

Hyperfine interactions of iron in ternary alloys with B8₂ type structures

S C BHARGAVA and P K IYENGAR

Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400085

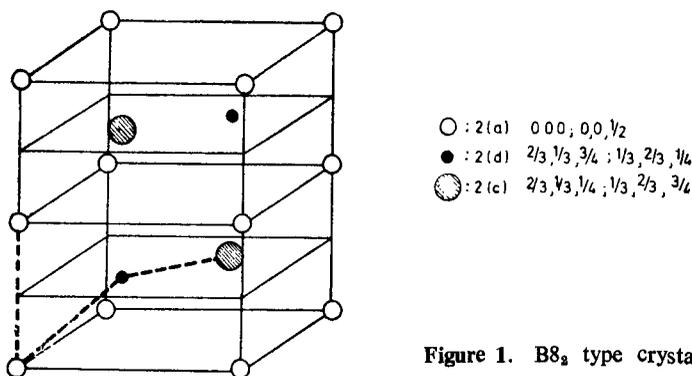
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Abstract. The recoilless absorption spectra of iron in the ternary alloys CoFeGe, CoFeSb and FeMnGe, which possess B8₂ type structure, reveal the existence of different ordering temperatures of moments at 2(*a*) and 2(*d*) sites. Using the Einstein model to describe the second order Doppler shift, it has been found that Θ_D appropriate to the thermal motions of iron atoms at 2(*a*) and 2(*d*) sites in CoFeGe are different, which is also suggested by the temperature dependences of the relative areas of the corresponding component spectra. In CoFeSb, on the other hand, relative areas of the component spectra are independent of temperature, and give the relative distribution of iron at the inequivalent sites. A large difference in the isomer shifts of 2(*a*) and 2(*d*) site spectra indicates a larger number of d-electrons in the atomic configuration for 2(*a*) atoms. The isomer shift change is negative for 2(*a*) site nuclei and positive for 2(*d*) site nuclei with increase in temperature. The magnetic fields at 2(*d*) site nuclei in CoFeGe and CoFeSb alloys indicate that the moments of the parent atoms are not much different from the value in iron metal.

Keywords. Ternary alloys with B8₂ type structure; hyperfine interactions; ordering of atomic moments; superparamagnetism; iron distribution at inequivalent sites.

1. Introduction

Earlier measurements of the magnetic properties of alloys with hexagonal closed packed structures have revealed several interesting features. It is known that while cobalt and iron atoms possess moments in hexagonal cobalt and Fe_{1.7}Ge respectively, the alloy Co_{1-x}Fe_xGe is Pauli paramagnetic. Kanematsu *et al* (1963) have shown that the results of susceptibility measurements on the ternary alloy (Co_{1-x}Fe_x)_{1.7}Ge, for small values of *x*, can be explained by assuming that the moment appears only on those cobalt atoms which possess more than a certain number of iron atoms in the first coordination sphere. In alloys possessing B8₂ type structure (figure 1) atoms of iron group occupy 2(*a*) and 2(*d*) sites. It has been found experimentally that the magnetic moment of the atom at a 2(*a*) site is considerably less than the moment of the atom at a 2(*d*) site. The nature of magnetic coupling also greatly depends on the type of atoms occupying the inequivalent sites. For example in Fe₂Ti, with MgZn₂ type of structure (Pearson 1958), when the iron atoms occupy 2(*a*) and 6(*h*) sites only, with first near neighbours at 2.4 Å, the coupling has been found to be antiferromagnetic (Nakamichi 1968), but as soon as iron starts occupying 4(*f*) sites as in Fe₂Ti (30.8 – 32.2 at. % Ti) which has the near neighbour shell at 2.8 Å, ferromagnetic coupling is favoured.

