PHYSICAL REVIEW VOLUME 172, NUMBER 2 10 AUGUST 1968

Temperature Dependence of the ^{57}Fe hfs in the Ordered Alloys $FePd_3$ and FePd near the Curie Temperature*

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(Received 15 February 1968)

The temperature dependence of the ^{57}Fe hfs in ordered $FePd_3$, FePd, and a disordered $Fe_{0.222}Pd_{0.778}$ alloy has been measured, using the Mössbauer effect near the Curie temperature T_c. These measurements yield values for the critical exponent β of 0.371 ± 0.01, 0.377 ± 0.01, and 0.394 ± 0.02, respectively, in the temperature region $0.85<T/T_c<0.99$. The values of β obtained for the ordered alloys are higher than the value $\beta=0.313\pm0.004$ predicted on the basis of a nearest-neighbor Ising model but lie within the range of values $0.36\leq\beta\leq0.41$ derived from a Heisenberg model. The values indicate that the long-range magnetic exchange interaction, known to exist in dilute Fe-Pd alloys, if it exists in these concentrated alloys, does not have an appreciable effect on the value of β. The fact that the present values of β are lower than those previously obtained ($\beta\simeq0.43$) for disordered Fe-Pd alloys containing $\simeq10\%$ iron verifies the suggestion that the latter higher values are due to the presence of a magnetization distribution arising from the spatial distribution of iron atoms in disordered alloys.

INTRODUCTION

In recent years measurements of the critical-temperature dependence of the spontaneous magnetization have been made in many magnetically ordered materials in the hope of relating them to the predictions of several models for ferromagnetism. In particular, both theory and experiment[1] suggest that the following relationship holds near the critical temperature (T_c): $M/M_{SAT}=A(1-T/T_c)^\beta$, where M_{SAT} is the magnetization at 0°K, and β and A are constants for a particular material. There is a large difference in the values for β of $\frac{1}{2}$ and $\frac{5}{16}$ predicted on the basis of the molecular-field model with an effectively infinite range for the magnetic interaction and of the nearest-neighbor Ising model, while measurements so far have tended to cluster around the value of $\beta\simeq0.33$.[1]

In this work we present similar measurements on the Fe-Pd system, which is of interest since it is known from neutron diffraction studies[2] at low iron concentrations that the ferromagnetic exchange interaction decreases exponentially with distance and extends to $\simeq10$ Å. Such an interaction was used by Woodhams *et al.*[3] to fit Mössbauer hyperfine spectra obtained using a disordered $Fe_{0.028}Pd_{0.972}$ alloy. One might therefore expect a different value of β than that of $\simeq0.33$ measured, e.g., for EuS,[4] which is thought to behave like a Heisenberg ferromagnet. Previous Mössbauer measurements on disordered Fe-Pd alloys[5–7] in which there is a distribution of magnetization gave a value for $\beta=0.43\pm0.03$ for $Fe_{0.132}Pd_{0.868}$ and $Fe_{0.075}Pd_{0.925}$, while for dilute iron concentrations ($\simeq0.4\%$ Fe), the value of β was considerably larger. It was suggested[5–7] that the higher values of β were due to the presence of the magnetization distribution arising from the spatial distribution of iron atoms, and to the fact that regions of differing magnetization were coupled via a long-range exchange interaction leading to a unique Curie temperature. The value of β was even larger for the dilute alloys because the relative fluctuations in local magnetization become larger as the alloy becomes more dilute. Because of this, measurements of β in dilute alloys in which the existence of a long-range interaction is well established[2] are difficult because the true value of β is obscured by the effect of the distribution in magnetization. These experiments also suggested that the long-range interaction was still appreciable in concentrated alloys.[7]

It is therefore of interest to measure the values of β in the ordered alloys $FePd_3$ and FePd, where the density of iron atoms is unique, to see if there is any evidence for long-range interactions in concentrated ordered alloys which could lead to a larger value of β.

