

Magnetic properties of  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  ( $x=0-3$ ) compounds prepared by arc melting

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

1995 J. Phys.: Condens. Matter 7 4251

(<http://iopscience.iop.org/0953-8984/7/22/008>)

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

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:23

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

## Magnetic properties of $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$ and $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ ( $x = 0-3$ ) compounds prepared by arc melting

Bing Liang, Bao-gen Sheng, Zhao-hua Cheng, Hua-yang Gong, Shao-ying Zhang and Jun-xian Zhang

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China

Received 8 November 1994

**Abstract.** The crystal structure and magnetic properties of  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  compounds were investigated. The results of the powder x-ray diffraction indicate that the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds crystallize in the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure and the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  compounds exhibit two phases of the hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure and the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure. The addition of Si results in a decrease in the lattice constants and the unit-cell volumes. The Curie temperature  $T_C$  of the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds is found to increase from 327 K for  $x = 0$  to 485 K for  $x = 2.5$  and then to decrease slightly with increasing  $x$ , whereas the  $T_C$  of their carbides  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  undergoes a small enhancement with increasing Si concentration. An approximately linear decrease in the saturation magnetization with increasing  $x$  is observed when the non-magnetic Si atom is substituted for Fe. Spin reorientation transitions are observed in  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ . Substitution of Si for Fe in  $\text{Er}_2\text{Fe}_{17}$  leads to an increase in the uniaxial anisotropy of the Er sublattice; therefore, the spin reorientation temperature  $T_{sr}$  increases with increasing Si concentration. The introduction of carbon has a marked effect on shifting the  $T_{sr}$  towards higher temperatures.

### 1. Introduction

The binary rare-earth(R)-iron intermetallic compounds with  $\text{Th}_2\text{Zn}_{17}$  or  $\text{Th}_2\text{Ni}_{17}$  structure are not useful as permanent magnets because of their low Curie temperatures and room temperature planar anisotropy [1]. Numerous investigations have been made to improve their magnetic properties. It has been discovered that the intrinsic magnetic properties of the  $\text{R}_2\text{Fe}_{17}$  compounds can be considerably improved upon the introduction of interstitial carbon or nitrogen atoms by means of the gas-solid reaction [2–4] or melt spinning [5, 6]. For example,  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  exhibits a high Curie temperature, strong axial anisotropy and large saturation magnetization [2, 7]. It has also been found that the partial substitution of Co, Ni, Al, Si and Ga for Fe in the  $\text{R}_2\text{Fe}_{17}$  compounds will strongly increase the Curie temperature [8–15]. Furthermore, many studies have shown that the addition of an appropriate amount of Ga, Si and Al in the  $\text{R}_2\text{Fe}_{17}$  ( $\text{R} = \text{Sm}, \text{Er}$ , etc) compounds leads to a strong enhancement in the uniaxial anisotropy.  $\text{Sm}_2\text{Fe}_{17-x}\text{M}_x$  ( $\text{M} = \text{Ga}$  or  $\text{Al}$ ) compounds with  $x > 2.0$  exhibit an easy-axis anisotropy at room temperature and their Curie temperatures are much higher than that of the parent compound  $\text{Sm}_2\text{Fe}_{17}$  [14, 16]. Recently, we studied the  $\text{R}_2\text{Fe}_{17-x}\text{M}_x$  and  $\text{R}_2\text{Fe}_{17-x}\text{M}_x\text{C}_y$  ( $\text{M} = \text{Ga}, \text{Al}$  or  $\text{Si}$ ) series to investigate the effect of the M atoms on the structure and intrinsic magnetic properties. It was found that the substitution of Ga, Al and Si for Fe in the  $\text{R}_2\text{Fe}_{17}$  compounds not only strikingly improves the hard-magnetic properties but also helps the formation of the 2:17-type rare-earth-Fe compounds

with high C concentration [17–20]. In this paper, the structure and magnetic properties of the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds and their carbides  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  ( $0 \leq x \leq 3$ ) are reported in detail.

