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Neutron diffraction study of $HoFe_{11}TiD_x$ deuterides

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Abstract

Powder neutron diffraction measurements have been performed on the $HoFe_{11}TiD_x$ ($x=0$, 0.7, 0.9) compounds. The results show the appearance of a spin–reorientation transition and a remarkable change of the crystallographic parameters and the magnetic moments of the Fe atoms after deuteration.

Keywords: Neutron diffraction; Deuterides; Fe atoms

1. Introduction

The intermetallic compounds of the type $RFe_{11}Ti$ (R= rare earth) crystallize in a tetragonal structure with a space group $I4/mmm$ and two formula units per unit cell. In this structure R (rare earth) occupies 2a crystallographic sites and the Fe (and Ti) occupies three crystallographically inequivalent sites—8i, 8j and 8f. The 8j and 8f positions are fully occupied by the Fe ions.

The intrinsic magnetic properties of the $HoFe_{11}Ti$ intermetallic compound have been previously investigated. According to the results of Boltich et al. [1], Sinha et al. [2], and Zhang et al. [3] the magnetic ordering temperature of this compound is $T_c=518$ K and it exhibits one successive spin reorientation (SR) transition at about 50 K. Hu et al. [4] and Kou et al. [5] assert that such SR transition does not exist. There are reports [4–6] on the existence of a field induced transition at a temperature $T=77$ K and in a magnetic field $H\sim19$ kOe. In the review paper [1] it is pointed out that a second transition from cone to plane can occur in this compound at lower temperatures.

Our previous investigations [7] including ac-susceptibility method and magnetization measurements in situ in hydrogen atmosphere under pressure showed that the investigated hydrides $HoFe_{11}TiH_x$ with $x<0.4$ do not exhibit a spin reorientation transition at low temperatures. Such a transition appears at $x>0.4$ and as a result of this the magnetization direction deviates from the c axis.

In this paper, we present the results of powder neutron diffraction experiments performed on the $HoFe_{11}TiD_x$ deuterides in the temperature range from 2 K to 250 K. The aim of these investigations was to check up the existence of SR transitions, to determine the magnetic structures of these compounds and the individual behavior of the magnetic moments of the rare earth and the transition metal magnetic sublattices.

2. Experimental procedure

The $HoFe_{11}Ti$ polycrystalline samples were prepared by arc melting of the constituent materials (Tb, Fe, and Ti) of 99.9% purity under purified Ar atmosphere. The buttons were remelted four times and then annealed for 80 h to achieve phase homogeneity. X-ray analysis showed that the samples have a tetragonal $ThMn_{12}$-type structure. A small amount of Fe impurity phase (about 5%) was observed in the alloy.

The preliminary deuterium content was determined by a gravimetric method. Finally the deuterium concentration was defined more precisely using the data of the numeric treatment of the experimental results.

Neutron diffraction studies of $HoFe_{11}TiD_x$ were performed using powder neutron diffractometer DN5 with a multidetector of 800 cells at the SILOE Reactor of the 'Centre d'Etudes Nucleaires' of Grenoble ($\lambda=1.342$ Å) in

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the temperature range 2–250 K. The treatment of the neutron data was carried out using the FULLPROF PROGRAM.

3. Experimental results

The investigated compounds are $HoFe_{11}TiD_x$ with $x=0$, 0.7 and 0.9. Further we shall discuss the deuteride with $x=0.7$, which according to our data undergoes a SR transition at $T=135$ K [7]. The experimental and the calculated patterns at $T=2$ K for the host compound are displayed in Fig. 1 and for the deuteride compound in Fig. 2. The results of the treatment with the FULLPROF PROGRAM at this temperature are presented in Table 1 Table 2.

Powder neutron diffraction studies show that $HoFe_{11}Ti$ has a collinear ferrimagnetic structure with magnetic moments oriented along the *c* axis. This structure reserves its character down to 2 K. In the deuteride sample $HoFe_{11}TiD_{0.7}$ remarkable changes in the magnetic and structural properties take place.

The crystallographic data are presented in Fig. 3. The lattice parameters change monotonously with the decreasing temperature down to 100 K. At this temperature they sharply decrease. Further temperature decrease down to 2 K does not influence the monotonous character of the parameter change. The unit cell volume undergoes a similar change.

