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Magnetic Behavior of the Pt+Fe System Near Pt_3Fe†

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The complex magnetic behavior of the Pt+Fe system near Pt_3Fe has been investigated by means of the Mössbauer effect. The temperature dependence of the hyperfine field has been measured for alloys with iron concentrations from 24 to 34.5%. For the 26.7% alloy in which two magnetic phases simultaneously exist at low temperature, the results corroborate the conclusion of Bacon and Crangle that the transition that takes place at the lower of the two transition temperatures is an order-order transition. Further, all iron moments, even those of atoms on planes interleaving the magnetic planes, are found to be aligned. Structure in the magnetically split Mössbauer patterns is shown to be due to the effects of local environment.

INTRODUCTION

NEUTRON diffraction measurements[1] have disclosed that several magnetic phases simultaneously exist in homogeneous dilute solid solutions of Fe in ordered Pt_3Fe. In order to further elucidate the nature of this complex magnetic behavior we have examined the temperature dependence of the magnetic hyperfine interaction by means of Mössbauer spectroscopy. The alloys in this investigation range in iron concentration from 24.0 to 34.5% Fe (all concentrations are given in at.%) and are ordered into the γ'-$FePt_3$ phase with the cubic Cu_3Au structure.[2] Crangle and Shaw[3] found that the γ'-$FePt_3$ phase is stable at room temperature over a composition range from 21 to 40% iron.

Crangle[4] measured mass susceptibility versus temperature for platinum-iron alloys near the composition Pt_3Fe and found behavior typical of a paramagnetic-antiferromagnetic transition. At about 32% Fe, he found evidence for superparamagnetism and exchange anisotropy. At 34.3% Fe, normal ferromagnetic behavior was observed.

Bacon and Crangle[1] used neutron-diffraction techniques to study the Pt+Fe system in the concentration range 24.8–36.0% Fe. The magnetic transition observed for concentrations greater than 25%, but near Pt_3Fe, was not of the simple paramagnetic-antiferromagnetic type expected from magnetic measurements. In 26.7% Fe, two antiferromagnetic phases, each having a different ordering temperature, are present. These phases were indexed as $\frac{1}{2}\,\frac{1}{2}\,0$ and $\frac{1}{2}00$ in terms of the ordinary chemical cell, that is, the magnetic cell is larger than the chemical unit cell. Their magnetic ordering temperatures are about 170 and 120°K, respectively. The temperature dependence of the neutron intensity from each kind of order clearly indicates that some of the material which at 160°K shows $\frac{1}{2}\,\frac{1}{2}\,0$ ordering changes over to $\frac{1}{2}00$ ordering below 120°K.

The relative intensities of these two types of magnetic ordering were found to be particularly sensitive to Fe concentration. Only the $\frac{1}{2}\,\frac{1}{2}\,0$ type is present for concentrations of 24–24.8% Fe. As the concentration of iron is increased beyond 25%, the $\frac{1}{2}00$ type appears; with further increase in iron concentration, the $\frac{1}{2}00$ ordering grows at the expense of the $\frac{1}{2}\,\frac{1}{2}\,0$ type. At 31.6% Fe, the $\frac{1}{2}\,\frac{1}{2}\,0$ order has been completely replaced by the $\frac{1}{2}00$ type. With further increase in iron concentration the $\frac{1}{2}00$ type diminishes as ferromagnetic ordering [100] sets in.

