

Influence of vanadium on the ^{57}Fe -site spin and charge densities in cobalt-vanadium alloys

S. M. Dubiel*

Max-Planck-Institut für Eisenforschung GmbH, Max Planck Strasse 1, D-4000 Düsseldorf, West Germany

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The influence of substitutional vanadium on spin and charge densities has been studied for a series of hcp $\text{Co}_{100-x}\text{V}_x$ alloys with $x \leq 12.5$, using ^{57}Fe -site Mössbauer spectroscopy. It has been shown that one V atom residing in the first-neighbor shell reduces the ^{57}Fe -site hyperfine field by $\Delta H_1 = 38.4$ kOe and the isomer shift by $\Delta I_1 = 0.020$ mm/s which means an increase of the charge density by $\Delta N_1^s = 0.01$ s electrons. The influence of one V atom as a second-nearest neighbor is similar in sign but three times smaller in magnitude. The maximum change of the charge density (i.e., that due to three V atoms per unit cell) which can be evaluated from the correlation between the average hyperfine field and the average isomer shift amounts to $\eta = 0.03$ – 0.05 s electrons. The results are compared with those obtained for the bcc Fe-V system.

I. INTRODUCTION

Substitution of Fe atoms by V atoms results in a change of both spin and charge density which can be conveniently studied by Mössbauer spectroscopy.¹ In particular, Fe nuclei having one V atom in their nearest-neighbor shell (NN) experience a hyperfine (HF) field reduced by $\Delta H_1 = 30$ kOe, while for those having such an atom in the next-nearest-neighbor shell (NNN) the reduction is $\Delta H_2 = 20$ kOe compared with the field at Fe nuclei residing in an undisturbed atomic configuration. Corresponding changes in the isomer shift, namely $\Delta I_1 = -0.0195$ mm/s and $\Delta I_2 = -0.0115$ mm/s, respectively, indicate an increase of the charge density. Assuming that only electrons from one subband are subject to the change, one could estimate the disturbance produced by one V atom in the NN shell to be equal to $\Delta N_1^s = 0.010$ spin-up s -like electrons, while that due to one V atom in the NNN shell corresponds to $\Delta N_1^s = 0.006$ electrons of the same kind.

It was further shown that the average HF field \bar{H} was linearly correlated with the average isomer shift \bar{I} and also with the average number of V atoms within the NN-NNN volume N . These two correlations enabled the increase of the charge density at the Fe site due to one V atom in unit cell $\eta = 0.05$ s electrons to be determined. It seems interesting to carry out a similar investigation for a system with a different crystallographic structure in order to see the role of the latter. For that purpose a $\text{Co}_{100-x}\text{V}_x$ system doped with 1 at. % ^{57}Fe was chosen. It has an hcp structure, which also, because of its parameters, can be regarded as the fcc structure,² to a good approximation. On the other hand, it must be realized that in the present case it is not only the crystallographic structure but also the host matrix (cobalt instead of iron) which distinguishes it from the previous experiment.¹ Consequently, an interpretation of possible differences would not be justified only in terms of the crystallographic nature.

Nevertheless, the experiment seems to be worth doing, all the more so since an interesting phenomenon may

additionally be expected. Namely, for Fe in the Co matrix a charge flow from Fe to Co is expected from the Miedema-van der Woude model³ (positive isomer shift relative to that of metallic iron) while a charge flow from V to Fe is expected from the same model for the Fe-V system (negative relative value of I). Consequently, for $(\text{Co}_{100-x}\text{V}_x)_{99}\text{Fe}$, one expects the isomer shift to change its sign from positive for $x = 0$ to negative for a certain value of x .

Motivated by the above-mentioned aim, Mössbauer-effect measurements were carried out on a series of $\text{Co}_{100-x}\text{V}_x$ alloys with $x \leq 12.5$. The results obtained are presented and discussed in this paper.

II. EXPERIMENT

A. Sample preparation

$\text{Co}_{100-x}\text{V}_x$ samples with $0 \leq x \leq 12.5$ and containing approximately 1 at. % ^{57}Fe isotope were prepared by melting appropriate amounts of cobalt (99.9% pure), vanadium (99.9% pure), and iron (99% pure) enriched to approximately 95% in the ^{57}Fe isotope, in an arc furnace under an argon atmosphere. The ingots so obtained were subject to a homogenizing treatment at 1100°C for 24 h followed by water quenching. The actual composition of each sample was obtained by chemical analysis.

