

# A Variable-Temperature Mössbauer Study into the Structure, Disorder and Formation Kinetics of Iron Nitrides

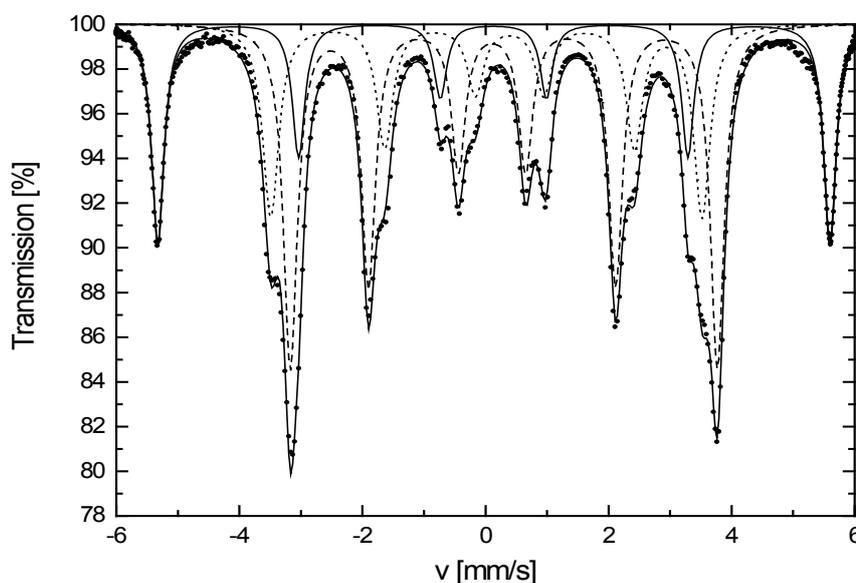
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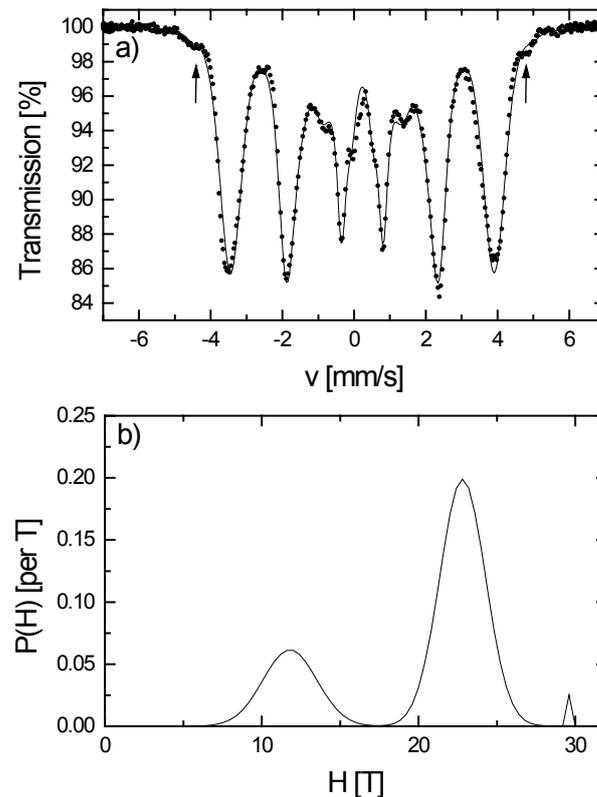
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Mössbauer spectra of the iron nitrides  $\gamma'$ -Fe<sub>4</sub>N<sub>1+ $\delta$</sub>  and  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub> have been measured at room temperature and at 550 °C.  $\gamma'$ -Fe<sub>4</sub>N<sub>1+ $\delta$</sub>  is well ordered and close to ideal stoichiometry even at high temperatures. Its room temperature Mössbauer spectrum exhibits three magnetically split subspectra due to the fact that the structurally equivalent Fe(1) sites are split into two spectroscopically inequivalent sites, Fig. 1. This is consequence of the simultaneous presence of magnetic and quadrupolar interactions at Fe(1) sites, see Refs. [1,2]. In the case of  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub>, however, the stoichiometry-dependent magnetically-split room temperature spectra demonstrate the extensive disorder of nitrogen in the compound, Fig. 2 [2,3]. At 550 °C, spectra of  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub> have been measured at various defined nitrogen activities. The quadrupole-split spectra are discussed in relation to structure and disorder of the nonstoichiometric material. In particular, it is shown that the composition dependent high-temperature spectra of  $\epsilon$ -Fe<sub>3</sub>N<sub>1+x</sub> can be modelled in the framework of a simple two-site model [2].



**Fig. 1** Mössbauer spectrum of  $\gamma'$ -Fe<sub>4</sub>N at room temperature. The fit is based on three subspectra which are indicated by a solid line due to Fe(2) and by dotted and dashed lines for subspectra which are due to Fe(1a) and Fe(1b), respectively.



**Fig. 2** a) Mössbauer spectrum of  $\epsilon\text{-Fe}_{3+x}\text{N}$  at room temperature, b) Distribution of local magnetic fields according to the fit shown in Fig. 2a.

By means of time-resolved Mössbauer measurements, the formation reaction of  $\gamma\text{-Fe}_4\text{N}_{1+\delta}$  has been followed at *in situ* conditions at 550 °C. The formation kinetics have been found to obey a parabolic rate law. The nitrogen activity dependence of the experimental rate constant for the formation of  $\gamma\text{-Fe}_4\text{N}$  is discussed in relation to the point defect structure of the compound the atomic diffusion of nitrogen. The analysis provides evidence for the diffusion of nitrogen by means of a vacancy and an interstitial mechanism in  $\gamma\text{-Fe}_4\text{N}_{1+\delta}$  where the latter is dominating the formation kinetics of the compound.

### References

- [1] C. A. Kuhnen, R. S. de Figueiredo, V. Drago, E. Z. da Silva, J. Magn. Mater. 111 (1992) 95.
- [2] O. Bartels, K.-D. Becker, Z. Phys. Chem. 221 (2007) 1509.
- [3] P. Schaaf, Prog. Mater. Sci. 39 (2001) 1.