

Effects of Cu on crystallographic and magnetic properties of $\text{Sm}(\text{Co,Cu})_7$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 5621

(<http://iopscience.iop.org/0953-8984/15/32/321>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 15:02

Please note that [terms and conditions apply](#).

Effects of Cu on crystallographic and magnetic properties of $\text{Sm}(\text{Co}, \text{Cu})_7$

J Luo¹, J K Liang^{1,2}, Y Q Guo³, Q L Liu¹, L T Yang¹, F S Liu¹, G H Rao¹
and W Li³

¹ Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, China

² International Centre for Materials Physics, Academia Sinica, Shenyang 110016, China

³ Institute of Functional Materials, Central Iron and Steel Research Institute, Beijing 100081, China

E-mail: jkliang@aphy.iphy.ac.cn

Received 28 May 2003

Published 1 August 2003

Online at stacks.iop.org/JPhysCM/15/5621

Abstract

We have investigated the structural stability and magnetic properties of $\text{SmCo}_{7-x}\text{Cu}_x$ compounds with the TbCu_7 -type structure using x-ray powder diffraction and magnetic measurement. A large solid solution with $0.8 \leq x \leq 4.0$ in $\text{SmCo}_{7-x}\text{Cu}_x$ compounds has been observed. Both the lattice parameters and unit cell volume increase with increasing Cu content. $\text{SmCo}_{7-x}\text{Cu}_x$ compounds exhibit ferromagnetic order. A strong uniaxial magnetocrystalline anisotropy with an anisotropy field as high as 20 T is obtained with $x = 0.8$ at 5 K. However, the saturation magnetization and Curie temperature decrease with increasing Cu content.

1. Introduction

In recent years, there has been much interest in Sm–Co alloys with the TbCu_7 -type structure due to their potential applications as novel high-temperature rare earth permanent magnetic materials [1–8]. The strong interatomic exchange between the Co atoms gives rise to a high Curie temperature and ensures a high anisotropy in the temperature region of interest, which is above 450 °C. The structure of the 1:7 phase can be regarded as a derivative of CaCu_5 structure through a disordered substitution of ‘dumbbell’ Co–Co pair atoms for Sm atoms [9]. Researchers are interested to see if the 1:7 composition could be given the merits of SmCo_5 , such as high anisotropy, and of $\text{Sm}_2\text{Co}_{17}$, such as large magnetization and high Curie temperature.

Usually the binary Sm–Co 1:7 phase with the TbCu_7 -type structure cannot be formed. However, a small amount of a third metal element dopant such as Ti, Zr, Cu can stabilize the 1:7 phase by casting, ball milling, and annealing [10–12]. The magnetic properties depend significantly on these synthesis processes. The formation and stability of the 1:7 phase are the

Table 1. Lattice parameters a and c , c/a ratio and unit cell volume V of $\text{SmCo}_{7-x}\text{Cu}_x$.

| x | a (Å) | c (Å) | c/a | V (Å ³) |
|-----|-----------|-----------|-------|-----------------------|
| 0.8 | 4.9348(1) | 4.0351(1) | 0.82 | 85.101(4) |
| 1.5 | 4.9403(2) | 4.0509(1) | 0.82 | 85.622(4) |
| 2.0 | 4.9427(1) | 4.0547(1) | 0.82 | 85.786(3) |
| 3.0 | 4.9619(1) | 4.0603(1) | 0.82 | 86.574(4) |
| 4.0 | 4.9736(2) | 4.0674(1) | 0.82 | 87.134(5) |

main problems in the study of the 1:7-type high-temperature permanent magnetic material. Therefore, it is very important to find a way to stabilize the 1:7 phase using only a simple casting and annealing process. According to the previous report, the 1:7 single phase cannot be obtained in $\text{SmCo}_{7-x}\text{Cu}_x$ alloys with a Cu content x beyond 0.8 [2]. However, in our work, we find that $\text{SmCo}_{7-x}\text{Cu}_x$ can be stabilized with a large Cu content ranging from $x = 0.8$ to 4.0 even after annealing at 600 °C for three weeks. Here we report the effects of Cu on crystallographic and magnetic properties of $\text{Sm}(\text{Co}, \text{Cu})_7$.

