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# The Structure and Magnetic Properties of $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$ Compounds<sup>\*</sup>

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**Abstract :** The effects of substituting small amounts of Si for Co on the structure and magnetic properties of  $\text{Ho}_2\text{Co}_{17}$  compounds were studied by means of X-ray diffraction and magnetization measurements. All samples are of single phase with the  $\text{Th}_2\text{Ni}_{17}$ -type structure. The substitution of Si for Co leads to an approximately linear decreasing in the unit cell volume. The analysis indicates that the saturation magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  is found to decrease as  $x$  increasing from 0 to 3. From thermomagnetization curves measurements, it is assumed that  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds display the plane anisotropy at  $x = 0.5$ . A spin reorientation occurs turning from base-plane into  $c$ -axis for  $0.5 < x < 3.0$ .  $T_{sr}$ , the temperature of spin reorientation, decreases firstly, and then after reaching a lowest point at  $x = 2.5$  increases with the increase of Si concentration.

**Key words :** Rare earths, Crystal structure, Saturation magnetization, Magnetocrystalline anisotropy

**PACC :** TG115.27+1

## 1 Introduction

Over the last two decades, 217-type rare earth (RE)-transition (T) metal intermetallic compounds have been extensively investigated<sup>[1,2]</sup>. In particular, their magnetocrystalline anisotropy, a fundamental intrinsic magnetic property has attracted much attention. Researches<sup>[3,4]</sup> show that the substitution of small amounts of non-magnetic atoms such as Al, Ga and Si for the transition metal atoms is capable not only of maintaining stable 217-type structure but also of elevating its Curie temperature. It can also reinforce uniaxial anisotropy of  $\text{RE}_2\text{Fe}_{17}$  and  $\text{RE}_2\text{Co}_{17}$  compounds or shift planar anisotropy to uniaxial anisotropy.

In this study, RE element Ho is selected. The structure of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  with  $x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$ , and the effects of substituting small amounts of Si for Co on the saturation magnetization and magnetocrystalline anisotropy are discussed in detail.

## 2 Experimental methods

Samples of the composition  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  with  $x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$  were prepared by weighting the constituent elements of a purity of at least 99.9% and putting into an arc-melting furnace.

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nance. High pure Argon was injected for protection, but before that the furnace was evacuated until the pressure was approximately  $10^{-3}$  Pa. The ingots were melted at least three times to ensure homogeneity. The as-cast ingots were sealed in an evacuated quartz tube and annealed in the vacuum at  $1040^{\circ}\text{C}$  for 88 h, then quenched to room temperature. X-ray powder diffraction using  $\text{CuK}\alpha$  radiation in a Rigaku Rint 3000 was used for characterization. The spin reorientation temperature of the powder samples was measured by using a vibrating sample magnetometer in a field of 0.1 T. The saturation magnetization of the powder samples was also measured by using an extracting sample magnetometer at low temperature 1.5 K.

### 3 Results and discussion

The X-ray diffraction patterns of the powder samples  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  ( $x = 0.5, 3.0$ ) are shown in Fig. 1, the results of X-ray powder diffraction indicate that  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds are of single phase with the hexagonal  $\text{Th}_2\text{Ni}_{17}$  type structure. In Table 1 shown the lattice parameters including  $a$ ,  $c$  and unit cell volume of the samples (shorting for  $V_X$  including  $x = 0$ ).  $\text{Ho}_2\text{Co}_{17}$  sample is ordered in the hexagonal  $\text{Th}_2\text{Ni}_{17}$  structure, the space groups is  $\text{Pb}_3/\text{mmc}$ , the lattice parameters  $a$ ,  $c$  is 0.834 nm, 1.217 nm respectively, and the unit-cell volume  $V$  is  $0.7340 \text{ nm}^3$ . Viewing from Table 1,  $V$  linearly decreases with increasing Si concentration. The reason is that the Si atom radius is smaller than Co atom radius, thus causing lattice parameters and the volume to decrease accordingly.

