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EXPERIMENTAL VERIFICATION OF THE MODELS DESCRIBING THE HYPERFINE MAGNETIC FIELDS IN Fe-Cr*

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In the first part of this study, four different ways of experimentally verifying two previously outlined models, describing the hyperfine fields at Fe sites in homogeneous Fe-Cr alloys, are suggested. They involve an investigation, using the Mössbauer effect, of the following quantities: 1)the field at Fe nuclei with no Cr atoms within the first two coordination spheres, $H(00)$, 2) the shape of the Mössbauer spectrum, 3) the critical concentration, at which the alloy loses its ferromagnetic character, and 4) the shape of the field distribution. In the second part, the proposed criteria are compared with the experimental results, obtained for two Fe-Cr samples containing 26.3 and 45.5 at% of chromium. The predictions based on model II are in a good agreement with the experimental results.

1. *Introduction*

The origin of the hyperfine magnetic field at Fe nuclei has not yet been finally revealed, despite numerous attempts on this problem, both by theorists and experimentalists. It is hoped, however, that further experimental evidence will help to make another step towards a better understanding of this phenomenon and will supply the theorists with a better starting point for their calculations.

This paper presents the results of our further study of Fe-Cr alloys. In a previous publication (Dubiel 1976) the hyperfine magnetic fields have been measured at ^{57}Fe nuclei in the configurations (00), (10) and (01) in a range of Cr concentration in Fe-Cr alloys. The alloys contained 1–15 at% of chromium. The results were interpreted as reflecting the dual i.e. localized-itinerant character of ferromagnetism in metallic iron. A change of the field versus Cr content, for the studied configurations, had been ascribed to a change in the conduction electron polarization (CEP), i.e. the experimental results were fitted with the following formula:

$$H_{\mathrm{CEP}}(c) = A\Delta\sigma(c), \tag{1a}$$

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where A is a constant, while $\Delta\sigma(c)$ stands for a change in CEP relative to iron. It was also assumed that $\Delta\sigma(c) = \sigma_{\mathrm{Fe}} f(c)$, where σ_{Fe} is the polarization of the conduction electrons in metallic iron and $f(c)$ is a concentration dependent function to be fitted.

It had turned out that the data could be equally well-fitted by the following two phenomenological functions:

$$f(c) = \begin{cases} 0.835c - 3.973c^2 \\ c^{1.62}(1-c)^{14.3} . \end{cases} \tag{1b}$$

The parabolic form of the function had been called model I, while the exponential one — model II.

As it can be clearly seen from figure 1, presented in the previous paper (Dubiel 1976), neither of the two models could be distinguished by the experimental data for the range of Cr concentration studied in that investigation — they both gave an equally good fit to the data.

The present paper shows the possibilities of verifying the two models as well as the experimental verification itself, based on the Mössbauer effect measurements of two homogeneous samples of Fe-Cr alloys containing 26.3 and 45.5 at% of chromium.

2. *Comparison of available models*

According to what has been mentioned in the Introduction, the two models could not be distinguished unless the Cr concentration was larger than 15 at%. Now we want to show that the predictions of these models are quite different for a sufficiently high Cr content in the alloy.

The predictions concern the following measurable quantities:

2.1. The field $H(00)$ i.e. the field at Fe nuclei with no Cr atoms within the first two coordination spheres.
2.2. The shape of the Mössbauer spectrum of the alloy.
2.3. The value of the critical chromium concentration i.e. the concentration at which the alloy loses its ferromagnetic character.
2.4. The shape of the field distribution corresponding to a given spectrum.

2.1. The field $H(00)$

Figure 1 of this paper presents the field $H(00)$, which is expected from the two models for the whole range of chromium concentration. One can readily see that the greater the content of Cr in an iron matrix the more pronounced the difference between the values of $H(00)$ as predicted by the two models. Such a behaviour of $H(00)$ means that there does exist the possibility of distinguishing between the models in an experimental way. Measurement should be carried out on samples with sufficiently high Cr concentration.

In addition, the magnetic field derived from Hasegawa and Kanamori's CPA calculations (1972) is also illustrated in this figure. Its behaviour is intermediate to those mentioned above.

