

Investigation of the MgO:Fe System using the Mössbauer Effect

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The MgO:Fe system as subjected to a variety of heat-treatments has been studied using the Mössbauer effect for Fe⁵⁷. On firing the MgO:Fe samples in air, iron initially dissolves in the lattice in its ferric state and is associated with a charge-compensating vacancy. However, on exceeding a certain concentration, magnesioferrite precipitates out. Hydrogen firing of these samples tends to create clusters of metallic iron and Fe²⁺ at Mg²⁺ sites. On refiring the samples in air, metallic iron is converted to Fe₂O₃ and Fe²⁺ to Fe³⁺ which subsequently reacts with the lattice to give magnesioferrite and a small fraction of Fe³⁺ dissolved in the lattice. These changes are found to be completely reversible. In some cases the magnesioferrite particle size is so small that it exhibits superparamagnetism. Although there is a limit to the solubility of Fe³⁺ in MgO, Fe²⁺ can be dissolved to any extent.

1. Introduction

The magnetic, electric and mechanical properties of the Mg-Fe-O system have attracted considerable attention in recent years because of the variety of its applications. These studies, particularly in the region of high concentration of iron have shown that the mechanical properties of the system depend sensitively on the heat-treatment given to the system. Thus, Groves and Fine [1] have observed that samples quenched from 1400° C in air showed considerable strengthening presumably due to the formation of Fe³⁺ in the lattice. Similarly, Phillips *et al* [2] have reported that MgO crystals containing 2% Fe/Fe + Mg are single phase at 1400° C in air, but on quenching and annealing below 1100° C, there is a possibility of forming a precipitate of magnesioferrite. Blackman [3] on the other hand tried to investigate the formation of ferrous ions in the system from the point of view of its effects on the microwave properties of magnesioferrite. In addition to the formation of Fe²⁺, Fe³⁺ and ferrimagnetic magnesioferrite in the MgO lattice, there is a possibility of precipitation of bcc metallic iron in MgO in view of certain dimensional relationships that were shown by Davidge [4] to exist between these two structures. All these different forms can perhaps be formed

by giving suitable heat-treatment and changing the iron concentration. The Mössbauer effect for Fe⁵⁷ is an excellent tool for detecting these various forms and determining precisely the conditions under which a particular form may be expected.

The Mössbauer effect – i.e. the resonance fluorescence of gamma rays or the zero phonon emission and absorption of gamma rays is realised when the emitting and absorbing nuclei are embedded in well bound crystal lattices. Under these conditions, Mössbauer showed that the recoil momentum during the emission and absorption of a gamma ray is taken up by the entire crystal, with the result that the emitted or absorbed gamma ray has complete transition energy. It was also shown that when the emitting and absorbing nuclei are embedded in well bound crystal lattices, the gamma emission and absorption in most cases takes place without any change in the phonon occupation number of the lattice. The probability of zero phonon process is referred to as the *f*-factor or the Lamb-Mössbauer factor and is similar to the Debye-Waller factor in X-ray scattering. When the lattice is not excited during gamma ray emission, the line width is determined entirely by the life-time of the nucleus in the excited state. In the

case of the 14.4 keV emission of Fe^{57} the line width of the gamma rays emitted during the zero phonon emission is 4.19×10^{-9} eV. This implies that one can detect and measure a change in energy levels of the nucleus of an order of 10^{-9} eV, or the accuracy in the determination of gamma ray energy is 1 part in 10^{18} . This makes it the most well defined electromagnetic radiation available for physical measurement.

In view of the accuracy obtainable in the Mössbauer effect, it has become possible to determine a variety of hyperfine interactions which nuclei have with the surrounding electron cloud. These interactions are (i) electric monopole interaction between the positively charged nucleus and the effective s electron density at the nucleus, (ii) electric quadrupole interaction between the quadrupole moment of the nucleus and the electric field gradient at the nucleus arising out of the asymmetric distribution of charges associated with the ion or in the crystal lattice, and (iii) magnetic dipole interaction between the magnetic moment of the nucleus and the hyperfine magnetic field at the nucleus. The electric monopole interaction is reflected by a shift of the centre of the spectrum called the isomer shift and yields information about the s electron density at the nucleus, and consequently the valence state of the ion. The quadrupole interaction and the magnetic dipole interaction cause splitting of the line, the amount of splitting giving information about the electric field gradient (efg) and the magnetic field (hf) at the nucleus.