## 2. Experiment

The  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  samples with  $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5$  and  $3.0$  were prepared by arc melting in an argon atmosphere of high purity. The raw materials of the Er, Fe, Si and Fe–C alloys had at least 99.9% purity. The ingots were remelted at least three times to ensure their homogeneity. The arc-melted ingots were wrapped in molybdenum foil, sealed in a steel tube, annealed at 1400 K for 48 h in a high-purity argon atmosphere and then quenched into water. Powder x-ray diffraction with  $\text{Cu K}\alpha$  radiation was used to determine the phase purity, crystal structure and lattice parameters. The Curie temperature and spin reorientation temperature were determined from the temperature dependence of magnetization measured with a vibrating-sample magnetometer in a magnetic field of 700 Oe and an extracting-sample magnetometer in a magnetic field of 1 kOe. The saturation magnetizations at 1.5 K were derived from magnetization curves measured in a magnetic field up to 70 kOe with an extracting-sample magnetometer.

## 3. Results and discussion

X-ray powder diffraction indicates that the annealed  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  samples consist of a single phase of hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure while two phases coexist in the annealed  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  samples of hexagonal  $\text{Th}_2\text{Ni}_{17}$ -type structure and rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure. The substitution of Si for Fe in the  $\text{Er}_2\text{Fe}_{17}$  compounds and their carbides results in a decrease in the unit-cell volumes. The lattice contents  $a$  and  $c$  and the unit-cell volumes  $v$  obtained from the x-ray diffraction patterns of the heat-treated samples are shown in figure 1 as functions of Si concentration. An approximately linear dependence of the unit-cell volume on Si concentration is observed. For  $\text{Er}_2\text{Fe}_{14}\text{Si}_3$ , a decrease of about 1.6% in the unit-cell volume is observed compared with the parent compound  $\text{Er}_2\text{Fe}_{17}$ . A similar decrease in the unit-cell volume has been observed for other  $\text{R}_2(\text{Fe}, \text{Si})_{17}$  compounds [13, 21].

The silicon concentration dependences of the Curie temperature  $T_C$  for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  are summarized in figure 2. An important effect of the substitution of Si for Fe in the  $\text{Er}_2\text{Fe}_{17}$  compound on the Curie temperature is observed.  $T_C$  is found first to increase sharply and then appears to decrease slightly with increasing  $x$ , having a maximum value at about  $x = 2.5$  for both  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ , as illustrated in figure 2. This dependence of  $T_C$  on  $x$  is very similar to that in Al-substituted [12, 16] and Ga-substituted [14]  $\text{R}_2\text{Fe}_{17}$  compounds with  $\text{R} = \text{Sm}, \text{Y}$  or  $\text{Ho}$ . Substitution of silicon for iron in the  $\text{R}_2\text{Fe}_{17}$  compounds strongly increases the Curie temperature, whereas the unit-cell volume decreases with increasing silicon content. This behaviour is rather peculiar, because the replacement of ferromagnetic iron by non-magnetic silicon and the lattice contraction upon silicon substitution would normally be expected to result in a decrease in the Curie temperature. Conventional arguments suggest that silicon would occupy the *antiferromagnetic correlative 6c(4f) sites*, which would reduce the negative Fe–Fe exchange interactions [22, 23] and lead to an increase in the Curie temperature. Another explanation was given by Long *et al* [24] on the basis of a neutron diffraction and Mössbauer effect