The composition dependence of the neutron intensities is explained by Bacon and Crangle[1] on the basis of the three magnetic structural arrangements depicted in Fig. 1. At the stoichiometric composition Pt_3Fe, the platinum-iron alloy has the Cu_3Au superlattice structure, i.e., fcc with the platinum atoms on

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the face centers and the iron atoms on the corner sites. All iron atoms have 12 nearest-neighbor platinum atoms. The coupling of the iron moments gives rise to (110) ferromagnetic sheets with adjacent sheets arranged antiferromagnetically. This ordering produces the $\frac{1}{2}\frac{1}{2}0$ phase [Fig. 1(A)]. As iron atoms are added to the system, they begin to occupy the face-center sites; nearest-neighbor iron atoms couple into (100) ferromagnetic sheets which in turn couple antiferromagnetically to give the $\frac{1}{2}00$ order [Fig. 1(B)]. It can be seen that the two types of antiferromagnetic ordering are mutually exclusive in a chemical cell. With further increase in the iron concentration, increasing numbers of iron atoms go into face centers and ferromagnetic ordering results as shown in Fig. 1(C). The order in all cases is long range. The iron moment was found to be $\sim 3.3\mu_B$ for both of the antiferromagnetic structures and $\sim 2\mu_B$ for the ferromagnetic one. The moment of platinum is less than $0.2\mu_B$ for all compositions studied (24–36% Fe).

This explanation of the neutron diffraction data leaves unanswered several interesting questions about the details of the three types of magnetic ordering. Some of these questions can be investigated by means of the Mössbauer effect.

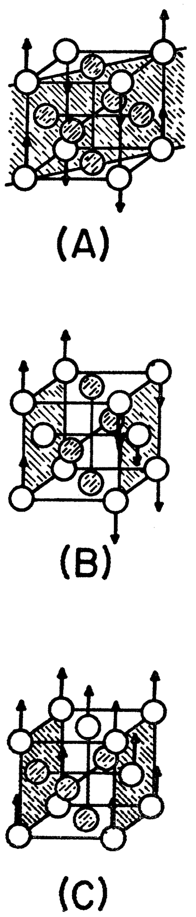

FIG. 1. Magnetic structural arrangements giving rise to (A) antiferromagnetic $\frac{1}{2}\frac{1}{2}0$, (B) antiferromagnetic $\frac{1}{2}00$, and (C) ferromagnetic 100 reflections. [From Bacon and Crangle (Ref. 1).]

How do the hyperfine interactions differ for the two types of antiferromagnetic ordering within the same lattice? In the concentration ranges where the two antiferromagnetic phases coexist at low temperature, is there a paramagnetic iron component below the higher ordering temperature? How do the ferromagnetic and the antiferromagnetic hyperfine interactions differ and can a correlation with the electronic structure of the Fe atoms (as reflected in atomic magnetic moments) be discerned? In the antiferromagnetic phases, what is the role of the Fe atoms that are on the nonmagnetic planes which interleave the magnetic planes?

It is important to note that only chemically ordered samples undergo antiferromagnetic transitions. Completely disordered alloys are ferromagnetic at room temperature. More dilute Pt-Fe alloys are also ferromagnetic, as has been demonstrated by the magnetization measurements of Crangle and Scott.[5] Segnan[6] has used the Mössbauer effect to measure the temperature dependence of the hyperfine field for ferromagnetic solid solutions with iron concentrations between 1 and 15%. He finds that for a range of temperatures below the temperature at which magnetic broadening first occurs, the spectra consist of a narrow component superimposed on a broad component. At somewhat lower temperatures, Segnan's patterns have structure due to the presence of several hyperfine fields in each sample. At very low temperatures, the hyperfine fields in a given sample all reach a common saturation value.

EXPERIMENT

The Mössbauer investigation was conducted at Northern Illinois University with a spectrometer which consists of a Kankeleit-type electromagnetic drive[7] and a multichannel analyzer operated in the time mode. For Co^{57} in Cu as source and a 0.5-mil natural iron foil as absorber, the experimental widths of the central lines of the absorption pattern are 0.21 mm/sec.