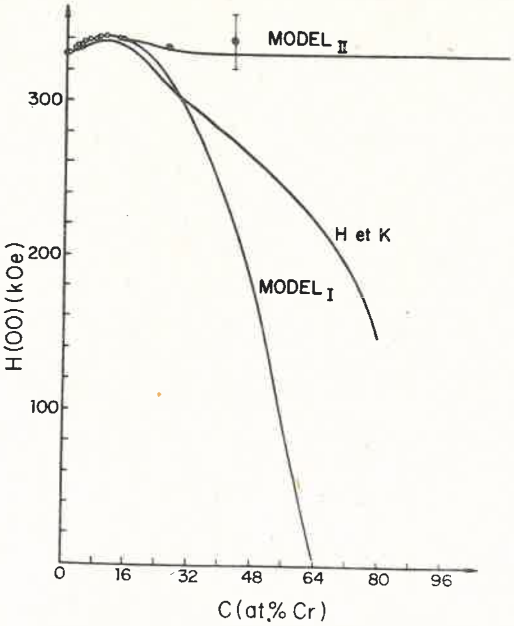

Fig. 1. The magnetic field at Fe nuclei in the configuration (00) obtained from model I, model II and from the calculation by Hasegawa and Kanamori versus Cr content. The open circles stand for the experimental results obtained previously (Dubiel, 1976), while the full circles mark the present data

2.2. The shape of the Mössbauer spectrum

The difference in the field behaviour for a given configuration predicted by the models should be reflected in the different shape of the Mössbauer spectra. To show this, such spectra have been simulated based on models I and II as well as on Hasegawa and Kanamori's calculations. Each simulated spectrum was a superposition of a number of six-line patterns, having different splittings, isomer shifts and relative intensities. The latter ones were assumed to be proportional to the probabilities of the configuration (m, n). The probabilities were calculated from the binomial distribution. In addition, to obtain the spectra the additivity of the field and the isomer changes as well as the previously measured values of $H(00)$, ΔH_1, ΔH_2, $IS(00)$, ΔIS_1 and ΔIS_2 were used (Dubiel 1976). The meaning of the symbols is as follows:

$$\begin{aligned} \Delta H_1 &= H(00)-H(10), & \Delta IS_1 &= IS(00)-IS(10), \\ \Delta H_2 &= H(00)-H(01), & \Delta IS_2 &= IS(00)-IS(01). \end{aligned} \tag{2}$$

To illustrate the difference between the three models, the simulated spectra for Fe-40%Cr and Fe-50%Cr are presented in Fig. 2a and Fig. 2b, respectively. A pronounced difference can be readily seen, especially for the sample with the higher Cr content. At this concentration it is possible, from the shape itself, to distinguish between the models.

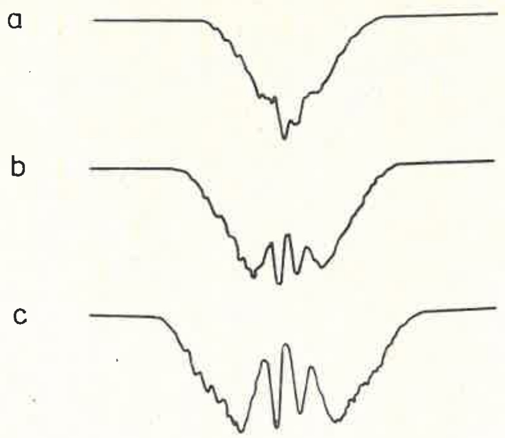

Fig. 2a. The simulated spectra for an Fe-Cr alloy containing 40 at % of chromium. Spectrum a) is based on model I, spectrum b) on Hasegawa and Kanamori's calculation and spectrum c) on model II

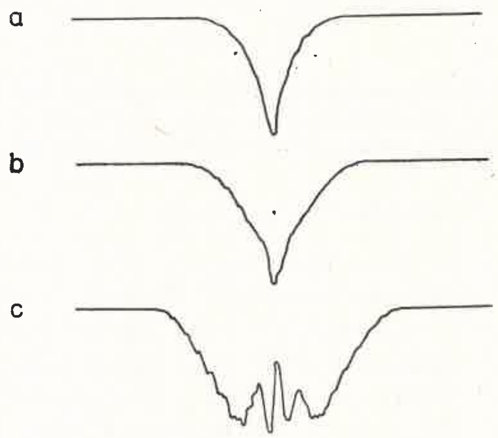

Fig. 2b. The simulated spectra for an Fe-Cr alloy containing 50 at % of chromium. Spectrum a) is based on model I, spectrum b) on Hasegawa and Kanamori's calculation and spectrum c) on model II

2.3. The critical concentration of chromium

Fig. 2b shows that for model I to be valid the hyperfine field of the alloy becomes zero at ~ 50% of chromium. This disagrees with the experimental observation that this alloy is ferromagnetic up to ~84% of Cr (Johnson et al. 1963, Loegel 1975, Loegel et al. 1975 and Burke and Rainford, 1978). Hence, model I will not be able to predict the value of the magnetic field for the alloy with higher Cr concentration.

