# Mössbauer study of ferromagnetic phase transitions in $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$ alloys<sup>\*</sup>

R. A. Levy,<sup>†</sup> J. J. Burton, and D. I. Paul

Henry Krumb School of Mines, Columbia University, New York, New York 10027

J. I. Budnick<sup>‡</sup>

Fordham University, Bronx, New York 10458

(Received 11 July 1973)

The effect of varying the host-matrix susceptibility of the  $Pd_{0.99}Fe_{0.01}$  alloy system has been investigated through Mössbauer analysis of several  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys with silver concentrations given by x = 0, 0.005, 0.025, 0.10, 0.25, and 0.50. We have shown that the Curie temperature varies linearly with the spin paramagnetic susceptibility of the Pd-Ag host matrix, in agreement with theoretical predictions. This was done for silver concentrations up to 25 at.% and assumes a constant value for the spin of the iron impurity. From the observed linear dependence of the ordering temperature on the host-matrix susceptibility evaluated at  $T_c$ , we obtain a value for the exchange parameter of  $0.11 \pm 0.01$  eV which is used in estimating the saturation moment per iron atom. Assuming a molecular-field model, values for the saturation hyperfine field are deduced from temperature-extrapolated hyperfine-field measurements. Changes in those values with silver addition suggest changes in the polarization of 3d electrons and a possible correlation with the saturation magnetization. Isomer-shift measurements of these alloys are found to be concentration independent up to x = 0.25 and to increase by 20% at about x = 0.50.

#### I. INTRODUCTION

The Pd<sub>1-x</sub>Fe<sub>x</sub> system has been extensively investigated by a variety of methods.<sup>1-4</sup> The interest in such a system stems from the fact that the addition of iron impurities to paramagnetic palladium induces a ferromagnetic phase transition at temperatures depending strongly on the iron concentration.<sup>5</sup> This is accompanied by the appearance of "giant moments" around the iron atom<sup>6</sup> (as large as 12.  $2\mu_B$  per iron atom for 0.28-at. % Fe in Pd, the Fe atom itself contributing about  $3.5\mu_B$ ) together with a polarization by the iron atom of the neighboring 4d palladium electrons to within a range of ~ 10 Å.<sup>7</sup> Both the appearance of the giant moments and the extensive Fe-Pd polarization range which depends on Fe concentration have received theoretical attention.<sup>8</sup> Long-range ferromagnetism occurs when there is coupling among the ferromagnetic complexes centered around the solute magnetic atoms.

Through Mössbauer spectroscopy, we have extended the study of the  $Pd_{1-x}Fe_x$  system to alloys of the type  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  (where x=0, 0.005, 0.025, 0.10, 0.25, and 0.50). Silver was chosen because it enters the lattice substitutionally, thus increasing the average number of electrons in the unfilled 4d band of palladium. We have used 1at.% iron in our alloys because at this concentration, nearest-neighbor iron-iron interactions are small, data are available for correlation of results, and the Fe<sup>57</sup> resonance has a narrow linewidth together with a large-percent-absorption effect.

The experimental results are analyzed to give

values for the Curie temperature, molecular-field coefficient, exchange-interaction parameter between the local moment and itinerant electrons, saturation moment per iron atom, saturation hyperfine field, and the isomer shift.

#### **II. EXPERIMENTAL PROCEDURE**

All  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys in the present Mössbauer experiments were used as absorbers. The starting elements, 99.999%-pure palladium sponge, 99.999%-pure silver powder, and enriched (98-99.9% pure)  $Fe^{57}$  powder, were pelletized in the form of a cylindrical button. Each sample was then placed in a recrystallized zirconium oxide crucible and melted by induction heating in a purified-argon atmosphere. The samples which were measured after the melting operation showed a slight percentage increase in weight (~1.5%) due to the sticking of a thin layer of zirconia at the bottom of the ingot. This layer was subsequently removed by filing. We estimate the accuracy limits of the nomical contents to be within 3%. The ingots were then rolled and hand polished to the desired thickness (0,001-0,0015 in.). Each foil was outgassed overnight at 300 °C in a quartz tube. These tubes were sealed under vacuum, and placed in an electric furnace at a 1000 °C for a week, to ensure homogeneity of the iron and silver atoms in the alloy, after which they were quickly cooled in air then water.

