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INVESTIGATIONS OF PHASE TRANSITIONS IN $RFe_{11}TiH_x$ (R = Dy, Ho, Er) INTERMETALLIC COMPOUNDS BY THE AC SUSCEPTIBILITY METHOD

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Радостина Дамянова, Андрей Апостолов, Руслан Бездушний, Любомир Илиев, Никола Станев. ИЗСЛЕДВАНЕ НА ФАЗОВИТЕ ПРЕХОДИ В $RFe_{11}TiH_x$ (R = Dy, Ho, Er) ИНТЕРМЕТАЛНИ СЪЕДИНЕНИЯ ЧРЕЗ АС-ВЪЗПРИЕМЧИВОСТ.

В настоящата статия са представени резултати от изследването на спин-преориентационните явления в интерметални съединения $RFe_{11}Ti$ и техните хидриди (R= Dy, Ho и Er), получени чрез изследване на ас-възприемчивост. В $DyFe_{11}TiH_x$ и $HoFe_{11}TiH_x$ при увеличаване на концентрацията на водорода спин-преориентационните преходи се отместват към по-високите температури и дори изчезват. В $ErFe_{11}TiH_x$ при температури, по-високи от 100 K, се наблюдава термомагнитен хистерезис.

Radostina Damianova, Andrei Apostolov, Ruslan Bezdushnyi, Ljubomir Iliev, Nikola Stanev. INVESTIGATIONS OF PHASE TRANSITIONS IN $RFe_{11}TiH_X$ (R = Dy, Ho, Er) INTERMETALLIC COMPOUNDS BY THE AC SUSCEPTIBILITY METHOD.

In this paper the spin reorientation behaviour of some $RFe_{11}Ti$ compounds and their hydrides (R = Dy, Ho and Er) determined by the ac susceptibility method is reported. In $DyFe_{11}TiH_x$ and $HoFe_{11}TiH_x$ upon hydrogenation in the unhydrogenated compounds existing spin reorientation transitions shift to higher temperatures and even disappear. In $ErFe_{11}TiH_x$ hydrogenated compound a thermomagnetic hysteresis appear above T = 100 K.

Keywords: intermetallic compounds, magnetic susceptibility, spin reorientation, hydrogen
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1. INTRODUCTION

Ternary alloys of the composition $RFe_{11}Ti$ have a body—centred tetragonal $ThMn_{12}$ structure. They become important as new magnetic materials because of their outstanding properties, such as fairly high magnetic ordering temperatures, large values and specific temperature dependence of the magnetocrystalline anisotropy. The Fe sublattice exhibits uniaxial anisotropy orientated along the c-axis [001] over all temperatures. Rare earth ions with negative second order Stevens' factors (Tb, Dy, and Ho) exhibite planar anisotropy contributions, whereas those with positive second order Stevens' factors (Sm, Er, Tm, and Yb) generally exhibit an easy axis. The temperature induced competition between the R and Fe sublattice anisotropies or the temperature induced changes in the R sublattice anisotropy only, lead to the appearance of complex spin—reorientation transitions [1–7].

Till now, the magnetic properties of the $RFe_{11}TiH_x$compounds have been scantily explored [8–11], in contrast with their host materials. In this paper we report the spin reorientation behaviour of some $RFe_{11}Ti$ compounds and their hydrides (R=Dy, Ho, and Er) determined by the ac susceptibility method.

2. EXPERIMENTAL PROCEDURE

$DyFe_{11}Ti$, $HoFe_{11}Ti$ and $ErFe_{11}Ti$ intermetallic compounds were prepared by induction melting of the constituent elements (99.9 % purity) under a high-purity argon atmosphere. The samples were remelted several times to achieve better homogeneity. The X-ray diffraction analysis showed the expected tetragonal $ThMn_{12}$-type structure. The alloys were almost single-phase materials. A small amount of Fe impurity phase (about 3%) was observed in the samples by X-ray and magnetic phase analysis.