Shirane *et al* [5] employed Mössbauer spectroscopy to study the FeO:MgO system and observed the Fe^{2+} state in MgO with a quadrupole interaction which was independent of concentration. On the other hand Simkin *et al* [6] have reported superparamagnetism of Fe^{2+} in MgO and have observed concentration-dependent quadrupole interaction. During our detailed investigation of this system, we observed divalent Fe, vacancy associated Fe^{3+} , ferromagnetic magnesioferrite, ferromagnetic bcc iron and antiferromagnetic Fe_2O_3 . This paper reports the results of our studies on MgO samples containing an iron concentration of more than 0.5 at. %.

2. Experimental

2.1. Sample Preparation

The iron-doped MgO absorbers were prepared

following the usual ceramic technique. The appropriate amounts of "specpure" (Johnson Matthey & Co) MgO and isotopically enriched $\text{Fe}_2^{57}\text{O}_3$ were taken and thoroughly mixed in an agate mortar. The mixture was then pressed into pellets and heated in air at 1000°C for 3 h. After cooling, the pellets were crushed, mixed, pressed and fired again in air at the same temperature for another 3 h. After this firing schedule, the pellets were crushed and the powder compressed into discs with the optimum thickness used for Mössbauer spectroscopy. The concentration of iron ranged between 0.5 and 8.0 at. %.

2.2. Mössbauer Spectrometer

The Mössbauer spectra were obtained using a conventional constant velocity mechanical drive reported earlier [7] in conjunction with a $\text{Co}^{57}:\text{Cu}$ source. The absorber was kept stationary. The usual velocity convention has been followed and the isomer shifts (IS) are given with respect to the copper source. The drive was calibrated using standard iron and Fe_2O_3 absorbers. With suitable arrangements, the spectra could be taken at any temperature between 78 and 700°K . In some cases, the absorbers were enclosed in a chamber which could be heated, and through which either hydrogen or argon could be made to flow.

3. Results and Discussion

The sample containing 0.5 at. % of iron ($(\text{Fe}/\text{Fe} + \text{Mg}) \times 100$) was heated in air at 1000°C for 4 h and was matched against a standard $\text{Co}^{57}:\text{Cu}$ source. The resulting spectrum is shown in fig. 1a. For a number of reasons such as isomer shift, nature of the host lattice, etc, the spectrum can be assigned to the quadrupole split partners of the Fe^{3+} state. The isomer shift is $+0.15 \pm 0.05$ mm/sec and the quadrupole interaction is 0.7 ± 0.05 mm/sec. The quadrupole splitting for the ferric ion in MgO cubic lattice is not altogether unexpected. MgO is a divalent lattice and hence for every pair of Fe^{3+} ions, there should be one charge compensating a Mg^{2+} vacancy. If this vacancy is associated with the Fe^{3+} ion then one can understand the occurrence of large efg at the Fe^{3+} site. Gonsler *et al* [8] tried to investigate the direction along which the associated vacancy might be situated. There are two possible directions viz $\langle 110 \rangle$ and $\langle 100 \rangle$. Using the point charge calculations, the observed efg can be explained satisfactorily if one assumes that the vacancies lie along the

$\langle 110 \rangle$ directions. It may be mentioned that in this sample in addition to the vacancy associated Fe^{3+} ion, a small quantity of unassociated Fe^{3+} is also present. For samples with lower concentration this fraction is totally absent.