2. Experiment

The starting material with the nominal composition $\text{SmCo}_{7-x}\text{Cu}_x$ ($x = 0\text{--}6.0$) was prepared by arc melting in a high-purity argon atmosphere. The ingots were melted four times to ensure homogeneity. Chemical analysis was carried out to determine the element composition in the $\text{SmCo}_{7-x}\text{Cu}_x$ alloy. Based on the chemical composition analysis, more accurate $\text{SmCo}_{7-x}\text{Cu}_x$ compounds were synthesized. The samples were annealed for three weeks at 600 °C, then quenched in water. Powder x-ray diffraction (XRD) was carried out to check the structure on a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation (50 kV \times 250 mA) and a graphitic monochromator using a step-scan mode with a step width of $2\theta = 0.02^\circ$ and a sampling time of 2 s. Samples for magnetic anisotropy studies were prepared by mixing the fine powder with epoxy on a glass slide and aligning in a magnetic field of 1 T. The magnetization of the samples was measured by a commercial SQUID magnetometer in fields ranging from 0 to 5 T. The temperature dependence of the magnetization of $\text{SmCo}_{7-x}\text{Cu}_x$ intermetallic compounds was measured by a magnetic balance at temperatures ranging from room temperature to 1273 K in a field of 0.5 T.

3. Results and discussion

3.1. Structural information

XRD patterns show that $\text{SmCo}_{7-x}\text{Cu}_x$ crystallizes in the hexagonal TbCu_7 -type structure in the range $0.8 \leq x \leq 4.0$ with lattice parameters of $a = 4.9348(5)\text{--}4.9736(5)$ Å and $c = 4.0351(2)\text{--}4.0674(2)$ Å as shown in figure 1. One minor phase with the CaCu_5 hexagonal structure appears when x is less than 0.8, and a small amount of face-centred-cubic Cu coexists with the main 1:7 phase when x exceeds 4.0. The structure has been refined using the Rietveld method. Table 1 shows the lattice parameters a and c . Both of the lattice parameters and the unit cell volume increase linearly with increasing Cu content. This is because the radius of a Cu atom is slightly larger than that of a Co atom, therefore the lattice parameters a and c increase when Co is partly substituted by Cu. The average c/a ratio for these compounds is about 0.82, which is very close to the value of 0.84 for the 1:7 compounds reported by Buschow

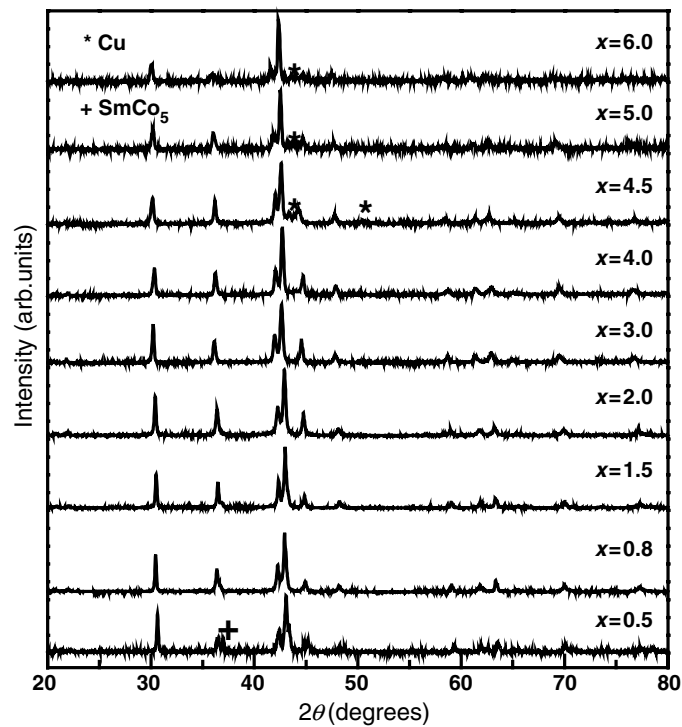


Figure 1. The XRD patterns of the as-cast $\text{SmCo}_{7-x}\text{Cu}_x$ alloys.

