

# Rietveld analysis of x-ray powder diffraction patterns for the new $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ nitride compound

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Considerable improvement of the magnetic properties has been achieved by nitrogen absorption in the  $R\text{Fe}_{10}\text{Mo}_2$  compounds with  $\text{ThMn}_{12}$ -type structure. A lattice expansion has been observed ( $a=8.6781$ ,  $c=4.8531$  Å for the nitride and  $a=8.5869$ ,  $c=4.8002$  Å for the nitrogen-free sample) from  $\text{N}_2$  absorption and a determination of the displaced Sm, Fe, and Mo positions has been achieved from Rietveld analysis for the  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$  compound. This structure determination provides some evidence for the site occupation of the nitrogen atoms in the tetragonal  $\text{ThMn}_{12}$ -type structure. Measurements of an oriented powder sample at 295 K show that the easy magnetization direction is in the  $(a,b)$  plane.

## I. INTRODUCTION

The 38% relative increase of Curie temperature ( $T_c = 421$  K and  $T_c = 581$  K for  $\text{SmFe}_{10}\text{Mo}_2$  and  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ , respectively) with the maximum relative increase (80%) observed in compounds with  $R=\text{Lu}$  in the series  $R\text{Fe}_{10}\text{Mo}_2\text{N}_x$ ,<sup>1</sup> makes studying their magnetic properties interesting. In this work, a crystallographic study of the  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$  compound is attempted and the possibility of locating the N atoms by Rietveld analysis of x-ray powder diffraction data is investigated. The low atomic scattering factor of the N atom, in contrast with the large values for the Sm, Fe, and Mo atoms, makes it difficult to be determined by x-ray diffraction studies. The final results of Rietveld refinement of the  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$  sample in comparison with those of  $\text{SmFe}_{10}\text{Mo}_2$ , gives a direct indication that the probable N site in the tetragonal  $\text{ThMn}_{12}$ -type structure, is the  $2b$  site (Wyckoff notation). An indirect verification comes from the correspondence of this site to the  $9e$  sites of the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure and the  $6h$  sites of the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure, which are occupied by N or C atoms in  $\text{RE}_2\text{Fe}_{17}\text{N}_x$  or  $\text{RE}_2\text{Fe}_{17}\text{C}_x$  compounds.<sup>2</sup>

## II. EXPERIMENTAL

### A. Sample preparation

The  $\text{SmFe}_{10}\text{Mo}_2$  compound was prepared by arc melting the constituents (all 99.99% pure) followed by an annealing in vacuum at 850 °C for a week. The annealed sample was pulverized to a very fine powder ( $<10$  μm) and heated in an atmosphere of purified  $\text{N}_2$  gas for 2 1/2 h at 500 °C.

### B. Data collection

X-ray powder diffraction data were collected in the  $2\theta$  range  $26^\circ$ – $100^\circ$ , using the Siemens D500 diffractometer with  $\text{CuK}\alpha$  radiation and diffracted beam graphite monochromator. The sample was positioned on a glass slide. The continuous step-scanning technique was used at steps of  $0.03^\circ$ , with measuring time of 30 s/step.

## III. REFINEMENT—RESULTS AND DISCUSSION

The Rietveld refinement of data was carried out using the program H.2.<sup>3</sup> A trial Rietveld refinement, using as starting structural parameters the ones given in Ref. 4 for the phase  $\text{YFe}_{11}\text{Ti}$ , revealed the complete agreement of the pattern with the 1:12 phase, except for those peaks that correspond to the  $\alpha$ -Fe phase. The  $\alpha$ -Fe phase was included in the refinement. Because of the enhanced background introduced by the glass slide at the  $2\theta$  range  $25^\circ$ – $30^\circ$ , the refinement was done in the  $2\theta$  range from  $38.5^\circ$  to  $100.0^\circ$ .

In Table I, the final values of the nonstructural parameters are given. The Pearson VII function for the 1:12 phase and  $U, V$  parameters of the half width (HW) were refined for both the upper and lower part of intensity distribution around a peak. For the  $\alpha$ -Fe phase the simple Pearson VII function was used and only the  $U$  value was refined for HW. The specimen displacement parameter was included in the refinement and the background was refined in the form  $Y_b = \sum_{m=0}^1 C_m x(2\theta)^m$ . The base of every peak is ranged 15 times the HW below and above the peak position. At every stage of the refinement, convergence was specified by average parameter shifts less than one tenth of the standard deviations.

