The anomalous charge state of Fe in Mg(Fe,Cr)O$_4$: a Mossbauer study

The anomalous charge state of Fe in Mg(Fe,Cr)O$_4$: a Mössbauer study

M R Singh and S C Bhargava

Solid State Physics Division, Bhabha Atomic Research Centre, Bombay 400 085, India

Abstract. Iron in MgFeCrO$_4$ and MgFe$_{0.6}$Cr$_{1.4}$O$_4$ is expected to be in the Fe^{3+} charge state. Mössbauer spectroscopy, however, reveals the formation of a significant amount of Fe^{2+} state. The electric quadrupole interaction as well as the linewidth of the Mössbauer spectrum of Fe^{2+} show temperature dependences.

1. Introduction

Mg(Fe$_{2-x}$Cr$_x$)O$_4$ possesses a spinel structure. The magnesium and chromium ions in it are expected to be in the Mg^{2+} and Cr^{3+} ionic states, respectively, when the oxide is prepared in air using the conventional ceramic procedure. Thus, we expect iron to exist in the Fe^{3+} charge state only. This has also been the assumption in the earlier interpretation of the macroscopic magnetization studies [1].

   Mössbauer spectroscopy, which can distinguish between the charge states of iron unambiguously, shows the formation of a significant amount of Fe^{2+}, even though features which generally characterize the Fe^{3+} state are not completely lost. Thus, even though isomer shifts and quadrupole splittings are characteristic of the Fe^{2+} state, the hyperfine magnetic field is characteristic of the Fe^{3+} state. Similar anomalous formation of Fe^{2+} was reported earlier [2] in CuCr$_{2(1-x)}$Fe$_{2x}$O$_4$, in which iron is expected to be in the Fe^{3+} state, but a significant amount of Fe^{2+} was found to be formed.

2. Experimental details

MgFe$_{0.6}$Cr$_{1.4}$O$_4$ and MgFeCrO$_4$ were prepared using the conventional ceramic procedure. The appropriate quantities of MgO, Cr$_2$O$_3$ and Fe$_2$O$_3$ (99.99% purity) were thoroughly mixed under acetone, pelletized and sintered at 950 °C for 48 h with an intermediate grinding. The final sintering was done at 1400 °C for 3.5 h. X-ray analyses at ambient temperature showed the presence of the cubic spinel phase. The cell constants of MgFe$_{0.6}$Cr$_{1.4}$O$_4$ and MgFeCrO$_4$ are 8.341 Å and 8.357 Å, respectively. These values are reasonable considering the lattice constants of MgCr$_2$O$_4$ ($a = 8.333$ Å) and MgFe$_2$O$_4$ ($a = 8.387$ Å). No impurity phase was detectable. The x-ray lines were found to be sharp, which makes the detection of any impurity phase with even slightly different lattice constants easy. Specifically, no trace of

$FeCr_2O_4$, which has a cubic spinel structure at ambient temperature ($a = 8.379$ Å) and contains iron in the Fe^{2+} state, was found even though it would be distinctly seen.

Mössbauer spectra have been obtained using a spectrometer operated in the constant-acceleration mode for temperatures above the liquid-nitrogen temperature and another spectrometer, operated using sine-wave drive, for spectra at low temperatures. ^{57}Co in Rh is used as the Mössbauer source. The calibration is done using sodium nitroprusside absorber for paramagnetic spectra and iron foil for the magnetic spectra of the oxide. The temperatures are measured using a Cu–constantan thermocouple at temperatures above the liquid-nitrogen temperature and a carbon glass resistor at lower temperatures.

3. Results

The Mössbauer spectra of $MgFe_{0.6}Cr_{1.4}O_4$ in the paramagnetic state are shown in figure 1. The spectra have been fitted using the least-squares procedure with two symmetric doublets. The linewidths and depths are different for the two doublets but the same for the two components of any doublet. The results are given in table 1. The temperature dependences of the centre shifts, quadrupole splittings, linewidths and relative intensities characterizing the two doublets of $MgFe_{0.6}Cr_{1.4}O_4$ are plotted in figures 2–5.