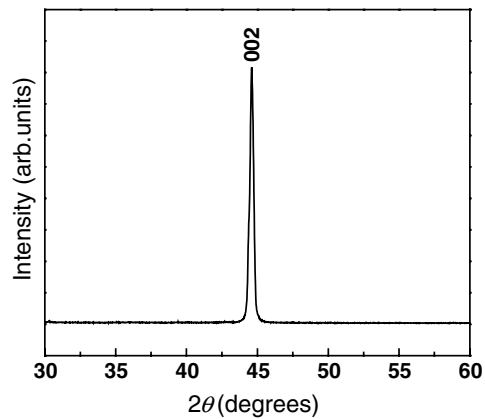


Figure 2. Typical XRD pattern for the aligned sample of $\text{SmCo}_{7-x}\text{Cu}_x$.

and Van der Goot [9]. Our experimental results indicate that over a large range of Cu content, doping with Cu can stabilize the 1:7 phase of the Sm–Co alloy.

3.2. Magnetocrystalline anisotropy

Figure 2 shows a typical XRD pattern for the aligned sample. The presence of a strong (002) peak indicates that the compound exhibits a uniaxial magnetocrystalline anisotropy.

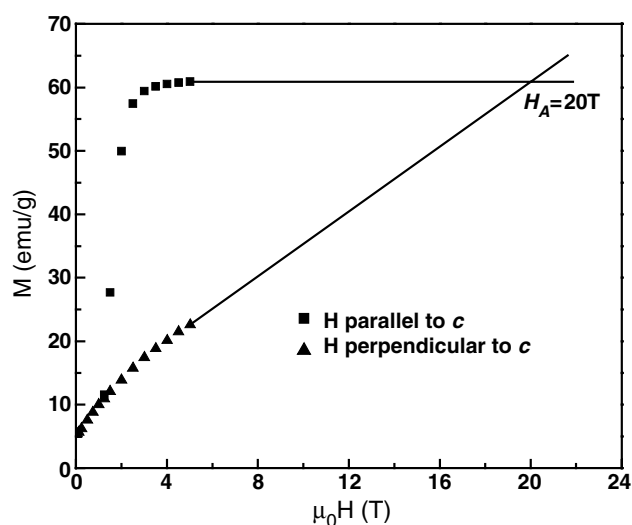


Figure 3. Magnetization as a function of magnetic field at 5 K for the magnetically aligned powder sample of $\text{SmCo}_{6.2}\text{Cu}_{0.8}$. The solid lines are extrapolations.

Other aligned samples exhibit the same result from their XRD patterns. Our result is the same as that of Ti- and Mn-doped SmCo_7 compounds [3, 4], but is different from that of Zr-doped compounds, which have two enhanced lines (110) and (200) indicating a plane magnetocrystalline anisotropy [1]. Figure 3 shows the magnetization versus the applied field curves for the aligned $\text{SmCo}_{6.2}\text{Cu}_{0.8}$ compound measured at 5 K. The anisotropy field is determined from the intersection point of two extrapolated magnetization curves measured in a magnetic field applied parallel and perpendicular, respectively, to the alignment direction of the powder samples. The experimental anisotropy field is about 20 T, which is between the value of 12 T for SmCo_7 and 30 T for SmCo_5 [3].