A 15-mCi  $\operatorname{Co}^{57}$  radioactive source (plated onto a copper matrix) was rigidly mounted on a speakertransducer assembly described by Cohen *et al.*,<sup>9</sup> while a time-sequence mode of operation was used to detect the emerging radiation. For the low-

9

temperature experiments (below 78 °K) the sensor was an Andonian-*CGIAC* calibrated germanium resistor accurate to within 0.1 °K; a calibrated Artronix-*PSIA* platinum sensor was used at higher temperatures. Our choice of these two sensors over a thermocouple or a carbon resistor was dictated by their known stability, reproducibility and sensitivity to low temperatures. An Artronix-5301 temperature controller was used to stabilize our temperatures to better than 0.01 °K.

## III. EXPERIMENTAL RESULTS AND DISCUSSION A. Curie temperature

The Curie temperature of the  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$ alloys with Ag concentrations given by x = 0, 0.005, 0.025, 0.10, and 0.25 was determined by measuring the maximum absorption resonance. The onset of ferromagnetism for all considered alloys was a gradual process with the Mössbauer spectra exhibiting both six-line and single-line components over a temperature range of several degrees below  $T_C$ . In our x = 0.25 sample, we did not go more than 1.3 °K below  $T_C$  and, therefore, did not observe any large resolved hyperfine splitting. Similar observations regarding the diffuseness of the magnetic transition have been reported<sup>10,11</sup> and attempts were made to correlate the effect to local statistical variations in the solute concentration.

Dekhtyar and Fedchenko<sup>12</sup> have observed changes in the paramagnetic susceptibility of the alloys Pd+1-at. % Fe and Pd+1-at. % Fe+25-at. % Ag. as a result of repeated quenching (from 900, 1000, and 1100 °C) in water. They report that the paramagnetic susceptibility (a) rises substantially and deviates from the Curie-Weiss law with an increase in the number of quenching cycles, and (b) exhibits a dependence on the magnetic field not seen for the alloys in the annealed state. Since it is known<sup>13-15</sup> that vacancies are preferably nucleated on impurities during quenching, one expects an increase in the diffusion rate of Fe atoms within the alloy. This, in turn, may generate the formation of complex groups of Fe atoms and quenching defects (ferromagnetic clusters) that explain the observed data. In view of these results, it is possible that, during the cooling period of the heattreatment process of our samples, there was a tendency for the Fe atoms to lose their uniform distribution which accounts for the coexistence of regions in the paramagnetic and ferromagnetic state.

The effect of annealing on the Mössbauer spectra of a 0.22-at. % Fe in Pd sample had been seen<sup>10</sup> to lower the maximum temperature at which hyperfine fields could be observed, to narrow enormously the spread in hyperfine fields just below  $T_c$ , and to sharpen the transition. This was interpreted by assuming that the annealing process breaks up iron clusters and in so doing lowers the temperature at which magnetization first begins to appear.

On the other hand, Clark and Meads<sup>16</sup> noted that a previously annealed  $Pd_{0.99}Fe_{0.01}$  sample heated at 1000 °C and quenched in liquid nitrogen caused considerable sharpening of the transition and displacement of  $T_C$  to a lower value. It is apparent, from these conflicting observations, that additional experimental and theoretical work on the effect of heat-treatment is needed to clarify this point. We might point out at this time that with our samples placed in a temperature-controlled exchange-gas environment, temperature gradients of the magnitude required to explain the effect are unlikely to exist during measurement across these samples.

Figure 1 shows the variation of  $T_c$  with silver concentration x; experimental results using other methods are also shown for comparison purposes. In the case of the  $Pd_{0.99}Fe_{0.01}$  alloy, our value for  $T_c$  lies between the reported value of  $T_c$  obtained by other Mössbauer measurements.<sup>16</sup> Agreement within the experimental error exists between our measurements of  $T_c$ , for the  $Pd_{0.99}Fe_{0.01}$  alloy, and reported values of  $T_c$  obtained by electrical resistivity measurements.<sup>5,17</sup>

We believe the discrepancy between our measured value of  $T_c$  and the one reported by saturation magnetization is due to the limitations of the various techniques used to determine  $T_c$ . The magnetization measurements involve a plot of H/M vs  $M^2$  (M is the magnetization per gram, H is the applied field), which is then extrapolated to zero applied field. Any deviation from linearity in the limit of zero applied field, as seen in the



FIG. 1. Variation of the Curie temperature  $T_C$  of several  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys with at.% Ag concentration. Closed circles: Mössbauer maximum absorption technique (this work); open circles: saturation magnetization (Ref. 6); triangles: electrical resistivity (Refs. 5 and 17); square: Mössbauer equal area technique (Ref. 16); crosses: low-field susceptibility (measured on our alloys at Fordham University, courtesy of Professor J. I. Budnick). The solid curve is explained in the text.