Figure 1. $B8_2$ type crystal structure

The technique of recoilless absorption of γ -rays is very useful to probe such microscopic properties of iron at the inequivalent sites. The magnetic and electric hyperfine interactions provide information about the charge and magnetic moment distributions around the nuclear sites. Besides, the relative distribution of iron atoms at the inequivalent sites can be determined, using this technique. In the present measurements, the hyperfine interactions of iron in the ternary alloys CoFeSb, CoFeGe and FeMnGe, have been determined. These alloys possess $B8_2$ type structure. The striking feature of the spectra is the coexistence of a paramagnetic doublet and magnetically split spectrum over a wide range of temperatures. Although such features can result from the presence of two phases in the alloys, which have different lattice or magnetic arrangements (antiferromagnetic and ferromagnetic domains coexisting), earlier measurements on certain alloys with similar structures (Murthy *et al* 1969, Sharon and Tsuei 1970, Wertheim *et al* 1970) suggest that in these three alloys the atoms at inequivalent sites order independently at different temperatures. Neutron diffraction analysis of FeMnGe by Murthy *et al* (1969) showed that the moments at 2 (d) and 2 (a) sites order at 385 K and 245 K respectively. Similar conclusions have been derived from the Mössbauer measurements (Sharon and Tsuei 1970, Wertheim *et al* 1970) on Fe_2Ti and $(Fe_{0.85}Mn_{0.15})_2Ti$, which possess $MgZn_2$ type structures. In the antiferromagnetic Fe_2Ti , although iron atoms at 6 (h) sites give magnetically split spectrum below T_N (279 K), the spectrum corresponding to iron at 2 (a) sites has been found to be a paramagnetic doublet even at 20 K. The intensity of the doublet reduces with increase of iron at 4 (f) sites which also give rise to ferromagnetic coupling in the alloy.

Neutron diffraction measurements on FeMnGe (Murthy *et al* 1969, Suzuoka *et al* 1968) have shown that 80% of iron atoms occupy 2 (d) sites which have point symmetry $\bar{6}m2$ and the sublattice moment at room temperature is $1.9\mu_B$ per atom; but the presence of an asymmetric doublet alone (quadrupole splitting = 0.62 mm/sec) has been reported in earlier Mössbauer measurements on the same alloy (Fatehally *et al* 1969). In the present study also, the intense doublet has been observed, which agrees with the discrepancy noted earlier, but the presence of a weak magnetic spectrum ($H_{eff} \approx 155$ kOe), in addition to the doublet, has been found, which was not noted earlier. This shows that the alloy is partly magnetic at room temperature. It is concluded that the discrepancy between the cation distribution determined using the neutron diffraction technique and the ratio of areas of the component Mössbauer spectra of FeMnGe can result from the presence of superparamagnetic clusters.

Neutron diffraction measurements on CoFeGe, at room temperature, show that the magnetic contribution to the scattered intensity is appreciable for one reflection only, making it difficult to obtain information about the moment distribution at different sublattices using this technique. This increases the desirability of Mössbauer investigation to determine the magnetic property of iron atoms at the different sites in the alloy.

2. Experimental

2.1 Sample preparation

The alloys have been prepared by melting the desired proportions of the constituent elements in an argon arc furnace. The resulting ingots of CoFeGe and CoFeSb were powdered and annealed at 1000° C in vacuum for seven days. For cooling from this temperature two processes, namely, slow cooling and quenching from 1000° C to room temperature, have been used. The recoilless absorption spectra of the two alloys remain unaltered by the thermal treatments. It is thus concluded that the population of iron at the inequivalent sites and the electronic properties responsible for the hyperfine interactions are not changed by the annealing processes. The alloy samples, which were annealed and then furnace cooled have been used for further investigations. The sample of FeMnGe alloy, used for the neutron diffraction studies by Murthy *et al* (1969), has been used in the present measurements also.

Using the x-ray fluorescence method the alloys have been found to possess the following compositions: $\text{Co}_{0.95}\text{FeGe}_{0.89}$, $\text{Co}_{0.83}\text{FeSb}_{1.02}$, and $\text{Mn}_{0.95}\text{FeGe}_{0.80}$.

The x-ray and the neutron diffraction patterns of these alloys can be indexed on the basis of B8_2 type structure. In the x-ray pattern of CoFeSb alloy, the reflection (101) is stronger than (102) and (110). Secondly (100) is not observable and the intensity of (002) is weak. These facts show (Castelliz 1953) that there is a large vacancy (more than 50%) at the 2 (*d*) sites in the alloy and a large fraction of the iron group atom, in place of 2 (*d*) sites, go to 2 (*a*) and 2 (*c*) sites equally. The accurate distribution of Co and Fe at different sites has been determined using Mössbauer measurements.