The hydrides were formed by exposing the host materials to high purity hydrogen at about 40 atm. The resulting alloys were checked by means of X-ray diffraction. Additional crystallographic phases (not existing in the host materials) have not been found. On hydriding an increase of the lattice parameters (a and c) and unit cell volume was observed to increase, but the ratio c/a remains constant.

The ac susceptibility of the samples was measured in magnetic fields up to 10 Oe, at a frequency 11–111 Hz, using a Hartshorn mutual inductance bridge. The nature of the observed transitions was inferred from the shape of the curve and the transition temperatures were identified with the inflection points. In order to define more exactly the temperatures of spin reorientation transitions at $T >$300 K the temperature dependence of the magnetization in a static magnetic field using a vibrating sample magnetometer was measured.

3. RESULTS AND DISCUSSION

A. $DyFe_{11}TiH_x$ ($x < 1.4$)

The intermetallic compound $DyFe_{11}Ti$ exhibits two phase transitions. The resulting spin reorientations temperatures identified by the peaks in χ_{ac} for polycrystalline samples, $T_{\mathrm{SR1}} = 215$ K, and $T_{\mathrm{SR2}} = 100$ K [3], are in good agreement to 235 K and 110 K, respectively, measured by a dc method [3] and also with our magnetization data [12]. The T_{SR1} and T_{SR2} values derived by Hu et al. [5] from the temperature dependence for the magnetization of a $\mathrm{DyFe_{11}Ti}$ single crystal are 200 K and 58 K, respectively.

The measurements of the anisotropy field in $\mathrm{YFe_{11}Ti}$ [13] pointed out that the Fe sublattice exhibits uniaxial anisotropy along the c-axis over all temperatures ($W_{\mathrm{an}}^{\mathrm{Fe}} = K_1^{\mathrm{Fe}} \sin^2 \vartheta$). An uniaxial 3d anisotropy can be assumed also for the present compound. The Dy sublattice is tetragonal ($W_{\mathrm{an}}^{\mathrm{Dy}} = K_1^{\mathrm{R}} \sin^2 \vartheta + K_2^{\mathrm{R}} \sin^2 \vartheta + K_2'^{\mathrm{R}} \sin^4 \vartheta \cos^4 \psi$) and only at temperatures higher than T_{SR2} its magnetic moment is aligned along the c-axis. The appearance of a spin reorientations in $\mathrm{DyFe_{11}Ti}$ is not at all surprising since the intrinsic rare earth anisotropy is opposite to that of the iron [3]. The temperature dependence of the rare earth and transition metal sublattice anisotropies are generally quite different. The Dy anisotropy is dominant at low temperatures, whereas the Fe anisotropy is dominant at temperatures larger than T_{SR1}. At 215 K the Dy sublattice magnetization deviates from the c-axis and a spin reorientation transition axis-to-cone takes place. At $T = 100$ K the easy magnetization direction becomes perpendicular to the c-axis, i.e. a SR transition cone-to-plane takes place.

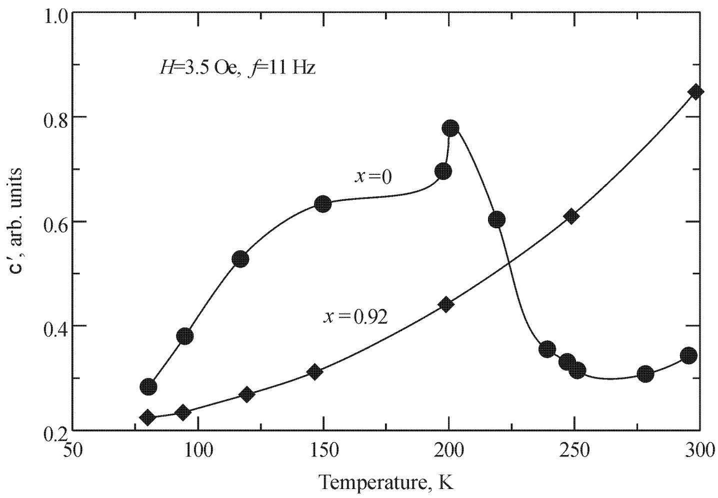

Fig. 1. Temperature dependence of ac susceptibility for $\mathrm{DyFe_{11}TiH}_x$

