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# Effects of iron substitution on magnetic properties of $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$ compounds

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## Abstract

The effects of iron substitution on the crystal structure and magnetic properties of  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  ( $x = 0.1, 0.3, 0.5,$  and  $0.7$ ) compounds were investigated by means of x-ray powder diffraction and magnetic measurements. The as-cast  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds crystallize in the  $\text{TbCu}_7$ -type structure with the space group  $P6/mmm$ . The lattice parameters  $a$  and  $c$  increase with the Fe content. The  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds exhibit ferromagnetic order with a strong room temperature uniaxial magnetocrystalline anisotropy. The Curie temperature and saturation magnetization increase with the Fe content. The magnetic anisotropy field of the compounds reaches a maximum value at  $x = 0.5$ . The anomalous concentration dependence of the anisotropy field is explained by considering the contribution of individual site anisotropy in combination with the preferential occupation of 3d ions on different sites.

## 1. Introduction

An excellent high temperature permanent magnet requires a high Curie temperature, large saturation magnetization, and strong uniaxial magnetocrystalline anisotropy. Interest has recently been focused on the Sm–Co intermetallic compounds with the  $\text{TbCu}_7$ -type structure due to their potential applications as novel high temperature permanent magnetic materials [1–3]. The  $\text{TbCu}_7$  structure is a derivative of the  $\text{CaCu}_5$ -type structure (space group  $P6/mmm$ ) and can be visualized as a  $\text{TbCu}_5$ -based compound in which 2/9 of the Tb sites are randomly replaced by ‘dumb-bell’ pairs of Cu–Cu [4]. The pure binary  $\text{SmCo}_7$  compound with the

TbCu<sub>7</sub>-type structure does not exist stably at room temperature and a third metal element is necessary to replace a proportion of the Co atoms in order to stabilize the Sm–Co 1:7 phase with the TbCu<sub>7</sub>-type structure. According to the previous reports, a small amount of the third metallic element M (M = Zr, Cu, Ti, and Mn) can stabilize the SmCo<sub>7–x</sub>M<sub>x</sub> compound with  $x \geq 0.2$  [1, 5–8]. In order to improve the magnetic properties of SmCo<sub>7–x</sub>M<sub>x</sub> compounds, it is desirable to minimize the content of the stabilizing element M and to replace some of the Co with Fe since the stabilizing element M usually dilutes magnetization whereas Fe has a larger moment than Co. In our previous work, we found that the Sm–Co 1:7 phase could be stabilized with the content of the doping Hf between 0.1 and 0.2 [9]. Partial substitution of Fe for Co is expected to improve the magnetic properties of SmCo<sub>7–x</sub>Hf<sub>x</sub> compounds. In this paper, we report the structure and magnetic properties, in particular magnetic anisotropy, of SmCo<sub>6.8–x</sub>Fe<sub>x</sub>Hf<sub>0.2</sub> compounds.

## 2. Experiment

The compounds with nominal composition SmCo<sub>6.8–x</sub>Fe<sub>x</sub>Hf<sub>0.2</sub> ( $x = 0.1, 0.3, 0.5, 0.7$ ) were prepared by arc melting starting metallic elements of at least 99.9% purity in an ultrapure argon atmosphere. To compensate for the Sm losses during the synthesis process, an excess of 10% Sm was added to each sample. The ingots were melted four times to ensure homogeneity. Phase identification of the samples was carried out by means of x-ray powder diffraction (XRD) using a Rigaku D/max 2500 diffractometer with Cu K $\alpha$  radiation (50 kV  $\times$  250 mA) and a graphitic monochromator. Aligned samples for magnetic anisotropy measurements were prepared by mixing fine powder with epoxy resin and by aligning it and letting it solidify in a magnetic field of about 10 kOe. The magnetization of the samples was measured on a superconducting quantum interference device (SQUID) magnetometer in a field ranging from 0 to 50 kOe. The temperature dependence of the magnetization was measured on a magnetic balance in an applied field of 1000 Oe.