B. Mössbauer-effect measurements

For the Mössbauer-effect measurements approximately 50 mg of an alloy per cm^2 was used in form of a powder. The spectra were recorded at room temperature in transmission geometry using a standard setup with a 1024-channel analyzer. The γ rays were emitted by a $^{57}\text{Co}:\text{Rh}$ source and calibration of the drive, moving in a sinusoidal mode, was done with a 12.5 μm thick iron foil.

C. Analysis of the spectra

The spectra, of which several examples are shown in Figs. 1(a)–1(e), were computer fitted by means of two in-

dependent methods: (a) superposition method, hereafter referred to as method I, and (b) hyperfine field distribution method,⁴ hereafter referred to as method II. Concerning method I, each spectrum was treated as consisting of a number of six-line Lorentzian-shaped subspectra having characteristic HF fields $H(m,n)$, isomer shifts $I(m,n)$, and statistical weights $P(m,n)$ where m and n are the number of V atoms in the NN shell and in the NNN shell, respectively. Each such subspectrum was then ascribed to a particular atomic configuration (m,n) . The number and kind of configurations, which were finally considered for a given alloy composition, were calculated from a binomial distribution of V atoms in the fcc Co lattice.

(The filing treatment transformed the samples into a purely hexagonal structure. Its lattice parameters, however, are such² that it can be treated as a fcc lattice, i.e., with maximum $m=12$ and maximum $n=6$ for the present considerations. Additional measurements on the $\text{Co}_{99}\text{Fe}_1$ sample which, through a proper heat treatment, were transformed to a significant proportion into the fcc phase, proved that the HF parameters, viz. H and I were for this sample identical with those found for the purely hexagonal sample). Only those subspectra with $P(m,n) \geq 0.01$ were considered as measurable, i.e., they were included into the fitting procedure. It was further assumed in the procedure that the influence of V atoms on H and I is additive, i.e., the following formulas hold:

