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1997 J. Phys.: Condens. Matter 9 2187

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The electronic and magnetic structure of the $\text{Y}(\text{FeV})_{12}$ compound and its carbides

J Deniszczyk[†] and W Borgiet[‡]

[†] Institute of Physics and Chemistry of Metals, Silesian University, Bankowa 12, 40-007 Katowice, Poland

[‡] Institute of Physics, Silesian University, 40-007 Katowice, Poland

Received 23 September 1996, in final form 9 December 1996

Abstract. The electronic and magnetic properties of body-centred-tetragonal YFe_8V_4 carbon-doped compounds have been analysed theoretically. The electronic structure was determined by a TB-LMTO-ASA method within the scalar-relativistic approximation. The crystal structure and lattice constant parameters were taken from experiment. The total and partial densities of states, and the magnetic moments for YFe_{12} , YFe_8V_4 , $\text{YFe}_8\text{V}_4\text{C}$ and $\text{YFe}_8\text{V}_3\text{C}$ compounds were calculated and discussed. In the calculations the unit volume for the carbides was assumed to be smaller than that for the parent YFe_8V_4 compounds; nevertheless, an increase in total magnetic moment for the compounds with carbon atoms in the positions 4(d) and 8(i) was observed.

1. Introduction

In the last decade iron-rich ThMn_{12} - and $\text{Th}_2\text{Mn}_{17}$ -type compounds have been the subject of intensive experimental as well as theoretical investigation. These compounds, having the uniaxial crystal structure and being characterized by high Curie temperatures and strong uniaxial magnetic anisotropy fields near room temperature are very promising starting materials for permanent-magnet applications. One of the most important recent developments in magnetism has been the realization of the great improvements in properties in binary and ternary intermetallic compounds. It has been recognized that the properties of the iron-rich rare-earth intermetallics with the structures 1:12 and 1:17 are very sensitive to carbon or nitrogen doping [1–3].

The nitrides and carbides can be prepared by using any of several techniques [4]. Among these, the most widely used is a solid–gas-phase reaction. The gas-phase carbonation, in common with nitrogenation of 1:12 compounds, results in the absorption of carbon (nitrogen) atoms into the interstitial 2(b) sites adjacent to the rare-earth sites [2, 3]. Investigations of $\text{RE}(\text{FeTM})_{12}$ (RE—rare earth; TM—transition metal) carbides and nitrides have shown that the insertion of carbon and nitrogen using the gas-phase interstitial modification technique dilates the lattice, enlarging its unit volume by several per cent (2.3% for $\text{DyFe}_{11}\text{TiC}_{1-\delta}$ [2] and 3.7% for $\text{DyFe}_{10}\text{Mo}_2\text{N}_x$ [5]). It is commonly argued that the volume expansion causes a narrowing of the 3d band and an enhancement of the Fe–Fe exchange interaction. Consequently it leads to an increase of the Curie temperature. The spontaneous magnetization remains almost unchanged [2]. The presence of carbon and nitrogen atoms at interstitial 2(b) sites causes the substantial changes in the magnetocrystalline anisotropy (MCA) of the parent $\text{RE}(\text{FeTM})_{12}$ compounds.

Another preparation technique recently used for 1:12 nitrides, carbides and borides is that of arc melting the constituents. By applying this method, carbides [6–8] and borides [9] have been prepared, and they were then examined. Investigations of the carbides have shown that the effect of carbon on the structural and magnetic properties of rare-earth–transition-metal compounds can be different from that observed for carbides produced by the gas-phase modification method. With increasing concentration of carbon the lattice parameters decrease and the unit volume is reduced by about 0.5–0.7% [6, 8]. Magnetic measurements reveal:

(i) a substantial enhancement of the average iron magnetic moment (by 5% in $\text{RETiFe}_{11-x}\text{C}_x$ with a small concentration of carbon ($x \leq 0.25$) [6] and by 25% in $\text{REFe}_{12-x}\text{V}_{x-y}\text{C}_y$ for $y \simeq 1$ [8]);

(ii) an increase of the Curie temperature by about 140 K for higher carbon concentrations [8];

(iii) the existence of a spin-reorientation transition (SRT) from the planar to the axial easy-magnetization direction in compounds with rare earths characterized by negative second-order Stevens factors α_J [6, 8, 10] (the SRT temperature shifts to higher values with increasing concentration of carbon [10]);

(iv) the axial anisotropy of the parent compounds SmTiFe_{11} ($\alpha_J > 0$) remains unchanged upon carbonation [6].