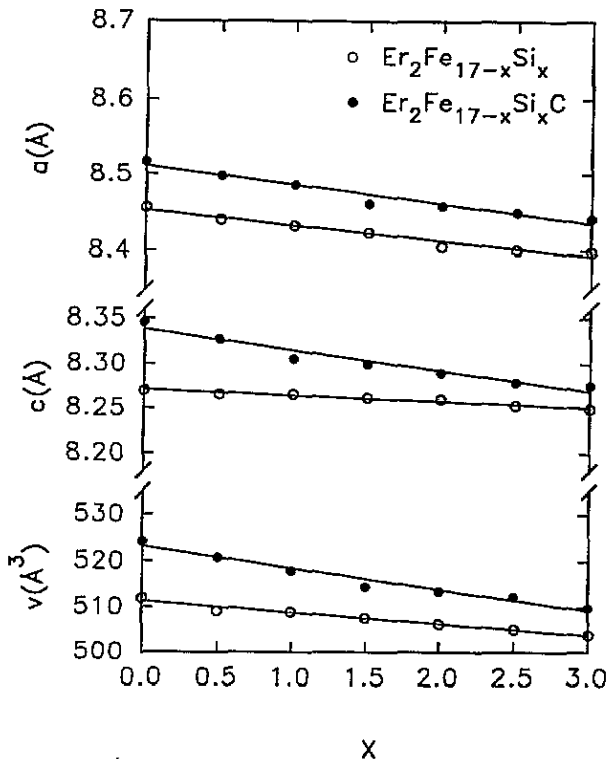


Figure 1. The crystallographic parameters  $a$  and  $c$  of the unit cell and unit-cell volume  $v$  according to Si content  $x$  for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ .

study of  $\text{Nd}_2\text{Fe}_{17-x}\text{Si}_x$  compounds, which indicated that silicon preferentially occupied the 18h sites with the largest number of rare-earth near neighbours. Their investigation suggests that the increase in Curie temperature is closely related to the expansion of the lattice in the 9d–18h plane of the unit cell. Recently, a neutron powder diffraction study of  $\text{Nd}_2\text{Fe}_{14}\text{Si}_3$  by Zhang *et al* [25] showed that silicon atoms preferentially occupy both 18h and 18f sites only and are absent in 6c and 9d sites. The Fe–Fe bond length of  $\text{Nd}_2\text{Fe}_{14}\text{Si}_3$  has an optimum value compared with that of the  $\text{Nd}_2\text{Fe}_{17}$  compound. From these results it may be inferred that the contraction of the unit cell induced by the silicon substitution for Fe in  $\text{R}_2\text{Fe}_{17}$  compounds would increase the Fe–Fe ferromagnetic exchange and decrease antiferromagnetic exchange; as a consequence, the Curie temperature increases enormously.

It can also be seen in figure 2 that the introduction of carbon has a drastic effect on the Curie temperature. For  $x = 0$  and 1, the  $T_C$  of the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  compounds increases by 183 K and 110 K, respectively, compared with those of the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds. This is attributed to the increase in Fe–Fe distance induced by the lattice expansion.

The saturation magnetic moments of  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  at 1.5 K are shown in figure 3 as functions of Si concentration  $x$ .  $M_s$  is found to decrease linearly with increasing  $x$ . This is in agreement with the previous study on the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds by Alp *et al* [13]. The decrease in  $M_s$  is associated with the dilution of Fe by non-magnetic Si atoms and the contraction in the unit-cell volume.

The temperature dependences of the magnetization of  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  are given in figure 4 and figure 5 respectively. The maxima or jumps observed in the  $M$

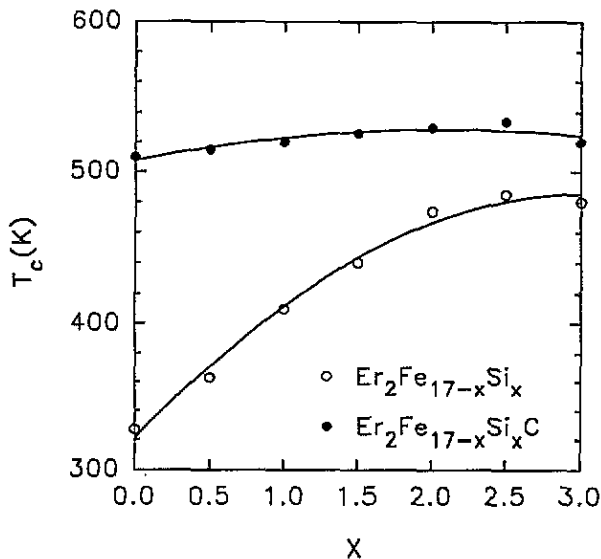


Figure 2. Silicon concentration dependences of the Curie temperatures for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ .

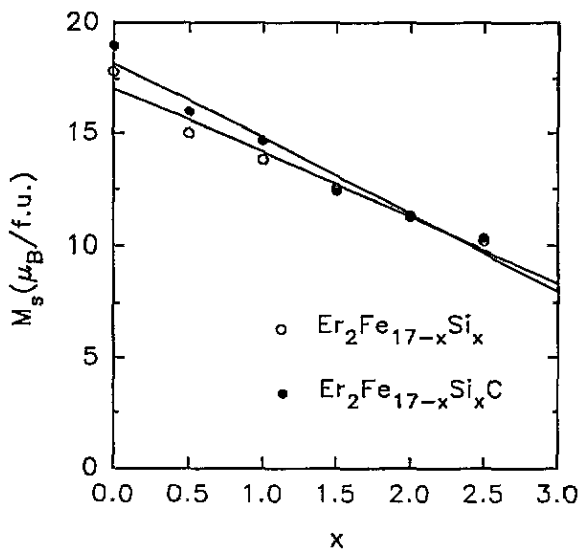


Figure 3. The saturation magnetic moments  $M_s$  at 1.5 K according to Si content  $x$  for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ .

versus  $T$  curves for these compounds are due to the occurrence of a spin reorientation. The value of the spin reorientation temperature  $T_{\text{sr}}$  is plotted as a function of Si concentration in figure 6. It should be noted that the increase in Si concentration leads to a marked increase in the spin reorientation temperature for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ . This concentration dependence of  $T_{\text{sr}}$  bears much resemblance to those observed recently for

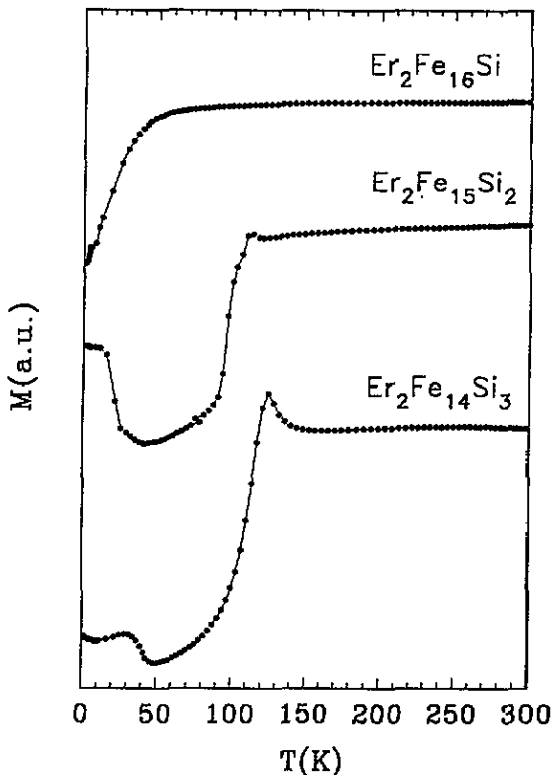


Figure 4. The temperature dependences of the magnetization for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  with  $x = 1.0$ , 2.0 and 3.0.