The x-ray diffraction pattern of CoFeGe shows that a minimum of 60% of the cobalt and iron atoms occupy 2 (*a*) sites. This is in agreement with the conclusions of Castelliz (1953) who found that 30% of 2 (*d*) sites remain vacant and all the germanium occupies 2 (*c*) sites only. The neutron diffraction pattern of CoFeGe at room temperature taken using unpolarised neutrons of wavelength 1.24 Å showed that the spins at the magnetically ordered sites are ferromagnetically coupled and the spins point along *c*-axis. The determination of the magnetic moments of Co and Fe atoms has not been attempted because the magnetic contribution (determined by applying an external magnetic field of 17 kOe) to (100) reflection is small and the contributions to other reflections are much smaller than this. The relative nuclear intensities also show that a large fraction of iron atoms occupy 2 (*a*) sites in this alloy.

2.2. Mössbauer measurements and analysis

The Mössbauer spectrometer employed in this work has been described elsewhere (Bhargava and Iyengar 1958). The source used is Co^{57} in chromium metal and has been kept at room temperature for all the measurements. The γ -rays are detected

using an argon-methane proportional counter. The spectrometer is operated in constant acceleration mode and the spectra are recorded on a 400-channel analyser, operated in the time mode. The velocity scale is calibrated using iron metal, potassium ferrocyanide, 310-stainless steel, and sodium nitroprusside absorbers. The calibration of velocity scale obtained using sodium nitroprusside ($0.065 \text{ mm. sec}^{-1}$ per channel) agreed with the calibration obtained using iron metal ($0.065 \text{ mm. sec}^{-1}$ per channel). The position of lines of potassium ferrocyanide, iron metal, and the stainless steel absorbers, calculated using sodium nitroprusside absorber spectrum agreed very well with the positions experimentally observed using these absorbers. The drift in the zero position and the change in the velocity scale has been found to be insignificant over a period of several weeks. The absorber powder pellets are enclosed between thin aluminium foils. The heating of the absorbers has been done in vacuum and the temperature controlled to within $\pm 0.5^\circ$.

The spectra of the alloys have been unfolded into the component spectra using a least squares fitting programme. All the lines have been assumed to be Lorentzian in shape.

The spectrum of CoFeGe has been unfolded into three component spectra, which consist of a quadrupole split doublet, arising from nuclei at 2 (*a*) sites (point symmetry $\bar{3}m$) where an axially symmetric field gradient due to lattice exists, and two magnetically split spectra, without appreciable quadrupole interaction, arising from nuclei at 2 (*c*) and 2 (*d*) sites (point symmetry $\bar{6}m2$). Since only a small fraction of iron group atoms occupy 2 (*c*) sites, the weaker magnetic spectrum has been ascribed to

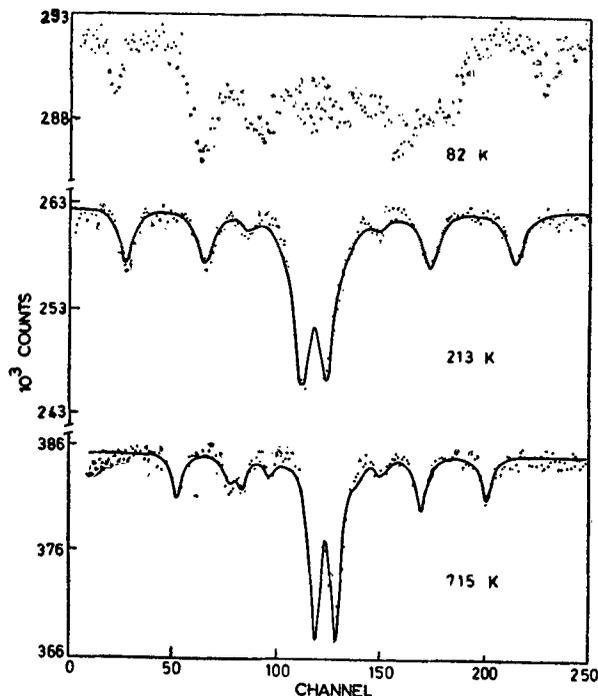


Figure 2. Mössbauer spectra of CoFeGe at 123, 293 and 715 K. The solid curves represent the least squares fitting to the raw data with 14 Lorentzian lines using the constraints described in the text. The three component spectra are clearly seen in the spectrum at 715 K.

