Mössbauer measurements in iron based alloys with transition metals

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Abstract. Results of Mössbauer measurements on dilute Fe based alloys with all soluble transition impurities are given; the spectra are analysed to obtain hyperfine field and isomer shift changes at first, second and average further neighbour shells. The hyperfine field changes are shown to be consistent with a model in which the conduction electron polarization has a linear response to the d moment changes induced by the impurity. The isomer shift changes are ascribed primarily to variations in the d↑ density at the Fe neighbour sites.

1. Introduction

If we put an impurity into an iron matrix, then the screening of the impurity excess charge causes a change in the charge and spin density at the neighbouring matrix atoms. In the case of magnetic transition element d impurities this charge screening takes place mainly by d electrons, owing to the large d electron density of states of the iron. The change in the spin density of the d electrons of the iron atoms surrounding the impurity results in a change in their magnetic moment. The total change due to the impurity in the d moment of the neighbouring iron atoms is

$$\sum_k c_k \Delta\mu_{Fe}^k = \frac{d\bar{\mu}}{dc} + (\mu_{Fe} - \mu_i) \tag{1}$$

where $\Delta\mu_{Fe}^k$ is the deviation of the iron moment from the pure iron value in the kth coordination sphere of the impurity, which contains c_k atoms; $d\bar{\mu}/dc$ is the change of the average magnetization of the alloy per substituted impurity atom; μ_i and μ_{Fe} are the impurity local moment and the pure iron moment, respectively. From an analysis of diffuse neutron scattering measurements (Collins and Low 1965) it is possible to obtain the individual moment changes $\Delta\mu_{Fe}^k$ and the impurity moments μ_i, but the accuracy is very limited. These values, as well as the $d\bar{\mu}/dc$ values, were well described by Campbell and Gomès (1967) within a simple picture, where the impurity was represented by localized potentials determined selfconsistently by the impurity excess charge through the Friedel sum rule.

For investigation of the charge and spin density perturbation caused by the impurity at the matrix atoms the Mössbauer effect is very suitable, because the hyperfine field

and the isomer shift are sensitive to changes in both the d and s electron spin and charge density, respectively. Of course, the artificial separation of the perturbations related to the d and s bands raises a difficult problem. In a simple semiempirical model (Shirley *et al* 1968, Campbell 1969), the change of the hyperfine field in the kth coordination sphere of the impurity consists of two contributions:

$$\Delta H^k = \Delta H^k_{CEP} + \Delta H^k_{CP} \tag{2}$$

where the change of the core polarization contribution $\Delta H^k_{CP} = a\Delta\mu^k_{Fe}$ is proportional to the change in the magnetic moment of the neighbour atoms (a is the core polarization constant, with a value 50–70 kG μ_B^{-1} for iron), and ΔH^k_{CEP} is due to changes in the polarization of the conduction electrons around the impurity.

In the following we shall deal mainly with dilute iron based alloys containing first, second and third transition series magnetic elements. As is well known, the Mössbauer spectra of iron alloys are generally superpositions of several six line patterns, each of which corresponds to the different impurity neighbourhoods and thus each having a different hyperfine field and isomer shift from that of pure iron. The probability of the different impurity configurations determines the relative amplitudes of these sextets. The greatest problem in the evaluation of the Mössbauer spectra is the determination of the individual contributions of the environmental impurities.

The first detailed Mössbauer investigation of the iron based alloys with such impurities was carried out by Wertheim *et al* (1964). In this work, it was assumed that the observable satellites correspond to the first and second iron neighbours of the impurity. However, these investigators did not perform a detailed least squares analysis to check this assumption and to obtain the parameters giving the best fit to the spectra.

In the work of Stearns (1966) data were presented for the change of the hyperfine field in the case of Mn, Cr and V impurities up to fifth neighbour of the impurity. However, the results of her decomposition of the Mössbauer spectra are in disagreement with data from recent spin echo (Dean *et al* 1971 on FeV) and CW NMR (Mendis and Anderson 1970) experiments, in which individual satellites are well resolved.

As will be shown later, a more careful analysis of the Mössbauer spectra is able to give parameters in good agreement with these 'direct' measurements. A new data evaluation procedure is also necessary, because the accuracy and reliability of the earlier reported isomer shift data are unsatisfactory.

In this paper we report the results of Mössbauer investigations at room temperature on iron based alloys with all the soluble magnetic d impurities. The data obtained are compared with the existing ideas used to explain the effect of the impurity on the hyperfine properties of the matrix, and an attempt is made to get a consistent picture with other known quantities. The temperature dependence of the Mössbauer spectra has also been measured, and the results have already been published in part (Vincze and Grüner 1972, Vincze 1972). Here a summary of these results is given in connection with the description of the spin and charge density oscillations produced by the impurities.

2. Experimental method and results

2.1. Apparatus

A conventional constant acceleration Mössbauer spectrometer was utilized in conjunction with a 1024 multichannel analyser and a 10 mCi ^{57}Co in chromium source. In

the measurements, the differential nonlinearity proved to be better than 0·1% and no measurable change of velocity or zero point could be observed even during runs taking several days. Each spectrum involved 100–300 × 10³ counts per channel collected over a 24 hour run. The measurements were performed from liquid nitrogen temperature to the Curie point of the alloys using a vacuum furnace above room temperature and a 'cold finger' cryostat at low temperatures, the sample temperature being stabilized by a temperature controller to within ±0·5 °C. Reproducibility was within the limits of the experimental error. We did not investigate all the samples as a function of temperature.