Deportes *et al* [13] pointed out that the uniaxial Co anisotropy in RCO_5 systems comes primarily from the $2c$ sites. When R is replaced by the Co–Co dumbbells of $2e$ sites, the environment changes in such a way as to reduce the anisotropy of Co in $2c$ sites and also that of the compound. For this reason, Huang *et al* [1, 14, 15] consider that the doping element partly replaces the Co–Co dumbbell occupying the $2e$ equivalent position, which will restore some of the lost anisotropy. According to neutron diffraction results on the TbCu_7 -type $\text{Ce}(\text{Ni}, \text{Cu})_6$ and CeNi_5Si [16–18], however, the third doping elements such as Cu and Si have no preference for occupying the $2e$ dumbbell sites, which agrees with our XRD refinement result. We also find that if the equivalent point $3g$ is fully occupied by Cu atoms, the molecular formula should be $(\text{Sm}_{0.78}\text{Co}_{0.44})\text{Co}_2\text{Cu}_3$ (or $\text{SmCo}_{3.14}\text{Cu}_{3.86}$), which is very close to the single-phase endpoint of SmCo_3Cu_4 in our experiment. Figure 4 show a typical Rietveld refinement XRD pattern for SmCo_4Cu_3 using the computer program DBWS-9411 [19]. The structural parameters of the SmCo_4Cu_3 compound are listed in table 2. According to the solid solution range and the neutron diffraction result, as well as the structural refinement, this implies that the Cu atom occupies the $3g$ equivalent crystal position. Streever [20, 21] argued that the $3g$ sites occupied by magnetic Co atoms make a small opposing contribution to the easy c -axis Co anisotropy. Therefore, the anisotropy of the compound increases if the nonmagnetic Cu atoms occupy the $3g$ sites.

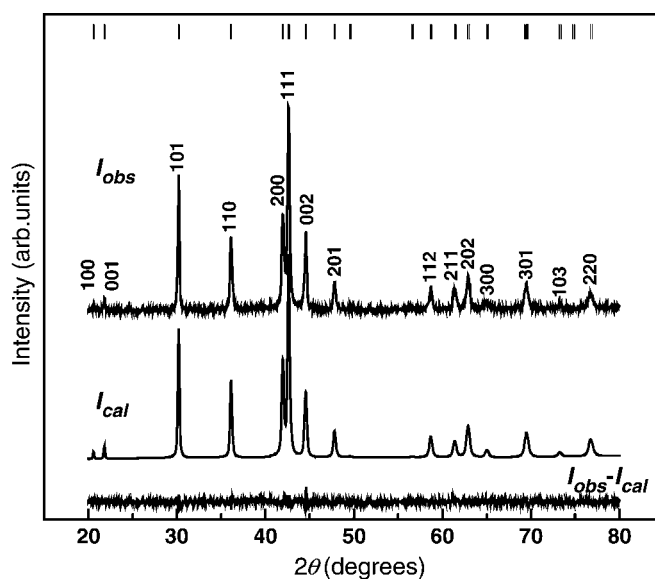


Figure 4. Typical XRD pattern of SmCo₄Cu₃ with $R_p = 4.49\%$, $R_{wp} = 5.95\%$ and $R_{exp} = 2.71\%$. The experimental and calculated XRD patterns are shown in pattern I_{obs} and I_{cal} , respectively. The lowest trace indicates the difference between the two patterns and the peak positions of the 1:7 hexagonal phase are denoted by the upper vertical lines.

Table 2. The structural parameters of SmCo₄Cu₃ compound.

| Atom | Site | x | y | z | Occupancy factor |
|------|------|-----|-----|--------|------------------|
| Sm | 1a | 0 | 0 | 0 | 0.78 |
| Co | 2e | 0 | 0 | 0.2813 | 0.22 |
| Co | 2c | 1/3 | 2/3 | 0 | 1 |
| Co | 3g | 1/2 | 0 | 1/2 | 0.78 |
| Cu | 3g | 1/2 | 0 | 1/2 | 0.22 |

3.3. Magnetization

SmCo_{7-x}Cu_x intermetallic compounds exhibit a ferromagnetic order. Figure 5 shows the temperature dependence of magnetization of SmCo_{7-x}Cu_x compounds with $x = 0.8, 1.5$ and 2.0 . The samples with $x = 0.8-2.0$ are ferromagnetic with Curie temperatures higher than 810°C . Curie temperatures of the 1:7 phase decrease from 855°C for $x = 0.8$ to 810°C for $x = 2.0$ due to the nonmagnetic element Cu substituting for magnetic Co, and weakening the ferromagnetic order. For the sample with $x = 2$, the magnetic domain affects the magnetic behaviour at low temperatures ($<200^\circ\text{C}$). This is evident from the field-cooled (FC) and zero-field-cooled (ZFC) curves. Figure 6 shows the magnetization hysteresis loop with $x = 2.0$ at room temperature. The field range was limited by our maximum field. An intrinsic coercivity around 0.361 T is obtained for this compound.

