

Diffusion Broadening of the Mössbauer Line in Wüstite*

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The temperature dependence of the diffusion broadening for Fe⁵⁷ in wüstite, FeO_x, from 800 to 1050 °C is reported. Measurements were done at various compositions *x* by adjusting the ratio of partial pressures of carbon dioxide to carbon monoxide in which the samples were annealed. Our data indicate that the Mössbauer line broadening is only about half of that predicted by the Singwi-Sjölander theory. Our results support the recent tracer-diffusion measurements of Chen, Peterson, and Robinson, which contradict several earlier studies on the diffusion of iron in wüstite. The temperature dependence of the recoil-free fraction is reported in the region where diffusion broadening is observed.

I. INTRODUCTION

We have measured the broadening of the Mössbauer line for Fe⁵⁷ in wüstite, FeO_x. Our observations indicate a broadening smaller than the original predictions of Singwi and Sjölander.¹ The Singwi-Sjölander (SS) theory predicts, for solid-state diffusion in the sudden-jump limit, that

$$\Delta\epsilon/\Gamma_N = 2\tau_N/\tau_D, \quad (1)$$

where $\Delta\epsilon$ is the incremental broadening of the Mössbauer line, Γ_N is the level width \hbar/τ_N , τ_N is the mean lifetime of the isomeric level, and τ_D is the mean time of occupying a lattice site before diffusing to an adjoining site.

Although the original SS theory is intended for a purely random-walk motion, most solid-state diffusion is via correlated mechanisms such as the vacancy mechanism. For cubic crystals the diffusion time τ_D is given by

$$\tau_D = r_0^2 f_C / 6D, \quad (2)$$

where r_0 is the jump distance, f_C is the Bardeen-Herring correlation factor (0.78 for diffusion via vacancies in fcc crystals), and D is the diffusion coefficient for the Mössbauer isotope in the host lattice. Equations (1) and (2) indicate a broadening proportional to the diffusivity D . The first solids where the proportionality was confirmed^{2,3} were Fe⁵⁷ in Cu and Au. Although these cases show a scaling-factor discrepancy between measured broadening and that inferred from the SS theory, phenomenological modification of the theory, including correlation effects, was found to restore agreement between theory and experiment.^{4,5}

Lewis and Flinn⁶ have reported a complete confirmation of the SS theory for Fe⁵⁷ diffusion in bcc iron stabilized with 3-wt. % silicon, and they have suggested that the reduced broadening found by Knauer and Mullen^{2,3} may have been a peculiarity of the particular impurity diffusion system studied. They also reported the usual Debye-Waller fall-

off in the recoil-free fraction in the temperature region where diffusive broadening was observed, in contrast to observations of an exceptionally rapid falloff in the recoil-free fraction for Fe diffusion in Cu and Au.

Recently, Greenwood and Howe^{7,8} found approximate agreement between their experimental results and the SS theory, studying Fe⁵⁷ diffusion in wüstite by the Mössbauer technique. Unfortunately the Greenwood-Howe experiment was limited to measurements at 801 and 900 °C, with only two variations of *x*, i. e., two values for the gas ratio (GR) of carbon dioxide to carbon monoxide (GR), at the latter temperature. Their 801 °C measurements gave only a slight broadening beyond their minimum observed width, making their reference width and the determination in the incremental broadening uncertain. Also the tracer-diffusion data⁹⁻¹¹ which they used to compare their results were on polycrystalline samples and have been contradicted by more detailed recent studies.¹²

In the present note we wish to report the temperature dependence of the Mössbauer line broadening for self-diffusion of Fe in FeO_x, and give our results for the falloff in the recoil-free fraction in the temperature interval where diffusive broadening was noticeable.

II. EXPERIMENTAL PROCEDURE

Mössbauer line broadening was studied from 800 to 1050 °C in a mixed homogeneous atmosphere of CO and CO₂ premixed in a specially constructed high-pressure tank. High-purity 99.99%-pure gases, supplied in tanks by Matheson Gas Co., were used throughout the experiment. Two natural-iron and two enriched-iron absorbers were used in the experiment. The natural-iron-absorber experiments were done with 99.999%-pure, 0.001-in.-thick foils, and the enriched foils were prepared by electroplating Fe⁵⁷ from an oxylate solution onto a 99.999%-pure foil, depositing sufficient Fe⁵⁷ to approximately double the total Fe⁵⁷

concentration of the original foil.