$\text{Er}_2\text{Fe}_{17}\text{C}_x$  [26] and  $\text{Tm}_2\text{Fe}_{17}\text{C}_x$  [27]. In general, this type of spin reorientation reflects the competition between the R sublattice anisotropy (favouring an easy  $c$ -axis magnetization) and the Fe sublattice anisotropy (favouring an easy-magnetization direction perpendicular to the  $c$  axis). To a first approximation, the total magnetocrystalline anisotropy constant is the sum of the first-order anisotropy constants of the rare-earth (R) and iron (Fe) sublattices:

$$K_1[\text{total}] = K_1[\text{Fe}] + K_1[\text{R}].$$

It is well known that  $K_1[\text{Fe}]$  is negative for the  $\text{R}_2\text{Fe}_{17}$  compounds [28]. The rare-earth sublattice anisotropy can be expressed in crystal-field terms as

$$K_1[\text{R}] = -\frac{3}{2}\alpha_J\langle r^2 \rangle \langle O_2^0 \rangle A_2^0$$

where  $\alpha_J$  is the second-order Stevens factor, and  $\langle r^2 \rangle$  and  $\langle O_2^0 \rangle$  are expectation values of the 4f radius and the operator equivalent function  $O_2^0$ , respectively. These quantities are well known for each of the various rare-earth elements. The second-order crystal-field parameter  $A_2^0$  depends strongly upon the crystal field associated with the environment of a given rare-earth element. In the case of  $\text{Er}_2\text{Fe}_{17}$ ,  $\alpha_J > 0$  for erbium and  $A_2^0 < 0$ , a positive  $K_1[\text{Er}]$ -value being responsible for the easy  $c$ -axis magnetization, but the Er sublattice anisotropy is too weak to overcome the Fe sublattice anisotropy ( $K_1[\text{total}] < 0$ ), so that

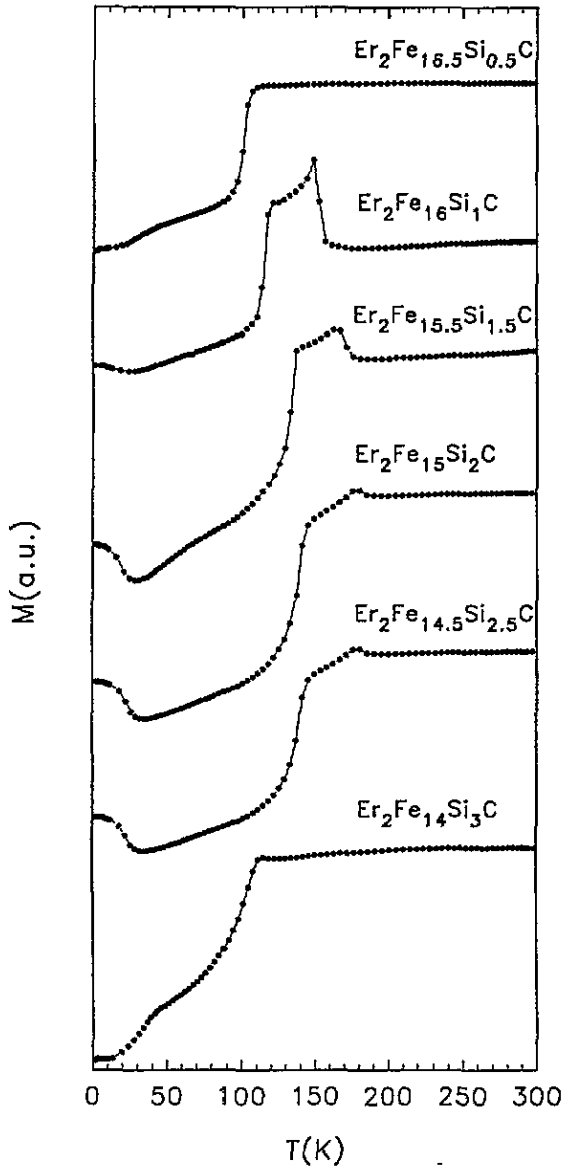


Figure 5. The temperature dependences of the magnetization for  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  with  $x = 0.5, 1.0, 1.5, 2.0, 2.5$  and  $3.0$ .