The applied field dependence of magnetization is shown in figure 7. The saturation magnetization was derived from the M versus $1/H$ plots by extrapolating M to $(1/H) = 0$. For compounds with $x = 1.5, 2.0$ and 3.0 , the magnetization did not approach saturation. Therefore, we only list the saturation magnetization of the compound with $x = 0.8$ in table 3.

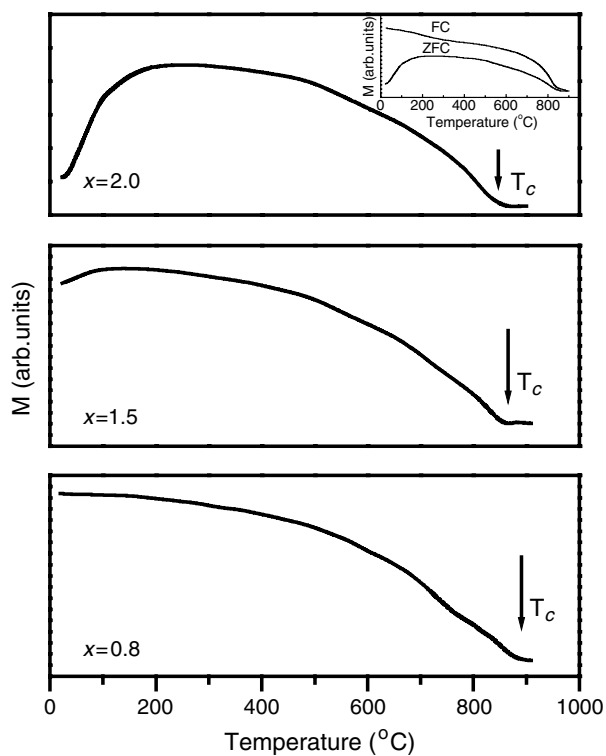


Figure 5. Magnetization as a function of temperature of $\text{SmCo}_{7-x}\text{Cu}_x$ alloys. The inset shows the FC and ZFC curves with $x = 2.0$.

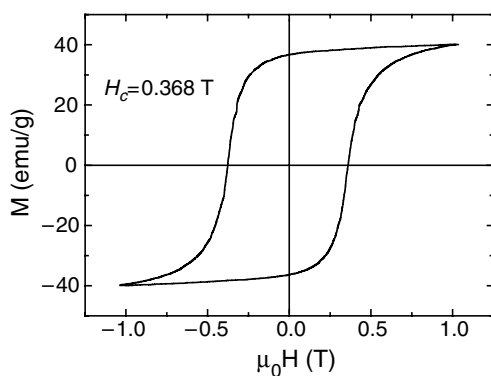


Figure 6. Hysteresis loop of the SmCo_5Cu_2 compound at room temperature.

However, it is obvious that the saturation magnetization decreases with increasing Cu content due to the substitution of nonmagnetic Cu for magnetic Co.

4. Conclusion

In conclusion, Cu doping can stabilize the TbCu_7 -type structure in $\text{SmCo}_{7-x}\text{Cu}_x$ alloys over a large Cu content range from 0.8 to 4.0. Both lattice parameters and the unit cell volume

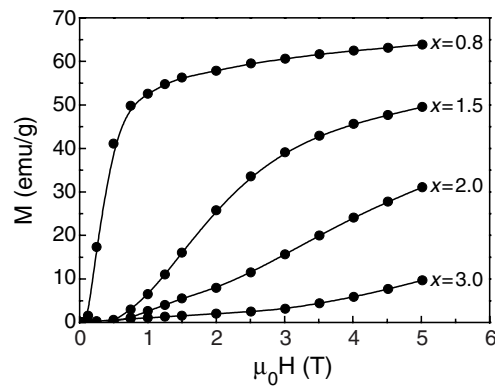


Figure 7. The field dependence of the magnetization of SmCo_{7-x}Cu_x alloys at 5 K.

