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Ab initio crystal structure solution of the novel intermetallic compound $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$

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Abstract

X-ray powder diffraction data have been used for the ab initio crystal structure solution of the novel intermetallic compound $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$. The structure has been determined by a combined use of the Patterson and Fourier synthesis methods and the Rietveld decomposition formula. The compound crystallizes in the monoclinic $A2/m$ space group: $a = 10.6463(7)$ Å, $b = 8.5958(6)$ Å, $c = 9.7534(7)$ Å, $\beta = 96.94(1)^\circ$. The 6 Nd atoms per cell occupy two crystallographically different sites (2a, 4i) and the 58 (Fe,Ti) atoms are distributed in 11 crystallographically different sites. The structure is a mixture of the tetragonal ThMn_{12} and the rhombohedral $\text{Th}_2\text{Zn}_{17}$ types of structures.

Keywords: Intermetallic compounds; X-ray powder diffraction

1. Introduction

The main problem concerning the ab initio crystal structure solution from powder X-ray diffraction (XRD) data is the difficulty in extracting accurate $|F_{\text{obs}}|$ values for each reflection, because of the extended overlap of the recorded intensities in a powder diffraction pattern. The intensity values of overlapping reflections estimated by using the standard full pattern decomposition approach [1] are not accurate [2]. Recently two methods have been developed for the deconvolution of intensities of overlapping reflections and the results on ab initio crystal structure solution are quite promising. The first method is based on the triplet and quartet relations that have been developed within the framework of direct methods for single-crystal structure analysis and correlate not only the phases of the reflections with the intensities but also the intensities with each other [2,3]. The second method uses a maximum entropy algorithm for estimation of the intensities of overlapping reflections [4]. The Rietveld intensity decomposition formula [5], which is a kind of deconvolution, has been used successfully in the past for ab initio crystal structure solution of compounds containing heavy atoms [6–9] or to find the whole structural model from a known part of it [10–12]. In order to apply this method to

XRD data a prior knowledge of a part of the structure is needed. The position of some starting atoms are found by using $|F_{\text{obs}}|$ values obtained by the full pattern decomposition method [1] for Patterson synthesis. Using these atoms as a starting model more accurate $|F_{\text{obs}}|$ values are obtained by applying the Rietveld intensity decomposition formula. Following the procedure of an iterative application of the Rietveld intensity decomposition formula, by adding each time in the starting model the new atoms located through a Patterson or a difference Fourier synthesis, the optimum values for $|F_{\text{obs}}|$ are obtained, which can be used for the complete crystal structure solution. A systematic presentation of the method described above with results on different compounds has been given [13].

In the present work, the method described above is applied for the ab initio crystal structure solution of the novel intermetallic compound $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$. Li et al. [14] have proposed a structure model based on a trial and error approach, which is a usual practice for compounds exhibiting superstructure relationships as is the case of the $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$ compound. This compound displays a strict superstructure relation with the CaCu_5 -type structure and the related intermetallic compounds with the rhombohedral $\text{Th}_2\text{Zn}_{17}$ (2:17R) and tetragonal ThMn_{12} (1:12) type structures. In Ref.

[14], the structure is considered as monoclinic with space group $P2_1/c$. There are 2 non-equivalent crystallographic sites for Nd atoms and 15 non-equivalent crystallographic sites for (Fe,Ti) atoms in the unit cell. In a recent paper [15] we have suggested that a more accurate description of the structure can be provided in the monoclinic space group $A2/m$. With this description the number of non-equivalent (Fe,Ti) atom sites in the cell is reduced to 11. Recently, this result has been confirmed by means of neutron diffraction data [16].

2. Experimental details

The $Nd_3(Fe,Ti)_{29}$ ingots with the nominal composition $Nd_3(Fe_{0.95}Ti_{0.05})_{29}$ were prepared by induction melting high purity elemental constituents (better than 99.9%). The sample was then wrapped in tantalum foil, heat treated in vacuum at 1373 K for 120 h and water quenched. From XRD, thermomagnetic analysis (TMA) and scanning electron microscopy (SEM) analysis it was concluded that the sample was of a single phase.

X-ray powder diffraction data were collected with a D500 Siemens diffractometer employing Cu $K\alpha$ radiation and a secondary beam graphite monochromator. The measured 2θ range (26° – 75°) was scanned in steps of 0.02° with a counting time of 5 per step. The aperture slits were set at 0.3° and the Soller slits were set of 0.1° .

