

Structural and magnetic properties of arc-melted $RFe_{10}V_2$ carbides (R = Y or Sm)

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

1996 J. Phys.: Condens. Matter 8 6079

(<http://iopscience.iop.org/0953-8984/8/33/014>)

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

Download details:

IP Address: 171.66.16.206

The article was downloaded on 13/05/2010 at 18:32

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

Structural and magnetic properties of arc-melted $RFe_{10}V_2$ carbides ($R = Y$ or Sm)

X L Dong[†], Z D Zhang[†], H T Kim^{†‡}, D Zhang[†], X C Kou[†], W Liu[†],
X K Sun[†], Y C Chuang[†], B S Zhang[§] and H L Du[§]

[†] Institute of Metal Research, Academia Sinica, Shenyang 110015, People's Republic of China

[‡] Department of Metallurgical Engineering, Chungnam National University, Taejon 306-764, South Korea

[§] Institute of Atomic Energy, Beijing 102413, People's Republic of China

Received 19 February 1996

Abstract. Using x-ray diffraction, powder neutron diffraction, high-field magnetization measurement and thermomagnetic analysis, we have studied the structural and magnetic properties of $RFe_{10}V_2C_{0.5}$ alloys ($R = Sm$ or Y) made by arc melting, in which the carbon was added using Fe–C alloy. Both samples are found to be nearly single phase with $ThMn_{12}$ -type structure and with a small amount of α -Fe phase (less than 4 wt%). The neutron diffraction of the Y-containing compound indicates that the real composition of the main phase is $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$, and that the carbon atoms occupy not only the interstitial 2b site but also the substitutional 8i site. The Fe moments of the 8i site as well as the 8j site are found to be reduced in the $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ compound compared with its carbon-free counterpart. The decrease in the Fe moment at the 8j site is due to the surrounding interstitial carbon atoms, while the decrease in the Fe moment at the 8i site is ascribed to the surrounding substitutional carbon atoms as nearest neighbours. The high-field magnetization measurements indicate that the anisotropy field of $SmFe_{10}V_2C_{0.5}$ and $YFe_{10}V_2C_{0.5}$ are slightly higher than those of $SmFe_{10}V_2$ and $YFe_{10}V_2$, respectively. In $SmFe_{10}V_2C_{0.5}$, the magnetization curve in the hard direction at 4.2 K shows a first-order-magnetization-process (FOMP)-like or quasi-FOMP-like transition.

1. Introduction

Since the discovery of $Sm_2Fe_{17}N_3$ [1] and $NdFe_{11}TiN$ [2, 3] produced by gas–solid reaction, it has been found that the magnetic properties of $ThMn_{12}$ -type compounds can be dramatically improved by the introduction of nitrogen or carbon atoms. Therefore many researchers have investigated the magnetic properties of $Nd(Fe,M)_{12}$ nitrides ($M = Ti, V, Mo$, etc). However, until now, little work has been done on $Nd(Fe,M)_{12}$ carbides [4–7]. Many studies have reported that nitrogen or carbon atoms occupy only octahedral interstitial sites: 9e sites in the Th_2Zn_{17} -type structure [8], and 2b sites in the $ThMn_{12}$ -type structure [9–11]. Recently Fujii *et al* [12] reported that, in a study of the $ThMn_{12}$ -type nitrides using neutron diffraction, only half of the 2b sites were occupied by the nitrogen atoms and suggested the occupation possibility of another site 4d. Hu *et al* [13] also presented the possibility of another site occupation of carbon atoms in the $ThMn_{12}$ -type carbides. In this work, $R(Fe,V)_{12}C_{0.5}$ ($R = Sm$ or Y) alloys are successfully synthesized by arc melting, and the structure and magnetic properties are studied by means of x-ray diffraction, powder neutron diffraction, high-field magnetization measurement and thermomagnetic analysis.

2. Experimental details

RFe₁₀V₂C_{0.5} alloy (R = Sm or Y) were prepared by arc melting, where the carbon was added using Fe–C alloy containing 5.25 wt% C. The as-cast samples were annealed at 950 °C for 3 weeks and then checked by x-ray diffraction, to be essentially single phase with the tetragonal ThMn₁₂-type structure.