Table 3. Curie temperature T_C , saturation magnetization per atom μ_s , magnetic anisotropic field H_A and easy magnetic direction (EMD) of SmCo_{7-x}Cu_x.

| x | T_C (°C) | μ_s (μ_B /atom) | H_A (T) | EMD |
|-----|------------|--------------------------|-----------|-----------------|
| 0.8 | 850 | 0.88 | 20 | <i>c</i> -axial |
| 1.5 | 830 | — | — | <i>c</i> -axial |
| 2.0 | 810 | — | — | <i>c</i> -axial |

increase with increasing Cu content because the radius of the Cu atom is larger than that of the Co atom. Cu tends to occupy the 3g crystal position. SmCo_{7-x}Cu_x compounds exhibit ferromagnetic order. A strong uniaxial magnetocrystalline anisotropy with an anisotropy field as high as 20 T is obtained with $x = 0.8$ at 5 K. However, the saturation magnetization and Curie temperature decrease with increasing Cu content.

Acknowledgments

This work was supported by the National High Technology Research and Development Program (863 Program) (Grant No 2002AA324050), National Natural Science Foundation of China and State Key Project of Fundamental Research.

References

- [1] Huang M Q, Wallace W E, McHenry M, Chen Q and Ma B M 1998 *J. Appl. Phys.* **83** 6718
- [2] Al-Omari I A, Yeshurun Y, Zhou J and Sellmyer D J 2000 *J. Appl. Phys.* **87** 6710
- [3] Zhou J, Al-Omari I A, Liu J P and Sellmyer D J 2000 *J. Appl. Phys.* **87** 5299
- [4] Gjoka M, Kalogirou O, Sarafidis C, Niarchos D and Hadjipanayis G C 2002 *J. Magn. Magn. Mater.* **242–245** 844
- [5] Liu J F, Chui T, Dimitrov D and Hadjipanayis G C 1998 *Appl. Phys. Lett.* **73** 3007
- [6] Zhou J, Skomski R, Chen C, Hadjipanayis G C and Sellmyer D J 2000 *Appl. Phys. Lett.* **77** 1514
- [7] Al-Omari I A, Zhou J and Sellmyer D J 2000 *J. Alloys Compounds* **298** 295
- [8] Jiang C, Venkatesan M, Gallagher K and Coey J M D 2000 *J. Magn. Magn. Mater.* **236** 49
- [9] Buschow K H J and Van der Goot A S 1971 *Acta Crystallogr. B* **27** 1085
- [10] You C, Zhang Z D, Sun X K, Liu W, Zhao X G and Geng D Y 2001 *J. Magn. Magn. Mater.* **234** 295
- [11] Venkatesan M, Jiang C and Coey J M D 2001 *J. Magn. Magn. Mater.* **242–245** 1350
- [12] Venkatesan M, Rhen F M F and Coey J M D 2002 *IEEE Trans. Magn.* **38** 2919
- [13] Deportes J, Givord D, Schweizer J and Tasset F 1976 *IEEE Trans. Magn.* **12** 1000

-
- [14] Huang M Q, Drennan M, Wallace W E, McHenry M E, Chen Q and Ma B M 1999 *J. Appl. Phys.* **85** 5663
 - [15] Huang M Q, Sankar S G, Wallace W E, McHenry M, Chen Q and Ma B M 2000 *J. Appl. Phys.* **87** 5305
 - [16] Moze O, Kockelmann W A, Brück E and Buschow K H J 1998 *J. Phys.: Condens. Matter* **10** 775
 - [17] Moze O, Kockelmann W A, Brück E and Buschow K H J 1998 *Mater. Sci. Forum* **278–281** 532
 - [18] Moze O, Brück E and Buschow K H J 1998 *J. Alloys Compounds* **281** 123
 - [19] Young R A, Sakthivel A, Moss T S and Paiva-Santos C O 1995 *J. Appl. Crystallogr.* **28** 366
 - [20] Streever R L 1978 *Phys. Lett. A* **65** 360
 - [21] Streever R L 1979 *Phys. Rev. B* **19** 2704