Let us see now what is the prediction of model II as for the critical concentration. To this end, several Mössbauer spectra have been simulated based on this model for adequate values of Cr content. The results obtained are shown in Fig. 3. These spectra

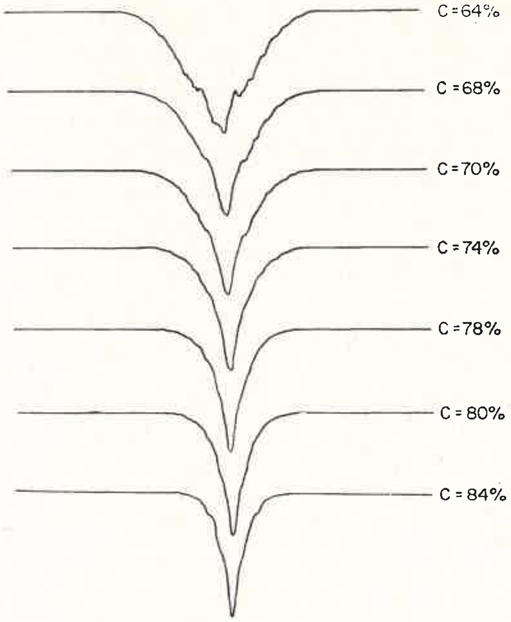

Fig. 3. The simulated spectra based on model II for an Fe-Cr alloy with different Cr content

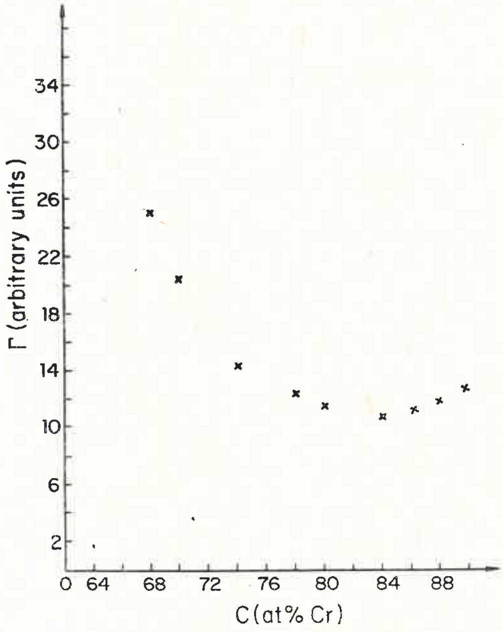

Fig. 4. The line width at half maximum, *Γ*, as a function of Cr concentration, *c*, as obtained by fitting the spectra shown in Fig. 3 with a single Lorentzian-shaped line

were then fitted with a Lorentzian-shaped single line to get the linewidth at half maximum. From the dependence of the linewidth on chromium concentration, which is illustrated in Fig. 4, it can be concluded that model II predicts that an Fe-Cr alloy exhibits ferromagnetism up to about 84 at% of chromium, which follows from the minimum of the linewidth at this concentration. This seems to be a reasonable estimate. It is hoped, therefore, that the field description predicted by this model is a correct one.

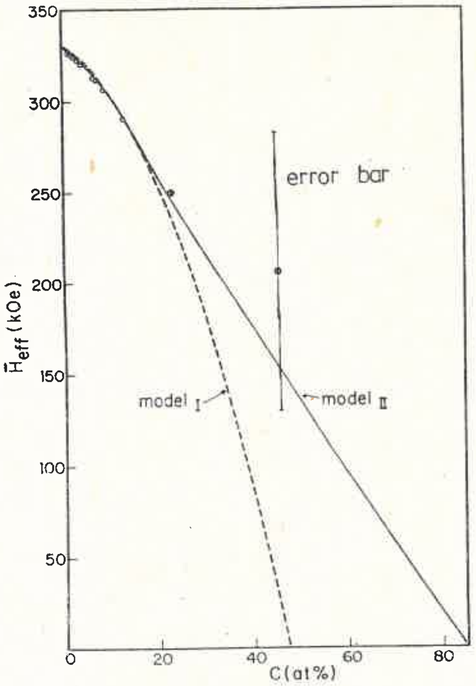

Fig. 5. The average magnetic field, $\overline{H}_{eff}$, calculated from model II and from model I. Open circles represent the experimental data obtained by Dubiel (1976) and the circles with dot inside show the present results