Even though it is known that the Mo atoms in 1:12 phase occupy the  $8i$  site,<sup>4</sup> at the early stages of refinement, this site was supposed to be fully occupied by Fe. The  $R$  factors were  $R_p = 11.30$ ,  $R_{wp} = 12.78$  and  $R_B = 12.24$ . At

TABLE I. Values for the nonstructural parameters of the sample  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ . In the first line are given the values for the  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$  and in the second the values for the  $\alpha$ -Fe phase. The  $W$  value for the  $\alpha$ -Fe phase corresponds to the whole HW value.

Pearson VII function	$m_0=0.13(3)$	$m_1=0.0124(8)$
shape parameters	0.90(4)	...
HW parameters		
Low angle	$V=0.20(1)$	$W=-0.057(5)$
	...	0.29(2)
High angle	$V=0.21(1)$	$W=-0.057(6)$
	...	...
Specimen displacement	0.009(3)	
Background parameters	$C_0=139(1)$	$C_1=-0.61(3)$

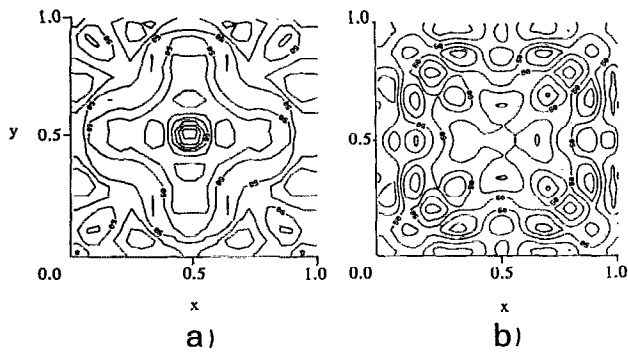


FIG. 1. Difference Fourier map at  $z=0.0$  for the nitride (a) and the nitrogen-free sample (b). The contours are in steps of  $0.5 \text{ e}/\text{\AA}^3$ .

this stage the occupancy factors of the three Fe atoms were left to refine freely. The occupancy factors of Fe at the  $8i$  site increase significantly from the ideal (1.0) to the value 1.440.<sup>3</sup> The remaining factors have values very close to the ideal ones. This is a strong indication that the  $8i$  site is also occupied by the Mo atoms. This site is supposed to be half occupied by Fe and Mo atoms. The composition formula, with respect to the metal atoms is thus  $\text{SmFe}_{10}\text{Mo}_2$ . With this hypothesis the  $R$  factors obtained were  $R_p = 7.65$ ,  $R_{wp} = 8.66$ , and  $R_B = 6.23$ . At this stage a difference Fourier synthesis was calculated.<sup>6</sup> In Fig. 1(a) the difference Fourier map at  $z=0$  is given. The peak at  $x=y=0.5$  is evident. This peak corresponds to the site with Wyckoff notation ( $2b$ ). Considering this as the N-atom site, it was included in the refinement. The final  $R$  values for the nitride sample are  $R_p = 6.94$ ,  $R_{wp} = 8.31$  and  $R_B = 5.07$ . The 1.16% reduction in  $R_B$  makes it probable that the  $2b$  site is the nitrogen site.

In Table II, the final structural parameters are given. The temperature factors of all the atoms were kept constant during the refinement and the values have been taken from Ref. 4. The observed, calculated, and difference patterns are shown in Fig. 2.

A nitrogen-free sample was measured also. The refinement was performed in exactly the same way. Table II lists the final structural parameters. The  $R$  factors were convergent to the values  $R_p = 6.62$ ,  $R_{wp} = 8.93$  and  $R_B = 3.70$ . The

TABLE II. Fractional atomic coordinates, isotropic temperature factors and occupancy factors for  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$  and for  $\text{SmFe}_{10}\text{Mo}_2$ . The fractional atomic coordinates for the nitrogen-free are given in brackets. The lattice constants are  $a=8.6781(3) \text{ \AA}$ ,  $c=4.8531(3) \text{ \AA}$  for the nitride sample and  $a=8.5869(3) \text{ \AA}$ ,  $c=4.8002(3) \text{ \AA}$  for the nitrogen-free sample. Space group  $14/mmm$ .

