# Influence of carbon introduced by arc melting on the structural and magnetic properties of $RFe_{12-x}V_x$ (R = Y and Dy)

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## Abstract

Carbon was introduced by arc melting into $RFe_{12-x}V_x$ compounds, where R = Y or Dy and $x$ = 2, 3 or 4, and its effects on the crystallographic and magnetic properties of these intermetallics were investigated by X-ray, magnetostatic and Mössbauer effect measurements. Experimental results show that the carbon atoms prefer the 4d sites to the 2b sites, or occupy the sites reserved for Fe atoms in the $ThMn_{12}$-type crystal structure. Carbon solution increases with increasing vanadium concentration, giving rise to an effect opposite to that of vanadium. An increase in vanadium content causes an increase in the cell volume and a linear decrease in Curie temperature and in the Fe magnetic moment, whereas the addition of carbon leads to a reduction in unit volume while maintaining a high $T_C$ and enhancing the Fe magnetic moment despite decreasing iron content in the samples.

*Keywords:* Rare earth-Fe-V compounds; Carbon addition; Magnetic properties

## 1. Introduction

It is known that the magnetic properties of iron-rich rare earth intermetallics with structure 2:17 and 1:12 may be dramatically altered when nitrogen or carbon is inserted into the interstitial sites by gas-solid reaction [1-5]. The gas-phase interstitial modification process leads to dilatation of the lattice causing an increase in the Curie temperature and iron magnetisation. The other effect concerns the magneto-crystalline anisotropy where a complete sign reversal of the rare earth sublattice due to modification of the crystal field experienced by the 4f rare earth shell takes place. A certain quantity of carbon can be introduced into intermetallics by the arc-melting method, but the results are open to discussion [6-8]. To our surprise, it was found that the addition of carbon to $RFe_{12-x}V_x$ compounds causes simultaneously a decrease in unit volume and an increase in Curie temperature [6]. To obtain a better insight into the

magnetic behaviour of the carbides with $ThMn_{12}$-type structure, an interstitial series $RFe_{12-x}V_xC_y$ and a substitutional stoichiometric series $RFe_{12-x}V_{x-y}C_y$ were prepared. Studies on the effect of carbon on the structural and magnetic properties of $RFe_{12-x}$ $V_x$ compounds are presented in this paper.

## 2. Experimental

Samples of the required compositions $RFe_{12-x}V_x$, $RFe_{12-x}V_xC_y$, and $RFe_{12-x}V_{x-y}C_y$ with R = Y or Dy, $x$ = 2, 3 or 4 and $0.3 \leqslant y \leqslant 1$ were synthesised by the arc-melting method in an Ar atmosphere. (Dy and Y with purity of 99.9% and Fe, V and C with purity of 99.999% were used.) The interstitial $RFe_{12-x}V_x$ carbides were prepared by arc-melting the parent compounds with carbon. For substitutional systems, carbon was introduced as Fe-C alloys. The ingots were remelted several times, crushed and melted again to ensure homogeneity. The samples were next annealed at about 1200 K for one week. Samples quality was checked by X-ray and magnetostatic measurements. X-Ray measurements were performed using conven-

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tional X-ray powder diffraction with a Siemens diffractometer and Cu-K$\alpha$ radiation. Magnetostatic measurements were carried out in the temperature range 4.2-1000 K in a magnetic field of up to 1.6 T using Farraday, Foner and torsion methods. Mössbauer measurements were performed on a constant acceleration spectrometer with a $^{57}$Co:Cr source. The Mössbauer spectra were recorded at room temperature and at about 120 K. Magnetic measurements were performed on the bulk, powder and magnetically aligned powder samples. The easy magnetisation direction at room temperature was determined from the X-ray diffraction patterns of the aligned samples.

## 3. Results and discussion

### 3.1. Crystallographic structure

All samples investigated were approximately single phase and had tetragonal ThMn$_{12}$-type structure (Fig. 1). A small quantity of a second phase was detected in YFe$_8$V$_4$ and its carbides. The typical X-ray diffraction patterns of RFe$_{12-x}$V$_x$, RFe$_{12-x}$V$_x$C$_y$ and RFe$_{12-x}$V$_{x-y}$C$_y$ are shown in Fig. 2. The X-ray reflections of RFe$_{12-x}$V$_x$ are shifted towards lower angles with increasing vanadium concentration because of the lattice expansion.



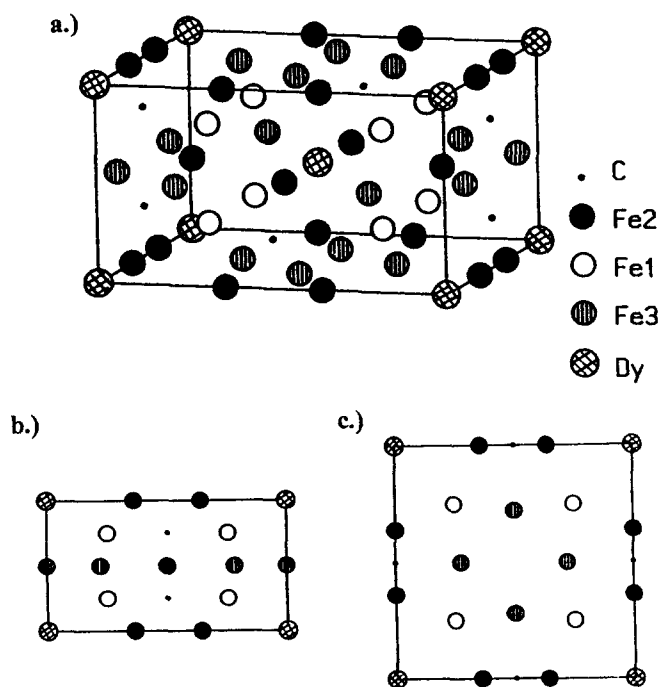Fig. 1. The crystal structure of RFe$_{12-x}$V$_x$ compounds. (a) Projection showing the 4d interstitial site occupied by C; (b) $a$-$c$ plane projection of this structure; (c) basal plane projection of this structure.