The magnetic moments of the 8i-Fe and 8j-Fe (Fig. 4) sublattices change considerably (nearly 15%) at $T \approx 130$ K, while the 8f-Fe sublattice magnetic moment decreases monotonously with the decreasing temperature (Fig. 4). The Ho sublattice magnetic moment is found to decrease monotonously with the temperature increase (from $\mu_{Ho}=9.4\ \mu_B$ at $T=2$ K to $\mu_{Ho}=4.8\ \mu_B$ at $T=250$ K), (Fig. 5).

The magnetic moment of the system tilts out from the c-axis by an angle of about 30 degrees in the temperature range from $T=250$ K to 150 K (Fig. 5). At $T=150$ K, the tilt angle increases rapidly to $\theta=70°$. This value remains down to 2 K.

4. Discussion

The neutron diffraction study of the $HoFe_{11}TiH_x$ compound shows the absence of a SR transition at $x=0$. The magnetic moment of the compound remains parallel to the *c*-axis. The SR transition does not appear at $x<0.4$ either [7].

The magnetocrystalline anisotropy of $RFe_{11}Ti$ intermetallic compounds can be explained as due to the contribution of two factors [8]: the crystal electric field effect and the changes in the charge density. In our case, the influence of the both factors is considerable.

At room temperature the deuterium entering the lattice of the host compound causes deformations, changes in the crystal electric field and a delocalization of the electronic charge of the metal matrix. This leads to an increase of the magnetic anisotropy in the basal plane [9]. As a result even

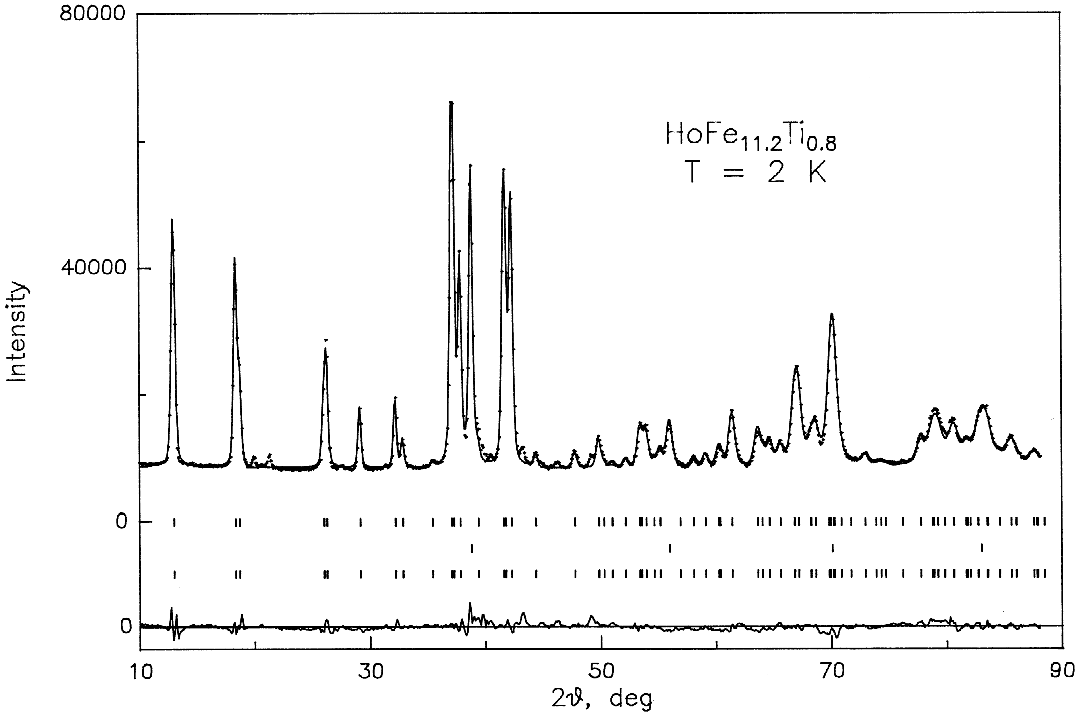

Fig. 1. Experimental (+) and calculated (line) neutron powder diffraction patterns of $HoFe_{11}Ti$ at $T=2$ K.