METHOD

In the Fe-Pd system there are two superlattices, fcc $FePd_3$ and face-centered tetragonal (fct) FePd, which exist as single phases over the approximate

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* This work was performed under the auspices of the U. S. Atomic Energy Commission. Prepared under Contract No. AT(04-3)-63 for the San Francisco Operations Office, U. S. Atomic Energy Commission.

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TABLE I. Linewidths and hyperfine fields of Fe-Pd alloys.

Alloy	Temperature (°K)	Hyperfine field H_{eff} (kOe)	Component linewidth (mm/sec)		
			Inner	Middle	Outer
Ordered $Fe_{0.50}Pd_{0.50}$	R.T.[a]	267.9±1	0.37±0.01	0.37±0.01	0.37±0.01
	4.2	281±3	...	...	...
Disordered $Fe_{0.50}Pd_{0.50}$	R.T.	320±1	0.38±0.02	0.64±0.03	0.90±0.04
Ordered $Fe_{0.27}Pd_{0.73}$	R.T.	285.5±1	0.37±0.01	0.37±0.01	0.37±0.01
	4.2	334±3	...	...	...
Disordered $Fe_{0.27}Pd_{0.73}$	R.T.	278±1	0.41±0.30	0.60±0.04	0.79±0.06
Disordered $Fe_{0.22}Pd_{0.78}$	R.T.	267±1	0.35±0.01	0.52±0.02	0.69±0.03
	4.2	312±3	...	...	...

[a] Room temperature.

concentration ranges 25–30 at.% Fe and 43–50 at.% Fe, respectively.[8] The following alloys $Fe_{0.268}Pd_{0.732}$ and $Fe_{0.496}Pd_{0.504}$ were prepared by melting 99.999% pure iron and palladium in an induction furnace in sufficient quantities to ensure that the losses were less than 0.1%. The alloy $Fe_{0.268}Pd_{0.732}$ was chosen since a previously prepared alloy, $Fe_{0.248}Pd_{0.752}$, remained disordered after substantial annealing. After being rolled to foils about 2 mil thick, the alloys were homogenized by being annealed at 900°C for 4 h, and quenched to room temperature to form the fcc disordered phase. The homogeneity and composition were checked using an electron-beam microprobe device and by spectrographic analysis. The largest impurity found was 100 ppm of silicon, although the presence of oxygen was not checked. The alloys were then ordered by being held at 550°C (FePd) and 620°C ($FePd_3$) *in vacuo* for about 50 days. X-ray diffraction patterns were measured before and after ordering with the following results: disordered $FePd_3$, fcc $a=3.856\pm 0.004$ Å, ordered $FePd_3$, fcc $a=3.849\pm0.001$ Å, disordered FePd, fcc $a=3.803\pm0.002$ Å, and ordered FePd, fct $c/a=0.960\pm0.005$, $a=3.86\pm0.01$ Å, in good agreement with previous measurements.[9] Since the samples were initially cold-rolled, there were preferred crystalline orientations that were not fully removed after ordering. Thus it was not possible to determine the long-range ordering parameter S conclusively from the ratios of intensities of normal and superlattice peaks in the x-ray diffraction pattern. [S is defined as $(r_A-F_A)/(1-F_A)$, where r_A is the fraction of A sites in the alloy occupied by the "correct," i.e., A atoms, and F_A is the fraction of A atoms in the alloy; see, e.g., Cullity.[10]] However, in the case of FePd, if one neglects the normal peaks which show preferred orientation effects, then a value for $S=0.97\pm0.03$ was found using four superlattice peaks. The samples therefore appear to be appreciably ordered.

The Mössbauer spectra were obtained using a constant-acceleration velocity drive and multichannel analyzer, the emitter being ^{57}Co in Pd. For temperatures above room temperature, a small vacuum furnace and proportional temperature controller were used, whereby the absorber temperature could be held constant to better than 0.2°C.

