

## Mössbauer Study of Two Pd-Fe Alloys Containing Absorbed Hydrogen†

WALTER C. PHILLIPS

*Argonne National Laboratory, Argonne, Illinois and National Aeronautics and Space Administration,  
Electronics Research Center, Cambridge, Massachusetts*

AND

CLYDE W. KIMBALL

*Argonne National Laboratory, Argonne, Illinois and Northern Illinois University, DeKalb, Illinois*

(Received 14 August 1967)

The temperature dependence of hyperfine fields and isomer shifts in the system Pd-Fe-H (2 and 5% Fe) has been investigated by means of the  $^{57}\text{Fe}$  Mössbauer effect. We observe hyperfine fields indicating that an ordered magnetic structure exists in the  $\beta$  phase at H concentrations high enough to cause filling of the Pd  $4d$  band (H/Pd  $\geq 0.59$  for 2% Fe). The  $\beta$ -phase transition temperature  $T_c(\beta)$  is considerably lower than the corresponding  $\alpha$ -phase transition temperature. For the 2%-Fe alloy,  $T_c(\beta) = (3 \pm 1)^\circ\text{K}$  and H ( $1.8^\circ\text{K}$ )  $\approx 240$  kOe; for the 5%-Fe alloy,  $T_c(\beta) = (10 \pm 3)^\circ\text{K}$  and H ( $1.8^\circ\text{K}$ )  $\approx 310$  kOe. The distribution of measured hyperfine fields has been correlated with the H near-neighbor configuration. Above  $T_c(\alpha)$  and also below  $T_c(\beta)$ , we observe an isomer shift of  $+0.045 \pm 0.003$  mm/sec in going from the  $\alpha$  to the  $\beta$  phase.

### I. INTRODUCTION

**F**ERROMAGNETISM in dilute solutions of iron (or cobalt) in a palladium matrix has been investigated using Mössbauer, neutron diffraction, NMR, and magnetic-susceptibility techniques.<sup>1-8</sup> It is well established that the  $3d$  moment on Fe impurity atoms induces a  $4d$  moment on surrounding Pd atoms out to distances  $\approx 6 \text{ \AA}$ .<sup>9</sup> Several viewpoints have been advanced to explain the ordering mechanism and long-range polarization. The interpretation of recent Mössbauer experiments relates the spatial extent of polarization to statistical fluctuations in the local concentration of Fe atoms.<sup>10,11</sup>

On the basis of recent de Haas-van Alphen measurements,<sup>12</sup> palladium has been ascribed an electron configuration of  $4d^{9.64} 5s^{0.36}$ . However, in alloying with Ag or H, Pd behaves as though 0.6 holes existed in the  $4d$  band and the valence electrons of the solute atoms

fill the  $d$ -band holes.<sup>13,14</sup> Burger has measured ferromagnetic susceptibilities in Pd-Fe-H (5-13% Fe) for H concentrations at which the  $4d$  band is presumably filled.<sup>15</sup> In the present work we investigate magnetic properties of Pd-Fe-H (2% and 5% Fe) for H concentrations from 0 to 0.65 H/Pd by means of Mössbauer spectroscopy.

#### A. Pd-H

At room temperature palladium metal readily absorbs large quantities of hydrogen which produce an expansion of the Pd lattice. Neutron diffraction experiments have shown that the absorbed-hydrogen nuclei occupy octahedral interstitial sites, forming an NaCl-type structure.<sup>16,17</sup> Two phases of the hydride coexist for hydrogen concentrations lower than about 0.65 H/Pd: an  $\alpha$  phase containing essentially no hydrogen (lattice parameter  $a_0 = 3.88 \text{ \AA}$ ), and a  $\beta$  phase containing  $\approx 0.65$  H/Pd ( $a_0 = 4.02 \text{ \AA}$ ). (All hydrogen concentrations will be expressed as the ratio of the number of H atoms to Pd atoms, H/Pd.) Pure  $\beta$ -Pd-H samples are obtained for a H/Pd ratio greater than  $\approx 0.65$  (at STP). Several experimental results support the hypothesis that electrons from hydrogen fill the unoccupied states in the Pd  $4d$  band: (1) Pd has a large paramagnetic susceptibility, while  $\beta$ -Pd-H is diamagnetic, (2) the measured electronic specific heat of Pd [ $\gamma = 9.3 \text{ mJ/deg}^2$  (g atom Pd)] is much greater than that of  $\beta$ -Pd-H [ $\gamma = 1.4 \text{ mJ/deg}^2$  (g atom Pd)], and (3) only 65% of the octahedral interstitial sites in the Pd lattice need be occupied in order to form the  $\beta$  phase.<sup>18,18</sup>

† Based on work performed under the auspices of the U.S. Atomic Energy Commission.