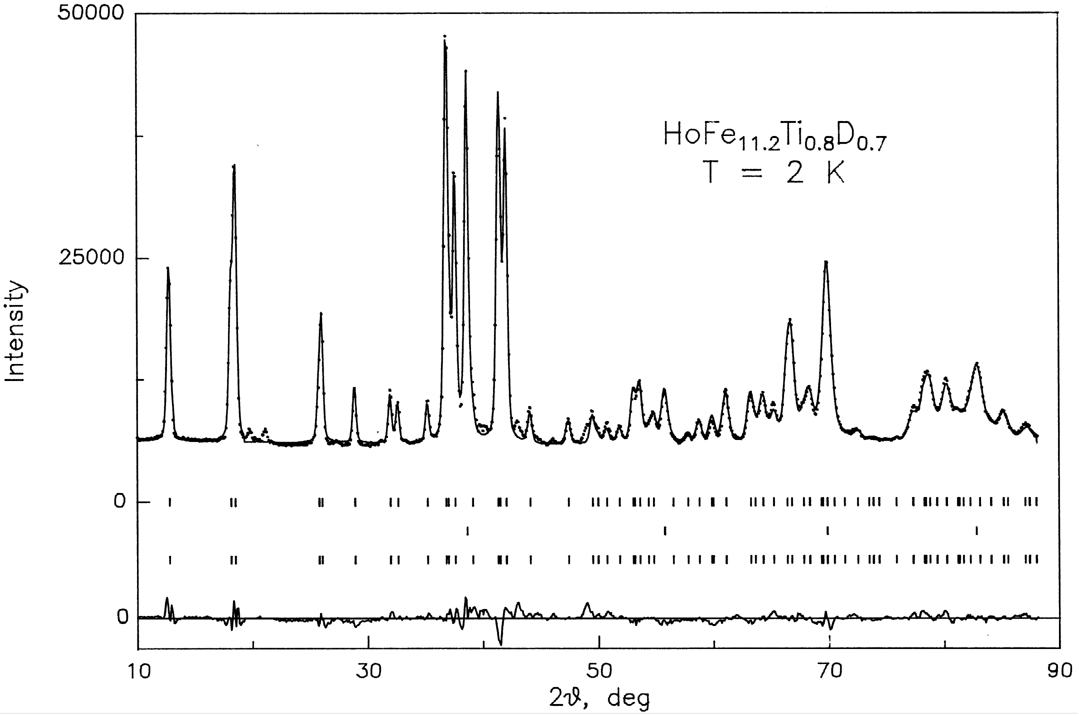

Fig. 2. Experimental (+) and calculated (line) neutron powder diffraction patterns of $HoFe_{11}TiD_{0.7}$ at 2 K.

Table 1
Crystal and magnetic parameters of refinements for $HoFe_{11}Ti$ at $T=2$ K. Lattice Parameters: $a=8.4687$ Å, $c=4.7659$ Å

At.	Pos.	x	y	z	Occ.	M (μ_B)	ϑ, deg
Ho	2a	0	0	0	1	9.8	180
Fe	8i	0.3530	0	0	0.82	2.2	0
Ti	8i	0.3530	0	0	0.18	–	–
Fe	8j	0.2765	.5	0	1	2.3	0
Fe	8f	0.25	0.25	0.25	1	1.9	0

at room temperature the magnetization direction deviates from the c-axis by an angle of 30°.

When the temperature decreases, the lattice form undergoes anisotropic changes, which influence the crystal electric field and consequently, the magnetic anisotropy. Variations appear in the charge distribution too, because for the 8j-Fe sublattice the interatomic distances $d_{Fe-D} \approx$ 1.9 Å depend slightly on the temperature. At $T=100 \div 120$ K, the overlap of the D-orbitals and the Fe d-orbitals increases and the delocalization of the s—electronic charge leads to a further increase of the magnetic anisotropy in the basal plane. Owing to this the tilt angle reaches the value $\theta=70°$.

Table 2
Crystal and magnetic parameters of refinements for $HoFe_{11}TiD_{0.7}$ at $T=2$ K. Lattice Parameters: $a=8.500$ Å, $c=4.777$ Å

At.	Pos.	x	y	z	Occ.	M (μ_B)	ϑ, deg
Ho	2a	0	0	0	1	8.9	110
D	2b	0	0	0.5	0.7	–	–
Fe	8i	0.3506	0	0	0.82	3.2	70
Ti	8i	0.3506	0	0	0.18	–	–
Fe	8j	0.2759	0.5	0	1	2.4	70
Fe	8f	0.25	0.25	0.25	1	1.6	70