The composition dependence of the lattice parameters $a$ and $c$ and unit volume are presented in Figs. 3-5. In RFe$_{12-x}$V$_x$ (R = Y, Dy), an increase in the lattice parameters $a$ and $c$ with a consequent increase in the cell volume (Figs. 3 and 4) was observed, as reported earlier for compounds with Tb, Er, Gd and Y [9,10]. Dilatation of the lattice is due to the substitution by the larger V$^{+3}$ ion of the Fe$^{+3}$ ion. The XRD patterns of RFe$_{12-x}$V$_x$C$_y$ reveal a shift of the peaks to higher angles when compared with those of RFe$_{12-x}$V$_x$ (Fig. 2(b)). It follows that introduction of a certain number of carbon atoms by the arc-melting method causes an unexpected decrease in values of the lattice parameters and a reduction in cell volume of the carbides as compared with the parent compounds. These results are shown in Figs. 3 and 4. (A certain increase in volume was only noticed for nonannealed samples RFe$_{10}$V$_2$C$_{0.3}$.) The changes in the lattice constant $a$ with changing composition were observed to be larger than those in $c$.

As the Fe traces were not detected on the diffraction patterns it would be reasonable to deduce that the carbon atoms do not occupy the 2b interstitial sites but prefer alternative positions such as 4d [11], or replace the 3d-metal in the crystal structure. For this reason a stoichiometric RFe$_{12-x}$V$_{x-y}$C$_y$ series was prepared. As shown in Fig. 2(a), the X-ray reflections of C substitutional systems are shifted to higher angles when compared with pure compounds, showing that in this case a reduction in the unit volume also occured (Fig. 3). The carbon atoms entering the 4d interstitial sites or substituting a 3d atom have as nearest neighbours mainly the 3d ions (Fig. 1). Owing to their greater electronegativity carbon atoms have a tendency to attract the electrons of nearest neighbours. Hence the chemical bond becomes more covalent, which could lead to some reduction of the cell volume for substitutional C and interstistial 4d modified RFe$_{12-x}$V$_x$ systems.

X-Ray diffraction and thermomagnetic analysis show that the formation of ThMn$_{12}$-type structures for samples with carbon depends on the concentration of iron and vanadium in the composition. In general, the dissolution of carbon in the composition increases with increasing $x$ ($y = 0.3$, 0.7-1 for $x = 2$, 3, respectively, reaching a maximum when vanadium content $x = 3$). From the composition-dependence of the structural parameters (Fig. 5) it may be deduced that the lattice parameters (especially $a$) and unit volume change markedly when an excess quantity of carbon is introduced into the compound. Excessive carbon addition violates the geometrical conditions for formation of the ThMn$_{12}$-type tetragonal structure. A tendency toward the formation of the R$_3$(FM)$_{29}$ phase [12] and distortion of the tetragonal structure are observed.