Our results of the χ_{ac} versus temperature behaviour for the $\mathrm{DyFe_{11}Ti}$ (Fig. 1) are in excellent agreement with those presented in the review paper [3]. The Fig. 1 shown temperature dependence of χ_{ac} for the hydrogenated sample $\mathrm{DyFe_{11}TiH_{0.92}}$ do not exhibit any peculiarities in the temperature range from 78 to 300 K. According to these data and also to our previous results concerning the magnetic properties of $\mathrm{DyFe_{11}TiH}_x$ [12] it can be concluded that the incorporation of hydro-

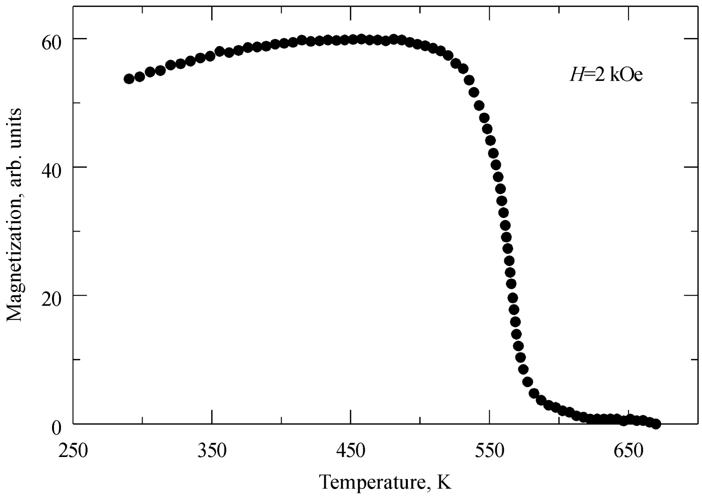

Fig. 2. Temperature dependence of magnetization for $DyFe_{11}TiH_{1.2}$

gen causes significant changes in the Dy sublattice anisotropy, which results in shifting T_{SR1} and T_{SR2} towards higher temperatures.

The magnetization versus temperature behaviour of $DyFe_{11}TiH_{1.2}$ compound (with high hydrogen content) in the temperature range from 78 to 700 K is shown in Fig. 2. As evidenced in the figure there are no indications for any spin reorientations up to the magnetic ordering temperature of the hydrogenated compound. It is believed that in this case the Dy magnetic moments are practically perpendicular to the c-axis in the whole temperature range from 0 K up to T_C.

B. $HoFe_{11}TiH_x$

Boltich et al. [1], Sinha et al. [3], and Zhang et al. [4] claim a spin reorientation transition in $HoFe_{11}Ti$ at about 50 K from a high-temperature easy c-axis spin configuration to a cone structure. In contrast with this Hu et al. [2] and Yang et al. [14] have pointed out that the easy magnetization direction of $HoFe_{11}Ti$ remains easy c-axis down to the lowest temperatures (up to 15 K).

Our results of the χ_{ac} versus temperature behaviour for the $HoFe_{11}TiH_x$ (Fig. 3) are in close agreement (in the investigated temperature range 77–300 K) with those presented in the review papers [3] and [7]. The Fig. 3 shown temperature dependence of χ' for $HoFe_{11}TiH_{0.8}$ hydrogenated compound shows that in the presence of hydrogen the spin reorientation transition (existing at about 50 K [1, 3, 4]) is shifted to higher temperatures. It means that hydrogen entering the lattice of the investigated compound causes a significant change in the Ho sublattice anisotropy constants, which results in an increase of the spin reorientation transition temperature. At this temperature the Ho magnetic moments deviate from the

