Mössbauer Studies of $Fe_{1-x}O$. Part III.† Diffusion Line Broadening at 1074 and 1173 K

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The diffusive line broadening of the Mössbauer spectrum of $Fe_{1-x}O$ has been studied at 1074 and 1173 K and leads to activation energies for the jump process of 140 ± 20 kJ mol^{-1} for $Fe_{0.940}O$ and 135 ± 20 kJ mol^{-1} for $Fe_{0.910}O$. The observed reduction in the average cation-jump frequency from 42 MHz to 30 MHz over the range $Fe_{0.940}O$ to $Fe_{0.910}O$ at 1074 K has been compared with the number of atoms statistically able to jump in random and clustered defect configurations, but the observed behaviour can only be simulated by the incorporation of an activation energy of jumping which increases with increasing cluster size. The absolute magnitude of the derived self-diffusion coefficient was in general agreement with values obtained from radioactive tracer studies.

SINCE Singwi and Sjölander predicted a relationship between the Mössbauer line broadening and the diffusive motion of atoms,[1] the effect, for the case of jump-type displacements, has been observed in metals [2,3] and recently by two independent groups in the oxide $Fe_{1-x}O$.[4,5] The technique offers a means of determining the average jump frequency τ^{-1} of the resonant nuclei and this can be more directly related to a mechanism of diffusion than can the self-diffusion coefficient measured by conventional techniques since correlation effects [6] are not involved. In addition, the experimental difficulties of surface scaling, inadequate equilibration, and possible diffusion *via* grain boundaries, which are inherent in the radioactive tracer method, are avoided since the Mössbauer sample is kept at equilibrium for the duration of the measurement and the effect is an average over all existing jump rates.

In the case of $Fe_{1-x}O$, the many reported measurements [7-10] of the self-diffusion coefficient of Fe in the high-temperature wüstite phase reveal a dependence on defect concentration which varies from linear at 1373 K [10] to almost zero dependence at 1073 K.[7] This suggests strong defect interaction at the lower temperatures and at higher defect concentrations. Recent diffraction experiments [11,12] have shown that the defects in $Fe_{1-x}O$ (cation vacancies and Fe^{3+} ions) form clustered arrays under these conditions. In order to investigate the diffusion mechanism in such a defect-cluster system, we have studied the Mössbauer line broadening over a range of compositions at 1173 and 1074 K, where the Mössbauer resonance is most pronounced and where the tracer measurements are least accurate. Previous Mössbauer experiments [4,5] did not provide quantitative results over a range of compositions.

EXPERIMENTAL

Sections of the controlled atmosphere furnace used to maintain the sample in the equilibrium state are shown in Figure 1. The Fe foil sample, of approximate exposed diameter 11 mm, was crimped at two points between platinum annulae and curved slightly so as to allow for thermal expansion and contraction. The assembly was held in the isothermal enclosure formed by mullite annulae and thin alumina radiation shields. The composition of the sample was maintained by a mixed stream of CO_2–CO passing along the furnace at 9 mm s^{-1} and between the spaces around the radiation shields and sample. In order to prevent thermal segregation of the components of the gas mixture [13] it was necessary to have a gradual temperature gradient along the inlet gas path and this was provided by the non-heating end of a 36-cm long helical silicon carbide element, for which the middle of the hot zone was 24 cm from the gas inlet end. Published data [14]

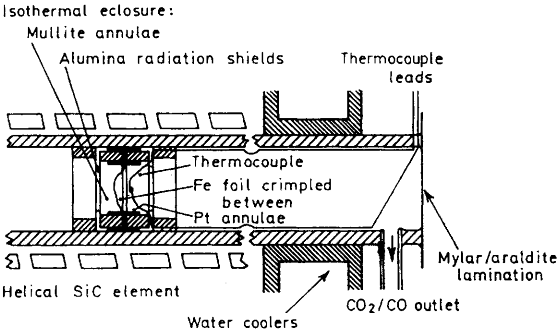

FIGURE 1 Sections of the controlled-atomsphere furnace showing the sample mounting

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

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[1] K. S. Singwi and A. Sjölander, *Phys. Rev.*, 1960, **120**, 1093.

[2] A. J. F. Boyle, D. St. P. Bunbury, C. Edwards, and H. E. Hall, *Proc. Phys. Soc.* (*London*), 1961, **77**, 129.

[3] R. C. Knauer and J. G. Mullen, *Appl. Phys. Letters*, 1968, **13**, 150; *Phys. Rev.*, 1968, **174**, 711.

