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DOI

[10.1063/1.355413](https://doi.org/10.1063/1.355413)

Publication date

1994

Published in

Journal of Applied Physics

[Link to publication](#)

Citation for published version (APA):

Liu, J. P., Zeng, D. C., Tang, N., Winkelman, A. J. M., Menovsky, A. A., de Boer, F. R., & Buschow, K. H. J. (1994). Structure and magnetic properties of interstitial compounds of the series $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{Z}_y$ (Z=N or H). *Journal of Applied Physics*, 75, 6247-6249. <https://doi.org/10.1063/1.355413>

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Structure and magnetic properties of interstitial compounds of the series $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{Z}_y$ ($\text{Z}=\text{N}$ or H)

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The interstitial nitrides $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ with $0 \leq x \leq 6$ and $0 \leq y \leq 2.7$ and hydrides $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{H}_y$ with $0 \leq x \leq 4$ and $0 \leq y \leq 4.2$ have been synthesized by means of melting and by means of the gas-phase-interaction method. The effect of the interstitial atoms on the structure and the lattice parameters has been investigated. For the nitrogenated compounds, it is found that nitrogen can be introduced until a maximum volume expansion is reached. The magnetic properties of the interstitial compounds, including high-field magnetization at 4.2 K and Curie temperatures, have been measured. The Dy-Fe exchange interaction is found to decrease upon introduction of the interstitial atoms.

I. INTRODUCTION

Since the discovery by Coey and Sun¹ that the introduction of interstitial nitrogen greatly improves the magnetic properties of Y_2Fe_{17} and $\text{Sm}_2\text{Fe}_{17}$, much work has been done to investigate the interstitial nitrides. It has been established that nitrogenation enhances the Curie temperatures and the saturation magnetization of R_2Fe_{17} ($\text{R}=\text{rare earth}$) compounds. A similar effect has been observed earlier for the introduction of interstitial hydrogen in R_2Fe_{17} compounds (see, for instance, Ref. 2). However, the influence of the interstitial atoms on the R - T ($T=\text{transition metal}$) exchange interaction in nitrides and hydrides has not been studied in very much detail. In the present work, we have investigated the effect of interstitial nitrogen and hydrogen on the Dy-Fe coupling in $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compounds.

II. EXPERIMENT

The parent compounds of the series $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ with $x=0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0$, and 7.0 were prepared by arc melting the starting materials with purities higher than or equal to 99.9%. After the melting, the ingots were annealed at 1000°C for three weeks. The homogenized ingots were checked by x-ray diffraction and found to be single phase.

The nitrogenation was carried out on fine powder particles (with diameters $\leq 40 \mu\text{m}$) in a furnace at about 500°C with flowing nitrogen gas. The time needed to reach sufficient nitrogenation varies from compound to compound. It was found that with increasing aluminum content in the parent series, the nitrogenation becomes increasingly difficult. Hydrogenation was performed by heating powdered samples for a few hours at about 250°C in flowing hydrogen gas. It was found that the hydrogenation can only be carried out for compounds with $x < 5$. The nitrogen and hydrogen contents were determined by weighing the samples. A detailed description of the synthesis of the interstitial nitrides and hydrides will be given in Ref. 3.

All nitrogenated and hydrogenated compounds have been checked by x-ray diffraction (with $\text{Cu } K\alpha$ radiation) to confirm the formation of the interstitial phases, to determine

the lattice constants, and to detect the presence of possible impurity phases.

High-field magnetization measurements up to 35 T at 4.2 K have been carried out in the Amsterdam high-field installation.⁴ The samples consisted of powder particles that were free to rotate in the sample holder. The Curie temperatures were measured by means of an automatic magnetization-temperature recorder based on the Faraday method. The magnetic field applied in the measurement was 0.14 T.

III. RESULTS AND DISCUSSION

A. Expansion of the unit cells upon the introduction of interstitial nitrogen and hydrogen

Figure 1 shows as an example the diffraction patterns of the $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ compound with $x=1$ and its nitride and

FIG. 1. X-ray diffraction patterns of the compound (a) $\text{Dy}_2\text{Fe}_{16}\text{Al}$ and its interstitial (b) hydride and (c) nitride. The dashed peaks are from the Si standard for calibration.

TABLE I. Structural data of $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ compounds with $x=0, 1, 2, 3, 4, 5, 6$ and 7 , and their interstitial hydrides and nitrides. The lattice parameters (a and c) are given in Å. The expansion $\Delta V/V$ is given in %.

x	Parent compounds			$Z=H$				$Z=N$			
	Type	a	c	a	c	y	$\Delta V/V$	a	c	y	$\Delta V/V$
0	hex.	8.476	8.312	8.552	8.408	4.0	3.1	8.648	8.473	2.7	6.1
1	hex.	8.494	8.316	8.554	8.412	3.2	2.6	8.645	8.490	2.2	5.8
2	hex.	8.538	8.344	8.575	8.438	2.6	2.1	8.652	8.472	1.7	4.3
3	rh.	8.566	12.615	8.610	12.673	2.5	1.5	8.670	12.660	1.2	2.8
4	rh.	8.609	12.564	8.615	12.674	1.8 ^a	1 ^a	8.665	12.682	1.3	2.3
5	rh.	8.632	12.592	8.632	12.592	0	0	8.668	12.949	0.7	1.7
6	rh.	8.667	12.616	8.667	12.616	0	0	8.659	12.716	0.3 ^a	0.8 ^a
7	rh.	8.709	12.636	8.709	12.636	0	0	8.709	12.636	0	0

^aThese data should be considered as less accurate.

hydride. It can be clearly seen that the unit-cell volume expands upon nitrogenation and hydrogenation, the expansion caused by the nitrogenation being the largest. Similar results have been obtained for the nitrides up to $x=6$ and for the hydrides up to $x=4$. In Table I, the structural data of the compounds are listed. In the calculation of the unit-cell volumes, the volumes of the compounds crystallizing in hexagonal structure have been multiplied by 1.5 to compare them with the unit-cell volumes of the compounds with rhombohedral structure.