The temperature dependences of the centre shifts of the two doublets, with respect to the sodium nitroprusside absorber at room temperature, are fitted with straight lines (figure 2). The linear temperature coefficients of the centre shifts are -5.173×10^{-4} and -7.887×10^{-4} mm s^{-1} K^{-1} for the two components. This is due to the second-order Doppler shifts. There is no anomaly in the temperature dependences of the centre shifts in the temperature range investigated. This shows that there is no phase change or change in valence state of Fe corresponding to either of the two components in the temperature range investigated. Such a change is expected to give an anomaly in the temperature dependence of the centre shift. The relative intensities of the two components are also independent of temperature. This also shows that the two components correspond to inequivalent ions which are independent of each other in the temperature range investigated. This is different from the behaviour found for $CuCr_{2(1-x)}Fe_{2x}O_4$ [2] in which the relative intensity of one of the two components increases and that of the other decreases simultaneously as the temperature changes. Thus, the origins of Fe^{2+} in the two cases are expected to be different.

The temperature dependences of the quadrupole splittings are shown in figure 3. One of the doublets has a low splitting which has no significant temperature dependence. The isomer shift shows that this component corresponds to the Fe^{3+} state. The other doublet has a large quadrupole splitting at lower temperatures, which decreases as the temperature increases and becomes small at the ambient temperature. Nevertheless, it is characterized by the isomer shift which is typical of iron in the Fe^{2+} state at all temperatures. Yet another remarkable feature of the second component is its large linewidth at 100 K, which decreases, together with the quadrupole splitting, as the temperature is increased (figure 4). This may be due to the presence of dynamical effects at 100 K in $MgFe_{0.6}Cr_{1.4}O_4$, which decrease as the temperature increases. The fluctuation frequency of the hyperfine field in this sample may be comparable with the nuclear precession frequency at 100 K and progressively becomes
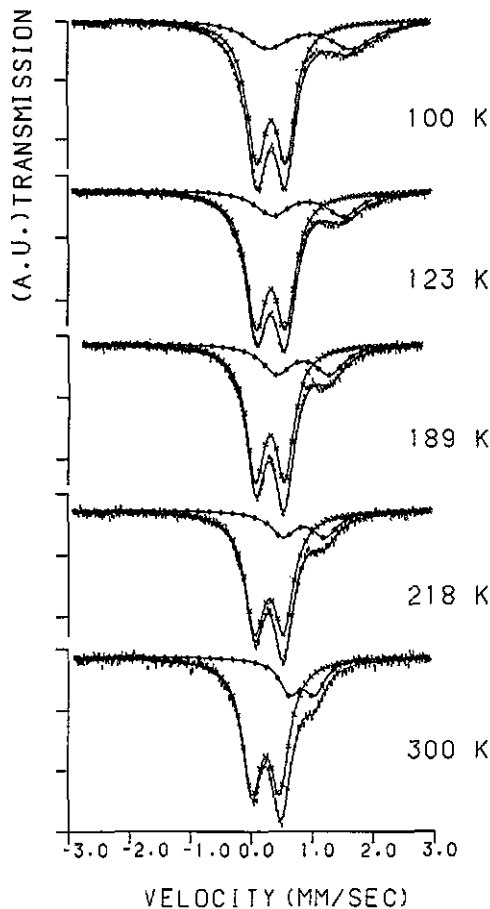
Figure 1. Mössbauer spectra of MgFe$_{0.6}$Cr$_{1.4}$O$_4$.

larger than the nuclear precession frequency as the temperature increases, such that the dynamical broadening disappears. The results imply that the origin of the line broadening at 100 K and the temperature variation in the electric field gradient (EFG) may be the same.