3. Results and discussion

The indexing and assignment of the proper space group have been based on the work of Li et al. [14] and Fuerst et al. [17]. The first group describes the structure in the $P2_1/c$ space group and the second group mentions for the first time that the lattice is probably A centred. A detailed discussion of the description of the structure in the $A2/m$ space group instead of $P2_1/c$ is given in Ref. [15]. In what follows the procedure for the ab initio crystal structure solution is described.

Approximate values for the observed structure factors were obtained by using the program FULLPROF [18] in the full pattern decomposition mode. As an input to the program, the approximate values for the unit cell and the space group were used. The Pearson VII function was used for the description of the intensity distribution. The unit cell parameters, the background parameters, the exponent of the Pearson VII function and the full width parameters were refined. The final values for the unit cell dimensions were $a = 10.6473(5)$ Å, $b = 8.5950(6)$ Å, $c =$

$9.7547(6)$ Å, $\beta = 96.93(1)^\circ$. The agreement indices (R factors [18]) converged to the following values: $R_p = 13.3\%$, $R_{wp} = 18.0\%$, $R_B = 8.24\%$, $R_{exp} = 11.8\%$.

The number of independent reflections in the refined 2θ range was 235. These approximate $|F_{obs}|$ values were used for Patterson synthesis with the SHELXS-86 [19a] program. The list of the sites for the atoms interpreting the peaks found in the Patterson map is given in Table 1. A simple comparison of this list with the atom positions given in Ref. [15] (or with the list of the atom positions of Table 1) gives the assignment of atoms listed in the last column of Table 1.

All attempts to locate more atoms with difference Fourier synthesis and using the $|F_{obs}|$ values derived with the full pattern decomposition method were unsuccessful. More accurate $|F_{obs}|$ values were obtained by applying the Rietveld intensity decomposition formula, that means Rietveld refinement with the atoms Nd(1), Nd(2), Fe(9), Fe(4), Fe(10), Fe(6), Fe(8), Fe(5) and Fe(1) at positions listed in Table 1, as starting model. With this incomplete model as a starting structural model for Rietveld refinement, only the unit cell dimensions and the background parameters were refined. The profile shape parameters (Pearson VII exponent) and the full width parameters were kept constant at the values derived from the full pattern decomposition run. These new $|F_{obs}|$ values were used for difference Fourier synthesis with the SHELX-76 [19b] program. The list of the five most intense peaks found with these calculations is given in Table 2. Comparing these positions with the atom positions given in Ref. [15] (or in Table 1) the assignment of atoms given in the last column of Table 2 is concluded. The final values of the atom positions are obtained by the standard Rietveld refinement method [20] and they are listed in Table 3.

A description of the structure is given in Refs. [14] and [15]. The relation of 3:29 with 1:12 and 2:17R (or

Table 1
List of atom sites for the atoms interpreting the peaks found in the Patterson map by using SHELXS-86 program

Site (sequence number)	x	y	z	Assignment
1	0.0	0.0	0.0	Nd(1)
2	0.597	0.0	0.185	Nd(2)
3	0.197	0.0	0.380	— ^a
4	0.700	0.0	0.900	Fe(9)
5	0.793	0.813	0.080	Fe(4)
6	0.379	0.743	0.052	Fe(10)
7	0.257	0.0	–0.106	— ^a
8	0.0	0.351	0.0	Fe(6)
9	0.766	0.243	0.343	Fe(8)
10	0.607	0.654	0.204	Fe(5)
11	0.5	0.0	0.5	Fe(1)

^a Ghost peaks.

Table 2

List of peaks found in difference Fourier maps (SHELX-76)

Peak number	x	y	x	Assignment
1	0.0	0.25	0.25	Fe(11)
2	0.429	0.243	-0.443	- ^a
3	0.239	0.0	0.538	Fe(3)
4	0.139	0.0	0.277	Fe(2)
5	0.886	0.0	0.261	Fe(7)

^a Ghost peak (0.53 Å from Fe(10)).