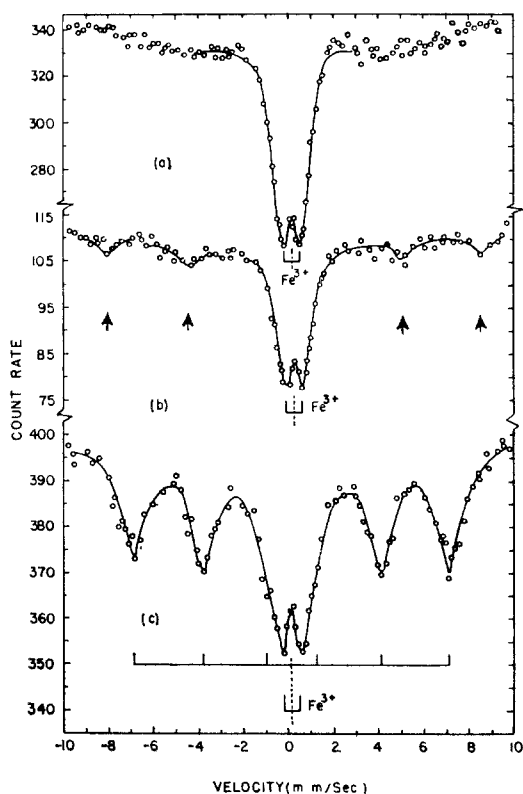


Figure 1 (a) Spectrum of sample containing 0.5 at. % Fe at 300° K. (b) Spectrum of the same sample at 78° K. (c) Spectrum of a sample containing 1.8 at. % Fe at 300° K.

In addition to the dominant quadrupole split partners at the centre, wings can be observed in the higher velocity region. The same sample was examined at 78° K (fig. 1b). Because of an enhanced f -factor at lower temperatures, the spectrum at 78° K shows the existence of a magnetic phase through the Zeeman split six finger pattern. It may be pointed out that the fraction precipitating out as a magnetic phase at this concentration is extremely small and just detectable. Indeed at lower concentrations there is hardly any evidence for the formation of a magnetic phase. In order to confirm the existence of a magnetic phase and to study it in detail, another sample containing 1.8 at. % iron was studied. This sample was identically treated and

its spectrum is shown in fig. 1c. This spectrum clearly indicates the precipitation of a magnetic phase. Although the relative amount of Fe^{3+} as compared to the magnetic phase is much less in this sample, the actual amount of Fe^{3+} appearing as dissolved in the lattice is nearly the same as in the lower concentration sample. This indicates that there is limit to the solubility of Fe^{3+} in the MgO lattice. After this limit is exceeded, the magnetic phase seems to precipitate out. At still higher concentration, it is expected that the magnetic phase would dominate, and that relatively, the amount of Fe^{3+} in MgO would be minute. Fig. 4a shows a spectrum corresponding to an 8% Fe/Fe + Mg sample treated similarly. In this sample we have used normal iron, in which Fe^{57} abundance is 2%, instead of enriched iron. This spectrum very convincingly demonstrates the existence of the magnetic phase while Fe^{3+} is hardly detectable, perhaps because natural iron was used. These studies clearly show that at low concentration most of the iron dissolves as Fe^{3+} associated with a vacancy. As the concentration is increased there is an indication of the existence of small concentrations of unassociated Fe^{3+} . On increasing the concentration further, beyond a certain limit (the solubility limit for Fe^{3+} in MgO), one observes a distinct magnetic phase precipitating out, whose concentration increases linearly as the iron concentration is increased.

For some time, the magnetic phase was mistakenly thought to be due to unreacted Fe_2O_3 , but several considerations at once show that this is not the case. The hf split spectrum of the magnetic phase is symmetrical without any evidence of quadrupole interaction and gives the hf field of 445 kOe as against the field [9] of 515 kOe corresponding to Fe_2O_3 . The temperature variation of this field was studied and its Curie temperature was determined by the stationary absorber method [10] to be $315 \pm 10^\circ \text{C}$. These considerations and particularly the phase diagram reported by Phillips [2] showed conclusively that this magnetic phase corresponded to magnesioferrite MgFe_2O_4 . It may be pointed out that the Zeeman split lines are broad. This is not surprising in view of the recent observation of Housley and Gonser [11] suggesting that in this mixed ferrite, there is a possibility of two patterns, both giving nearly the same field, 450 kOe, and superposed one over the other. These two patterns can be distinguished by applying an external magnetic field, and arise out of two non-

equivalent sites. The Curie temperature of $315 \pm 10^\circ \text{C}$ observed in our experiment agrees with that reported by Dekker [12] and yields a magnetic moment of $1.1 \mu_B$ per molecule of MgFe_2O_4 . Gorter [13] has shown that this value is possible for $\text{Mg}_x\text{Fe}_{1-x}(\text{Mg}_{1-x}\text{Fe}_{1+x})\text{O}_4$ with $x = 0.11$. It should be noted that x can be altered by giving suitable heat-treatment.