The above-described structural and magnetic properties of arc-melted 1:12 carbides cannot be caused by carbon occupying the 2(b) interstitial sites. On the basis of experimental evidence it has been concluded that also in the carbides $\text{RE}(\text{FeVC})_{12}$ produced by the arc-melting method, the carbon atom prefers to enter an interstitial position—4(d)—or to replace one of the 3d atoms at 8(i) sites [8, 10]. Since the changes of the magnetic properties of 3d sublattices upon carbonation are similar to those observed upon reduction of the vanadium concentration [11], we assume that carbon replaces vanadium at an 8(i) site.

Among the rare-earth–transition-metal intermetallic series of compounds, yttrium compounds are particularly convenient as regards studying the 3d-sublattice contribution to the magnetism of $\text{RE}(\text{FeTM})_{12}$ compounds. Yttrium is nonmagnetic, so it provides an opportunity to focus on the transition-metal contribution to the magnetic properties of RE–TM compounds. The key to the understanding of the magnetic properties of a material is its electronic structure. Many band-structure calculations have been done for the prototype yttrium intermetallic 1:12, 2:17 and 2:14 compounds [12–16] and their interstitial nitrides and carbides [3, 17–19]. Consistently with the earlier experimental evidence, the calculations for 1:12 carbides and nitrides were performed assuming the nitrogen or carbon to occupy the 2(b) interstitial sites (as in the case of compounds produced by the gas-phase interstitial modification process).

In this paper we present self-consistent band-structure calculations of the electronic structure of the parent YFe_8V_4 compound and its carbides. For the sake of providing a comparative study, band-structure calculations for the hypothetical binary YFe_{12} compound are also presented. The aim of our investigations was a theoretical analysis of the influence of carbon on the electronic and magnetic properties of YFe_8V_4 carbides produced by the arc-melting method. We focus our attention on the dependence of the electronic and magnetic properties of the carbides on the crystal position of the carbon within the unit cell of the reference system. To answer the question of what the occupation preference of the carbon is, we calculated the electronic structure for two interstitial carbides: $\text{YFe}_8\text{V}_4\text{C}$ (with C at 2(b) and 4(d) sites) and substitutional $\text{YFe}_8\text{V}_3\text{C}$ (C replaces one vanadium atom at an 8(i) site). For these three positions the effect of carbon on the magnetization and electronic

structure was studied. The calculated total and local moments are compared with the results of low-temperature magnetization and Mössbauer spectroscopy measurements.

2. Crystal structure

In the $ThMn_{12}$ -type structure of the base YFe_{12} compound there exist three nonequivalent positions occupied by Fe atoms (8(f)— $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$, 8(i)—(0.361, 0, 0) and 8(j)—(0.277, $\frac{1}{2}$, 0), one position (2(a)—(0, 0, 0)) occupied by an yttrium atom, and several empty interstitial positions (2(b) and 4(d)) which can be occupied by small atoms. Experimentally it was observed that in the ternary $YFe_{12-x}TM_x$ compounds the substituted transition-metal atoms preferentially occupy the 8(i) positions [20, 21]. In the unit cell of $Y(FeV)_{12}$ structure there is one position of type 2(b) with coordinates (0, 0, $\frac{1}{2}$), two equivalent positions of type 4(d) ($\frac{1}{2}, 0, \frac{1}{4}$), and four equivalent positions of type 8(i). The symmetry of $Y(FeV)_{12}$ structure doped with one carbon atom depends on the position that it occupies. When the 2(b) position is occupied the symmetry of the parent structure is preserved. The nearest neighbours of carbon are four Fe (j) and two Y (a) atoms. A single carbon atom placed into one of the 4(d) sites reduces the space group from the group $I4/mmm$ (No 139) of the parent compound YFe_8V_4 to the group $I4m2$ (No 119) of carbide. The nearest neighbours of C at a 4(d) site are four V atoms at 8(i) positions. Replacement of one of the vanadium atoms at an 8(i) site by carbon lowers the symmetry to orthorhombic $I2mm$ (No 44). Consequently the number of classes of inequivalent atoms in the unit cell is enlarged. The distances from C placed at position 8(i) to nearest-neighbour atoms are significantly larger than those for C in positions 2(b) or 4(d).