2.2. Samples

The disordered bcc alloys were prepared in an induction furnace from constituents of 99·99% purity by melting either in vacuum or under argon atmosphere. After melting, the samples were annealed at 1100°C for half an hour, then rolled to plates of 20–30 μm thickness which were homogenized at 850°C in an H_2 atmosphere for three days. A powder sample of grain size less than 50 μm was filed from the alloys containing W impurities, because of their hardness. Since the weight losses on melting were negligible, the nominal compositions of all the alloys were assumed to be correct. After the above heat treatment no appreciable change was detected in the parameters measured at room temperature following measurements at higher temperatures, except for Mn impurity. In this case a loss of Mn was observed during the measurements above 500°C; this was taken into account in the evaluation of the spectra.
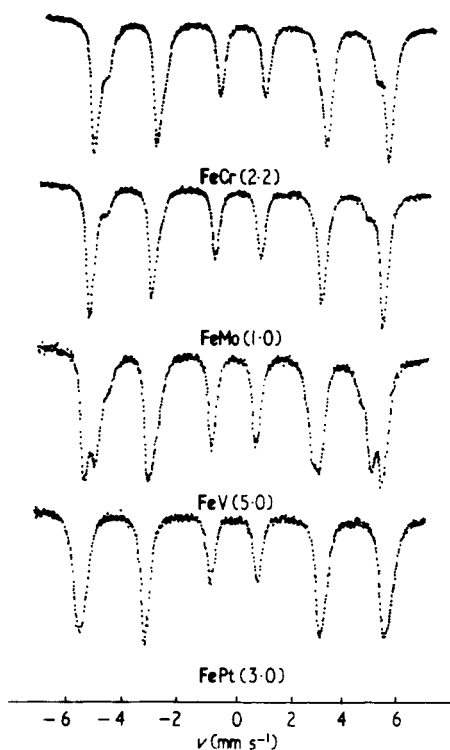

Figure 1. Typical room temperature Mössbauer spectra.

The impurity concentrations were the following:
3d impurities: Ti (3·0 at %), V (2·0 and 5·0 at %), Cr (2·2 at %), Mn (2·5 and 3·4 at %), Co (1·5 and 3·0 at %) and Ni (1·5, 3·0 and 5·0 at %).
4d impurities: Mo (1·0 at %), Ru (3·6 at %), Rh (3·0 and 5·0 at %) and Pd (1·0 at %).
5d impurities: W (3·0 and 5·0 at %), Re (2·0 and 3·0 at %), Os (1·5 at %), Ir (3·0 at %) and Pt (3·0 at %).

2.3. Evaluation of the data

Some typical spectra at room temperature are shown in figure 1. The depth of the outer peaks on the figure generally reaches 60×10^3 counts per channel. With Ti, V, Cr, Mn, Mo, Ru, W, Re and Os impurities one or two well observable satellites can be seen besides the main line while in case of Co, Ni, Rh, Pd, Ir and Pt impurities we found only an asymmetrical line broadening. In analysing the data we considered the whole spectra (not just the outer peaks as was done in earlier work). The assumptions used in the decomposition of the spectra into their individual contributions were very similar to those of Wertheim *et al* (1964), except that we made a detailed analysis by the method of least squares using an iterating program on an ICT 1905 computer.

First of all it was assumed that the observed satellites correspond to the effects of impurity neighbours in the coordination shells containing $z_1, z_2, \ldots$ etc atoms. It was found that only the perturbations in the first and second ($z_1 = 8$ and $z_2 = 6$) or third ($z_3 = 12$) coordination spheres of the impurity could be resolved. The spectra were fitted with six line patterns, each pattern corresponding to Fe atoms in a given configuration constrained to satisfy the symmetry and splitting ratio characteristic of a metallic iron Mössbauer spectrum. The relative amplitude of these sextets was assumed to be given by the binomial distribution, because of the randomness of the alloys; that is

$$p(z_1, z_k, n, m, c) = p_{z_1}(n, c) p_{z_k}(m, c) = \binom{z_1}{n} c^n (1 - c)^{z_1 - n} \binom{z_k}{m} c^m (1 - c)^{z_k - m} \tag{3}$$

is the probability of having n and m impurities in the first and kth shell, respectively, for impurity concentration c. We were able to check this assumption for the group of impurities producing well observable satellites by iteration for the impurity concentration, and no deviation was found from the nominal concentration. Such a check is not possible for the other group of alloys, because of the absence of a resolvable satellite. Short range ordering which would alter the relative intensities of the various sextets was not observed.

The line shape was assumed to be lorentzian, and to limit the number of parameters all linewidths were assumed to be the same. The linewidth was considered as an iteration parameter which specifies the broadening and distortion of the lines due to the finite thickness of the absorber and source (Frauenfelder *et al* 1962) as well as to the instability and nonlinearity of the apparatus. The asymmetric line broadening is identical for each resolved line, since the unresolved effects of impurities in more distant shells remain small compared to the observed linewidth, according to the spin echo and cw NMR measurements (Budnick *et al* 1970, Mendis and Anderson 1970). The finite thickness of the absorber should in principle be included explicitly; however, the changes in the final parameters compared with the simple calculation will be small.

It was assumed that the contributions coming from the multiple impurity neighbours in the same or different shells are additive and independent of their relative positions; that is

$$H(n, m) = H_0 + n\Delta H_1 + m\Delta H_k \tag{4}$$

for the hyperfine field and analogously

$$i(n, m) = i_0 + n\Delta i_1 + m\Delta i_k \tag{5}$$

for the isomer shift. Here ΔH_1, ΔH_k and Δi_1, Δi_k are the changes of the hyperfine field and isomer shift in the first and kth coordination sphere due to the impurity, while H_0 and i_0 contain the effects of unresolved satellite lines and are dependent on the impurity concentration. Additivity for the hyperfine field changes was observed at low concentrations ($\lesssim 1$ at %; Mendis and Anderson 1967), but this is not a very important assumption because the low impurity concentrations used means that the probability of two impurity neighbours is ten times smaller than one. However, if we want to determine $H(n, m)$ without the assumption of additivity, as was done, for example, by Schurer *et al* (1971), then correlations between a large number of badly determined parameters leads to systematic uncertainties which are much more important than the statistical errors.

There was no indication of any quadrupole splitting within experimental error for all environments.

