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LETTER TO THE EDITOR

The magnetization of $\alpha''\text{Fe}_{16}\text{N}_2$

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Abstract. Powder and foils containing up to 40% $\alpha''\text{Fe}_{16}\text{N}_2$ have been prepared by annealing nitrogen-martensite. The magnetization of the α'' phase is deduced from magnetization measurements, coupled with a quantitative phase analysis based on Mössbauer spectra. At room temperature the values are 225–270 J T⁻¹ kg⁻¹ corresponding to $J_s = 2.1$ –2.5 T. The average iron moment at $T \sim 0$ K is 2.3–2.6 μ_B , which is in accord with the results of spin-polarized band structure calculations.

It would be useful to have a ferromagnet with a magnetization substantially greater than that of αFe . The relevant property for many applications is the spontaneous polarization J_s , which is 2.15 T for iron at room temperature. Related quantities are the magnetic moment per unit mass $\sigma = 220$ J T⁻¹ kg⁻¹ and the magnetic moment per atom $\mu_{\text{Fe}} = 2.2 \mu_B$ [1]. Since αFe is known to be a weak ferromagnet with an incompletely filled 3d \uparrow band there should be scope for increasing the moment, but the greatest polarization that has been achieved with binary iron-based substitutional alloys is $J_s = 2.45$ T for Fe₆₅Co₃₅. Ferrites contain iron ions with much larger atomic moments (5 μ_B for Fe³⁺) yet J_s does not exceed 0.6 T because the order is ferrimagnetic and most of the volume is occupied by non-magnetic O²⁻.

The ordered, metastable iron nitride $\alpha''\text{Fe}_{16}\text{N}_2$ was discovered by Jack in 1951 [2]; its magnetic properties remained unexplored until 1972 when Kim and Takahashi produced thin films, where $\alpha''\text{Fe}_{16}\text{N}_2$ was the major phase, by evaporating iron in nitrogen. Some of these films were found to have a polarization as high as 2.64 T, and the polarization of pure $\alpha''\text{Fe}_{16}\text{N}_2$ was inferred to be 2.76 T, corresponding to an average iron moment of 3.0 μ_B [3].

In recent years, several other Japanese groups have made films containing $\alpha''\text{Fe}_{16}\text{N}_2$ by different methods, with quite variable results [4–7]. Most remarkable are those of Sugita and co-workers, who produced films by molecular beam epitaxy on (Ga_{0.8}In_{0.2})As substrates where the polarization of Fe₁₆N₂ was found to be 2.9 T [5]. Their result was recently corroborated by a ferromagnetic resonance experiment [8]. The corresponding average moment per iron atom μ_{av} is 3.2 μ_B at room temperature rising to 3.5 μ_B at $T \sim 0$ K. Such a large moment seems to be incompatible with the band theory of metals; three independent band-structure calculations have yielded average moments per iron atom of approximately 2.4 μ_B [9–11]. Other workers, however, report values of the magnetization of their thin films which are consistent with the calculations [4, 7].

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In an effort to clarify the magnetic properties, we have investigated the magnetization of bulk material containing a significant proportion of the α'' phase, prepared according to Jack's original method [2]. Nitrogen has an extended solubility range in austenite (γ Fe), which is stable above 590 °C. Nitrogen austenite was prepared by heating powders or foils in an atmosphere of flowing NH_3/H_2 at 760 °C for several hours. The product was rapidly quenched to yield nitrogen martensite, thereby avoiding decomposition into the equilibrium phases, $\alpha\text{Fe} + \text{Fe}_4\text{N}$. Annealing the martensite at 120 °C for seven days yielded samples composed of αFe , γFe and $\alpha''\text{Fe}_{16}\text{N}_2$ in varying proportions. Some of the samples also contained Fe_4N , which may result from insufficiently rapid quenching. Figure 1 shows some typical x-ray diffraction patterns after quenching (martensite plus residual austenite) and annealing (multiphase mixture).