The YFe_{12} and YFe_8V_4 compounds are hypothetical and the lattice parameters were taken from fits of a linear function to the measured variation of the unit-cell volume of $YFe_{12-x}V_x$ versus the concentration x of vanadium atoms [15, 20]. The ratio of the lattice parameters c/a is taken equal to 0.562. The lattice parameters of the carbides were taken from experiments [8].

3. Computational method

We performed the band-structure calculations using the tight-binding linear muffin-tin orbital (TB-LMTO) method of Andersen *et al* [22]. The calculations were scalar relativistic, neglecting the spin-orbit interaction. The exchange-correlation potential was taken within local spin-density approximation, with the use of the von Barth-Hedin [23] parametrization:

$$\begin{aligned} v_{xc}(n(r), n_{\sigma}(r)) = & -\frac{\alpha}{r_s} - c^P \ln\left(1 + \frac{r^P}{r_s}\right) \\ & + \left[c^P g\left(\frac{r_s}{r^P}\right) - c^F g\left(\frac{r_s}{r^F}\right) \right] \left[\gamma((2n'_{\sigma})^{1/3} - 1) - \frac{4}{3} f(n'_{\sigma}) \right] \\ & + \left[c^P \ln\left(1 + \frac{r^P}{r_s}\right) - c^F \ln\left(1 + \frac{r^F}{r_s}\right) \right] f(n'_{\sigma}) \end{aligned}$$

with the functions $f(x)$ and $g(z)$ defined as follows:

$$\begin{aligned} f(x) &= (x^{4/3} + (1-x)^{4/3} - 2^{-1/3}) / (1 - 2^{-1/3}) \\ g(z) &= (1 + z^3) \ln\left(1 + \frac{1}{z}\right) + \frac{z}{2} - z^2 - \frac{1}{3}. \end{aligned}$$

