Mössbauer Studies of $Fe_{1-x}O$. Part II.† Disproportionation between 300 and 700 K

By **N. N. Greenwood** *‡ and **A. T. Howe**, Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU

A Mössbauer investigation of the disproportionation of quenched samples of $Fe_{1-x}O$ between 300 and 700 K has been carried out. At temperatures above 500 K the prior rearrangement of $Fe_{1-x}O$ into $Fe_{1-x-y}O$ and $Fe_{1-x+y}O$ (see Part I) was too rapid to be recorded on the Mössbauer spectra, but the observed reduction in the quadrupole splitting as a function of time at constant temperature can be discussed in terms of the reaction:

$$(1-4z)Fe_{1-x}O \longrightarrow (1-4x)Fe_{1-z}O + (x-z)Fe_3O_4$$

In the limit, z becomes very small and the monoxide approaches stoicheiometry. The phase $Fe_{0.99}O$ had a Néel temperature of 196 ± 3 K and a range of hyperfine magnetic fields of 340 ± 20 kG at 77 K. At temperatures above about 570 K further disproportionation of $Fe_{1-z}O$ itself becomes rapid and the spectrum of metallic iron begins to appear, according to the reaction:

$$4Fe_{1-z}O \longrightarrow (1-4z)Fe + Fe_3O_4$$

The rate of precipitation of Fe_3O_4 at a given temperature was found to depend not only on the initial composition of $Fe_{1-x}O$, but also on the temperature from which the initial samples were quenched during preparation. The effect is interpreted in terms of the defect aggregations present in the initial samples.

It has been recognised for some time[1,2] that the disproportionation of $Fe_{1-x}O$ below the eutectic temperature of 843 K occurs in two stages. The compound first disproportionates into Fe_3O_4 and a phase richer in iron than $Fe_{1-x}O$, and this phase ($Fe_{1-z}O$) then disproportionates further into Fe_3O_4 and Fe:

$$(1-4z)Fe_{1-x}O \longrightarrow (1-4x)Fe_{1-z}O + (x-z)Fe_3O_4 \quad (1)$$

$$4Fe_{1-z}O \longrightarrow Fe_3O_4 + (1-4z)Fe \quad (2)$$

The growth of the products Fe_3O_4 in reaction (1) and Fe_3O_4 and Fe in reaction (2) has been monitored magnetically,[2c] and both stages can be described by the kinetics of nucleation and growth. The completion of the first stage was separated from the observable commencement of the second stage by a substantial induction period.

† Part I, N. N. Greenwood and A. T. Howe, preceding paper.

‡ *Present address:* Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT

[1] (*a*) W. A. Fischer and A. Hoffmann, *Arch. Eisenhüttenwesen*, 1958, **29**, 107; (*b*) A. Hoffmann, *Z. Electrochem.*, 1959, **33**, 207.

[2] (*a*) O. K. Shabalina and G. I. Chufarov, *Fiz. Metal. Metalloved.*, 1961, **12**, 697; (*b*) *ibid.*, 1962, **13**, 766; (*c*) *ibid.*, 1963, **15**, 690.

However, the structural changes which the non-stoicheiometric monoxide must undergo during the initial precipitation of Fe_3O_4 in reaction (1) are not well established. Fischer and Hoffmann [1] showed that during this process the cubic unit-cell dimension of $Fe_{1-z}O$ increased to a maximum corresponding to the composition $Fe_{0\cdot99}O$ (*i.e.* $z = 0\cdot01$) and Hentschel [3] has recently claimed a maximum cell dimension corresponding to $Fe_{1\cdot00}O$ when extrapolated from the dimensions of samples with lower iron content. The quadrupole splitting of the paramagnetic Mössbauer peak of several partially decomposed samples was also shown to have decreased,[3,4] but no deductions as to the local structural parameters as determined by defect concentration and possible aggregation were made.

