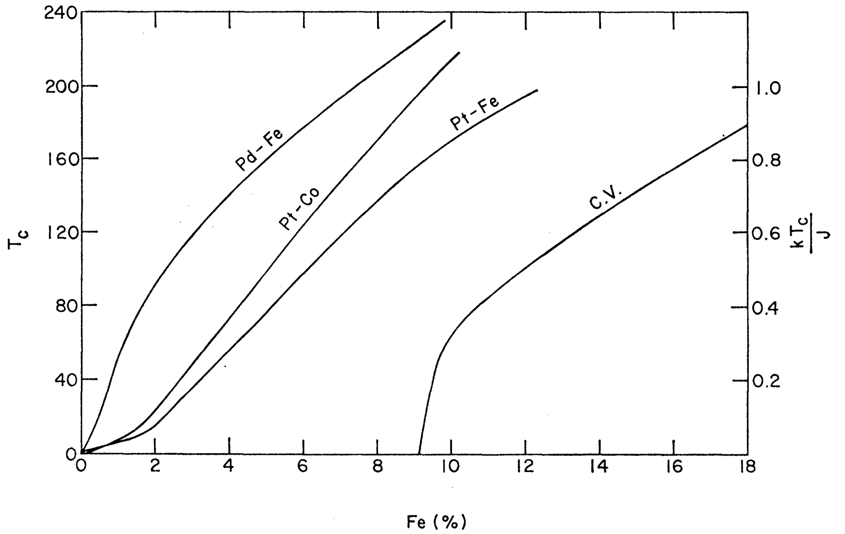

FIG. 5. Transition temperature (°K) in the Pd–Fe, Pt–Co and Pt–Fe systems as deduced by means of bulk magnetization (Crangle) and Mössbauer measurements. The curve C. V. represents the result of the cluster-variation theory.

interaction between the conduction electrons. Giovannini, Peter, and Schrieffer[11] considered the exchange correction to the RKKY interaction. They find that the *d*-electron exchange interactions in the matrix strongly modify the form of the induced polarization surrounding the localized moment (in our case Fe atoms). The main effect is to increase the polarization on the sites neighboring the localized moment. Recently, Kim[12] has considered the problem of ferromagnetism in dilute alloys. Of his results the one of importance to us is the linear dependence of the critical temperature T_c versus concentration of magnetic atoms. An examination of the T_c-versus-concentration curve (Fig. 4) suggests that one may divide it into two regions: one between about 0- and 1-at.% Fe concentration and the other between about 2 and 8 at.%. From Fig. 4 one observes that T_c depends linearly on concentration between 2 and 8 at.% Fe. However, if a fit is made between the experimental data and Kim's results, a rather high value for the conduction-electron–impurity-spin exchange integral is found ($J\sim1$ eV). If one assumes that the region between nearly 0 and 1 at.% Fe concentration is also linear, one obtains a value for J of 0.5 eV. Both values seem unrealistically high. [*Note added in proof*. By using more recent magnetic-susceptibility measurements (see Ref. 13), for the region up to 1 at.% of Fe, one obtains a smaller value ($J\sim0.14$ eV) for the spin-exchange integral. The author is indebted to Dr. D. J. Kim for bringing to his attention the magnetic-susceptibility data.]

By extrapolating the region between 2 and 8 at.% Fe to zero T_c, one obtains a value of about 2 at.% for the concentration. This concentration corresponds to a 20% probability that any iron atom will have a second iron atom as nearest neighbor. On the other hand, one can make an estimate of the average separation between magnetic atoms. On the average, for a 2 at.% Fe concentration, two magnetic atoms are at a distance of about 5.2 Å from each other. This corresponds for an fcc system to roughly a four-nearest-neighbor separation (the first-nearest-neighbor distance is about 3 Å). It is tempting to speculate that in the region between about 2 and 8 at.% concentration there exists a short-range exchange mechanism which extends to a few nearest neighbors and which contributes additively to the exchange polarization. In this concentration region, the short-range effect appears to be the dominant one and may have its origin in the fact that the iron atoms induce a magnetic moment on surrounding Pt atoms which is, however, local in character. In other words, it seems quite possible that the localized wave functions corresponding to the so-called giant moments extend further spacially than the bare-iron localized wave functions. There exists, therefore, a short-range exchange interaction corresponding to the spacially extended but still localized wave functions. For concentrations lower than 1 at.% the short-range direct-exchange contribution becomes small, and the interaction is primarily caused by longer-range weaker indirect exchange between magnetic impurities via the enhanced conduction-electron polarization of the platinum matrix. Two linear regions at low concentrations, in the T_c-versus-concentration curve, can also be observed in the Pd–Fe and Pt–Co alloys (Fig. 5). The behavior of all the alloys is qualitatively very similar. The curve labeled C.V. represents the result of the theoretical treatment discussed by Sato *et al.*[14] The theoretical curve gives a critical concentration of 9 at.% for the onset of ferromagnetic ordering, which is much higher than the extrapolated experimental one. It must

