PHYSICAL REVIEW B VOLUME 37, NUMBER 4 1 FEBRUARY 1988

Platinum-induced changes in the electronic structure of iron

S. M. Dubiel*
Max-Planck-Institut für Eisenforschung, Max-Planck-Strasse 1, D-4000 Düsseldorf, West Germany

(Received 21 April 1987)

By means of the Mössbauer-effect spectroscopy and the nuclear magnetic resonance the influence of substitutional platinum on spin- and charge-density changes in a metallic iron is studied in order to further test the Miedema–van der Woude model which for a change of the charge-density caused by one Pt atom in a unit cell predicts a value of $\eta = -0.34(4)$. From linear correlations between the average hyperfine field $\bar{H}$ and the average isomer shift, as well as between $\bar{H}$ and the concentration of platinum, a value of $\eta = -0.21(1)$ is found. The influence of Pt atoms turns out to be extremely long ranged, as the impurities residing at least up to the thirteenth coordination shell must be included in order to properly describe the observed effects.

I. INTRODUCTION

It is well known that substitutional impurities induce changes in the electronic structure of metallic iron which can be successfully studied by means of the Mössbauer spectroscopy. Two hyperfine (hf) quantities are measurable by this technique: the hf field H proportional to the spin density of s-like electrons within the probe nucleus and the isomer shift I related to the charge density of those electrons. In a study of Fe-Cr alloys[1] one has, among other things, shown that the average hf field $\bar{H}$ was linearly correlated with the corresponding average isomer shift $\bar{I}$ as well as with the concentration of the impurity x. Using these two correlations it was possible to evaluate a change of a spin (charge) density at the ^{57}Fe nucleus due to one impurity atom per unit cell η. Such correlations turned out to also hold for other binary iron-based alloys[2] and they permitted to determine η for various impurities studied.

As mentioned above, with the Mössbauer spectroscopy one measures spin (charge) density changes only within the volume of a probe nucleus. In order to infer the related changes in the electronic structure of the lattice, which is of a primary interest, one has to know a relationship between them. This, however, remains still an theoretically unresolved problem, though the authors of a recent paper[3] have succeeded to theoretically explain the linear correlation between $\bar{H}$ and $\bar{I}$ in the line with the previous empirical interpretation,[2] i.e., only the density of s-like electrons from one subband is affected by the substitution (in this case spin and charge density are equivalent). A phenomenological model originally introduced by Miedema and van der Woude[4] permits for a binary alloy, in particular Fe-X, to calculate a model value of η (η_M) from a simple formula:

$$\eta_M = 0.5 \left[P'\Delta\phi^* + Q' \frac{\Delta n_{\mathrm{WS}}}{n_{\mathrm{WS}}^{\mathrm{Fe}}} \right] \tag{1}$$

where P' and Q' are constants characteristic of a given Mössbauer isotope, $\Delta\phi^* = \phi_X^* - \phi_{\mathrm{Fe}}^*$, ϕ^* being a chemical potential of a constituent and $\Delta n_{\mathrm{WS}} = n_{\mathrm{WS}}^X - n_{\mathrm{WS}}^{\mathrm{Fe}}$, n_{WS} being a density of electrons at the boundary of the Wiegner-Seitz cell, both quantities are to be taken for a pure state of the constituents. The model was successfully applied to explain η's for various binary alloys of iron.[5]

In order to further test the model, one should first of all consider extreme cases, i.e., for such X atoms which induce possibly large η. To this end we have recently studied Fe-P alloys.[6] The measured η was, however, three times smaller than the value expected from Eq. (1), $\eta_M = -0.40(5)$. It is not clear whether this discrepancy should be taken as an argument against the model, at least in its present two-parameter version, or the predicted η_M was not correctly evaluated because the value of ϕ_P^* has not yet been measured for phosphorus (instead a model value was used according to Ref. 7) and the value of n_{WS}^P can be also questioned as P is not a good metal. In view of the above, a further experimental test of the model seems to be justified.

