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Mössbauer Spectra of Wustite at High Temperatures: Diffusion Line Broadening†

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In this work, Mössbauer spectra of wustite are studied in the temperature interval 600–910°C. Owing to self-diffusion of iron atoms in the defect wustite lattice, a pronounced broadening of the spectrum is observed. The values of the energy of activation and of the preexponential factor computed from the Mössbauer spectra amount respectively to 25 ± 3 kcal/g-atom and 0.6×10^{-4} cm^2/sec. The error for $\log D_0$ equals ±0.8. These magnitudes are in satisfactory agreement with the values found by isotopic methods.

The Mössbauer experiments on nonstoichiometric iron oxide FeO_{1+x} (wustite) were conducted on quenched samples at low temperatures (*1*, *2*), as this compound is thermodynamically stable only above 570°C. On the other hand, it is known that wustite poorly lends itself to quenching. The high sensitivity of the Mössbauer spectra of wustite to the thermal history of the samples is reported in (*2*). An investigation of the Mössbauer spectra of wustite in the region of its thermodynamic stability was, therefore, of interest.

The method used in the experiment given for studying the Mössbauer spectra of FeO_{1+x} at a high temperature is based on the possibility of carefully oxidizing without mechanical destruction, a thin iron foil in a controlled gaseous atmosphere [as was done, for example, in (*3*) during the investigation of the electrical conductivity of wustite]. Iron foil of a thickness equivalent to 3 mg/cm^2, enriched 60% in the isotope ^{57}Fe, was formed electrolytically. The sample oxidized spontaneously in a mixture of CO_2 and CO in the furnace which permitted Mössbauer spectra to be taken at temperatures up to 1000°C. The composition of the iron oxide was set by the ratio of P_{CO_2}/P_{CO} (*4*, *5*). One can judge the attainment of this equilibrium from the constancy of the Mössbauer spectra. Such methods permit the investigation of iron oxides of varying composition with no change in the geometry of the sample. The negligible area of contact of the sample with the platinum holder practically eliminates the diffusion of foreign impurities into the sample.

The spectra of wustite of composition $FeO_{1.05}$ in a temperature interval of 600–910°C are presented in Fig. 1. The parameters of the spectra are given in Table I. Isomer shifts are relative to the source ^{57}Co in Pd.

As is seen in the figure, when the temperature is raised, one observes a sharp broadening of the Mössbauer line of the wustite. For comparison, two

TABLE I

PARAMETERS OF THE MÖSSBAUER SPECTRA OF $FeO_{1.05}$ IN THE TEMPERATURE INTERVAL INVESTIGATED

Temp., °C	Γ, mm/sec	δ, mm/sec
600	1.13 ± 0.02	0.28 ± 0.04
650	1.11 ± 0.02	0.26 ± 0.04
700	1.20 ± 0.03	0.26 ± 0.04
750	1.48 ± 0.04	0.24 ± 0.04
800	1.76 ± 0.06	0.21 ± 0.04
825	1.97 ± 0.07	0.21 ± 0.04
850	2.18 ± 0.09	0.18 ± 0.04
910	3.0 ± 0.2	0.10 ± 0.08

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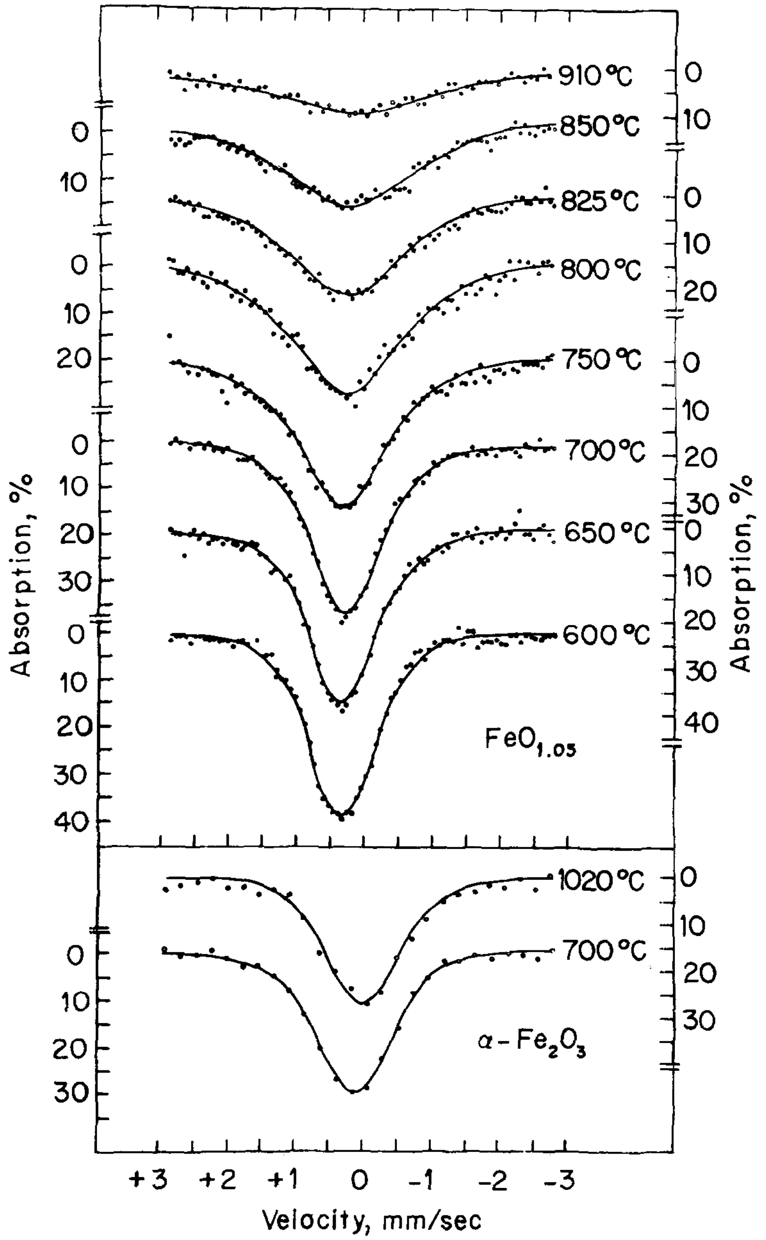