<sup>1</sup> J. Crangle, *Phil. Mag.* **5**, 335 (1960); J. Crangle and W. R. Scott, *J. Appl. Phys.* **36**, 921 (1965).

<sup>2</sup> R. M. Bozorth, D. D. Davis, and J. H. Wernick, *J. Phys. Soc. Japan* **17**, Suppl. **B1**, 112 (1962).

<sup>3</sup> A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, *Phys. Rev.* **125**, 541 (1962).

<sup>4</sup> J. W. Cable, E. O. Wollan, and W. C. Koehler, *J. Appl. Phys.* **34**, 1189 (1963).

<sup>5</sup> P. P. Craig, B. Mozer, and R. Segnan, *Phys. Rev. Letters* **14**, 895 (1965); F. W. D. Woodhams, R. M. Meads, and J. S. Carlow, *Phys. Letters* **23**, 419 (1966).

<sup>6</sup> P. P. Craig, R. C. Perisho, R. Segnan, and W. A. Steyert, *Phys. Rev.* **138**, 1460 (1965).

<sup>7</sup> Walter C. Phillips, *Phys. Rev.* **138**, A1649 (1965).

<sup>8</sup> J. I. Budnick, J. Lechaton, and S. Skalski, *Phys. Letters* **22**, 405 (1966).

<sup>9</sup> G. G. Low, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 133; G. G. Low and T. M. Holden, *Proc. Phys. Soc. (London)* **89**, 119 (1966).

<sup>10</sup> W. L. Trousdale, T. A. Kitchens, and G. Longworth, *J. Appl. Phys.* **38**, 922 (1967).

<sup>11</sup> B. D. Dunlap and J. G. Dash, *Phys. Rev.* **155**, 460 (1967).

<sup>12</sup> Joseph H. Vuillemin, *Phys. Rev.* **144**, 369 (1966).

<sup>13</sup> J. S. Dugdale and A. M. Guénault, *Phil. Mag.* **13**, 503 (1966).

<sup>14</sup> D. W. Budworth, F. E. Hoare, and J. Preston, *Proc. Roy. Soc. (London)* **A257**, 250 (1960).

<sup>15</sup> Jean-Paul Burger, *Ann. Phys. (Paris)* **9**, 345 (1964).

<sup>16</sup> J. E. Worsham, Jr., M. K. Wilkinson, and C. G. Shull, *J. Phys. Chem. Solids* **3**, 303 (1957).

<sup>17</sup> G. A. Ferguson, Jr., A. I. Schindler, T. Tanaka, and T. Morita, *Phys. Rev.* **137**, A483 (1965).

<sup>18</sup> C. A. Mackliet and A. I. Schindler, *Phys. Rev.* **146**, 463 (1966).

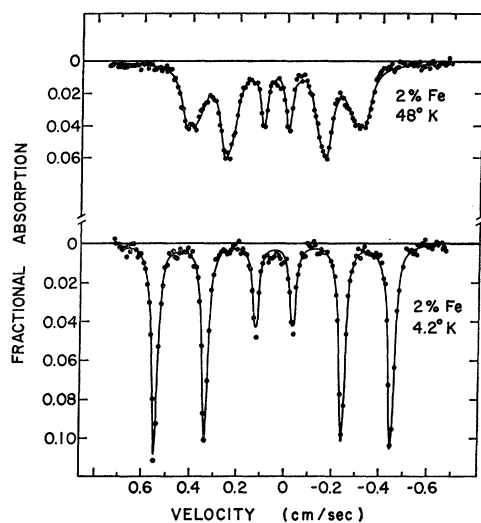


FIG. 1.  $\alpha$ -Pd-Fe-H Mössbauer spectra for the 2% -Fe alloy at 48 and 4.2°K. At 4.2°K all fields have approached their saturation values and the spectrum has collapsed to six lines. The zero of the velocity scale is at the centroid of an Fe versus Fe absorption spectrum at 300°K. The solid lines are the calculated least-squares fits.