The samples were prepared by arc melting 99.999% Pt and $99.99^{+}\%$ Fe. The alloys were homogenized, powdered with a diamond file, and annealed at 1000°C for 17 h. The powder was encapsulated in a cold-setting plastic. The compositions given are the values as cast; there was virtually no weight loss upon melting. All the alloys had x-ray patterns which showed the fcc structure with superlattice lines of the Cu_3Au ordering. The lattice parameters are in agreement with those of Crangle and Shaw.[3] Further evidence for the nearly complete ordering into the γ'-$FePt_3$ phase is given by the temperature dependence of the Mössbauer spectra which do not show the magnetic splitting at high temperatures, which would be expected for disordered solid solutions as well as for FePt with the CuAu I structure.

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DISCUSSION OF RESULTS

Magnetic Hyperfine Fields

The temperature dependence of the hyperfine fields, shown in Figs. 2 and 3, was measured for iron percentages of 24, 24.5, 26.7, 30, and 34.5% for chemically ordered alloys. The spectra differ in two ways from Segnan's spectra for ferromagnetic alloys of lower iron concentration.[6] First, unlike the spectra of very dilute alloys, the temperature dependence of the spectra for both the antiferromagnetic (24–30%) and the ferromagnetic (34.5%) alloys is like that of iron. That is, at each concentration all the magnetic splitting goes rapidly, but continuously, to zero near a single well-defined magnetic ordering temperature (Figs. 2 and 3). The ferromagnetic clustering that would lead to superparamagnetic behavior above T_N is not evident in the Mössbauer spectra. Second, in each sample a distribution of hyperfine fields is observed at all temperatures below T_N down to 4.3°K, as is evident from the unequal broadening of corresponding lines on opposite sides of the centroid of each magnetically split spectrum (Fig. 4). That is, the hyperfine fields in alloys of a given concentration do not reach a common low-temperature saturation value as they do in the alloys of lower iron concentration.[6]

The nature of the transition from $\frac{1}{2}\,\frac{1}{2}\,0$ to $\frac{1}{2}00$ magnetic order was investigated by examining the hyperfine fields over a temperature range that extends across the $\frac{1}{2}00$ ordering temperature in the 26.7% alloy as shown in Fig. 3. At 171°K the system has begun to order with the $\frac{1}{2}\,\frac{1}{2}\,0$ arrangement of spins. Below 171°K but above the $\frac{1}{2}00$ ordering temperature of $\sim$140°K, there is no paramagnetic component in the Mössbauer pattern. This result is in agreement with the deduction of Bacon and Crangle that the transition at the lower temperature is an order-order transition, but shows further that all iron moments participate in the $\frac{1}{2}\,\frac{1}{2}\,0$ type of order before some of them transform to the $\frac{1}{2}00$ type at the lower transition temperature. However, the transition from antiferromagnetic $\frac{1}{2}\,\frac{1}{2}\,0$ to antiferromagnetic $\frac{1}{2}00$ takes place smoothly in the hyperfine field. It appears that when both types of order exist simultaneously at a given temperature, the effective hyperfine fields are approximately equal, so that the changeover from one

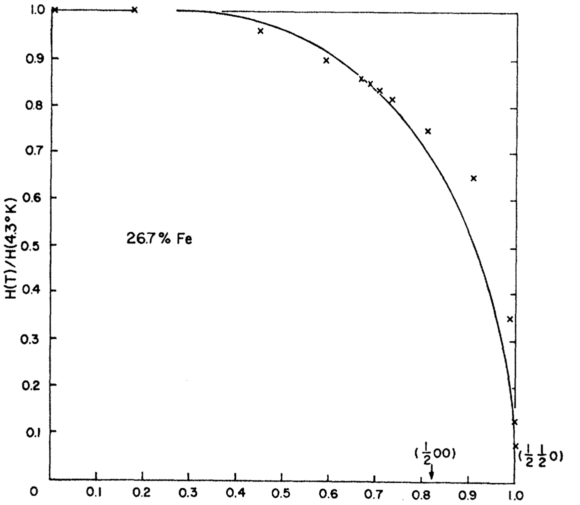

FIG. 3. Temperature dependence of the hyperfine field for the 26.7% alloy. The solid curve is the Brillouin function for $J=\frac{1}{2}$. The magnetic ordering begins at the Néel temperature for $\frac{1}{2}\,\frac{1}{2}\,0$ antiferromagnetic ordering and shows no anomalous behavior as part of the alloy undergoes the order-order transition to the $\frac{1}{2}00$ type at the lower temperature indicated in the figure.