The goodness of fit of the data to the theoretical curve was tested by computing the χ^2 value, defined in the usual way as a sum of terms of the form: ((observed value − computed value) × standard deviation of the observed value)². The expected value of this sum is: $\langle \chi^2 \rangle$ = the number of measured points − the number of fitted parameters. The value of the χ^2 obtained for the fits to the spectra was generally one to five times the expected value, and even for pure iron and it depended on the statistics. The value of $\chi^2/\langle \chi^2 \rangle$ was larger the more counts there were in the channel. This can be well illustrated by the pure iron case: if we reduce the number of channels to 512 for the same spectrum, adding the contents of the channels in pairs, then the value and the error of the evaluated parameters remain unchanged, but the $\chi^2/\langle \chi^2 \rangle$ value increases by about 20%. These discrepancies can probably be attributed to the large statistics, which has the results (i) that the average over the channel on the theoretical curve is not necessarily a good representation of a point of the curve and (ii) that the possible deviation (Evans and Black 1970) of the line shape from the lorentzian used will be more important. The errors noted for the parameters take no account of systematic errors; they are only the statistical errors obtained from the error matrix in the fitting program corrected by $\chi^2/\langle \chi^2 \rangle$.

The fitting of the spectra to the curve discussed above was performed gradually, by a step by step analysis. The problems are quite different for the two groups of impurities.

In the case of Ti, V, Cr, Mn, Mo, W, Re and Os impurities the observed satellite in the spectrum was attributed to the effect of the impurity in the first shell. The spectra of FeMn and FeOs can be well described with this assumption: the value of $\chi^2/\langle \chi^2 \rangle$ is about 2·2 and the evaluated linewidth agrees well with that of pure iron (the full linewidth at the half maximum of the outer peaks is $0·33$ mm s^{-1}). If we attempt to determine the effect of impurities in the second or third shell, then the χ^2 value decreases by about 10%, but a strong correlation appears between the value of the ΔH to be determined and the linewidth, which decreases the latter under the pure iron value and thus makes the parameters evaluated from the fit unreasonable. The cw NMR data of Mendis and Anderson (1970) and the spin echo measurement of Rubinstein *et al* (1966) give the same result as our own in the case of FeMn alloys; comparable data are not at present

available for FeOs. The similar decomposition of the FeRu spectrum gives an adequate description ($\chi^2/\langle\chi^2\rangle = 2\cdot3$), but the decomposed linewidth ($0\cdot36$ mm s^{-1}) is somewhat larger than that of pure iron. The best fit was obtained by attributing this broadening to the effect of the third neighbour impurity, in very good agreement with the spin echo measurement of Budnick and Skalski (1967), although the drop in the reduced χ^2 value is only $0\cdot3$. After the decomposition of the third neighbour contribution we reach the linewidth of the pure iron, and thus it is not possible to determine contributions of the other shells. In the case of FeMo the broadening of the line is different from that found for FeRu because only the observed satellite line is broadened, while the linewidth of the main line is the same as in pure iron (in FeRu both the satellite and the main line are equally broadened). Analysis of the intensity relations shows that the contribution from the second shell is the reason for the observed broadening. A similar situation was found for Re and W impurities, except that the difference between the contributions from the first and second shell is larger, and thus their decomposition is easier. The intensity of the satellite line caused by Ti, V or Cr impurities indicates that it comes from the perturbation of the first two shells of the impurity. The χ^2 value is the same whether calculated on the assumption that $\Delta H_1 = \Delta H_2$ and $\Delta i_1 = \Delta i_2$ or on the assumption these differ. The decomposed linewidth agrees with that for pure iron in both cases, so it was concluded that, on the basis of Mössbauer measurements, the contributions from the two shells are not separable and the effects of the more distant impurity neighbours are unresolvable. This conclusion is supported by the recent spin echo measurements of Dean *et al* (1971) on FeV alloys, in spite of the better resolution of the method.

In the case of Co, Ni, Rh, Pd, Ir and Pt impurities the decomposition of the Mössbauer spectra is more complicated than for the first group of impurities, because there is no resolvable satellite line in the spectra, only an asymmetrical line broadening. The problems are connected with the fact that the values of the hyperfine field changes due to the impurity are relatively small and nearly every contribution causes an increase of the hyperfine field. The difficulties in the data evaluation can be illustrated by the typical example of the Co impurity which has already been thoroughly investigated by various methods, including cw NMR (Mendis and Anderson 1967), spin echo (Budnick *et al* 1970, Rubinstein 1968 and Stauss 1971) and Mössbauer effect (Wertheim *et al* 1971). When the contributions from the first shell only are determined we get a large decrease in the value of the reduced χ^2 as compared with the one sextet fit (from $\chi^2/\langle\chi^2\rangle = 7\cdot7$ to $3\cdot6$). The value of ΔH_1 is $11\cdot8$ kG and the decomposed linewidth is somewhat larger than that for pure iron. Evaluation of the change of the hyperfine field in the second coordination sphere gives two solutions, which within the error of χ^2 have the same reduced χ^2 value (about $2\cdot8$), the program oscillating between the two minima. The two solutions are $\Delta H_1 = 13\cdot3$ kG, $\Delta H_2 = 6\cdot0$ kG, and $\Delta H_1 = 11\cdot1$ kG, $\Delta H_2 = 9\cdot5$ kG. In both cases the decomposed linewidth is equal to the pure iron value. No particular change was found in these parameters when we took into account in the iteration procedure the fixed value of $\Delta H_3 = 4\cdot3$ kG obtained from the cw NMR measurements (Mendis and Anderson 1967). It seems to us that it is not possible to prefer one of the two solutions solely on the basis of Mössbauer measurements. If the results of the spin echo measurements of Budnick *et al* (1970) are taken into account then we choose the solution with the larger ΔH_1, in a very good agreement with the decomposition of the new spin echo measurements of Stauss (1971), while the second solution corresponds to the Mössbauer results of Wertheim *et al* (1971). Our data also contradicts the assignments of the satellites proposed by Rubinstein (1968), according to whom the largest satellite in the NMR spectra of FeCo alloys corresponds to the first neighbour contribu-

tion, but are consistent with the finding of Wertheim *et al* (1971) that it is a third neighbour effect.