The nucleation of magnesioferrite in the MgO lattice is rather easy. Magnesioferrite is formed by aggregating Fe^{3+} ions and vacant Mg^{2+} sites on the cation lattice and moving half of the Fe^{3+} ions into tetrahedral interstices. Magnesioferrite forms with its $\{111\}$ planes in common with those of MgO matrix. These planes provide a low energy interface since $\{111\}$ planes in both these structures contain identical sheets of close packed O^{2-} ions and hence no movement of large O^{2-} ions is involved.

3.1. Effect of Heat-Treatment

These samples were subjected to a variety of heat-treatments and very interesting results were obtained. Fig. 2 shows the series of spectra for the 0.5% iron concentration sample, when it was subjected to firing at various temperatures in a hydrogen atmosphere. Fig. 1a is the spectrum of the same sample fired in air at 1000°C . On firing this sample in hydrogen at 780°C , we obtain a spectrum as shown in fig. 2a. This spectrum shows the existence of a magnetic phase and also of Fe^{2+} ions dissolved in the lattice. The hf associated with the Zeeman split spectrum is 330 kOe at room temperature with an isomer shift of -0.15 mm/sec . The Zeeman split spectrum is symmetrical and there is no evidence of any quadrupole interaction superposed over magnetic splitting. The magnitude of the hf field, its temperature variation and the isomer shift all indicate that this magnetic phase is bcc metallic iron. In addition to the disappearance of the ferrite phase and the precipitation of bcc metallic iron instead, one observes the emergence of an Fe^{2+} spectrum. As the firing temperature is increased, more and more Fe^{3+} ions are converted into Fe^{2+} . However, there is no change in the intensity of the bcc metallic iron spectrum. It is interesting to see that Fe^{2+} is a single line showing no evidence whatsoever of quadrupole interaction. Even at higher concentrations, a typical case of which is shown in fig. 4b, it is seen that hydrogen firing causes the ferrite to convert into bcc iron. Since, in this sample, natural iron was used, Fe^{3+} in the lattice

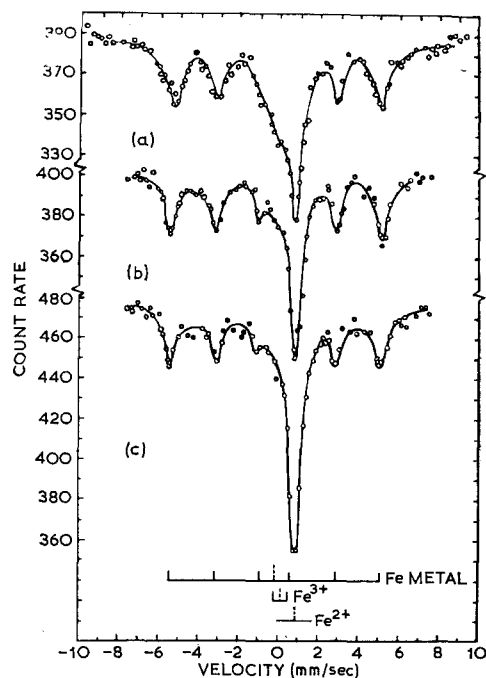


Figure 2 Spectra at 300°K of sample of fig. 1a after it had been fired in hydrogen at successively higher temperatures: (a) at 780°C , (b) at 900°C , (c) at 1100°C .

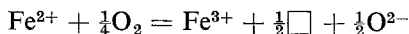
could not be detected in air fired samples (fig. 4a) and perhaps for the same reason, the Fe^{2+} dissolved in the lattice arising out of the conversion of Fe^{3+} on hydrogen firing cannot be detected. It may be mentioned that although ferrite is easily and quickly converted into metallic iron on hydrogen firing, the conversion of Fe^{3+} into Fe^{2+} is a comparatively slow process. We tried to investigate the intermediate stages through which ferrite converts itself into metallic iron, but we could not obtain any evidence of an intermediate phase. It appears that the conversion of ferrite into metallic iron proceeds in one step and there is no intermediate compound formed.

