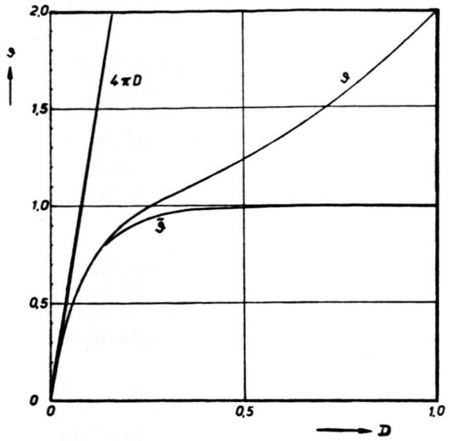


Abb. 2. Kennwerte bei freier gedämpfter Schwingung.

aus Gl. (12)

$$\vartheta = \vartheta(D) = 4\,\pi\,D\,\lambda\,. \tag{20}$$

Darin ist $\lambda = \Omega/\omega$ die Abstimmung des Systems. Die spezifische Dämpfung ϑ gemäß Gl. (20) ist somit bei erzwungenen Schwingungen abhängig von der Abstimmung λ des Systems; demgegenüber lautet die meistens im Schrifttum wiedergegebene Umrechnungsbeziehung stark abweichend

$$\tilde{\vartheta} = 4\,\pi\,D\,. \tag{21}$$

Bestimmt man bei der Auswertung erzwungener Schwingungen das Dämpfungsmaß D und berechnet die spezifische Dämpfung nach Gl. (21), so weicht das Ergebnis um so mehr vom tatsächlichen Wert (20) ab, je weiter man von der Abstimmung $\lambda = 1$, der Resonanzlage, entfernt ist.

Stoichiometric FeO as Metastable Intermediate of the Decomposition of Wustite at 225 °C

BERNHARD HENTSCHEL

Institut für Physikalische Chemie der Universität Münster
Münster (Westfalen), West Germany

(Z. Naturforsch. **25 a**, 1996—1997 [1970]; received 16 October 1970)

If a wustite sample prepared above 1000 °C is annealed at 225 °C stoichiometric FeO occurs as a metastable decomposition intermediate, as has been demonstrated röntgenographically and by means of the Mössbauer-effect.

In 1954 HALLA[1] and coworkers suggested that in the decompositon of wustite below 570 °C the system passes through a metastable wustite phase which is richer in iron than the starting specimen. HOFFMAN and FISCHER[2] were able to corroborate this suggestion by demonstrating that during the annealing of wustite specimens below 570 °C the lattice constant increases, such that the final value attained depends not upon the initial composition $Fe_{1-y}O$, but only upon the value of the annealing temperature. From the linear relationship between the lattice constant (a) and the iron deficiency (y) according to the values of MARION[3] (which have been confirmed by ENGELL[4]) HOFFMANN was able to determine the iron content of the metastable wustite formed during decomposition; in the case of some specimens with particularly high iron contents the relationship was extrapolated to the iron-rich side.

For the present investigations the initial wustite specimens of definite composition were prepared by oxidation of vacuum-melted sheets of pure iron, 30 μm thick. The oxidation was carried out at 1100 °C in a vertical furnace with $CO - CO_2$ mixtures. During the preparation the sample was hung by means of a platinum wire from a hollow iron cylinder which was suspended in a magnetic field within the gas-inlet tube above the furnace. By rapid dropping of the electromagnet the sample could be transferred in less than half a second from the furnace to a water-cooled section of the reaction tube. The composition of the samples was determined gravimetrically; the values were very reproducible. Neither magnetite nor α-iron, which could have been produced by decomposition during quenching, could be observed by x-ray diffraction or by means of the Mössbauer-effect.

Mössbauer spectra were recorded for a number of wustite samples, the composition of which varied throughout the range of phase stability at 1100 °C. These spectra do not agree with the interpretation of COX and SHIRANE[5] for Mössbauer spectra of wustite; their form corresponds far better to that published by ELIAS and LINNETT[6]. The lattice constants were measured on the [400] reflex of wustite (between 63 and 65°) by means of a goniometer calibrated against silver. The values thus determined agree well with those of MARION (compare Fig. 1, range $y > 0.05$).

For the investigation of the subeutectic wustite decomposition, samples of the composition $Fe_{0.940}O$ were

Reprints request to Dipl.-Chem. B. HENTSCHEL, Institut für Physikalische Chemie, Westfälische Wilhelms-Universität, *D-4400 Münster (Westfalen)*, Schloßplatz 4.

[1] L. CASTELLIZ, W. DE SUTTER, and F. HALLA, Mh. Chem. **85**, 487 [1954].

[2] W. A. FISCHER and A. HOFFMANN, Arch. Eisenhüttenwesen **29** (No. 2), 107 [1958]. — A. HOFFMANN, Z. Elektrochem. **33** (No. (2), 207 [1959].

[3] F. MARION, Doc. Métallurg. **24**, 87—136 [1955].

[4] H.-J. ENGELL, Arch. Eisenhüttenwesen **28**, 109 [1957].