The situation is very similar in the case of the other impurities. When we want to determine the contributions from the first and second neighbour impurities, then in every case we get an oscillation behaviour between the possible solutions due to the very similar value of ΔH_1 and ΔH_2, and we cannot decide between them on the basis of least square analysis. In all cases the change in the value of ΔH_1 evaluated from the one shell model is not more than 5–10% for the two shell analysis. In every case we chose the solution with the largest ΔH_1, getting a very good agreement with the spin echo measurements of Budnick *et al* (1970), and the well resolved satellite with large amplitude in their spectra can be attributed to the third neighbour contribution. From our Mössbauer experiments we cannot resolve this contribution because the evaluated linewidth was the same as that of the pure iron (except the case of Pt impurity) and the strong correlation between ΔH_1 and ΔH_2 makes the fit of a new parameter hopeless.

Evaluation of the isomer shift changes in the different shells is much more problematical because of the badly resolvable satellites, and so we determined only the average change in the isomer shift.

The total change of the hyperfine field and isomer shift due to one impurity atom, that is $d\bar{H}/dc$ and $d\bar{i}/dc$, were determined. If the assumption about the additivity of the contributions from the shells holds—which is not improbable because of the low impurity concentrations—then these quantities should be simply $\Sigma_k c_k \Delta H^k$ and $\Sigma_k c_k \Delta i_k$. Thus we have two possibilities of determining the values of $d\bar{H}/dc$ and $d\bar{i}/dc$. In the first case, a single sextet can be fitted to the spectra to determine the value of the average hyperfine field and isomer shift, and the required quantities are calculated from these values. The second method (which is not rigorously exact for finite absorber thickness) is to determine the contribution from each shell, and then sum them up. The first method involves a systematic error because the values of the parameters of the average curve deviate from the average value of the individual parameters. Figure 2 shows the deviation between the values of the averaged centre of two lorentzian curves and the centre of the single
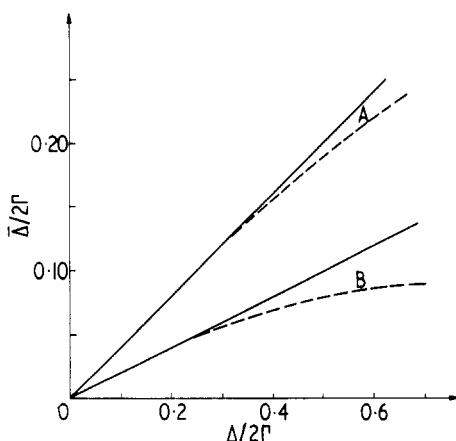

Figure 2. Deviation of the fitted centre of two lorentzian lines from the theoretical value: Δ is the separation of the two lines. $\bar{\Delta}$ is the central position, 2Γ is the whole linewidth at the half maximum of the starting lines; r is the amplitude ratio of the two line. A, $r = 0.67$; B, $r = 0.25$. The full curve is the calculated value of the centroid of the two curves while the broken curve signifies the value obtained from the one curve fit.

Table 1. The evaluated data from the decomposition of the Mössbauer spectra at room temperature, together with the $d\bar{\mu}/dc$ and μ_i values. The values of $d\bar{H}/dc$ calculated on the basis of equation (7) are also given. (Isomer shift data in mm s^{-1}, hyperfine field data in kG, magnetic moment data in μ_B). Positive signs signify increases in the absolute value of the hyperfine field. The impurity moment data are taken from the work of Collins and Low (1965), Campbell (1966) and Shirley *et al* (1968).

3d Solutes	Ti	V	Cr	Mn	Co	Ni
Δi_1	−0·013 (2)	−0·023 (2)	−0·020 (2)	−0·016 (2)		
Δi_2	−0·013 (2)	−0·023 (2)	−0·020 (2)	——		
Δi_3						
di_0/dc	0·09 (3)	0·15 (2)	0·12 (3)	0·07 (1)		
di/dc	−0·08 (5)	−0·17 (3)	−0·16 (4)	−0·06 (2)	0·16 (3)	0·23 (2)
ΔH_1	−19·1 (0·3)	−24·3 (0·2)	−26·9 (0·2)	−23·0 (0·1)	13·3 (0·3)	9·4 (0·3)
ΔH_2	−19·1 (0·3)	−24·3 (0·2)	−26·9 (0·2)	(<5)	6·0 (1·0)	7·0 (1·0)
ΔH_3						
dH_0/dc	20 (10)	110 (5)	140 (15)	30 (5)	65 (5)	40 (5)
$(d\bar{H}/dc)_{exp}$	−270 (20)	−230 (10)	−240 (20)	−150 (10)	205 (10)	160 (10)
$(d\bar{H}/dc)_{calc}$	−290	−290	−150	−95	+200	+180
μ_i	−0·9	−0·7	−0·8	0·1	1·9	0·9
$d\bar{\mu}/dc$	−3·4[a]	−3·3[b]	−2·4[b]	−1·6[c]	1·2[d]	0·6[c]

4d Solutes	Mo	Ru	Rh	Pd
Δi_1	−0·035 (5)	−0·014 (3)		
Δi_2	−0·003 (7)	——		
Δi_3		0·001 (5)		
di_0/dc	0·20 (1)	0·11 (4)		
di/dc	−0·10 (4)	0·00 (5)	0·58 (3)	0·90 (10)
ΔH_1	−38·7 (0·5)	−20·2 (0·3)	11·6 (0·3)	11·8 (0·3)
ΔH_2	−31·6 (0·7)	(<5)	7·9 (1·0)	6·0 (2·0)
ΔH_3		5·8 (0·3)		
dH_0/dc	120 (10)	5 (10)	50 (10)	110 (10)
$(d\bar{H}/dc)_{exp}$	−380 (15)	−90 (15)	190 (15)	240 (20)
$(d\bar{H}/dc)_{calc}$	−115	−125	+255	
μ_i	−0·7	0·8	0·7	0·2
$d\bar{\mu}/dc$	−2·1[c]	−1·5[f]	1·0[f]	