Manenc *et al.*[5] have further shown that for samples of $Fe_{1-x}O$ having a low initial concentration of defects, the above two stages are preceded by a rapid aggregation of defects within the oxide structure which can be represented as

$$2Fe_{1-x}O \longrightarrow Fe_{1-x-y}O + Fe_{1-x+y}O \qquad (3)$$

Since the above disproportionations involve migration of defects within the monoxide lattice, an understanding of the overall structure adopted at any particular defect concentration requires a knowledge of the preferred local defect configurations. The recent X-ray analysis of Koch and Cohen,[6] from which a clustered configuration of defects was proposed, has provided this basis on which micro-structure-sensitive experiments such as Mössbauer spectroscopy can be interpreted over a wide range of conditions not amenable to detailed X-ray studies. Such investigations would be of particular value in deciding whether reaction (3) was spinodal or not,[7,8] and also in determining the effect of the reduction in the total defect concentration on the cluster size in the iron-rich oxide $Fe_{1-z}O$ present in the multiphase disproportionation product of reaction (2). The results of Part I [9] indicate that the cluster size is significantly reduced in rapidly quenched samples of $Fe_{1-x}O$ between $x = 0\cdot100$ and $0\cdot053$, and a further reduction may occur as the defect concentration diminishes.

The present study was designed to follow the Mössbauer spectra of the monoxide phase during the above disproportionation reactions. Because of the short time-scale of the initial step (of the order of minutes at 573 K) [5] spectra were recorded at the temperature of disproportionation. This eliminated the uncertainties inherent in repeated heatings and coolings and enabled the conditions necessary for the observation of the various steps to be easily established. The results of the Mössbauer study in Part I [9] enabled the structure of the initial starting compounds to be carefully controlled so as to minimise any reaction occurring during the quenching of the samples.

EXPERIMENTAL

Samples were prepared as previously described.[9,10] Those used for the kinetic runs were quenched into water from the equilibrium state at 1520 K as established by a CO_2–CO gas stream. Other samples were quenched into water from specified temperatures.

The room-temperature spectra were the same as those given in Part I [9] for the appropriate compositions and quench conditions. For the kinetic runs the finely powdered sample was supported on a horizontal plate of boron nitride in a small temperature-controlled vacuum furnace (Ricor Ltd.). Before the temperature was raised the sample was pumped at 10^{-4} mmHg for 12 h to remove adsorbed gases, and the furnace was pumped continuously during the kinetic runs. At temperatures below 620 K there was no evidence of oxidation even over periods of several days. The temperature was controlled to ±1 K. Samples enriched in ^{57}Fe were loaded to 2 mg cm^{-2} and unenriched samples to 20 mg cm^{-2}. The spectrometers used were of standard design.[11] The Néel temperatures were determined as previously described.[12] The low-temperature spectra were obtained from the P.C.M.U., Harwell. Chemical isomer shifts are expressed relative to iron metal at 295 K.

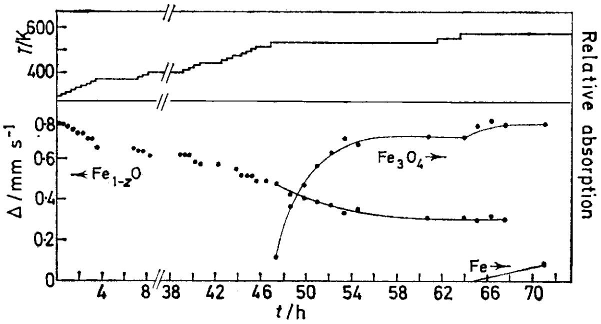

FIGURE 1 Changes in the Mössbauer spectrum of $Fe_{0\cdot940}O$ prior to and during decomposition. The increase in intensity of the Fe_3O_4 peaks (right-hand scale) is accompanied by a simultaneous decrease in the quadrupole splitting, Δ, of the residual $Fe_{1-z}O$ (left hand scale), which finally decomposed to Fe_3O_4 and Fe. The temperatures at which the spectra were recorded are shown on the top scale. Spectra were accumulated for 0·25, 1, or 5 h

RESULTS AND DISCUSSION

Disproportionation Reactions above Room Temperature.—Changes in the Mössbauer spectrum as a sample of $Fe_{0.940}O$ was heated *in vacuo* are summarized in Figure 1. The time spent at each temperature is shown, during which period the spectra were recorded. The short

---

[3] B. Hentschel, *Z. Naturforsch.*, 1970, **25a**, 1996.