[4] P. M. Valov, Ya. V. Vasil'ev, G. V. Veriovkin and D. F. Kaplin, *J. Solid State Chem.*, 1970, **1**, 215.

[5] (*a*) A. T. Howe, Thesis, University of Newcastle upon Tyne, 1970; (*b*) N. N. Greenwood, Plenary Lecture at the Conference of the German Chemical Society (Solid State Group), Bonn, 2nd October 1970, *Angew. Chem. Internat. Edn.*, 1971, **10**, 716.

[6] M. O'Keeffe, in 'The Chemistry of Extended Defects in Non-Metallic Solids,' L. Eyring and M. O'Keeffe, eds., North-Holland, Amsterdam, 1970, p. 609.

[7] L. Himmel, R. F. Mehl, and C. E. Birchenall, *J. Metals*, 1953, **5**, 827.

[8] R. E. Carter and F. D. Richardson, *Trans. Met. Soc., AIME*, 1954, **200**, 1244.

[9] P. Desmarescaux and P. Lacombe, *Mem. Sci. Rev. Met.*, 1963, **60**, 899.

[10] P. Hembree and J. B. Wagner, *Trans. Met. Soc., AIME*, 1969, **245**, 1547.

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

[12] A. K. Cheetham, B. E. F. Fender, and R. I. Taylor, *Solid State Physics*, 1971, **4**, 2160.

[13] L. S. Darken and R. W. Gurry, *J. Amer. Chem. Soc.*, 1945, **67**, 1398.

[14] R. J. Ackermann and R. W. Sandford, jun., U.S. Atomic Energy Commission Research and Development Report, 1966, ANL-7250.

were used to determine x to $\pm 0{\cdot}001$ from the CO_2–CO ratio. The compositions were checked *in situ* at the phase boundaries by observing changes in the Mössbauer spectrum and the results agreed well with published data.

The furnace temperature was measured and controlled using a standardised Pt/(Pt–13% Rh) thermocouple housed in the isothermal enclosure. The temperature could be maintained over extended periods of time to $\pm 0{\cdot}5$ K using a Ricor Ltd. TC4B controller. Siliceous material was excluded from the furnace materials and high purity gases were used to prevent long-term sample contamination.

The Mössbauer equipment included a 50 mCi source and a Goodman-type transducer driven from the time mode of a 400-channel R.I.D.L. multichannel analyser and mounted independently of the furnace in order to prevent vibrational transfer to the sample. Chemical isomer shifts are quoted relative to Fe metal at 295 K as zero.

Because of the extended dimensions of the furnace, it was not necessary to correct the linewidth for baseline curvature since this was only 0·02% of the total number of counts at the maximum velocity used and this was less than the statistical error for the weakest absorption encountered. The velocity ranges used (± 9 and ± 13 mm s^{-1}) were chosen so that the spectra could be computed over the number of channels approximately equivalent to five times the resonance linewidth.

In the work reported earlier[5] a 95% enriched ^{57}Fe foil 0·0025 mm thick was used and spectra were accumulated during 10 h at 1073 K. The times needed for equilibration at the various temperatures and compositions were used as a basis for the second set of experiments reported here using an unenriched foil. This was used to eliminate the possible effects on the diffusion rate of impurities in the enriched foil (*ca.* 1·5%). A high purity foil (<20 p.p.m., Koch–Light Chemicals Ltd.) was electropolished in a chilled phosphoric–acetic acid bath from a thickness of 0·075 to 0·025 mm (equivalent to 18 mg cm^{-2}) before mounting. The Mössbauer absorption, although less than that obtained with the enriched foil, was adequate and the increased sturdiness of the foil enabled data to be collected over several weeks. Results obtained at the start and at the completion of the series were in good agreement and showed that contamination of the sample had not occurred.

A spectrum of the mounted foil was first collected at room temperature to establish the effective linewidth in the absence of diffusion broadening.[15] The sample was then heated to 1273 K during 3 h in a stream of purified hydrogen so that scaling would not occur due to slow oxidation and also to avoid the use of the CO_2–CO mixture below the temperature at which carbon is deposited (*ca.* 1040 K).[14] The sample was then oxidised to $Fe_{0{\cdot}91}O$ in CO_2–CO and maintained at 1273 K for 10 h to ensure complete equilibration. Spectra were then collected for periods of 20—200 h at either 1173 or 1074 K. The composition was reset by raising the temperature to 1273 K for 1 h followed by cooling to the lower temperature with the gas ratio readjusted to maintain the high-temperature composition.

