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MÖSSBAUER STUDY OF HIGH-TEMPERATURE DIFFUSION IN MAGNETITE

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A Mössbauer investigation has been made of the temperature dependence of cation diffusion in magnetite, $Fe_{3-\delta}O_4$. In the temperature range 1100 to 1400 °C, spectral line shapes are influenced characteristically by cation diffusion processes. At high oxygen partial pressures, p_{O_2}, the in-situ spectra give clear evidence of rapid migration of cations on octahedral sites by a vacancy mechanism, while interstitial processes involving the tetrahedrally coordinated iron ions dominate at low p_{O_2}.

1. Introduction

Magnetite, $Fe_{3-\delta}O_4$, crystallizes in the spinel structure. With its two cation sites of different coordination (tetrahedral and octahedral) and its considerable range of nonstoichiometry, δ, magnetite provides an interesting example for the investigation of the microscopic ionic migration processes in complex solid state systems. Despite the fact that Mössbauer spectra are highly sensitive to solid state diffusion (see, e.g., the pioneering experimental work of Mullen et al. [1] and Flinn et al. [2]) Mössbauer spectroscopy has not been widely used in this respect. In this contribution, we report results which extend our earlier work [3]. We present the first high-temperature Mössbauer study of diffusion in this compound. Mössbauer transmission spectra of magnetite have been measured at temperatures in the range 900–1400 °C using defined oxygen partial pressures, p_{O_2}, produced by flowing CO/CO_2 gas mixtures, to define and control the composition of the crystal.

2. Results and discussion

The Mössbauer spectra of magnetite depend upon stoichiometry, as shown in fig. 1 for $T = 1300\,^{\circ}\mathrm{C}$. These changes in line shape may be discussed in terms of defect-induced cationic migration processes. In binary oxide crystals, defect concentrations can be varied in a defined way by introducing the appropriate external gas atmospheres: the formation of cation vacancies (V) occurs by reaction of oxygen with magnetite according to

$$3\mathrm{Fe}^{2+}_{\mathrm{Fe}} + \tfrac{2}{3}\mathrm{O}_2 \rightleftharpoons 2\mathrm{Fe}^{3+}_{\mathrm{Fe}} + V_{\mathrm{Fe}} + \tfrac{1}{3}\mathrm{Fe}_3\mathrm{O}_4. \qquad (1)$$

Iron ions on interstitial sites (I) are formed through the Frenkel disorder reaction

$$\mathrm{Fe}^{n+}_{\mathrm{Fe}} + V_{\mathrm{I}} \rightleftharpoons \mathrm{Fe}^{n+}_{\mathrm{I}} + V_{\mathrm{Fe}}. \qquad (2)$$

Application of the concepts of point defect thermodynamics to the above defect equilibria shows that the concentration of cation vacancies varies as $p_{\mathrm{O}_2}^{2/3}$, while that of the iron interstitials changes as $p_{\mathrm{O}_2}^{-2/3}$. Indeed, in quantitative agreement with this prediction, the isothermal cation tracer diffusion coefficients, D^{T}, exhibit a minimum as a function of p_{O_2} with $D^{\mathrm{T}} \sim p_{\mathrm{O}_2}^{2/3}$ at high and $D^{\mathrm{T}} \sim p_{\mathrm{O}_2}^{-2/3}$ at low oxygen partial pressures [4]. This behaviour unambiguously demonstrates that at high oxygen partial pressures, corresponding to an iron deficit ($\delta > 0$), cation diffusion is dominated by a vacancy mechanism, whereas for iron excess ($\delta < 0$), at low P_{O_2}, interstitial processes dominate.

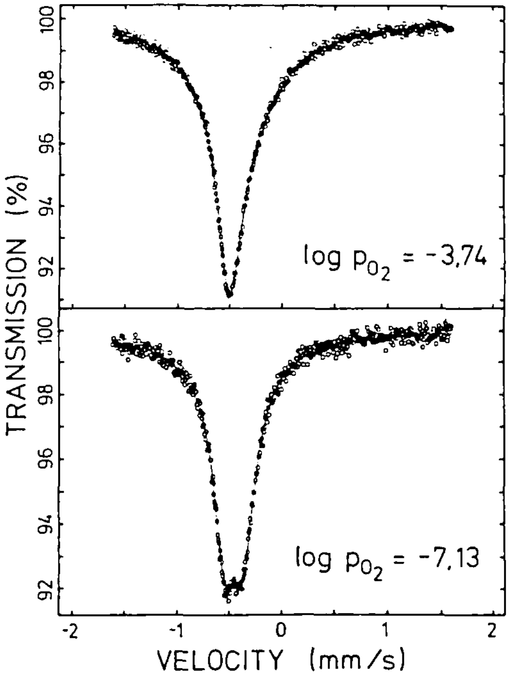

Fig. 1. Mössbauer spectra of magnetite at 1300 °C as a function of oxygen partial pressure, p_{O_2}.