[4] H. Shechter, P. Hillman, and M. Ron, *J. Applied Phys.*, 1966, **37**, 3043.

[5] (*a*) T. Herai, B. Thomas, J. Manenc, and J. Benard, *Compt. rend.*, 1964, **258**, 4528; (*b*) J. Manenc, T. Herai, and J. Bénard, in Fifth International Conference on the Reactivity of Solids, ed. G. Schwab, North-Holland, Amsterdam, 1964, p. 432; (*c*) J. Manenc, *Bull. Soc. Franc. Mineral Cryst.*, 1968, **91**, 594.

[6] F. Koch and J. B. Cohen, *Acta Cryst.*, 1969, *B*25, 275.

[7] M. E. Fine, 'The Chemistry of Extended Defects in Non-Metallic Solids,' eds. L. Eyring and M. O'Keeffe, North-Holland, Amsterdam, 1970, p. 575.

[8] S. K. Evans and I. B. Cutler, *J. Material Sci.*, 1970, **5**, 141.

[9] N. N. Greenwood and A. T. Howe, preceding paper.

[10] A. T. Howe, Ph.D. Thesis, University of Newcastle upon Tyne, 1970.

[11] N. N. Greenwood and A. T. Howe, Proc. Apollo 11 Lunar Science Conf. vol. 3, *Geochim. Cosmochim. Acta*, Suppl. I, 1970, 2163.

[12] N. N. Greenwood, A. T. Howe, and F. Ménil, *J. Chem. Soc.* (*A*), 1971, 2218.

15-min runs for spectrum accumulation were made possible by the use of a sample enriched to 95% in ^{57}Fe, though this inevitably led to some line broadening due to absorber thickness.

Initially the spectrum showed only an asymmetrical doublet [9] the splitting of which was constant at constant temperature but decreased regularly as the temperature was increased in accord with the increasing thermal population of the higher electronic levels of Fe^{2+}.[13] At 513 K peaks of Fe_3O_4 appeared, and during a prolonged stay at 533 K these rapidly increased to a maximum; concurrently there was a steady reduction in the quadrupole splitting of the residual $Fe_{1-x}O$ despite the constant temperature. After a further increase in the temperature to 573 K the intensity of the Fe_3O_4 peaks again increased and this was accompanied by the appearance of Fe peaks. The complexity of the spectrum at this stage can be gauged from the room-temperature spectrum shown in Figure 4 (to be discussed later).

The stages of decomposition represented by equations (1) and (2) can be identified in Figure 1, and occur under conditions which are in approximate agreement with those found by Shabalina and Chufarov [2c] from magnetic data. There was no evidence of a sudden change in the quadrupole splitting of the monoxide before Fe_3O_4 appeared, as might have been anticipated had an initial disproportionation occurred according to equation (3). However, the effect may have been masked by the collapse of the quadrupole splitting due to the normal temperature effect and the line broadening due to the use of the enriched ^{57}Fe sample.

The steady decrease in the quadrupole splitting of the monoxide which accompanied the isothermal precipitation of Fe_3O_4 was studied in more detail using unenriched samples at two compositions, $Fe_{0·940}O$ and $Fe_{0·880}O$. Figure 2 shows spectra which were recorded during the precipitation of Fe_3O_4 from $Fe_{0·940}O$. The growth of the Fe_3O_4 peaks is accompanied by a reduction in the quadrupole separation of the monoxide peak envelopes until, when Fe is just apparent in the last spectrum, the uncorrected linewidth of the peak was 0·52 mm s^{-1}. A value of 0·58 mm s^{-1} was found after the sample had been cooled and reinvestigated at room temperature.

The results of a similar series of experiments on a sample of composition $Fe_{0·880}O$ are shown in Figure 3. The quadrupole splitting of the monoxide again decreased with the increase in Fe_3O_4 until a sharp peak was obtained by the time peaks from Fe began to emerge.