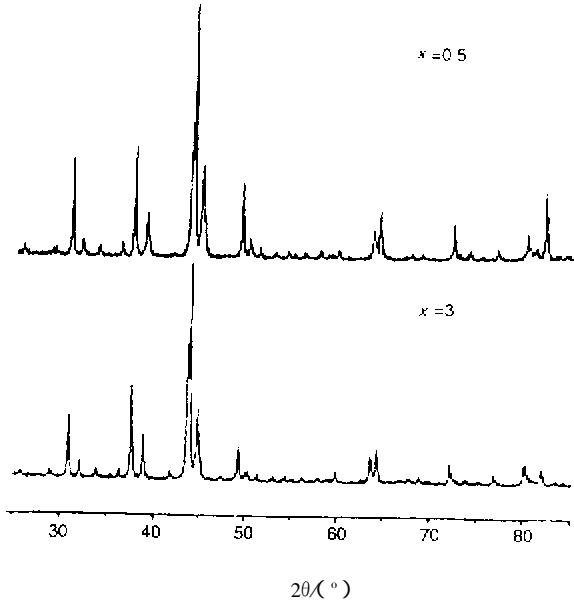


Fig. 1 The X-ray diffraction patterns of the powder samples  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  ( $x = 0.5, 3.0$ )

In  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds, the saturation magnetization is attributed to the interplay of  $\text{Ho}^{3+}$  and  $\text{Co}^{3+}$  moments. In order to find the respective contribution of Ho atom and Co atom to the saturation magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds, the saturation magnetization of  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  powder

Table 1 The lattice parameters  $a$ ,  $c$  and unit cell volume  $V$  of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds

Composition	$a/\text{nm}$	$c/\text{nm}$	$V/\text{nm}^3$
$\text{Ho}_2\text{Co}_{17}$	0.834	1.217	0.7340
$\text{Ho}_2\text{Co}_{16.5}\text{Si}_{0.5}$	0.833	1.216	0.7305
$\text{Ho}_2\text{Co}_{16}\text{Si}_1$	0.832	1.216	0.7289
$\text{Ho}_2\text{Co}_{15.5}\text{Si}_{1.5}$	0.831	1.215	0.7274
$\text{Ho}_2\text{Co}_{15}\text{Si}_2$	0.831	1.215	0.7264
$\text{Ho}_2\text{Co}_{14.5}\text{Si}_{2.5}$	0.830	1.213	0.7246
$\text{Ho}_2\text{Co}_{14}\text{Si}_3$	0.830	1.211	0.7238

Table 2 The magnetic moment of  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds

Composition	$\mu_s/\mu_B$	$\mu_{\text{Co}}/\mu_B$
$\text{Y}_2\text{Co}_{17}$	28.7	1.69
$\text{Y}_2\text{Co}_{16}\text{Si}_1$	23.0	1.44
$\text{Y}_2\text{Co}_{15}\text{Si}_2$	19.3	1.28
$\text{Y}_2\text{Co}_{14}\text{Si}_3$	14.0	1.00

samples was firstly measured, then the average magnetic moment of  $\text{Co}^{3+}$ ,  $\mu_{\text{Co}}$  (shown in Table 2), in this structure can be obtained, and the saturation magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  powder samples was also measured so as to calculate the  $\mu_s$  of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds, the magnetic moment of Ho,  $\mu_R$ , as is shown in Table 3.

Table 3 The magnetic moment of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds

Composition	$\mu_s/\mu_B$	$\mu_{\text{Co}}/\mu_B$	$\mu_R/\mu_B$
$\text{Ho}_2\text{Co}_{16.5}\text{Si}_{0.5}$	5.77	1.69	11.06
$\text{Ho}_2\text{Co}_{16}\text{Si}_1$	2.95	1.44	10.04
$\text{Ho}_2\text{Co}_{15.5}\text{Si}_{1.5}$	0.76	1.44	10.78
$\text{Ho}_2\text{Co}_{15}\text{Si}_2$	0.38	1.28	9.41
$\text{Ho}_2\text{Co}_{14.5}\text{Si}_{2.5}$	2.45	1.28	8.06
$\text{Ho}_2\text{Co}_{14}\text{Si}_3$	4.04	1.00	4.98

There exist two following reasons for choosing  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds: (I) Y is a non-magnetic atom without atomic moment, thus the magnetic moments of these compounds are exclusively derived from the contribution of  $\text{Co}^{3+}$ . (II)  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds and  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds correlate to the similar structure, and the value of  $\mu_{\text{Co}}$  in the two compounds is equivalent. The calculated results, including  $\mu_s$  of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds, the average magnetic moment of RE Ho,  $\mu_R$ , and Co,  $\mu_{\text{Co}}$ , are presented in Table 3.