case of 0.15-at. % Fe in Pd, <sup>18</sup> may result in serious errors in the determination of  $T_c$ . Craig et al.<sup>3</sup> have discussed the limitations of the various extrapolation techniques used to obtain  $T_c$  from saturation magnetization data and have shown that, in the particular case of Pd<sub>0.9735</sub>Fe<sub>0.0265</sub>, the extrapolated value of  $T_c$  is always higher than the value of  $T_c$  obtained from Mössbauer spectroscopy as in our case. Our method of measuring the Curie temperature involves finding the maximum absorption resonance in the Mössbauer spectrum of the alloys in the paramagnetic state just above the transition temperature. If one plots the intensity at the Doppler velocity corresponding to this maximum absorption resonance as a function of temperature. the first significant decrease in relative count rate. that occurs as the temperature is lowered, corressponds to the onset of an internal field and determines the magnetic transition temperature. This operational technique, which is commonly used, has the advantage of requiring no applied field but sets an upper limit to the ordering temperature. The discrepancy between our  $T_c$  measurement of the  $Pd_{0.99}Fe_{0.01}$  alloy and the other Mössbauer measurement reported by Clark and Meads<sup>16</sup> is basically due to the difference in choice of technique used to determine  $T_c$ . They determined the "mean Curie temperature"; our method determines the onset of ferromagnetism.

The gradual addition of Ag to the  $Pd_{0.99}Fe_{0.01}$ alloy in the range of concentrations  $0 \le x \le 0.25$  is seen to result in a large decrease in the values of the magnetic transition temperature  $T_c$  as shown in Fig. 1. This can be interpreted qualitatively by assuming that the valence electrons of Ag are donated to the partially filled 4d band of Pd, thus reducing the magnetic susceptibility of the Pd-Ag matrix and thereby making it harder for the solute iron atoms to polarize the host alloy conduction electrons.

The ferromagnetism of Pd alloys containing small concentrations of iron has been treated by Takahashi and Shimizu<sup>19</sup> based on a band model for 4d electrons. The authors assume that the magnetic moments of the dissolved iron atoms are localized at their sites and interact only with the magnetic moments of itinerant 4d electrons so as to induce a uniform polarization in the 4d band. These assumptions led to the following equation:

$$T_{c} = N_{i} g^{2} \mu_{B}^{2} S(S+1) \alpha^{2} \chi_{0} (T_{c})/3k , \qquad (1)$$

where  $N_i$  is the number of dissolved Fe atoms, S is the spin quantum number of dissolved iron atoms,  $\chi_0(T_c)$  is the host matrix susceptibility evaluated at the  $T_c$ , and  $\alpha$  is the molecular-field coefficient for the interaction between the iron moments and the 4d electrons.

Figure 2 shows the variation of our measured values of  $T_c$  with reported values of  $\chi_0$  ( $T_c$ ). In the particular case of the x = 0.25 alloy where no value for  $\chi_0$  ( $T_c$ ) is available,  $\chi_0$  ( $T_c$ ) was chosen at T = 20 °K rather than at 7.5 °K. Such a decision was based on the fact that for low temperatures (< 40  $^{\circ}$ K) and high silver concentrations (> 22.5 at. %),  $\chi_0$  for Pd-Ag alloys is nearly temperature independent.<sup>20,21</sup> From the slope of the linear fit shown in Fig. 2, we obtained a value for the molecular-field coefficient  $\alpha = (0.17 \pm 0.02) \times 10^4$  mole/ emu in agreement with the theoretically predicted  $\alpha = 0.16 \times 10^4$  mole/emu. A linear dependence between the Curie temperature  $T_c$  and the host matrix susceptibility  $\chi_0(T_c)$  is hence established as a result of the concentration-independent behavior of  $\alpha$  in  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys. The full theoretical curves in Fig. 1 represent Eq. (1) using the known host matrix susceptibility evaluated at  $T_c$ , the calculated molecular-field coefficient  $\alpha = (0.17)$  $\pm 0.02$ )×10<sup>4</sup> mole/emu, the reported <sup>19</sup> value for the magnitude of the impurity spin  $S = \frac{3}{2}$ , and a value for the spectroscopic factor g = 2.