In order to characterise more precisely the monoxide $Fe_{1-x}O$ which remains after the first precipitation of Fe_3O_4, as represented by equation (1), samples were decomposed in evacuated silica ampoules at one particular temperature for short periods of time and then requenched. The linewidths and isomer shifts of the room-temperature spectra of these samples are given in the Table and a typical spectrum is shown in Figure 4, for sample 4. In the Table, Γ refers to the approximate full width at half height of the total asymmetrical envelope of the room temperature spectra of the initially quenched samples of composition $Fe_{1-x}O$, whereas Γ′ refers to the full width at half height of the room-temperature spectra after disproportionation to $Fe_{1-x}O$ at temperature T_{decomp} for time t_{decomp}. The initial samples were prepared by quenching from a temperature T_{prep} into chilled water. Samples 1 and 2 were disproportionated during the kinetic runs described above and only the highest temperature used is recorded in the Table. Samples 1—4 all showed small proportions of free Fe in addition to Fe_3O_4 whereas in samples 5—8 Fe was not yet present. The halfwidths Γ′ were computed over the minimum number of channels so as to minimise the effects of the shoulder peaks from Fe_3O_4 and Fe (see Figure 4). These overlapped less for the samples having narrow monoxide peaks and the value of Γ′ in these cases was not affected. The results will be discussed in more detail after the results on the magnetically ordered phases at low temperature have been presented.

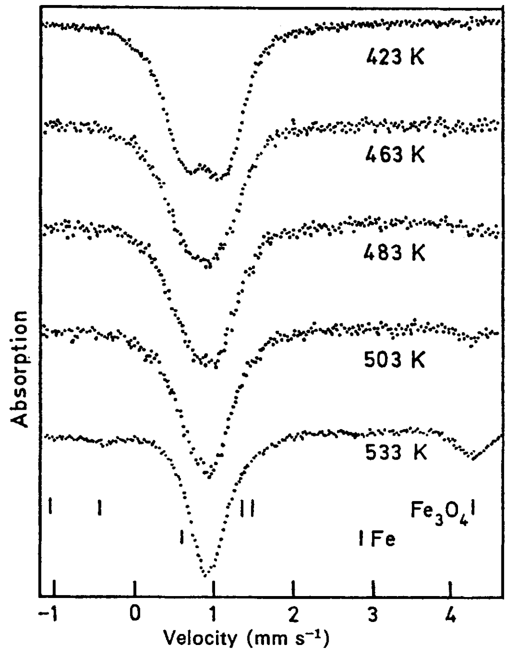

FIGURE 2 Mössbauer spectra recorded during the precipitation of Fe_3O_4 from $Fe_{0·940}O$ at 423 K (11 h), 443 K (2 h, not shown), 463 K, 483 K, 503 K (2 h each), 523 K (3 h, not shown) and 533 K (22 h). The sample had previously been at 323 K (9 h), 353 K (3 h), 383 K (3 h), and 403 K (5 h)

Effect of heat treatment on the room-temperature line width for various samples of $Fe_{1-x}O$

No.	T_{prep}/K	$1 - x$	Γ/(mm s^{-1})	T_{decomp}/K	t_{decomp}/h	Γ′/(mm s^{-1})	δ/(mm s^{-1})
1	1520	0·940	1·1	533	11	0·58	1·10
2	1520	0·880	1·2	613	0·6	0·49	1·09
3	1520	0·940	1·1	623	1	0·48	1·08
4	1520	0·940	1·1	673	0·5	0·39	1·09
5	1200	0·944	1·1	573	0·3	0·38	1·07
6	1520	0·940	1·1	583	1·1	0·60	1·08
7	1420	0·902	1·2	573	0·3	0·41	1·07
8	1420	0·870	1·2	573	0·3	0·40	1·05

---

[13] R. Ingalls, *Phys. Rev.*, 1964, **133A**, 787.