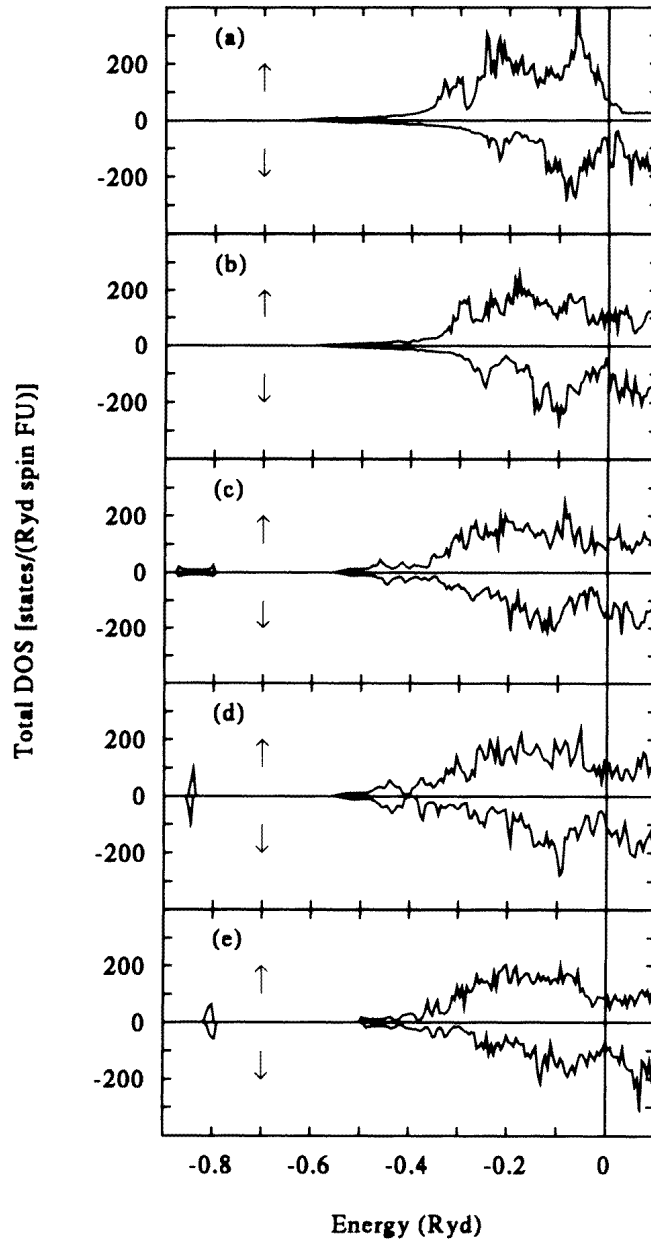


Figure 1. Total densities of states (states Ryd⁻¹/cell) for (a) YFe₁₂, (b) YFe₈V₄, (c) YFe₈V₄C 2(b), (d) YFe₈V₃C 4(d), and (e) YFe₈V₃C 8(i) versus energy (Ryd). The vertical line which goes across each of the partial pictures marks the position of the Fermi level.

r_s is the dimensionless parameter related to the electron charge density $n(r)$ by the equation $4\pi r_s^3 a_0^3 = 1/n$, $n'_\sigma = n_\sigma/n$, and the numerical parameters take the values $\alpha = 1.221774$, $\gamma = 5.1297628$, $c^P = 0.0504$, $c^F = 0.0254$, $r^P = 30.0$, $r^F = 75.0$.

In the TB-LMTO method the crystal potential is treated within the atomic-sphere approximation (ASA). The crystal is divided into overlapping Wigner–Seitz (W–S) spheres with a spherically symmetric potential in each of the W–S spheres. The sum of the W–S spheres’ volumes is equal to the unit-cell volume. The remaining small interstitial region is neglected. For calculations on compounds in which there always exist nonequivalent sites, the ASA approximation introduces adjustable parameters. In order to establish uniquely the radii of inequivalent W–S spheres the volume equation is used, and additionally a choice must be made for the ratios of the radii of the spheres centred at inequivalent atomic positions. In the calculations for the YFe_{12} and YFe_8V_4 compounds we applied the ratios proposed by Coehoorn [13, 15]: $r_Y/r_{Fe} = 1.35$ and $r_V/r_{Fe} = 1.06$. These values are close to the corresponding ratios of atomic radii for Y, Fe and V. For the YFe_8V_4C compounds with the carbon placed at small-volume interstitial positions we assume the W–S sphere ratio $r_C/r_{Fe} = 0.5$. This choice provides a carbon W–S sphere which overlaps with the nearest neighbours by less than 30%. In the case of the YFe_8V_3C compounds, carbon replaces one vanadium atom which has a relatively large radius. In this case we choose the set of ratios of radii of different W–S spheres which give effective potentials on different spheres which are almost the same (the zero-step-potential approach). Within this approach we found $r_Y/r_{Fe} = 1.15$, $r_V/r_{Fe} = 1.06$, and $r_C/r_{Fe} = 0.81$. We assumed the same W–S sphere radius for all inequivalent Fe atoms.

The number of k -points in the irreducible part of the Brillouin zone (IBZ) was: 288 for YFe_{12} , YFe_8V_4 and YFe_8V_4C 2(b); 262 for YFe_8V_4C 4(d); and 510 for YFe_8V_3C . For the purpose of the calculation of the densities of states (DOS), using the tetrahedral integration method, one iteration has been performed for every composition with a greater number of k -vectors in the IBZ: 1183 for YFe_{12} , YFe_8V_4 and YFe_8V_4C 2(b); 1116 for YFe_8V_4C 4(d); and 1160 for YFe_8V_3C .

Table 1. Calculated values of the total densities of states at the Fermi level in units of states $\text{Ryd}^{-1} \text{FU}^{-1}$.

	YFe_{12}	YFe_8V_4	YFe_8V_4C 2(b)	YFe_8V_4C 4(d)	YFe_8V_3C 8(i)
$D_{\uparrow}^{\text{total}}(\epsilon_F)$	69.2	123.8	90.9	109.5	78.4
$D_{\downarrow}^{\text{total}}(\epsilon_F)$	145.4	70.3	174.8	108.7	66.5
$D^{\text{total}}(\epsilon_F)$	214.6	194.1	265.7	218.2	144.9

4. Results and discussion

4.1. Densities of states

The total densities of states obtained for the series of compounds are plotted in figure 1. Values of the total densities of states at the Fermi level are collected together in table 1.