### B. Pd-Fe

For iron concentrations of less than 25%, Fe and Pd form face-centered-cubic solid solutions. For the compositions examined in this study the alloys are completely disordered and retain the fcc Pd structure with a slightly reduced lattice parameter ( $a_0 = 3.87 \text{ \AA}$  for 8% Fe).<sup>19</sup> (All iron concentrations will be given in at. %.) Alloys with Fe concentrations of 1% or greater are ferromagnetic.<sup>2</sup> Magnetization and neutron diffraction measurements have shown that both Fe and Pd atoms possess an aligned moment. For an alloy with 1.3% Fe, the aligned  $3d$  moment is  $\approx 3.9\mu_B$  per Fe atom and the aligned  $4d$  moment is  $\approx 6.9\mu_B$  per Fe atom (at 0°K).<sup>7</sup> The  $4d$  moment is distributed over many Pd atoms around an Fe impurity, the size of the moment depending upon the distance from an Fe atom.<sup>9</sup> Mössbauer measurements made by Craig *et al.* have shown that the magnitude of the  $Fe^{57}$  magnetic hyperfine field in Pd-Fe alloys (1) increases as the Fe concentration increases and (2) is proportional to the bulk magnetization.<sup>5,6</sup>

### C. Pd-Fe-H

For Fe concentrations less than 10%, Pd-Fe alloys readily absorb hydrogen. As in the case of Pd-H, two phases are formed in the Pd-Fe-H system: an  $\alpha$  phase containing very little or no hydrogen and a  $\beta$  phase containing essentially all of the absorbed hydrogen. As the Fe concentration increases, less hydrogen is required to form the  $\beta$  phase. Each Fe atom appears to contribute about three electrons to the Pd  $4d$  band.<sup>20</sup>

<sup>19</sup> W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

<sup>20</sup> J. P. Burger, E. Vogt, and J. Wucher, *Compt. Rend.* **149**, 1480 (1959).

For 5% Fe the alloy is completely transformed to the  $\beta$  phase at 0.51 H/Pd and for 2% Fe at 0.60 H/Pd. Our Mössbauer data are consistent with this model. It has been assumed that the addition of hydrogen to the fcc solid solutions of Fe in Pd at low Fe concentrations results in a  $\beta$ -Pd-Fe-H phase having the same crystal structure as  $\beta$ -Pd-H. As discussed below, the  $\beta$ -Pd-Fe-H alloys are magnetic with ordering temperatures lower than those of the corresponding  $\alpha$ -Pd-Fe alloys. In view of Burger's saturation magnetization measurements for Pd-Fe-H alloys, the transition observed by the Mössbauer effect is assumed to be ferromagnetic in the following discussion.

## II. EXPERIMENTAL

A standard electromechanical Mössbauer spectrometer<sup>21</sup> with the source driven by a loudspeaker and a multichannel analyzer in pulse-height mode were used. The single-line  $Co^{57}$ -in-Cu source versus Fe absorber had a linewidth of 0.22 mm/sec. Extensive low-temperature runs were made only at 1.8 and 4.2°K where accurate temperature control was possible. Temperatures were measured by means of carbon resistors.

Two Fe concentrations were studied. The alloys were made by arc melting Fe (enriched to 50%  $Fe^{57}$ ) and approximately 3 g of Pd metal (99.995% purity) in an Argon atmosphere. The compositions of these alloys, determined from the weights of the starting materials, were  $(2.1 \pm 0.2)\%$  Fe and  $(5.5 \pm 0.6)\%$  Fe. The uncertainties result from weight lost during arc melting. We shall refer to the alloys as being nominally 2 and 5% Fe, respectively.

The samples were rolled to thin foils 1.0-mil thick (2% Fe) and 0.7-mil thick (5% Fe). These were annealed in vacuum at 800°C for 40 min. Foils were sandwiched between Lucite and aluminized Mylar discs in the cryostat in order to minimize temperature gradients across the sample. Both single  $\beta$ -phase and two-phase samples were prepared by maintaining foils in a hydrogen atmosphere at constant temperature for times between 5 and 100 h. Various hydrogen pressures (from 7 to 60 psi) and temperatures (from 0 to 120°C) were used to produce samples with differing hydrogen concentrations. Before hydrogenation, foils were out-gassed in a vacuum for several hours at 300°C. The weight of hydrogen in each sample was determined to  $\pm 1\%$  by weighing the foil before and after hydrogenation. Each foil was reweighed immediately after the Mössbauer data were collected to check for loss of hydrogen. Foils were found to retain initial hydrogen compositions if not left at room temperature in the atmosphere for more than 30 min. At liquid-nitrogen temperature in vacuum, the composition was unchanged for periods of several weeks. The H/Pd ratios required to completely transform to the  $\beta$  phase as

<sup>21</sup> F. J. Lynch and J. B. Baumgardner, Argonne National Laboratory Report No. ANL-6391, 1961, p. 10 (unpublished).