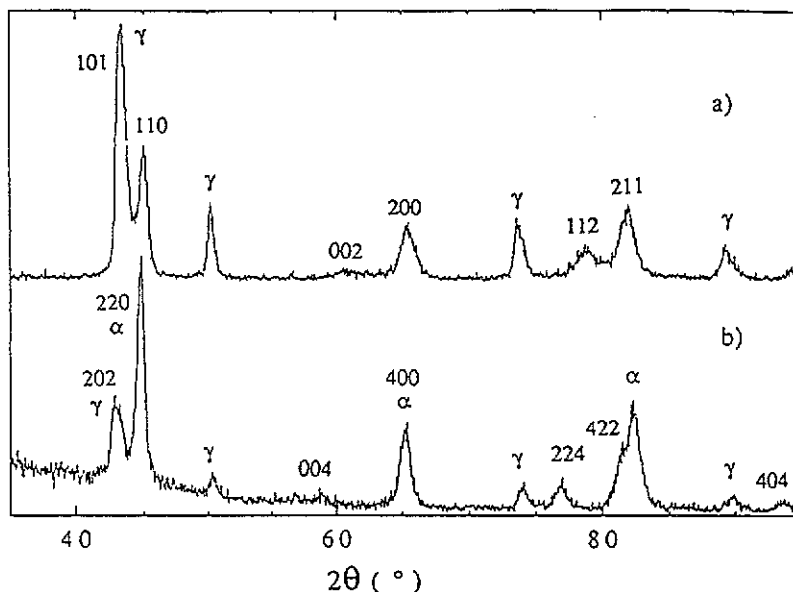


Figure 1. X-ray diffraction pattern ($\text{Cu K}\alpha$) of pieces of iron foil from sample 5: (a) as-quenched and (b) annealed at 120 °C for 7 days. The reflections of (a) α' nitrogen martensite, and (b) $\alpha''\text{Fe}_{16}\text{N}_2$ are marked by their indices, whereas the peaks of α and γ iron are indicated by a Greek letter.

Quantitative phase analysis was based on the absorption areas of Mössbauer spectra taken at 15 K. A typical result is shown in figure 2(a). The parameters of the spectra of αFe and Fe_4N measured at the same temperature were fixed in the least-squares fits of the data, and $\alpha''\text{Fe}_{16}\text{N}_2$ was fitted with three subspectra having an intensity ratio 1:1:2. The γFe gives rise to a broadened central peak. The distinctive feature of the Mössbauer spectrum of $\alpha''\text{Fe}_{16}\text{N}_2$ is the hyperfine component with $B_{\text{hf}} = 41$ T [12–16], which is attributed to iron in 4d sites. The subspectra of iron in 4e and 8h sites, which form an octahedron around the nitrogen interstitial [2], have hyperfine fields of 31 T and 32 T, respectively. This assignment is in accord with that of Nakajima *et al.*, based on conversion-electron spectra of ion-implanted films [16], and with previous work on bulk samples [13–15]. It also agrees with the order of the hyperfine fields calculated by Coehoorn *et al.* using a full-potential linearized augmented plane wave method [11]. Moriya *et al.* assigned the highest moment

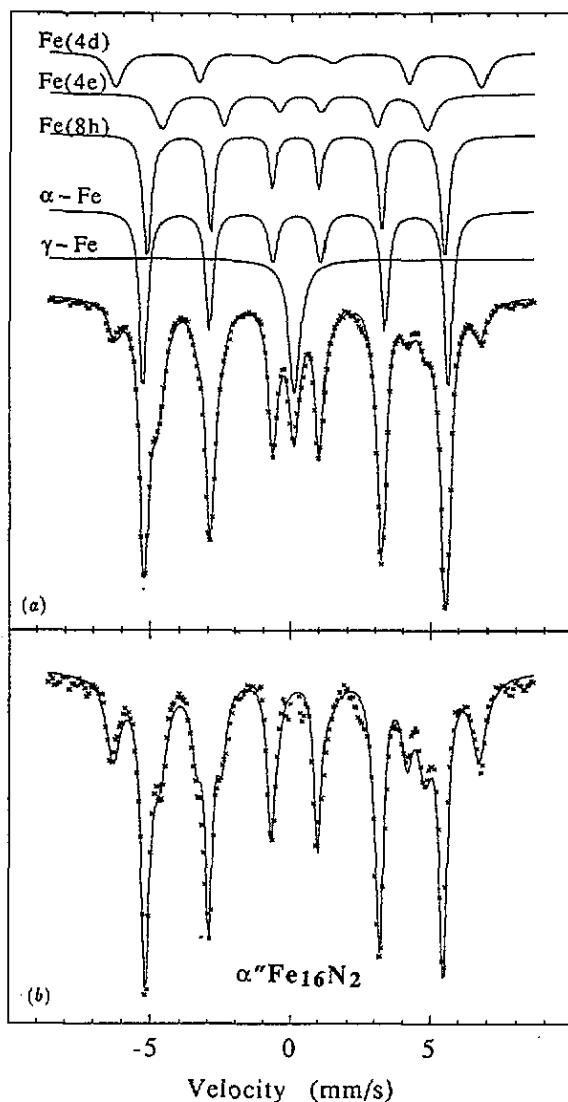


Figure 2. Mössbauer spectra at 15 K of a multiphase sample containing $\alpha''\text{Fe}_{16}\text{N}_2$: (a) whole spectrum and (b) spectrum stripped to remove α -Fe and γ -Fe absorption.

to the 8h site [12], but their interpretation is inconsistent with the expectation that 8h and 4e sites, each with one nitrogen neighbour, should have similar hyperfine fields [14]. The spectrum of $\alpha''\text{Fe}_{16}\text{N}_2$ obtained after stripping off the other constituents is shown in figure 2(b). Fitted hyperfine parameters are given in table 1.