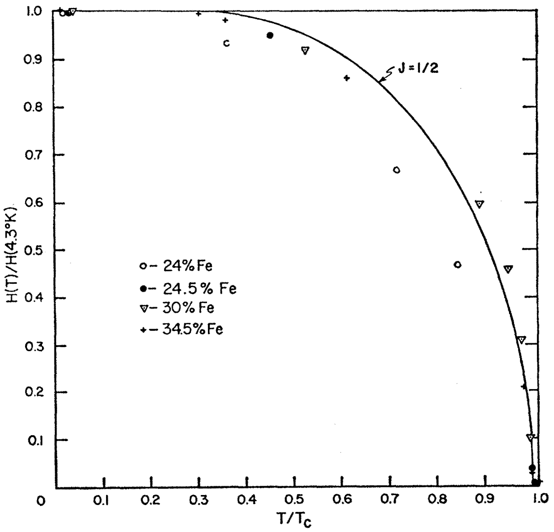

FIG. 2. Temperature dependence of the hyperfine field for 24, 24.5, 30, and 34.5% alloys. The solid curve is the Brillouin function for $J=\frac{1}{2}$.

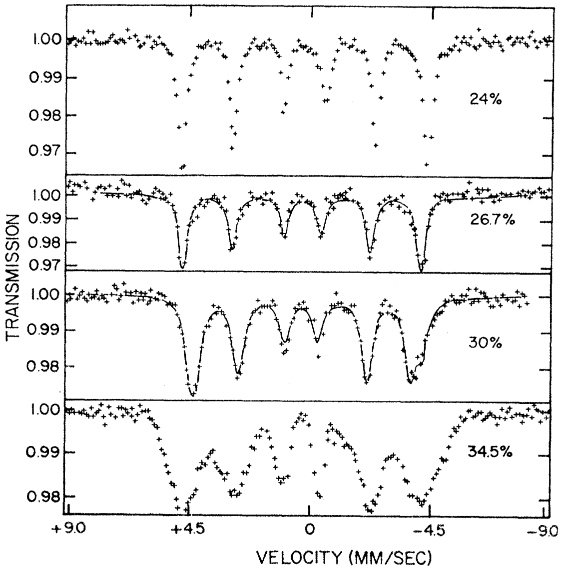

FIG. 4. Mössbauer spectra at 78°K. The solid lines are the spectra calculated on the basis of the model discussed in the text.

type of ordering to the other produces no marked anomaly in the temperature dependence of the hyperfine field. In fact, the Mössbauer results contain no hint of the presence of two magnetic phases or the existence of two ordering temperatures.

There is also a new conclusion to be drawn from the absence of a paramagnetic component below the higher ordering temperature T_N. About two-thirds of the excess Fe above the stoichiometric 25% goes into sites on the interleaving planes. This amount would easily be seen as a paramagnetic component in the spectra. The absence of this paramagnetic component indicates that the moments of the iron atoms in interleaving planes are also aligned and that the resulting hyperfine fields for these atoms are comparable to those for atoms on ordered planes.

The magnetic order-disorder temperatures T_c (Table I) as determined by the Mössbauer technique are in fair agreement with the neutron results for the 24.5, 30, and 34.5% alloys. The Néel temperature for the 24% alloy as measured by the Mössbauer technique is ~25° higher than that determined by the neutron technique. In addition, if the behavior is assumed to be Brillouin-like, the temperature-dependence curve of H_{eff} is shifted toward large J. Both of these facts might be attributed to imperfect chemical order in our 24% sample.