The above estimate has been independently confirmed by calculation of the average magnetic field based on model II. The result is presented in Fig. 5. It clearly shows that this model predicts the existence of ferromagnetism in the studied alloy up to ~85% of chromium, while according to model I the critical concentration is ~48%.

2.4. The field distribution shape

Finally, we want to point at another way of distinguishing between the three models. This lies in obtaining the field distributions from the Mössbauer spectra of the samples. Such distributions have been obtained based on the method outlined by Window (1971) and they are presented in Fig. 6 for the sample containing 50 at% of chromium. It is clear that the distributions obtained from each of the models are different. This makes it, therefore, also possible to distinguish between them in this way.

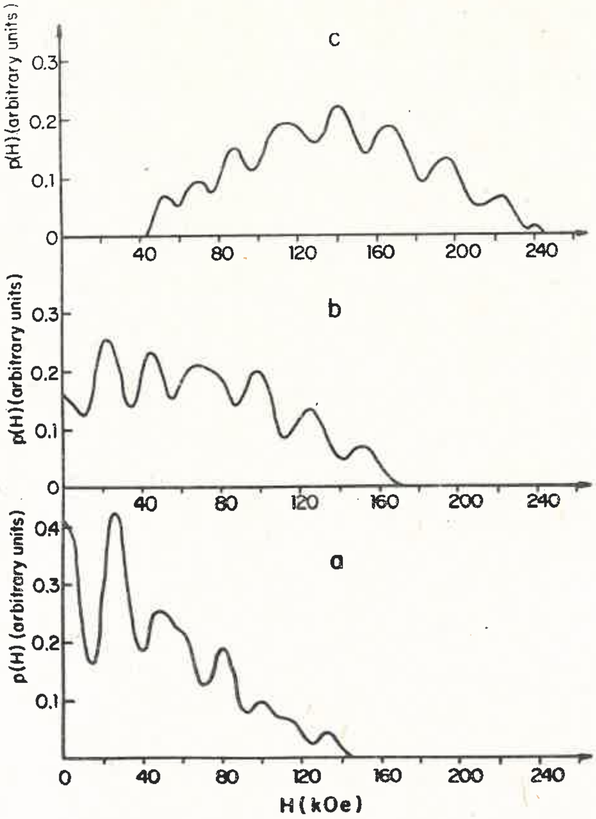

Fig. 6. The field distributions, $p(H)$, obtained from the spectra shown in Fig. 2b. $P(H)$ is a probability density of the field H

3. *Experimental procedure and spectra analysis*

3.1. Preparation of samples

Two samples of an Fe-Cr alloy were prepared in the form of 0.1 mm thick foil from Armco-iron and 0.999 purity chromium. They contained 26.3 and 45.5 at% of Cr. The method of preparation of the samples was similar to that described elsewhere (Dubiel et al. 1975). To obtain a more homogeneous distribution of Cr atoms in the iron matrix the foils were sealed in a vacuum quartz tube and then annealed for 6 hours at 1140±30°C. The tube was then quenched in a mixture of dry ice and C_2H_5OH. From the foils the final samples of ~35 μm thickhess were obtained by electropolishing.

3.2. Experiment

A 50 mCi source of ^{57}Co dissolved in a chromium matrix was used to provide monoenergetic 14.4 keV gamma rays. The Mössbauer spectra were recorded at room temperature by the constant-acceleration NOKIA spectrometer with a 400-channel analyser operating in the time-mode.

An iron foil of 12.5 μm thickness was used as a calibration standard.

3.3. Analysis of spectra

The spectra obtained were computer fitted, using a least-squares iteration procedure. Each spectrum was assumed to be a superposition ot a number of six-line patterns having different magnetic splittings, isomer shifts and statistical weights. It was also assumed that the lines were Lorentzian-shaped and that all corresponding lines had the same line-width, which was, however, a parameter to be fitted. The number of the contributing six-line patterns was calculated from the binomial distribution, taking into account only those that had the most significant probabilities to fulfil the condition that the overall probability of them was greater than 98%. These probabilities were not constrained, but were free parameters.