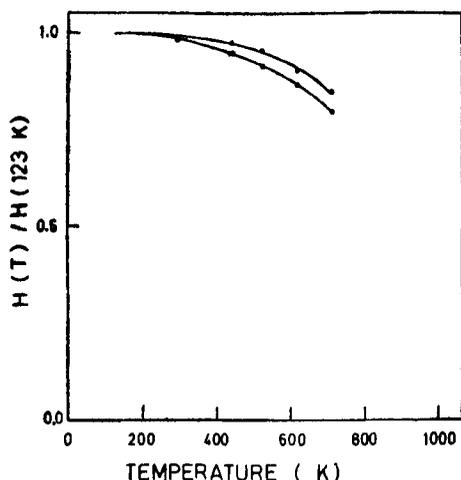


Figure 3. The temperature dependences of $H(T)/H(123\text{ K})$ corresponding to the two component spectra of CoFeGe spectrum.

nuclei at 2 (c) sites. The following assumptions have been made in the analysis of the spectra :

- (1) The intensity of the two lines of the quadrupole split doublet are equal. It is characterised by $H_{int} = 0$.
- (2) The line widths of all the fourteen lines in the spectrum are equal.
- (3) The two component spectra with $H_{int} \neq 0$, have zero quadrupole splittings.
- (4) The intensity ratio of first, second, and third pairs of lines, in the two component spectra with $H_{int} \neq 0$, are 3:2:1.

The typical fits to the raw data are shown with solid curves in figure 2. The fitting is good. The small deviations in certain parts of the spectra are present at all temperatures and reflect a small systematic error in the constraints used to analyse the data. The values of the various quantities thus determined, are given in table 1. In this table and table 2 the velocity shift represents shift in the centre of the spectrum relative to centre of iron metal spectrum at room temperature. Due to considerable overlap of 2 (c) site spectrum with other component spectra, a significant error may be present in velocity shifts of 2 (c) site spectra. This also introduces appreciable fluctuations in the component areas determined using the least squares fitting procedure. The presence of the three component spectra is clearly seen in the spectrum at 715 K and the results obtained at this temperature are expected to be free from any systematic error due to overlap. The temperature dependences of the magnetic fields are shown in figure 3.

The experimental values of the velocity shifts of 2 (a) and 2 (d) site spectra have been fitted using least squares technique to the formula (Perkins and Hazony 1972)

$$F(T) = \delta E_I^0 + \epsilon T - 7.306 \Theta_E \left[\frac{1}{2} + (\exp(\Theta_E/T) - 1)^{-1} \right] \times 10^{-4} \text{ mm sec}^{-1} \quad (1)$$

Here δE_I^0 represents isomer shift at 0 K, ϵT accounts for the temperature dependent contribution to the isomer shift, the last term represents the contribution of the second order Doppler shift to the velocity shift, and Θ_E represents the Einstein temperature appropriate to the thermal motion of the atom. The curves obtained

Table 1. Absorber CoFeGe

Temperature K	Magnetic field (kOe)		Quadrupole splitting at 2 (a) site (mm sec ⁻¹)	Velocity shifts (mm sec ⁻¹)		Relative area (%)		FWHM (mm sec ⁻¹)		
	2 (c) site	2 (d) site		2 (a) site	2 (c) site	2 (d) site	2 (a) site		2 (d) site	
123	199	43	0.662	0.37	0.43	0.204	49	15	36	0.509
293	196	338	0.657	0.33	0.297	0.149	59	11	30	0.39
443	194	325.4	0.621	0.23	0.22	0.04	65.5	9.5	25	0.40
525	190	314	0.593	0.17	0.15	-0.01	61.5	12.5	26	
621	179.5	298	0.56	0.099	0.097	-0.05	59	11	30	0.462
715	168.6	272	0.568	0.047	0.207	-0.134	53.6	16.7	29.7	0.327

Table 2. Absorber CoFeSb

Temperature K	Velocity shift (mm sec ⁻¹)		Magnetic field (kOe)	B spectrum	Relative area %		FWHM (mm sec ⁻¹)			
	A	B			A	B	1st and 6th	2nd and 5th	3rd and 4th	4th
85	0.495	0.13	367	35.7	64.3	0.77	0.51	0.3	0.67	
293	0.438	0.06	361	35.6	64.4	0.65	0.47	0.35	0.66	

