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Electronic structure and magnetism of transition-metal-stabilized $\mathrm{YFe}_{12-x}M_x$ intermetallic compounds

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Self-consistent *ab initio* band-structure calculations using the augmented-spherical-wave method were performed for the hypothetical compounds YFe_{12} and YFe_8M_4 (M = Ti, V, Cr, Mn, Mo, and W) with the ThMn_{12} structure, in which the M atoms occupy the 8(i) crystallographic sites. We found that YFe_{12} is a weak ferromagnet: For none of the three Fe sites is the majority-spin $3d$ band completely occupied. Using extrapolated experimental lattice parameters, the calculated total magnetization ($24.2\mu_B$/formula-unit) and the calculated moment reduction after replacement of the Fe(i) atoms by an M atom are in good agreement with experimental data on $\mathrm{YFe}_{12-x}\mathrm{M}_x$ ($1 \le x \le 3$) compounds. The calculated local magnetic moments are compared with the results of neutron-diffraction and Mössbauer-spectroscopy experiments, as well as with the results of band-structure calculations on some structurally related compounds.

I. INTRODUCTION

Recently, the preparation, structure, and physical properties of compounds of the type $R\mathrm{Fe}_{12-x}M_x$ have attracted much interest because of their potential application in permanent magnets. These compounds crystallize in the body-centered-tetragonal ThMn_{12} structure. The Th site is occupied by a rare-earth (R) atom, while the Mn sites are occupied mainly by Fe atoms. The binary compounds $R\mathrm{Fe}_{12}$ do not exist, but de Mooij and Buschow[1] discovered that the structure can be stabilized by replacing a small fraction of Fe by the M atoms Ti, V, Cr, Mo, W, or Si. Independently, Ohashi *et al.*[2,3] and Müller[4] also reported the discovery of a member of this class of compounds, containing Ti (with $x = 1$) and Mo, respectively, as the stabilizing element. $R\mathrm{Fe}_{12-x}\mathrm{Mn}_x$ and $R\mathrm{Fe}_{12-x}\mathrm{Al}_x$ had already been known for some time, but only with relatively low Fe concentrations: $x \ge 4$ for $\mathrm{YFe}_{12-x}\mathrm{Mn}_x$ (Ref. 5) and $6 \le x \le 8$ for $\mathrm{GdFe}_{12-x}\mathrm{Al}_x$.[6] Xiang-Zhong *et al.*[7] have recently prepared metastable $\mathrm{GdFe}_{12-x}\mathrm{Al}_x$ compounds with $2 \le x \le 6$ by melt spinning. The stability range of $R\mathrm{Fe}_{12-x}\mathrm{M}_x$ compounds shown in Fig. 1. As far as is known at present, this range only depends on the M element, and not on the R element.

For permanent-magnet applications the compounds with the highest Fe concentration are the most interesting, because the substitution of M for Fe leads to a decrease of the saturation magnetization and of the Curie temperature. For $x < 2$ the transition-metal contribution to the saturation magnetization is fairly high. Generally, it is $(16\text{–}21)\mu_B$ per formula unit at 4.2 K.[8] The Curie temperature is well above room temperature.[1] As is usual in rare-earth–iron compounds, the R and Fe moment couple ferromagnetically for the light-rare-earth elements and antiferromagnetically for the heavy-rare-earth elements. Sm is the most favorable rare-earth element. First, its magnetic moment couples ferromagnetically to the magnetization due to the Fe sublattice. Secondly, its second-order Stevens factor, α_J, is positive, which is necessary in order to obtain uniaxial magnetocrystalline anisotropy (c-axis preferred), because the second-order crystal-field parameter A_2^0 is negative.[9] The magnetic anisotropy fields at room temperature of the compounds which have been studied most extensively up to now, $\mathrm{SmFe}_{11}\mathrm{Ti}$, $\mathrm{SmFe}_{10}\mathrm{V}_2$, and $\mathrm{SmFe}_{10.5}\mathrm{Mo}_{1.5}$, are all 8–10 T.[3,4,10,11] From measurements on the corresponding Y compounds $\mathrm{YFe}_{11}\mathrm{Ti}$ and $\mathrm{YFe}_{10}\mathrm{V}_2$, it follows that the contribution of the Fe sublattice to the uniaxial anisotropy field at room temperature is in both cases approximately 2 T.[12] The anisotropy fields at room temperature are quite high, which is a necessary condition for high-coercivity permanent magnets. The highest values for the coercive fields $\mu_0 H_c$ obtained so far are 0.6 T for melt-spun Sm-Fe-Ti alloys[13] and 0.48 T for Sm-Fe-Mo alloys that were prepared by mechanical alloying.[14]