The fitting procedure was constrained by the additivity relations, both as for the magnetic field and the isomer shift changes i.e. it was assumed that

$$\begin{aligned} H(m,n) &= H(00)+m\Delta H_1+n\Delta H_2, \\ IS(m,n) &= IS(00)+m\Delta IS_1+n\Delta IS_2, \end{aligned} \tag{3}$$

where $H(m, n)$ stands for the field at Fe nuclei with m Cr atoms in the first and n atoms in the second coordination sphere. $IS(m, n)$ describes the isomer shift of an Fe atom occupying a similar configuration.

It is worth noticing that the above relations were experimentally verified for a range of Fe-Cr alloys containing 1–15 at%Cr (Dubiel and Krop, 1974).

4. Results and their comparison with the model predictions

The recorded Mössbauer spectra are shown in Fig. 7a and Fig. 8a. They were both successfully fitted by the procedure described above. The best-fit parameters are displayed in Table I.

To see how the experimental results agree with those predicted by model II, they are compared below.

The values of $H(00)$ fields obtained from the fits to the experimental spectra are presented as full circles in Fig. 1. One can see that they agree very well with the prediction of model II. Another way of verifying the predictions of model II is by comparing the shape of the experimental spectra with the predicted ones. This is done in Fig. 7 and Fig. 8. Namely, Fig. 7b and Fig. 8b show the best-fit to the experimental spectra for the samples containing 26.3 and 45.5 at% of chromium, respectively. Fig. 7c and Fig. 8c illustrate the predicted spectra for the two compositions, based on model II and using the ΔH and ΔIS values obtained for lower concentrations of Cr. Finally, Fig. 7d and Fig. 8d present the difference between the model and the fit spectra. One can readily see that for the Fe-26.3%Cr sample there is practically no difference between the experimental and the model spectrum as for the shape. For the Fe-45.5%Cr sample the difference is more pronounced, but it is still rather minute. It is partly due to the difference in $H(00)$ values. Namely, the predicted value is equal to 330 kOe, while the measured one — 340.2±30 kOe. The difference of 10 kOe (3%) lies within the experimental error and it can be explained in the following