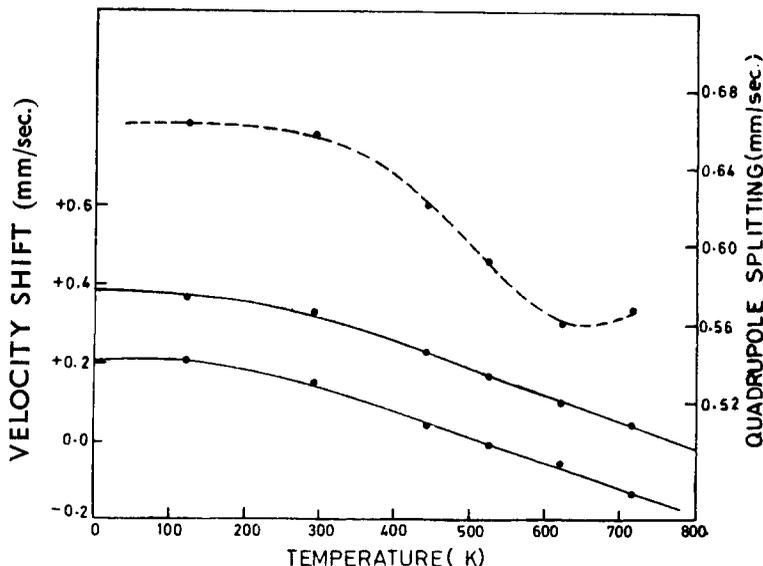


Figure 4. The temperature dependences of the velocity shifts of the spectra of nuclei at 2(a) and 2(d) sites with respect to the centre of iron metal spectrum at 293 K. The solid curve represents the least squares fit to the experimental points with the expression, $F(T) = \delta E_I^0 + \epsilon T - 7.306 \Theta_E \times [\frac{1}{2} + (\exp(\Theta_E/T) - 1)^{-1}] \times 10^{-4} \text{ mm sec}^{-1}$. The quadrupole splitting values for the nuclei at 2(a) sites, which are not magnetically ordered at these temperatures, are also shown in the figure.

by least squares fitting of the experimental data with the above function are shown in figure 4. The values of the parameters thus determined are:

for 2(a) site

$$\begin{aligned} \delta E_I^0 &= (0.66 \pm 0.01) \text{ mm sec}^{-1} \\ \epsilon &= -(7.0 \pm 1.0) \times 10^{-5} \text{ mm sec}^{-1} \text{ } ^\circ\text{K} \\ \Theta_E &= (750 \pm 20) \text{ K} \end{aligned}$$

for 2(d) site

$$\begin{aligned} \delta E_I^0 &= (0.41 \pm 0.01) \text{ mm sec}^{-1} \\ \epsilon &= (2.0 \pm 1.0) \times 10^{-5} \text{ mm sec}^{-1} \text{ } ^\circ\text{K} \\ \Theta_E &= (540 \pm 30) \text{ K} \end{aligned}$$

The spectrum of CoFeGe in an external magnetic field of 8 kOe, transverse to the direction of propagation of γ -rays, shows that the iron moments at the two magnetically ordered sites are ferromagnetically coupled.

The spectrum of FeMnGe at room temperature is shown in figure 5. The doublet has quadrupole splitting of 0.65 mm sec^{-1} and velocity shift 0.33 mm sec^{-1} with respect to iron metal absorber at room temperature, in agreement with the results of the earlier Mössbauer investigation (Fatehally *et al* 1969). The magnetically split spectrum is unresolved and very weak compared to the doublet. A rough estimate of the magnetic field gives the value $(155 \pm 10) \text{ kOe}$.

The spectra of CoFeSb at room temperature and 85 K are similar in shape. The paramagnetic line is broad, due to small quadrupole interaction. The magnetic spectrum, coexisting with the paramagnetic line, becomes broader at higher velocities, indicating small spread in the value of the internal field. Only the average value of the magnetic field has been determined. The following assumptions have been made in unfolding the spectra into the two component spectra A and B:

- (1) The linewidths of the pairs of lines, first and sixth, second and fifth, and third and fourth, are equal but different for different pairs
- (2) The quadrupole splitting is zero for the paramagnetic component.

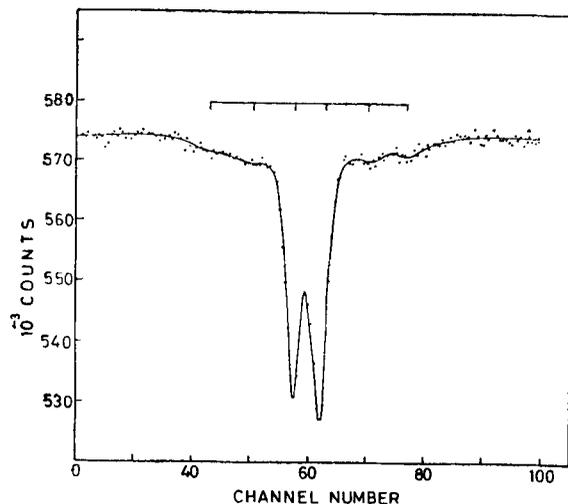


Figure 5. Mössbauer spectrum of FeMnGe at room temperature.