FIG. 1. Mössbauer spectra of wustite and hematite at high temperatures. Ordinate is absorption (%); abscissa is velocity (mm/sec).

spectra of α-Fe_2O_3 taken under the same conditions at temperatures of 700 and 1020° are presented in the same figure. We note that the area under the curve of the resonance absorption for $FeO_{1.05}$ and α-Fe_2O_3 changes approximately equally. The temperature dependence of the wustite linewidth that was observed can be connected only with an intensive self-diffusion of the iron atoms in the defect lattice of this oxide. The influence of diffusion of the absorbing (or radiating) nuclei in the Mössbauer spectra is theoretically examined in (*6, 7*). According to (*6*), when there is no correlation between two successive atom jumps, the broadening of the spectral line, $\Delta\Gamma$, is connected with the atom's life time at a given lattice site, τ, by the relationship:

$$\Delta\Gamma = \frac{2\hbar}{\tau}\left[1 - \int \exp\,(i\boldsymbol{\varkappa}\cdot\mathbf{r})h(\mathbf{r})d\mathbf{r}\right]. \qquad (1)$$

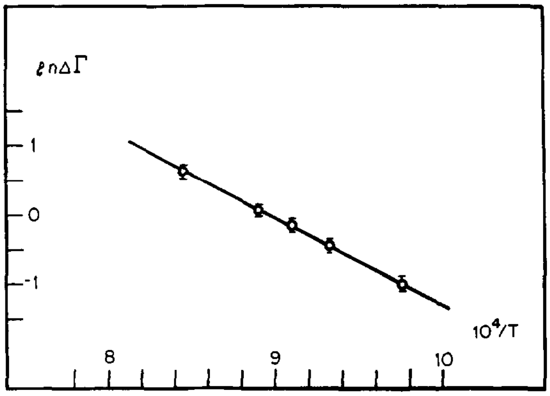

FIG. 2. The dependence of the logarithm of the linewidth of $FeO_{1.05}$ on inverse temperature.

Here $\varkappa$ is the wave vector of the incident γ quantum; $h(\mathbf{r})$ is the function which defines the probability of finding the particle after one jump at point $\mathbf{r}$, if before the jump it is found at the origin of the coordinates. It is not difficult to be convinced that for a polycrystalline sample under the condition $\kappa r \gg 2\tau$ the integral in the right part of Eq. (1) is negligible in comparison with unity. Assuming a NaCl-type lattice with $\tau \approx a_0^2/12D$ and considering that the temperature dependence of the diffusion coefficient in a solid is usually described by the equation $D = D_0 \exp(-E/kT)$, we get:

$$\Delta\Gamma \approx 24\hbar_{D_0}/a_0^2 \exp(-E/kT], \qquad (2)$$

where E is the energy of activation for self-diffusion and a_0 is the lattice constant.

The dependence of the logarithm of the line broadening on temperature from 700°C on up is presented in Fig. 2. As can be seen from the figure, the line broadening of wustite that was observed experimentally is described very well by the exponential dependence of Eq. (2) with values of $E = 25 \pm 3$ kcal/g-atom and $D_0 = 0.6 \times 10^{-4}$ cm²/sec. The error for $\log D$ amounts to ± 0.8.

In the determination of self-diffusion coefficients in wustite by the method of radioactive indicators values for the energy of activation and for the preexponential factor of 29.7 kcal/g-atom and 1.2×10^{-2} cm²/sec* and 30.2 kcal/g-atom and 1.4×10^{-2} cm²/sec were found for oxides of composition $FeO_{1.103}$ (*8*) and $FeO_{1.087}$ (*9*), respectively. In the temperature interval investigated, the magnitudes of the self-diffusion coefficients obtained from the Mössbauer data are 1.5–3 times less than the average values gained from the isotopic methods.

Bearing in mind the approximate nature of the observations presented above, such an agreement of results in experiments which are different in principle can be considered satisfactory. In the same way, the truth of the interpretation of the temperature dependence of the linewidth in wustite is convincingly confirmed.

In conclusion, it is interesting to note that the spectral lines of wustite are symmetrical, although one might expect that the presence of a certain amount of Fe^{III} in FeO_{1+x} would lead to an asymmetry in the spectrum because of the difference in the isomer shifts of the lines of Fe^{II} and Fe^{III}. Not long ago, the Mössbauer spectra of the solid solutions $FeO_{1+x} \cdot zMgO$ were studied. The oxides of this system, in contrast to wustite, are easily quenched. The Mössbauer-spectra lines of these solutions in the temperature interval 80–300°K also turned out to be symmetrical (*10*). This allows one to suppose that the asymmetry of the Mössbauer line found for FeO_{1+x} in (*1*) is apparently connected with changes produced during the quenching of the samples, which are difficult to control.

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* In Eq. (4) of Ref. (8), the value of the preexponential factor is presented as 0.118 cm/sec. This, obviously, is an error, as can be seen from the data of Table III and Fig. 7 of the same work.