As the next good candidate for such a test we have chosen platinum, which is a good transition metal, hence the conditions for the formula (1) to hold are fulfilled. Taking for ϕ_{Pt}^* and $n_{\mathrm{WS}}^{\mathrm{Pt}}$ the values after Ref. 7 and using Eq. (1) we arrive at $-0.38 \le \eta_M \le -0.30$, i.e., the expected change in the spin (charge) density is large. The present paper presents the results obtained for a series of $\mathrm{Fe}_{100-x}\mathrm{Pt}_x$ alloys with $x \le 10$.

II. EXPERIMENT

A. Sample preparation and analysis

$\mathrm{Fe}_{100-x}\mathrm{Pt}_x$ samples were prepared by melting in a vacuum furnace high purity Fe and Pt. The mass of each sample was 1 g and the melting process was repeated several times to assure a homogeneous distribution of impurities.

The actual concentration of platinum x was revealed by a microprobe analysis of the samples. Table I shows x values averaged over ten randomly chosen points for each sample. The error quoted is a standard deviation.

TABLE I. Results of the microprobe analysis of $Fe_{100-x}Pt_x$ samples.

Probe	1	2	3	4	5	6	7
x	0.15(8)	0.42(8)	1.19(9)	2.80(5)	4.9(2)	7.3(4)	10.3(8)

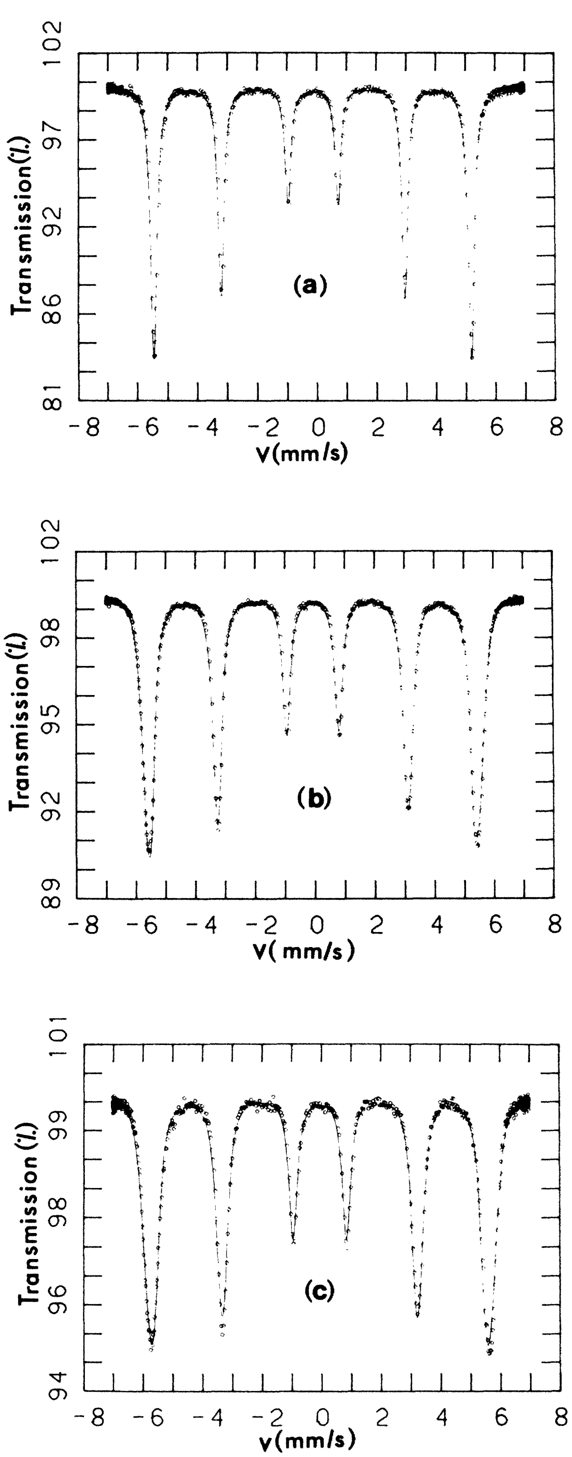

FIG. 1. Room temperature ^{57}Fe Mössbauer spectra of $Fe_{100-x}Pt$ alloys (a) $x = 0$, (b) $x = 4.9$, and (c) $x = 10.3$. The solid lines are for the corresponding fits as obtained with method I.