Neutron diffraction measurement was performed in a powder diffractometer setting at a heavy-water research reactor. The powder sample was packed in a thin-wall cylindrical vanadium cell 5.0×10^{-3} m in diameter and 5.0×10^{-2} m high. The diffraction data were collected at room temperature with the neutron wavelength 1.184×10^{-10} m by scanning from $2\theta = 10^\circ$ to $2\theta = 80^\circ$ in steps of 0.15° . The diffraction patterns obtained were analysed by means of the Rietveld [14] profile technique. For the coherent scattering lengths, we used the values 0.775×10^{-14} m for yttrium, 0.954×10^{-14} m for iron, -0.0382×10^{-14} m for vanadium and 0.665×10^{-14} m for carbon. An indication of the agreement between the observed and calculated intensities (both nuclear and magnetic) is given by the reliability factor R_{total} :

$$R_{total} = \left(\sum_i S_{i(obs)}^2 - c^{-1} \sum_i S_{i(calc)}^2 \right) / \sum_i S_{i(obs)}^2$$

where $S_{i(obs)}$ and $S_{i(calc)}$ are the observed and calculated integrated intensities, to be summed over all reflections, and c is a scaling factor. Similar expressions are used to obtain the separate R_{nucl} - and R_{magn} -values.

The Curie temperatures of these compounds were determined from the thermomagnetic analysis curves performed from 4 to 673 K. In order to perform high-field magnetization measurements up to 35 T at 4.2 K, powder samples of cylindrical shape were aligned in a magnetic field of 1 T, and then the high-field isotherms at 4.2 K were recorded with the external field parallel and perpendicular to the alignment field. The anisotropy fields were derived from the intersection points of the extrapolated magnetization curves measured parallel and perpendicular to the aligned direction. The values of saturation magnetization M_s were derived from the high-field part of the magnetization curves.

3. Results and discussion

X-ray diffraction patterns show that the arc-melted YFe₁₀V₂C_{0.5} and SmFe₁₀V₂C_{0.5} are nearly single phase with the ThMn₁₂-type structure and with small amounts of α -Fe phase. The α -Fe content calculated by the Rietveld analysis is less than 4 wt%. No single-phase samples could be obtained using arc-melted ingots containing carbon contents higher than that (C = 0.5) because these alloys exhibit a relatively high volume of α -Fe. This result shows the same trend as for the arc-melted 2:17 carbides reported by others [15–17]. The neutron diffraction diagram for YFe₁₀V₂C_{0.5} obtained at room temperature is shown in figure 1. The observed diffraction lines are interpreted by nuclear and magnetic coherent scattering. The diffraction patterns of YFe₁₀V₂C_{0.5} can be indexed in a body-centred tetragonal cell (space group, $I4/mmm$), with parameters $a = (8.526 \pm 0.004) \times 10^{-10}$ m and $c = (4.794 \pm 0.003) \times 10^{-10}$ m. The results of the refinement procedure including the coordinates of crystallographic sites, the occupations of atoms in these sites and the magnetic moments are presented in table 1. Powder neutron diffraction has been widely used because this technique is a particularly powerful tool for locating the light elements, for measuring accurately the changes in intermetallic distances and for determining the magnetic moment. The position parameters for Y, Fe and V for YFe₁₀V₂C_{0.5} are very close to those obtained

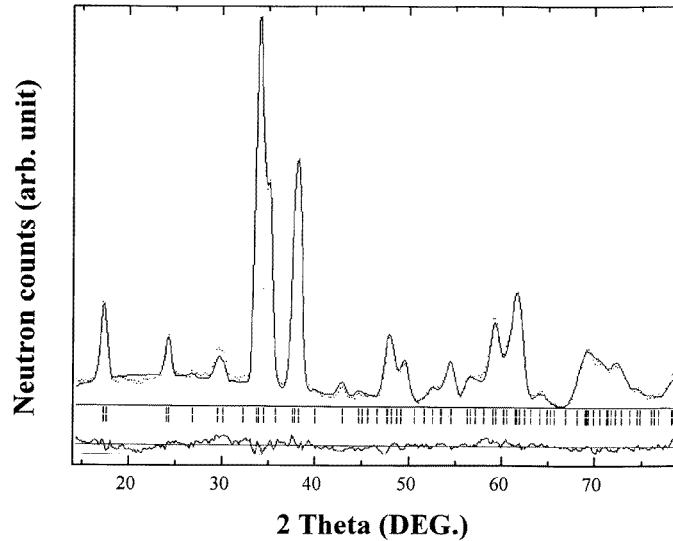


Figure 1. Neutron diffraction pattern of $YFe_{10}V_2C_{0.5}$ obtained at room temperature: ●, measured intensities; —, the calculated profiles. Positions of possible reflections are marked.