Magnetically Ordered Spectra.—The spectrum of sample 4 at 77 K is also shown in Figure 4. It is made up of the superposition of the magnetically-split patterns of three different phases, and subtraction of the spectra of Fe and Fe_3O_4, using the reported values,[14,15] gave the magmetic spectrum of $Fe_{1-x}O$ as shown. The linewidths and peak positions are very similar to those reported in Part I[9] for the spectrum of undecomposed $Fe_{0\cdot947}O$. The broad outer lines again indicate a range of magnetic hyperfine interactions characteristic of a range of environments of Fe^{2+}.[12] The value of H_{eff} is 340 ± 20 kG. The quadrupole splitting, evident from the asymmetry of the line positions, results from the rhombohedral distortion which occurs in $Fe_{1-x}O$ below the Néel temperature.[16]

The Néel temperature of $Fe_{1-x}O$ (sample 5) after decomposition was determined to be 196 ± 3 K; this is essentially the same as the value of 198 ± 3 K found for an undecomposed sample of $Fe_{0\cdot870}O$ quenched from 1420 K into water, and both values agree within experimental error with the values of 200 ± 3, 195 ± 3, and 203 ± 3 K for $Fe_{0\cdot980}O$, $Fe_{0\cdot932}O$, and $Fe_{0\cdot896}O$ respectively, which were derived from measurements of Young's modulus.[17,18] This constancy of the values over a wide range of defect concentration is consistent with the presence of defect clusters rather than a random array of point defects in the lattice.

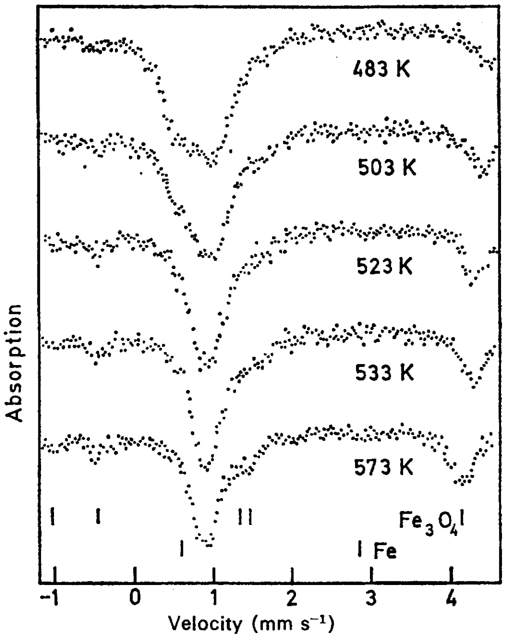

FIGURE 3 Mössbauer spectra recorded during precipitation of Fe_3O_4 from $Fe_{0\cdot880}O$ at 483 K, 503 K, 533 K (1·5 h each), 533 K (1·5 h, not shown), 553 K (3 h, not shown) and 573 K (1·5 h). The sample had previously been at 453 K for 4 h, and was heated further at 593 K (1 h) and 613 K (0·6 h) before cooling

The transition from a paramagnetic to a magnetically ordered spectrum occurred rapidly within 1 K and no evidence for ordered magnetic behaviour in the monoxide phase was found above the Néel temperature. This conflicts with the interpretation of earlier Mössbauer data[4] in terms of magnetic clusters induced above the Néel temperature by the presence of intergrown Fe_3O_4.