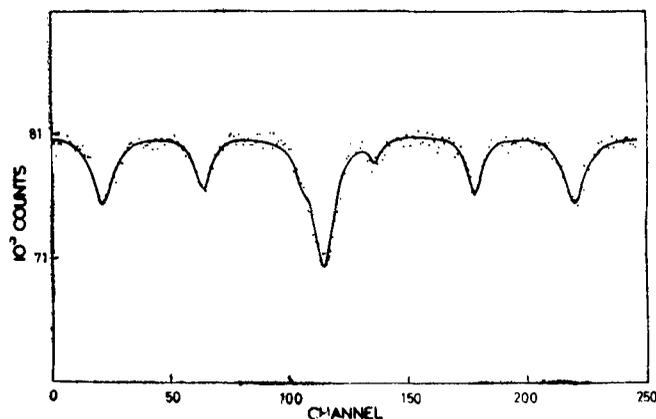


Figure 6. Mössbauer spectrum of CoFeSb at 293 K. The solid curve is obtained by least squares fitting the raw data with seven Lorentzian lines. The constraints used have been described in the text.

The results thus obtained are shown in table 2.

The value of the quadrupole splitting has been found to be negligible for the magnetically split spectrum B, at these temperatures. The spectra are shown in figure 6.

3. Discussion

The alloys with $B8_2$ type structure (figure 1) are formed by combining transition metals with elements of group III B, IV B, V B, or VI B of the periodic table. In $B8_1$ structure the hexagonal closed packed lattice is formed by 2 (*c*) sites and the transition elements sit in the 2 (*a*) interstices formed by the *hcp* lattice. In ionic compounds like FeS, where cations are smaller compared to anions, there is no deformation caused by filling of 2 (*a*) sites and the axial ratio is found to be 1.63. But as the ionic nature of the bond decreases, the axial ratio also decreases. In $B8_2$ type of structures, not only 2 (*a*) interstices but the 2 (*d*) interstices of the *hcp* lattice are also filled. In ternary alloys discussed here, like in other $B8_2$ type of alloys (Kanematsu 1962), the

axial ratio has been found to be close to 1.25. The interatomic distances in the three alloys are given in table 3. Evidently the volume available at 2 (*a*) sites is larger than at 2 (*d*) sites. This may be the reason for the large vacancy at 2 (*d*) sites, generally found in such alloys.

3.1 Distribution of iron at inequivalent sites

The area under the component spectrum is proportional to the product of the actual population of the site and the recoilless fraction appropriate to the atoms at these sites. In the expression of the recoilless fraction, the factor $(\Theta_D/T)^2$ occurs in the exponential. A difference in the value of Θ_D introduces temperature dependences in the fractional areas of the component spectra, even if the distribution of iron atoms remain unaltered.

The fractional area has been found to be temperature independent in CoFeSb and thus it is concluded that Θ_D is same for the atoms at inequivalent sites, and 35.7% of iron atoms occupy 2 (*a*) sites. On the other hand, the small spread observed in the value of the internal field of the magnetically split spectrum can arise from some contribution from iron nuclei at 2 (*c*) sites or it may be the result of local inhomogeneity in the near neighbour shell of the nuclei at 2 (*d*) sites. Thus it is uncertain whether the remaining 64.3% iron atoms occupy 2 (*d*) sites alone or are distributed between 2 (*c*) and 2 (*d*) sites, although the relative intensities of the lines in the x-ray diffraction pattern favour (Castelliz 1953) the later possibility.

In CoFeGe spectra, there is a tendency of the fractional area of 2 (*a*) site spectrum to decrease at low temperatures, which indicates that the Debye temperature appropriate to the thermal motions of the atoms at 2 (*a*) sites is higher than its value for the other sites. The values of Θ_E determined from the velocity shift data agrees with this conclusion, although there is large uncertainty (Perkins and Hazony 1972) in the values of Θ_E , thus determined, due to correlations between Θ_E and ϵ , and δE_I^0 and Θ_E in eq. 1. Nevertheless, it can be concluded that a maximum of 49% iron atoms occupy 2 (*a*) sites. The remaining atoms are distributed at 2 (*c*) and 2 (*d*) sites as shown in table 1.