Two runs were made on the one sample, separated by a period at room temperature, and spectra were collected for samples produced both by oxidation and by reduction. The results obtained were reproducible to within the standard deviation of the statistical counting errors.

RESULTS AND DISCUSSION

Determination of the Average Jumping Frequency τ^{-1}.—Typical Mössbauer spectra obtained from an unenriched foil at 1074 and 1173 K are shown in Figure 2. Table 1 shows the computed linewidth Γ obtained over a range of compositions at the two temperatures. These values are *ca.* 10% lower at 1170 K and consistently 30% lower at 1076 K than those reported for the enriched sample;[5] for example the enriched sample of composition $Fe_{0{\cdot}938}O$ had $\Gamma = 4{\cdot}95$ mm s^{-1} at 1170 K and for compositions $Fe_{0{\cdot}934}O$, $Fe_{0{\cdot}914}O$, and $Fe_{0{\cdot}895}O$ at 1076 K the values of Γ were 2·28, 1·85, and 1·21 mm s^{-1} respectively. Calculations show that only a difference of *ca.* 10% could arise from thickness broadening due to the isotopic enrichment, and the difference is attributed to impurities present in the earlier enriched sample. The values found in the present study were also lower by *ca.* 10% at 1073 K and by *ca.* 30% at 1173 K than those reported for $Fe_{0{\cdot}95}O$ by Valov *et al.*[4] using 60% enriched ^{57}Fe of unspecified elemental purity.

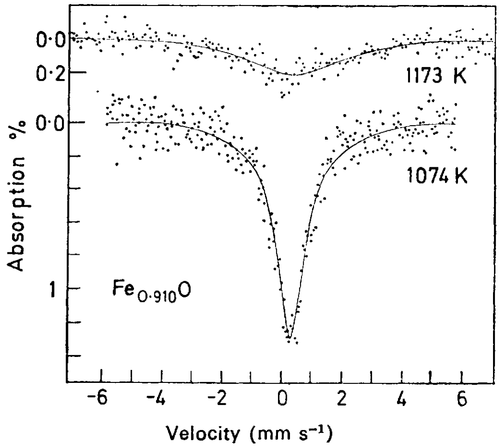

FIGURE 2 Diffusion-broadened Mössbauer spectra of $Fe_{0{\cdot}910}O$ showing the marked dependence on temperature.

TABLE 1

The dependence on composition and temperature of the linewidth Γ of the Mössbauer spectrum of $Fe_{1-x}O$ collected for the times shown.

Composition $(1 - x)$	Prep.	t/h	T/K	Γ/mm s^{-1}
0·940	red	27	1074	1·56
0·941	ox	44	1074	1·56
0·940	red	62	1074	1·56
0·934	red	20	1074	1·47
0·923	red	42	1074	1·57
0·920	red	21	1074	1·33
0·910	red	45	1074	1·20
0·910	ox	25	1074	1·18
0·940	red	39	1173	4·41
0·910	ox	216	1173	3·88

The non-diffusive contributions to the linewidths were calculated as follows. Firstly, the sum of the natural linewidth and instrumental broadening was estimated to be 0·35 mm s^{-1} from the linewidths of the six-line room temperature spectrum of the unoxidised iron foil measured *in situ* and corrected for desaturation[16] arising

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[15] N. N. Greenwood and A. T. Howe, *J.C.S. Dalton*, 1972, 110.
[16] T. C. Gibb, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1968, 890.

from the reduced f factor and increased linewidth at the high temperature used. Secondly, a quadrupole splitting at 1074 K was estimated as 0·03 mm s^{-1} by extrapolation from the values of 0·90,[5a] 0·75,[5a] and 0·40 mm s^{-1} [17] reported for two-peak fits to the spectrum of $Fe_{0\cdot88}O$ at 225, 295, and 483 K respectively. Thirdly, no significant line broadening arose from the presence of both Fe^{2+} and Fe^{3+} since a single resonance only was observed due to rapid electron hopping at these elevated temperatures. Thus, a minimum electron hopping frequency τ_e^{-1} of 120 MHz at 1074 K can be calculated from the observed mobility [18] of 0·121 cm^2 V^{-1} s^{-1} for the Fe^{3+} charge carriers at this temperatures using the expression $\mu = ea^2/(kT\tau_e)$ where μ is the mobility and a is the hop distance. Since this frequency is much higher than that corresponding to the reciprocal of the lifetime of the ^{57}Fe excited state (10 MHz) an averaged resonance is expected.