The foils were clamped between quartz tubes in a furnace assembly with contact only at the outer edges of the iron-foil samples, the foil being freely exposed to the CO₂-CO atmosphere used. The furnace arrangement was similar to that used in our earlier work,¹³ except for the following changes. Indium seals were used between the end caps and the outer quartz tubes. The sample support was kept in compression by means of quartz flax placed at the edges of the end caps. BeO was used for a baffle material in these experiments.

The metallic foils were oxidized by first heating them in an H₂ atmosphere to 950 °C and then replacing the hydrogen with an oxidizing CO₂-CO atmosphere. Precautions were taken to verify that the CO₂-CO gas flow rate was compatible with thermal and compositional equilibrium, and the thermal gradients across the absorber were measured to be less than 2 °K. The oxidation annealing was done in the same furnace where the Mössbauer measurements were made, making it possible to proceed directly to the Mössbauer measurements after sample oxidation without any thermal cycling that might cause a phase transformation.

The problem of determining the minimum reference linewidth, where diffusion does not occur, is compounded in the present experiment as a result of magnetic hyperfine splittings at lower temperatures, where diffusive broadening is negligible. In our experiment the minimum reference linewidth was taken to be 0.4 mm/sec for the natural foils and 0.45 mm/sec for the enriched foils. The errors in these values of the reference width are conservatively estimated to be 0.2 mm/sec. Since we were able to observe broadening of the order of 100 times the natural width, errors in the assumed reference width are negligible for the high-temperature runs. Only in the low-temperature region, such as studied by Greenwood and Howe,⁷ can the error due to an inaccurate reference width be significant.

The experiment was done with a 30-mCi Co⁵⁷-in-Pd source, which was moved with a double-coil transducer at room temperature (22 °C), and the transmission intensity was recorded by means of a multichannel analyzer. The experiment was done in the constant acceleration mode and a parabolic correction was made for the small intensity variation resulting from changes in source-to-detector distance.

III. EXPERIMENTAL RESULTS

Typical Mössbauer spectra are shown in Fig. 1, where the gas ratio (GR) is 0.9, i. e., the relative partial pressure of CO₂ to CO is 0.9. Similar measurements were made at a GR of 0.5 and 1.6, and the temperature dependence of the line broad-

ening is given in Fig. 2 for all three gas ratios studied. The line shape in the temperature interval 800 to 1050 °C was found to be Lorentzian with the expected χ^2 . It should be noted that at 700 °C the line shape could not be satisfactorily fitted to a single Lorentzian. Our curve fit for this case indicated a slight quadrupole splitting of 0.3 ± 0.1 mm/sec, which is small enough to preclude the possibility of a temperature-dependent quadrupole splitting contributing significantly to the temperature dependence of the line broadening. For the higher-temperature runs the count-rate statistics were always greater than 10^6 .

A point of caution should be made concerning comparison of older diffusion data with our present experiment. We have presented our value of the line broadening as a function of the relative gas pressure of CO₂ to CO. Diffusivity measurements have generally been referred to x values, which reflect the degree of deviation from stoichiometry. This is usually done by referring to the widely accepted results of Darken and Gurry,¹⁴ which are