The spectra of MgFeCrO$_4$ and MgFe$_{0.6}$Cr$_{1.4}$O$_4$ at ambient temperature are similar, except for the different relative intensities of the two doublets (table 1). The spectra of MgFeCrO$_4$ at 4.2 K in zero field and in a longitudinal field of 3 T are shown in figure 6. The spectrum in the absence of a field is fitted with two sextets. It is assumed that the widths and depths of the pairs of corresponding lines in a sextet are equal. The area ratios of the three pairs of lines of the smaller component spectrum have been constrained to 3:2:1. This is necessitated by the large overlap of the two component spectra. The results are given in table 2. The spectrum in a field of 3 T cannot be fitted with two sextets alone. This is obvious from a visual inspection of the smaller sextets. The outer lines of a weaker sextet are narrow. If the inner lines of this sextet are also narrow, they must overlap with the inner lines of the intense sextet, because no separate narrow lines are experimentally observed. A fit assuming overlap of the inner lines gives an isomer shift characteristic of Fe^{3+}.

Table 1. Results of the analysis of Mössbauer spectra of MgFe$_{2-x}$Cr$_x$O$_4$ in the paramagnetic state. The isomer shift is with respect to sodium nitroprusside absorber.

| x	Temperature (K)	A site				B site			
		Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Γ (mm s^{-1})	Relative intensity (%)	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	Γ (mm s^{-1})	Relative intensity (%)
1.0	300	0.593	0.502	0.458	82.0	1.078	0.855	0.486	18.0
1.4	300	0.601	0.456	0.383	77.4	1.183	0.413	0.418	22.6
1.4	218	0.653	0.474	0.394	77.5	1.209	0.695	0.501	22.5
1.4	189	0.672	0.482	0.372	72.9	1.217	0.869	0.592	27.1
1.4	170	0.683	0.478	0.372	72.8	1.260	0.957	0.634	27.2
1.4	150	0.690	0.476	0.369	71.5	1.272	1.084	0.713	28.5
1.4	123	0.696	0.484	0.405	75.2	1.310	1.157	0.657	24.8
1.4	100	0.698	0.482	0.397	68.3	1.337	1.346	0.853	31.7
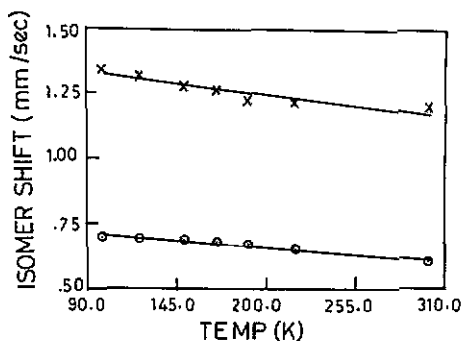
Figure 2. The temperature dependences of the centre shifts of the two component Mössbauer spectra of MgFe$_{0.6}$Cr$_{1.4}$O$_4$.
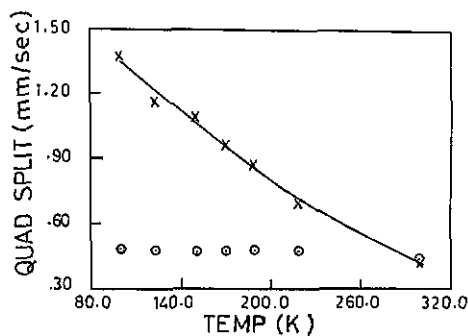

Figure 3. The temperature dependences of the quadrupole splittings of the two component Mössbauer spectra of MgFe$_{0.6}$Cr$_{1.4}$O$_4$.
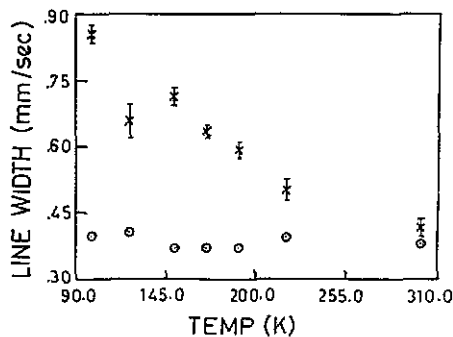