atoms	$x$	$y$	$z$	$B$	$n$
Sm( $2a$ )	0.0	0.0	0.0	0.59	1.0
Fe/Mo( $8i$ )	0.3603(2)	0.0	0.0	0.72	0.5/5
Fe( $8j$ )	[0.3601(2)]	0.5	0.0	0.65	1.0
	0.2782(4)				
Fe( $8f$ )	[0.2780(3)]	0.25	0.0	0.37	1.0
	0.25				
N( $2b$ )	0.0	0.0	0.5	1.0	1.0

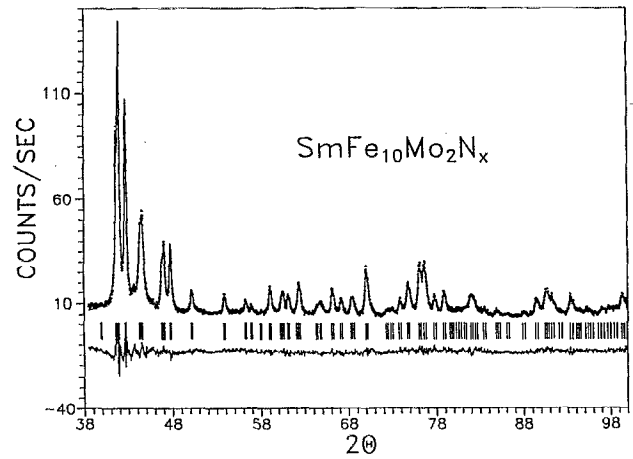


FIG. 2. Observed (dots), calculated (continuous line) and difference (below in the figure) patterns for the sample  $\text{SmFe}_{10}\text{Mo}_2\text{N}_x$ .

weight fraction of the  $\alpha$ -Fe phase was 15.14% for the nitride and 8.63% for the nitrogen-free sample.

In Fig. 1(b) the same difference Fourier map as calculated for the sample  $\text{SmFe}_{10}\text{Mo}_2$  is given. It is clear that the interpretation of the map is complete, and this fact makes it more probable that the peak shown in Fig. 1(a) is not a ghost peak.

The relative volume increase of the nitride sample compared to the non-nitride one is 3.3%. The Fe atoms at the ( $8j$ ) sites around the (0.5, 0.5, 0.0) position are the most distant for the 1:12 structure. The  $\text{Fe}(8j)[x,y,z] - \text{Fe}(8j)[1-x,1-y,1-z]$  distance increases from 3.812(2)  $\text{\AA}$  for the nitrogen-free sample to 3.850(2)  $\text{\AA}$  for the nitride.

Another fact supporting this result, is that this site is analogous to the  $6h$  or  $9e$  sites, which are occupied by the N or C atoms in the hexagonal or rhombohedral structures of compounds  $RE_2\text{Fe}_{17}\text{N}_x$ ,  $RE_2\text{Fe}_{17}\text{C}_x$ , respectively. Following the study of Ref. 5, the relation of the hexagonal 2:17 ( $R_2T_{17}$   $R$  = rare earth,  $T$  = transition element) and 1:12 ( $RT_{12}$ ) structures to the 1:5 structure can be expressed as a direct relation between them, through the transformation of reciprocal vectors:

$$\begin{pmatrix} h \\ k \\ l \end{pmatrix}_{1:12} = \begin{pmatrix} -1 & -1 & 0 \\ 0 & 0 & 1 \\ -1/3 & 1/3 & 0 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{2:17} \det = 2/3$$

In Fig. 3(a) this relation is shown schematically. Figure 3(b) shows the reverse transformation. Comparing the two figures it is clear that the similarity of the structures comes from a rearrangement of rare-earth atoms and dumb-bell Fe atoms [crosses in Figs. 3(a), 3(b)] at  $z=1/4$  (or  $3/4$ ) level of 2:17 structure and  $y=0$  ( $1/2$ ) level of 1:12 structure. The unit cell volume of  $RT_{12}$  is two-thirds that of hexagonal  $R_2T_{17}$ .  $Z=2$  for the two structures. The precise site relations are (with the 2:17 sites in brackets)  $2/3[T(12k) + T(6g)] = T(8f) + 1/2T(8j)$ ,  $2/3[T(12j)] = 1/2T(8i) + 1/2T(8j)$  and  $[2R(2b) + T(4f) + 2R(2d)] = 2R(2a) + 1/2 T(8i)$ .