## 3. Results and discussion

### 3.1. Structural information

Figure 1 shows the XRD patterns of the as-cast SmCo<sub>6.8–x</sub>Fe<sub>x</sub>Hf<sub>0.2</sub> compounds, which reveal that all the samples crystallize in the TbCu<sub>7</sub>-type structure. A trace amount of 2:7 phase (Sm<sub>2</sub>Co<sub>7</sub>) with the Ce<sub>2</sub>Ni<sub>7</sub>-type structure (space group  $P6_3/mmc$ ) coexists with the main 1:7 phase. As shown in table 1, the lattice parameters  $a$  and  $c$  increase with increase of the Fe content, since the atomic radius of Fe (1.27 Å, coordination number = 12) is larger than that of Co (1.24 Å, coordination number = 12). The nearly linear dependence of the lattice constants on concentration (see figure 2) also indicates that the samples are single-phase solid solution. The  $c/a$  ratio is between 0.82 and 0.83, which is very close to the value of 0.84 for TbCu<sub>7</sub> binary compound reported by Buschow and Van der Goot [4]. According to our investigation of the SmCo<sub>7–x</sub>Hf<sub>x</sub> compounds [9], Hf shows a distinct preference for occupying the 2e site. Owing to the small difference in x-ray scattering power of Co and Fe atoms, no attempts were made to differentiate between them in the crystal structure with XRD data. However, it can be concluded from the variation of the lattice parameter that Fe is likely to substitute for Co since the atomic radius of Fe is larger than that of Co but smaller than that of Hf or Sm.

### 3.2. Curie temperature

Figure 3 shows the temperature dependence of the magnetization of the SmCo<sub>6.8–x</sub>Fe<sub>x</sub>Hf<sub>0.2</sub> compounds. All samples are ferromagnetic and the Curie temperature increases with

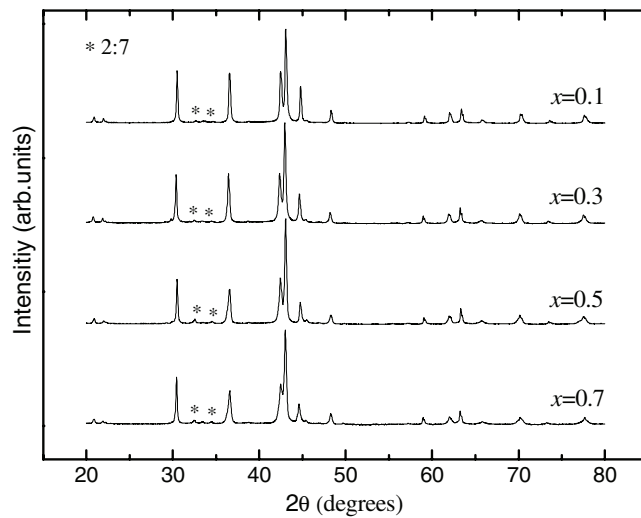


Figure 1. XRD patterns of the as-cast  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds.

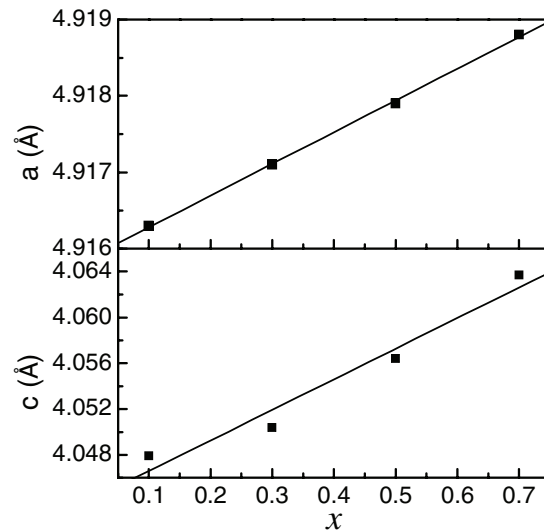
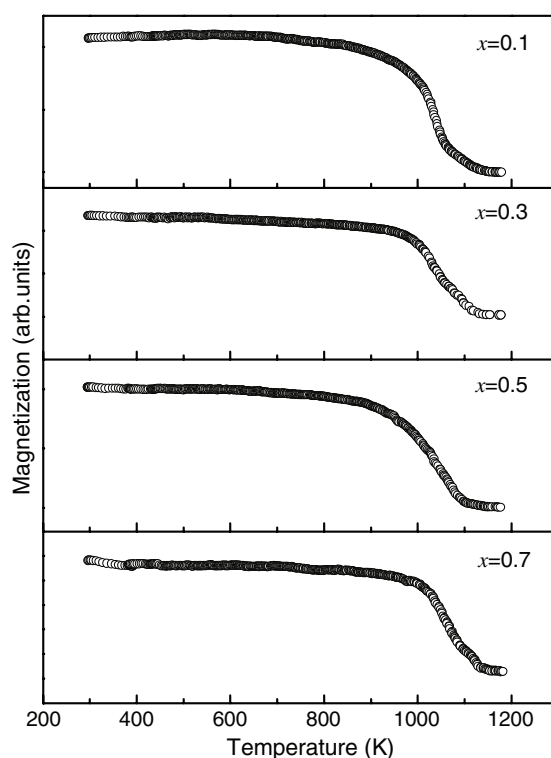