TABLE I. Analysis of hyperfine spectra for  $\alpha$ -Pd-Fe-H. Data are fitted to two six-line patterns which approximately fit a nearest-neighbor model.  $A$  is the measured fractional area associated with the corresponding random probability  $P(n)$  of having  $n$  Fe nearest neighbors (12 nearest-neighbor positions in the  $\alpha$  phase).  $T_c$  is the ordering temperature for a specified substructure of the hyperfine field. Data at 4.2°K are fitted to a single six-line spectrum.

$\alpha$ Phase							
% Fe	$T$ (°K)	$T/T_c$	$H$ (kOe)	$A$	$n$	$P(n)$	$T_c$ (°K)
2	48	0.68	207	0.65	0	0.79	$67 \pm 1$
			233	0.35	1, 2	0.20	75
			259	0.52	0	0.55	158
5	77	0.47	274	0.48	1, 2	0.44	168
			309 $\pm$ 2				
5	4.2	0.03	316 $\pm$ 3				

determined from our Mössbauer spectra are in agreement for both alloys with those found previously for Pd-Fe-H by Burger, Vogt, and Wucher.<sup>20</sup> Spectra were analyzed with a computer program which fit the data with from 1 to 12 Lorentzian lines as necessary.<sup>22</sup>

### III. DISCUSSION OF RESULTS

#### A. Hyperfine Fields

##### 1. $\alpha$ -Pd-Fe-H

The onset of ferromagnetism was determined from the broadening of the hyperfine patterns and occurs in a given alloy over a range of temperatures. For the 5% alloy  $T_c = (163 \pm 5)^\circ\text{K}$ , in agreement with Crangle's value.<sup>1</sup> (The spread in  $T_c$  represents the temperature range over which the broadening occurs.) For the 2% Fe alloy  $T_c = (71 \pm 4)^\circ\text{K}$ ; this value is lower than that measured by Crangle but in approximate agreement with other measurements.<sup>6,7</sup> For  $1 > T/T_c \gtrsim 0.1$  the spectra exhibit more than one internal field. Trousdale, Kitchens, and Longworth observe a similar distribution of fields below the transition temperature in Pd-Fe.<sup>10</sup> As  $T/T_c$  approaches zero, the subpatterns expand so that the total spectrum collapses to a six-line pattern characteristic of a single saturation field ( $H_0$ ). Figure 1 shows spectra for the 2%-Fe alloy at two temperatures below  $T_c$ . The magnitude of the hyperfine fields was determined by comparing the line splittings with those of an Fe absorber (330 kOe at 20°C). For both the 2 and 5%-Fe alloys, the fields measured at 4.2°K are in good agreement with the saturation values obtained by Craig *et al.* (see Table I).

For the Pd-Fe system the Curie temperature is a much stronger function of Fe concentration than the splitting at saturation so that both composition and temperature fluctuations can lead to structure in absorption patterns at temperatures not low enough to yield saturation values. As previously indicated, precautions were taken to ensure homogenization of the alloys and uniformity of temperature in the sample.

The pattern for 2% Fe at  $T/T_c \approx 0.68$  corresponds in form to that observed by Trousdale *et al.* for 0.4% Fe at  $T/T_c \approx 0.52$ . This behavior is consistent with the findings of the latter authors that the rate of change of the average hyperfine field below  $T_c$  increases with increasing Fe content. They interpret their spectra using a model which relates the distribution of hyperfine fields to Fe concentration fluctuations and determine a range parameter which describes the interaction between two Fe atoms suspended in a palladium matrix.