Table 3

Crystallographic data for the $\text{Nd}_3(\text{Fe},\text{Ti})_{29}$ compound

Atom	Site	x	y	z
Nd(1)	2a	0.0	0.0	0.0
Nd(2)	4i	0.5974(7)	0.0	0.1850(7)
Fe(1)	2c	0.5	0.0	0.5
Fe(2)	4i	0.140(2)	0.0	0.298(2)
Fe(3)	4i	0.251(2)	0.0	0.517(2)
Fe(4)	8j	0.799(1)	0.782(1)	0.089(2)
Fe(5)	8j	0.623(1)	0.646(2)	0.179(1)
Fe(6)	4g	0.0	0.355(2)	0.0
Fe(7)	4i	0.891(2)	0.0	0.275(2)
Fe(8)	8j	0.801(2)	0.244(2)	0.344(2)
Fe(9)	4i	0.704(2)	0.0	0.901(2)
Fe(10)	8j	0.404(1)	0.750(2)	0.062(2)
Fe(11)	4e	0.0	0.25	0.25

Space group no. 12 (A2/m), $A 1 2/m 1$, unique axis b , cell choice 2 on p. 161 of ref. [21]; unit cell dimensions, $a = 10.6463(7)$ Å, $b = 8.5958(6)$ Å, $c = 9.7534(7)$ Å, $\beta = 96.94(1)^\circ$ and $V = 886.03$ Å³; agreement indices (R factors), $R_p = 7.23\%$, $R_{wp} = 13.54\%$, $R_B = 5.74\%$, $R_{exp} = 11.70\%$

2:17H) is derived from the fact that the 3:29 phase also presents a layered structure consisting of mixed R and Fe atom layers and layers of only Fe atoms. Following the Stadelmaier [22] scheme, the composition of these compounds can be described with the series formula $\text{R}_{m-n}\text{T}_{5m+2n}$, where T is a transition element, R a rare earth atom, m the unit cell volume relation and n the number of R atoms replaced by pairs of dumbbell T atoms in the mixed R and T layers. We have to notice that in a table given in Ref. [20], where all the possible formulae for different m and n values are listed, at the entry with $(m, n) = (10, 4)$ (values that correspond to the 3:29 compound) there is a “gap”. The comment for this gap is, “these R/T ratios are less likely to occur”. R:T = 3:29 is met at the entry $(m, n) = (5, 2)$. We believe that this gap arises from the fact that Stadelmaier [21] has not evaluated the importance of the m value (10 for the 3:29 compound) to predict the existence of the 3:29 phase although it is reported that the unit cell volume relation is important for the existence of a structure.

The arrangements of R and dumbbell sites in the

mixed R–Fe atom layers of the 3:29 compound are described in Ref. [15]. The stacking of the layers is described in Ref. [14]. From these two descriptions it is concluded that the 3:29 structure is a mixture of the 2:17R and 1:12 structures, with a part of the structure having a strict relation with the 2:17R and a part of it having a strict relation with the 1:12 structure. These strict structure relations give a basis for a deeper understanding of the physical properties for compounds with the 3:29 structure and predict some of them.

Theoretical calculations of the second-order crystal field coefficients give a negative value for the 4i R site (2:17R like) and a positive value for the corresponding value for the 2a R site (1:12 like) [23]. The T_c values of $\text{R}_3(\text{Re},\text{Ti})_{29}$ ($\text{R} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ and Gd) are lower than those of RFe_{11}Ti and higher than those of R_2Fe_{17} rhombohedral compounds [21].

The first prediction concerns the probable positions of nitrogen atoms in the nitrided 3:29 compounds. Following the procedure described in [10], that is using transformations which relate the structures and are derived from the relation of the unit cell crystallographic axes of the 3:29 structure with the corresponding axes of the 1:12 and 2:17H structures, the probable positions of nitrogen atoms are predicted. In Fig. 1 the unit cell relations are shown schematically. Combining the transformation matrices which relate the 3:29 [15] phase with the 1:5 phase, and the 1:12 and 2:17H phases with the 1:5 phase [24], the following transformation matrices result for the relation of the 3:29 phase with the 1:12 and 2:17H phases:

$$(hkl)3:29 \rightarrow (hkl)1:12, \begin{bmatrix} 0 & -1 & 0 \\ 1/2 & 0 & 1 \\ -2 & 0 & 1 \end{bmatrix}, \text{ determinant of } 5/2 \quad (1)$$

$$(hkl)3:29 \rightarrow (hkl)2:17H, \begin{bmatrix} -2/3 & -1 & 1/3 \\ 2/3 & -1 & -1/3 \\ 1/2 & 0 & 1 \end{bmatrix},$$

$$\mathbf{p} = \begin{bmatrix} 0 \\ 0 \\ 1/4 \end{bmatrix}, \text{ determinant of } 5/3 \quad (2)$$

where \mathbf{p} is the shift vector of origin. Using the inverse matrices of the above transformations [25], the probable x, y, z coordinates for the nitrogen atoms in the 3:29 phase can be derived. The N sites in the 1:12 structure are 2b: (0, 0, 1/2). The probable nitrogen atoms sites in the 3:29 structure, derived by applying the inverse transformation (1), is (-0.2, 0.0, 0.1). By applying the symmetry operation $(-x, y, 1-z)$ we obtain the 4i sites ($x, 0, z$) with $x \approx 0.2$ and $z \approx 0.9$ suggested in Ref. [15]. The N sites in the 2:17H structure are the 6h: ($x, 2x, 1/4$) with $x = -1/6$ or the