In this paper we present the first *ab initio* self-consistent band-structure calculations of the electronic structure of hypothetical YFe_{12} and of transition-metal-

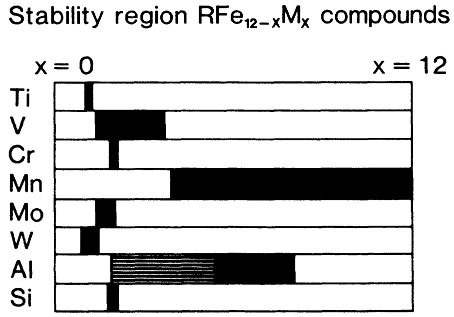

FIG. 1. Stability range of $R\mathrm{YFe}_{12-x}M_x$ compounds. In the shaded range ($2 \le x \le 6$) for M = Al, only metastable compounds have been prepared.

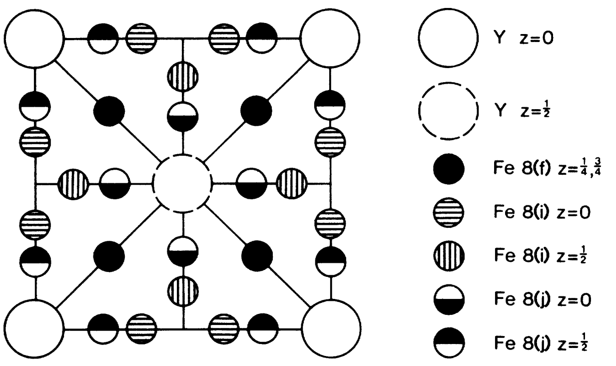

FIG. 2. Projection of the tetragonal unit cell of YFe_{12} in the $ThMn_{12}$ structure on the $z=0$ plane.

stabilized $YFe_{12-x}M_x$ ($M=$Ti, V, Cr, Mo, and W) compounds. Yttrium is chemically similar to the rare-earth elements but it is nonmagnetic, which gives us the opportunity to focus on the transition-metal contribution to the magnetic properties. The results can be compared with those obtained earlier for the stable Y-Fe compounds Y_2Fe_{17}, Y_6Fe_{23}, YFe_3, and YFe_2, and for hypothetical YFe_5.[15] A brief report on these results was given in Ref. 16. After replacing the atoms on one of the Fe sites by Ti, V, Cr, Mo, and W, the effect of the stabilizing elements on the magnetization was studied. The total and local moments obtained by these calculations are compared with the results of low-temperature magnetization measurements, neutron diffraction, and Mössbauer spectroscopy.

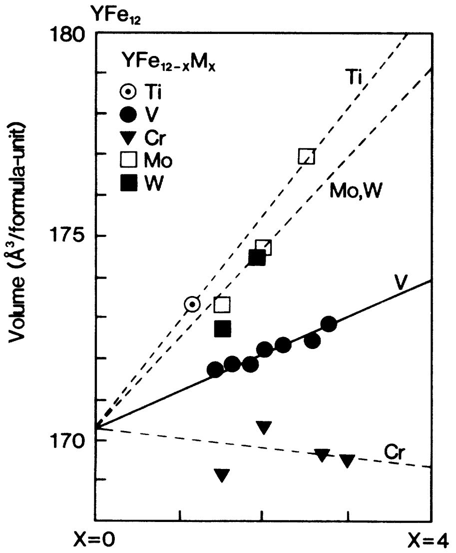

FIG. 3. Experimental composition dependence of the unit-cell volume of $YFe_{12-x}M_x$ compounds (from Ref. 1). The data for $M=$V have been used to estimate the volume of hypothetical YFe_{12} (solid line). The dashed lines indicate the extrapolations made to estimate the volume of the YFe_8M_4 compounds.