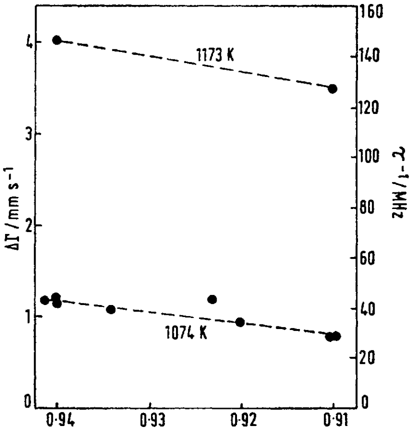

FIGURE 3 Diffusion broadening $\Delta\Gamma$ of the Mössbauer spectra over a range of compositions and temperatures. The average jump frequency $\tau^{-1} = \Delta\Gamma/(2\hbar)$ is also shown

Although calculations based on accepted formulae [19,20] show that a small line broadening of 0·04 mm s^{-1} would result from such a hopping rate, similar calculations for the case of Fe_3O_4 [19] have shown that such estimates are larger than the broadening actually observed because of correlation effects; in view of this the correction can safely be ignored. At room temperature a minimum hopping frequency of 2·8 MHz can be calculated from the reported conductivity,[18] and exchange averaging would, therefore, not occur, which is in agreement with the Mössbauer spectral analysis reported in Part I.[15]

The diffusive broadening of the linewidths $\Delta\Gamma$, obtained by subtraction of the sum of the above non-diffusive contributions (0·38 mm s^{-1}) from the observed linewidths are shown in Figure 3. The standard deviations obtained from the computer fits were *ca.* 0·1 and 0·5 mm s^{-1} for the spectra at 1074 and 1173 K respectively.

For atomic jumping at a frequency τ^{-1}, Singwi and Sjölander [1] have shown that

$$\Delta\Gamma = \frac{2\hbar}{\tau}[1 - \int \exp{(i\boldsymbol{k}.\boldsymbol{r})}h(\boldsymbol{r})d\boldsymbol{r}] \qquad (1)$$

where $\boldsymbol{k}$ is the wave vector of the incident γ-ray and $h(\boldsymbol{r})$ is a function which defines the probability of finding the atom at point $\boldsymbol{r}$ after one jump from a position $\boldsymbol{r} = 0$. For the case of the 14·4 keV γ-ray from ^{57}Fe and for typical jump distances in the lattice of polycrystalline $Fe_{1-x}O$ the integral is negligible in comparison to unity.[3] Hence $\tau^{-1} = \Delta\Gamma/(2\hbar)$ and values for this are also shown in Figure 3.

Activation energies E for the jump process can be calculated from the expression $\Delta\Gamma = (\Delta\Gamma_0) \exp{(-E/RT)}$; values of 140 ± 20 and 135 ± 20 kJ mol^{-1} were found for $Fe_{0\cdot940}O$ and $Fe_{0\cdot910}O$ from the data obtained at the two temperatures. The results are in reasonable agreement with the activation energies of the self-diffusion coefficient determined by the tracer technique, which range from 110 kJ mol^{-1} for $Fe_{0\cdot94}O$ to 125 kJ mol^{-1} for $Fe_{0\cdot91}O$.[7,9] A value of 105 ± 12 kJ mol^{-1} was estimated from Mössbauer data on $Fe_{0\cdot95}O$ using an over-simplified treatment of the data.[4]

Comparison of the absolute values of the diffusion parameters obtained from the two techniques involves several uncertain factors which will be discussed in the last section.

Diffusion Mechanism.—For a given cation with n adjacent vacancies the jump frequency of the cation into any of the vacancies expressed can be as

$$\tau^{-1} = n\tau_0^{-1}e^{-E/RT} \qquad (2)$$

where τ_0^{-1} is a constant and E the activation energy of jumping. For an assembly of cations, for which the probability of a particular cation having n adjacent vacancies is p_n, the average jump frequency is then given by

$$\tau^{-1} = \sum_n np_n\tau_0^{-1}e^{-E/RT} \qquad (3)$$

where $\sum_n np_n$ is the average number of adjacent vacancies per cation. For $Fe_{1-x}O$, which has a defect face-centred cubic lattice, $p_1 = 12x$, $p_2 \approx 0$ for the limiting case of low concentrations of vacancies ($x \rightarrow 0$). For higher vacancy concentrations, general calculations have been performed [6,21] which assume a repulsion between the vacancies such that jumps which would create vacancy–vacancy pairs are prohibited. The resulting maximum in the function $\sum_n np_n$, when evaluated over a wide composition range, reproduces the observed behaviour of the ionic conductivity in anion-deficient oxides of the type $Th_{1-2x}Y_{2x}O_{2-x}$.[22] However, in the case of $Fe_{1-x}O$

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

[18] I. Bransky and D. S. Tannhauser, *Physica*, 1967, **37**, 547.