5d Solutes	W	Re	Os	Ir	Pt
Δi_1	−0·034 (3)	−0·029 (3)	−0·017 (2)		
Δi_2	−0·010 (6)	−0·003 (7)	——		
Δi_3					
di_0/dc	0·31 (2)	0·14 (4)	0·23 (2)		
di/dc	−0·02 (5)	−0·09 (7)	0·09 (4)	0·20 (3)	1·80 (7)
ΔH_1	−45·8 (0·4)	−47·2 (0·3)	−36·0 (0·3)	10·3 (0·4)	15·0 (0·3)
ΔH_2	−24·7 (0·6)	−22·5 (0·5)	(<5)	(<5)	11·3 (1·0)
ΔH_3					
dH_0/dc	115 (10)	105 (5)	50 (5)	−20 (15)	370 (10)
$(d\bar{H}/dc)_{exp}$	−400 (15)	−410 (10)	−240 (10)	60 (20)	560 (20)
$(d\bar{H}/dc)_{calc}$	−110	−60	−100	230	410
μ_i	−0·6	−0·4	0·0	0·2	0·1
$d\bar{\mu}/dc$	−2·0[a]	−1·6[a]	−1·6[f]	0·6[f]	1·7[f]

[a] Aldred (1968); [b] Nevitt and Aldred (1963); [c] Arajs (1969); [d] Bardos (1969); [e] Peschard (1925); [f] Fallot (1938).

average curve fitted to them, as a function of the distance and relative intensity of the two curves. It is quite clear that averaging with one curve is a much worse approximation for the distant satellites with small amplitude. The tendency of this systematic error is in each case to decrease the absolute value of $d\bar{H}/dc$. If the distance of the satellite is not more than 5–6 kG, the measure of this systematic error will not exceed 10%. This explains why, for example, in the case of FeCo alloys the value $dH/dc = 170$ kG obtained from the single sextet fit (Johnson *et al* 1963) is lower than the sum of the values of the decomposed hyperfine field change $\Sigma_k c_k \Delta H^k = 210$ kG, and this is a generally observed property. If we compare the change dH_0/dc of the unresolved components obtained by us with the sum of the corresponding contributions of the more distant satellites determined by cw NMR method (Mendis and Anderson 1970), the agreement is satisfactory for Mn, Co and Ni (and also for Al and Sn; Vincze and Cser 1972a, 1972b), while in the case of Cr and V impurities we get a two to five times larger value from the Mössbauer data. The reasons for this deviation (if the assignments of the satellites are right) may be (i) that the different impurity concentration ranges investigated in the two experiments have the result that in the Mössbauer experiments the overlap effect of the perturbed magnetic moment regions around the impurity is observed, which causes a simple shift of the main line, and (ii) difficulties in the determination of the central NMR line shift due to distortion and broadening.

2.4. Results

The room temperature data evaluated from the Mössbauer spectra in the way described above are given in table 1. In cases where several samples with different impurity concentrations were used we present average values of the parameters. The following remarks should be added to what has gone before. In the case of FeIr after the decomposition of the first neighbour effect a linewidth equal to that of pure iron is obtained, so that searching for the contribution of second neighbours was not reliable. The linewidth decomposed up to the second shell for Pt was about 0.40 mm s^{-1}, indicating the presence of a large number of satellites with nearly the same distance, in agreement with the very large dH_0/dc value obtained. Because of the difficulties mentioned earlier, the attempt to evaluate the further shell contributions was not successful.

In table 1 we present the values of $d\bar{H}/dc$ and $d\bar{i}/dc$, which are the sums of the decomposed values and the change of the unresolved contributions. The $d\bar{H}/dc$ data mostly agree within 20% with those of Wertheim (1966), although the difference is much larger in the case of Os and Pt impurities. For Mo, Re and W solutes the above reported values are the first determinations of $d\bar{H}/dc$.

The good agreement between our ΔH data and those of the different NMR methods in the investigated cases has already been mentioned, so here the data are only compared with the earlier reported Mössbauer measurements. The ΔH values in the different coordination shells likewise generally agree to within 20% with the earlier determined data of Wertheim *et al* (1964) for Ti, V, Cr, Mn, Co and Ru impurities but appreciable deviations occur, too. For instance, in the case of Ru these investigators attributed a value of -8.2 kG to the second neighbour contribution, whereas we have observed a third shell contribution of $+5.8$ kG. In the work of Bernas and Campbell (1966) practically only the average values of ΔH_1 and ΔH_2 are given for Re, Os, Ir and Pt impurities, and our data are in qualitative agreement. In the case of Mo, W and Re only data evaluations (Sauer and Reynik 1971), Marcus and Schwartz 1967) $\Delta H_1 = \Delta H_2$ and $\Delta i_1 = \Delta i_2$ were performed (that is the impurity nearest neighbour and next nearest

neighbour iron atoms were assumed to be identical). Our analysis shows that the assumptions are not valid for these alloys, and thus explains their deviations from our data (the same is true for Mn). As far as we know values for the ΔH hyperfine field changes in the different shells for Ni, Rh, Pd, Ir and Pt solutes have not yet been reported.

It is of course impossible from these spectra alone to assign sextets to definite neighbour sites other than by intensity measurements and plausability arguments. Implicitly in this section and §2.3 we have followed the conventional assignments where the large shifts are taken to be on first and second neighbours. Cranshaw (1972) from single crystal data suggests for FeCr that the site normally called second neighbour is in fact fifth neighbour. We will continue to use the conventional nomenclature; none of our conclusions are in fact dependent on this site assignment.
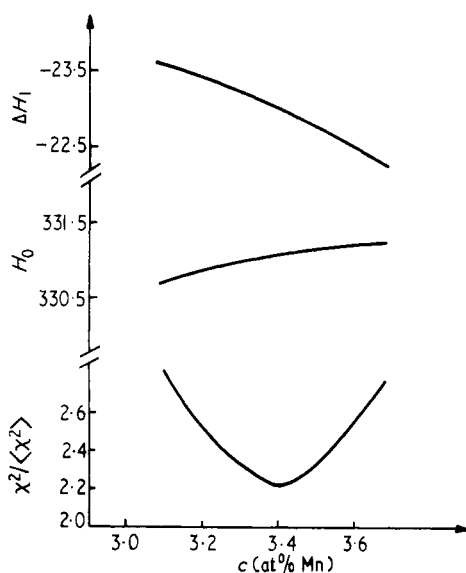

Figure 3. The dependence of $\chi^2/\langle\chi^2\rangle$, ΔH_1 and H_0 obtained from the fit of a FeMn (3·4 at %) alloy assuming different impurity concentrations in the fit.