Figure 4. The temperature dependences of the linewidths of the two component Mössbauer spectra of MgFe$_{0.6}$Cr$_{1.4}$O$_4$.
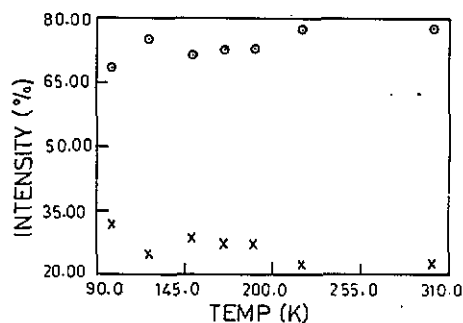

Figure 5. The temperature dependences of the relative intensities of the two component Mössbauer spectra of MgFe$_{0.6}$Cr$_{1.4}$O$_4$: ⊙, A sites; ×, B sites.

We do not expect this to correspond to the paramagnetic component with an isomer shift of Fe^{2+}. If we constrain isomer shift of the weaker sextet including outer narrow lines to Fe^{2+} like, the innermost lines are forced to be broader than outer lines. There is no known mechanism of line broadening which will broaden inner lines more than the outer lines of a sextet. Consequently, we fitted the spectrum in a field of 3 T with three sextets. The fit obtained is good. Two of the sextets belong to Fe^{3+} and the third belongs to Fe^{2+}. The analyses thus show that the external field splits the component spectrum of the Fe^{3+} ions occupying equivalent sites into two sextets. Such a phenomenon is, however, well known in ferrites [3–5] and is due to 'spin reversal', as explained later.

The two component spectra observed in the absence of any external field, corresponding to Fe^{3+} and Fe^{2+} ions, may originate from the same site or from inequivalent A and B sites of the spinel. The external field enables us to distinguish between the two possibilities as follows.

The two sublattices A and B of the ferrite are antiparallel to each other according to the Néel model of ferrimagnetism. When Yafet–Kittel non-collinearity appears on
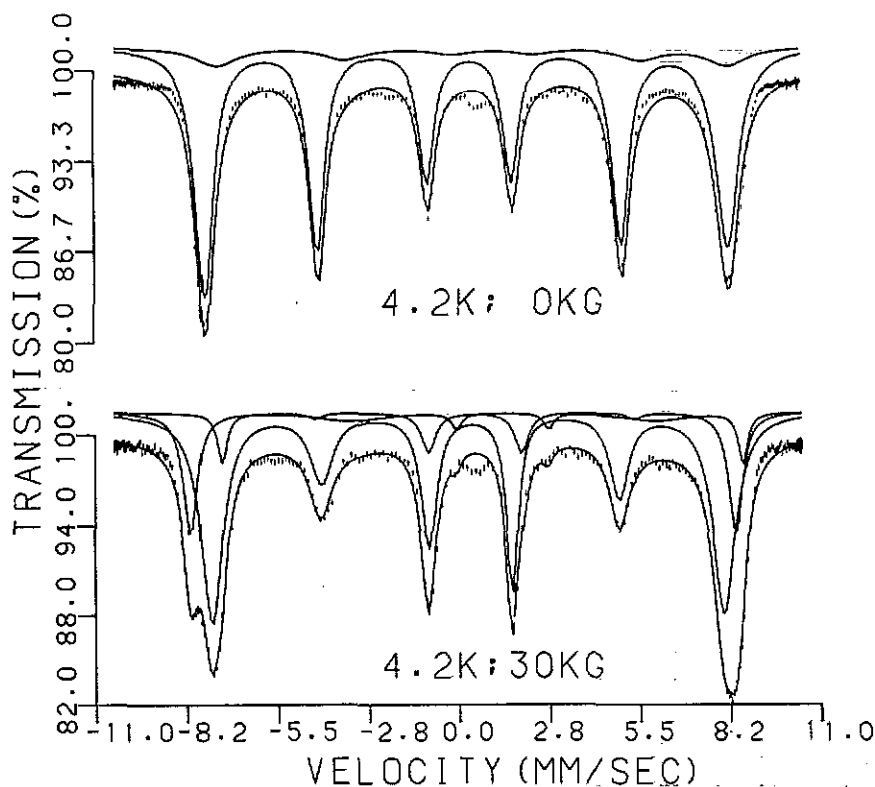
Figure 6. Mössbauer spectra of MgFeCrO$_4$ at 4.2 K in the presence of longitudinal external magnetic fields of 0 T and 3 T. The fitted curve and the component spectra are shown by full curves.