We also tried to reduce the lattice in vacuum instead of in hydrogen. However, on vacuum-firing no metallic iron spectrum was observed. Vacuum-firing merely causes the conversion of Fe^{3+} into Fe^{2+} . It appears that, as in other oxide lattices such as Al_2O_3 [14], SrTiO_3 [15], heating in hydrogen is essential for the formation of metallic iron clusters. The exact mechanism for this process is not known but several authors [16, 17] have suggested that the formation of OH^- ions in the lattice during hydrogen firing

helps the formation of metallic iron clusters. It may be of interest to recall the observation of Davidge [4] who reported the precipitation of bcc iron in similar samples, due to hydrogen firing. An X-ray oscillation photograph showed detectable diffraction due to bcc iron with the orientation $[000]_{\text{MgO}} \parallel [001]_{\text{Fe}}$ and $[110]_{\text{MgO}} \parallel [100]_{\text{Fe}}$. The two structures have a dimensional relationship such that

$$\begin{aligned} d[100]_{\text{MgO}} (2.98 \text{ \AA}) &\simeq d[100]_{\text{Fe}} (2.78 \text{ \AA}) \\ 2d[001]_{\text{MgO}} (8.42 \text{ \AA}) &\simeq 3d[001]_{\text{Fe}} (8.61 \text{ \AA}). \end{aligned}$$

To see whether the effects produced on hydrogen-firing are reversible, the samples were heated in air at successively higher temperatures. The series of spectra thus obtained are shown in fig. 3. When the hydrogen-treated sample which exhibited metallic iron and Fe^{2+} dissolved in the lattice (fig. 2c), was heated in air at 525°C , we obtained the spectrum as shown in fig. 3a. This spectrum clearly shows the partial conversion of Fe^{2+} to Fe^{3+} and the precipitation of yet another magnetic phase. On analysing the spectrum, it was clear that this magnetic phase corresponds to Fe_2O_3 ($H_n = 515 \text{ kOe}$, IS 0.15 mm/sec.). The oxidation of Fe^{2+} to Fe^{3+} in MgO can be regarded in several ways depending upon the precise form of Fe^{3+} . If Fe^{3+} is unassociated as happens in the early stages of oxidation, we can write



where \square represents a vacant Mg^{2+} site. High total Fe content will favour a low $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio. However, an association reaction between Fe^{3+} ions and vacancies may occur to form dimers or trimers. This vacancy association as has been shown earlier takes place along $\langle 110 \rangle$ directions. The conversion of metallic iron to Fe_2O_3 due to air-firing is understandable because metallic iron existed as a distinct phase in the MgO lattice.

On subsequent firing at 700°C , one obtains a spectrum as shown in fig. 3b. This spectrum is complex: the Fe^{2+} has been converted into vacancy associated Fe^{3+} ; superposed on this is another spectrum which shows faint ferrite lines with wings. Fig. 3c shows the spectrum for the same sample at 78°K . The wings which existed in fig. 3b have disappeared and instead the ferrite lines have become quite prominent. These changes could possibly be explained on two grounds. On lowering the temperature, the f -factor may have increased considerably so that

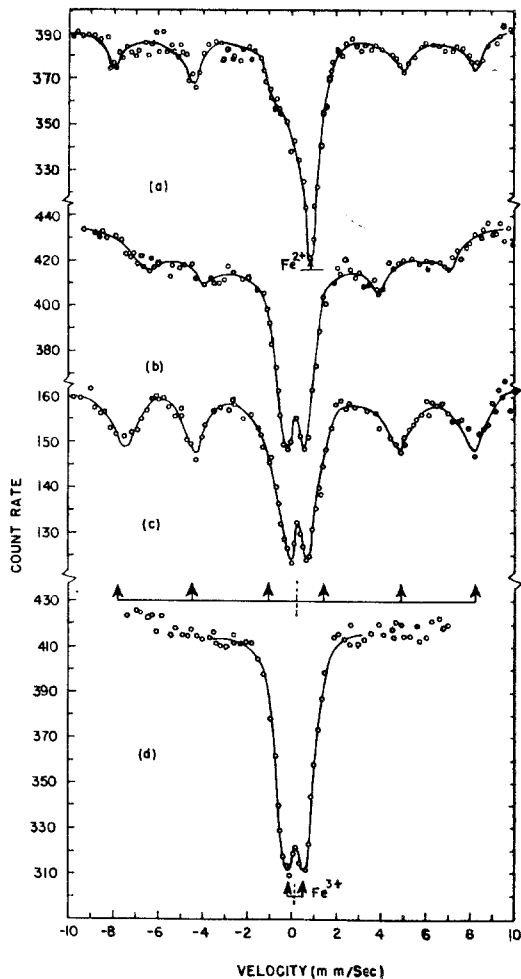


Figure 3 Spectra of the sample of fig. 2c after it had been fired in air at successively higher temperatures: (a) fired at 525°C , (b) fired at 700°C , (c) sample of fig. 3b examined at 78°K , (d) fired at 900°K .