$\text{Er}_2\text{Fe}_{17}$  exhibits no magnetic transition down to 4.2 K. The addition of Si atoms ( $x > 0.5$ ) in the lattice of  $\text{Er}_2\text{Fe}_{17}$  could induce a weakly uniaxial anisotropy above  $T_{\text{sr}}$  and trigger a spin reorientation transition at low temperatures. Previous studies of the  $^{169}\text{Tm}$  Mössbauer effect of  $\text{Tm}_2\text{Fe}_{15}\text{Si}_2$  [29] have shown that silicon substitution leads to a marked shift in the second-order crystal-field parameter  $A_2^0$  to more negative values; as a result, the positive value of  $K_1[\text{R}]$  may be large enough to overcompensate for the negative value of  $K_1[\text{Fe}]$  which is already at higher temperatures than for the parent compounds. As a consequence,

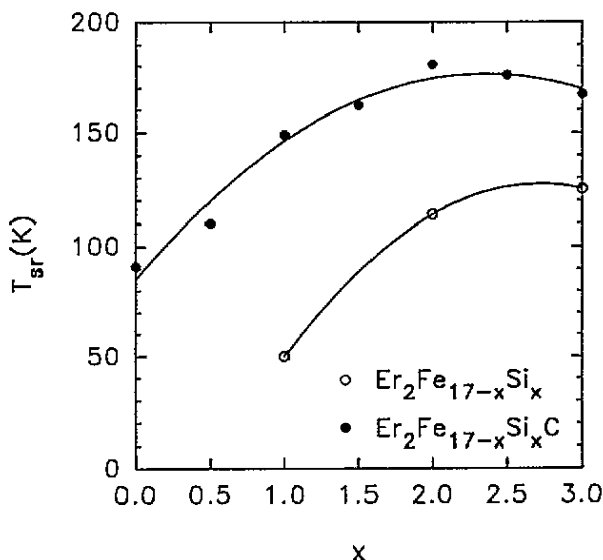


Figure 6. Silicon concentration dependences of the spin reorientation temperatures  $T_{sr}$  of  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  and  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$ .

$T_{sr}$  is shifted to a higher temperature with increasing silicon concentration  $x$ .

It can be seen from figure 6 that the  $T_{sr}$  of the carbides  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  is considerably higher than those of the  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x$  compounds. The introduction of carbon induces a larger negative value of  $A_2^0$ ; simultaneously the spin reorientation transition moves to a higher temperature [27]. For the carbides  $\text{Er}_2\text{Fe}_{17-x}\text{Si}_x\text{C}$  with  $x > 0.5$ , two spin reorientation transitions can be observed at  $T_{sr1}$  and  $T_{sr2}$ , respectively, which suggests that with decreasing temperature the magnetization of the carbides starts to depart from the basal plane at  $T_{sr1}$  and coincides completely with the  $c$  axis at  $T_{sr2}$ . For temperature between  $T_{sr1}$  and  $T_{sr2}$ , an easy cone can be expected. The complex magnetic behaviour at lower temperatures may be attributed to the change in the higher-order crystal-field terms. As has been shown for other carbides [30], the crystal-field coefficients  $A_2^0$  and  $A_6^0$  become more negative with increasing carbon content whereas  $A_4^0$  becomes more positive. It can be inferred that the easy-cone anisotropy is the result of the changes in the magnitude and signs of  $K_1$  and  $K_2$  due to the changes in  $A_2^0$ ,  $A_4^0$  and  $A_6^0$ .

### Acknowledgments

This work was supported by the National Natural Science Foundation of China and the State's Sciences and Technology Commission. The authors are grateful to T S Ning for his x-ray diffraction measurement.