Kim<sup>22</sup> has also related  $T_c$  to  $\chi_0(T_c)$  using a quantum mechanical exchange enhancement model, i.e.,

$$T_{C} = 2N_{i}J^{2}S(S+1)\rho(\epsilon_{F})/3kN^{2}[1-V\rho(\epsilon_{F})], \qquad (2)$$

where J is the exchange interaction parameter between the local moment and the itinerant electrons,  $\rho(\epsilon_F)$  is the density of states of conduction electrons at the Fermi level, V is an effective interaction potential, and N is the total number of lattice points.



FIG. 2. Variation of the Curie temperature of several  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys with host matrix susceptibility evaluated at  $T_C$ . Closed circles: Mössbauer maximum absorption technique (this work); open circles: saturation magnetization (Ref. 6); triangles: electrical resistivity (Refs. 5 and 17); square: Mössbauer equal-area technique (Ref. 16); crosses: low-field susceptibility (measured on our alloys at Fordham University, courtesy of Professor J. I. Budnick). The solid curve is a linear least-square fit of the data,

 $\chi_0$  is related to  $\rho(\epsilon_F)$  through<sup>21</sup>

$$\chi_0 = 2\mu_B^2 \rho(\epsilon_F) / [1 - V\rho(\epsilon_F)] . \tag{3}$$

As in the case of  $\alpha$ , we computed the value of  $J=0.11\pm0.01$  eV from the slope of the linear fit of the curve shown in Fig. 2. This value is comparable to the value of  $J=0.15\pm0.02$  eV reported by Doniach and Wohlfarth.<sup>23</sup> The small discrepancy is not fundamental but may reflect the methods used, i.e., they used the slope of the linear fit of the saturation magnetization per iron atom  $\mu_{sat}$  vs  $\chi_0$  (T=0°K) for various alloys to determine J, while we used the Curie-temperature data for the (Pd<sub>1-x</sub>Ag<sub>x</sub>)<sub>0.99</sub>Fe<sub>0.01</sub> alloys, in our analysis. This difference may also reflect a small alloying effect on J, more significant at the highest silver concentration we used.

We now consider the saturation magnetization per iron atom  $\mu_{sat}$ . Doniach and Wohlfarth<sup>23</sup> have obtained the following relation for this quantity:

$$\mu_{\text{sat}} = \mu_0 \frac{1 + 2J\chi_0(T=0 \,^\circ\text{K})}{Ng^2 \,\mu_B^2}$$
$$\simeq \mu_0 [1 + \alpha \,\chi_0 \,(T=0 \,^\circ\text{K})] , \qquad (4)$$

where  $\mu_0$  is the moment localized on the iron atom. Our calculated value of J was used to estimate values of  $\mu_{sat}$ . These calculations, based on  $\mu_0 = 3.5 \mu_B$ , show that—as predicted— $\mu_{sat}$  falls sharply with increasing silver content. The results summa-rized in Table I are in qualitative agreement with the low temperature saturation magnetization measurements of Clogston *et al.*<sup>6</sup>

### B. Hyperfine field

All values of the hyperfine field at temperature T, Hi(T), were determined from the outer peaks of the computer fitted six-line spectra. These spectra were not characterized by well-defined lines below  $T_c$ , but rather by six smeared and broadened lines which became sharper and narrow-er with decreasing temperatures, in agreement with similar reported observations.<sup>10,24</sup> Although this line broadening, which intensifies as the temperature is increased, may be caused by relaxa-tion effects, <sup>25</sup> it may also be due to a wide distribution of hyperfine fields arising from the spread in exchange fields caused by statistical fluctuations in the density of iron atoms.<sup>10,11</sup>

In order to estimate an absolute value for the hyperfine field at zero temperature  $H_{sat}$ , we used the Weiss molecular-field spontaneous-magnetization equation in zero external field<sup>26</sup>:

$$\frac{H_i(T)}{H_{sat}} = B_s \frac{3ST_C H_i(T)}{(S+1)T H_{sat}},$$
(5)

where  $H_i(T)$  and  $H_{sat}$  refer to the hyperfine field

at temperature T and zero temperature, and  $B_s$ is the Brillouin function of spin S. In using Eq. (5), we made the assumption (borne out by experimental results<sup>3</sup>) that the hyperfine field is proportional to the bulk sample magnetization.