the ferrite lines become prominent. However, one cannot explain the disappearance of the wings on this assumption. Furthermore, the intensity of the Fe^{3+} spectrum has not changed considerably due to cooling. The other possibility is that in this sample we have clusters of ferrite of various sizes such that there are some clusters which exhibit superparamagnetism and for which the particle relaxation time [18], $\tau \propto e^{\kappa V / k_{\beta} T}$, is much smaller than the Larmor precession time (the time required for the spin vector to precess around the magnetic field axis). For such clusters, one would obtain an unrelaxed single line spectrum indicating zero time averaged field at the nucleus. Such spectra have

been observed for small Fe_2O_3 [19], NiO [20] and ferrite [21] particles. On lowering the temperature, the relaxation time increased. If the relaxation time is greater than the Larmor precession time, these clusters would give a well resolved Zeeman split spectrum, indicating the existence of a finite time averaged field at the nucleus. That this seems to be a valid explanation for the changes observed on lowering the temperature is further confirmed by the observation of the spectrum of the same sample at 150°C . At 150°C , the magnetic lines are totally absent and instead there is a central line associated with wings. Gonsler *et al* [22] has very recently reported superparamagnetism of magnesioferrite small particles.

If this sample is further heated in air at 900°C , one obtains a relatively simple spectrum (fig. 3d) which is similar to that shown in fig. 1a. This shows that the effects of hydrogen-firing can be reversed by heating the hydrogen-fired samples in air at fairly high temperatures. This figure does not show any evidence for the existence of ferrite. All the iron in the sample now exists in the form of Fe^{3+} at Mg^{2+} sites associated with a charge compensating vacancy. It is significant to note that the ferrite which existed in samples heated at 700°C (figs. 3b and c) has disappeared and dissolved in the lattice. This is understandable if one assumes that the limit of solubility for Fe^{3+} in MgO decreases as the temperature is reduced. At 700°C , all the iron could not be assimilated in MgO as Fe^{3+} and hence ferrite precipitated out. However, at 900°C , the solubility of Fe^{3+} in MgO is much greater and hence no ferrite precipitated out at this temperature. All other samples with higher concentrations gave similar results.

In another series of experiments, these samples were subjected to another heat-treatment. The hydrogen-treated samples, which contained clusters of bcc iron and Fe^{2+} in the lattice (fig. 4b), were heated in argon. A typical spectrum arising out of argon-firing is shown in fig. 4c. This is a partially resolved quadrupole split spectrum attributable to Fe^{2+} at Mg^{2+} sites ($IS = 0.85 \pm 0.05$ mm/sec). The splitting is 0.30 ± 0.05 mm/sec and is concentration-dependent. In this particular sample, the $\text{Fe}/\text{Fe} + \text{Mg}$ %, was 8%. It is interesting to note that all the iron that was present as bcc metal reacted on argon firing to give Fe^{2+} at Mg^{2+} . It is significant to point out that whereas there is a limit to the solubility of Fe^{3+} in MgO

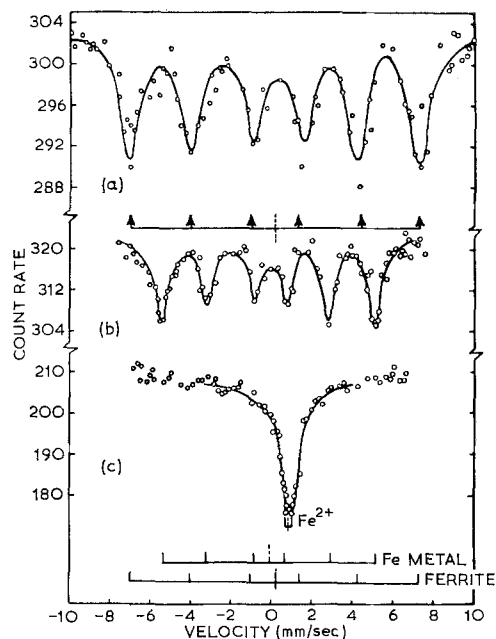


Figure 4 (a) Spectrum of a sample containing 8 at. % Fe. (b) Spectrum of this sample fired in hydrogen. (c) Spectrum of the same sample fired in argon. All spectra are at 300°K .