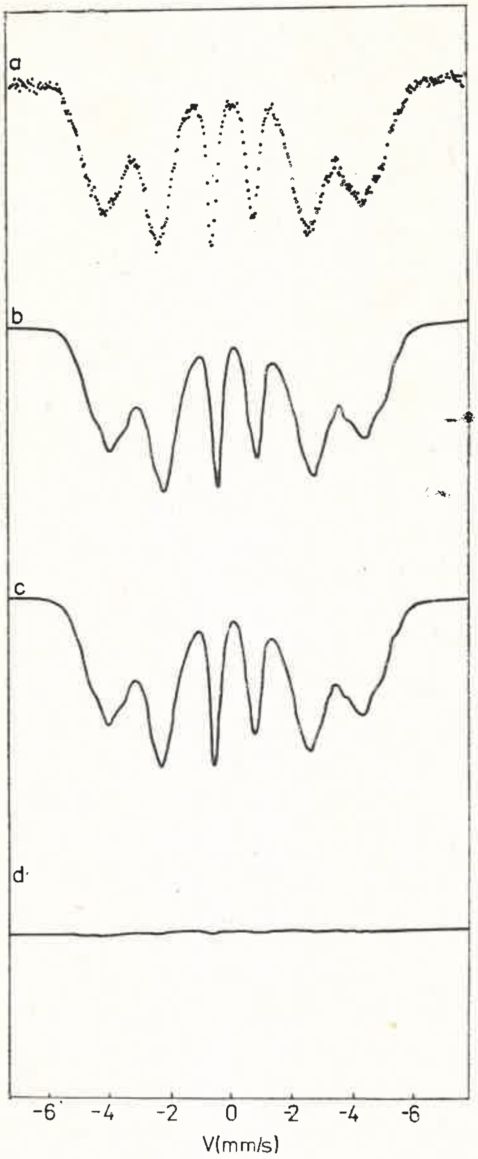

Fig. 7

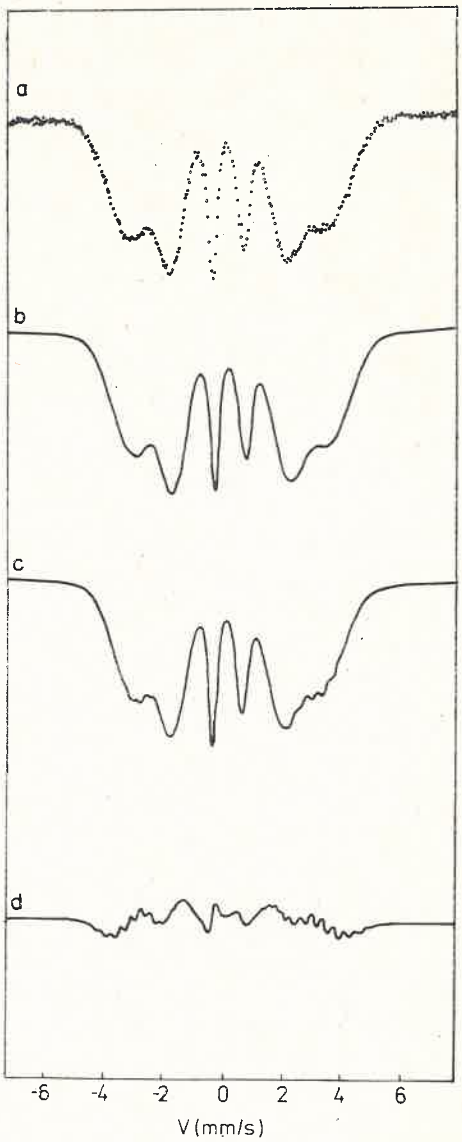

Fig. 8

Fig. 7. The Mössbauer spectra of Fe-Cr containing 26.3 at% of chromium: a — experimental, b — the best-fit to the experimental, c — based on model II and d — the difference between b and c

Fig. 8. The Mössbauer spectra of Fe-Cr containing 45.5 at% of chromium. The meaning of the symbols labelling the spectra is the same as in Fig. 7

way: the sample was not perfectly homogeneous. For a perfectly homogeneous alloy the average magnetic field would be equal to 197.8 kOe, assuming the same values of parameters. This figure differs by 4% from the measured value. Hence it seems likely that

TABLE I

The values of the best-fit parameters obtained from the measured Mössbauer spectra of Fe-Cr alloys containing 26.3 and 45.5 at % of chromium. The meaning of the symbols used is given in the text

c (at %)	$H(00)$ (kOe)	ΔH_1 (kOe)	ΔH_2 (kOe)	$\overline{H}_{\mathrm{eff}}$ (kOe)	ΔIS_1 (mm/s)	ΔIS_2 (mm/s)	$\overline{IS}^{a}$ (mm/s)	Γ (mm/s)
26.3	334.0 ± 2.4	-33.3 ± 1.0	-22.1 ± 1.0	248.4 ± 5.4	-0.020 ± 0.008	-0.020 ± 0.008	-0.06 ± 0.03	0.40 ± 0.07
45.5	340.2 ± 30	-22.9 ± 13	-19.4 ± 14	205.4 ± 75	-0.021 ± 0.015	-0.015 ± 0.016	-0.09 ± 0.017	0.47 ± 0.08

[a]-relative to metallic iron

it was the nonhomogeneity, that caused the 10 kOe deviation in $H(00)$. Furthermore, it is easy to show that for Fe-Cr the greater the degree of order the greater the value of the average field.

Using the best-fit parameters the average fields have been calculated based on the formula

$$\bar{H}_{\text{eff}}(c) = \frac{\sum H(m, n : c)P(m, n : c)}{\sum P(m, n : c)}, \tag{4}$$

where $P(m, n{:}c)$ is a relative population of the configuration (m, n) in the alloy, whose concentration of chromium is c. $P(m, n{:}c)$ was one of the parameters in the fitting procedure. The values obtained from that formula are presented in Table I and they are also illustrated in Fig. 5 as open circles with a dot inside. One can see that for the less concentrated alloy the measured value of the average field agrees perfectly with that predicted by model II. For the more concentrated sample the experimental value is greater than for the model value by ~50 kOe. It agrees, however, with it within the experimental error. The observed difference may be partly due to a lack of perfect homogeneity of Cr distribution in the iron matrix. This is able to account for the 7.5 kOe difference, assuming the same values of the parameters involved in calculating the average field. However, as can be seen from