From a known  $H_i(T)/H_{sat}$  ratio and an experimentally measured  $H_i(T)$  at  $T/T_c$ , the value of  $H_{sat}$ was calculated (see Fig. 3). In the case of the  $Pd_{0.99}Fe_{0.01}$  alloy, our estimated value of  $H_{sat}$ =  $314 \pm 3$  kOe is about 3% larger than the reported value  $H_{\text{sat}} = 304 \pm 3 \text{ kOe}^4$  obtained by extrapolation of the hyperfine field at very low temperatures. Such a discrepancy may be explained if the molecular-field model fails to fit the hyperfine-field data for all possible spins at intermediate  $T/T_c$ values (as reported for Pd-Fe alloys<sup>3,27</sup>), or if the assumed proportionality factor between hyperfine field and bulk magnetization is temperature dependent possibly due to a difference in coupling strength between impurity-host and host-host atoms.<sup>28</sup>

The measured hyperfine field corresponds mainly to the polarization of the s electrons by the outer unpaired 3d electronic spins of the Fe<sup>57</sup> impurity. The decrease in the estimated value of  $H_{sat}$  with silver addition suggests a change in the polarization of 3d electrons. Furthermore, the tional decrease in  $H_{sat}$  in going from Pd<sub>0.99</sub>Fe<sub>0.01</sub> to (Pd<sub>0.90</sub>Ag<sub>0.10</sub>)<sub>0.99</sub>Fe<sub>0.01</sub> (~ 22%) is in close agreement with the fractional decrease in the saturation moment per iron atom (~ 23%), as calculated in Table I, using Doniach's model. This suggests that in the case of the Pd-rich (Pd<sub>1-x</sub>Ag<sub>x</sub>)<sub>0.99</sub>Fe<sub>0.01</sub> alloys the saturation hyperfine field is approxi-



FIG. 3. Graphical representation of  $H_i(T)/H_{sat}$  and the Brillouin function  $B_S(Z)$  of spin  $S = \frac{3}{2}$  vs  $Z \equiv [3S/(S+1)] \times (T_C/T) H_i(T)/H_{sat}$  at the following values of  $T/T_C$ : x = 0,  $T/T_C = 0.41$ ; x = 0.005,  $T/T_C = 0.51$ ; x = 0.025,  $T/T_C = 0.24$ ; and x = 0.10,  $T/T_C = 0.34$ . The intersection of the two curves yield the ratio  $H_i(T)/H_{sat}$  at a specified  $T/T_C$  value.

Alloy	T <sub>C</sub> (°K) Curie temperature (±1, 3 °K)	$\begin{array}{c} \chi_0(T_C) \\ (10^{-4} \ \mathrm{emu/mole}); \\ \mathrm{host \ matrix} \\ \mathrm{susceptibility \ evaluated} \\ \mathrm{at} \ T_C \\ (\pm 0.1 \times 10^{-4} \ \mathrm{emu/mole}) \end{array}$	Estimate of $\mu_{sat}$ ( $\mu_B$ ); saturation moment per Fe atom (±1.0 $\mu_B$ )	Estimate of  H <sub>sat</sub>   (kOe) saturation hyperfine field at 0°K (±3 kOe)
Pd <sub>0.99</sub> Fe <sub>0.01</sub>	37.3	7.8 (Ref. 20)	8.1	314
$(Pd_{0.995}Ag_{0.005})_{0.99}Fe_{0.01}$	34.6	7.2 (Ref. 21)	7.8	313
$(Pd_{0.975}Ag_{0.025})_{0.99}Fe_{0.01}$	29.9	6.3 (Ref. 21)	7.1	288
$(Pd_{0.90}Ag_{0.10})_{0.99}Fe_{0.01}$	20.1	4.6 (Ref. 20)	6.1	244
$(Pd_{0,75}Ag_{0,25})_{0,99}Fe_{0,01}$	7.5	2,3 (Ref. 20)	4.9	

TABLE I. Summary of results.

mately proportional to the average saturation magnetization.

### C. Isomer shift

In the paramagnetic range of temperatures, the spectra for our  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys exhibited broadened single lines which were computer fitted to a Lorentzian shape. The absence of a magnetic hyperfine structure within the considered velocity scan (±10 mm/sec) indicates that the iron atoms have not segregated during the induction melting operation but have dissolved in the  $Pd_{1-x}Ag_x$  host matrix. Previous investigators<sup>29,30</sup> have reported difficulties in obtaining such solid solutions using other sample preparation techniques.

The average room-temperature isomer-shift measurements shown in Fig. 4 are all determined relative to a metallic-iron absorber containing enriched Fe<sup>57</sup> (90.73%). The following results were observed: (i) the isomer shift for each of the alloys exhibits a large positive value with respect to metallic iron; (ii) in the range of silver concentration extending from x = 0 to x = 0.25, there is no noticeable variation in the isomer shift; and (iii) at the silver concentration corresponding to x = 0.50, an increase of 20% in the positive isomer shift was recorded.