Figure 2. The dependence of the lattice parameters  $a$  and  $c$  on  $x$  for  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds.

the Fe content. This is usual for the rare earth–3d transition metal compounds such as  $\text{R}(\text{Fe}, \text{Co})_3$  [10],  $\text{R}(\text{Fe}, \text{Co}, \text{M})_5$  [11–15],  $\text{R}(\text{Fe}, \text{Co}, \text{M})_{12}$  [16–18], and  $\text{R}(\text{Fe}, \text{Co}, \text{M})_{13}$  [19] compounds ( $\text{R}$  = rare earths,  $\text{M}$  = doping element). Generally, the Curie temperature first increases with increasing content of Fe, goes through a maximum value when the content of Fe reaches a certain value, then decreases with further increasing Fe content. The same variation of the Curie temperature can be expected for the  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds.

According to [18], the exchange interaction  $J_{\text{Fe}-\text{Co}}$  plays a more important role than  $J_{\text{Fe}-\text{Fe}}$  and  $J_{\text{Co}-\text{Co}}$  in the Curie temperature, since  $J_{\text{Fe}-\text{Co}}$  is the largest among  $J_{\text{Fe}-\text{Fe}}$ ,  $J_{\text{Co}-\text{Co}}$ , and  $J_{\text{Fe}-\text{Co}}$  in the  $\text{Y}(\text{Fe}, \text{Co})_{10}\text{Si}_2$  compound.  $J_{\text{Fe}-\text{Fe}}$ ,  $J_{\text{Co}-\text{Co}}$ , and  $J_{\text{Fe}-\text{Co}}$  are the exchange



**Figure 3.** The temperature dependence of the magnetization for the  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds.

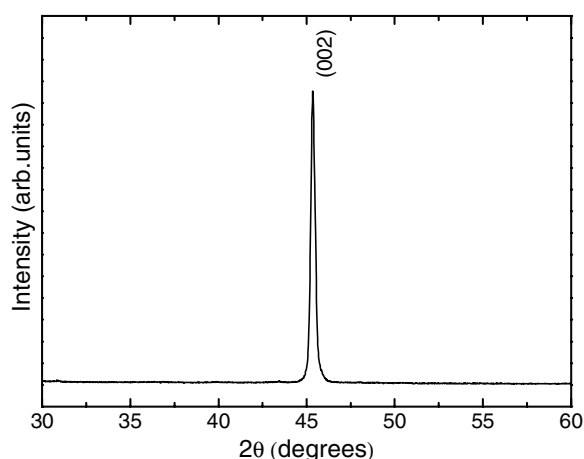
**Table 1.** The lattice parameters  $a$  and  $c$ ,  $c/a$  ratio, Curie temperature ( $T_C$ ), saturation magnetization ( $M_S$ ), and magnetic anisotropy field ( $H_A$ ) of  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds.