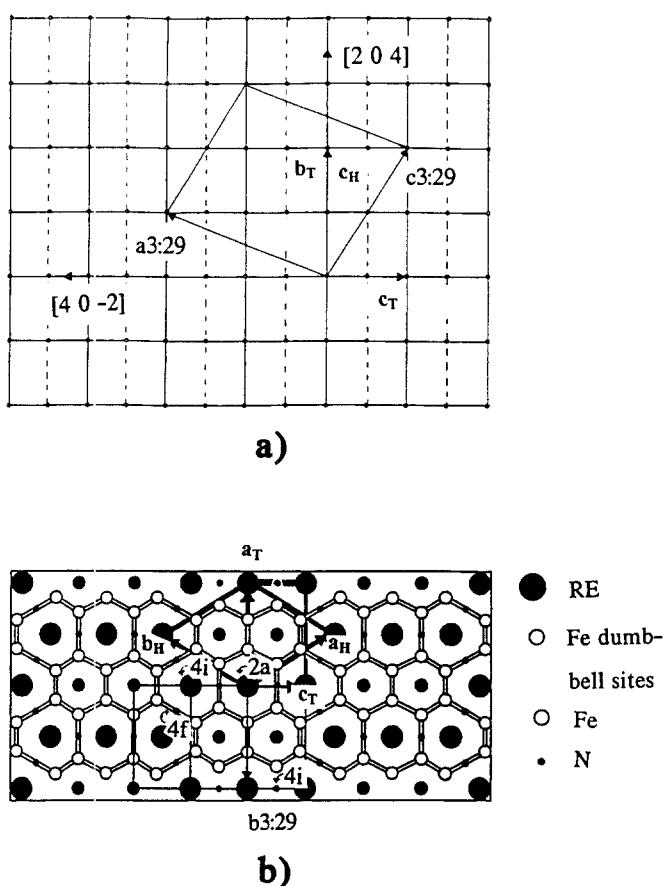


Fig. 1. (a) The unit cell relation of the 3:29-type structure with the tetragonal 1:12-type structure (b_T and c_T axes) and the hexagonal 2:17H-type structure (c_H axis). The projection is along the [100] axis direction for the 1:12-type structure or along the [110] crystallographic direction for the 2:17H-type structure. (b) Unit cell relations in the (204) plane of the 3:29-type structure projected along the [204] crystallographic direction. The axes a_T , c_T correspond to the 1:12-type structure and the axes a_H , b_H to the 2:17H-type structure.

symmetry-equivalent site $(-2x, 1-x, 1/4) = (1/3, 7/6, 1/4)$. The corresponding sites in 3:29 derived by applying the inverse transformation (2) are $(1/2, -3/4, -3/4)$. By applying the translation $(0, 1, 1)$ we obtain the 4f sites $(1/2, 1/4, 1/4)$ suggested in Ref. [15].

The second prediction concerns the importance of the $[20\bar{1}]$ and $[102]$ crystallographic directions (or their parallel directions $[40\bar{2}]$ and $[204]$ respectively) (Fig. 1(a)) for the description of the magnetocrystalline anisotropy of the 3:29 compounds. The unit cell transformations described above give the result that the $[20\bar{1}]$ direction corresponds to the c axis of the 1:12 phase and the $[102]$ direction corresponds to the c axis of the 2:17H (or 2:17R) structure. XRD patterns of magnetically aligned powder samples of $\text{Nd}_3(\text{Fe,Ti})_{29}$ and $\text{Nd}_3(\text{Fe,Ti})_{29}$ have revealed the importance of these directions [15].

4. Conclusions

As far as we know an ab initio crystal structure solution of the novel $\text{Nd}_3(\text{Fe,Ti})_{29}$ compound is presented for the first time. The structure was solved by applying the Rietveld intensity decomposition formula to X-ray powder diffraction data. The fact that one part of the structure has a strict relation with the 2:17R-type structure and one part of it has a strict relation with the 1:12-type structure gives a basis for a deeper understanding of the physical properties for the compounds with the 3:29-type structure (e.g. values for the second-order crystal field coefficients) and predict some of them (e.g. positions of N atoms in the nitrided compounds).

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