Table 2. Mössbauer parameters of MgFeCrO$_4$ at 4.2 K. The values for the isomer shift are with respect to α-Fe at ambient temperature and the quadrupole splitting is half the observed splitting.

H_{ext} (T)	Site	Isomer shift (mm s^{-1})	Quadrupole splitting (mm s^{-1})	H_{eff} (kG)	$I_{16}:I_{25}:I_{34}$	α_{YK} (deg)	Relative intensity (%)
0.0	A	0.396	−0.038	496.5	2.2:1.6 :1.0	0.0	85.0
0.0	B	0.83	−0.3	484.8	3.0:2.0 :1.0	0.0	15.0
3.0	A	0.38	−0.025	485.7	2.1:0.7 :1.0	67.3	71.0
3.0	A	0.33	−0.18	511.9	3.0:0.05:1.0	60.6	18.7
3.0	B	0.96	−0.29	485.5	3.0:3.8 :1.0	89.6	10.3

one of the sublattices, it splits it into two sublattices. The case when the B sublattice is split into two sublattices B$'$ and B$''$ is schematically shown in figure 7(a). The two sublattices B$'$ and B$''$ are oriented at an angle α_{YK} to the A sublattice. The external field affects the two component spectra similarly if they originate from ions at equivalent sites of sublattice A or B (B$'$ or B$''$).

On the contrary, if the two components correspond to ions at the two inequivalent sites A and B (B$'$ or B$''$), the two component spectra are affected differently, as shown in figure 7. The external field aligns the larger magnetization parallel to it and the
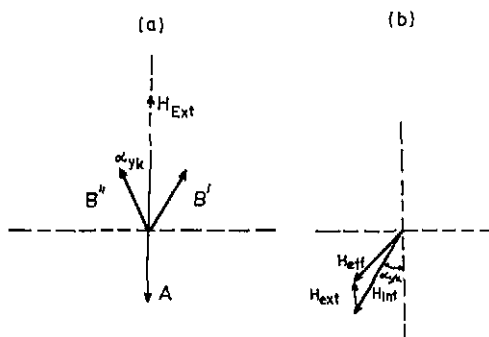
Figure 7. Schematic representation of non-collinearity angle α in the spinel structure. (*a*) The B sublattice splits into two sublattices B' and B''. (*b*) The external field affects the hyperfine field at the two sites as shown.

other sublattice magnetization antiparallel to it. The external field thus reduces the hyperfine magnetic field at one site and increases the field at the nuclei at other sites, in this case. The change in hyperfine field due to the external field in the presence of non-collinear spin structure is given by

$$H_{\text{eff}}^2 = H_{\text{int}}^2 + H_{\text{ext}}^2 \pm 2H_{\text{int}}H_{\text{ext}}\cos\alpha_{\text{YK}}. \tag{1}$$

The plus and minus signs correspond to when the magnetization of the sublattice is antiparallel and parallel, respectively, to H_{ext}. Thus, as a result of the application of the external field, the splitting of one of the components decreases, and that of the other increases. However, when the concentration of the diamagnetic ions is large, a third magnetic component appears because of the phenomenon of 'spin reversal' [3–5] as explained below.