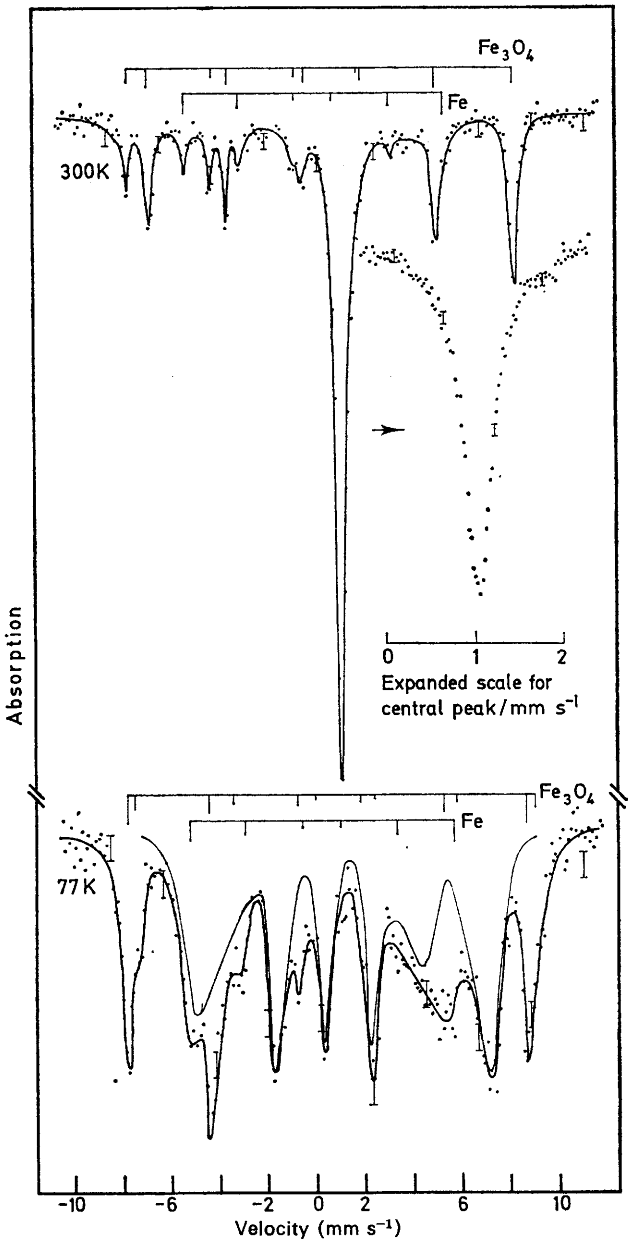

FIGURE 4 Mössbauer spectra at 300 K and 77 K of $Fe_{0\cdot940}O$ previously heated at 673 K for 0·5 h (sample 4). The paramagnetic peak is inset on an expanded scale. The spectrum at 77 K (feint line) has been obtained by subtraction of the spectra due to Fe_3O_4 and Fe

Defect Structure.—It has been shown previously[9] that

---

[14] R. S. Preston, S. S. Hanna, and J. Heberle, *Phys. Rev.*, 1962, **128**, 2207.

[15] W. Kündig and R. S. Hargrove, *Solid State Comm.*, 1969, **7**, 223.

[16] B. T. M. Willis and H. P. Rooksby, *Acta Cryst.*, 1953, **6**, 827.

[17] F. B. Koch and M. E. Fine, *J. Appl. Phys.*, 1967, **38**, 1470.

[18] M. E. Fine and F. B. Koch, *J. Appl. Phys.*, 1968, **39**, 2478.

the range of quadrupole-split resonances which is responsible for the broad Mössbauer spectra of the directly quenched samples of $Fe_{1-x}O$ can be related to the average defect concentration and to the extent of defect aggregation. A similar relationship can be obtained for samples having defect concentrations in the range found in the disproportionated samples.

The types of Fe^{2+} environment in such samples can be conveniently divided into those having no neighbouring defects (Fe^{3+} or vacant cation sites) at any of the 12 nearest-neighbour or 6 next-nearest-neighbour cation positions, and those having one or more defects at any of these 18 sites. The quadrupole splitting of the first type is expected to be approximately zero, since the lattice is cubic, whereas that of the second type will range from approximately 0·5 to 1·0 mm s^{-1}.[9] An analysis, as described in Part I, of the structures with random and aggregated defects, yields the proportion of Fe^{2+} with 1 or more neighbouring defects shown in Figure 5, for the range $Fe_{1{\cdot}00}O$ to $Fe_{0{\cdot}95}O$. The relative intensity of that portion of a resonance showing a quadrupole splitting should parallel this value. A random array of defects is seen to result in a significantly larger proportion of cations with neighbouring defects than a structure containing clusters of defects having the same overall composition. The results can now be discussed in terms of these model structures.