[5] G. SHIRANE and D. F. COX, Phys. Rev. **125** (No. 4) [1962].

[6] D. J. ELIAS and J. W. LINNETT, Trans. Faraday Soc. **65** (No. 562), 2673 [1969].

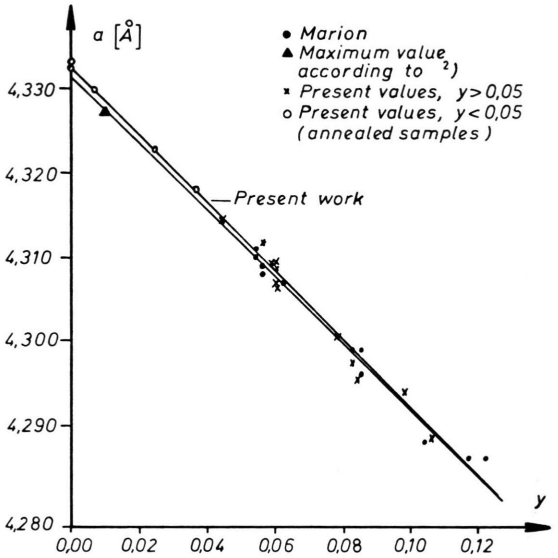
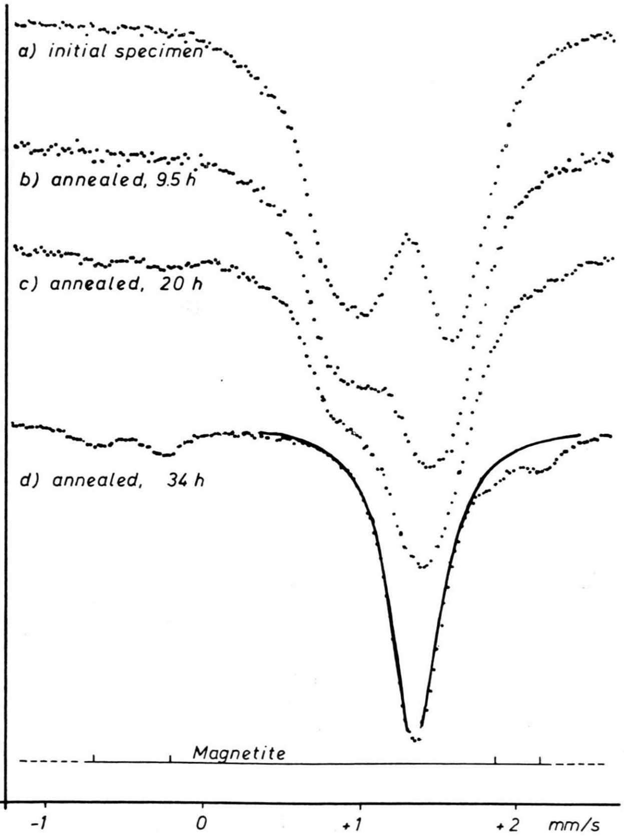


Fig. 1. Dependence of the lattice constant a upon iron deficiency y.



placed in an aluminum furnace at 225 °C (constant within ±0.05°) for times ranging between 20 minutes and 72 hours. These annealed specimens yielded lattice constants exceeding 4.310 Å, the limit of the stable iron-rich wustite; the deficiency of iron is correspondingly less than $y = 0.05$ (see Fig. 1). The presence of magnetite, which must thus occur as an oxygen-rich product, could be demonstrated, both by x-ray diffraction and by means of the Mössbauer-effect, for specimens which had been annealed for a long period.

A few typical Mössbauer spectra are compared in Fig. 2. Curve a reproduces the spectrum of the initial wustite; the splitting into two nonequal peaks indicates that not all iron ions have the same electron density at the nucleus. A specimen which was annealed for 9.5 hours yields spectrum b, wherein the splitting is less noticeable. After 20 hours of annealing the lines of the decomposition product magnetite may already be recognized (curve c). With further annealing the splitting completely disappears; the specimens now yield a single line. Curve d in Fig. 2 exhibits this peak, obtained for a sample annealed for 34 hours, in comparison with an individual theoretical Lorentzian-line with which it agrees well. The line width amounts to 0.34 mm/s. From the disappearance of the splitting it may be concluded that all iron ions of the lattice possess the same electron density and exhibit no electric field gradient at the nucleus. The lattice constants of the corresponding specimens attain values which, according to Fig. 1, correspond to stoichiometric FeO. After an annealing period of more than 50 hours the lines of α-iron appear beside those of magnetite. Thus the decomposition of wustite under the conditions applied here appears to occur in two steps: in the first one magnetite and stoichiometric FeO are formed; subsequently the stoichiometric FeO decomposes into α-iron and more magnetite.

The author wishes to thank Prof. Dr. E. Wicke for suggesting this research project and for his steady interest in the progress thereof.

Fig. 2. Mössbauer spectra of wustite and FeO. Velocity with respect to sodium nitroprusside.