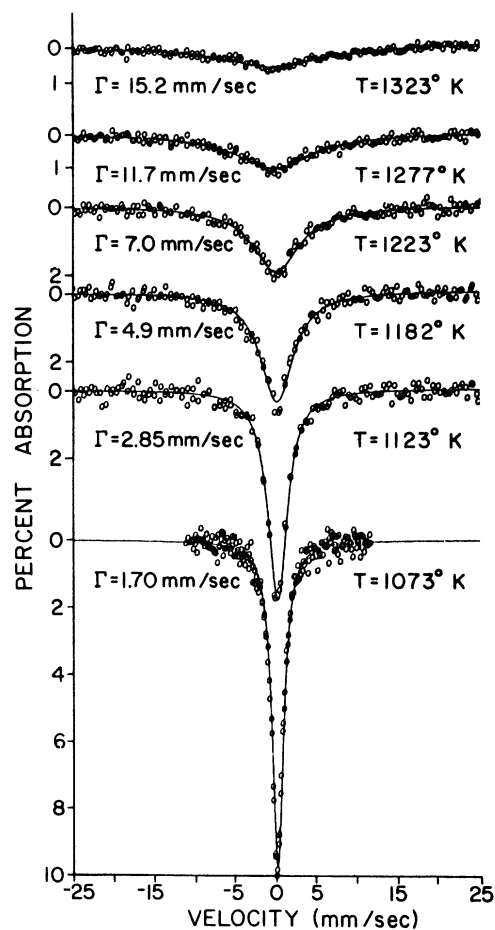


FIG. 1. Typical Mössbauer spectra for enriched wüstite with a GR of 0.9.

TABLE I. Least-squares-fit parameters [Eq. (3)] for measured line broadening.

GR, $[P(\text{CO}_2)/P(\text{CO})]$	Curve	E (kcal/mole)	$10^{-2}(\Delta\epsilon/\Gamma_N)_0$
1.6	A	30.3 ± 0.4	$1.6_2 \pm 0.3$
0.9	B	27.1 ± 0.7	$0.4_3 \pm 0.2$
0.5	C	27.0 ± 0.8	$0.4_7 \pm 0.2$

not in good agreement, when extrapolated to $T < 1100^\circ\text{C}$, with the recent results of Ackerman and Sandford,¹⁵ who find that the value of x is essentially constant for all temperatures (roughly covering the same temperature range as our experiment) provided GR is fixed. By these latter results the curves A, B, and C in Fig. 2 would represent x values of 1.10, 1.08, and 1.06, respectively.

The data for the line broadening fit an exponential relation of the form

$$\Delta\epsilon/\Gamma_N = (\Delta\epsilon/\Gamma_N)_0 e^{-E/RT}. \quad (3)$$

The best-fit parameters are given in Table I. The slopes are in reasonably good agreement with data of Chen *et al.*, although for a GR of 0.5 our activation energy is about 2 kcal/mole less than their value. This slight discrepancy is probably within experimental errors.

In addition, we find, as in our earlier experiments,^{2,3,16,17} that a plot of $\ln f$ versus T yields an extremely rapid falloff in the recoil-free fraction in the temperature interval where diffusion broadening effects are observed. The results shown in Fig. 3 are similar to other systems which we have studied where an exceptionally rapid fall-off in $f(T)$ (nearly proportional to area A under the Mössbauer resonance) was found in the temperature region where noticeable diffusive broadening effects are seen. Unfortunately wüstite is not stable below 570°C and it was not possible to extend our measurements to low enough temperatures to get a reliable Mössbauer characteristic temperature θ_M for the region between $\theta_M/2$ and 800°C , where appreciable Mössbauer line broadening is first observed. Based on studies of other similar oxides, however, we would expect a slope in the $\ln f$ -vs- T curve considerably less than found in the interval from 800 to 1050°C . No noticeable compositional dependence on recoil-free fraction was observed.

IV. DISCUSSION

Our experimental results agree with those of Greenwood and Howe,⁷ where they overlap, but do not agree as well with the findings of Valov *et al.*¹⁸ We find a serious discrepancy with the SS theory, similar to our earlier measurements^{2,3} on Fe in Cu and Au, which have been reasonably accounted for on the basis of correlation.^{4,5} Comparing our results with the recent tracer-sectioning measure-

ments by Chen *et al.*¹² on single-crystal wüstite, we find that the broadening is proportional to the diffusivity within the experimental errors, but that the proportionality constant is only about 60% of that indicated by the SS theory, taking the corre-