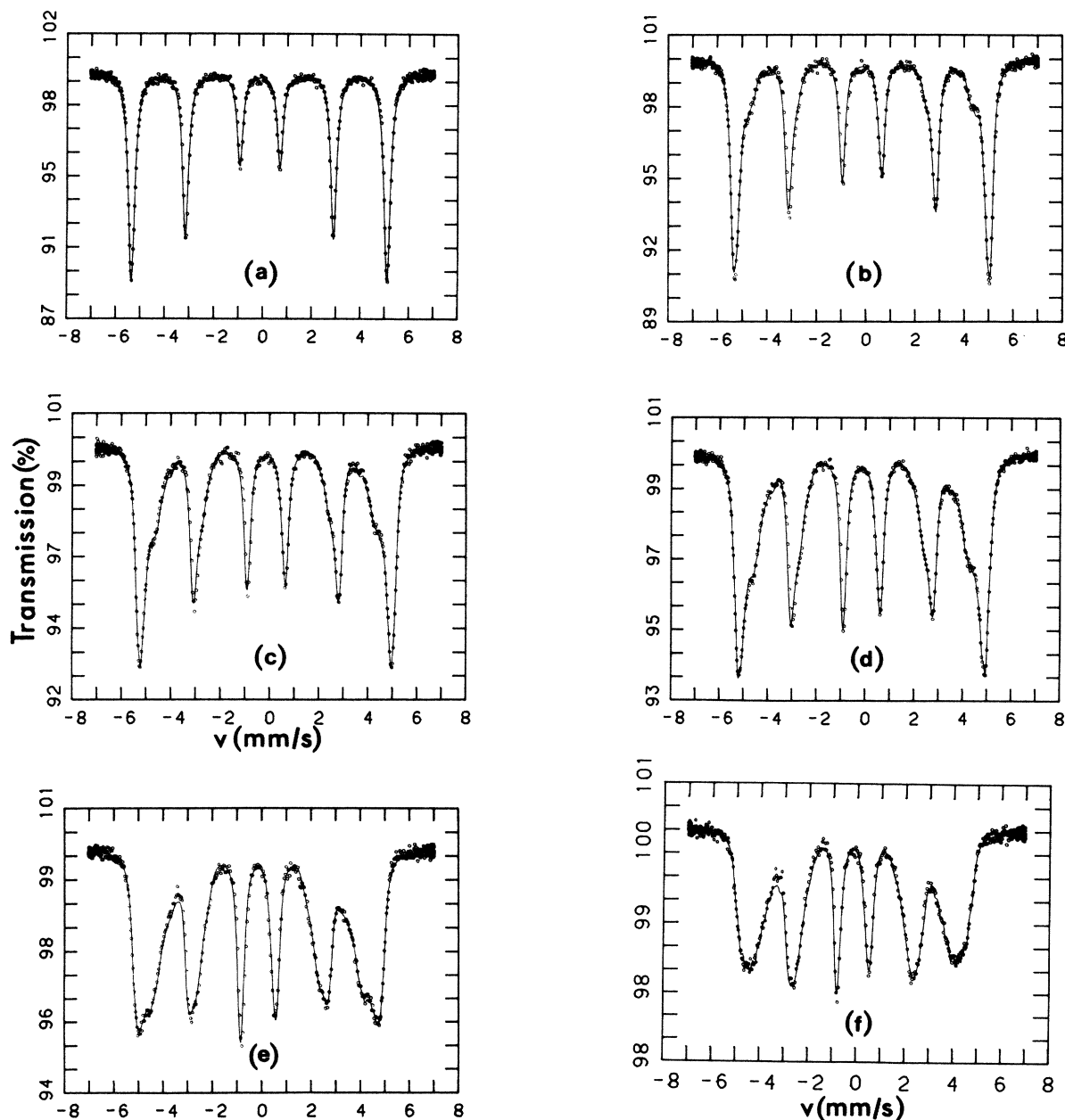


FIG. 1. Room-temperature ^{57}Fe Mössbauer spectra of $\text{Co}_{100-x}\text{V}_x$ alloys for (a) $x=0$, (b) $x=1.9$, (c) $x=3.6$, (d) $x=4.9$, (e) $x=7.5$, and (f) $x=10.0$. The solid lines represent the best-fit spectra.

$$H(m,n) = H(0,0) + m\Delta H_1 + n\Delta H_2, \quad (1a)$$

$$I(m,n) = I(0,0) + m\Delta I_1 + n\Delta I_2, \quad (1b)$$

where $\Delta H_1 = H(1,0) - H(0,0)$ and $\Delta H_2 = H(0,1) - H(0,0)$. ΔI_1 and ΔI_2 have a similar meaning.

It was possible by the alternative fitting procedure, i.e., method II, to obtain, from the measured spectra, the HF field distribution curves $p(H)$. The average HF field \bar{H}_{II} can be determined from them:

$$\bar{H}_{II} = \int_{H_1}^{H_2} H p(H) dH, \quad (2)$$

where H_1 and H_2 are the lower and the upper value of the H range, respectively, within which $p(H) \geq 0$.

The advantage of method II is that, contrary to method I, it is model independent. It cannot, however, supply as detailed information as method I. Therefore, method II will be treated here only as a check for the results obtained with method I.

III. RESULTS AND DISCUSSION

Hyperfine parameters, as obtained by means of both methods, are displayed in Table I. Here \bar{H}_I and \bar{I}_I stand for the average H and I calculated from the following formula:

$$\bar{X}_I = \sum_{m,n} X(m,n)P(m,n) / \sum_{m,n} P(m,n), \quad (3)$$

where $X = H$ or I , respectively. N is the average number of V atoms within the NN-NNN neighborhood which was also calculated from Eq. (3) putting $X(m,n) = m + n$.

A. Shift of H and of I due to one V atom in the NN shell or in the NNN shell

It follows from Table I that H is reduced on average by $\Delta H_1 = 38.4$ kOe if one V atom resides in the NN shell, and by $\Delta H_2 = 11.6$ kOe if such atom is in the NNN shell. Corresponding figures for Fe-V are 30 and 20 kOe, respectively.¹ Thus one can see that $\Delta H_1(\text{bcc}) \approx \Delta H_1(\text{hcp})$, while $\Delta H_2(\text{bcc}) \approx 2\Delta H_2(\text{hcp})$. Similar relationships are valid for the changes in the isomer shift.