3.2 Isomer shifts

The charge density at the nuclear site is related to the isomer shift by the relation

$$\delta E_I = \alpha |\psi(0)|^2 + \text{constant.} \quad (2)$$

Thus the isomer shift in the alloys relative to metallic iron absorber can be expressed as

$$\delta E_I - \delta E_{I_{Fe}} = \alpha [|\psi(0)|^2 - |\psi_{Fe}(0)|^2] \quad (3)$$

Table 3. The interatomic distances in the three alloys

Site	Symmetry	Neighbour	C.N.	Distances in Å		
				CoFeGe	CoFeSb	FeMnGe
2 (<i>a</i>)	$\bar{3}m$	2 (<i>a</i>)	2	2.51	2.57	2.59
		2 (<i>c</i>)	6	2.63	2.64	2.72
		2 (<i>d</i>)	6	2.63	2.64	2.72
2 (<i>c</i>)	$\bar{6}m2$	2 (<i>d</i>)	3	2.31	2.30	2.40
		2 (<i>d</i>)	2	2.51	2.57	2.59
		2 (<i>c</i>)	6	3.41	3.45	3.53

Here α is a nuclear constant and depends on the difference of the nuclear radii in the excited and ground states. Several authors have attempted to estimate the value of α by comparing the isomer shifts in ionic ferrous compounds and in iron metal absorber (Duff and Das 1971, Ingall 1967, Shinohara and Fujioka 1973), as well as by using the results of pressure experiments on iron metal (Drickamer *et al* 1969, Ingall *et al* 1967). Contributions to $|\psi(0)|^2$ from 1s, 2s and 3s electrons calculated by Watson (1960) for 3dⁿ free ion configurations have been used, and values of $|\psi_{4s}(0)|^2$ have been obtained using band calculations of iron metal (Duff and Das 1971, Ingall 1967). These estimates indicate that the value of α lies between -0.32 and $-0.4 a_0^3 \text{ mm sec}^{-1}$, although the value -0.37 has been preferred by several authors.

The velocity shift of the centre of the spectrum relative to the centre of iron metal spectrum at room temperature is given by

$$V_{\text{alloy}} - V_{\text{Fe}} = [\delta E_{\text{alloy}} - \delta E_{\text{Fe}}] - [\langle v^2 \rangle_{\text{alloy}} - \langle v^2 \rangle_{\text{Fe}}] / 2c \quad (4)$$

The last term depends on the thermal motions of the atoms in the alloy and iron metal. In CoFeGe alloy, this contribution at room temperature for 2 (a) and 2 (d) sites are -0.32 and $-0.27 \text{ mm sec}^{-1}$ respectively (using the Einstein model to describe $\langle v^2 \rangle$), whereas for iron metal the contribution is $-0.235 \text{ mm sec}^{-1}$ ($\Theta_E = 320 \text{ K}$, as determined by Lafleur and Goodman 1971). In CoFeSb alloy, on the other hand, this contribution is same for 2 (a) and 2 (d) site atoms, although the value is not known. It is, however, reasonable to assume a value of -0.3 mm sec^{-1} in CoFeSb, which is the average of the values found in CoFeGe alloy. Using these values, values of $[|\psi_{\text{Fe}}(0)|^2 - |\psi_s(0)|^2]$ can be estimated and are given in table 4.

In alloys, the changes in isomer shifts are not only due to changes in the number of electrons with s and d character, but also due to changes in the volume available to the atom at different sites in the alloy (Drickamer *et al* 1969). For example, in bcc iron the charge density at the nuclear site increases with decrease of volume due to external pressure, although there is little change in the number of s and d electrons. The increase in density results from the compression of the 4s-band as well as due to expansion of 3d-orbitals (Ingall 1967). In closed packed structures, however, s \rightarrow d transfer has been found to be significant (Drickamer *et al* 1969), which considerably reduces the increase of charge densities due to the above causes.