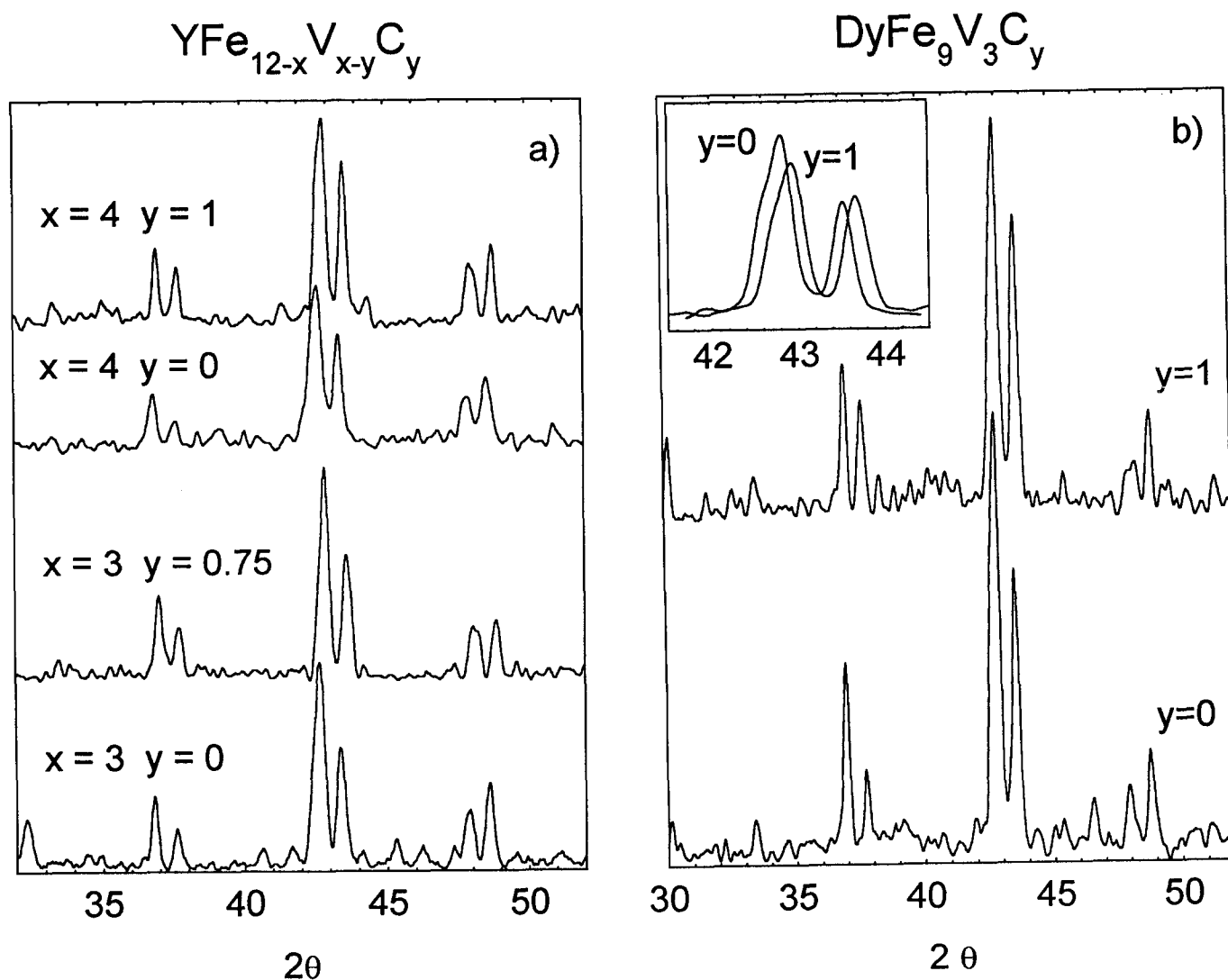## $YFe_{12-x}V_{x-y}C_y$

## $DyFe_9V_3C_y$



Fig. 2. X-Ray diffraction patterns of (a) $YFe_{12-x}V_x$ and $YFe_{12-x}V_{x-y}C_y$, (b) $DyFe_9V_3$ and $DyFe_9V_3C$.

### 3.2. Curie temperature and magnetic moment

The compositon dependence of the Curie temperature for different systems is reported in Fig. 6. In the $RFe_{12-x}V_x$ compounds a linear decrease in $T_C$ with increasing V content is observed. This decrease in $T_C$ is consistent with a simple dilution of the overall exchange, to be expected with decreasing the Fe concentration [9,10]. Moreover with increasing vanadium content in $YFe_{12-x}V_x$ and in $DyFe_{12-x}V_x$ (Fig. 6) the Fe sublattice magnetisation is reduced. In the dysprosium system the magnetic moment of the Fe sublattice may be estimated as the resultant moment when assuming $D^{+3}$ free ion magnetic moment and antiparallel coupling between the Dy and Fe moments. The temperature variation of magnetisation [6] confirmed the

antiparallel coupling between the Dy and Fe magnetic moments in both the primary (parent) compounds and those with carbon. The linear decrease of the Fe moment with increasing $x$ is in agreement with that found in Refs. [9] and [10]. The decrease of the Fe moment in these materials was explained qualitatively on the basis of Friedel's model [13] and confirmed by calculations of the electronic structure [14]. However the introduction of carbon substantially changes the behaviour of the Curie temperature and the Fe magnetic moment with variations in $x$ and $y$. The high $T_C$ is maintaned despite the fact that the Fe content is decreasing in the sample (Fig. 6). It is noteworthy that $T_C$ is high for both the stoichiometric and nonstoichiometric intermetallics. It may be concluded that the effect of substitutional and interstitial C is generally
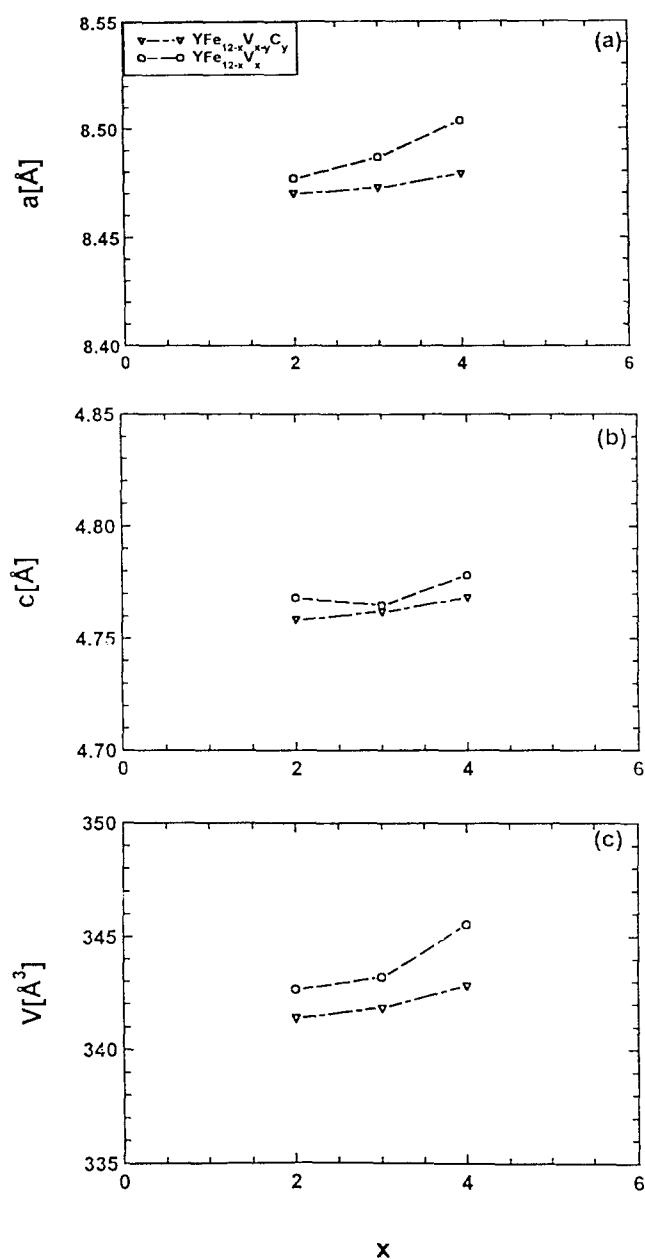
Fig. 3. Dependence of (a) the lattice parameters $a$, (b) the lattice parameters $c$ and (c) the unit cell volumes $V$ on vanadium content ($x$) in $YFe_{12-x}V_x$ and $YFe_{12-x}V_{x-y}C_y$ compounds.