As regards the isomer shifts, similarly detailed data have yet to be reported. The same criticism applies to the isomer shift change determined in the earlier mentioned 14 nearest neighbour model as to the hyperfine field change data. Wertheim *et al* (1964) reported Δi_1 data among others for Ti, V, Cr, Mn, Co and Ru solutes, but these are not reliable, since no least squares analysis was carried out and the evaluation method used was rather crude (only the outer peaks were taken into account).

As an example of the sensitivity to impurity concentration, figure 3 shows the dependence of the parameters on the different impurity concentrations assumed in the evaluation for the FeMn (3·4 at %) alloy. The large minimum in the χ^2 value at the real concentration is very prominent.

The temperature dependence of the Mössbauer spectra has been determined for most of the alloys under investigation (Vincze and Grüner 1972, Vincze 1972). The aim of these measurements was to compare the temperature dependences of the hyperfine field at iron atoms with different impurity environments, because it is expected that such a comparison can give valuable information both about the origin of the hyperfine field perturbations due to the impurities and about the origin of the anomalous temperature

dependence of the impurity hyperfine field first observed by Koi *et al* (1964) in FeMn. The evaluations of the spectra were performed in the same way as with the room temperature data, except that owing to the difficulties already referred to only the first neighbour hyperfine field change was determined for the second group of solutes. In respect to the temperature dependence this approximation seems to be reasonable, since we are comparing similarly evaluated data and, as was emphasized, the effect of the other neighbours is taken into account in the linewidth.

We found no deviations from pure iron in the temperature dependences of the hyperfine field at the iron atoms with different number of impurities in their neighbourhood for Ti, V, Cr, Co, Mo, Rh, W, Re and Ir solutes, whereas for Mn, Ru, Os, Ni, Pt and Pt the hyperfine field at iron atoms with nearest neighbour impurities declined much faster with increasing temperature than the hyperfine field at iron atoms without first neighbour impurities, which showed the same temperature dependence as that of pure iron. The hyperfine field at the third iron neighbour of Ru and Ni impurities exhibits a similar behaviour (the former follows from Mössbauer measurements (Vincze 1972) and the latter from NMR measurements by Riedi (1970)). The temperature dependence of the hyperfine field at iron atoms further away than the first neighbour shell, for impurities where the anomaly was observed, the case of Mn only has been investigated by cw NMR method (Vincze and Grüner 1972). No anomaly was found, but the highest temperature at which measurements were made was room temperature.

The first investigation of the temperature behaviour of the hyperfine field at iron atoms close to Mn impurity was the Mössbauer measurements of Cranshaw *et al* (1967). Our own hyperfine field data agree well with their results up to the highest temperature they used, as similar assumptions were made in the data evaluation. The temperature dependence of the iron hyperfine fields were also studied by Schurer *et al* (1971) in FeSi and FeMn. However, in both cases it was assumed without any check that the first two neighbouring shells around the impurity give important contributions, and five configurations with different peak positions were used. The erroneous assignments of the satellites (in the case of Si the third neighbour contribution is important, whereas for Mn the second neighbour effect is not resolvable by Mössbauer method), together with the overlarge number of parameters considered causes a much greater error in the peak positions than the statistical error. This is particularly noticeable for FeSi, in which the relative hyperfine fields at iron atoms with different configurations are the same within the given error, but deviate from the unperturbed value, indicating the inconsistency and uncertainty of the data.

The change of the isomer shift due to the impurity was found to be temperature independent. To illustrate this figure 4 shows Δi_1 for Mn impurity as a function of temperature. The temperature dependence of the isomer shift for the central line was the same as that for pure iron.
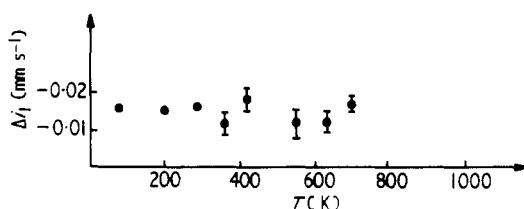

Figure 4. The temperature dependence of Δi_1 in FeMn (3·4 at %) alloy.

The decomposed linewidth narrowed with increasing temperature, which was consistent with the reduction of the effective sample thickness due to decrease of the Debye–Waller factor.

3. Discussion

We will first recall what is already known about the electronic structure of these alloys (mainly from magnetic and neutron scattering experiments); we will then point out the systematic trends that appear in the analysed Mössbauer data, and we will finally attempt to see what information can be drawn from the results.

3.1. Electronic structure

Fe is a weak ferromagnet with d band Fermi surfaces for both spin $\uparrow$ and spin $\downarrow$. Introduction of impurities to the left of Fe in the transition series reduces the average moment per atom, that is $d\bar{\mu}/dc$ is negative; the local moment on the impurity is near zero or slightly negative and the neighbour Fe sites have reduced moments for first and second neighbour sites and increased moments for some further neighbour sites (Collins and Low 1965). As we have just discussed the impurities Mn, Ru and Os are special cases in which the local moment varies strongly with temperature.

Introduction of impurities to the right of Fe leads to a positive average moment change $d\bar{\mu}/dc$, even though the local moment on the impurity is always less than that on an Fe site. The positive moment change on the Fe neighbours extends out to at least third or fourth neighbour sites (Collins and Low 1965).

The overall behaviour can certainly be ascribed to the same basic cause as in Ni and Co based alloys explained by Friedel (1967). In addition it has been suggested that in the case of Fe the high susceptibility associated with its weak ferromagnet character plays an important modifying rôle, especially in producing the positive $d\bar{\mu}/dc$ values for right hand side impurities (Campbell 1968).

3.2. Systematic trends

We will list the main trends that appear from an inspection of table 1 (some of these points have already been made by other authors).

(i) Impurities with small local moments and negative values of $d\bar{\mu}/dc$ (eg Cr) induce negative ΔH_1 and ΔH_2. For first series impurities ΔH_1 is approximately equal to ΔH_2, but for second and third series impurities of this type $|\Delta H_1| > |H_2|$.