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

[20] G. A. Sawatzky, J. M. D. Coey, and A. H. Morrish, *J. Appl. Phys.*, 1969, **40**, 1402.

[21] W. W. Barker, *Material Sci. Eng.*, 1967, **2**, 208.

[22] B. C. H. Steele and C. B. Alcock, *Trans. Met. Soc., AIME*, 1965, **233**, 1359.

it has been shown that the vacancies are mutually attracted to a small proportion of tetrahedral Fe^{3+}. Diffraction experiments [11,12] suggest clusters of the type $\{^{t}Fe^{3+}{}_{4}(\square_{+})_{13}\}^{14-}$ and $\{^{t}Fe^{3+}(\square_{+})_{4}\}^{5-}$, although the extent to which these occur at a particular composition and temperature is not well established. Since the vacancy-repulsion model is not relevant to such clustered systems, the evaluation of τ^{-1} in the vacancy-clustered $Fe_{1-x}O$ is now considered. The calculations may be expected to predict the features of the transport properties of the few other clustered systems so far identified (*e.g.* $V_{0\cdot79}O$ [23] and $Fe_{x}Mg_{1-x}O$ [24]).

In the limit of a very high energy of cluster formation the cations in such a system can only make jumps in a co-operative fashion, such that the identity of the clusters would be preserved; this would result in a very low jump frequency. A more realistic approach is to assume an equilibrium between appreciable numbers of single vacancies and clusters ranging in size from $\{^{t}Fe^{3+}(\square_{+})_{4}\}^{5-}$ to $\{^{t}Fe^{3+}{}_{4}(\square_{+})_{13}\}^{14-}$. The sums $\sum_{n} np_{n}$ for any one of these distributions alone have been calculated and are shown in Figure 4 as a function of composition. The values of p_{n} were evaluated for a completely non-interacting array of defects using standard statistical procedures.[21] In the case of the clustered structure the number of adjacent vacancies per cation was calculated directly for each of the two sizes of cluster, from which the value at any cluster concentration could be calculated. The concentrations considered were such that cations adjacent to one cluster were never also adjacent to another, assuming an even cluster distribution throughout the lattice.

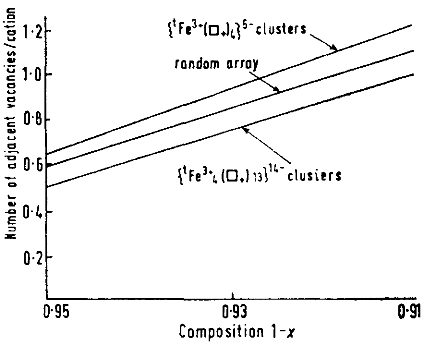

FIGURE 4 The average number of adjacent vacancies per cation $\sum_{n} np_{n}$ as a function of composition in $Fe_{1-x}O$ for various defect arrangements

The similarity of the values shown in Figure 4 for the clustered and random distributions is somewhat unexpected, and arises from the balancing of two factors, (*a*) the increase in the number of vacancies produced by transfer of cations from the octahedral sites to the tetrahedral sites to form the nucleus of the clusters, and (*b*) the reduction in the number of sites from which cations have access to the vacancies when clustering occurs. A ratio of vacant cation sites to tetrahedral Fe^{3+} of 4·0 and 3·25 is demanded by the two cluster structures. No tetrahedral occupancy was assumed for the random distribution.

The rate of change of the sums $\sum_{n} np_{n}$ (Figure 4) with composition agrees to within experimental error with the rate of change of the self-diffusion coefficient [10] with composition measured at 1373 K, and shows that a clustered structure, as suggested by the observed value of *ca.* 4 for the ratio of vacancies to tetrahedral sites measured at 1458 K for $Fe_{0\cdot906}O$,[12] is consistent with the diffusion measurements at these temperatures.