RESULTS

The spectra obtained for the ordered alloys at room temperature are shown in Fig. 1. The values of hyperfine field are tabulated in Table I together with the linewidths and fields obtained at 4.2°K. At room temperature there was an appreciable spread in field in the disordered samples, while the lines in the ordered samples were narrower and approximately equal in width. The field in $FePd_3$ at room temperature changed slightly on ordering from 278±1 to 286±1 kOe, but there was a decrease in field from 320±1 to 268±1 kOe in FePd. The change in spatial arrangement of Fe atoms on ordering could change the field via a change in the Pd conduction-electron polarization by the Fe atoms. However, Craig *et al.*[11] assume that the contributions to the polarization from Fe atoms having one or more than one Fe nearest neighbor are the same, and since the probability of having one or more Fe neighbors in $FePd_3$ increases by only 3% on ordering, we may expect only a small change in field in $FePd_3$. The decrease in field for $Fe_{0.50}Pd_{0.50}$ is presumably due to the change in structure from fcc to fct when the iron-iron nearest-neighbor distance increases from 2.69 to 2.73 Å. In the case of FePd, there was a quadrupole

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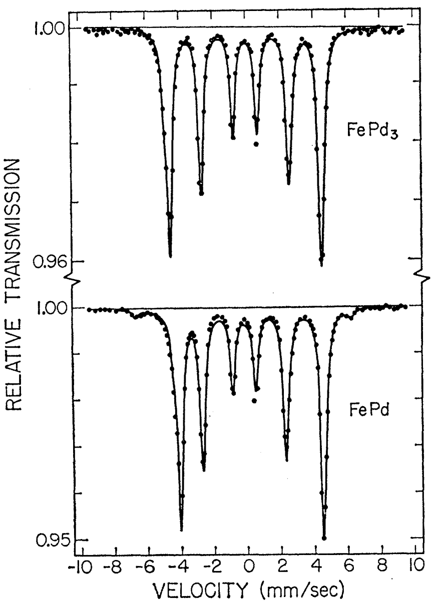

FIG. 1. Hyperfine spectra for ordered $Fe_{0.27}Pd_{0.73}$ and ordered $Fe_{0.50}Pd_{0.50}$ at room temperature. The solid lines represent the calculated least-squares fits.

interaction with a shift in the energy levels of

$$\tfrac{1}{4}(e^2qQ)\left[\tfrac{1}{2}(3\cos^2\theta-1)\right]=0.215\pm0.003\ \text{mm/sec}$$

(see, e.g., Wertheim[12]). The widths of the lines in the ordered alloys at room temperature, 0.37±0.01 mm/sec, were in good agreement with those obtained above the Curie temperatures, 0.38±0.02 mm/sec. In addition, at temperatures $0.86<T/T_c<0.99$, the outer lines were $\simeq 20\%$ broader than the inner lines. These facts seem to indicate that there could still be a small amount of disorder present. In FePd, the angle θ between the directions of the electric field gradient and the magnetic hyperfine field seems to be almost unique, but there is evidence for an asymmetry in the outer limb (Fig. 1) of the left-hand outer line. This asymmetry could be due to a small anisotropic distribution in angle θ, which could give rise to a combination of a quadrupole shift in the lines together with a small amount of quadrupole broadening. Alternatively, this asymmetry, which is also present to a lesser degree in ordered $FePd_3$, could be due to the presence of a second hyperfine field about 10% higher in value than the main field and with about 10% of the probability of the main field. It is difficult to see how this could arise; since the crystal structure is well defined from x-ray analysis, the impurity level should be small enough not to produce such a large shift in field, and it seems unlikely that a small amount of disorder would give rise to an essentially unique field.

There is some evidence for the presence of two fields in disordered $Fe_{0.132}Pd_{0.868}$ from NMR measurements by Budnick *et al.*,[13] who find fields at 317 and 327 kOe, although Craig *et al.*[11] find only one field at 327 kOe using the Mössbauer technique. In the ordered FePd sample there is also evidence for another field at 400 kOe. This could be due to the presence of a small amount of oxidation in the sample, although the field is considerably smaller than those of the iron oxides.