(nearly 0.3 at. % at 1000°C), as much as 8 at. % of Fe^{2+} can be dissolved in the lattice.

The origin of the efg at Fe^{2+} occupying Mg^{2+} sites is rather difficult to understand. Shirane *et al* [5] explained the efg on the assumption that Fe^{2+} has a larger ionic radius than Mg^{2+} . On the other hand, Simkin *et al* [6] have attributed quadrupole splitting to superparamagnetic clusters of Fe^{2+} in MgO. These points of view have been discussed in great detail and need no further comment.

If these argon-fired samples (fig. 5a) are fired in hydrogen, one returns to the situation wherein iron clusters exist with Fe^{2+} (fig. 5b). Thus the argon- and hydrogen-firing effects are reversible. Now if this argon-fired sample (fig. 5c) is heated in air one obtains the spectrum shown in fig. 5d indicating clearly the precipitation of magnesioferrite. The process through which Fe^{2+} in argon-fired MgO samples converts into magnesioferrite, takes place in two steps. Air-firing initially converts Fe^{2+} into Fe^{3+} . Since there is a limit to the solubility of Fe^{3+} in the lattice, the excess of Fe^{3+} precipitates out as magnesioferrite. The conversion of Fe^{2+} into Fe^{3+} is quite a slow process since it involves the capture of a hole by a Fe^{2+} ion. Since the precipitation of a

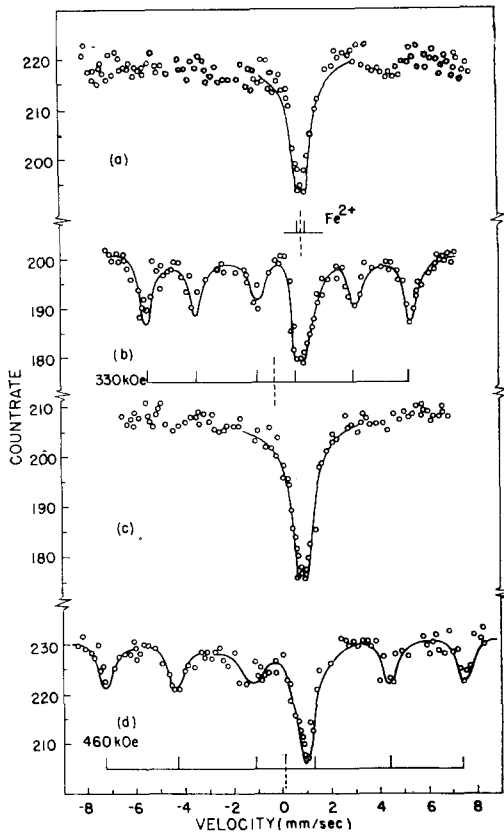


Figure 5 (a) Spectrum of argon fired sample containing 8 at. % Fe. (b) Spectrum of the same sample fired in hydrogen. (c) Spectrum of the sample fired in argon. (d) Spectrum of the sample fired in air. All the spectra are taken at 300° K.

ferrite is dependent on the formation of Fe^{3+} in the lattice, the rate of formation of magnesio-ferrite is indeed very slow. In fact the ferrite formation proceeds from the surface to the interior of the crystal.

In all these studies we have not been able to detect the presence of Fe^{1+} which has been reported in a $\text{MgO}:\text{Co}^{57}$ source [23]. Perhaps this may be due to the fact that the solubility of Fe^{1+} ion in the lattice is extremely small and hence its presence in the absorber cannot be detected. Alternately the presence of Fe^{1+} in the $\text{MgO}:\text{Co}^{57}$ source may be a consequence of the electron capture decay of Co^{57} . A similar situation has been reported, in $\text{SrTiO}_3:\text{Co}^{57}$ systems. In this system, one gets low spin ferric

ions in addition to the high spin ferric ions which are known to be stable in SrTiO_3 [24].

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