Fig. 4. Dependence of (a) the lattice parameters $a$, (b) the lattice parameters $c$ and (c) the unit cell volumes $V$ on vanadium content ($x$) in $DyFe_{12-x}V_x$ and $DyFe_{12-x}V_xCy$ compounds.

the same, although it may be different in origin because of the different sites occupied in the crystal structure (2b [4,5,8], 4d, (8i, 8f, 8j) [6,7]). In Ref. [7] $RTiFe_{11-x}C_x$ with only a small carbon content ($x = 0.25$) was studied. Its effect on $T_C$ was negligible but the Fe magnetic moment was influenced by the carbon. In our samples the Fe magnetic moment is also markedly influenced by carbon addition. Carbon, unlike vanadium, inhibits the decrease in the iron magnetic moment. For sufficiently large carbon con-
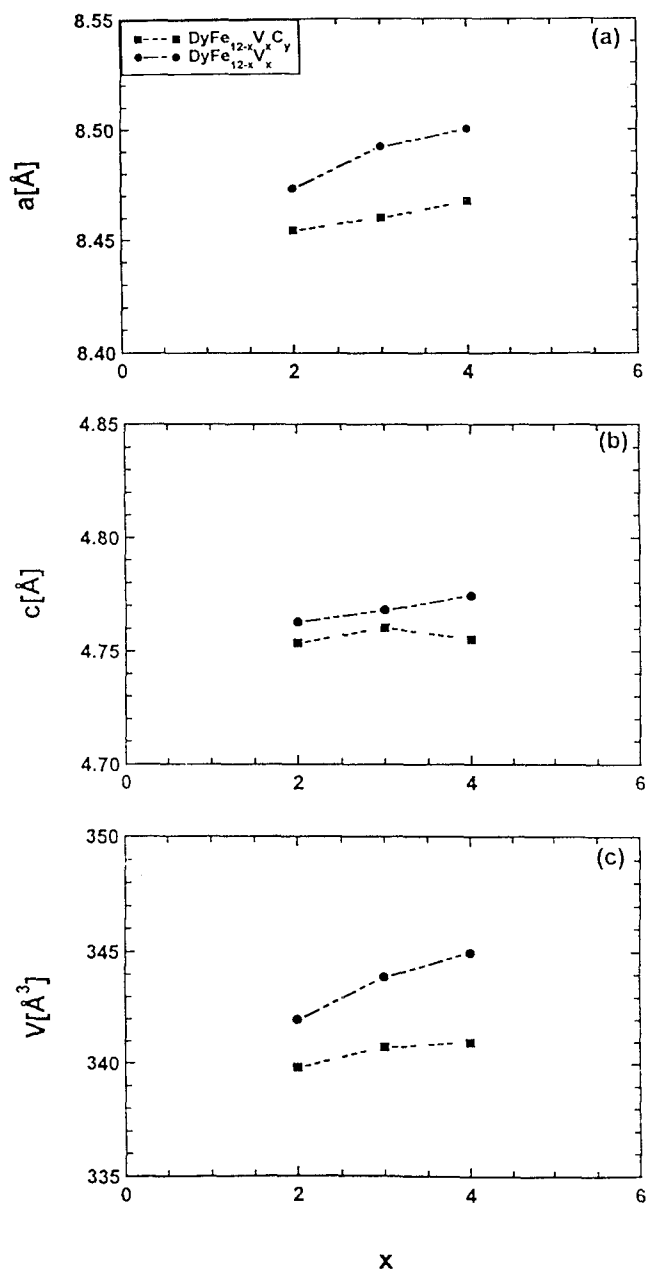
tents, an increase in magnetic moment of Fe is even observed (Fig. 7). In stoichiometric compounds substituting C for $V^{+3}$ exlusively in 8i sites is especially beneficial in preventing the creation of a large magnetic moment in the iron sublattice.