One can further express the observed changes in H and N in terms of a related number of s -like electrons. To this

end one has to evaluate the corresponding HF coupling constants. For the NN shell,

$$\alpha_1 = \Delta H_1 / \Delta N_1^s = (\Delta H_1 / \Delta I_1) / (\Delta I_1 / \Delta N_1^s) \approx 3840 \text{ kOe}$$

per s electron, ($\Delta I_1 / \Delta N_1^s \approx 2$ mm/s per s electron was used after Ref. 5). This figure is close to $\alpha_1 = 3240$ kOe found for the Fe-V system.¹ Knowing α_1 one arrives at $\Delta N_1^s = 0.01$ s electrons which agrees perfectly with the corresponding figure found for Fe-V.¹ Concerning ΔN_2^s , one is not able to directly determine α_2 because of the small values of ΔI_2 . Instead, based on the results obtained for the Fe-V system, one can assume that here also $\alpha_1 \approx \alpha_2$. In such a case one arrives at $\Delta N_2^s = 0.003$ against 0.006 for Fe-V. From these two figures one would be tempted to conclude that the disturbance of the Fe-site spin or charge density by neighboring V atoms is, to a first approximation, similar for both the hcp Co-V system and the bcc Fe-V system. One has to realize, however, that because of the different crystallographic structure the distance between the probe Fe nuclei and the neighboring V atoms is different also for the two systems. Namely, for the former the NN distance $d_1 = 1.773$ Å and the NNN distance $d_2 = 2.508$ Å, while the corresponding figures for the latter are $d_1 = 2.482$ Å and $d_2 = 2.866$ Å. (Lattice parameters $a = 2.866$ Å for pure iron and $a = 2.508$ Å for pure cobalt were taken and their dependence on V content was neglected). It would be more reasonable to compare the disturbance in the spin or charge density due to one V atom situated at the same distance in both systems, in order to infer the role of the structure and the matrix. In other words, $\Delta N_1^s(\text{bcc})$ should be compared with $\Delta N_2^s(\text{hcp})$. One can here readily see that $\Delta N_1^s(\text{bcc}) \approx 3\Delta N_2^s(\text{hcp})$, i.e., the influence of V atoms on the electronic structure is in fact different for the two systems.

B. Average charges

1. \bar{H} versus x

Figure 2 illustrates \bar{H} versus the vanadium content x . For comparison, the corresponding behavior for the Fe-V system as found previously¹ is also indicated by a dashed line ($d\bar{H}/dx = -2.9$). One can readily note that for the

TABLE I. Best-fit spectral parameters as obtained for the $\text{Co}_{100-x}\text{V}_x$ alloys (H in kOe and I in mm/s) by means of method I (index I) and by method II (index II). For details see the text. Typical errors: ± 1 kOe for $H(0,0)$ and $\Delta H_{1,2}$; ± 0.002 mm/s for $I(0,0)$ and $\Delta I_{1,2}$; $\pm 10\%$ for the average quantities.

x	$H(0,0)$	ΔH_1	ΔH_2	\bar{H}_I	\bar{H}_{II}	$I^a(0,0)$	ΔI_1	ΔI_2	\bar{I}_I	N
0	321.9			321.9		0.011			0.011	
1.1	321.0	-38.8	-12.0	316.3		0.008	-0.018	0.013	0.0095	0.23
1.9	319.9	-38.8	-11.6	310.0		0.007	-0.019	0.014	0.009	0.60
3.6	317.9	-37.2	-11.3	300.3		0.005	-0.023	0.007	0.0055	0.81
4.9	316.5	-37.2	-11.3	292.9		0.006	-0.019	0.005	0.002	1.15
7.5	310.8	-37.6	-11.2	273.4	274.3	0.015	-0.019	0.001	-0.002	1.72
8.5	308.3	-38.4	-12.0	264.6	265.2	0.014	-0.021	-0.001	-0.003	1.86
10.0	303.7	-39.0	-13.0	254.7	255.2	0.025	-0.026	-0.007	-0.0055	2.31
12.5	295.3	-38.4	-12.2	229.0	229.5	0.024	-0.021	-0.005	-0.011	2.63

^aRelative to metallic Fe.