B. ME and NMR measurements

For both the Mössbauer-effect (ME) and the nuclear magnetic resonance (NMR) measurements samples in form of powder of an average particle size of 60 μm were used. ^{57}Fe Mössbauer spectra were recorded at room temperature using a standard setup with a 1024-channel analyzer and a sinusoidal drive. The calibration was done with a 12.5-μm-thick iron foil.

^{57}Fe NMR spectra of $Fe_{100-x}Pt_x$ with $x = 0.15$, 1.19, and 2.80 were determined by a Fourier transform of the real and imaginary parts of the echo shape as described elsewhere.[8] The domain-enhanced spin echoes were recorded at 4.2 K.

Figure 1 illustrates some examples of the recorded ME spectra. At a first glance, Pt hardly affects a spectrum of a pure iron; in fact, all spectra, irrespective of Pt concentration, are similar to each other and they consist of six spectral lines only. A closer inspection, however, permits one to reveal that the maximum splitting of the spectrum, hence H increases rather rapidly with x. Also its center, i.e., the isomer shift I does not stay constant but shifts with x. In order to quantitatively discuss the mentioned changes, the spectra were computer fitted with two independent methods. (i) method I, because of a lack of any structure within the spectral lines, each spectrum was fitted in terms of only one sextet. This permitted to determine the average values of $H, \bar{H}_{\mathrm{I}}$ and of $I, \bar{I}_{\mathrm{I}}$. (ii) method II yielded the hf field distribution curves from the measured spectra by means of a Fourier transform.[9] Some examples of them are shown in Fig. 2. As expected, each distribution curve can be described by a single peak only which shifts toward a larger H with growing x. Another effect is an increase of its width,

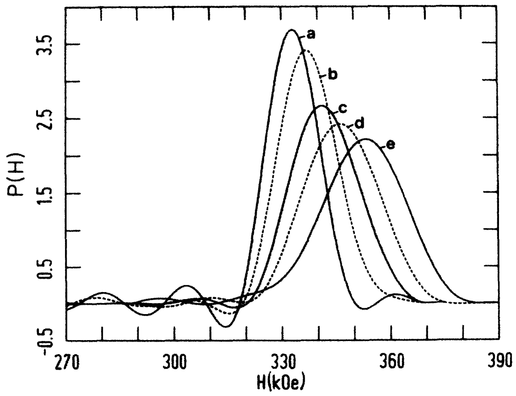

FIG. 2. Hyperfine field distribution curves $P(H)$ as obtained from the Mössbauer spectra of $Fe_{100-x}Pt_x$ samples (a) $x = 1.19$, (b) $x = 2.80$, (c) $x = 4.9$, (d) $x = 7.3$, and (e) $x = 10.3$.

TABLE II. The best fit hf parameters as obtained from ^{57}Fe Mössbauer spectra of $Fe_{100-x}Pt_x$ samples by means of method I (index I) and method II (index II), $\bar{H}$ is in kOe and $\bar{I}$ in mm/s.

x	$\bar{H}_{\text{I}}$	$\bar{I}_{\text{I}}$	$\bar{H}_{\text{II}}$	$\bar{I}_{\text{II}}$	$\Delta\bar{H}_{\text{II}}$
0	331.1	0.000	330.9	0.000	14.0
0.4	331.2	0.001	330.9	0.001	14.5
1.2	333.8	0.010	332.9	0.011	17.0
2.8	337.9	0.024	336.7	0.025	19.7
4.9	342.5	0.046	341.5	0.047	23.4
7.3	346.9	0.057	346.5	0.0575	26.0
10.3	351.1	0.084	352.9	0.0845	27.4

ΔH_{II}. Integration of the curves yielded the average values of $H, \bar{H}_{\text{II}}$. The average $I, \bar{I}_{\text{II}}$ could also be obtained from this procedure. Table II displays the values of the best fit hyperfine parameters as obtained by both methods. A good agreement between their corresponding values can readily be seen.