The density of states for the Fe-rich YFe_{12} compound (figure 1(a)) resembles that of pure Fe. In the region extending some eV below the Fermi level it is easy to recognize pure 3d Fe structure. Substitution of vanadium for four Fe atoms is associated with the lowering of the total electron number by 12 and causes drastic changes in the spin-up density of states. The occupancy of the majority-spin band is lowered by more than 12, and consequently the spin-up DOS decreases uniformly (figure 1(b)). In YFe_8V_4 as compared with YFe_{12} the spin splitting is reduced. Substantial changes in the DOS for both spin directions in the

vicinity of the Fermi level can be observed. The considerable peak of the spin-up DOS at -0.06 Ryd below the Fermi level almost disappears. A strong enhancement of the spin-up DOS at the Fermi level and in the valence band is observed. The spin-down DOS at ε_F is reduced to half of its value in YFe_{12} (see table 1 for details).

Parts (c), (d) and (e) of figure 1 present the total DOS of YFe_8V_4 carbides for different positions of carbon within the unit cell. In all cases the $2s$ part of the carbon electronic structure at about -0.8 Ryd is visible. It is worth also noting the reverse spin splitting of carbon $2s$ states for carbide with carbon at 4(d) interstitial sites (the possibility of such an inverse splitting was discussed by Nolting *et al* [24]). As a result of hybridization of $2p$ states of carbon located at -0.45 Ryd with $3d$ states of neighbouring TM atoms, the low-energy tail of the DOS is truncated and the band edges become sharper. Independently of the crystal position of the carbon, the characteristic iron sharp peak structure of the DOS disappears, and the shapes of the up-spin DOS and the down-spin DOS both become smoother.

Table 2. Occupation numbers of the majority (N_\uparrow) and minority (N_\downarrow) subbands for inequivalent crystallographic sites of YFe_8V_4 . The magnetic moment (in units of μ_B) and total electron number are defined as $\mu = N_\uparrow - N_\downarrow$ and $N = N_\uparrow + N_\downarrow$, respectively. ΔQ represents the deviation from charge neutrality.

	Y 2(a)	Fe 8(f)	V 8(i)	Fe 8(j)
N_\uparrow	1.569	4.840	2.095	4.896
N_\downarrow	1.864	3.186	2.841	3.034
N_{total}	3.433	8.026	4.936	7.930
μ	-0.295	1.653	-0.746	1.862
ΔQ	0.433	0.026	-0.064	-0.070

Total majority electrons = 48.886
 Total minority electrons = 38.114
 Total electrons = 87.000
 Magnetization = $10.78 \mu_B \text{FU}^{-1}$
 Average Fe moment = $1.3 \mu_B$

Table 3. Calculated values for $\text{YFe}_8\text{V}_4\text{C}$ with C at the interstitial site 2(b) (the notation is the same as in table 2).

	Y 2(a)	Fe 8(f)	V 8(i)	Fe 8(j)	C 2(b)
N_\uparrow	2.018	4.982	2.043	4.770	1.088
N_\downarrow	2.223	2.931	2.775	3.629	1.148
N_{total}	4.241	7.913	4.818	8.399	2.236
μ	-0.205	2.051	-0.732	1.141	-0.060
ΔQ	1.241	-0.087	-0.181	0.399	-1.764

Total majority electrons = 50.288
 Total minority electrons = 40.712
 Total electrons = 91.000
 Magnetization = $9.58 \mu_B \text{FU}^{-1}$
 Average Fe moment = $01.2 \mu_B$

Table 4. Calculated values for YFe_8V_4C with C at the interstitial site 4(d) (the notation is the same as in table 2).