The large difference in the isomer shifts at 2 (a) and 2 (d) sites, however, cannot be due to changes in atomic volume alone (10% change in volume causes a change of $0.075 \text{ mm sec}^{-1}$ in isomer shifts in hcp metals; see Drickamer *et al* 1969) and indicates a difference in the number of electrons in the d-orbitals of the atomic configurations of the two sites. Theoretical values of $|\psi(0)|^2$ for different 3d-configurations

Table 4. The electron densities at the nuclear sites in the alloys ($|\psi_s(0)|^2$) compared to the value in iron metal at room temperature (assuming $\alpha = -0.37 a_0^3 \text{ mm sec}^{-1}$)

Alloy	$[\psi_{\text{Fe}}(0) ^2 - \psi_s(0) ^2] (a_0^{-3})$	
	S = 2(a)	S = 2(d)
CoFeGe ..	1.12	0.5
CoFeSb ..	1.36	0.34

show that a minimum of 0.3 electrons are more in the 3d orbital of 2 (a) site compared to 2 (d) site configuration, at the expense of s-electrons (Walker *et al* 1961). This is consistent with the observation that the moment of the atom at 2 (a) site is lower than the moment at 2 (d) site.

3.3 Magnetic fields

The internal fields at 2 (d) sites in CoFeGe and CoFeSb are not appreciably different from the value in iron metal. The spin dipolar contribution is expected to be small due to negligible ordered moment in the first coordination sphere of 2 (d) sites. The result indicates that the moment on iron atoms on these sites is nearly same as found in iron metal. This implies that spin up and spin down d-electron populations responsible for the magnetic moment of the parent atoms have been equally affected in these alloys in comparison to their occupation in iron metal. On the other hand, the magnetic splitting, at liquid nitrogen temperature, in the spectrum of FeMnGe corresponds to a low value of the internal magnetic field. The result is consistent with the observations (Gonser *et al* 1963, Nakamura and Masayuki 1967) that in antiferromagnetic environment, the internal field at iron nuclei is generally low. The moment on iron atom has also been found (Abrahams *et al* 1962) to be low in antiferromagnetic alloys ($\approx 0.7 \mu_B$) compared to the value ($\approx 2.2 \mu_B$) in ferromagnetic alloys. However, the crude proportionality between internal field at nucleus and the moment on the parent atom found in a number of ferromagnetic alloys, appears to break down in these cases.

An interesting feature of the results of neutron diffraction measurements on FeMnGe alloy is that while 2 (a) moments at (0, 0, 0) and (0, 0, $\frac{1}{2}$) are antiferromagnetically coupled, the mutual alignment of 2 (d) site moments is ferromagnetic. This shows that the influence of one sublattice on moments on another sublattice are weaker compared to intra sublattice interactions, which may be responsible for the existence of two transition temperatures in these alloys. When there is a tendency of successive 2 (a) layers, parallel to basal plane, to couple antiferromagnetically, the direct exchange between moments occupying 2 (d) sites with 2 (a) site moments in upper and lower layers are equal and opposite. The ordering of 2 (d) site moments will not depend on whether 2 (a) moments are ordered or not.

Neutron diffraction analysis (Murthy *et al* 1969) also showed that moments at 2 (d) sites alone are magnetically ordered at room temperature with the sublattice moment of $1.9 \mu_B$ per atom, and 80% of the iron atoms in the alloy occupy these ordered sites. On the other hand, the Mössbauer spectrum at 293 K shows that most of the iron nuclei contribute to a paramagnetic doublet with isomer shift close to the values determined for 2 (a) site spectra in CoFeGe and CoFeSb. The quadrupole splitting value is also close to the splitting of the doublet in CoFeGe spectrum. Moreover, the magnetic spectra of CoFeGe and CoFeSb alloys, corresponding to 2 (c) and 2 (d) sites with point symmetry $\bar{6}m2$, do not show appreciable quadrupole splittings. The asymmetry of the doublet at room temperature is not significant and results from the difference in the isomer shifts of the two component spectra.

Thus the discrepancy can be accounted for if the observed nuclear intensities in the neutron diffraction pattern of FeMnGe are also consistent with an alternative

arrangement of iron and manganese atoms in which a large fraction of iron occupies 2 (*a*) sites, which the neutron diffraction results show to be disordered at room temperature, or this indicates the presence of motional narrowing of the magnetic spectra due to superparamagnetism. The size of the cluster should be small because a magnetic field of 6 kG has been found unable to provide enough magnetic energy to stabilise the direction of magnetisation of the cluster. The ionic spin relaxation cannot give rise to such a behaviour due to the fact that, below the magnetic transition temperature, the magnetic splitting cannot be zero for any value of the relaxation time (Bhargava and Iyengar 1972).

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