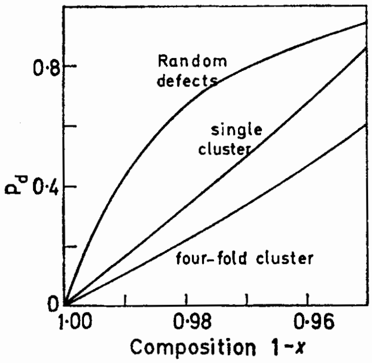

FIGURE 5 The proportion P_d of Fe^{2+} cations having one or more neighbouring defects over the range $Fe_{1{\cdot}00}O$ to $Fe_{0{\cdot}95}O$ for (a) a random defect distribution; (b) single clusters of 1 tetrahedral Fe^{3+} and 4 vacant cation sites; and (c) fourfold clusters of 4 tetrahedral Fe^{3+} and 13 vacant cation sites

The data in Figure 1 and the spectra in Figures 2 and 3 show that the average width at half height of the envelope is reduced as the average concentration of defects diminishes, as evidenced by the increase in the proportion of Fe_3O_4. The spectra finally produced have a half-width approaching that expected from a single unsplit resonance (*ca.* 0·25 mm s^{-1} under the experimental conditions used). At intermediate stages in the disproportionation some of the spectra (*e.g.* the sample at 503 K in Figure 3) showed a marked asymmetry, which was also a feature of previously reported spectra of partially disproportionated samples.[3]

The most obvious interpretation of the disproportionation process, especially in view of the observed asymmetry of the spectra, is that the monoxide of the reaction mixture represented by equation (1) is composed of two phases—the initial quadrupole-split $Fe_{1-x}O$ and the iron-rich product phase $Fe_{1-z}O$ $(0 \leqslant z < 0{\cdot}01)$ having one sharp peak at an isomer shift displaced to higher velocities from that of the initial oxide by the absence of defects around the Fe^{2+} ions. However, the calculations represented by Figure 5 show that such a spectrum could also result from a one-phase monoxide which had undergone a gradual depletion of defects during the elimination of Fe_3O_4, and which could be represented in equation (1) by $Fe_{1-z}O$ where $0 \leqslant z < x$. For instance, at the composition of approximately $Fe_{0{\cdot}965}O$ either of the clustered configurations of defects considered alone would have *ca.* 50% of the total number of Fe^{2+} ions producing a quadrupole-split resonance while an equal number would produce a sharp peak. The one-phase mechanism is in accord with the present understanding of the wide stability range of the phase.[19] This interpretation is also suggested by the gradual increase in the unit-cell dimensions with the extent of the reaction as found by Hoffmann,[1] although the *X*-ray parameters are only average values and could conceal the presence of microdomains of slightly different composition.

The narrow-line spectrum of the monoxide found at the completion of the reaction (1) indicates that the composition approaches that of the stoicheiometric oxide FeO, which has only been prepared in the absence of other phases under high pressure conditions.[20] The minimum observed linewidth of 0·38 mm s^{-1} (for sample 5) shows a residual broadening of *ca.* 0·13 mm s^{-1} over that expected for a single resonance under the same experimental conditions (*ca.* 0·25 mm s^{-1}) or for Fe^{2+} doped into the cubic lattice of MgO (0·25 mm s^{-1}).[21] The increased linewidth could in principle result from a single unsplit resonance from stoicheiometric FeO which had been broadened by local distortions from cubic symmetry caused by lattice strain, the effect of which was observed as a broadening of the *X*-ray lines for some samples. In addition, broadening could arise from the presence of residual grains of incompletely decomposed monoxide (of quadrupole splitting 0·5—1·0 mm s^{-1}) within the bulk of the defect-free material. Such an explanation would be in accord with the earlier interpretation of the spectrum (having $\Gamma = 0{\cdot}34$ mm s^{-1})[3] in terms of stoicheiometric FeO.

However, the present calculations show that such a broadening could also arise if the composition of the whole phase differed significantly from stoicheiometry. Spectral simulations show that a linewidth of 0·35 mm s^{-1} can result from the superposition of a quadrupole

---

[19] J. S. Anderson in ' The Chemistry of Extended Defects in Non-Metallic Solids,' eds. L. Eyring and M. O'Keeffe, North-Holland, Amsterdam, 1970, p. 1.

[20] T. Katsura, B. Iwasaki, S. Kimura, and S. Akimoto, *J. Chem. Phys.*, 1967, **47**, 4559.