Enhancement of the 3d magnetic behaviour was confirmed by Mössbauer measurements. The Mössbauer spectra for $DyFe_9V_3$, $DyFe_9V_3C$ and $DyFe_8V_3C$ performed at room temperature are presented in Fig. 8. The average hyperfine field ($\langle H_{hf} \rangle$)is
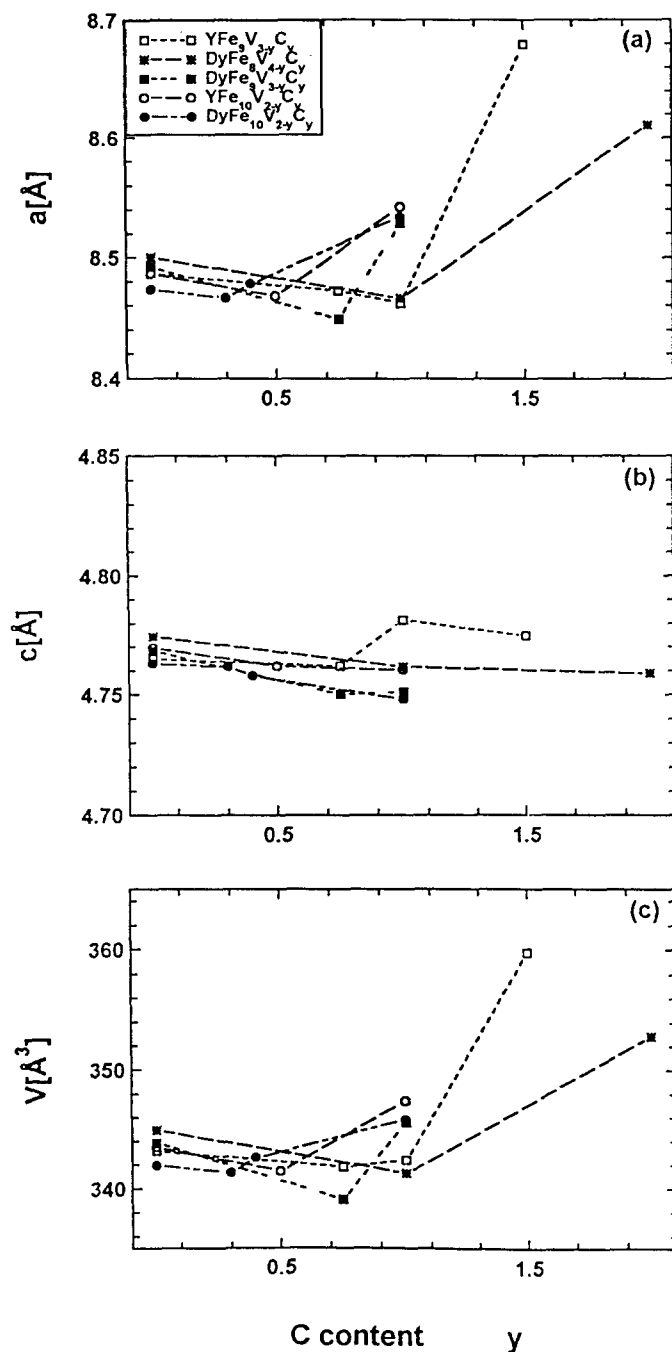
Fig. 5. Dependence of (a) the lattice parameters $a$, (b) the lattice parameters $c$ and (c) the unit cell volumes $V$ on carbon content ($y$) in $YFe_{12-x}V_{x-y}C_y$ and $DyFe_{12-x}V_{x-y}C_y$ compounds.

markedly changed in the carbides investigated, unlike those modified by the gas-solid state process [4]. Details of the Mössbauer spectra analysis will be reported elsewhere [15].

It is interesting to estimate the average magnetic moment of iron ($\langle \mu Fe \rangle$) according to the approximation $H_{hf}(Fe) = A \langle \mu Fe \rangle$, where $A = 14.4$ T $\mu_B^{-1}$ [16]. The values of the iron magnetic moment derived at

temperatures of about $T = 120$ K for the various studied compositions are presented in Fig. 7. The results agree quite well with data obtained from magnetostatic measurements. Some deviations in the experimental data may be due to small departures from the nominal composition and irregular distribution of the vanadium atoms in the crystal structure. The saturated magnetisation at 4.2 K for $YFe_9V_3$,
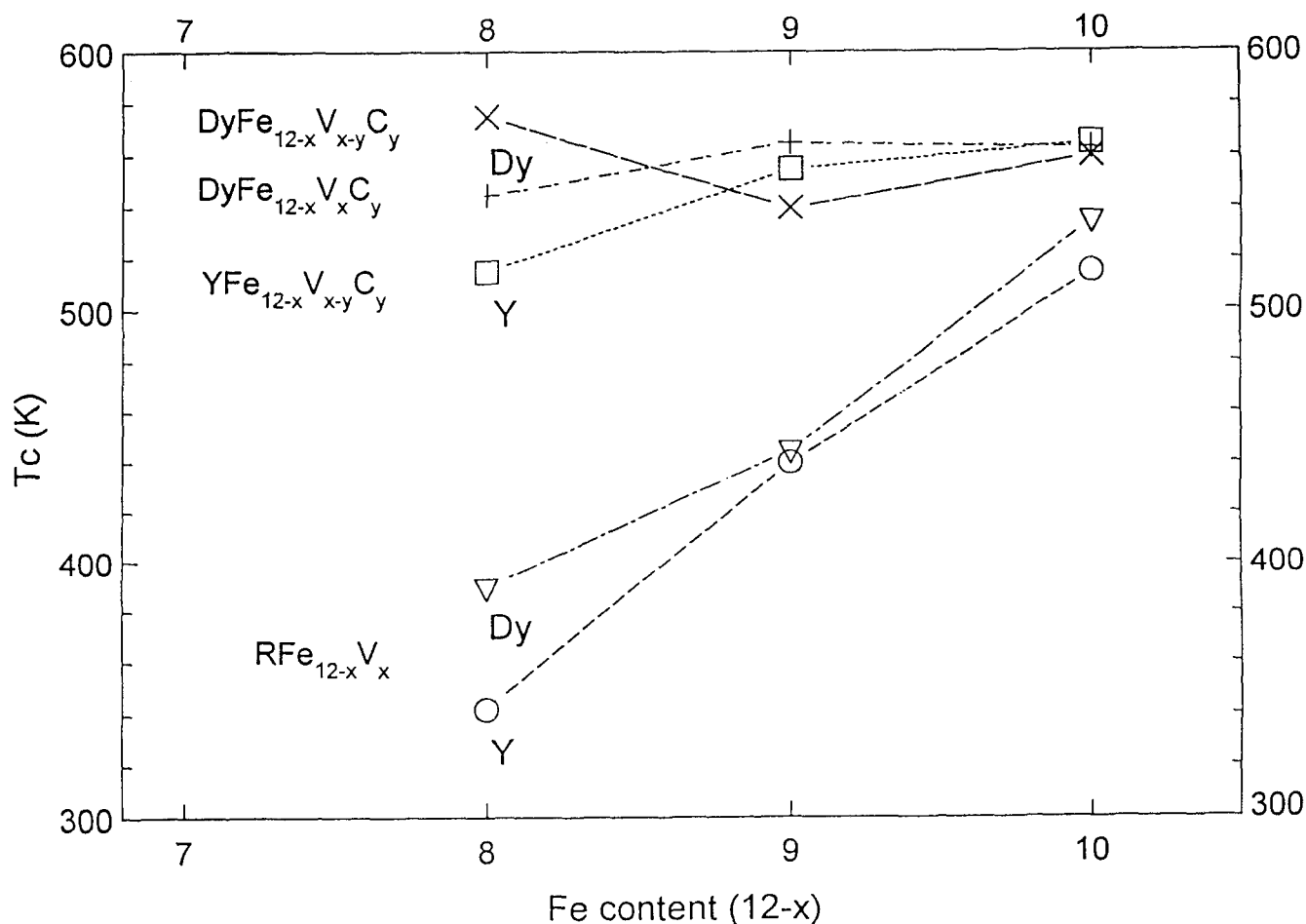
Fig. 6. Dependence of the Curie temperature on iron content (12-$x$) in RFe$_{12-x}$V$_x$, RFe$_{12-x}$V$_{x-y}$C$_y$ and RFe$_{12-x}$V$_x$C$_y$ compounds.