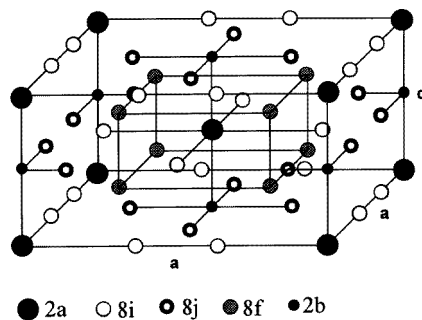


Figure 2. Schematic structural diagram of $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$.

for $YFe_{10}V_2$ reported by Helmholtz *et al* [18]. The Fe atoms are found to occupy the 8i, 8j and 8f sites, whereas the V atoms almost all reside in the 8i site. This is in agreement with the results of others [19, 20]. Moreover, our result shows that about 10% of the vanadium atoms reside in the 8f site. The most important result is the position of the carbon atoms. It was found that the carbon atoms not only occupy the interstitial 2b site coinciding with the results reported until now but also enter the substitutional 8i site up to nearly 50% with respect to the total carbon contained in the alloy. The real composition of the main phase is $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$. A schematic structural diagram of $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ is shown in figure 2. In this arc-melted carbide, the total carbon content, which can form a single phase, is about 0.5 per formula unit.

To discuss the effects of carbon atoms on the magnetic moments at the three non-equivalent iron sites, the moments at the three sites of $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ are compared with the reported values for $YFe_{10}V_2$ [18] as shown in table 1. The Fe moments of 8j and 8i sites are found to be reduced in the $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ compound compared with

Table 1. Coordinates of sites, occupation of atoms and magnetic moments in different sites of $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$. $a = (8.526 \pm 0.004) \times 10^{-10}$ m and $c = (4.794 \pm 0.003) \times 10^{-10}$ m; $R_{nucl} = 6.29\%$, $R_{magn} = 5.79\%$ and $R_{total} = 5.30\%$. The values in parentheses are taken from [18] for $YFe_{10}V_2$.

Atom	Site	Coordinates of sites			Number of atoms	μ_z (μ_B)
		x	y	z		
Y	2a	0.0000	0.0000	0.0000	2.00	0
Fe	8i	0.3573	0.0000	0.0000	4.07	1.23 (1.70)
V	8i	0.3573	0.0000	0.0000	3.46	0
C	8i	0.3573	0.0000	0.0000	0.47	0
Fe	8j	0.2742	0.5000	0.0000	8.00	1.13 (1.16)
Fe	8f	0.2500	0.2500	0.2500	7.66	2.02 (1.53)
V	8f	0.2500	0.2500	0.2500	0.34	0
C	2b	0.0000	0.0000	0.5000	0.53	0

Table 2. Lattice parameters, unit-cell volumes and Curie temperatures for the $RFe_{10}V_2C_{0.5}$ and $RFe_{10}V_2$ ($R = Sm$ or Y) compounds.

Compounds	Lattice parameters (nm)		Volume V (nm^3)	Δ	T_c (K)
	a	c			
$SmFe_{10}V_2C_{0.5}$	0.857	0.479	0.352	1.1%	612
$SmFe_{10}V_2$	0.854	0.477	0.348		603
$YFe_{10}V_2C_{0.5}$	0.853	0.479	0.349	1.4%	547
$YFe_{10}V_2$	0.849	0.477	0.344		534

Table 3. Magnetic properties for the $RFe_{10}V_2C_{0.5}$ and $RFe_{10}V_2$ ($R = Sm$ or Y) compounds at 4.2 K.