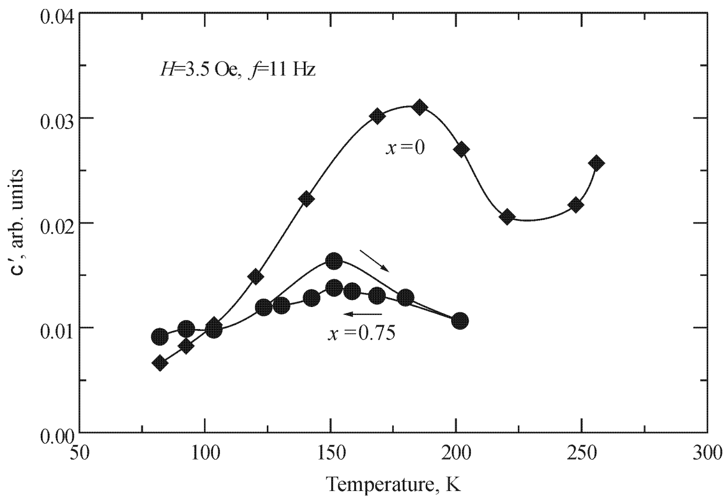

Fig. 3. Temperature dependence of ac-susceptibility for $HoFe_{11}TiH_x$

easy axis and a spin reorientation transition axis-to-cone takes place. These results confirm the obtained earlier by us magnetization data for $HoFe_{11}TiH_x$ hydrides [15].

C. $\mathbf{ErFe_{11}TiH_x}$

A very surprising result is the appearance of a spin reorientation phenomenon in $ErFe_{11}Ti$. A change of the easy magnetization direction has been detected at about 50 K from the c-axis above this temperature to a cone at lower temperatures [5]. As discussed above, Er with a positive α_j is expected to prefer uniaxial anisotropy over all temperatures. The exhibition of a spin reorientation in $ErFe_{11}Ti$ may be attributed to the significance of higher-order crystal field parameters and the dominance of a higher anisotropy constant at low temperatures [3].

Our investigation of the $ErFe_{11}Ti$ intermetallic compound by the ac susceptibility method gave nearly the same results as those presented in [3] (Fig. 4). But the hydrogenated compound exhibited two anomalies ($ErFe_{11}TiH_{0.75}$ on Fig. 4). First, the peak in $\chi_{ac}(T)$ is shifted to lower temperatures ($\Delta T = 50$ K), which may be a consequence of the effect of the absorbed hydrogen on the crystalline electric field of the Er ions. Secondly, above T=100 K, χ' exhibits a thermomagnetic hysteresis. The latter one can be interpreted as a result of the alternation in the exchange interactions and crystalline electric field, caused by the hydrogen atoms. Hydrogen entering the lattice of the investigated compound forms (on the conditions of the present experiment, i.e. P=6 atm and $x = 0.75$ at.H./f.u.) an α-hydride, i.e. the distributed between the Er atoms hydrogen leads to the fluctuations in exchange interactions, which results in appearance of a thermomagnetic hysteresis just above the spin reorientation temperature. A similar behaviour was observed in other hydrogenated intermetallic compounds, e.g., $R_2Co_7H_x$ [16].