The isomer shifts obtained for disordered and ordered $Fe_{0.50}Pd_{0.50}$ and for disordered and ordered $Fe_{0.27}Pd_{0.73}$ were +0.027±0.005, +0.034±0.005, +0.006±0.006, and +0.007±0.003 mm/sec with respect to the ^{57}Fe in Pd source. Thus the S electron density at the nucleus in these alloys is slightly less than that in the source. With respect to an iron-metal absorber, this source has an isomer shift of −0.188±0.003 mm/sec, which indicates that the S electron density at the nucleus in the source is itself less than that in iron metal. From a comparison of the areas of the transmission curves obtained at room temperature for different thicknesses of ordered $Fe_{0.27}$ $Pd_{0.73}$ and $Fe_{0.50}Pd_{0.50}$, a value for the recoilless fraction of $f_A=0.50\pm0.02$ was obtained, which corresponds on a Debye model to a Debye temperature $\Theta=245\pm10°K$. The recoilless fraction of the source is $f_s=0.61\pm0.03$.

The Curie temperatures of the alloys were determined by measuring spectra at 1° intervals for temperatures where the spectrum had collapsed to a single broadened line. The width of this line was then plotted as a function of temperature, and there was a sharp discontinuity in the slope of the curve which allowed the Curie temperature to be defined to ±0.5°C. Values for T_c of 499.1±0.5 and 728.2±0.5°K for $FePd_3$ and FePd were found. These may be compared with the values 513 and 743°K obtained by Fallot[14] and 731°K by Kuprina *et al.*[15] from magnetization measurements. The measurements of Fallot[14] have been rejected by Elliot[8] since they are not in agreement with other features of the phase diagram for the Fe-Pd system.

Spectra were obtained for temperatures $0.85<T/T_c<0.99$ for FePd and $0.6<T/T_c<0.99$ for $FePd_3$. The hyperfine fields were determined from computer fits to the spectra using Lorentzian line shapes. For $T/T_c>0.99$ the spectrum consisted of a single broadened line, which made analysis difficult. The hyperfine field was assumed to be proportional to the magnetization, at least close to the Curie temperature. It is not known whether this proportionality holds for these alloys, but Craig *et al.*[16] have shown it to be the case for a disordered $Fe_{0.0265}Pd_{0.9735}$ alloy over an extended range of temperatures.

The usual method for determining β and A in the relationship $M/M_{\mathrm{SAT}}=A(1-T/T_c)^{\beta}$ is to assume that

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the value of T_c is known from other measurements and to perform a least-squares fit to the data with two variable parameters β and A. It seems more meaningful, however, to allow T_c also to be determined in the least-squares fit. For this purpose, a nonlinear least-squares program was used which yielded the following values of the parameters (Fig. 2): for ordered $FePd_3$, $0.85 < T/T_c < 0.99$, $\beta = 0.371 \pm 0.01$, $T_c = 499.6 \pm 0.5$°K, $A = 1.33 \pm 0.07$, and for ordered FePd, $0.85 < T/T_c < 0.99$, $\beta = 0.377 \pm 0.01$, $T_c = 728.6 \pm 1.0$°K, $A = 1.36 \pm 0.04$. These values of T_c are in good agreement with those determined from the onset of paramagnetism.