It is interesting to note that the amount of interstitial atoms that can be introduced into the compounds decreases with increasing aluminum concentration. Above $x=6$ nitrogenation was not found to be possible and above $x=4$ hydrogenation was not possible, even after treatments for a very long time. All nitrogenated compounds have almost the same lattice parameters, appearing to reach a maximum expansion. The same phenomenon has previously been observed for other series.⁵ In the case of the hydrides, this "maximum expansion" phenomenon was not observed.

As is usually observed, α -Fe precipitates in the samples during the nitrogenation, which contributes to the magnetization of the compounds. A method to correct for this impurity contribution is presented elsewhere.⁶

B. Magnetic properties of the interstitial nitrides and hydrides

The Curie temperatures of the compounds $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x$ and $\text{Dy}_2\text{Fe}_{17-x}\text{Al}_x\text{N}_y$ are listed in Table II. In the range $x \leq 3$, substitution of Fe by Al causes an increase in the Curie temperature, which has been discussed in Refs. 7 and 8. The expansion of the unit cell caused by the introduction of nitrogen is accompanied by an increase of the Curie temperature. The amount of nitrogen that can be introduced, however, decreases with increasing Al concentration, which is accompanied by a reduced increase of the Curie temperature.

In R - T compounds, the magnetic properties change from ferromagnetic to ferrimagnetic when R proceeds from the light rare earths to the heavy rare earths.⁹ If the applied external field is sufficiently high, the ferrimagnetic spin structure is affected, the magnetic moments start to bend, and the magnetization increases. A simple model that describes the magnetization process of (single-crystalline) powder par-

ticles that are free to rotate in the applied field has been presented by Verhoef *et al.*¹⁰ According to this model, the intersublattice molecular-field coefficient n_{RT} can be derived directly from the magnetic susceptibility in the region where the departure from the ferrimagnetic structure occurs:

$$n_{RT} = B/M. \quad (1)$$

The exchange constant J_{RT} (the exchange parameter appearing in a nearest-neighbor Heisenberg-type Hamiltonian) can be obtained by means of the equation

$$J_{RT} = \frac{g_R \mu_B^2 N_T}{(g_R - 1) Z_{RT}} n_{RT}, \quad (2)$$

where g_R is the Landé factor of the R ion, N_T is the number of T atoms per formula unit, and the Z_{RT} is the number of nearest T -atom neighbors of an R atom.

As examples, in Fig. 2 the free-powder magnetization curves are presented for the hydride and the nitride with $x=4$. The J_{RT} values that could be derived for the investigated nitrides and hydrides are collected in Table II, together with the J_{RT} values for the parent compounds taken from Ref. 7. It can be seen clearly from the table that the introduction of hydrogen or nitrogen leads to a decrease of $|J_{\text{DyFe}}|$, which is the strongest for the nitrides. This decrease of the R - T coupling upon introduction of interstitial atoms has also been observed in other series.¹¹ The decrease may be inter-

TABLE II. Curie temperatures (T_C) and the intersublattice-coupling constants (J_{DyFe}/k), both expressed in K, for the $\text{Dy-Fe}_{17-x}\text{Al}_x$ compounds and the corresponding interstitial hydrides and nitrides. The T_C values of the parent compounds have been taken from Ref. 7.

x	Parent compounds		$Z=H$			$Z=N$	
	T_C	$-J_{\text{DyFe}}/k$	$-J_{\text{DyFe}}/k$	$-J_{\text{DyFe}}/k$	$-J_{\text{DyFe}}/k$	T_C	
0	371	...	...	...	...	699	
1	404	...	...	...	...	671	
2	436	...	...	...	...	592	
3	451	10.6 ^b	9.8	8.6	5.25	525	
4	436	9.04	8.5	7.5	4.57	457	
5	395	8.77	...	7.3 ^b	423 ^b	423 ^b	
6	319	9.25	...	...	...	...	
7	237	10.1	...	...	...	...	

^aNo values available.

^bData should be considered as less accurate.

FIG. 2. Magnetic isotherms at 4.2 K of the interstitial hydride $\text{Dy}_2\text{Fe}_{13}\text{Al}_4\text{H}_{1.8}$ and nitride $\text{Dy}_2\text{Fe}_{13}\text{Al}_4\text{N}_{1.3}$.

preted to result from the increase of the unit-cell volume and the associated increase of the spatial separation of the ions. Since the $3d$ - $4f$ interaction which is mediated by the hybridization of the $3d$ - and $5d$ -electron states is distance depen-

dent, a decrease of $|J_{RT}|$ upon introduction of interstitial atoms seems natural.

ACKNOWLEDGMENTS

This work has been partially carried out within the scientific exchange program between China and the Netherlands. The authors thank Professor P. F. de Châtel for fruitful discussions.

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