The appearance of non-collinearity is related to weakening of the intersublattice exchange interaction in comparison with the intrasublattice interactions. This occurs when some of the magnetic ions on the other sublattice in the immediate neighbourhood are substituted by diamagnetic ions. In the present case, the Mg^{2+} ions are such diamagnetic ions. The non-collinearity angle increases as the number of diamagnetic ions in the neighbourhood increases. This neighbourhood of ions on a sublattice, however, varies as we go from site to site on the sublattice for statistical reasons also. The localized canting model [4] of non-collinearity takes into consideration the variation in the environments of different sites on a sublattice, which produces variation in non-collinearity from site to site. This model further shows that a fraction of ions on this sublattice have a finite probability that all their neighbouring sites are occupied by Mg^{2+}. For such ions which have all neighbouring sites occupied by diamagnetic ions, the non-collinearity angle exceeds 90° and is equal to $180° - \alpha_{\text{YK}}$ [3, 4]. The effect of the external field on such ions will be opposite to the effect on other ions with the non-collinearity angle α_{YK} less than 90°. Thus, there are ions on the sublattice with the non-collinearity angles $180° - \alpha_{\text{YK}}$. This is known as the 'spin reversal' of ions and has been found whenever the concentration of the diamagnetic ions is large [3, 5]. The effects of the external field will be opposite on the two types of Fe^{3+} ion; it reduces the hyperfine field at ions with non-collinearity angle α_{YK}, less than 90° and it increases the field at the ions with non-collinearity angle $180° - \alpha_{\text{YK}}$. Thus, the external field splits the component spectrum corresponding to Fe^{3+} further into two component spectra, as has been found in the present case.

4. Discussion

The presence of Fe^{2+} in the oxide shows the formation of either Cr^{4+} or vacant oxygen sites. Thus, the chemical formula should be either $Mg^{2+}Fe^{3+}_{0.82}Fe^{2+}_{0.18}Cr^{3+}O_{3.91}$ or $Mg^{2+}Fe^{3+}_{0.82}Fe^{2+}_{0.18}Cr^{3+}_{0.82}Cr^{4+}_{0.18}O_4$ or an intermediate composition, to satisfy the condition of charge neutrality.

The relative site stabilization energies of various ions for the two sites indicate that Mg^{2+}, Fe^{2+} and Cr^{3+} have strong preferences for the B sites in comparison with Fe^{3+} ions. It has been shown [6] that Cr^{3+} exclusively goes to the octahedral site. The relative preference of Mg^{2+} in comparison with Fe^{3+} for the B sites is well known from the fact that $MgFe_2O_4$ is a partially inverse spinel. Fe^{2+} ions too have a higher preference for the B site in comparison with Fe^{3+} ions, as is clear from the cation distribution in Fe_3O_4. Thus, we are inclined to think that the smaller component given in table 2 is caused by Fe^{2+} at the octahedral site. In this case, the magnetization of the A sublattice in $MgFeCrO_4$ is larger than that of the B sublattice. This, however, cannot be verified from the Mössbauer data.

The isomer shifts, quadrupole splittings and internal magnetic fields corresponding to the paramagnetic component spectrum with larger intensity are typical of the Fe^{3+} state. They do not show any significant temperature dependences. On the other hand, the hyperfine interaction parameters characterizing the other component show interesting behaviours. The centre shifts are typical of the Fe^{2+} state and show no significant temperature dependence. The relative areas of the two component spectra also have no appreciable temperature dependences. This implies that the ionic state corresponding to the smaller component in $Mg(Fe,Cr)O_4$ is $2+$ at any temperature and the temperature dependence of the electric quadrupole interaction which is discussed below is not due to a transformation from the $3+$ to the $2+$ state. This is different from the behaviour observed for $CuCr_{2-x}Fe_xO_4$ [2] in which the relative intensities of Fe^{3+} and Fe^{2+} showed strong temperature dependences. The presence of Fe^{2+} ions in the oxides is surprising. The magnesium and chromium ions are in the $2+$ and the $3+$ states, respectively. Thus, we expect Fe to be in the $3+$ state only.