Under the present experimental conditions, <sup>31</sup> positive values for the measured isomer shifts indicate that the *s*-electron density at the Fe<sup>57</sup> nucleus in the six considered alloys is smaller than in metallic iron. Our measured value of the isomer shift for the Pd<sub>0.99</sub>Fe<sub>0.01</sub> alloy,  $\delta = 0.193 \pm 0.005$  mm/sec, is close to that for very dilute iron in palladium,  $\delta = 0.185 \pm 0.01$  mm/sec<sup>32</sup> and agrees with the values found by Bemski *et al.* to 25-at.% iron in palladium.<sup>33</sup> Thus, for our range of concentrations, the electron density at the Fe<sup>57</sup> nucleus appears to be independent of the iron content.

The fact that the average isomer shift remains positive and concentration independent up to the considered silver concentration x = 0.25 suggests a transfer of s electrons from both iron and silver to the partially filled palladium 4*d* band due to its high density of states. Any spilling of charge in the broad overlapping *s* band which would tend to increase the average value of the isomer shift is counterbalanced by the volume expansion of the Pd-Ag unit cell, <sup>34</sup> thus leaving the *s*-electron density at the Fe<sup>57</sup> nuclear site essentially unchanged upon addition of silver. The functional behavior of our Fe<sup>57</sup> isomer shifts with increasing silver content is in agreement with the functional behavior reported for Sn<sup>119</sup> isomer-shift measurements in Pd-Ag-Sn alloys.<sup>35</sup>

The substantial increase in the observed isomer shift at the iron concentration x = 0.50 suggests that the palladium 4d band in our alloys has been filled. The addition of silver beyond the filled palladium d band causes the transfer of the 5s silver electrons to other bands (i. e., 3d), that shield the s electrons of iron from the Fe<sup>57</sup> nucleus and cause the larger positive isomer shift recorded. The situation here is similar to what was observed in Cu-Ni alloys containing small amounts of iron. <sup>36</sup> Above a concentration of copper at which the d band of nickel is completely filled, a further increase in copper tends to give addition-



FIG. 4. Variation of the room-temperature  $Fe^{57}$  isomer shifts (relative to  $Fe^{57}$  in metallic iron) of several  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys as a function of at. % Ag concentration. The solid curve represents a linear least-square fit of the data.

al d electrons near the iron atoms thereby decreasing the *s*-electrons density at the iron nucleus.

The thermal contribution to the isomer shift  $\delta_{th}$  has been calculated for the specified  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys over a wide range of temperatures using the Debye temperature value of pure palladium<sup>37</sup>  $\Theta_D = 275$  °K in the second-order Doppler equation

$$\frac{\partial \delta_{th}}{\partial T} = -\frac{C_L}{2Mc^2}, \qquad (6)$$

where  $C_L$  is the specific heat of the lattice, M is the gram atomic weight, and c is the speed of light.

The agreement between the experimental data and calculated curve shown in Fig. 5 indicates that the mean-squared velocity of the iron atoms in palladium and Pd-Ag allovs is close in value to that of palladium atoms in pure palladium and Pd-Ag alloys, in agreement with specific heat measurements of Pd-Ag <sup>37</sup> and of dilute iron in palladium alloys.<sup>38</sup> When the observed shift is converted to isomer shift by subtracting the expected contribution from the second-order Doppler shift, the isomer shift of the Fe<sub>0.01</sub>Pd<sub>0.99</sub> remains temperature independent within the experimental error. Furthermore, in the silver-concentration range given by  $0 \le x < 0.25$ , the gradual addition of silver to the basic  $Fe_{0.01}Pd_{0.99}$  alloy does not affect the temperature independence of its isomer shift. This supports Phillips and Kimball's measurements<sup>24</sup> on Fe-Pd-H alloys (2- and 5-at. % iron) with hydrogen concentrations from 0 to 0.65 H/Pd, but does not concur with the results in Fe-Pd and Fe-Pd-H alloys of Bemski et al. 33

## **IV. CONCLUSION**

The behavior of dilute iron in Pd-Ag alloys has been investigated by Mössbauer measurements of the Curie temperature, hyperfine field, and isomer shift.

One examining the temperature variation of the spectrum, it was apparent that a paramagnetic component persisted several degrees below the quoted Mössbauer Curie temperatures, indicating, most probably, the existence of a range of ordering temperatures arising from local environment fluctuations. This has been a persistent feature in the study of the Fe-Pd system and does appear to be related to the metallurgical treatment of these alloys.