Results of the Mössbauer phase analysis of five samples containing varying proportions of the four constituents are given in table 2. Equal recoilless fractions are assumed for all the phases, and finite absorber thickness effects are neglected.

Magnetization was measured using a vibrating-sample magnetometer at room temperature in a field of 1.4 T and at 4.2 K in a field of up to 6 T. Room temperature

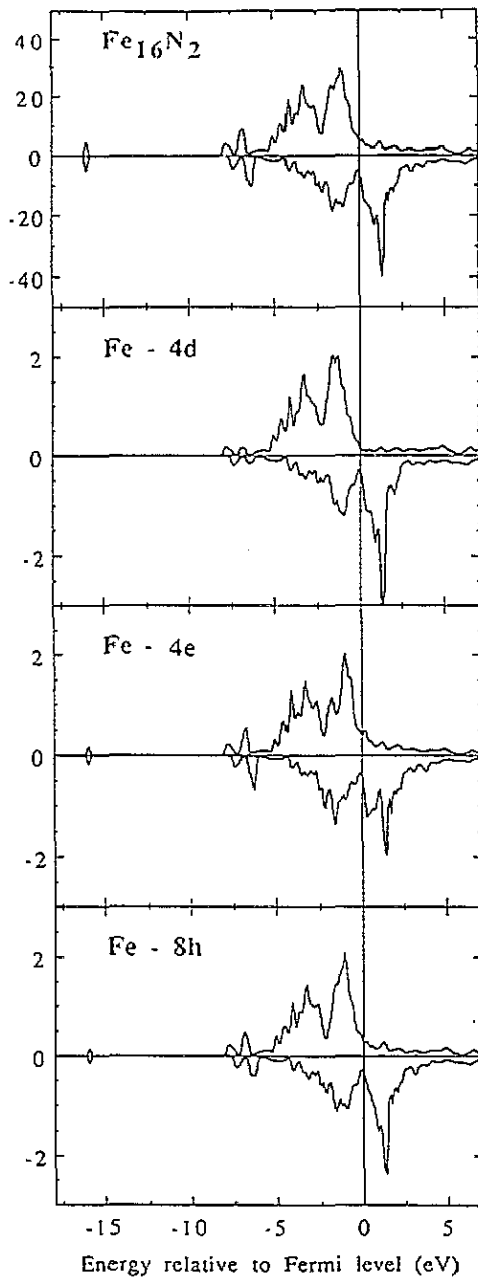


Figure 3. Local density of states at the three crystallographic sites in $\alpha''\text{Fe}_{16}\text{N}_2$ calculated by the LMTO method. Spin moments are $2.81 \mu_{\text{B}}$ (4d), $2.21 \mu_{\text{B}}$ (4e) and $2.39 \mu_{\text{B}}$ (8h).

values included in table 2 are obtained in 1.5 T, whereas the 4.2 K values are extrapolated to zero applied field. The room-temperature magnetization of $\alpha''\text{Fe}_{16}\text{N}_2$ was then deduced using the values of σ_{s} for αFe ($220 \text{ J T}^{-1} \text{ kg}^{-1}$) and Fe_4N ($210 \text{ J T}^{-1} \text{ kg}^{-1}$) measured using exactly the same conditions. The γFe has no magnetic moment. In order to convert

Table 1. Mössbauer fit parameters for $\alpha''\text{Fe}_{16}\text{N}_2$ at 15 K.

Site	Isomer shift (mm s ⁻¹) *	Quadrupole shift (mm s ⁻¹)	Hyperfine field (T)
4e	0.05	-0.49	30.7
8b	0.21	0.21	31.6
4d	0.25	-0.18	40.6

* Relative to αFe at room temperature.

Table 2. Phase composition (wt.%) and magnetization ($\text{J T}^{-1} \text{kg}^{-1}$) of samples containing $\alpha''\text{Fe}_{16}\text{N}_2$.