| $x$ | $a$ (Å) | $c$ (Å) | $c/a$ | $T_C$ (K) | $M_S$ (emu g <sup>-1</sup> ) |       | $H_A$ (kOe) |       |
|-----|---------|---------|-------|-----------|------------------------------|-------|-------------|-------|
|     |         |         |       |           | 5 K                          | 300 K | 5 K         | 300 K |
| 0.1 | 4.9163  | 4.0479  | 0.823 | 991       | 101                          | 96    | 131         | 74    |
| 0.3 | 4.9171  | 4.0504  | 0.824 | 1036      | 102                          | 97    | 214         | 122   |
| 0.5 | 4.9179  | 4.0564  | 0.825 | 1055      | 104                          | 101   | 230         | 211   |
| 0.7 | 4.9188  | 4.0637  | 0.826 | 1084      | 107                          | 102   | 173         | 157   |

interactions between Fe moments, between Co moments, and between Fe and Co moments respectively. The  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  and  $\text{Y}(\text{Fe}, \text{Co})_{10}\text{Si}_2$  compounds have closely related crystal structures (both of them have a crystal structure derived from  $\text{CaCu}_5$ ), and the same microscopic physical mechanism can be expected for the Fe concentration dependences of their Curie temperatures. The contribution of  $J_{\text{Fe-Co}}$  to the Curie temperature increases with increase of the Fe content, leading to the increase of the Curie temperature of the  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  ( $x = 0.1-0.7$ ) compound.

### 3.3. Magnetization and magnetic anisotropy

Figure 4 shows the XRD pattern of the aligned sample with  $x = 0.1$  at room temperature. The appearance of only one strong (002) peak in the XRD pattern indicates that the compound

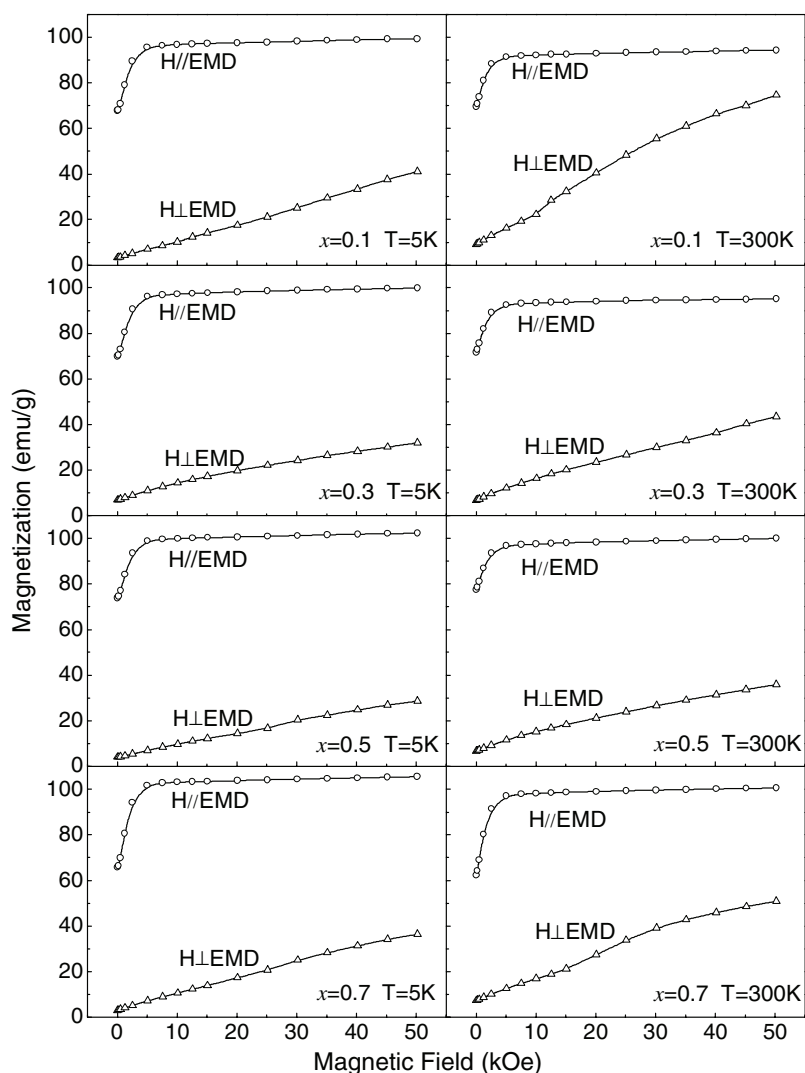


**Figure 4.** The XRD pattern for the aligned  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds with  $x = 0.1$ .

exhibits a uniaxial magnetocrystalline anisotropy. Other aligned samples show the same feature in the XRD patterns. The saturation magnetization  $M_S$  is derived from the magnetization curves (see figure 5) with the applied field along the easy magnetization direction (EMD) according to the law of approach to saturation, by extrapolating  $1/H$  to zero on the linear part of the  $M$  versus  $1/H$  curves [20]. As shown in table 1, the saturation magnetization increases with the Fe content at both 5 and 300 K as expected, since the magnetic moment of Fe is larger than that of Co.