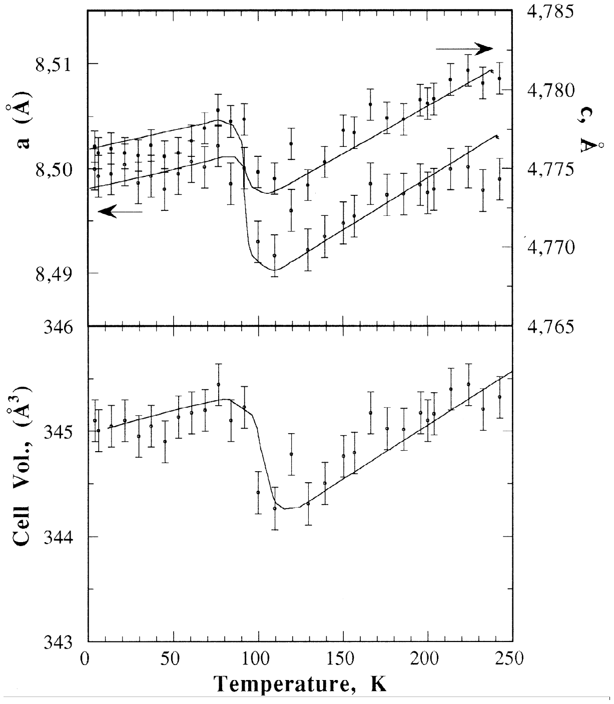

Fig. 3. Temperature dependence of the crystallographic lattice parameters a, c and of the cell volume for $HoFe_{11}TiD_{0.7}$. (lines are guide for the eye).

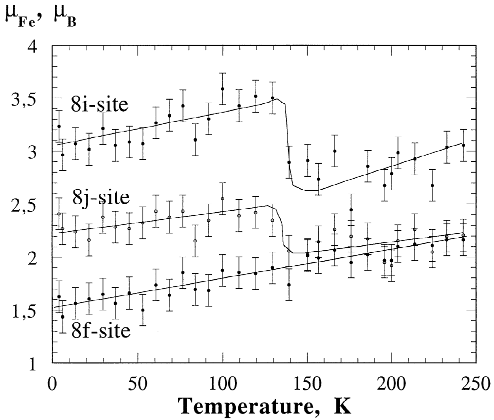

Fig. 4. Temperature dependence of the magnetic moment of the 8i, 8j and 8f iron sublattices for $HoFe_{11}TiD_{0.7}$.

The peculiarities in the behavior of the 8i-Fe and the 8f-Fe sublattice magnetic moments are a direct consequence of the changes in the lattice parameters observed at $T=100$–120 K, i.e. these peculiarities are caused by the changes in the hybridization provoked by the presence of deuterium.

Probably the different temperature dependence of the Ho and the Fe sublattice magnetic anisotropy is of great importance in our case too. The simultaneous influence of the following three factors-the crystal electric field, the charge delocalization and the different temperature dependence of the Ho and the Fe sublattice magnetic anisotropy-leads to a sharp change of the tilt angle at $T=135$ K.

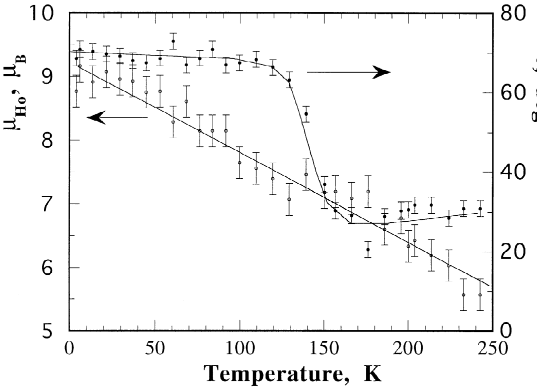

Fig. 5. Temperature dependence of the magnetic moment of the Ho sublattice and of the magnetic moment for $HoFe_{11}TiD_{0.7}$.

In all cases mentioned above the exchange energy ensures the collinearity of the Ho and the Fe magnetic sublattices.

5. Conclusion

Powder neutron diffraction experiments have been used to determine the crystallographic parameters, the magnetic moments and the magnetic anisotropy of $HoFe_{11}TiD_x$ for $x=0$ and $x=0.7$ in the temperature range from 2 to 250 K.

A remarkable change of the unit cell volume (a first order phase transition) and of the magnetic anisotropy has been found in the temperature range 100–150 K.

Acknowledgments

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