Compounds	M_s (μ_B Fu^{-1})	μ_R (μ_B)	μ_{Fe} (μ_B)	μ_M (μ_B)	B_A (T)	B_{FOMP} (T)
$Sm(Fe, V)_{12}C_{0.5}$	19.25	0.71	1.86	1.54	18	11.0
$SmFe_{10}V_2$	19.2	0.71	1.85	1.54	14	11.0
$Y(Fe, V)_{12}C_{0.5}$	16.42	0	1.64	1.37	4.5	
$YFe_{10}V_2$	15.9	0	1.59	1.3	—	

those of its carbon-free compound. Meanwhile, in this carbide the highest value of the Fe moment is found at the 8f site. This can be explained as follows. The Fe moment is very sensitive to the local coordination and the nearest-neighbour distance. So it can be well accepted that the iron moment of the 8j site is reduced because the iron atom in the 8j site is surrounded by the interstitial carbon atoms, 0.27 per formula unit as nearest neighbours [21]. For the same reason, it seems reasonable to expect a similar value for the iron moment in the 8i site, which also shows a lower moment because the iron atom is surrounded by the substitutional carbon atoms (0.23 per formula unit). Although the high 8f moment cannot be explained easily, one can assume a moment enhancement due to the location of carbon atoms presenting in the substitutional 8i site and the interstitial 2b site. The sum of all

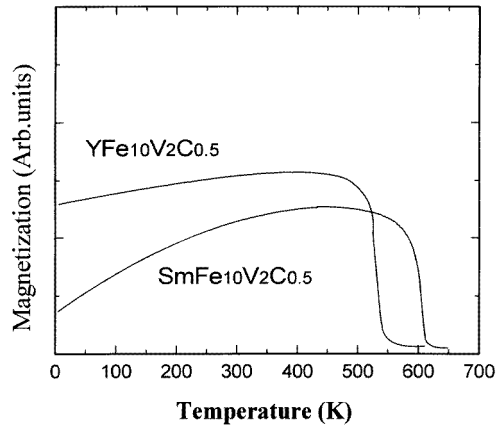


Figure 3. Temperature dependence of magnetization for $SmFe_{10}V_2C_{0.5}$ and $YFe_{10}V_2C_{0.5}$ compounds.

the magnetic moments at room temperature for $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ is $14.76\mu_B Fu^{-1}$, taking into account that the magnetic moment derived from the high-field magnetization measurements on aligned powder samples at 4 K is $16.42\mu_B Fu^{-1}$ as shown later in table 3. These values are exceptional, considering the effect of temperature.

The lattice parameters a , c and the unit-cell volume v determined from x-ray diffraction experiments are listed in table 2, together with the values of the Curie temperature obtained from a thermomagnetic analysis shown in figure 3. The lattice parameters a and c of $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$ are slightly changed, and subsequently the unit cell volume expansion is found to be 1.4% compared with the carbon-free $YFe_{10}V_2$. This volume increment of 1.4% found for this arc-melted carbide is slightly lower than that of 1.7% reported for $YFe_{10}V_2C_x$ [6] produced by gas–solid reaction using ethane (C_2H_6) and/or methane (CH_4). Consequently the increase in the Curie temperature is lower in our carbide also. It is well established that the Curie temperature depends strongly on the Fe–Fe distance [22]. It is thought that the lower volume expansion originates from the lower occupation at the 2b sites, i.e. 0.27 carbon atoms per formula unit, which is nearly 50% of the total amount of carbon contained in $Y(Fe_{9.87}V_{1.90}C_{0.23})C_{0.27}$. This implies that the carbon at the 8i site cannot contribute to the volume expansion. Therefore the smaller increase in Fe–Fe distance results in a smaller increase in the Curie temperature.

Figure 4 shows the high-field magnetization curves measured parallel (full circles) and perpendicular (full triangles) to the alignment direction at 4.2 K. The magnetic moments, the values of the anisotropy field and the first-order magnetization process (FOMP) derived from these curves are listed in table 3 together with the previous reported data [23]. The values of the magnetization for $SmFe_{10}V_2C_{0.5}$ and $YFe_{10}V_2C_{0.5}$ are $19.25\mu_B Fu^{-1}$ and $16.42\mu_B Fu^{-1}$. Owing to the introduction of carbon atoms, the values of the magnetization increase insignificantly by $0.05\mu_B Fu^{-1}$ and $0.52\mu_B Fu^{-1}$ for $SmFe_{10}V_2C_{0.5}$ and $YFe_{10}V_2C_{0.5}$, respectively. This is the same trend as that reported by Gubbens *et al* [24] in their study R_2Fe_{17} carbides.