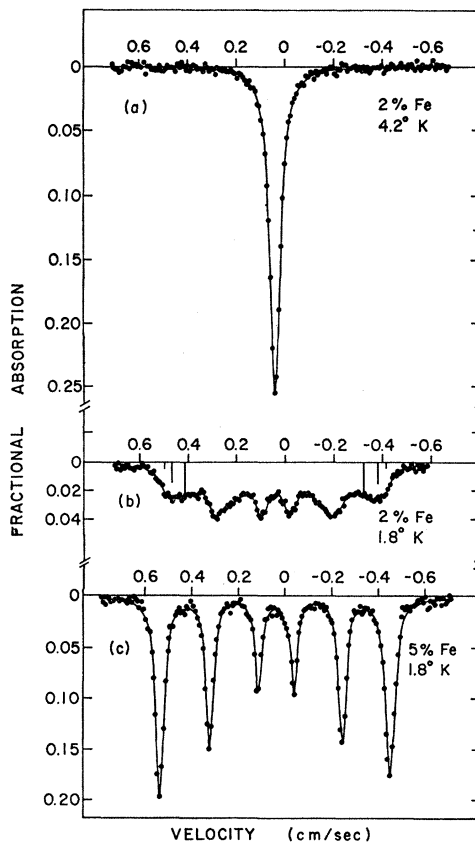


FIG. 2.  $\beta$ -Pd-Fe-H spectra for the 2%-Fe alloy (a) and (b), and the 5%-Fe alloy (c). The solid curves are the calculated least-squares fits. In (a) only one peak is present. The ferromagnetic spectrum in (b) is fitted with three subpatterns; the positions and relative areas of the three outermost peaks are shown by lines under the spectrum. Each set of lines (hyperfine field) is associated with atoms having a different number of H nearest neighbors. The 5%-Fe spectrum in (c) is fitted with twelve peaks. The zero of the velocity scale is at the centroid of an Fe versus Fe absorption spectrum at 300°K.

<sup>22</sup> R. S. Preston (private communication).

TABLE II. Analysis of superposed hyperfine spectra for  $\beta$ -Pd-Fe-H. Data for the 2% Fe-alloy are fitted to three subpatterns which correspond to a hydrogen nearest-neighbor model.  $A$  is the measured fractional area associated with the corresponding random probability  $P(n)$  of having  $n$  H nearest neighbors (6 H nearest-neighbor positions). Data for the 5%-Fe alloy are fitted to two subpatterns.

$\beta$ Phase							
% Fe	$T(^{\circ}\text{K})$	H/Pd	$H(\text{kOe})$	$A$	$n$	$P(n)$	$T_c(^{\circ}\text{K})$
2	1.8	0.59	$255 \pm 3$	0.57	0	0.54	$2.5 \pm 0.3$
			262	0.33	1	0.35	$2.9 \pm 0.3$
			283	0.10	2, 3	0.11	$3.7 \pm 0.2$
2	1.8	0.65	242	0.43	0	0.51	
			265	0.34	1	0.36	
			282	0.23	2, 3	0.13	
5	1.8		$304 \pm 3$				8-11
			313				8-11

Dunlap and Dash developed a similar theory to analyze Mössbauer results obtained from dilute Pd-Co alloys.<sup>11</sup>

Our data are analyzed using a simple model in which just two hyperfine spectra are superposed. The relative populations of Fe atoms in these spectra are proportional to the ratio of the areas associated with absorption due to all six lines in each subpattern. The model in which the ratio of areas corresponds to the ratio of the random probability of an Fe atom having zero Fe first neighbors to the probability of an Fe atom

having one or more Fe first neighbors only approximately fits the data (see Table I). When lines one and six are fit well, lines two and five are not. Within the framework of this model the best fit indicates that Fe atoms with one or more Fe first neighbors have a higher ordering temperature than Fe atoms with zero Fe first neighbors. However, it appears that models which take into account other than first-neighbor configurations are needed to adequately describe the field distribution.

## 2. $\beta$ -Pd-Fe-H

The Mössbauer spectra show that a single  $\beta$  phase is formed for the 2%-Fe alloy at H/Pd=0.59 and for the 5%-Fe alloy at H/Pd=0.54. The  $\beta$  phase of both alloys undergoes a magnetic transition; these transitions take place at considerably lower temperatures than those of the corresponding  $\alpha$  phase. For the 2% alloy the onset of ordering in the  $\beta$  phase occurred at  $T_c = (3.7 \pm 0.2)^{\circ}\text{K}$ . The hyperfine spectra taken at 1.8 and 4.2°K are shown in Figs. 2(a) and 2(b). Note that a distribution of fields occurs below  $T_c$ , as for  $\alpha$ -Pd-Fe-H. At 4.2°K the alloy is paramagnetic. At 1.8°K the field has not yet reached its saturation value. For the 5% alloy the magnetic transition in the  $\beta$  phase occurs at  $T_c = (10 \pm 3)^{\circ}\text{K}$ . Both transition temperatures are considerably lower than the Curie temperature determined by Burger from susceptibility data. The values of  $T_c$  in Table II were calculated from the corresponding hyperfine-field values using a simple Weiss function with  $1 \leq J \leq 5$  and the  $\alpha$ -phase saturation-field value.