III. RESULTS AND THEIR DISCUSSION

A. Evaluation of η

In order to evaluate η one can use the following alternative equations:

$$\frac{d\bar{H}}{dM}=\alpha\eta \tag{2}$$

or

$$\bar{H}(x)=H^{\text{Fe}}+M(x)\alpha\eta \tag{3}$$

where M is a number of Pt atoms in a unit cell and α is the average hf coupling constant, $\alpha=d\bar{H}/dN_s$ (N_s is a number of polarized s-like electrons). If the ME spectra of Fe-X alloys show structure within their spectral lines (satellite lines) then they can be analyzed in terms of different subspectra associated with different atomic configurations and for such case $d\bar{H}/dM$ can be experimentally determined.[1] This is, however, not the case for Fe-Pt. Based on the microprobe analysis one can here assume that the distribution of Pt atoms is random, i.e., $M=0.02x$. In this case Eqs. (2) and (3) are equivalent.

The value of α can be evaluated from the linear correlation between $\bar{H}$ and $\bar{I}$ which, as shown in Fig. 3, holds for the presently investigated system, too. The best fit to the data is given by

$$\bar{H}=330.8+263.7\bar{I}\ . \tag{4}$$

A value of $\alpha=d\bar{H}/dN_s=(d\bar{H}/d\bar{I})/(d\bar{I}/dN_s)=527(15)$ kOe per s electron follows. ($d\bar{I}/dN_s\approx 2$ mm/s per s electron after Ref. 10 was used.) Combining next the linear correlation between $\bar{H}$ and x (see Fig. 4):

$$\bar{H}=330.9+2.175x \tag{5}$$

with Eq. (3) one arrives at $\eta=-0.21(1)$ (the negative sign follows from $\bar{I}>0$). This value agrees in sign with the model value but its magnitude is about 50% less. This disagreement is, however, much smaller than that for phosphorus, and as illustrated in Fig. 5, the new point rather nicely joins the up-to-date systematic in the (η,η_M) plane which with the exception of P and Sn can be described by $\eta\approx 0.8\eta_M$. A systematic 20% deviation between the measured and the model values of η can certainly be accounted for by a nonaccurate value of $d\bar{I}/dN_s$.

It also seems worth noting that although the average influence of Pt atoms on the charge density of iron is

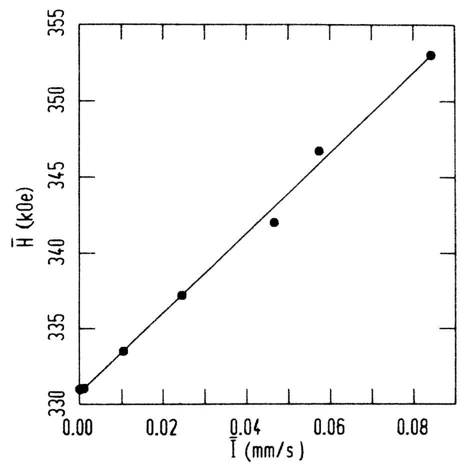

FIG. 3. Average hf field $\bar{H}$ as a function of the average isomer shift $\bar{I}$. The solid line stands for the best fit to the data.

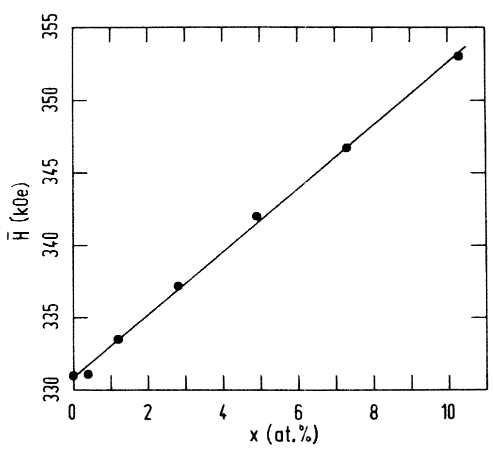

FIG. 4. Average hf field $\bar{H}$ vs Pt concentration x. The solid line is for the best fit to the data.