(ii) For the 'anomalous temperature dependence' impurities Mn, Ru and Os ΔH_1 is negative but ΔH_2 is small.

(iii) For all right hand side impurities ΔH_1 and ΔH_2 are positive.

(iv) For all impurities, right across the series, the hyperfine field changes when further neighbours represented by dH_0/dc are positive.

(v) The total hyperfine field change $d\bar{H}/dc$ changes sign with $d\bar{\mu}/dc$.

(vi) For left hand side impurities the isomer shift for first neighbours is negative and for second neighbours is small, whenever these can be distinguished.

(vii) The average isomer shift change $d\bar{i}/dc$ is negative or small for left hand side impurities, and becomes positive for right hand side impurities. There are marked series effects.

(viii) It appears reasonable to suppose that the isomer shift for further neighbours represented by di/dc is positive for all impurities.

3.3. Hyperfine field changes

The hyperfine field changes can be taken as due to a core polarization term arising directly from the d moment changes on the Fe sites, and a conduction electron polarization (CEP) term arising from changes induced by the d moment distribution on the impurity and on the Fe sites. A first approximation is to assume that the core polarization hyperfine field on each site is proportional to the d moment on that particular site, and that the conduction electron polarization (CEP) is nonlocalized but again linear response to the d moment distribution

$$P(r) = \sum_{r'} f(r - r')\,\mu_d(r').$$ (6)

When an impurity is introduced at site $r' = 0$ with an accompanying d moment distribution at and around it, the hyperfine field changes (with respect to the pure metal) will be

$$\Delta H(r) = \alpha_{CP}\,\Delta\mu_d(r) + \alpha_{CEP}\sum_{r'} f(r - r')\,\Delta\mu_d(r')$$ (7)

where α_{CP}, α_{CEP} are atomic core polarization and CEP coupling constants respectively.

If we knew exactly the moment distribution at and around an impurity $\Delta\mu_d(r')$ we could test this hypothesis directly. However, the accuracy of existing neutron diffraction data does not permit us to do this. Without knowing exact distributions we can, however, use as a test the behaviour of *average* hyperfine field changes.

First of all, if we include the value of the impurity hyperfine field in our average and neglecting changes in the atomic hyperfine coupling constants (approximately valid for first series impurities) the linear response hypothesis and the averaging over the non-localized distribution gives immediately the relation

$$\frac{d\bar{H}}{dc} + (H_i - H_{Fe}) = \left(\frac{H}{\mu}\right)_{\text{pure Fe}} \frac{d\bar{\mu}}{dc}.$$ (8)

Experimental values (figure 5) fit this expression very reasonably (with no adjustable parameters).
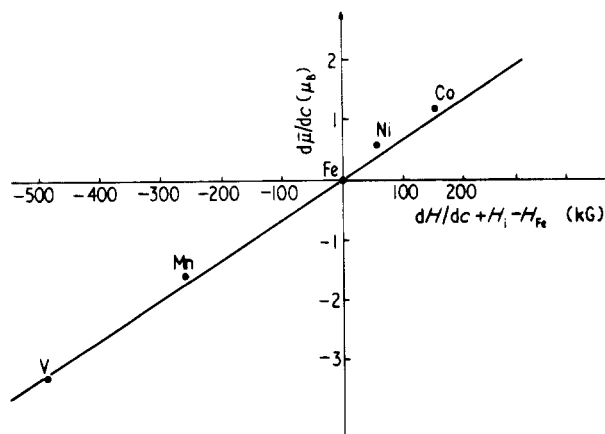

Figure 5. $d\bar{H}/dc + (H_i - H_{Fe})$ against $d\bar{\mu}/dc$ for the 3d impurities.

As a next step, if we know from the neutron diffraction data the local moment at the impurity site μ_i, then the hyperfine field at the impurity site will be

$$H_i = \alpha_{CP}^i \mu_i + \alpha_{CEP}^i \left(f(0) \mu_i + \sum_{r' \neq 0} f(r') \mu_d(r') \right) \tag{9}$$

For the case $\mu_i = 0$

$$H_i \simeq \alpha_{CEP}^i \left(\sum_{r' \neq 0} f(r') \right) \mu_d^n \tag{10}$$

while the sum of changes of fields at host sites due to the zero moment at the impurity site is

$$\sum_{r \neq 0} \Delta H(r) = \alpha_{CEP}^h \left(\sum_{r \neq 0} f(r) \right) (-\mu_d^h) = - \left(\frac{\alpha_{CEP}^h}{\alpha_{CEP}^i} \right) H_i. \tag{11}$$

For the general case we obtain an expression for the total change in neighbour site fields:

$$\frac{d\bar{H}}{dc} = A \left(\frac{d\bar{\mu}}{dc} + \mu_{Fe} - \mu_i \right) + B(\mu_i - \mu_{Fe}). \tag{12}$$

Here the first term is due directly to induced d moment changes on the Fe sites (both CP and CEP terms included) and the second term represents the effect on the conduction electrons at the Fe sites of the moment change at the impurity site. From the discussion above we have the *a priori* estimates

$$A \simeq \left(\frac{H}{\mu} \right)_{\text{pure Fe}} = 150 \, \text{kOe} \, \mu_B^{-1}$$

$$B \simeq \left(\frac{H_i}{\mu_{Fe}} \right) \left(\frac{\alpha_{CEP}^{Fe}}{\alpha_{CEP}^i} \right) = 80 \, \text{kOe} \, \mu_B^{-1}.$$

For estimating B we have taken the hyperfine field on Cu in Fe as representing a transition impurity with $\mu_i = 0$.

Calculated values of $d\bar{H}/dc$ using these estimates of A, B are given in table 1. The greatest difficulty in comparing the measured with the calculated values is the badly known impurity moment, but agreement is good for first series impurities and qualitatively correct for second and third series. It can be seen that the quantitative disagreement for Mo, W, Re and Os impurities is due to the exceptionally large values of ΔH_1 observed compared with the values for Ti, V and Cr. This may be due to series effects in the d–s interaction strenth.