In order to look for the effect of a distribution in magnetization on β, another alloy, $Fe_{0.222}Pd_{0.778}$, was prepared which was outside the concentration range for ordered $FePd_3$. Iron enriched to 25% in ^{57}Fe was used for this alloy, since losses were not as critical as for the ordered alloys and hence smaller quantities of material could be used. After annealing for 7 days at 600°C, there was no evidence for superlattice lines in the x-ray diffraction spectrum, so the alloy was assumed to be disordered ($a = 3.855 \pm 0.001$ Å). In the Mössbauer spectrum, the outer lines were roughly twice as broad as the inner lines (Table I) and the widths were essentially independent of temperature. Spectra were measured in the temperature range $0.86 < T/T_c < 0.98$. The value of the average hyperfine field was determined from the positions of the centroids of the lines. Values of the parameters $\beta = 0.394 \pm 0.02$, $T_c = 475.8 \pm 1.0$°K, and $A = 1.43 \pm 0.03$ were determined from the least-squares fit (Fig. 2).

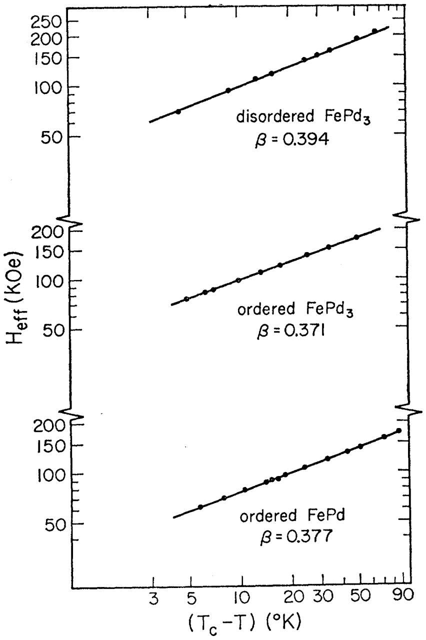

FIG. 2. Plots of $\log_{10}H_{eff}$ versus $\log_{10}(T_c - T)$ for disordered $Fe_{0.22}Pd_{0.78}$, $T_c = 475.8$°K, ordered $Fe_{0.27}Pd_{0.73}$, $T_c = 499.6$°K, and ordered $Fe_{0.50}Pd_{0.50}$, $T_c = 728.6$°K. The errors are no larger than the plotted points.

DISCUSSION

The good agreement between the values for the Curie temperature T_c as determined from the least-squares analysis and from the disappearance of the six-line hyperfine pattern encourages us to believe that the least-squares analysis method is a reliable one to determine T_c. The usual method of allowing only A and β to vary in the fit, using several fixed values for T_c, and determining T_c from the best fit to the data is inferior since the errors obtained in A and β are not strictly meaningful when a fixed value of T_c is used. The 3-parameter least-squares analysis used here reveals the presence of correlations between the errors in β, A, and T_c. In the case of the data for $Fe_{0.27}Pd_{0.73}$, the correlations between the errors in T_c and β, T_c and A, and β and A were 0.69, 0.59, and 0.97, respectively. Thus if the value of T_c were fixed at 499.6°K (derived from the 3-parameter least-squares fit) and if we were to perform a 2-parameter least-squares fit to the data in which A and β were varied, then the standard deviations in β and A would be reduced from 0.01 to 0.006 and 0.07 to 0.05, respectively. In the 2-parameter fit, for a change in T_c of one standard deviation (0.5°K), the value of β also changes by one standard deviation (0.01), and vice versa.

The values of β obtained for ordered FePd and $FePd_3$ are only slightly higher than those obtained in other magnetically ordered materials ($\beta \simeq 0.33$),[1] and are much closer to those values than to the value $\beta = 0.5$ predicted by the molecular-field model. The values of β for ordered and disordered $FePd_3$ are not significantly different, but it may be that the values for the average magnetization in the disordered sample as determined from the positions of the centroids of appreciably broadened lines are not accurate since they represent the most probable magnetization, which could differ from the average magnetization. In the previous work on disordered alloys[5] the values of β were determined from the spacing of the inner hyperfine lines, which are also subjected to the overlap of strong neighboring lines. However, the trend towards higher values of β in more dilute disordered alloys as compared to the present ordered alloys confirms the suggestion[9] that the higher values arise from fluctuations in magnetization due to the spatial arrangement of iron atoms in disordered alloys.