	Y 2(a)	Fe 8(f)	V 8(i)	Fe 8(j)	C 4(d)
N_{\uparrow}	1.489	4.827	2.624	4.895	1.121
N_{\downarrow}	1.792	3.067	3.026	2.951	1.036
N_{total}	3.281	7.894	5.650	7.846	2.157
μ	-0.303	1.760	-0.402	1.944	0.085
ΔQ	0.281	-0.106	0.650	-0.154	-1.843
Total majority electrons = 51.9944					
Total minority electrons = 49.004					
Total electrons = 91.000					
Magnetization = 12.99 μ_B FU ⁻¹					
Average Fe moment = 1.62 μ_B					

Table 5. Calculated values for YFe_8V_4C with carbon replacing one vanadium atom at an 8(i) site (the notation is the same as in table 2).

	Y 2(a)	Fe 8(f)	V 8(i)	Fe 8(j)	C 8(i)
N_{\uparrow}	1.096	5.023	1.870	5.052	2.041
N_{\downarrow}	1.374	3.089	3.061	3.016	1.980
N_{total}	2.470	8.112	4.931	8.068	4.021
μ	-0.278	1.934	-1.191	2.046	0.061
ΔQ	-0.530	0.112	-0.069	0.068	0.021
Total majority electrons = 49.05					
Total minority electrons = 36.95					
Total electrons = 86.000					
Magnetization = 12.10 μ_B FU ⁻¹					
Average Fe moment = 1.51 μ_B					

The influence of carbon on the details of the DOS in the vicinity of the Fermi level depends on its crystal position (see figure 1). Carbon introduced into YFe_8V_4 at a 2(b) interstitial site enhances the total DOS at ε_F by 36%, from 194 Ryd⁻¹ FU⁻¹ for YFe_8V_4 to 266 Ryd⁻¹ FU⁻¹ for YFe_8V_4C , increasing the exclusively spin-down channel (the spin-up DOS is reduced by 25%). Carbon placed at a 4(d) interstitial site gives $D^{total}(\varepsilon_F) = 218$ Ryd⁻¹ FU⁻¹ which is lower than the value in the former case but still higher than that for YFe_8V_4 . The values of the minority- and majority-spin DOS at ε_F are nearly the same. Substantial changes in the DOS are produced by carbon insertion into a substitutional 8(i) site. For both spin directions the value of the DOS at the Fermi level is reduced, giving a value of the total DOS equal to 145 Ryd⁻¹ FU⁻¹, 25% lower than in the parent YFe_8V_4 compound. Furthermore, one can observe the narrowing of the band as compared with those for the other carbides for which calculations were made (see figure 1).

4.2. Local magnetizations

For all of the compounds the calculations led to a ferrimagnetic solution. In tables 2–5 we list the values of the partial occupation numbers, local and total magnetic moments, and

deviations from charge neutrality for YFe_8V_4 , and its carbides with carbon at different crystal positions. For all of the compounds the direction of the effective magnetic moment coincides with that of the iron sublattice magnetization, while the yttrium and vanadium magnetic moments are always oriented in opposite directions. In our calculations we obtained a reduction of the magnetic moment of YFe_8V_4 by over $16\mu_B$ as compared to that of the YFe_{12} structure, which we found to be equal to $26.9\mu_B$. A similar, strong reduction of magnetic moment of the YFe_{12} structure stabilized by vanadium was also observed experimentally [8, 25]. A theoretical explanation of this effect, from the electronic structure point of view, was proposed recently by Coehoorn [15].

In the carbides the magnitude of the magnetic moment of carbon is very small. Its direction with respect to that of the effective moment, and its influence on the magnetic properties of YFe_8V_4 depend on the position it occupies. Having analysed the directions of the local magnetic moments we found that the magnetic moment on the carbon always orients oppositely to the moments of its nearest neighbours. In the case of carbon placed at a 2(b) position the nearest neighbours are the iron atoms at 8(j) sites, and the carbon atom is slightly polarized in the direction opposite to that of the bulk magnetic moment. The nearest neighbours of carbon at a 4(d) position are the vanadium atoms at 8(i) sites whose moments are negative. As a result, the carbon is polarized toward the effective moment of the sample.