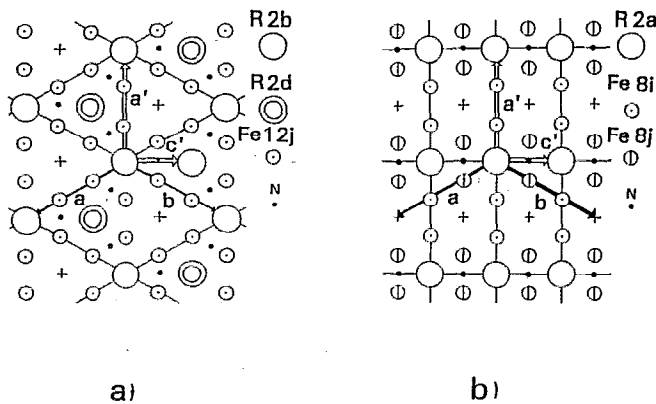


FIG. 3. Arrangement of atoms at  $z=1/3$  for the hexagonal  $R_2T_{17}$  phase (a) and at  $z=0$  for the tetragonal  $RT_{12}$  (b)

In Fig. 3(a) are also shown the positions of C or N atoms ( $6h$  sites). It is clear that the C or N atoms are positioned in the middle of the line connecting two neighboring rare-earth atoms. From the three sites of this type in the 2:17 structure around its rare-earth atom, only one remains in the 1:12 structure [Fig. 3(b)], that is the  $2b$  site. This is because of the linear arrangement of rare-earth atoms along the  $c$  axis in the 1:12 structure. Using the transpose of the inverse matrix of the above transformation the equivalence of a fraction of the  $6h$  sites (2:17) with the  $2b$  sites (1:12) becomes obvious. The  $(x, -x, 1/4)$  of the  $6h$  sites with  $x = -1/6$  is transformed to the  $(0, 1/4, 1/2)$  from which with a shift by  $1/4 b$ , in order to match the standard origin setting of the 1:12 structure, we get the  $2b$  site  $(0, 0, 1/2)$ .

In Fig. 4(a) is shown the XRD pattern measured from an unoriented nitride sample. In Fig. 4(b) is given the measured pattern from an oriented sample. The magnetic field was applied parallel to the plane of the sample. From the direct comparison of the two patterns it is clear that in the oriented one, the intensities of only the general reflections have been reduced significantly. This suggests that the easy magnetization direction is in the  $(a, b)$  plane.

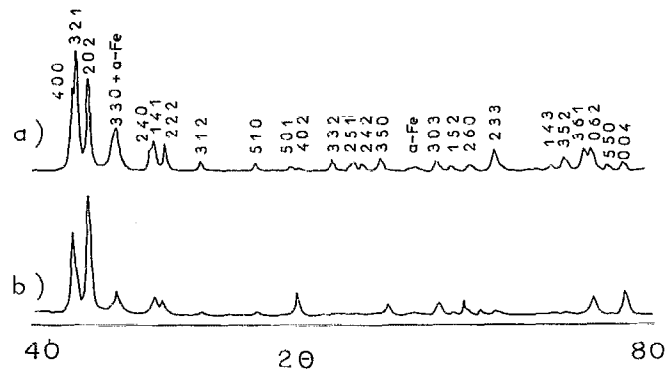


FIG. 4. X-ray patterns of  $SmFe_{10}Mo_2N_x$  for an unoriented (a) and an oriented sample (b). In the oriented sample the field was applied parallel to the plane of the sample.

#### IV. CONCLUSIONS

In this study we have presented the results, derived from Rietveld analysis and difference Fourier maps, related to the nitrogen position in the compound  $SmFe_{10}Mo_2N_x$ . The structure remains the same, with a slight expansion in the unit cell volume compared to the nitrogen-free sample, and the probable site for nitrogen is the  $2b$  site (Wyckoff notation). This result is supported from preliminary data using neutron diffraction and EXAFS studies.

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