An analysis of the dynamic Mössbauer line shapes has to account for the existence of the two cation sites of different symmetry. Due to the exact tetrahedral symmetry around the tetrahedrally coordinated sites, the quadrupolar interaction at these sites vanishes; at the octahedrally coordinated sites, the EFG is nonvanishing and possesses axial symmetry with respect to the ⟨111⟩ directions. Since the direction of the EFG major axis changes for jumps between neighbouring sites, the line shape problem is complicated not only by the existence of two cationic sublattices, but also by the field gradient fluctuations which finally in the fast diffusion limit lead to a vanishing of the quadrupole splitting for the octahedrally coordinated sites. Independent of the microscopic migration mechanism, the cationic dynamics in magnetite are completely specified by three elementary jump rates: that for octa-octa jumps, w_{oo}, that for tetra-tetra jumps, w_{tt}, and those for the cation exchange between the two sublattices, $w_{\mathrm{to}} = 2\ w_{\mathrm{ot}}$. Two limiting cases can be distinguished: either (i) cations jumps between sites on the same sublattice or (ii) jumps between the two sublattices are dominating [3]. As will be discussed elsewhere [5], we can exclude the case of rapid sublattice exchange of cations. Therefore, we have analyzed our data using a model of cation diffusion that accounts only for diffusion on sublattices. The line shape function consequently is given by a superposition of the two contributions due to the iron ions on the two separate sublattices.

The diffusion-induced relaxation process for cation migration on one sublattice is described by the following shape function [6]:

$$\phi_n(\omega) \sim \mathrm{Re}\int_{\text{powder}} \frac{\sin\vartheta\ \mathrm{d}\vartheta\ \mathrm{d}\varphi}{\mathrm{i}\omega_n + (\Gamma/2) + w_{nn}[1 - g(\boldsymbol{k})] + \dfrac{Q_n^2}{\mathrm{i}\omega_n + (\Gamma/2)w_{nn}}} \tag{3}$$

Here Γ is the line width in absence of relaxation; $\omega_n = \omega - S_n$, with ω denoting the Doppler velocity and S_n the isomer shift of Fe in the sublattice of type n ($n =$ o, t). Q_n stands for the quadrupole interaction $\frac{1}{2}e^2q_nQ$. ϑ and φ are the angles determining the directions of the γ-wave vector $\boldsymbol{k}$ versus the crystal axes. S_{o} and S_{t} were determined at each temperature from the spectra with slowest relaxation. Q_{o} is nearly temperature independent with $Q_{\mathrm{o}} = 0.18$ mms^{-1} and $Q_{\mathrm{t}} = 0$. In the framework of the encounter model of atomic diffusion [7] $g(\boldsymbol{k})$ is given by $g(\boldsymbol{k}) = \Sigma_r g(\boldsymbol{r})\ \mathrm{e}^{\mathrm{i}(\boldsymbol{k},\boldsymbol{r})}$. The probabilities $g(\boldsymbol{r})$ for a displacement of the Mössbauer atom to a position $\boldsymbol{r}$ with respect to its initial position in the encounter were determined from Monte-Carlo simulations [5]. Note that the EFG fluctuations are treated by spheric approximation which is assumed to be a reasonable approach to the EFG reorientations. The intensities of ϕ_{o} and ϕ_{t} were fixed to 2 : 1.

Cationic jump rates w_{oo} and w_{tt} thus can be determined from the experimental spectra. Results for $T = 1300\,^{\circ}\mathrm{C}$ are shown in fig. 2. They provide detailed information on the cation dynamics on octahedrally and tetrahedrally coordi-

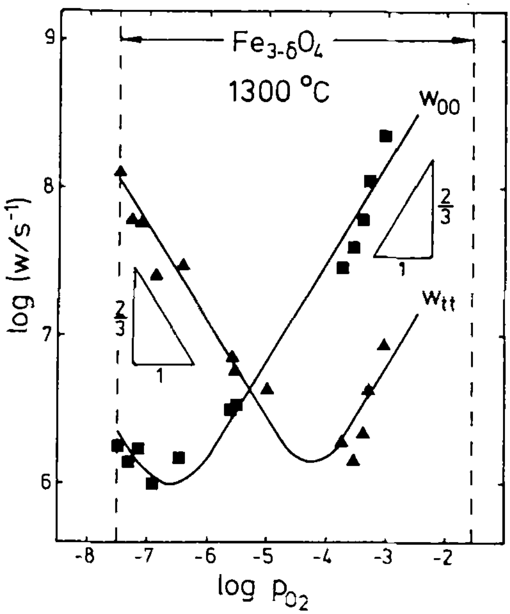

Fig. 2. Cation jump rates on the two sublattices of magnetite at 1300 °C as a function of oxygen partial pressure, p_{O_2}.

nated sites. In particular, by virtue of the observed p_{O_2} dependencies, they indicate that on both kinds of sites ions perform vacancy – as well as interstitial-induced migration processes at high and at low p_{O_2}, respectively. Further details and additional data at 1000, 1100, 1200, 1300, 1350, and 1400 °C, including a comparison of our spectroscopic data with the data obtained from macroscopic tracer diffusion studies [4], will be given elsewhere [5].

3. Conclusion

The present work constitutes the first experimental documentation and quantitative determination of cation migration on the two sublattices of magnetite. In the case of an iron deficit, $\delta > 0$, cation diffusion on the octahedral sublattice dominates. Cation diffusion on the tetrahedral, as well as exchange processes between the two cation sublattices, play only a minor role. The diffusion broadening of the octahedral component of the signal varies as $p_{O_2}^{2/3}$, which is evidence for a vacancy mechanism for cation diffusion. The diffusion data calculated from our spectroscopic data are in good agreement with the macroscopic tracer diffusion data. In the region of iron excess, $\delta < 0$, the line shapes are dominated by interstitial processes involving the tetrahedrally coordinated iron ions.

Acknowledgements

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