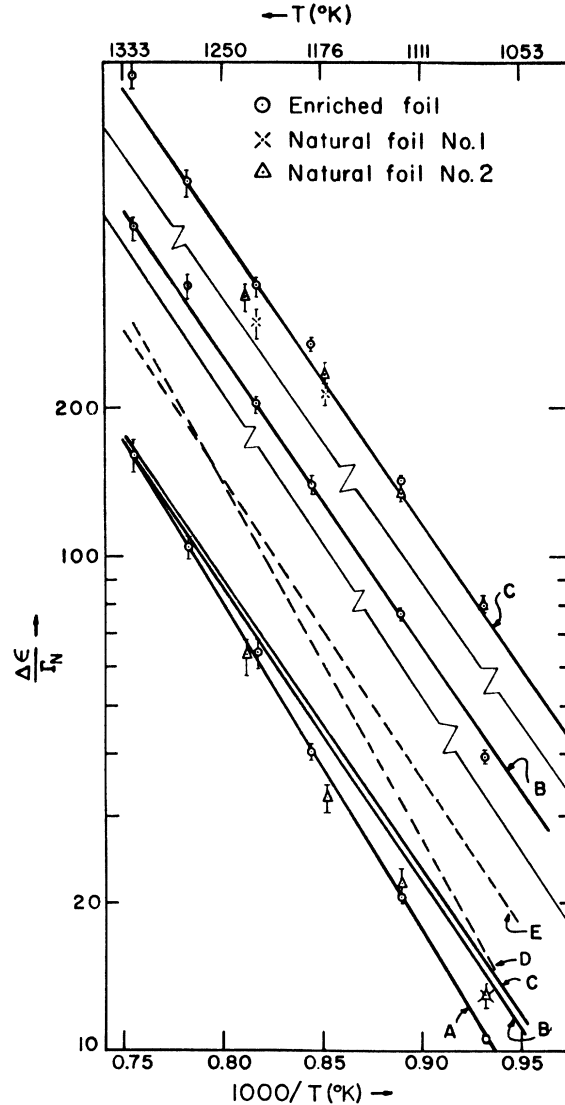


FIG. 2. Temperature dependence of the diffusive broadening of Fe^{57} in FeO_x . Solid lines A, B, and C represent the best fit to our experimental data for relative gas pressures of $P(\text{CO}_2)/P(\text{CO})$ of 1.6, 0.9, 0.5, respectively. Curves D and E give the expected broadening given by the Singwi-Sjölander theory using the data of Ref. 12, for a GR of 1.7 and 0.55, respectively. Curves B and C are plotted twice, with the upper plots representing a simple vertical displacement from the lower cases, with the data shown only in the upper plots to avoid overlapping. The error bars represent only the statistical errors, while the systematic errors in the incremental broadening are such that the real errors are larger than shown for the lowest-temperature data.