For both of the interstitial positions of carbon the calculations showed that a charge equal to that of 1.8 electrons is transferred from the carbon to its nearest neighbours (see tables 3 and 4). The influence of carbon at interstitial sites on its surroundings is that it tends to reduce the magnitude of the neighbouring local atomic moments. When carbon occupies the 2(b) interstitial site it causes the lowering of local magnetization on iron at 8(j) positions, which in effect leads to a reduction of the unit-cell magnetic moment (as compared to that of YFe_8V_4). A similar phenomenon was observed for carbon placed at a 4(d) site, but now carbon forces a reduction of the magnitude of the vanadium magnetic moments. Since the vanadium moments are oriented oppositely to the bulk magnetization, the presence of carbon leads to an enhancement of the total magnetic moment of the unit cell.

The influence of carbon replacing vanadium at an 8(i) site on the magnetic properties of $\text{YFe}_8\text{V}_3\text{C}$ compounds is of a different kind. The presence of carbon gives rise to the enhancement of the local magnetic moments within both of the magnetic sublattices toward their original orientation. This means that the replacement of one vanadium atom by carbon enhances both the V–V and the Fe–Fe exchange interactions. The average iron and vanadium magnetic moments increase by $0.22\mu_B$ and $0.41\mu_B$, respectively.

The calculated magnetic moments of Y–Fe–V–C compounds are consistent with the moments derived from magnetostatic and Mössbauer measurements [8, 25] and calculated previously [15, 19]. We have obtained overestimated magnetic moments for hypothetical YFe_{12} and YFe_8V_4 , for which the measured magnetic moments (per formula unit) are $24.5\mu_B$ [25] and $8\text{--}9\mu_B$ [8, 25], respectively. The experiments reported by Drzazga *et al* [8] show that the magnetic moment of YFe_8V_4 carbides is of the order of $13\mu_B$. The results of our calculations reveal that the observed enlargement of the magnetic moment of the carbides (with respect to that of the reference YFe_8V_4 system) is possible only under the assumption that the carbon atoms occupy interstitial 4(d) positions or replace the vanadium atoms at 8(i) sites. Carbon placed at 2(b) interstitial sites lowers the unit-cell magnetic moment considerably. In this respect our results follow the argumentation presented in [8]. Further theoretical investigations of the carbides are in progress.

4.3. The Curie temperature

Having calculated the magnetization data and spin densities of states, it is natural for us to ask whether the observed increase in Curie temperature of YFe_8V_4 on carbonation can be explained theoretically. Within the spin-fluctuation theory of Mohn and Wohlfarth [26], the Curie temperature (T_c) can be found by solving the quadratic equation

$$(T_c/T_{ST})^2 + T_c/T_{SF} - 1 = 0$$

where T_{ST} is the Stoner Curie temperature and T_{SF} is the characteristic temperature describing the influence of the spin fluctuations. Following papers by Jaswal *et al* [18] and Qi *et al* [3] we assume that the magnetic behaviour of the compounds considered by us is driven mainly by the spin fluctuations, and consequently we neglect the first term, proportional to the inverse of the square of the Stoner Curie temperature. Within this approximation, the Curie temperature is given by the spin-fluctuation temperature T_{SF} [26]:

$$T_c = T_{SF} = m_0^2 / (10k_B \chi_0)$$

where m_0 is the ground-state magnetic moment per atom, k_B is the Boltzmann constant and

$$\chi_0^{-1} = (4\mu_B^2)^{-1} [D_{\uparrow}(\epsilon_F)^{-1} + D_{\downarrow}(\epsilon_F)^{-1}] - I/2\mu_B^2$$

is the inverse of the exchange-enhanced susceptibility. $D_{\sigma}(\epsilon_F)$ ($\sigma = \uparrow, \downarrow$) are the up- and down-spin DOS at the Fermi level, and I is the Stoner parameter. For the purpose of estimations we use the Stoner parameter $I = 0.068$ Ryd given by Jaswal *et al* for Y_2Fe_{17} and its nitrides [18].

Within the spin-fluctuation approach, the Curie temperature is determined by the average magnetization per magnetic atom (in our case Fe) and by the average value of the spin density of states at the Fermi level. An increase of the Curie temperature can be obtained as the result of a decrease of the spin DOS at the Fermi level or an increase of the average magnetization. Since the exchange-enhanced susceptibility is a result of the difference of two small quantities (the inverse DOS and the Stoner parameter), the decisive role in the determination of T_c is played by the behaviour of the DOS in the vicinity of the Fermi level.