In the case of the x=0 and x=0.25 samples, our experimental values of  $T_c$  confirm the existence of a discrepancy between the results obtained by Mössbauer and magnetization methods. The variation of the magnetic transition temperature  $T_c$ with silver addition was seen to be essentially



FIG. 5. Variation of combined  $Fe^{57}$  isomer and thermal shifts (relative to  $Fe^{57}$  in metallic iron) as a function of temperature for several  $(Pd_{1-x}Ag_x)_{0.99}Fe_{0.01}$  alloys with x = 0 (open circles), x = 0.005 (closed circles), x = 0.025 (crosses), x = 0.10 (squares), and x = 0.25 (triangles). The theoretical Debye curve is shown for  $\Theta_D = 275$  °K.

determined by the spin paramagnetic susceptibility of the host matrix, as computed by Takashi and Shimizu<sup>19</sup> and Kim.<sup>22</sup> From the observed linear dependence of the Curie temperature on the hostmatrix susceptibility evaluated at  $T_C$ , the molecular-field coefficient and exchange parameter were evaluated and shown to be in agreement with reported values.<sup>19,23</sup>

At the lowest temperatures used to initiate the search for  $T_c$ , values for the hyperfine field were evaluated from the outer peaks of the computer fitted six-line spectra. These values were extrapolated to T = 0 °K in order to estimate the saturation hyperfine field and observe its dependence on silver concentration. The decrease in our estimated value of  $H_{sat}$  with silver addition suggests a change in the polarization of 3d electrons. As it has been suggested, <sup>39,40</sup> the observed sharpening and narrowing of our spectral lines with decreasing temperatures may correspond to the development of more uniform hyperfine field. This presumably would occur at  $T/T_c \ll 1$  even if the longrange conduction electron polarization would have a small oscillatory part over distances long compared to composition fluctuation distances.

The concentration-independent behavior of the isomer shift in the palladium-rich range of concentration and the 20% increase in this shift at the silver concentration x = 0.50 were discussed in terms of a charge-transfer model in which valence electrons from iron and silver are thought to be donated to the partially filled palladium 4d band. Although the conceptual simplicity of such a model has led us to its use, we do recognize its limited validity and the need for correlation with higher levels of approximation such as described for instance in the recent coherent-potential-approximation model.<sup>41</sup>

#### ACKNOWLEDGMENTS

One of the authors (R.A.L.) wishes to thank

- \*Work supported by the U. S. Naval Research Office.
- <sup>†</sup>Present address: Carnegie-Mellon University, Pittsburgh, Pa.
- <sup>‡</sup>Present address: National Science Foundation, Washington, D. C.
- <sup>1</sup>J. Crangle and W. R. Scott, J. Appl. Phys. <u>36</u>, 921 (1965).
- <sup>2</sup>M. P. Kawatra, J. I. Budnick, and J. A. Mydosh, Phys. Rev. B <u>2</u>, 1587 (1970).
- <sup>3</sup>P. P. Craig, R. C. Perisho, R. Segnan, and W. A. Steyert, Phys. Rev. <u>138</u>, A 1460 (1965).
- <sup>4</sup>J. I. Budnick, J. Lechaton, and S. Skalski, Phys. Lett. 22, 405 (1966).
- <sup>5</sup>For a recent summary as well as for additional data,
- see J. A. Mydosh, J. I. Budnick, M. P. Kawatra, and S. Skalski, Phys. Rev. Lett. <u>21</u>, 1346 (1968).
- <sup>6</sup>A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwitt, and R. C. Sherwood, Phys. Rev. 125, 541 (1962).
- <sup>7</sup>G. G. Low and T. M. Holden, Proc. Phys. Soc. Lond. 89, 119 (1966).
- <sup>8</sup>A. M. Clogston, Phys. Rev. Lett. <u>19</u>, 583 (1967); B. Giovannini, M. Peter, and J. R. Schrieffer, Phys. Rev. Lett. <u>12</u>, 736 (1964); D. J. Kim and B. B. Schwartz, Phys. Rev. Lett. <u>20</u>, 201 (1968).
- <sup>9</sup>R. L. Cohen, P. G. McMullin, and G. K. Wertheim, Rev. Sci. Instrum. 34, 671 (1963).
- <sup>10</sup>W.L. Trousdale, G. Longworth, and T. A. Kitchens, J. Appl. Phys. 38, 922 (1967).
- <sup>11</sup>T. A. Kitchens and W. L. Trousdale, Phys. Rev. <u>174</u>, 606 (1968).
- <sup>12</sup>I. Ya. Dekhtyar and R. G. Fedchenko, Fiz. Met. Metalloved. <u>21</u>, 833 (1966).
- <sup>13</sup>C. M. Wayman, K. M. Thein, and N. Nakaninski, J. Appl. Phys. <u>34</u>, 2842 (1963).
- <sup>14</sup>G. Thomas and J. Washburn, Rev. Mod. Phys. <u>35</u>, 992 (1963).
- <sup>15</sup>Ju-Pu Huang, Sci. Sinica. <u>12</u>, 891 (1963).
- <sup>16</sup>P. E. Clark and R. E. Meads, J. Phys. C <u>3</u>, 308 (1970).
- <sup>17</sup>G. Longworth and C. C. Tsuei, Phys. Lett. A <u>27</u>, 258 (1968).
- <sup>18</sup>A. J. Manuel and M. McDougald, J. Phys. C <u>3</u>, 147 (1970).
- <sup>19</sup>T. Takahashi and M. Shimizu, J. Phys. Soc. Jap. <u>20</u>,