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be pointed out, however, that the theoretical result was obtained considering direct interactions involving only nearest-neighbor magnetic atoms in a diamagnetic matrix. The induced moments on the host-metal Pt atoms would increase the extent of the short-range interaction and decrease the critical concentration. A fit of the linear part of the C.V. curve to the 2–8 at.% part of the experimental curve gives a value for the exchange coupling constant $J=0.5$ eV, which is somewhat high.

ACKNOWLEDGMENTS

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Magnetic Phase Equilibrium in Chromium-Substituted Calcium Ferrite*,†

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The structure of $CaFe_2O_4$ has orthorhombic symmetry (space group D_{2h}^{16}-*Pnam*) and is characterized by Fe–O–Fe–O chains within which the Fe–O–Fe bond angle is ~130°. These chains are cross-linked by means of Fe–O–Fe bonds in which the angle is ~99°. The compounds $Ca(Cr_xFe_{1-x})_2O_4$, with $0\leq x\leq 0.5$, have been found, by means of neutron measurements, to exhibit two magnetic structures in each of which the chains are internally antiferromagnetic, with spins alternating $+--+--$ along a chain. In one structure the chains are linked ferromagnetically through the 99° bonds, with magnetic symmetry *Pn′a′m*, and in the second they are antiferromagnetically coupled, corresponding to the space group *Pna′m*. A phase diagram has been constructed showing both single-phase regions and a region in which the two phases exist in equilibrium. Transition temperatures as well as the temperature dependence of magnetic moments and phase concentration have been determined as a function of chromium content. The problem posed by the coexistence, at equilibrium, of two magnetic phases belonging to a single crystal structure is discussed.

INTRODUCTION

In this paper we present the results of a systematic study of the magnetic structures occurring in the compounds $Ca(Cr_xFe_{1-x})_2O_4$ for $0\leq x\leq 0.5$. It is proposed that in certain broad temperature and composition ranges, two distinct magnetic phases coexist in thermal equilibrium. This phenomenon has not, to our knowledge, been previously reported in the literature. In the course of preparing this work for publication, we have received several communications[1] reporting work in other laboratories on unsubstituted $CaFe_2O_4$. All groups agree on the magnetic structure of $CaFe_2O_4$ at low temperatures, but only Watanabe *et al.*[1] confirm our observation of a second magnetic phase at higher temperatures. The case of $CaFe_2O_4$ is discussed in greater detail below in the section devoted to the pure compound.

CRYSTAL STRUCTURE

The crystal structure of $CaFe_2O_4$ was first studied by Bertaut, Blum, and Magnano,[2] who also reported the isomorphism with β-$CaCr_2O_4$, and further established by the detailed determinations of Hill, Peiser, and Rait[3] and of Decker and Kasper.[4] The compound is orthorhombic and the coordination of oxygen atoms around iron is approximately octahedral. Following Decker and Kasper, the space group is D_{2h}^{16}-*Pnam* with $a_0=9.230\pm0.012$ Å, $b_0=10.705\pm0.014$ Å, $c_0=3.024\pm0.004$ Å, and all atoms are in position

$$4(c):\quad \pm(x,y,\tfrac{1}{4};\tfrac{1}{2}+x,\tfrac{1}{2}-y,\tfrac{1}{4}).$$

The structure is shown in (001) projection in Fig. 1. Iron atoms are distributed in staggered Fe–O–Fe–O–··· chains (heavy lines of Fig. 1) with Fe–O–Fe bond angle approximately 130°. These chains are cross-linked by means of Fe–O–Fe bonds in which the angle is about 99°.

SAMPLE PREPARATION

Samples were prepared in a variety of ways to insure that the observed phenomena were not accidentally

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‡ Short accounts of this work were presented at the Seventh International Congress of the International Union of Crystallography, Moscow, 1966, and at the Twelfth Annual Conference on Magnetism and Magnetic Materials, Washington, D. C., 1966.

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