The parameters necessary for the estimation of T_c as obtained from band-structure results can be found in tables 1 to 5. In order to explain the behaviour of T_c upon carbonation we again pay attention to the DOS near the Fermi level. In carbide with carbon at a 2(b) site (figure 1(c)) the up-spin DOS decreases by about 25% while the density of down-spin states increases drastically by almost 150% as compared with the values for YFe_8V_4 (figure 1(b)). In effect, the total DOS in the carbide becomes larger by about 50%. When the second interstitial position, 4(d), of carbon is taken into account (figure 1(d)), calculations yield a value of the total DOS at the Fermi energy which is still larger than that obtained for the parent compound (by about 12%). Partial spin DOS are distributed equally between the two spin directions. For substitutional carbide (carbon at 8(i) sites) we observe an overall narrowing of the band and a substantial decrease of the DOS at the Fermi level (figure 1(e)). The total DOS becomes smaller by almost 25%, mainly due to the decrease in the up-spin component of the DOS.

For the parent YFe_8V_4 compound the estimated value of T_c is 300 K which agrees reasonably well with the experimental one ($T_c^{\text{exp}} \simeq 340$ K [8, 11]). The increase of the DOS calculated for both interstitial carbides results in a lowering of the Curie temperature—especially for 2(b) interstitial carbide, where the drastic increase of the DOS results in a negative value of the exchange-enhanced susceptibility. For 4(d) interstitial carbide our results give $T_c = 100$ K. The remarkable reduction of the DOS at the Fermi level observed

for 8(i) substitutional carbide gives rise to a strong enhancement of T_c , which we found to be equal to 780 K. The above-estimated values of the Curie temperature are of qualitative character.

The value of the Curie temperature determined experimentally for the carbides of YFe_8V_4 obtained by arc melting is about 500 K [8]. On the basis of our estimations of T_c it can be concluded that the real structure of the carbides probably consists of carbon atoms randomly distributed over 4(d) interstitial and 8(i) substitutional sites.

5. Concluding remarks

Previous band-structure calculations of $\text{Y}(\text{FeTM})_{12}$ carbides and nitrides have shown [3, 17] that the interstitial atoms tend to reduce the magnetic moments of neighbouring TM atoms and that the improvement of the magnetic parameters upon carbonation is mainly due to lattice dilatation. Our results for carbide with carbon placed at 2(b) interstitial sites are consistent with the results obtained by Qi *et al* for $\text{Y}(\text{Fe}_{11}\text{Ti})\text{C}$ [3]. We found that the presence of carbon alone leads to a reduction of the saturation magnetization on account of the covalent bonding with the neighbouring iron at the 8(j) sites, whose effect is to reduce the iron local magnetic moment slightly.

For carbides with carbon at the interstitial site 4(d) and the substitutional site 8(i) our results have shown that the presence of carbon may lead to an incrementation of the saturation magnetization in spite of the reduction of the unit-cell volume. The effect of carbon placed at the 4(d) sites on neighbouring atoms is of a similar kind to that for carbon at 2(b) sites. This time, however, carbon forms a covalent bond with the nearest vanadium atoms and as a result reduces the magnitude of their antiferromagnetically aligned local magnetic moments. As a result the bulk magnetization increases. The mechanism of the increase of magnetization caused by carbon replacing a vanadium atom at an 8(i) site is not clear. We suggest the following interpretation of our results. The replacement of one vanadium atom by carbon leads to the narrowing of the 3d bands (an effect similar to that of volume expansion). Associated with the band-narrowing, enhancement of the exchange–correlation interaction gives rise to the incrementation of the magnetization within both the antiferromagnetically aligned magnetic sublattice of V and that of Fe. It can be concluded that in this case disorder introduced by replacement of one vanadium atom by carbon is responsible for the observed changes in the magnetic properties of the carbide $\text{YFe}_8\text{V}_3\text{C}$.

Acknowledgments

The authors thank Z Drzazga for many helpful discussions of the experimental results. The band-structure calculations were performed in the Fachbereich Physik of Osnabrück University, and one of the authors (JD) is indebted for financial support to a DAAD Scholarship. This work was supported in part by the Polish Government Agency KBN under contracts No 2 P30224403 and PB 1108/p03/95/08 (WB).

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