The hyperfine magnetic field corresponding to the smaller component in the spectrum of $MgFeCrO_4$ at 4.2 K is, however, large and characteristic of the Fe^{3+} state, although the centre shift of this sextet is characteristic of the Fe^{2+} state and the lines are broader. Thus, the positive contribution to it from the orbital moment is small, which is expected also because of its complete quenching in the singlet ground state as discussed below.

The effect of the external field shows that the two components correspond to the two inequivalent sites of the spinel. It is, however, not possible to assign uniquely the two components to the two sites on the basis of Mössbauer data alone. Nevertheless, the known preference of Mg^{2+}, Fe^{2+} and Cr^{3+} for the B sites of the spinel indicates that the component with the smaller intensity which corresponds to Fe^{2+} originates from B sites, and the stronger component which corresponds to Fe^{3+} originates from A sites.

We consider the possibility of either of the two components originating from the presence of Fe^{2+} and Fe^{3+} at the same sublattice, as in Fe_3O_4. This possibility is ruled out for the stronger component in the spectrum of $MgFe_{0.6}Cr_{1.4}O_4$ as it is characterized by temperature-independent parameters characteristic of Fe^{3+} in the temperature range investigated. Thus, we consider the possibility of the weaker

component, which has a temperature-dependent EFG and linewidth, originating from a combination of Fe^{2+} and Fe^{3+}. Such a phenomenon is well known in Fe_3O_4. At low temperatures, when the electron hopping frequency between Fe^{2+} and Fe^{3+} ions at B sites is low, the two ions give separate component spectra. Above the Verwey transition temperature of 112 K, the two components merge to give a single average spectrum. The isomer shift in Fe_3O_4 also changes from an average of the two ionic states at higher temperatures to two distinct values corresponding to the two ionic states as the temperature is lowered, which lowers the hopping frequency. In our case the smaller component is not split into two doublets as the temperature is lowered to 100 K and the isomer shift is also temperature independent. We thus rule out the possibility of electron hopping in our sample.

The EFG has two contributions:

$$V = (1 - \tau_\infty)V_{\text{lattice}} + (1 - R)V_{\text{valence}}.$$

The Sternheimer shielding factors τ_∞ and R are approximately -10 and 0.3, respectively. The lattice contribution has little temperature dependence (in the absence of a phase transition) and is generally about 10% of the valence contribution. V_{valence} has a temperature dependence. The lattice decides the electronic energy states and their splittings. In the high-spin state of Fe^{2+}, the sixth valence electron alone contributes to the EFG. The contribution depends on the states which are thermally populated at the experimental temperatures. When the ion occurs at the octahedral site, the t_{2g} states are low lying and the e_g states are not thermally populated at ambient temperature. The trigonal distortion of the octahedral environment results in an orbital singlet and a doublet, which alone can be thermally populated at the temperatures of interest. In the case of elongation along the (111) axis, the doublet has a lower energy. On the other hand, in the case of compression along the trigonal axis, the singlet has a lower energy. In cubic spinels the close packing of oxygen ions leaves little space at the tetrahedral site. Therefore the occupancy of this site by a cation is expected to cause a trigonal compression at the adjacent octahedral site along $\langle 111 \rangle$ and consequently the singlet state may have a lower energy. As the temperature increases, the excited states with different contributions to the EFG become thermally populated, thereby making the EFG temperature dependent. Accordingly, we have fitted the quadrupole splitting values for Fe^{2+} in $MgFe_{0.6}Cr_{1.4}O_4$ at various temperatures with the expression [7]

$$V_{zz} = V_{zz}^{\text{lat}} + V_{zz}^{\text{val}}(0)\{[1 - \exp(-\delta/kT)]/[1 + 2\exp(-\delta/kT)]\}.$$