However, at the lower temperatures of 1173 and 1074 K investigated in this work, the calculated jump frequency does not parallel the sums given in Figure 4. One possible interpretation is that the activation energy of jumping into a vacancy increases as that vacancy is involved in cluster formation; the expression (3) for τ^{-1} would thus need to be evaluated over the full range of activation energies. The values of τ^{-1} would then be successively lower for larger cluster sizes and the results would imply an increasing cluster size as the concentration of defects increased over the range $Fe_{0\cdot940}O$ to $Fe_{0\cdot910}O$.

In summary, when defect clustering occurs the experimental results can only be interpreted by considering both the geometrical probability factor and the variation in activation energy of jumping, whereas for isolated defects a satisfactory fit can be obtained on the vacancy-repulsion model by considering the geometrical factors only.

Self-diffusion Coefficient.—The self-diffusion coefficient D of the cations in a cubic lattice is related to the average cation jump frequency τ^{-1} by the relation [25]

$$D = \frac{r_0^2 f}{6\tau} \tag{4}$$

where r_0 is the jump distance and f is the correlation factor which allows for the probability of a cation jumping back into the vacancy it has just created thereby contributing to the average jump frequency but not to the net transport. A direct comparison of τ obtained from the Mössbauer line broadening with the values of D obtained from tracer studies should yield an estimate of the correlation factor, which could be related to the diffusion mechanism in the manner described by O'Keeffe.[6] However, the uncertainty in the tracer determinations and the possible need of modification of the Singwi and Sjölander relationship [1] preclude such a comparison being made at present. For example, results from the diffusion of ^{57}Fe in Cu and Au[3] suggest that the theory should be modified by omission of the factor 2, such that $\Delta\Gamma = \hbar\tau^{-1}$ rather than $2\hbar\tau^{-1}$. The result follows from a comparison of the accurate values of D obtained by the tracer method, the value of $f = 0\cdot8$ determined independently from isotope

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[23] S. Westman, Dept. of Army Contract, 1970, No. D.A.-91-591-EUC-1319, AD 248, 112.

[24] K. N. Woods and M. E. Fine, *J. Appl. Phys.*, 1969, **40**, 3425; *J. Amer. Ceram. Soc.*, 1969, **52**, 186.

[25] R. J. Friauf, *J. Appl. Phys.*, 1962, **33S**, 494.

measurements, and the value of τ obtained from the Mössbauer experiments. It was proposed that in the case of vacancy diffusion, the relaxation of an ion out of a lattice site may not be a simple exponential in time, as assumed by the theory, but may approximate more to a step function.

Table 2 compares the self-diffusion coefficients of $Fe_{1-x}O$ determined from tracer measurements with those obtained from the Mössbauer data assuming $\Delta\Gamma = 2\hbar\tau^{-1}$, $f = 1$ and using values of r_0 calculated from the appropriate high-temperature unit cell dimensions.[26] The corrections arising from the isotope mass difference between the Mössbauer measurement (using ^{57}Fe) and the radioactive tracer measurements (using ^{55}Fe or ^{59}Fe) are very small and have been ignored. The data of Hembree and Wagner [10] are consistently lower than the other determinations, possibly because of the reported visual absence of surface cracking and scaling in the CO_2–CO atmosphere used compared to that observed in H_2O–H_2 mixtures in which the other measurements were performed. The Mössbauer results agree well with these lower values, and thus provide support for the original formulation of Singwi and Sjölander, namely that $\Delta\Gamma \simeq 2\hbar\tau^{-1}$.

TABLE 2

Values of the self-diffusion coefficient D as determined by tracer methods and by Mössbauer line broadening (Möss). Some of the values have been interpolated from references cited for ease of comparison

1073 K		1173 K		1373 K		
$1 - x$	$D/10^{-8}$ cm^2 s^{-1}	$1 - x$	$D/10^{-8}$ cm^2 s^{-1}	$1 - x$	$D/10^{-8}$ cm^2 s^{-1}	Ref.
0·921	0·97	0·921	3·1	0·921	22	C and R [8]
0·94—0·91	0·9—1·0	0·94—0·91	2·2—3·5	—	—	H, M, and B [9]
0·91	0·85	0·91	2·6	0·94—0·87	8—30	D and L [9]
—	—	—	—	0·921	14	
0·94—0·91	0·68—0·46	0·94—0·91	2·3—2·0	—	—	Möss (this work)
0·926	(0·4—0·7)	—	—	0·94—0·87	10—24	H and W [10]
				0·921	14	

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[26] A. K. Cheetham, B. E. F. Fender, and R. I. Taylor, unpublished results.