YFe$_9$V$_3$C, and YFe$_8$V$_3$C, deduced by extrapolation to 1/B→0, was 11.0, 13.84 and 14.42 $\mu_B$ (f.u.)$^{-1}$, respectively. This yields an increase of up to 0.4$\mu_B$ for the iron magnetic moment under the influence of carbon addition. It gives a value of 1.8 $\mu_B$ per Fe atom in YFe$_8$V$_3$C. A higher value of 2.01 $\mu_B$ per Fe atom was derived for DyFe$_8$V$_3$C at 4.2 K.

The enhancement of the Fe magnetic sublattice may be associated with the change of electronic structure under the influence of carbon. Electron transfer can take place from the nearest neighbours to the C-2p orbitals centered on the metalloid atoms since C atoms have larger electronegativity than the R, V and Fe atoms (although the electronegativity differences between them decrease, respectively). The presence of carbon seems to have an effect opposite to that of vanadium in electron transference to the iron 3d band. However, the increase in the Fe magnetic moment could be seen as the result of some increase of the localisation of magnetic moment due to the more covalent character of the chemical bond in the carbon-containing samples.

### 3.3. Magnetocrystalline anisotropy

All the samples of RFe$_{12-x}$V$_x$ have the c-easy direction of magnetisation at room temperature. Torsion measurements show that the magnetocrystalline anisotropy decreases with increasing vanadium concentration, but increases a little with the addition of carbon to YFe$_{12-x}$V$_x$ and with decreasing temperature [6]. However, it should be noted that the determination of the easy magnetisation direction from the relative intensity of some peaks of the diffraction patterns for oriented and nonoriented samples is not quite clear for samples with carbon. For Dy systems the increase in the high-order terms $K_2$ and $K_3$ with decreasiing temperature observed in the torque curves indicates the competition between Dy and Fe sublattice anisotropy. It proves that the sign of the magnetocrystalline rare earth anisotropy is not completely reversed as in the case of the 2b interstitial modified carbides [4,5]. An increase in dysprosium magnetocrystalline anisotropy can lead to spin reorientation phenomena (Fig. 9). However, the magnetocrystalline anisotropy be-
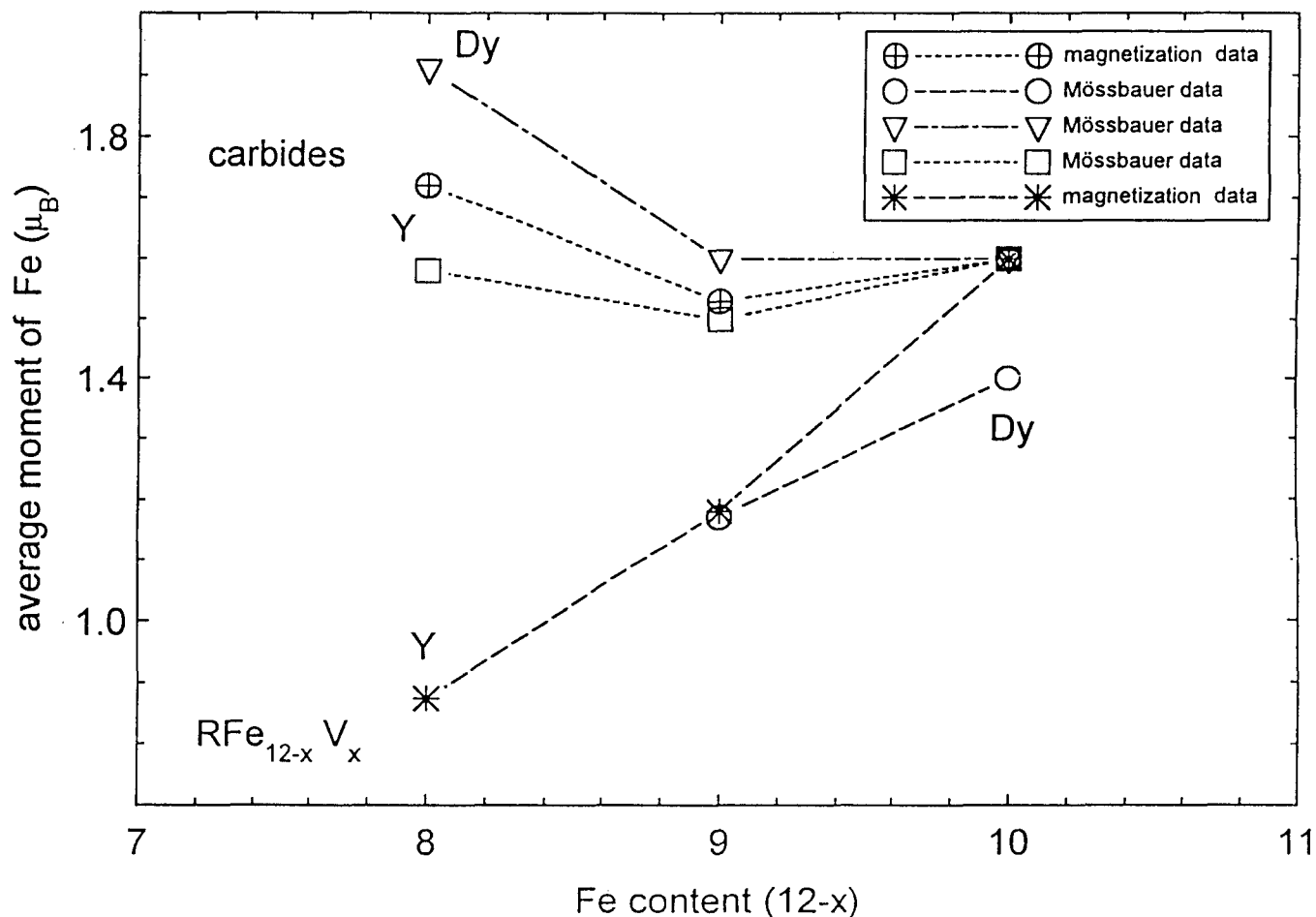
Fig. 7. Comparison of the concentration dependence of $\langle \mu_{Fe} \rangle$ in $RFe_{12-x}V_x$ and the carbides $RFe_{12-x}V_xC_y$ derived from magnetostatic and Mössbauer measurements.