One might expect that the long-range magnetic interaction known to exist for Fe-Pd alloys in which the iron concentration ≤5 at.% would become less effective in more concentrated alloys where the nearest-neighbor interactions become appreciable. However, Trousdale *et al.*[7] have shown that there is still an appreciable contribution from a long-range interaction in disordered $Fe_{0.132}Pd_{0.868}$. The Mössbauer spectra for this alloy were fitted on the basis of a simple cell model in which a given iron atom interacts magnetically with other iron atoms within a cell via a short-ranged interaction and with the average magnetization via a long-range interaction. From the fits, the cell size and effective strengths of the interactions were determined. The two interactions were found to be equally effective, while the long-range interaction, $\simeq$6 Å, is comparable to that in very dilute alloys.

In the present experiment we find no evidence for the existence of this long-range interaction via its effect on the value of β, which is not significantly different from the value $\beta = 0.35$[17] obtained for pure iron. However, it was recently pointed out by Fisher[18] that the presence of a long-range magnetic interaction of this form does not necessarily lead to a different value of β but could instead reduce the size of the critical-temperature range over which such a value of β is appropriate. The critical-temperature regions obtained here, however, also seem to be similar to those obtained for other materials.[1]

The experimental values of β obtained here are higher than the predictions of the three-dimensional Ising model,[1] $\beta = 0.313 \pm 0.004$, and of a model[1] based on a scaling-law analysis, $\beta = 0.33 \pm 0.03$, which starts from the Ising model and assumes that there exist relations between the various critical parameters governing the behavior of the magnetization, susceptibility, and specific heat. There has recently been a prediction for β by Baker *et al.*[19] based on the Heisenberg model, of $0.36 \leq \beta \leq 0.41$, whose limits enclose the present values of β.

ACKNOWLEDGMENTS

The author would like to thank Dr. Felix Boehm for his advice and encouragement, Dr. P. Duwez and Dr. C. C. Tsuei for many valuable discussions, and E. N. Kaufmann for providing the nonlinear least-squares fitting program.

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PHYSICAL REVIEW VOLUME 172, NUMBER 2 10 AUGUST 1968

Disappearance of a Vibrational Mode in the Ferroelectric Phase Transition of KH_2PO_4

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(Received 21 December 1967)

With the aid of a cold-neutron spectrometer, the time-of-flight spectra of KH_2PO_4 single crystals were measured with different orientations of the momentum exchange vector with respect to the crystallographic axis. In the case where the momentum exchange vector points mainly in the direction of the hydrogen bond, the temperature dependence of the spectrum was investigated. It was found that below the Curie temperature a band mode of 50 cm^{-1} disappears, and the mean square displacement of the protons in the direction of their bonds is strongly lowered.

THE structure of KH_2PO_4 in the para- and ferroelectric phase was established by Bacon and Pease.[1] In the paraelectric phase, the protons have two equivalent off-center positions along the hydrogen bond, only one in the ferroelectric phase, and conform with the assumptions of Slater's[2] order-disorder model for the ferroelectric phase transition in KH_2PO_4-type ferroelectrics. Blinc[3] proposed that the disorder in the paraelectric phase may be a dynamic one and that hydrogens may tunnel from one equilibrium position in the H bond to another, thus producing a reorientation of Slater's H_2PO_4 dipoles. Early inelastic neutron scattering experiments by Pelah *et al.*[4] and the "fluctuating double minimum potential well" model of Imry *et al.*[5] suggested the splitting of the ground level of the double minimum potential well to be about 400–500 cm^{-1}. Recent infrared absorption measurements by Wiener *et al.*[6] with samples of different oxygen isotopes allowed the definite assignment of a number of infrared absorption lines, showing also PO_4 modes near 500 cm^{-1} at room temperature. Pursuing the search for a "ferroelectric mode" or a definite measurement of the splitting energy of the ground state, a number of elastic and inelastic neutron scattering experiments have been

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