A new structure of $Nd_{1+\varepsilon}Fe_4B_4$ phase in NdFeB magnet

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Sintered NdFeB magnets are relatively complex multi-phase systems containing $Nd_2Fe_{14}B$ matrix and about 15% of other intermetallics such as $Nd_{1+\varepsilon}Fe_4B_4$, Nd-oxides (Nd-rich phase), etc. Boron rich $Nd_{1+\varepsilon}Fe_4B_4$ forms in irregularly distributed heavily faulted grains of roughly the same size as those of the $Nd_2Fe_{14}B$ phase [1]. The Curie temperature of this phase is 13 K and, therefore, it is not ferromagnetic at room temperature and is deleterious to the magnetic properties of the magnets.

$Nd_{1+\varepsilon}Fe_4B_4$ (where $\varepsilon \approx 0.1$) have been constructed by two different repeat units of Nd and Fe-B substructures along the c-axis with the identical a [2, 3]. The Nd substructure has a body-centred tetragonal (bct) structure with I4/mmm space group, and the Fe-B sub-structure has a primitive tetragonal structure with $P4_2/ncm$ space group [2, 4]. The corresponding atomic coordinates for two substructures are shown in Table I. The combination of two substructures with slightly different c_{Fe-B} and c_{Nd} parameters will form different commensurate structure for $Nd_{1+\varepsilon}Fe_4B_4$. Up to now, three kinds of structures have been reported as shown in Table II. The c parameter for $Nd_{1+\varepsilon}Fe_4B_4$ can be deduced from $c = m \cdot c_{Fe-B} = n \cdot c_{Nd}$, where m and n are integers. And the corresponding composition coefficient $\varepsilon = n/m - 1$. In this study, we will report a new commensurate structure which contains seven units of Fe-B sub-structure and eight units of Nd sub-structure.

The NdFeB magnets used for this study were supplied by Philips Component Ltd. and had nominal composition $Nd_{15}Fe_{76.5}B_7(Dy,Nb,Al)_{1.5}$(at.%) [6]. The magnets were produced by a powder metallurgy method (ingot → HD → jet milling → powder alignment → pressing → sintering) and were finally demagnetised. TEM foils were prepared using ion milling (see [7] for detail). TEM observations were carried out in a JEOL 4000FX.

Fig. 1 shows a TEM bright field micrograph of $Nd_{1+\varepsilon}Fe_4B_4$ phase surrounded by $Nd_2Fe_{14}B$ matrix in the as-received sample. Figs 2a and b show two selected area electron diffraction (SAD) patterns from $Nd_{1+\varepsilon}Fe_4B_4$ phase. To determine the n/m value, two substructures of Nd and Fe-B with the relationship of $[100]_{Nd}//[100]_{Fe-B}$ & $[001]_{Nd}//[001]_{Fe-B}$, have been used to simulate the patterns. It is found that the commensurate structure with $n/m = 8/7$, as shown in Fig. 3 (double diffractions are not considered), can elucidate the basic patterns of Fig. 2. Such a structure has not been given so far in this compound family, but the same n/m value was reported in $Gd_{1+\varepsilon}Fe_4B_4$ [8] with the space group of Pccn. Based on the atomic coordinates of $Gd_{1+\varepsilon}Fe_4B_4$, [001] and [010] zones have been simulated as shown in Figs 4a and b (using Diffract 1.2 software, Birmingham University). Comparing to the correspondences of Figs 2a and b, the simulated diagrams explain very well the real diffraction patterns, in both intensities and spacings of diffractions. The lattice parameters for $Nd_{1+\varepsilon}Fe_4B_4$ are $a = 0.71 \pm 0.005$ nm,

TABLE I The substructures reported unit cell parameters for $Nd_{1+\varepsilon}Fe_4B_4$

Space group	Atom	Site	Coordinate		
I4/mmm	Nb	2*a*	0	0	0
$P4_2/ncm$	Fe	8*i*	0.127	0.127	0.1349
	B	8*i*	0.068	0.068	0.639

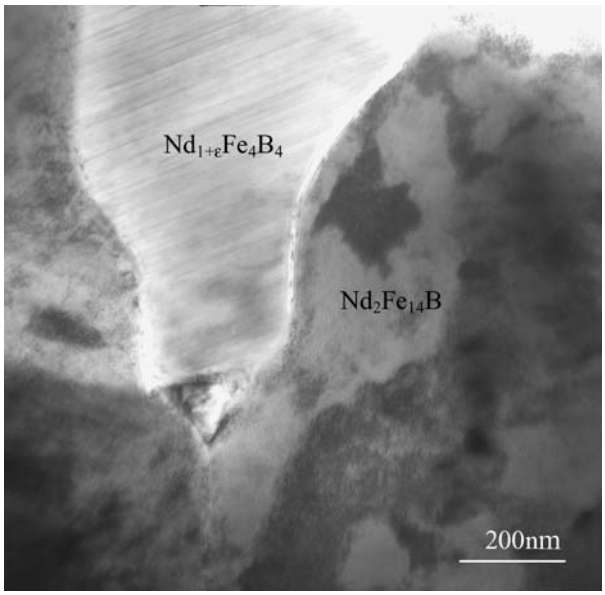

Figure 1 Bright field image of the $Nd_{1+\varepsilon}Fe_4B_4$ phase in the as-received sample.