haviour is complicated due to the simultaneous influences of vanadium and carbon. Moreover, torque and magnetisation measurements at the lowest temperatures suggest a noncollinear spin arrangement. The question of magnetocrystalline anisotropy requires more profound analysis and will be reported in a separate paper.

## 4. Conclusion

The introduction of carbon into $RFe_{12-x}V_x$ intermetallic compounds by arc-melting leads to results differing from those found for the gas-phase interstitial modification process, probably due to the different carbon occupation preference in the crystal structure. In gas-solid reaction carbon is inserted into the 2b interstitial sites while in the arc-melting method a preference for occupying the sites taken by Fe atoms and other 4d interstitial sites is observed. The structur-

al and magnetic properties of the investigated intermetallics depend on the concentrations of both vanadium and carbon.

An increase in vanadium content results in an increase in the cell volume and a linear decrease in the Curie temperature and the 3d magnetic moment with $x$.

The influence of carbon is opposite to that of vanadium and affects mainly the 3d magnetic sublattice because of its occupation preference (the nearest neighbours of a C atom are Fe and V atoms in the cases discussed). The samples containing carbon have high $T_C$ and enhanced Fe magnetic moment despite the decrease in number of Fe atoms. The rare earth sublattice is less influenced by carbon atoms which prefer the 4d interstitial sites or to take the place of Fe atoms.