Sample	αFe	γFe	$\alpha''\text{Fe}_{16}\text{N}_2$	Fe_4N	$\sigma(\text{RT})$	$\sigma(4.2)$
1 powder 30 μm	61	7	28	4	210	232
2 foil 100 μm	52	5	32	11	213	220
3 foil 100 μm	59	11	20	10	205	226
4 foil 25 μm	55	11	34	—	208	253
5 foil 25 μm	51	9	40	—	202	—

Table 3. Lattice parameters and magnetization deduced for $\alpha''\text{Fe}_{16}\text{N}_2$.

Sample	a (pm)	c (pm)	$\sigma(\text{RT})$ ($\text{J T}^{-1} \text{kg}^{-1}$)	$J(\text{RT})$ (T)	$\mu_{\text{av}}(4.2)$ ($\mu_{\text{B}}/\text{iron atom}$)
1	572	630	241	2.25	2.40
2	568	625	236	2.20	2.27
3	568	625	271	2.52	2.34
4	580	613	238	2.22	2.62
5	573	628	225	2.10	—

σ_s to J_s , the density is deduced from the measured lattice parameters of the $\alpha''\text{Fe}_{16}\text{N}_2$ phase. These parameters, together with the average magnetic moment per iron atom at 4.2 K are included in table 3. Experimental errors arise both from uncertainty in the phase analysis and in the magnetization measurements. The variations among the samples may or may not be significant. We conclude from the data that the magnetization of $\alpha''\text{Fe}_{16}\text{N}_2$ at room temperature lies in the range 225–270 $\text{J T}^{-1} \text{kg}^{-1}$, corresponding to $J_s = 2.1\text{--}2.5$ T. The average iron moment at $T \sim 0$ K is 2.3–2.6 $\mu_{\text{B}}/\text{atom}$. The most likely value is 2.4 $\mu_{\text{B}}/\text{atom}$.

We also carried out a series of self-consistent spin-polarized linearized muffin-tin orbital (LMTO) calculations for $\alpha''\text{Fe}_{16}\text{N}_2$, varying the unit cell volume, c/a ratio and special position parameters. These calculations are based on the atomic sphere approximation, which is well justified by the charge density distributions obtained by Coehoorn *et al* using a full potential approach [11]. Both methods give calculated moments for Fe_3N and Fe_4N which agree well with experimental values. There is some site variation in the iron moments calculated for $\alpha''\text{Fe}_{16}\text{N}_2$, but the average moment per iron atom is quite similar to that deduced experimentally. In no case did the calculated average moment exceed 2.5 μ_{B} . The largest moment (2.8 μ_{B}) is on 4d sites, where the local density of states indicates strong ferromagnetism, whereas the smallest is on 4e sites, which are nearest-neighbours to nitrogen and where the moment is reduced by hybridization (figure 3). The average moment per iron atom is significantly greater than for αFe , but the increased volume of the nitride makes for a less impressive improvement in the polarization.

Our experimental magnetization values are in broad agreement with those reported in

[4, 7, 17] and with all band-structure calculations, including our own. The giant moments claimed for some thin films [3, 5, 8] are not observed in bulk material. They would lead to values of magnetization far beyond our experimental errors, e.g. $\sigma = 243 \text{ J T}^{-1} \text{ kg}^{-1}$ for sample 5 in table 2, at room temperature.

It might be argued that some of the αFe in the annealed samples may be supersaturated in nitrogen, and consequently have a magnetization lower than $220 \text{ J T}^{-1} \text{ kg}^{-1}$. But even assuming that σ for the αFe is as low as $210 \text{ J T}^{-1} \text{ kg}^{-1}$, the values deduced for the magnetization of the $\alpha''\text{Fe}_{16}\text{N}_2$ will only increase by about 10%.

In conclusion, the average iron moment and the polarization of $\alpha''\text{Fe}_{16}\text{N}_2$ inferred from measurements on multiphase mixtures are found to be higher than for αFe , but the giant moments that have been reported in some thin films are not confirmed. Nevertheless, it is worth exploring ways of preparing the α'' phase in a purer form, and investigating alloy additions with a view to optimizing the properties for applications which call for bulk material with the greatest possible magnetic polarization.

References

- [1] Magnetization is expressed as magnetic moment per unit mass, σ , or magnetic moment per unit volume, M . It is usually the former that is measured experimentally. Units of σ ($\text{J T}^{-1} \text{ kg}^{-1}$) are numerically equivalent to emu g^{-1} . Units of magnetic polarization $J = \mu_0 M$ are tesla, equivalent to 10^4 gauss.
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