We emphasize that it is not possible to distinguish between a ferromagnetic and an antiferromagnetic

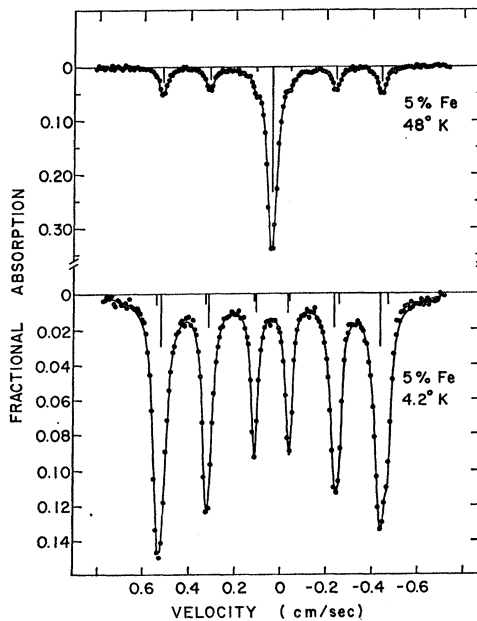


FIG. 3. Spectra from a two-phase sample of the 5%-Fe alloy at 48 and 4.2°K. The sample is composed of 23%  $\alpha$  phase and 77%  $\beta$  phase. At 48°K only the  $\alpha$  phase is ferromagnetic. The area under the  $\beta$ -phase peak is reduced by exponential absorption. Since both phases are well below their respective ordering temperatures, the spectrum at 4.2°K is approximated quite well by fitting to twelve absorption peaks, (solid-line) six associated with each phase. The lines under the absorption peaks show the positions and relative areas of the calculated peaks in the least-squares fit. The zero of the velocity scale is at the centroid of an Fe versus Fe absorption spectrum at 300°K. The relative isomer shift between the  $\alpha$  and  $\beta$  phases is not easily seen on this velocity scale.

TABLE III. Pd-Fe-H isomer shift in mm/sec relative to Fe in Fe at 300°K for the 2%-Fe alloy. The data are accurate to  $\pm 0.003$  mm/sec.

Temp. ( $^{\circ}\text{K}$ )	300	77	48	4.2	1.8
$I_{\beta}$	0.218	0.359	0.373	0.374	0.382
$I_{\alpha}$	0.176	0.311	0.335	0.337	0.337
$I_{\beta} - I_{\alpha}$	0.042	0.048	0.038	0.037	0.045

arrangement of Fe moments by means of Mössbauer spectroscopy (unless applied external fields are employed). The transition observed in the  $\beta$  phase is assumed to be ferromagnetic on the basis of Burger's results and the similarity of the  $\alpha$ - and  $\beta$ -phase spectra.

The detailed structure of the  $\beta$ -Pd-Fe-H spectra for 2% Fe was analyzed more successfully than the  $\alpha$ -phase spectra by a nearest-neighbor model in which the distribution of fields corresponds to the random distribution of hydrogen atoms in the allowed interstitial sites (see Table II). (Three parameters are available for the  $\beta$ -phase calculation, whereas only two are available for the  $\alpha$ -phase calculation because  $H/Pd \gg Fe/Pd$ ; this may to some degree account for the success of the  $\beta$ -phase fits.) This model suggests the largest field and highest ordering temperature are associated with Fe atoms having two or more H nearest neighbors, the smallest field with Fe atoms having zero H nearest neighbors. (A proton then spends a time long compared to  $10^{-7}$  sec at a given site at 1.8°K.) For the 5% alloy the intermediate structure is poorly resolved since 4.2 and 1.8°K are relatively far below the  $\approx 10^\circ$ K ordering temperature. The saturation fields for all environments are again approximately the same, the majority of Fe atoms in the 5% alloy being associated with the 313-kOe field. The distribution of fields is altered by the presence of absorbed hydrogen (and the filled 4d band), apparently masking the influence of the distribution of the Fe nearest neighbors observed in the  $\alpha$  phase.