In order to derive a detailed explanation for the increase in iron magnetisation and Curie temperature with a reduction in cell volume in substitutional C and interstitial 4d site-modified intermetallics further ex-
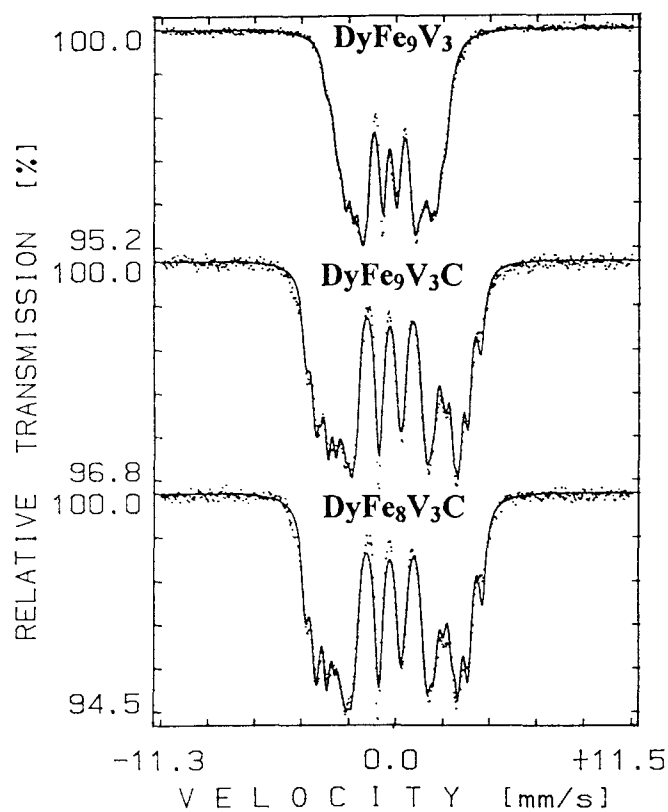
Fig. 8. The Mössbauer spectra for $DyFe_9V_3$ and its stoichiometric ($DFe_8V_3C$) and nonstoichiometric ($DyFe_9V_3C$) carbides obtained at room temperature. Points, experimental data; lines, fitted spectrum.
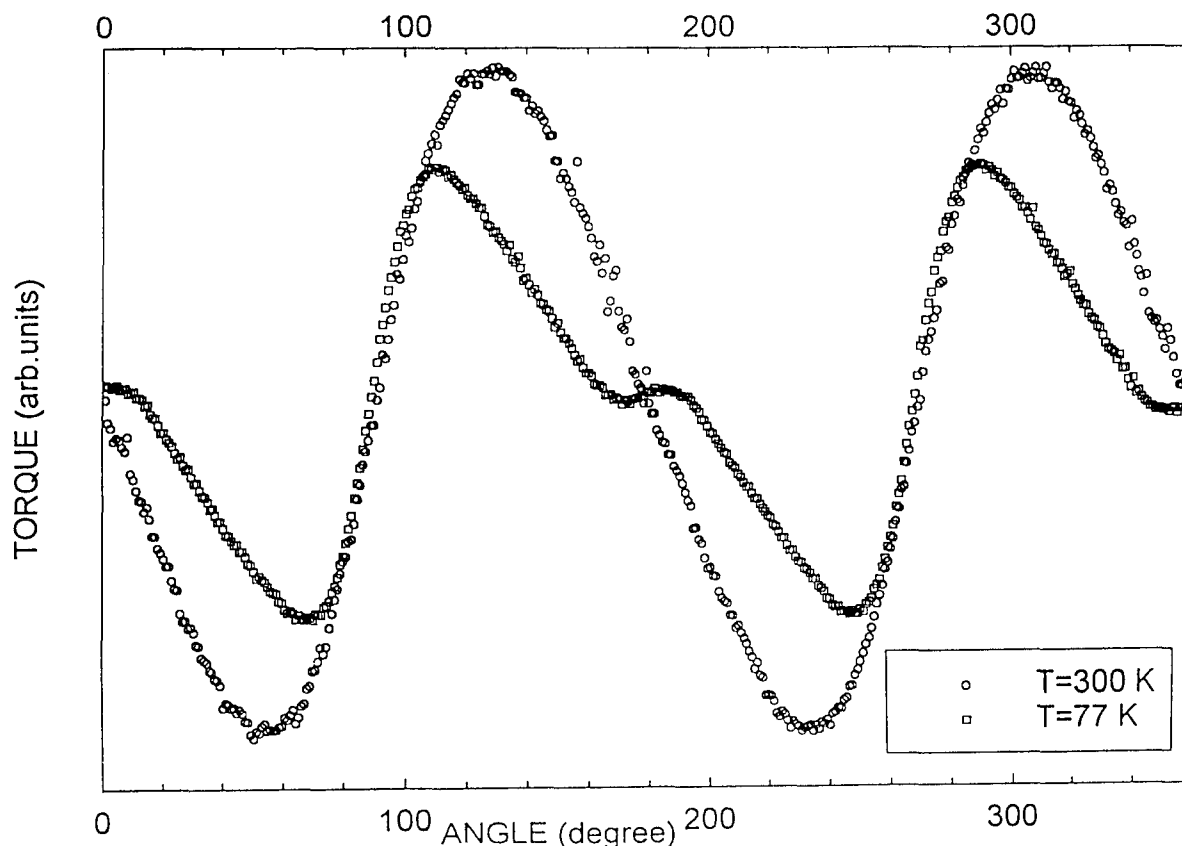


Fig. 9. The torque curves obtained for $DyFe_{10}V_{1.7}C_{0.3}$ at $B = 1.6$ T.

perimental studies and electronic structure calculations are required.

## Acknowledgements

## References

[1] J.M.D. Coey and H. Sun, J. Magn. Magn. Mater., 87 (1990) L251.

[2] H. Sun, J.M.D. Coey, Y. Otani and D.P.F. Hurley, J. Phys. Condens. Matter, 2 (1990) 6465..

[3] Y-C Yang, X-D Zhang, L-S Kong and Q. Pan and S-L G; Appl. Phys. Lett., 58 (1991) 2042. [4] D.P.F. Hurley and J.M.D. Coey, Phys. Condens. Matter, 4 (1992) 5573.

[5] Qi-nian Qi, Y.P. Li and J.M.D. Coey, J. Phys. Condens. Matter, 4 (1992), 8209.

[6] Z. Drzazga, A. Winiarska and W. Zarek, in C.A.F. Manwaring, D.G.R. Jones, A.J. Williams and I.R. Harris (eds.), Proc. 8th Int. Symp. on the Magnetic Anisotropy and Coercivity in Rare Earth-Transition Metal Alloys, Birmingham, UK, 1994, p. 377.

[7] Y-C Yang, X-D Zhang, S-Z Dong and Q Pan, J. Appl. Phys., 74 (1993) 6847.

[8] X-F Xu, Y-X Sun, Z-X Liu and C Lin, Solid State Commun., (1994) 409.

[9] D.B. de Mooij and K.H.J. Bushow, J. Less-Common Met., 136 (1988) 207.

[10] L. Pareti, M. Solzi, G. Marusi, M.R. Ibarra and P.A. Algarabel, J. Appl. Phys., 70 (1994) 3753.

[11] H. Fujii, Y. Miyzaki, K. Tatami, H. Sun, Y. Morii, M. Akayama and M.S. Funahashi, Int. Conf. on Magnetism, 1994, Warsaw.

[12] J.M. Cadogan, H-S Li, A. Margarian, J.B. Dunlop, D.H. Ryan, S.J. Collocott and R.L. Davis, J. Appl. Phys., 76 (1994) 6138.

[13] R. Verhoef, F.R. de Boer, Zhang Zhi-dong and K.H.J. Bushow, J. Magn. Magn. Mater., 75 (1988) 319.

[14] R. Coehoorn, Phys. Rev., B 41 (1990) 11790.

[15] E. Popiel, Z. Drzazga, A. Winiarska and W. Zarek, in preperation.

[16] T.H. Sinnemann, M. Rosenberg, K.H.J. Bushow, J. Less-Common Met., 146 (1989) 223.