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# Mössbauer study of gamma‴-iron nitride film

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**Abstract** A single-phase $\gamma'''$-FeN film with the rock-salt structure was produced by pulsed laser deposition of Fe onto an Al substrate in a $N_2$ atmosphere. Its Mössbauer spectra and powder X-ray diffraction patterns were measured. $\gamma'''$-FeN was found to be antiferromagnetic exhibiting a hyperfine magnetic field of 30 T at a temperature of 5 K. It was found to have a Néel temperature of 220 K. A minor component with a higher hyperfine magnetic field of 49 T at 5 K was also observed. It is thought to originate from defects in $\gamma'''$-FeN.

**Keywords** Iron nitride film · $\gamma'''$-FeN · Pulsed laser deposition · Mössbauer spectroscopy · Néel temperature

## 1 Introduction

Iron nitrides are important industrial materials because of its mechanical and magnetic properties. Iron nitride films and particles have been prepared by various methods [1–5]. FeN has been reported to have two phases: $\gamma''$-FeN (ZnS structure) and $\gamma'''$-FeN (NaCl structure). These two phases are generally formed simultaneously, making it difficult to produce a single phase [2, 6]. We previously reported that the yields of the two phases could be varied and that pure $\gamma''$-FeN and $\gamma'''$-FeN could be obtained by varying the substrate temperature during pulsed laser deposition (PLD); we also reported that Mössbauer spectra revealed that $\gamma''$-FeN and $\gamma'''$-FeN

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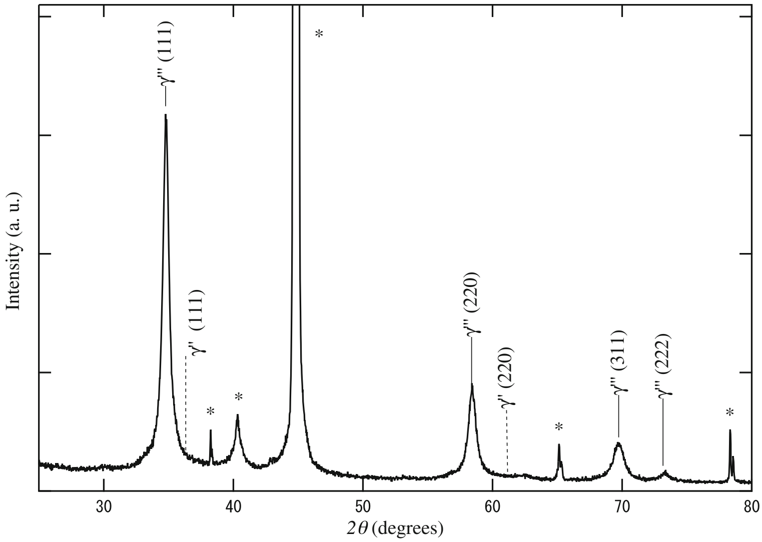


**Fig. 1** XRD pattern of $\gamma'''$-FeN film. Peaks marked with '*' indicate the Al substrate, and *dashed lines* indicate expected peak positions of $\gamma''$-FeN

are respectively paramagnetic and antiferromagnetic at low temperatures [7]. In the present study, Mössbauer spectra of a $\gamma'''$-FeN film were measured at temperatures between 5 and 300 K to observe the temperature dependence of the hyperfine magnetic field.

## 2 Experimental

PLD was performed using a Nd:YAG laser (wavelength: 532 nm; pulse energy: 85 mJ; repetition rate: 10 Hz). Fe metal was employed as the target material. The vapor was deposited on an Al substrate by irradiating the target with $1.1 \times 10^5$ pulses. During deposition, the $N_2$ pressure was maintained at 70 Pa and the Al substrate temperature was maintained at 520 K to produce a pure $\gamma'''$-FeN film. The film samples were measured by Mössbauer spectroscopy (Wiessel, MDU1200) at temperatures between 5 and 300 K. Powder X-ray diffraction (XRD; RINT2500, Rigaku; Cu-K$\alpha$) patterns were measured to confirm the assignments.

## 3 Results and discussion

A single-phase $\gamma'''$-FeN film was produced according to the method described in our previous study [7]. As $\gamma'''$-FeN and $\gamma''$-FeN tend to form simultaneously, we obtained XRD patterns of the sample film to confirm that single-phase $\gamma'''$-FeN had formed. Figure 1 shows the XRD pattern of the sample film, which belongs to $\gamma'''$-FeN with the lattice parameter of $a = 0.45$ nm. The XRD patterns of $\gamma''$-FeN produced by different experimental conditions were measured in our previous study [7], but $\gamma''$-FeN was not observed in the present XRD pattern. Although XRD is not