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TABLE II The reported unit cell parameters for $Nd_{1+\varepsilon}Fe_4B_4$

Lattice parameters of $Nd_{1+\varepsilon}Fe_4B_4$		*c* Parameters of substructures				
a (nm)	*c* (nm)	c_{Fe-B}(nm)	c_{Nd}(nm)	*n*/*m*	Composition of sintered alloy (at. %)	Reference
0.7133	14.457	0.3899	0.3519	41/37	$Nd_{12}Fe_{44}B_{44}$	[2]
0.7117	3.507	0.3897	0.3502	10/9	$Nd_{12.5}Fe_{43.8}B_{43.8}$	[3]
0.71	6.631	0.39	0.349	19/17	$Nd_{14}Fe_{44}B_{42}$	[5]

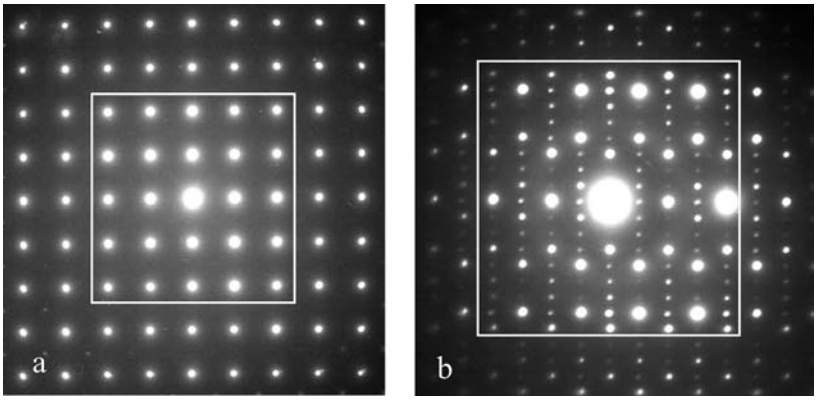

Figure 2 (a, b) Selected area electron diffraction patterns from $Nd_{1+\varepsilon}Fe_4B_4$ phase.

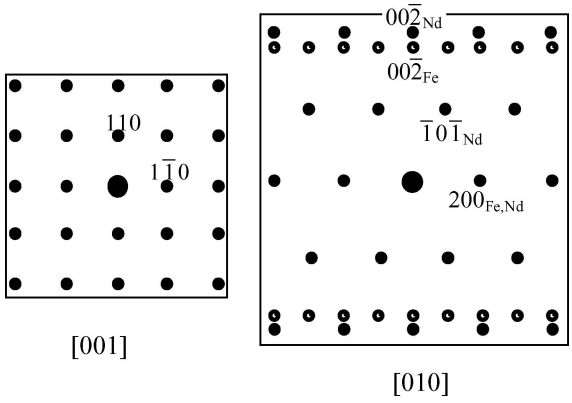

Figure 3 The indexed diagrams of two sub-structures of Nd and Fe-B with the relationship of $[100]_{Nd}$ // $[100]_{Fe-B}$ & $[001]_{Nd}$ // $[001]_{Fe-B}$. The solid and shadowed circles represent Nd sub-structure (I4/mmm, $a = 0.71$ nm, $c = 0.343$ nm) and Fe-B sub-substructure (P42/ncm, $a = 0.71$ nm, $c = 0.392$ nm), respectively. The double diffractions are not considered.

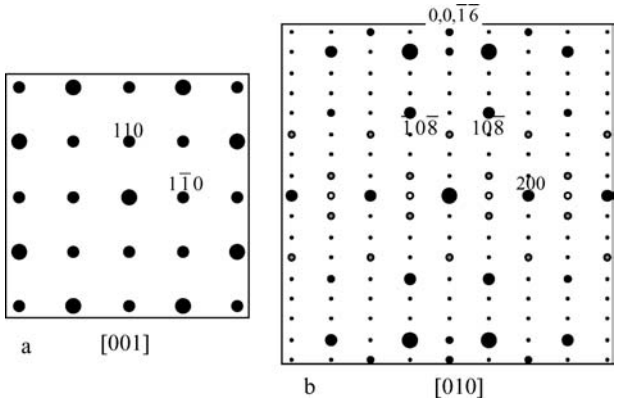

Figure 4 (a–b) The indexed diagrams for [001] & [010] zones of $Nd_{1+\varepsilon}Fe_4B_4$ based on Pccn ($\varepsilon \sim 0.143$) with lattice parameters $a = 0.71$ nm, $c = 2.74$ nm. The solid and open circles represent the actual and double diffractions, and the shadowed circles are attributed by both.

$c = 2.74 \pm 0.05$ nm, and the composition of the phase is deduced to be $Nd_2Fe_7B_7$ ($\varepsilon = 0.143$).

The reason for the existence of such a structure is unknown. However, we notice that the higher ratio of n_{Nd}/m_{Fe-B} (column 5 of Table II) corresponds to the higher ratio of Nd/Fe in as cast alloys (column 6 of Table II). Accordingly, it is argued that the formation of the new structure is related to the alloy composition.

In conclusion, a new structure for $Nd_{1+\varepsilon}Fe_4B_4$ phase has been observed, which has the same structure as $Gd_{1+\varepsilon}Fe_4B_4$. The compound has Pccn structure with $a = 0.71$ nm and $c = 2.74$ nm, and its composition was found to be $Nd_2Fe_7B_7$.

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