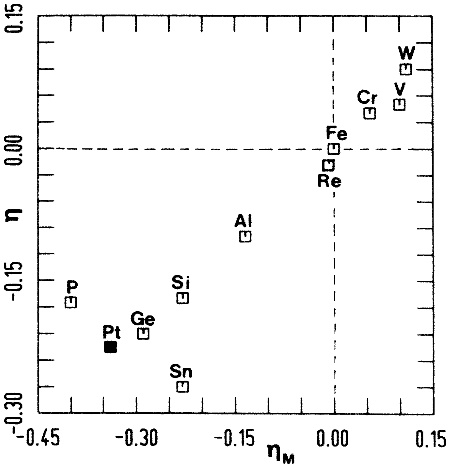

FIG. 5. Measured value of the ^{57}Fe-site charge-density η versus the corresponding Miedema-van der Woude model value η_M.

similar to that of Ge, these are the spin-up electrons which are responsible for the change in the former case, while the spin-down electrons cause the change in the latter (this follows from $\overline{H}-\overline{I}$ correlations for the both systems).

B. Shift of H and of I due to one Pt atom

Another problem which will be addressed in this paper is a magnitude of the ^{57}Fe hf field shift due to one Pt atom residing in the vicinity of the probe ^{57}Fe nuclei. If this disturbance is large enough, then the resulting ME spectra exhibit some structure mainly within the outermost lines and one is usually able to determine ΔH_1 and ΔH_2 from their computer analysis, i.e., the shift of H due to one impurity atom in the first (index 1) and in the second (index 2) neighbor shell. The authors of Ref. 11 reported for $Fe_{97}Pt_3$ $\Delta H_1 = 15.0$ kOe and $\Delta H_2 = 11.3$ kOe from their ME measurements. Attempts to fit the present ME spectra with those values failed. Therefore, NMR method as having a better resolution has been used. The resulting NMR spectra are presented in Fig. 6(a) through 6(c). The spectra recorded for $x = 0.15$ and 1.19 show a structure of three peaks whose positions f and statistical weights P have been computer determined with the values as given in Table III.

In order to answer the posed question, one has to identify the observed peaks with atomic configurations. There is no doubt as far as the main (0) peak is concerned. It can certainly be ascribed to ^{57}Fe nuclei of unperturbed atomic configuration (no Pt atoms within a certain vicinity). Its statistical weight of 0.63 for the less and 0.28 for the more concentrated sample can be understood in case of a random distribution of Pt atoms if more than 13 neighbor shells for the former and 8 for the latter are taken into account—see Fig. 7. This indicates a long-range or itinerant character of the influence of Pt on the electronic structure of iron (the change concerns mainly the conduction electrons).

TABLE III. Positions f and the statistical weights P of the peaks in the NMR spectra of $Fe_{100-x}Pt_x$ samples.

	$x = 0.15$		$x = 1.19$	
Peak no.	f (MHz)	P	f (MHz)	P
0	46.644	0.63	46.589	0.28
1	47.044	0.14	46.948	0.29
2	47.886	0.23	47.927	0.43