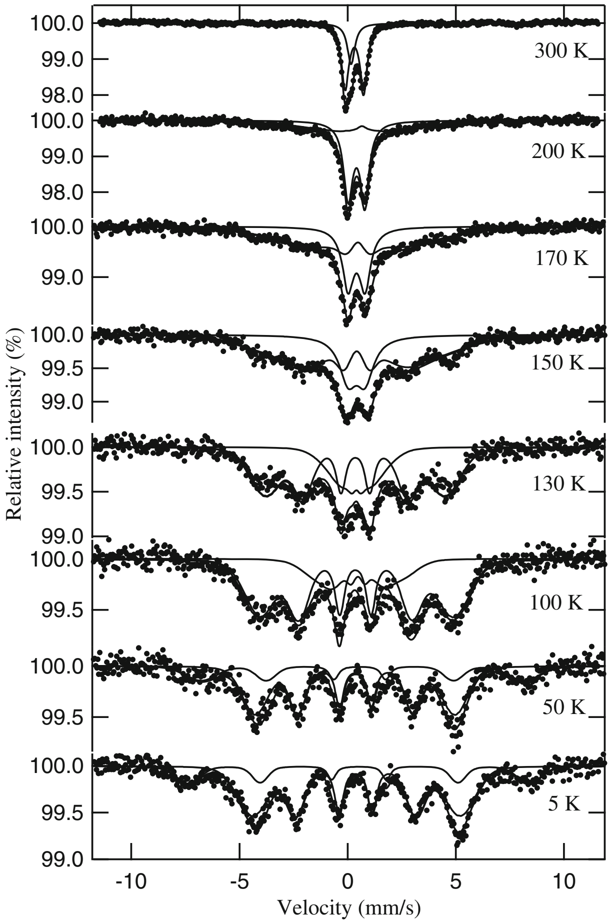


**Fig. 2** Mössbauer spectra of $\gamma'''$-FeN film measured at temperatures between 5 and 300 K

**Table 1** Mössbauer parameters of $\gamma'''$-FeN film at 5 and 300 K

| Component | Measured at 300 K | | | Measured at 5 K | | |
|---|---|---|---|---|---|---|
| | $\delta$ (mm/s) | $\Delta Eq$ (mm/s) | Yields (%) | $\delta$ (mm/s) | $H$ (T) | Yields (%) |
| I | 0.312(2) | 0.851(4) | 76 | 0.38(1) | 30(4) | 77 |
| II | 0.160(4) | – | 24 | 0.51(3) | 49(3) | 23 |

sensitive to lattice defects, it revealed that no other phases besides $\gamma'''$-FeN were present. Mössbauer spectra of the $\gamma'''$-FeN film were measured for temperatures between 5 and 300 K (Fig. 2) to investigate the magnetic properties. The spectrum measured at 5 K exhibited two sets of sextets, which have relatively broad absorption due to lattice defects. The spectra were fitted by assuming narrow distributions of hyperfine magnetic fields $H$: a Gaussian distribution with a half width $\Gamma_H$ of $\sim$4 T was assumed for the $H$ distribution. The two components (I and II) had hyperfine magnetic fields $H$ of 30 and 49 T, respectively (Table 1). The major component (I) corresponds to antiferromagnetic $\gamma'''$-FeN. The minor component

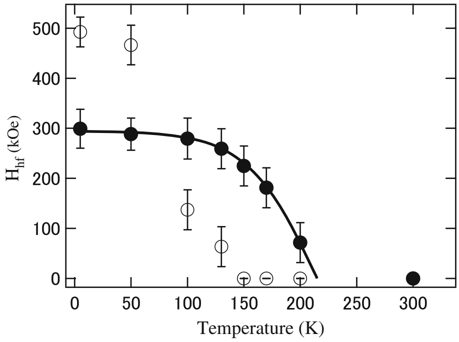


**Fig. 3** Temperature dependences of hyperfine fields of $\gamma'''$-FeN film. *Filled* and *open circles* indicate components I and II, respectively

(II) with the large $H$ has been observed in previous studies [6, 7]; it may originate from defects in the $\gamma'''$-FeN lattice. Figure 3 shows the temperature dependences of $H$ for the two components. For both components, $H$ decreases with increasing temperature. The temperature dependence of $H$ of $\gamma'''$-FeN (component I) could be fitted with a Brillouin function, giving a Néel temperature of 220 K. The other component (II) does not show a well-defined Néel temperature, because it originates from defects. The spectrum measured at 300 K consists of a singlet and a doublet. Comparison of the peak area intensities of the spectra reveals that the doublet corresponds to component I and that the singlet corresponds to component II. These two components have a ratio of 4:1. Table 1 lists the Mössbauer parameters.

Density functional calculations using the WIEN2k package [8] were performed to clarify the structures of $\gamma'''$-FeN and the effects of defects on the Mössbauer parameters. Previous theoretical studies of $\gamma'''$-FeN predict that Fe atoms in the (111)-plane will be ferromagnetically ordered and that the spin direction will alternate in adjacent planes in the [111]-direction. They also predict that the unit cell will be trigonal [9]. The calculations in those studies were performed for $\gamma'''$-FeN and the hyperfine magnetic field $H$ was calculated to be 34 T, which agrees well with the experimental result of 30 T. When a defect of a N atom is present in a $2 \times 2 \times 2$ trigonal structure, two Fe sites are predicted to appear with $H = 30$ and 35 T. Although a N atom defect generates higher hyperfine magnetic fields for Fe, they are still considerably smaller than the observed value. We also performed calculations for an Fe atom defect, but the results did not fit the experimental results. Thus, the origin of component II is unclear.

## 4 Conclusion

A single-phase $\gamma'''$-FeN film was produced by PLD in $N_2$ ambient gas and Mössbauer spectra of the $\gamma'''$-FeN film were measured at temperatures between 5 and 300 K to observe the temperature dependence of the hyperfine magnetic field. Antiferromagnetic $\gamma'''$-FeN showed $H = 30$ T at 5 K and a Néel temperature of 220 K. The results of density functional calculations of $\gamma'''$-FeN agreed well with the experimental results. A minor component was also observed with $H = 39$ T at 5 K; it was paramagnetic above 150 K. This minor component may originate from defects, but further theoretical calculations are required to confirm this.

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