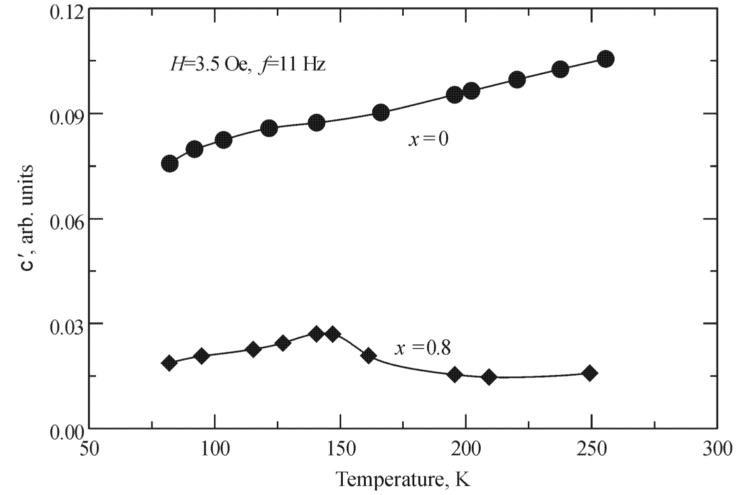

Fig. 4. Temperature dependence of ac susceptibility for $ErFe_{11}TiH_x$

4. CONCLUDING REMARKS

The $DyFe_{11}TiH_x$ and $HoFe_{11}TiH_x$ systems, investigated by the ac susceptibility method, have been observed to exhibit spin reorientation transitions. It has been found, that in contradiction to the small effect of the absorbed hydrogen on the Fe sublattice magnetic anisotropy, the Dy sublattice anisotropy energy appears to be highly influenced even by the relatively low hydrogen concentration. Upon hydrogenation in the host compounds existing spin reorientation transitions are observed to shift to higher temperatures and even to disappear. Similar conclusions about the influence of hydrogen on the rare earth sublattice behaviour in other compounds with a similar structure are presented in a review paper [6]. The $\chi_{\mathrm{ac}}(T)$ behaviour for $ErFe_{11}TiH_x$ is more complicated and additional investigations are needed to explain the obtained results.

REFERENCES

1. Boltich, E. B., B. M. Ma, L. Y. Zhang, F. Pourarian, S. K. Malik, S. G. Sankar and W. E. Wallace. *J. Magn. Mater.*, **78**, 1989, 365.
2. Hu Bo-Ping, Hong-Ahuo Li, J. P. Gavigan and J. M. D. Coey. *J. Phys.: Condensed Matter*, **1**, 1989, 755.
3. Sinha, V. K., S. K. Malik, D. T. Adroja, J. Elbicki, S. G. Sankar and W. E. Wallace. *J. Magn. Magn. Mater.*, **80**, 1989, 281.
4. Zhang, L. Y., E. B. Boltich, V. K. Sinha and W. E. Wallace. *EEE Trans. Magnetics*, **25**, 1989, 3303.
5. Bo-Ping Hu, Hong-Shuo Li, J. M. D. Coey and J. P. Gavigan. *Phys. Rev. B*, **41**, 1990, 2221.
6. Garcia, L. M., J. Bartolome, P. A. Algarabel, M. R. Ibarra and M. D. Kuzmin. *J. Appl. Phys.*, **73**, 10, pt. 2A, 1993, 5908.
7. Kou, X. C., T. S. Zhao, R. Grossinger, H. R. Kirchmayr, X. Li and F. R. de Boer. *Phys. Rev. B*, **47**, 1993, 3231.

8. Zhang, L. Y., S. G. Sankar, W. E. Wallace and S. K. Malik. *Sixth International Symposium on Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, Pittsburg, PA, USA, 25 October*, 1990. Paper No. SP33.
9. Nikitin, S. A., I. S. Tereshina, V. N. Verbetski and A. A. Salamova. *Physics of the Solid State*, **40**, 1998, 258.
10. Nikitin, S. A., I. S. Tereshina, Yu. V. Skourski, N. Yu. Pankratov, K. P. Skokov, V. V. Zubenko and I. V. Telegina. *Physics of the Solid State*, **43**, 2001, 290.
11. Tereshina, I. S., S. A. Nikitin, G. A. Bezkorovajnaya, W. Suski, D. Badurski. *Europ. Conf. on Physics of Magnetism, POZNAN, PL*, 2002.07 01-05.
12. Apostolov, A., R. Bezdushnyi, R. Damianova, N. Stanev, I. Naumova. *J. Magn. Magn. Mater.*, **150**, 1995, 393.
13. Zhang, L. Y. and W. E. Wallace. *J. Less-Common Metals*, **149**, 1989, 371.
14. Ying-Chang Yang, Lin-Shu Kong, Yuan-Bo Zha, Hong Sun and Xie-Di Pei. *J. Phys. (Paris) Collog.*, **49**, 1988, C8-543.
15. Apostolov, A., R. Bezdushnyi, N. Stanev, R. Damianova, D. Fruchart, J. L. Soubeyroux, O. Isnard. *J. Alloys and Comp.*, **265**, 1998, 1.
16. Apostolov, A., L. Bozukov, N. Stanev and T. Mydlarz. *J. Physique* , **49**, 1988, 518.

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