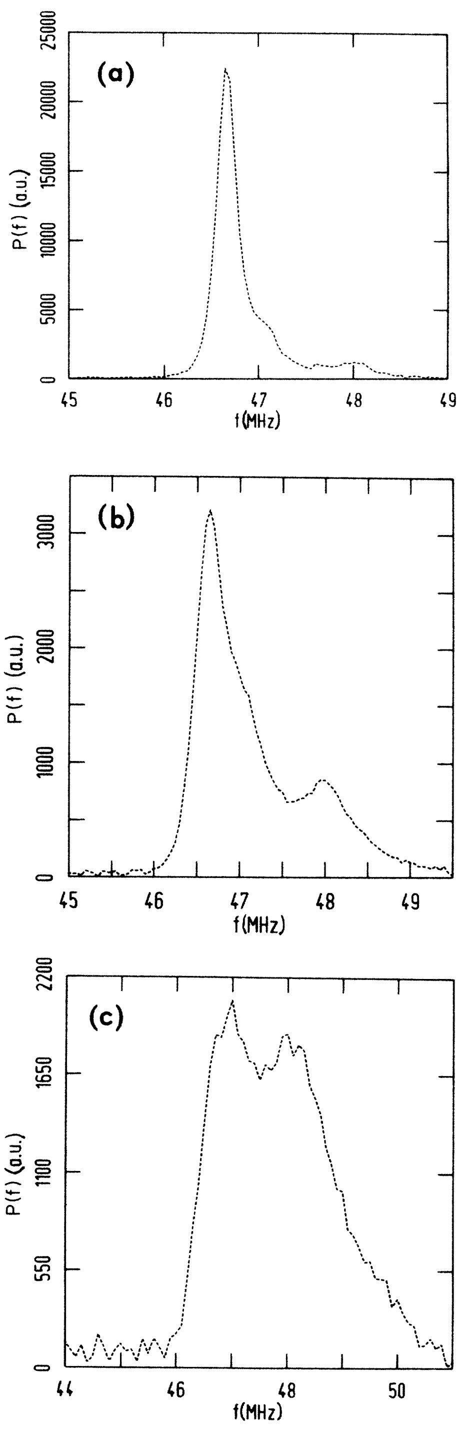

FIG. 6. 4.2-K ^{57}Fe NMR spectra of $Fe_{100-x}Pt_x$ samples for (a) $x = 0.15$, (b) $x = 1.19$, and (c) $x = 2.80$.

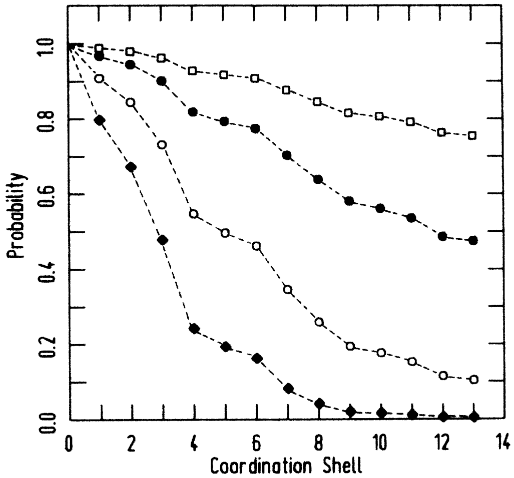

FIG. 7. Probabilities of an unperturbated atomic configuration (only Fe atoms) for an $Fe_{100-x}A_x$ alloy with a random distribution of atoms A vs the coordination shell number for different impurity concentration x: $x=0.15$ (□), $x=0.42$ (●), $x=1.19$ (○), and $x=2.80$ (◆).

Concerning now the peaks 1 and 2 one has to note that $P(2)\geq P(1)$ for both samples. Assuming further a random distribution, one would have to ascribe peak 2 to ^{57}Fe nuclei having one Pt atom within a volume of at least 13 shells and peak 1 to ^{57}Fe nuclei having two or more Pt atoms within this volume. Such interpretation seems, however, not to be correct because: (i) the influence of two or more Pt atoms on H would have to be smaller than that of a single Pt atom, and (ii) the linewidth of peak 1 Γ_1 should be larger than that of peak 2 Γ_2 which is not the case here (for $x=0.15$, $\Gamma_1=3.0$ kOe and $\Gamma_2=7.4$ kOe; and for $x=1.19$, $\Gamma_1=4.7$ kOe and $\Gamma_2=9.4$ kOe). It seems, therefore, more reasonable to treat peak 1 as due to ^{57}Fe nuclei having one Pt atom in their vicinity and peak 2 as due to those having two or more Pt atoms in their vicinity. Such interpretation permits to explain both the positions of the two satellite peaks as well as their widths. In the line with such interpretation, it follows then that $\Delta H_1=2.6-2.9$ kOe. Such a small value proves that the localized changes in the electronic structure of iron due to substitutional Pt have a residual meaning and the itinerant changes are dominant. Larger statistical weights of peak 2 would indicate a tendency for Pt atoms to cluster.