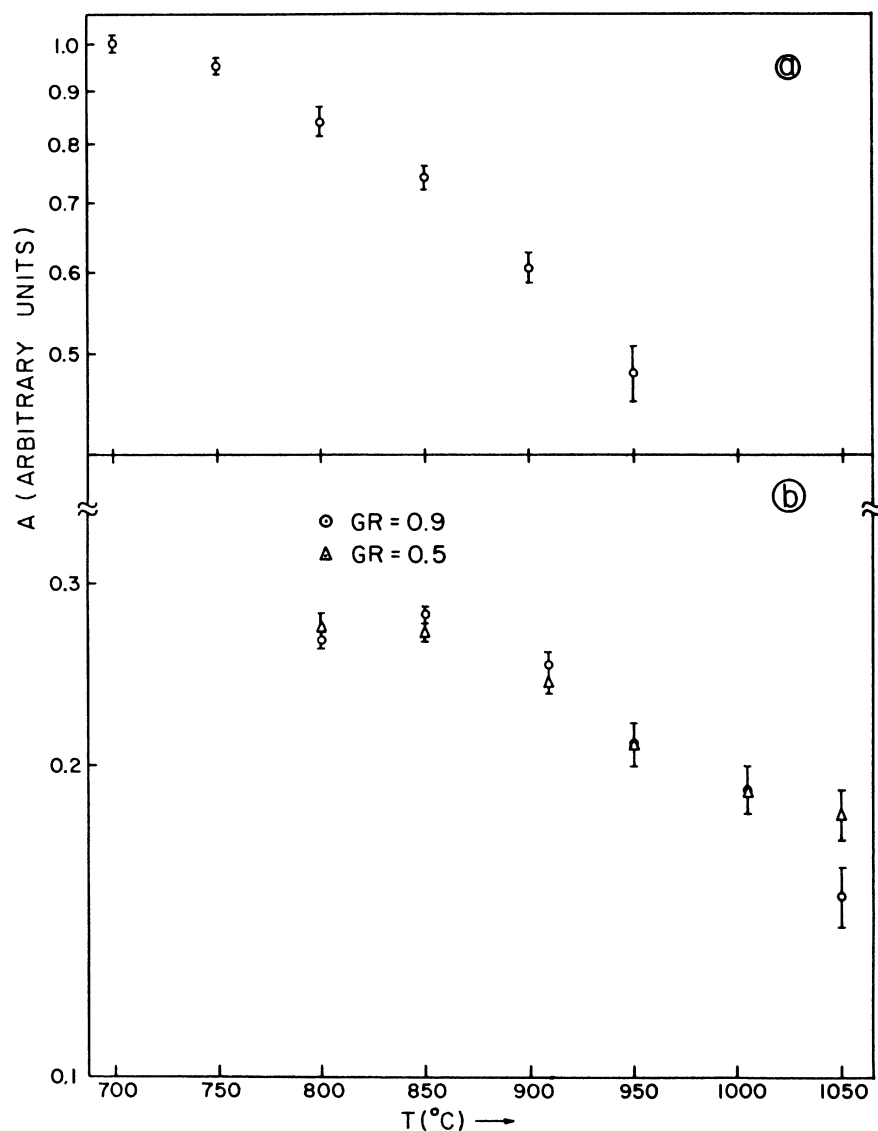


FIG. 3. Plot of $\ln A$ vs T for (a) natural wüstite foil with GR adjusted in order to maintain $x=1.055$ using Darken and Gurry (Ref. 15) calibration for nonstoichiometry and (b) enriched wüstite with a GR of 0.9 and 0.5.

lation factor to be $f_c = 0.78$. Curves A, B, and C in Fig. 2 represent the changes in the diffusion broadening when GR is changed from 1.6 to 0.9 to 0.5. The measured trend in $\Delta\epsilon$ is the same as that indicated in curves D to E, computed by means of Eqs. (1) and (2) from the data of Chen *et al.*¹² If the wüstite system was described by the SS theory then curves D and E should nearly agree with A and C, respectively.

The trends found in the present work are opposite to those of Desmarescaux *et al.*,⁹ Himmel *et al.*,¹⁰ and Hembree *et al.*¹¹ Each of these studies reports a large increase in diffusivity as the cation vacancy concentration is increased in the temperature region 800 to 1050 °C, where the present measurements were made. Our results indicate only a slight dependence of $\Delta\epsilon$ on GR and it

is opposite to that required by the older polycrystalline studies if $\Delta\epsilon \propto D$. This point is strikingly illustrated by the data of Hembree *et al.*,¹¹ who observe at 1100 °C (50 °C above the upper limit of our data) that the diffusivity increases by 50% as GR is changed from 0.5 to 1.6, while our data extrapolated to this temperature indicate that $\Delta\epsilon$ varies by less than 5% over the same range of GR. Chen *et al.*¹² found very little composition dependence to D at this temperature and their findings are in good agreement with our results.

Why our results and those of Chen *et al.* are in conflict with the earlier tracer-diffusion measurements is not certain. The failure to see an increase in the diffusivity with increasing x is not understood, but it is probably connected with clustering of vacancies in wüstite, as has been dis-

cussed by Greenwood and Howe.⁸ Such clustering has been observed in x-ray diffraction studies¹⁹ and neutron diffraction studies,²⁰ and if this clustering is connected with the mechanism of diffusion, then our assumed correlation factor of 0.78 may be only a rough approximation. A correlation factor of unity would only add to the problem, however, as there would be a large discrepancy between our results and those predicted by SS theory, and with $f_C = 1$, correlation would then no longer be a tenable explanation. Predictions would change, of course, if the jump distance in a vacancy cluster were not

the nearest-neighbor cation-cation distance. The most reasonable alternative would be a jump from a site of octahedral symmetry to one of tetrahedral symmetry, resulting in a shortened jump distance and a worsening in the agreement between the SS theory and our experiment.

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