26 (1965).

- <sup>20</sup>F. E. Hoare, J. C. Matthews, and J. C. Walling, Proc. R. Soc. Lond. <u>216</u>, 502 (1953).
- <sup>21</sup>R. Doclo, S. Foner, and A. Narath, J. Appl. Phys. 40, 1206 (1969).
- <sup>22</sup>D. Kim, Phys. Rev. <u>149</u>, 434 (1966).
- <sup>23</sup>S. Doniach and E. P. Wohlfarth, Proc. R. Soc. A <u>296</u>, 422 (1967).
- <sup>24</sup>W. C. Phillips and C. W. Kimball, Phys. Rev. <u>165</u>, 401 (1968).
- <sup>25</sup>F. Van der Woude and A. J. Dekker, Phys. Status Solidi 9, 775 (1965).
- <sup>26</sup>J. S. Smart, Effective Field Theories of Magnetism (Saunders, Philadelphia, Pa., 1966), p. 27.
- <sup>27</sup>T. A. Kitchens and P. P. Craig, J. Appl. Phys. <u>37</u>, 1187 (1966).
- <sup>28</sup>Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Jap. <u>19</u>, 1493 (1964).
- <sup>29</sup>G. Longworth, J. Phys. C 1, 81 (1970).
- <sup>30</sup>A. T. Grigorev, L. A. Pantelsimonov, Z. P. Ozerova, and E. V. Akatova, Russ. J. Inorg. Chem. <u>5</u>, 1160 (1960).
- <sup>31</sup>R. A. Levy, Doctoral thesis (Columbia University, 1973) (unpublished).
- <sup>32</sup>Mössbauer Effect Data Index 1958 1965, edited by A.
   H. Muir, K. J. Ando, and H. M. Coogan (Interscience, New York, 1966), p. 26.
- <sup>33</sup>G. Bemski, J. Danon, A. M. DeGraaf, and X. A. Da-Silva, Phys. Lett. <u>18</u>, 213 (1965).
- <sup>34</sup>B. R. Coles, J. Inst. Met. <u>84</u>, 346 (1956).
- <sup>35</sup>I. R. Harris and M. Cordey-Hayes, J. Less Common Metals <u>16</u>, 223 (1968).
- <sup>36</sup>G. K. Wertheim and J. H. Wernick, Phys. Rev. <u>123</u>, (1961).
- <sup>37</sup>H. Montgomery, G. P. Pells, and E. M. Wray, Proc. R. Soc. A 301, 261 (1967).
- <sup>38</sup>B. W. Veal and J. A. Rayne, Phys. Rev. <u>135</u>, A 442 (1964).
- <sup>39</sup>S. Skalski, J. I. Budnick, and J. Lechaton, J. Appl. Phys. <u>39</u>, 965 (1968).
- <sup>40</sup>J. I. Budnick, Colloque Ampere XV (North-Holland, Amsterdam, 1969).
- <sup>41</sup>G. M. Stocks, R. W. Williams, and J. S. Faulkner, Phys. Rev. B 4, 4390 (1971); K. Levin, R. Bass, and
- K. H. Bennemann, Phys. Rev. B 6, 1865 (1972).

T. Novinski and C. Bryant for experimental assistance as well as Dr. J.A. Rayne and Dr. M. Gutzwiller for fruitful discussions.