From the overall form of the results, we can estimate (in agreement with other authors, Stearns 1966, Grüner *et al* 1972) that $\alpha_{CEP} f(0) + \alpha_{CP} \simeq 80 \, \text{kOe} \, \mu_B^{-1}$, $\alpha_{CEP} f(r_1) \simeq -10 \, \text{kOe} \, \mu_B^{-1}$, $f(r_2)$ is near zero and $f(r_n)$ is positive for some $n > 2$ (here r_n is the nth neighbour distance). However, to establish the exact form and uniqueness of the function f, it would be necessary to know the d moment distributions much more accurately. Thus the fact that the fields at distant neighbours always increase can be ascribed to the positive $f(r_n)$ for $n > 2$ combined with the fact that the impurity moment is always less than that of Fe, but the neutron data suggests that μ_d is also positive at these neighbours for all impurities, which will give a direct contribution to the hyperfine field changes.

It is interesting to compare the hyperfine field distributions with those in FeAl (Grüner *et al* 1972) which we can take as representing an entirely localized hole in the d moment. For FeAl, $\Delta H_2 = 0$ as for the impurities Mn, Ru and Os. This would seem to confirm the neutron diffraction data which indicate that among the transition impurities,

these three approximate the best to well localized moments in Fe. It is precisely these impurities which have anomalous hyperfine characteristics as a function of temperature. Also, in FeAl the positive field changes on distant neighbours again appear, suggesting that this is at least partially a CEP effect.

3.4. Isomer shifts

The isomer shift reflects the changes in the 4s and 3d occupations; a positive change indicates a decrease in s occupation or increase in d occupation.

From table 1 it appears that the isomer shifts for all impurities tend to behave in a very similar way to the site moment changes (eg see figure 6). This is consistent with
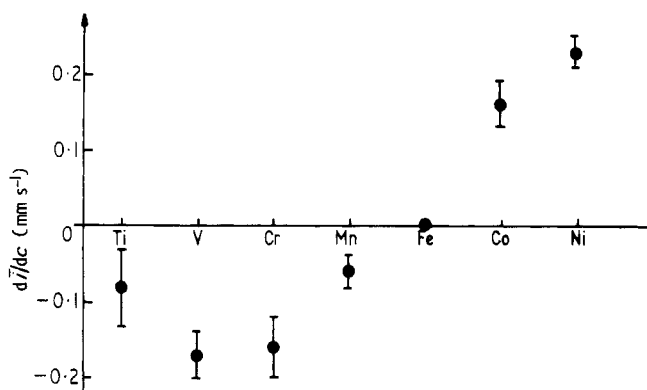

Figure 6. The total change of the isomer shift due to the 3d impurities.

effects principally in the d↑ band rather than the d↓ band. (For the d↓ band, site moment and d occupation have opposite signs.) This is reasonable because the band structure of Fe would indicate d↓ effects as very short ranged. If we ascribe the isomer shift changes primarily to d occupation changes, then the left hand side impurities provide repulsive d↑ potentials, which reduce the number of d electrons at sites near the impurity. Right hand side impurities provide attractive d↑ potentials giving increased moments and increased d occupation at sites around the impurity.

From the standard Fe isomer shift calibrations (Walker *et al* 1961) we can estimate that the Δi_1 values for left hand side impurities represent a total loss of about 0·2 d electrons from the eight Fe near neighbour sites, or alternatively an increase of 0·2 s electrons. This is a fairly small effect, and while of interest on its own merit does not invalidate to any great extent the preceding discussion of hyperfine fields. For a Pt impurity, however, (and to a lesser extent for Pd and Rh) shifts are much greater—the $d\bar{i}/dc$ measured represents a gain of 1·2 d electrons to the Fe sites per Pt atom, or alternatively an s to d transfer of about 0·6 electrons on the Fe sites. Because the effect is obviously associated with the high induced moment on the Fe sites surrounding the Pt, we suggest the s to d transfer is more probably correct. From the form of the Fe density of states it can be seen that an effective potential which increases Fe moments will also cause an s to d transfer because the d↑ density of states is greater than d↓ at the Fermi surface.

Again, it is interesting to compare with results in **FeAl** and **FeSi** (Grüner *et al* 1972). For these alloys, $\Delta i_2 \simeq 0$ as for all the transition impurities for which Δi_2 could be estimated separately. What is more important is that, while the hyperfine field changes induced by these impurities are close to those induced by left hand side transition impurities, the Δi_1 is of the opposite sign. This suggests that in **FeAl** the Δi_1 has a different origin and is due to a strong potential acting on the s electrons.

4. Summary and conclusion

Mössbauer spectra were taken for samples of Fe containing all soluble transition impurities. The spectra were analysed so as to estimate the hyperfine field and isomer shift changes at the various neighbour shells around the impurity. Care was taken in the evaluation of these parameters to eliminate alternative decompositions and to be as certain as possible of the assignments of the sites. Complimentary NMR data were used as a check whenever possible. The consistent treatment of the data for the different samples brings out the regularity in the systematic variation of the various parameters when the impurity species is changed; these trends are noted in §3.2.

In order to try to provide a unified explanation of the hyperfine field changes these are discussed in the usual phenomenological terms of a core polarization contribution and a CEP contribution, the latter reflecting a linear but nonlocalized response of the conduction electrons to changes in the d moment distribution due to the presence of an impurity. Quantitatively the average field changes are in reasonably good agreement with an expression established *a priori* on this approach, equation (7). Qualitatively within the limited accuracy of the d moment distribution data the hyperfine fields at different neighbour shells for the various impurities appear to be explained correctly by this picture. We conclude that the linear response is a good first approximation.

The isomer shift changes produced by different impurities show similar systematic behaviour to the hyperfine field changes; thus near neighbour shifts are positive for right hand side impurities, negative for left hand side impurities. We ascribe the shifts primarily to changes in the number of d↑ electrons at the Fe sites. Relatively large shifts (eg in **FePt**) are associated with large d moment changes on the Fe sites induced by the impurity, which suggests they are due to s to d transfer; there seems no evidence for any major departure from local change neutrality in the transition impurity alloys. This is in contrast to s–p impurity alloys such as **FeAl** where both the sign and the size of the isomer shift change indicate conduction electron screening effects.

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