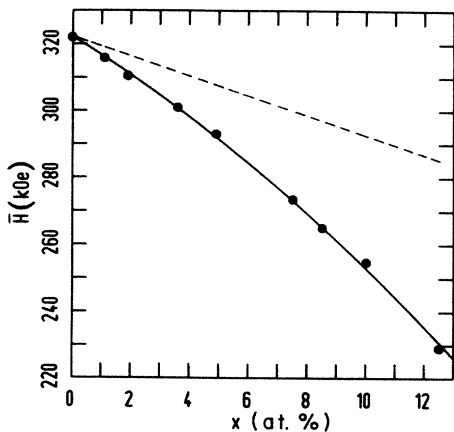


FIG. 2. Average HF field, \bar{H} vs x for $\text{Co}_{100-x}\text{V}_x$ alloys. The solid line is the best fit to the data while the dashed line shows the corresponding behavior found for $\text{Fe}_{100-x}\text{V}_x$ (Ref. 1).

presently studied system the behavior is nonlinear ($\bar{H} = 322.2 - 25.4x - 0.15x^2$) and that \bar{H} drops now much faster with x than it does for Fe-V.

2. \bar{H} versus N

\bar{H} turns out to be also correlated with the average number of V atoms in the NN-NNN vicinity of the probe Fe nuclei N (see Fig. 3). However, unlike the Fe-V system, the \bar{H} - N correlation is here nonlinear and the best fit to the data is $\bar{H} = 322.0 - 21.6N - 3.8N^2$. It is worth noting that the linear term is almost the same as that found previously for the Fe-V system, viz. $d\bar{H}/dN = -21$. In order to compare adequately the influence of V atoms on \bar{H} for both systems, one has to again take account of their different crystallographic structures. One

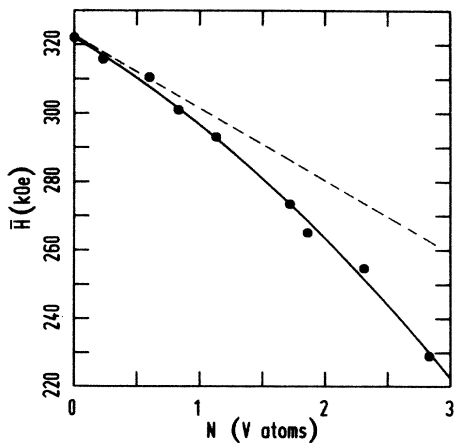


FIG. 3. Average HF field, \bar{H} as a function of the average number of V atoms within the first two neighbor shells, N for $\text{Co}_{100-x}\text{V}_x$ alloys. The solid line gives the best fit to the data and the dashed line represents the behavior found for $\text{Fe}_{100-x}\text{V}_x$ (Ref. 1).

can, for instance, evaluate a change of \bar{H} due to one V atom in unit cell, $d\bar{H}/dM$. For Fe-V one had $d\bar{H}/dM = -147$ kOe while for Co-V the corresponding figure is only -97 kOe. This proves that the effectiveness of V atoms is substantially different in both systems.

3. Correlation between \bar{H} and \bar{I}

A linear correlation between \bar{H} and \bar{I} was a typical relationship which was found to hold for binary Fe-based alloys⁶ including Fe-V.¹ Figure 4 supplies evidence that this is the case also for the Co-V system. Here, however, the \bar{H} - \bar{I} relationship can be described in terms of two linear branches:

$$(1) \text{ for } \bar{I} \geq 0, \quad \bar{H} = 286.6 + 3013\bar{I},$$

$$(2) \text{ for } \bar{I} \leq 0, \quad \bar{H} = 282.4 + 4987\bar{I}.$$

Branch 1, which includes the experimental points with $x \leq 4.9$, describes the samples for which the Fe-site charge density is smaller than that characteristic of a pure metallic iron. Branch 2, on the other hand, includes the data for $x \geq 7.5$ characterizing the samples in which the Fe-site charge density is larger than that in pure iron. It is obvious from the plot that the compensation composition, x_c , i.e., the composition for which the Fe-site charge density is equal to that of pure iron, lies between 4.9 and 7.5 at. %. Its exact value can be determined from both branches. Branch 1 gives $\bar{H} = 286.6$ for $\bar{I} = 0$. From the \bar{H} - x relationship (see Fig. 2) it follows that this value of \bar{H} occurs at $x_c = 5.7$. In a similar way one arrives at $x_c = 6.3$ using branch 2. The two figures are reasonably consistent. Using the \bar{H} - \bar{I} correlation one is further able to evaluate the maximum deficit (at $x = 0$) and the maximum excess (at $x = 12.5$) of the charge density at Fe nuclei. For the former one has first to determine the HF coupling constant $\alpha(1) = d\bar{H}/dN^s = (d\bar{H}/d\bar{I})/(d\bar{I}/dN^s) = 6026$ kOe per s electron ($d\bar{I}/dN^s = 2$ mm/s per s electron was used). The maximum charge-density deficit can now be obtained by dividing the difference in \bar{H} between its value for $x = 0$ and for $\bar{I} = 0$ by $\alpha(1)$. Doing so one arrives at the value -0.007 s -like electrons. In a similar way one estimates

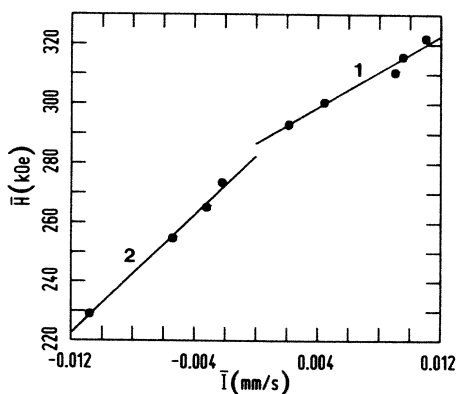


FIG. 4. Average HF field, \bar{H} vs the average isomer shift, \bar{I} for $\text{Co}_{100-x}\text{V}_x$ alloys. The straight lines 1 and 2 represent the best fit to the data for $\bar{I} \geq 0$ and $\bar{I} \leq 0$, respectively.

the HF coupling constant for branch 2, $\alpha(2)=9974$ kOe per s electron, and finally the charge-density deficit to be equal to 0.005 s -like electrons. As \bar{H} is negative, its systematic decrease with x can be explained in terms of an increase of the density of spin-up electrons in light of the \bar{H} - \bar{I} correlation.

The observed behavior of \bar{I} , and in particular the change in sign at $x_c=5.7-6.3$, gives at least qualitative evidence in favor of the Miedema-van der Woude model. Therefore, it seems interesting to estimate the model value of the compensation concentration, x_c^M . To this end the Co-V-Fe system will be treated as consisting of three binary subsystems: Fe-V, Fe-Co, and Co-V. For each such subsystem one next estimates the model value of a maximum change of the charge density at Fe site (at Co in Co-V) due to impurities η_M :

$$\eta_M = 0.5P'\Delta\phi^* - Q'\Delta n_{WS}/n_{WS}^{\text{Fe}}, \quad (4)$$

with $\Delta\phi^* = \phi_x^* - \phi_{\text{Fe}}^*$, ϕ^* being the chemical potential of the constituent and $\Delta n_{WS} = n_{WS}^x - n_{WS}^{\text{Fe}}$ and n_{WS} being the density of electrons at the boundary of the Wigner-Seitz atomic cell. Using for P' and Q' the same values as those derived for binary Fe-based alloys⁷ (the constants P' and Q' turn out to be characteristic of a given Mössbauer isotope⁸ and they seem not to depend much on the crystallographic state of the system^{6,9}) one arrives at (a) $\eta_M = 0.105$ for Fe-V which means a charge flow from V to Fe, (b) $\eta_M = -0.10$ for Fe-Co which means a charge flow from Fe to Co, and (c) $\eta_M = 0.195$ for Co-V which means a charge flow from V to Co. The last figure may be distorted as P' and Q' constants for Co may have different values from those for Fe used in the estimation.