[21] H. R. Leider and D. N. Pipkorn, *Phys. Rev.*, 1968, **165**, 494.

split resonance representing 20% of the Fe^{2+} having 1 or more neighbouring defects ($\Gamma = 0{\cdot}25$ mm s^{-1}, $\Delta = 0{\cdot}5$ mm s^{-1}) [9] and a single peak ($\Gamma = 0{\cdot}25$ mm s^{-1}) from the 80% Fe^{2+} having no neighbouring defects. From Figure 5 it can be seen that the compositions corresponding to this situation are $Fe_{0{\cdot}982}O$, $Fe_{0{\cdot}988}O$, and $Fe_{0{\cdot}996}O$ for the cases of four-fold clusters, single clusters, and a random array of defects respectively. In this light (assuming that all the line broadening arose from non-stoicheiometry rather than from lattice strain or incomplete disproportionation) the limiting composition that can be deduced will fall in the range between $Fe_{0{\cdot}98}O$ and $Fe_{1{\cdot}00}O$ depending on the extent of defect clustering. Comparison with unit-cell dimensions extrapolated from the values of $Fe_{1-x}O$ ($0{\cdot}05 < x < 0{\cdot}12$) reveals a range of results which give the composition as $Fe_{0{\cdot}99}O$ for 4·327 Å,[1] and 4·326 Å (present work) and $Fe_{1{\cdot}00}O$ for 4·332 Å.[3] The unit cell of the pure stoicheiometric FeO prepared under high pressure was reported to be 4·323 Å,[20] which is quite anomalous on the above extrapolated scale.

In the present experiments the composition of the disproportionating monoxide samples could not be sufficiently accurately determined from the proportion of Fe_3O_4 for a distinction to be made between a random and a clustered arrangement of defects, although the constancy of the Néel temperature argues for a clustered structure. The defects in the initial sample of $Fe_{0{\cdot}880}O$ would be expected to be arranged in four-fold clusters of the type present in $Fe_{0{\cdot}902}O$,[6] whereas the defects in $Fe_{0{\cdot}940}O$ would be expected to be grouped only in single clusters,[9] and differences in the defect configuration may remain at low defect concentrations. However, within the limits of interpretation mentioned, the two compositions investigated showed the same behaviour during disproportionation.

The results also indicate a dependence of the rate of the first decomposition stage [equation (1)] on both the composition and preparative conditions of the initial samples. The rates at a given temperature can be estimated by the rate of reduction of the quadrupole splitting of the monoxide spectra. For samples having the same initial value of x, the decomposition rate, at a given temperature, increased with a lower temperature of preparation. For example, $Fe_{0{\cdot}940}O$ quenched from 1520 K (sample 6) showed a linewidth of 0·60 mm s^{-1} after decomposition for 1·1 h at 583 K, whereas $Fe_{0{\cdot}944}O$ (sample 5), quenched from the lower temperature of 1200 K showed a narrow linewidth of 0·38 mm s^{-1} after only 0·3 h at 573 K.

For samples quenched from similar temperatures, a more rapid rate of precipitation of Fe_3O_4 was observed for the samples with larger values of x. For example, more than twice the quantity of Fe_3O_4 was precipitated from $Fe_{0{\cdot}870}O$ to give a linewidth of 0·40 mm s^{-1} for the monoxide in 0·3 h at 573 K than was precipitated from $Fe_{0{\cdot}940}O$ in 1·1 h at 583 K to give a linewidth of 0·60 mm s^{-1} (compare samples 8 and 6).

The different rates correlate with the extent of defect aggregation already present in the initial quenched samples, since it has been shown [9] that the extent of aggregation increases with both lower temperatures from which the samples were quenched, and with larger values of x. Thus, the preliminary step to precipitation of Fe_3O_4, namely defect aggregation within the $Fe_{1-x}O$ structure, has already occurred to some extent during the passage of the sample through the temperature zone below 843 K during the cooling process. It is clear that further kinetic studies of the decomposition will need to take into consideration the defect aggregation present in the initial samples.

We thank the Association of Commonwealth Universities for a Scholarship (to A. T. H.) and the S.R.C. for financial support.

[1/925 *Received, June 7th,* 1971]