The fitted curve is shown as a full curve in figure 3, where $\delta = 267.7$ cm^{-1} (385.2 K), $V_{zz}^{\text{lat}} = -0.4886$ and $V_{zz}^{\text{val}} = 1.9439$. The observed lattice contribution is about 25% of the valence contribution. This process is, however, not associated with any dynamical effects in the Mössbauer spectrum, but line broadening experimentally found to be present can be explained as follows. The requirement of charge neutrality implies that Fe^{2+} is accompanied by the formation of Cr^{4+} ions or there are vacancies in the oxygen environment of the Fe^{2+} ion. The disorder in the distribution of the Cr^{4+} ions (or vacant oxygen sites) can result in a variation in the ionic level splitting of the Fe^{2+} ion from site to site. At low temperatures, when the excited state is not significantly populated for any of the Fe^{2+} ions, the EFG due to the ground singlet is large and the lines are not broadened. At high temperatures, when the singlet and the

excited doublet are equally populated for any of the Fe^{2+} ions, the EFG is the same at all the sites and the lines are not broadened again. At intermediate temperatures, when the thermal populations of the excited electronic states are different at different sites, the EFG will vary from site to site and consequently the lines will appear broad and the fit to Lorentzian lines will be of poor quality. This explanation does not require the presence of any dynamical effects in the Mössbauer spectrum.

This randomness in the environment broadens lines in a magnetic sextet also. The randomness introduces variation in the angle θ between the direction of spin moment and V_{zz} from site to site, which broadens all the lines of a sextet equally. The line shift due to the quadrupole interaction is proportional to $(e^2Qq/2)[(3\cos^2\theta-1)/2]$ and is thus larger for Fe^{2+} than for Fe^{3+}, for which e^2qQ is smaller. The external field reduces this variation by aligning spin moments and thus narrows the lines of the sextet also. This is clearly seen in the magnetic spectrum of Fe^{2+}.

Another mechanism which can lead to a reduction in EFG as the temperature increases as well as the fluctuation effects is the Jahn–Teller effect. This has been found in several cases when Fe^{2+} occupies A sites. At low temperatures, static Jahn–Teller distortion occurs in any of the three distortions of the oxygen tetrahedra of minimum energy [8]. In this case, the EFG corresponds to the distorted environment and is large. As the temperature increses, the system acquires dynamical behaviour, where the tetrahedra keep on distorting dynamically in all possible directions of minimum energy, thereby averaging the EFG to a smaller value over the period of nuclear Larmor precession.

In the cases of ions occupying octahedral sites, when elongation along the $\langle 111 \rangle$ axis occurs, an orbital doublet is the ground state and can lead to a Jahn–Teller distortion, although no example of such a distortion in spinel is known. The presence of Jahn–Teller distortion when Fe^{2+} occupies octahedral sites has, however, been identified in other structures, such as $KMgF_3$.

5. Conclusions

In $MgFe_{2-x}Cr_xO_4$, we find Fe^{2+} ions which are not expected. This indicates either the formation of Cr^{4+} or the appearance of vacancies at the oxygen sites. The temperature dependence of the EFG is due to the increase in the population of the electronic excited state on increase in temperature. The disorder in the distribution of the Cr^{4+} ions (or vacant oxygen sites) can result in line broadening, which is experimentally observed at 100 K.

References

[1] Blasse G 1964 *Philips Res. Rep. Suppl.* **3** 84
[2] Gerard A and Grandjean F 1979 *J. Phys. C: Solid State Phys.* **12** 4601
[3] Bhargava S C 1985 *Hyperfine Interact.* **22–24** 435
[4] Rosencwaig A 1970 *Can. J. Phys.* **48** 2857
[5] Morrish A H and Clark P E 1975 *Phys. Rev.* B **11** 278
[6] Romeijn F C 1953 *Philips Res. Rep.* **8** 304
[7] Hartmann-Boutron F and Imbert P 1968 *J. Appl. Phys.* **39** 775
[8] Tanaka M, Tokoro T and Aiyama Y 1966 *J. Phys. Soc. Japan* **21** 262