Concerning the NMR spectrum for $x=2.8$, one can see that the main peak has almost disappeared while peaks 1 and 2 have nearly the same intensity. The disappearance of peak 0 supports the interpretation of the intensities of the peaks for $x=0.15$ and 1.19 in terms of a long-range interaction. It can be, namely, readily seen from Fig. 7 that for this concentration, i.e., $x=2.8$ its expected intensity must be of the order of 0.05 if at least 8 neighbor shells are to be taken into account. The above interpretation based on the NMR spectra can be further supported by the following analysis of the Mössbauer spectrum of $Fe_{99}Pt_1$ sample which was successfully fitted in terms of two subspectra with the following best fit parameters: $H=330.2$ kOe, $I=-0.1017$ mm/s, $P=0.60(5)$ for subspectrum 1; subspectrum 2: $H=338.9$ kOe, $I=-0.0909$ mm/s, $P=0.40(4)$. Subspectrum 1 can be identified with ^{57}Fe nuclei having no or one Pt atom in their vicinity (the resolution of ME does not permit the resolution of the two configurations because of a small value of ΔH_1). Its statistical weight of 0.60(5) agrees well with $P(0)+P(1)=0.57$ as determined for this sample from its NMR spectrum. Subspectrum 2 corresponds then to ^{57}Fe nuclei having two or more Pt atoms in their neighborhood. Its statistical weight of 0.40 is in accord with $P(2)=0.43$ as determined by the NMR method.

In the light with this interpretation and assuming that the effect of Pt atoms on H and I is additive, one is further able to estimate the influence of one Pt atom on the isomer shift. To this end one considers the difference in I between subspectrum 1 and 2 $\Delta I=0.0108$ mm/s. The corresponding difference in H, $\Delta H=9$ kOe, i.e., $\Delta H\approx 3\Delta H_1$. If one sets now $\Delta I=3\Delta I_1$ than $\Delta I_1\approx 0.0035$ mm/s follows.

IV. CONCLUSIONS

The following conclusions can be drawn from the present investigation:

(1) The substitution of Fe atoms of metallic iron by Pt atoms results in a charge flow from Fe atoms.

(2) One Pt atom per unit cell "removes" 0.21 spin-up s-like electrons from an Fe atom as compared to 0.34(4) expected from Miedema-van der Woude model.

(3) The observed changes have itinerant character (conduction electrons are involved in the transfer), and Pt atoms residing at least up to 13 neighbor shell must be taken into account.

(4) The influence of one Pt atom residing within this 13-shell volume on the ^{57}Fe hf field is $\Delta H_1=2.6-2.9$ kOe and on the isomer shift $\Delta I_1=0.0035$ mm/s.

ACKNOWLEDGMENTS

I am grateful to Ing. R. Staegemann for making the samples, to Frl. H. Falkenberg for their microprobe analysis, to Dr. H. Lütgemeier for recording the NMR spectra and the illuminative discussion of the results and to Professor G. Inden for a support of the experiment.

---

[*] Present address: Department of Solid State Physics, Institute of Metallurgy, Academy of Mining and Metallurgy, PL-30059 Krakow, Poland.

[1] S. M. Dubiel and J. Zukrowski, J. Magn. Magn. Mater. **23**, 214 (1981).

[2] S. M. Dubiel and W. Zinn, J. Magn. Magn. Mater. **45**, 298 (1984).

[3] M. E. Elzain, D. E. Ellis, and D. Guenzburger, Phys. Rev. B

34, 1430 (1986).

[4] A. R. Miedema and F. van der Woude, Physica (Utrecht) B **100**, 145 (1980).

[5] S. M. Dubiel and W. Zinn, Phys. Rev. B **28**, 67 (1983); **29**, 2279 (1984).

[6] S. M. Dubiel, Phys. Lett. A **120**, 151 (1987).

[7] A. K. Niessen and F. R. de Boer, J. Less-Common Met. **82**, 75 (1981).

[8] H. G. Bohn, R. R. Arons, and H. Lütgemeier, Physica (Utrecht) B **80**, 6 (1975).

[9] B. Window, J. Phys. E **4**, 401 (1971).

[10] L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Lett. **6**, 98 (1961).

[11] I. Vincze and I. A. Campbell, J. Phys. F **3**, 647 (1973).