In Fig. 2 shown the Si content dependence of the saturation magnetization for  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds. As is shown in Fig. 1, the increase of Si substitution  $x$  leads to a sharp linear decrease of the saturation magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds. This is due to that Si atoms are non-magnetic in  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds. So the saturation magnetization,  $\mu_s$ , consists of the summation of Ho and Co magnetic moments. In Table 3, it indicates that average magnetic moments of both Ho and Co in the

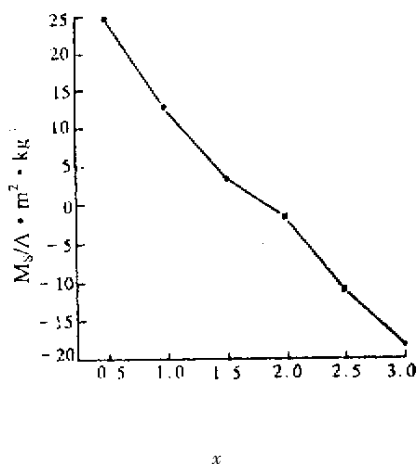


Fig. 2 The concentration dependence of the saturation magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds

$\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds decrease with increasing Si concentration. Obviously, the phenomenon that the total magnetic moment of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds decreases linearly with the increase of Si concentration is due to not only magnetic dilution of non-magnetic Si atoms but also the interplay of Si magnetic dilution and electron hybridization<sup>[5]</sup>.

In an external magnetic field of 0.1T, the thermomagnetic curves of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds above room temperature were obtained by using a vibrating sample magnetometer, whereas the curves below room temperature were obtained by using an extracting sample magnetometer.  $M-T$  thermomagnetic curves measured by extracting sample magnetometer are shown in Fig. 3. It is found that the magnetization  $M$  declines with increasing temperature  $T$ , disappears at a certain temperature

, and then increases with the temperature further increased. As is known, the magnetic moment of Ho sub-lattice is higher than that of Co sub-lattice at low temperature. When the temperature increases, the greater magnetic moment of Ho sub-lattice decreases at a higher speed and lays anti-parallelly to that of Co sub-lattice which is smaller and decreases more slowly. Therefore, when the temperature increases, there must be a point where the magnetic moments of Ho and Co sub-lattices have equal magnitude and opposite orientation so that the total magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  series compounds becomes zero. This temperature point is called offsetting point and this temperature is called compensating temperature. From Fig. 3, it can be seen that the compensating temperature rises with increasing Si content which leads to the decrease of Co sub-lattice magnetic moment. Therefore Co and Ho sub-lattice magnetic moments can offset each other totally at a higher temperature.

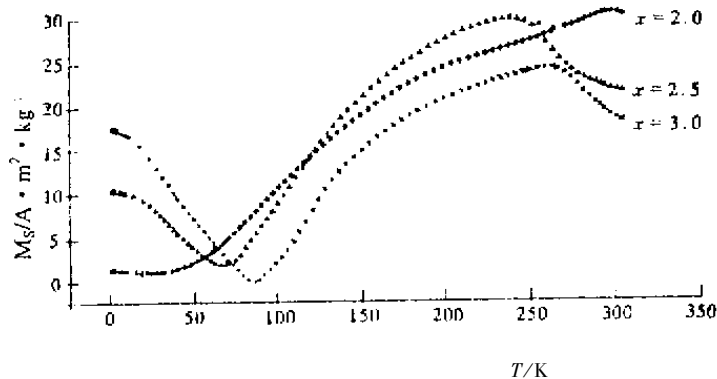


Fig. 3 Temperature dependence of the magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds measured in a field of 0.1T

Magneto-crystalline anisotropy is an important intrinsic property of RE-T intermetallic compounds. The magneto-crystalline anisotropy of  $\text{RE}_2\text{Co}_{17}$  compounds is determined by both Co sublattice and RE sublattice magneto-crystalline anisotropy. For  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds, Y atoms are non-magnetic and do

not contribute to magnetocrystalline anisotropy. Thus, it is reasonable to assume that the magnetocrystalline anisotropy of  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds is merely derived from Co sublattice. Planar anisotropy decreases due to the increasing of Si content, and the easy magnetization direction changes from easy-plane to easy-axis as  $x > 2.0$ , whereas that of  $\text{Y}_2\text{Fe}_{17-x}\text{Si}_x$  compounds is invariable. It may be due to that the anisotropy constant of  $\text{Y}_2\text{Co}_{17}$  compound is approximately an order of magnitude lower than that of  $\text{Y}_2\text{Fe}_{17}$  compound. Therefore, the easy magnetization direction of  $\text{Y}_2\text{Co}_{17-x}\text{Si}_x$  compounds is easier to shift from easy-plane to easy-axis with increasing Si content in comparison with  $\text{Y}_2\text{Fe}_{17-x}\text{Si}_x$  compounds<sup>[6]</sup>. In Fig.4 drawn the temperature  $T$  dependence of the magnetization  $M$  of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds ( $x = 1.0$ ) measured by using a vibrating sample magnetometer.