### References

- [1] Buschow K H J 1977 *Rep. Prog. Phys.* **40** 1179
- [2] Coey J M D and Sun H 1990 *J. Magn. Magn. Mater.* **87** L251



- [3] Liao L X, Chen X, Altounian Z and Ryan D H 1992 *Appl. Phys. Lett.* **60** 129
- [4] Sun H, Coey J M D, Otani Y and Hurlry D P F 1990 *J. Phys.: Condens. Matter* **2** 6465
- [5] Shen B G, Kong L S and Cao L 1992 *Solid State Commun.* **83** 753
- [6] Cao L, Kong L S and Shen B G 1992 *J. Phys.: Condens. Matter* **4** L515
- [7] Schnitzki K, Schultz L, Wecker J and Katter M 1990 *Appl. Phys. Lett.* **57** 2853
- [8] Narasimhan and Wallace W E 1974 *AIP Conf. Proc.* **18** 1248
- [9] van Mens R 1986 *J. Magn. Magn. Mater.* **61** 24
- [10] Hu B P and Coey J M D 1988 *J. Less-Common Met.* **142** 295
- [11] Hu B P, Rao X L, Xu J M, Dong X L, Li H, Yin L and Zhao Z R 1992 *J. Magn. Magn. Mater.* **114** 138
- [12] Jacobs H, Buschow K H J, Zhou G F, Li X and de Boer F R 1992 *J. Magn. Magn. Mater.* **116** 20
- [13] Alp E E, Umarji A M, Malik S K, Snenoy G K, Huang M Q, Boltich E B and Wallace W E 1987 *J. Magn. Magn. Mater.* **68** 305
- [14] Shen B G, Wang F W, Kong L S and Cao L 1993 *J. Phys.: Condens. Matter* **5** L685
- [15] Weitzer F, Hiebl K and Rogl P 1989 *J. Appl. Phys.* **65** 4963
- [16] Wang Z and Dunlap R A 1993 *J. Less-Common Met.* **5** 247
- [17] Shen B G, Kong L S, Wang F W and Cao L 1993 *Appl. Phys. Lett.* **63** 2288
- [18] Shen B G, Wang F W, Kong L S, Cao L and Guo H Q 1993 *J. Magn. Magn. Mater.* **127** L267
- [19] Shen B G, Kong L S, Wang F W, Cao L and Zhan W S 1994 *Acta Phys. Sin.* **43**
- [20] Cheng Z H, Shen B G, Wang F W, Zhang J X, Gong H Y and Zhao J G 1994 *J. Phys.: Condens. Matter* **6** L185
- [21] Shen B G, Liang B, Wang F W, Cheng Z H, Gong H Y, Zhang S Y and Zhang J X 1995 *J. Appl. Phys.* at press
- [22] Pedziwiatr A T and Wallace W E 1986 *J. Less-Common Met.* **126** 41
- [23] Strnat K 1988 *Ferromagnetic Materials* vol 4, ed E P Wohlfarth and K H J Buschow (Amsterdam: North-Holland) p 131
- [24] Long G J, Marasinghe G K, Mishra S, Pringle O A, Grandjean F, Buschow K H J, Middleton D P, Yelon W B, Pourarian F and Isnard O 1993 *Solid State Commun.* **88** 761
- [25] Zhang Z Y, Yan Q W, Zhang P L, Sun X D, Shen B G, Cheng Z H, Gong H Y, Laing B, Gou C and Chen D F 1995 *J. Phys.: Condens. Matter* submitted
- [26] Kou X C, Grossinger R, Jacobs T H and Buschow K H J 1991 *Physica B* **168** 181
- [27] Gubbens P C M, Van der Kraan A M, Jacobs T H and Buschow K H J 1989 *J. Magn. Magn. Mater.* **80** 265
- [28] Buschow K H J 1991 *Rep. Prog. Phys.* **54** 1123
- [29] Gubbens P C M, Van der Kraan A M, Jacobs T H and Buschow K H J 1990 *J. Less-Common Met.* **159** 173
- [30] Li Hong-shuo and Cadogan J M 1992 *Solid State Commun.* **82** 121