Neither the line shape nor intensity ratio of the subpatterns in the Mössbauer data of the magnetically ordered alloys corresponds in a simple way to the model suggested by the neutron results. Figure 4 shows the Mössbauer absorption patterns taken at 78°K. For 24.5% Fe, which orders in the magnetic $\frac{1}{2}\frac{1}{2}0$ phase, a six-line pattern is observed. At 26.7% Fe, there are at least two superimposed six-line patterns, but they do not have the 2:3 intensity ratio expected at 78°K if the Mössbauer subpatterns were to correspond to the neutron scattering intensities from Fe with the $\frac{1}{2}\frac{1}{2}0$ and $\frac{1}{2}00$ magnetic order, respectively. At 30% Fe, the spectra indicate two major fields, whereas the neutron measurements indicate a predominance of the $\frac{1}{2}00$ magnetic sublattice. At 34.5% Fe, the Mössbauer patterns for the ferromagnetic state have become complex superpositions of a number of subpatterns and the maximum value of the internal field has increased over that for either antiferromagnetic alignment.

TABLE I. Numerical results for various platinum-iron alloys. $\bar{\epsilon}_{\text{IS}}$ is the mean isomer shift at 300°K relative to the centroid of the absorption spectrum for pure iron at 300°K. Γ is the line width at 300°K. T_c is the temperature of the magnetic order-disorder transition. Type of order is indicated by A (antiferromagnetic) or F (ferromagnetic).

% Fe	$\bar{\epsilon}_{\text{IS}}$(300°K) (mm/sec)	Γ(300°K) (mm/sec)	H_{max}(4.3°K) (kOe)	T_c (°K)	Order
24.0	+0.32 (±0.01)	0.43	305	212	A
24.5			305	170±1	A
26.7	+0.31	0.47	297	171±1	A
30.0	+0.30	0.58	288	145±1	A
34.5	+0.29	0.68	310	255±2	F

Another mechanism is sought to explain the pattern structure. The effect of local environment has been observed in ferromagnetic systems by several investigators.[8] At concentrations greater than 25%, all Fe atoms in body corners have only Fe atoms as next nearest neighbors (nnn), but the nearest neighbor (nn) environment differs. Under the assumption that the excess Fe is randomly distributed into the face centers, the majority of Fe atoms in the body corners will have either zero or one nn Fe. The data have been successfully fitted with this simple model for alloys with 26.7 and 30% Fe. In Fig. 4 the solid lines show the calculated spectra. For 26.7% Fe, the Mössbauer spectrum at 78°K is decomposed into two six-line subspectra with an intensity ratio of 3.6:1; the resulting hyperfine fields are H (zero nn) = 281 kOe. For 30% Fe at 78°K, two subspectra with the intensity ratio 1.2:1 give the best fit: H (zero nn) = 261 kOe and H (one nn) = 267 kOe. In both cases the intensity ratio is approximately that expected on the assumption that the excess iron distributes itself at random in the face-center sites.

The hyperfine field at 4.3°K decreases with increasing iron content for the antiferromagnetic ordering. However, over the range of compositions for which the alloy is ordered antiferromagnetically, the variation in the hyperfine field is quite small (~20 kOe).

At present it is not possible to calculate quantitatively the magnitude of the various contributions to the hyperfine field because of the complexity of the problem. A naive application of current arguments as to the origin of the hyperfine field at the iron nucleus leads to the expectation that the (negative) hyperfine field will be roughly proportional to the $3d$ spin moment.[9,10] In fact, in the 34.5% alloy, which is ferromagnetic, the ratio of the observed hyperfine field to that in pure iron is about the same as the ratio of the respective atomic moments. However, the situation in the antiferromagnetic alloys (24–30% Fe) is quite different. Bacon and Crangle found that the average moment per atom in these alloys is 50% larger than in pure iron and that the moment on the platinum is zero. If the holes in Pt $5d$ shells are filled by charge transfer from $3d$ shells of Fe, then an increase in the $3d$ spin moment of Fe, and therefore of the total Fe atomic moment, would result. The naive view of the origins of the hyperfine field would then suggest that the hyperfine field would also be increased by about 50%. Instead, the Mössbauer measurements show that the hyperfine field is actually decreased by 10–15%. This

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indicates that the positive contributions to the hyperfine field, which are usually thought of as being relatively small, are in these cases greatly enhanced so that the net effect on the hyperfine field is to make it less negative than in pure iron, rather than more negative.