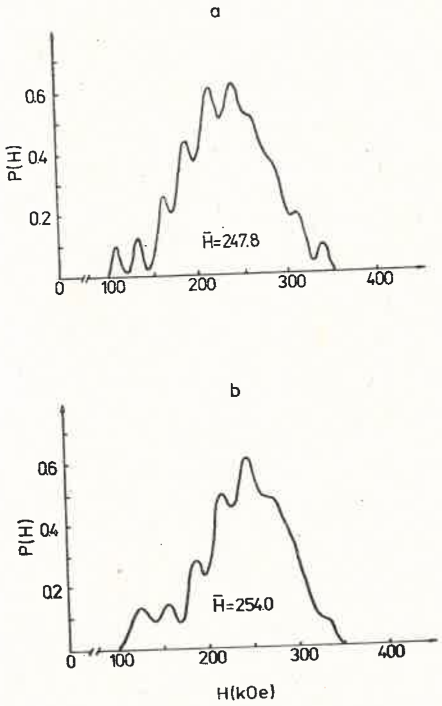

Fig. 9. The field distributions obtained for Fe-26.3 % Cr: a — from the experimental spectrum and b — from the corresponding spectrum based on model II. $P(H)$ is the probability density of the field H

Table I, the values of ΔH_1 and ΔH_2 for this sample are different than the corresponding ones for the sample with lower content of Cr. Namely, the ΔH_1 value is significantly smaller for Fe-45.5% Cr. This might be caused by the over-simplifications assumed in the fitting procedure, e.g. using the additivity formula, which may not be valid for more highly concentrated samples or the neglected further-than-the second neighbour Cr atoms may reflect their influence on the field by diminishing the value of ΔH_1. To see the role of this damping effect in the average field value, we have calculated it for Fe-45.5% Cr, taking for ΔH_1 and ΔH_2 the values obtained for Fe-26.3% Cr sample. In this case the average field has the value of 160.9 kOe, which is almost equal to the value predicted by model II.

Thus, one may conclude that concerning the average field the measured values do not disagree with model II predictions.

Finally, we want to compare the shapes of the field distributions. The comparison is shown in Fig. 9 and Fig. 10, where one can see the distributions derived from the experimental spectra — Fig. 9a and Fig. 10a, as well as those obtained from the simulated spectra based on model II — Fig. 9b and Fig. 10b. Similarity in the shapes and in the values of the average fields $\bar{H}$ is close.

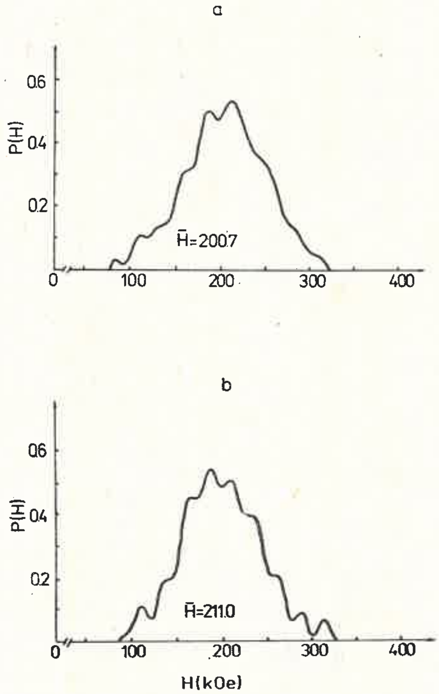

Fig. 10. The field distributions obtained for Fe-45.5% Cr: a — from the experimental spectrum and b — from the corresponding spectrum based on model II. $P(H)$ is the probability density of the field H

8. *Summary*

In the first part of this study four different ways of experimental verification of two models describing the hyperfine magnetic fields versus chromium concentration have been suggested for homogeneous Fe-Cr alloys. The suggestions have involved such measurable quantities as: $H(00)$ field, the shape of the Mössbauer spectrum, the critical Cr concentration in the alloy and the shape of the field distribution. It was shown that available experimental data had eliminated model I, because it failed to predict a correct value of the critical concentration.

In the second part the suggested criteria have been verified by comparing the predicted values with the measured ones, using the Mössbauer effect for two samples of Fe-Cr with sufficiently high content of chromium. The comparison has proved that the predictions derived from model II agree well with the corresponding experimental data. One hopes, therefore, that the model II description, which was previously introduced to describe the magnetic fields for a range of Fe-Cr alloys containing 1–15 at% of chromium, is correct for any Cr concentration.

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