### 3. Mixed Phases

For hydrogen concentrations below  $H/Pd \approx 0.54$  the samples are two-phase. The ratio of  $\alpha$  to  $\beta$  can be calculated from the known quantity of hydrogen in the sample. These intensity ratios were corroborated by taking spectra at a temperature which is below  $T_c$  for the  $\alpha$  phase but above the ordering temperature of the  $\beta$  phase. The resulting pattern is a superposition of spectra from the paramagnetic  $\beta$  phase (single line) and the magnetically broadened  $\alpha$  phase. Typical spectra for a mixed phase are shown in Fig. 3.

### B. Isomer Shifts

For both 2- and 5%-Fe alloys, the isomer shifts of the  $\alpha$  and  $\beta$  phases were measured as a function of temperature. The corresponding phases of both alloys have the same isomer shift to within our accuracy of  $\pm 0.003$  mm/sec at temperatures at which both are paramagnetic or both ferromagnetic. The data for the 2% alloy are shown in Table III. In two-phase samples, each phase exhibits the expected isomer shift (see Fig. 3). On passing through the Curie temperature (of either phase) from higher to lower temperatures, there is a suggestion of an additional isomer shift of

$\approx +0.01$  mm/sec associated with the onset of ferromagnetism. A similar observation for iron has been reported by Preston *et al.*<sup>23</sup>

In  $\beta$ -Pd-H a crystallographic transformation occurs at 55°K. Some hydrogen nuclei migrate from octahedral to tetrahedral sites, with an accompanying change in crystallographic symmetry and heat capacity.<sup>17,24</sup> We observe no isomer shift associated with this transition. This is not unexpected since the change in charge density at an Fe nucleus due to the rearrangement of the protons in the lattice is probably small, and only a fraction of the H nuclei occupy tetrahedral sites.

The measured temperature dependence of the shift of either phase is within a few per cent of that calculated from the measured specific heat of pure Pd (except near  $T_c$ ). Thus, the mean displacement of Fe atoms is nearly the same as that of Pd atoms in Pd. An anomalous temperature dependence of the isomer shift reported by Bemski *et al.* in Pd-Fe was not seen.<sup>25</sup>

If the electrons from H in  $\beta$ -Pd-Fe-H enter the Pd *d* band (as is consistent with previous remarks concerning the formation of the  $\beta$  phase as a function of Fe concentration), then in going from the  $\alpha$  to the  $\beta$  phase the Fe electron configuration remains unchanged while the volume per Fe atom increases by 11%. In general, a volume increase produces a charge density decrease at the nucleus with a corresponding positive isomer shift (in Fe). We observe a shift of  $(+0.045 \pm 0.003)$  mm/sec in going from the  $\alpha$  to the  $\beta$  phase, of the magnitude predicted from the volume change of Fe in Laves-phase compounds<sup>26</sup> and about one-third that extrapolated from measurements of the volume change of Fe produced by the application of pressure in bcc iron.<sup>27</sup> Obviously these volume considerations are an oversimplification of the physical situation.

### ACKNOWLEDGMENTS

We thank R. S. Preston for making available a computer program and for many very helpful discussions, J. L. Groves for assistance in preparing samples and collecting data, J. W. Downey for making the Pd-Fe alloys, and H. Montgomery for his many valuable comments on our manuscript.

<sup>23</sup> R. S. Preston, S. S. Hanna, and J. Heberle, *Phys. Rev.* **128**, 2207 (1962).

<sup>24</sup> P. Mitacek, Jr., and J. G. Aston, *J. Am. Chem. Soc.* **85**, 137 (1963).

<sup>25</sup> G. Bemski and X. A. Da Silva, *J. Appl. Phys.* **35**, 1081 (1964); G. Bemski, J. Dannon, A. M. De Graaf, and X. A. Da Silva, *Phys. Letters* **18**, 213 (1965).

<sup>26</sup> M. V. Nevitt, C. W. Kimball, and R. S. Preston, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 137.

<sup>27</sup> D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De-Pasquali, H. G. Drickamer, and H. Frauenfelder, *Phys. Rev.* **135**, A1604 (1964).