The anisotropy fields of $SmFe_{10}V_2C_{0.5}$ and $YFe_{10}V_2C_{0.5}$ are 18 T and 4.5 T, respectively, which are slightly higher than those of $SmFe_{10}V_2$ and $YFe_{10}V_2$, respectively. It is well known that in the $ThMn_{12}$ -type compounds, upon the introduction of interstitial atoms into the 2b site, the sign of the second-order crystal-field coefficient A_{20} is changed to the

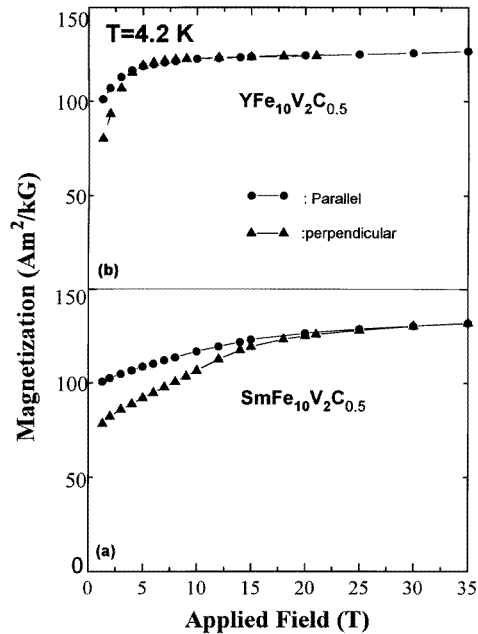


Figure 4. High-field magnetic isotherms of (a) $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ and (b) $\text{YFe}_{10}\text{V}_2\text{C}_{0.5}$ compounds at 4.2 K, measured parallel (\bullet) and perpendicular (\blacktriangle) to the alignment direction.

opposite sign. In the case of ThMn_{12} -type nitrides or carbides containing Sm which have a positive second-order Stevens coefficient ($\alpha_j > 0$), the anisotropy is expected to be changed towards in-plane anisotropy. Nevertheless the anisotropy field of $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ prepared in the present work is higher than that of $\text{SmFe}_{10}\text{V}_2$. This may be due to the contribution of the carbon atoms in the 8i site, i.e. the effect of substitutional carbon (8i site) on the crystalline electric field overrides the contribution of the interstitial carbon (2b site), resulting in an increase in the anisotropy field. In our previous investigation we have already reported that the boron atoms prefer to occupy the substitutional 8i site [25] in the ThMn_{12} -type intermetallic and, in another report, boron-containing $\text{Sm}(\text{Fe}, \text{V}, \text{B})_{12}$ [23] showed higher anisotropy fields than $\text{SmFe}_{10}\text{V}_2$, when studied by high-field magnetization measurements. From those results, it can be concluded that the enhancement of the anisotropy field found for $\text{Sm}(\text{Fe}, \text{V}, \text{B})_{12}$ [23] is caused by the boron atoms which occupy the substitutional 8i site. Similar to $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$, in which the carbon atom has nearly the same covalent-bond radius as that of the boron atom but much higher than that of nitrogen atoms, the carbon atom or boron atom can reside in the 8i site. Consequently the anisotropy field of $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ was found to be higher than that of $\text{SmFe}_{10}\text{V}_2$. In the magnetic isotherm for $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ as shown in figure 4, a slight upward curvature of the magnetization for the hard-direction magnetization is found, which may be explained by the assumption of a FOMP-like or quasi-FOMP-like transition [26].

4. Conclusion

Rare-earth transition-metal carbides with a ThMn_{12} -type structure have been reported by arc melting. The neutron diffraction study indicates that the carbon atoms occupy not

only the interstitial 2b site but also the substitutional 8i site. The lattice expansion, Curie temperature and saturation magnetization at 4 K are found to increase slightly by 1.4%, 10 K and $0.52\mu_B \text{ Fu}^{-1}$, respectively for $Y(\text{Fe}_{9.87}\text{V}_{1.90}\text{C}_{0.23})\text{C}_{0.27}$ compared with the carbon-free compound. The anisotropy fields of $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ and $\text{YFe}_{10}\text{V}_2\text{C}_{0.5}$ are slightly higher than those of $\text{SmFe}_{10}\text{V}_2$ and $\text{YFe}_{10}\text{V}_2$, respectively. In addition, $\text{SmFe}_{10}\text{V}_2\text{C}_{0.5}$ shows a FOMP-like or quasi-FOMP-like transition at 4.2 K.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China, the Commission of Sciences and Technology of Shenyang, and the Science Foundation for the Nuclear Industry, China.