The peak of  $M - T$  curves occurred at the spin reorientation temperature. The anisotropy of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  includes Ho sublattice anisotropy and Co sublattice anisotropy. At low temperatures, Ho sublattice in  $\text{Ho}_2\text{Co}_{17}$  compounds exhibits planar anisotropy, while there exists four lattice sites 6c, 18f, 9d and 18h for Co sublattice. The Co atoms on 18f lattice sites exhibit axis anisotropy compared to extremely clear planar anisotropy on 6c sites<sup>[7]</sup>. The anisotropy of Ho and Co sublattices change with temperature. The planar anisotropy dominates the axis anisotropy in  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds at lower temperature.

In view of Fig.4, it can be assumed that there may exist only planar anisotropy at  $x = 0.5$  for  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds, and a spin reorientation from easy-plane to easy-axis may occur for  $0.5 \leq x \leq 3.0$ . With the increase of Si content the spin reorientation temperature  $T_{sr}$  firstly decreases, then increases, and a minimum of  $T_{sr}$  occurred at  $x = 2.5$ . It is known that substituting non-magnetic Si atoms for Co atoms may occupy 6c, 18h, 9d lattice sites for  $x < 2.5$ , thus the planar anisotropy of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds decreases and the axis anisotropy is relatively reinforced; When  $x > 2.5$ , Si atoms may occupy 18f lattice sites, thus the axis anisotropy of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds relatively decreases, which leads to the occurrence of a minimum of  $T_{sr}$  at  $x = 2.5$ <sup>[6]</sup>.

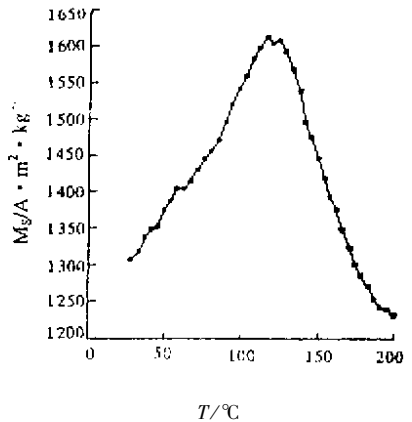


Fig.4 Temperature dependence of the magnetization of  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  compounds with  $x = 1.0$

## References

- [1] Chen Hai-Ying, Ho Wen-Wang, Sankar S G, et al. *Journal of Magnetism and Magnetic Materials*, 1989, **78**:203
- [2] Hu Bo-Ping, Coey J M D. *Journal of the Less - Common Metals*, 1991, **171**:33
- [3] Jacobs T H, Buschow K H J, Zhou G F, et al. *Journal of Magnetism and Magnetic Materials*, 1992, **116**:220
- [4] Shen B G, Cheng Z H, Liang B, et al. *Appl. Phys. Lett.*, 1995, **67**:1621
- [5] Shen B G, Liang B, Cheng Z H, et al. *Chin. Phys. Lett.*, 1998, **15**:223
- [6] Zhang Shao-Ying, Shen Bao-Gen, Li Run-Wei, et al. *J. Phys. Condens. Matter.*, 1998, **10**:2445
- [7] De Groot C H, Buschow K H J, de Boer F R, et al. *Physica B*, 1997, **229**:213

# 金属间化合物 $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$ 的结构和磁性研究\*

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**摘 要:** 研究了非磁性原子 Si 替代 Co 对  $\text{Ho}_2\text{Co}_{17}$  金属间化合物结构和磁性的影响。X 射线衍射结果表明,所有  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  ( $x = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$ ) 化合物都为  $\text{Th}_2\text{Ni}_{17}$  型六角结构,化合物的晶格常数和单胞体积都随 Si 含量的增加而呈线性下降。磁性测量结果表明,  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  化合物的饱和磁化强度随 Si 含量的增加而呈线性下降。从热磁曲线测量观察到,  $\text{Ho}_2\text{Co}_{17-x}\text{Si}_x$  化合物在  $x = 0.5$  时可能呈面各向异性,当  $0.5 \leq x \leq 3.0$  时出现由易面到易轴的自旋重取向,自旋重取向温度  $T_{sr}$  随 Si 原子含量的增加先下降,而后再上升,在  $x = 2.5$  处出现最低点。

**关键词:** 稀土;晶体结构;饱和磁化强度;磁晶各向异性

**中图分类号:** TG 115.27<sup>+</sup> 1      **文献标识码:** A

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