Isomer Shifts

Figure 5 shows the absorption patterns observed at 300°K. The mean isomer shift and line width at 300°K are also given in Table I. The average electron density at Fe nuclei increases slightly with increasing iron content. The volume of the unit cell decreases with increase in iron concentration.[3] Estimates of the influence of volume change can be made using the rate of change of isomer shift with fractional volume change from pressure measurements on iron,[11] or from atomic-size dependence in intermetallic compounds.[12] Using the former rate, one-half the concentration dependence of the shift can be accounted for; using the latter rate, one third.

The addition of one nn iron results in a shift of ~ -0.2 mm/sec at 78°K as determined from resolved magnetic spectra. The mean shift with concentration at 300°K is considerably smaller than would be expected on the basis of superposition of absorption spectra shifted in steps of ~ 0.2 mm/sec as a result of differing local environments.

The broad line widths at 300°K reflect both quadrupolar broadening and superposition of lines that are isomer shifted from one another. The quadrupolar broadening arises from the breakdown of local cubic symmetry as a result of random occupation of face-centered sites by excess iron (over the stoichiometric 25%).

CONCLUSIONS

When the two kinds of antiferromagnetic order coexist in one of these alloys, all the iron moments, even those in planes interleaving the magnetically ordered planes, begin to be aligned at one temperature, i.e., the higher ordering temperature. The transition at the lower temperature is an order-order transition. When the two kinds of antiferromagnetic order coexist, the Mössbauer effect is unable to distinguish between atoms in one or the other antiferromagnetic phase. The antiferromagnetic hyperfine field decreases with increasing iron content. The hyperfine fields are only slightly different for atoms in the ferromagnetic and antiferromagnetic phases in spite of the large difference in atomic moments. There is no evidence for the ferromagnetic clustering above T_N that was suggested by Bacon and Crangle.[1] If such clustering takes place, the relaxation of the coupled magnetic moments is rapid enough to yield a time average field of zero at each Fe nucleus.

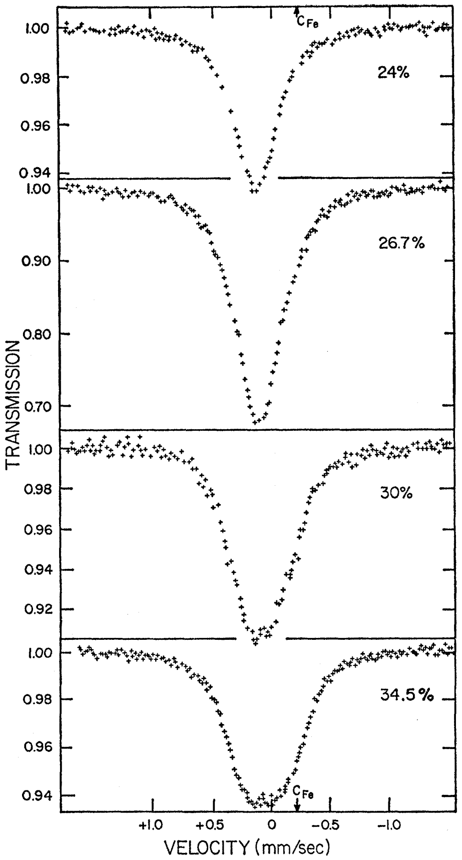

FIG. 5. Mössbauer spectra at 300°K.

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