References

- [1] Coey J M D and Hong Sun 1990 *J. Magn. Magn. Mater.* **87** L251
- [2] Yang Y C, Zhang X D, Kong L S, Pan Q and Ge S L 1990 *Proc. 11th Int. Workshop on Rare Earth Magnets and Their Application* vol 2 (Pittsburgh, PA: Carnegie Mellon University Press) p 190
- [3] Yang Y C, Zhang X D, Kong L S, Pan Q and Ge S L 1991 *Appl. Phys. Lett.* **58** 2042
- [4] Hurley D P F and Coey J M D 1992 *J. Phys.: Condens. Matter* **4** 5573
- [5] Qi-Nian Qi, Li Y P and Coey J M D 1992 *J. Phys.: Condens. Matter* **4** 8209
- [6] Tang Z X, Singleton E W and Hadjipanayis G C 1992 *IEEE Trans. Magn.* **28** 2572
- [7] Skolozdra R V, Tomey E, Gignoux D, Fruchart D and Soubeyrou J L 1995 *J. Magn. Magn. Mater.* **139** 65
- [8] Miraglia S, Soubeyrou J L, Kolbeck C, Isnard O, Fruchart D and Guillot H 1991 *J. Less-Common Met.* **171** 51
- [9] Ying-Chang Yang, Xiao-Dong Zhang, Lin-Shu Kong, Qi Pan, Sen-Lin Ge, Ji-Lian Yang, Yong-Fan Ding, Bai-Sheng Zhang, Chun-Tang Ye and Lan Jin 1991 *Solid State Commun.* **78** 313
- [10] Li Y P and Coey J M D 1992 *Solid State Commun.* **81** 447
- [11] Asano S, Ishida S and Fujii S 1993 *Physica B* **190** 155
- [12] Fujii H, Miyazaki Y, Tatami K, Hong Sun, Morii Y, Akayama M and Funahasi S 1995 *J. Magn. Magn. Mater.* **140-4** 1089
- [13] Hu Z, Yelon W B, Zhang X and James W J 1995 *Proc. Ann. 40th Conf. on Magnetism and Magnetic Materials (Philadelphia, PA, 1995)* p DS-12
- [14] Rietveld H M 1969 *J. Appl. Crystallogr.* **2** 65
- [15] Grossinger R, Kou X C, Jacobs T H and Buschow K H J 1991 *J. Appl. Phys.* **69** 5596
- [16] Kou X C, Grossinger R, Jacobs T H and Buschow K H J 1991 *Physica B* **168** 181
- [17] Sun H, Hu B, Li H and Coey J M D 1990 *Solid State Commun.* **74** 727
- [18] Helmholtz R B, Vleggaar J J M and Buschow K H J 1988 *J. Less-Common Met.* **138** L11
- [19] de Mooij D B and Buschow K H J 1988 *J. Less-Common Met.* **136** 207
- [20] Helmholtz R B, Vleggaar J J M and Buschow K H J 1988 *J. Less-Common Met.* **144** 209
- [21] Soubeyrou L, Fruchart D, Isnard O, Miraglia S and Tomoy E 1995 *J. Alloys Compounds* **219** 16
- [22] Isnard O and Fruchart D 1994 *J. Alloys Compounds* **205** 1
- [23] Chuang Y C, Zhang D, Zhao T, Zhang Z D, Liu W, Zhao X G, Sun X K and de Boer F R 1995 *J. Alloys Compounds* **221** 60
- [24] Gubbens P C M, Van der Kraan A M, Jacobs T H and Buschow K H J 1989 *J. Magn. Magn. Mater.* **80** 265
- [25] Zhang Dan, Zhang Zhi-Dong, Chuang Y C, Zhang Bai-Sheng, Yang Ji-Lan and Du Hong-Lin 1995 *J. Phys.: Condens. Matter* **7** 2587
- [26] Zhao Tong, Sun X K, Zhang Zhi-Dong, Wang Qun, Chuang Y C and de Boer F R 1992 *J. Magn. Magn. Mater.* **104-7** 2119