The evaluation of x_c^M can now proceed in two ways: (i) one calculates the amount of V which must be added into $\text{Co}_{99}\text{Fe}_1$ in order to compensate for the charge deficit of 0.007 electrons, or (ii) one calculates the amount of V which must be removed from the alloy already containing 12.5 at. % V in order to compensate for the charge excess of 0.005 electrons. For the first method one can write $0.007 = x_c^M(0.105/50)0.35$ which yields $x_c^M = 9.5$ ($0.105/50$ is a charge flow to Fe due to 1% V and the factor of 0.35 originates from the fact that in Co-V-Fe only 35% of the charge flows from V to Fe, while the rest flows to Co). Similarly, one arrives at $x_c^M = 5.7$ based on the second method of evaluation. One sees, therefore, that the expected value of x_c^M , $x_c^M = 6.7-9.5$ agrees rather well with the experimentally estimated value of 5.7-6.3.

Finally, it is of interest to evaluate the maximum change of the Fe-site charge density in the studied system experimentally in order to compare it with the corresponding figure of $\eta = 0.05$ found previously for the Fe-V system. The value of η can be determined from the following relationship:

$$3 d\bar{H}/dM = \alpha\eta. \quad (5)$$

(Maximum change in the charge density occurs when the probe Fe nucleus is surrounded only by V atoms which

corresponds to the concentration of vanadium $x = 75$, or 3 V atoms per unit cell). Based on Eq. (5) and using for α its value estimated from branch 1, i.e., $\alpha(1)$, one arrives at $\eta = 0.05$ or at $\eta = 0.03$ if $\alpha = \alpha(2)$. Though the figure of 0.03-0.05 is close to the value of 0.05 found for the maximum charge-density change in the bcc Fe-V system, one must remember that 75% V was needed in Co-V to produce it, while only 50% was enough in Fe-V. In other words, the effectiveness of V atoms as far as the Fe-site charge density is concerned is, in the bcc Fe-V system, twice as large as in the hcp Co-V system. (This can also be seen if one calculates η for Co with 50% V, viz. $\eta = 0.02-0.03$. This figure is only 50% of that found for Fe with 50% V). This weakened effectiveness of V atoms as observed in Co-V can be, at least qualitatively, understood in terms of the Miedema-van der Woude model which predicts that twice as much charge flows from V to Co than from V to Fe ($\eta_M^{\text{Co-V}} = 2\eta_M^{\text{Fe-V}}$). Factor 2 could even suggest that the charge flow from V to Co and from V to Fe in a ternary system Co-V-Fe can in fact be described in terms of a charge flow in two subsystems, viz. Co-V and Fe-V.

IV. CONCLUSIONS

The results obtained in the present investigation permit the following conclusions to be drawn.

(1) Substitutional V in $\text{Co}_{100-x}\text{V}_x$ alloys changes the Fe-site electronic structure in the following way. (a) V atoms residing in the first-neighbor shell reduce the Fe-site HF field by $\Delta H_1 = 38.4$ kOe and the isomer shift by $\Delta I_1 = 0.02$ mm/s, i.e., they increase the corresponding charge density by $\Delta N_1^s = 0.01$ spin-up s -like electrons. (b) V atoms residing in the second-neighbor shell have an influence similar in sign but three times smaller in magnitude on the charge density ($\Delta N_2^s = 0.003$).

(2) The values of $\Delta N_{1,2}^s$ are similar in sign and magnitude to those found for the Fe-V system. They are, however, due to V atoms situated at different distances from the probe nuclei, i.e., the radial disturbance in the charge densities is different for the two systems.

(3) With increasing V content, x Fe nuclei experience a change in the charge density from a negative (charge deficit of 0.007 electrons) at $x = 0$ to a positive (charge excess of 0.005 electrons) at $x = 12.5$ with a compensation at $x_c = 5.7-6.3$.

(4) The effectiveness of V atoms as far as the Fe-site charge density is concerned, is in the Co-V system two times smaller than in the Fe-V system which can be qualitatively understood in terms of the Miedema-van der Woude model.

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*Present address: Department of Solid State Physics, Academy of Mining and Metallurgy, Al. Mickiewicza 30, PL-30-059 Krakow, Poland.

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