Figure 5 shows the magnetization versus the applied field curves for the aligned sample measured at 5 and 300 K. The anisotropy field is determined from the intersection point of the two extrapolated magnetization curves with the applied field parallel and perpendicular to EMD. The anisotropy field at both 5 and 300 K first increases with the Fe content, reaches a maximum value at  $x = 0.5$ , then decreases with the Fe content (see table 1). The anomalous concentration dependence of the anisotropy field of the  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds is similar to those of  $\text{R}(\text{Fe}, \text{Co})_3$  [10],  $\text{R}(\text{Fe}, \text{Co})_5$  [21–23], and  $\text{R}_2(\text{Co}, \text{Fe})_{14}\text{B}$  [24] compounds, which can be explained by a simple model of individual site anisotropy in combination with the preferential occupation of iron atoms on different sites.

The anisotropy of these compounds is considered to be the sum of two separate contributions arising from the rare earth and the 3d sublattices. The anisotropy of the rare earth sublattice can be satisfactorily described in terms of the crystal-field model (or the single-ion model). However, the Co–Fe contribution is more complex. In most intermetallic compounds, the 3d ions are known to occupy different crystallographic sites which are expected to give different contributions to the total anisotropy. According to the neutron diffraction analysis for the  $\text{R}(\text{Co}, \text{Fe})_5$  compounds, the larger Fe atoms prefer to occupy the 3g site whereas the smaller Co prefer to occupy the 2c site [21]. Franse *et al* [22] calculated the individual site contribution to the anisotropy of  $\text{Y}(\text{Co}, \text{Fe})_5$  compounds based on the nuclear magnetic resonance (NMR) results [25]. They found that the first-order magnetocrystalline anisotropy constant  $K_1$  had different signs for the Fe and Co on both the 2c and 3g sites and, moreover, that the absolute values of  $K_1$  for the Fe and Co differ by almost one order of magnitude.  $K_1$  (unit:  $10^6 \text{ J m}^{-3}$ ) for Fe and Co at room temperature takes the values  $-51.3$  and  $5.7$  on the 2c site, and  $11.0$  and  $-1.7$  on the 3g site respectively [22]. Since the crystal structure of  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds is similar to that of  $\text{Y}(\text{Fe}, \text{Co})_5$  compounds, it is reasonable to



**Figure 5.** Magnetization as a function of applied field at 5 and 300 K for the aligned powder samples of  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$ .

expect the preferential occupancies of Fe and Co in  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds to also be similar to those in  $\text{Y}(\text{Fe}, \text{Co})_5$  compounds. At low Fe content, the Fe atoms prefer to occupy the 3g site and make a positive contribution to the total anisotropy, leading to the increase of the anisotropy field with the Fe content. With further increasing Fe content, more and more 2c sites will be occupied by Fe atoms, which makes a negative contribution to the total anisotropy and gives rise to the decrease of the anisotropy field with the Fe content. Considering the sign and magnitude of  $K_1$  for Fe and Co on the 2c and 3g sites, the anisotropy field should reach a maximum value at some small content of Fe.

#### 4. Conclusions

In summary, the as-cast  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$  compounds crystallize in the TbCu<sub>7</sub>-type structure. The lattice parameters  $a$  and  $c$  increase with the Fe content in the  $\text{SmCo}_{6.8-x}\text{Fe}_x\text{Hf}_{0.2}$

compounds. Both the Curie temperature and the saturation magnetization increase with increase of the Fe content. However, the magnetic anisotropy field reaches a maximum value at  $x = 0.5$ . The complex composition dependence of the magnetic anisotropy can be well explained in terms of a model considering the contribution of individual site anisotropy.

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