II. CRYSTAL STRUCTURE

In the body-centered-tetragonal $ThMn_{12}$ structure of hypothetical YFe_{12}, there are three inequivalent Fe sites–8(f), 8(i), and 8(j)—and one Y site, 2(a), which are indicated in the projection on the basal plane in Fig. 2. Substituted transition-metal atoms preferentially occupy the (i) site, as was observed by x-ray diffraction for Mo (Ref. 1) and by neutron diffraction for V (Ref. 17) and Ti.[18] Figure 3 shows the experimental variation of the unit-cell volume at room temperature with x for some M atoms. In the case of vanadium substitution, the volume varies linearly with x. From the best fit we have estimated the lattice parameters of hypothetical YFe_{12} (see Table I). The table also gives the nearest-neighbor distances of the atoms.

III. CALCULATIONAL METHOD

The band-structure calculations were performed using the augmented-spherical-wave (ASW) method of Williams, Kübler, and Gelatt.[19] Exchange and correlation were treated within the local-spin-density-functional (LDSF) approximation, using the form given by von

TABLE I. Lattice parameters of hypothetical YFe_{12}, refined positions of the inequivalent sites (Ref. 17), and nearest-neighbor distances up to 3.5 Å^3. Space group no. 139, $I4/mmm$.

$a=8.464$ Å
$c=4.754$ Å
$c/a=0.5617$
$V=170.3$ Å^3/formula-unit

Coordinates:	1(a) site (0,0,0)
	4(f) site $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$
	4(i) site $(x_1,0,0)$ $(x_1=0.3574)$
	4(j) site $(x_2,\frac{1}{2},0)$ $(x_2=0.2783)$

Surroundings of the atoms

Y(a):	4 Fe(i) at 3.025 Å
	8 Fe(f) at 3.028 Å
	8 Fe(j) at 3.220 Å
Fe(f):	2 Fe(f) at 2.377 Å
	4 Fe(j) at 2.439 Å
	4 Fe(i) at 2.592 Å
	2 Y(a) at 3.220 Å
Fe(i):	1 Fe(i) at 2.414 Å
	4 Fe(f) at 2.592 Å
	2 Fe(j) at 2.647 Å
	2 Fe(j) at 2.647 Å
	4 Fe(i) at 2.926 Å
	1 Y(a) at 3.025 Å
Fe(j):	4 Fe(f) at 2.439 Å
	2 Fe(i) at 2.640 Å
	2 Fe(i) at 2.647 Å
	2 Fe(j) at 2.654 Å
	2 Y(a) at 3.028 Å

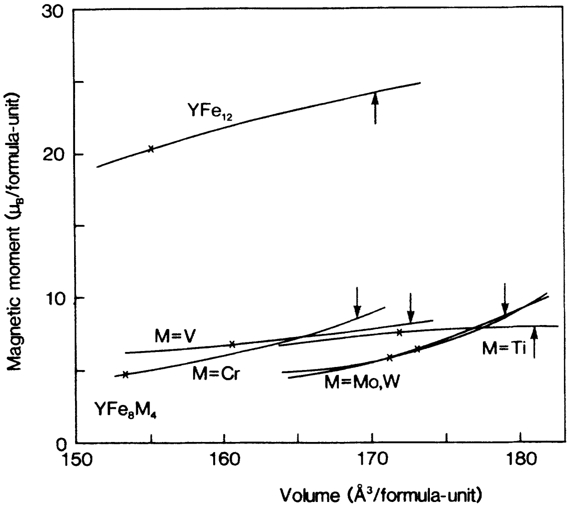

FIG. 4. Volume dependence of the calculated magnetic moment per formula unit of YFe_{12} and YFe_8M_4 compounds. Crosses denote the calculated equilibrium volumes. Arrows indicate the estimated experimental volumes.

Barth and Hedin,[20] with the parameters given by Janak.[21] The calculations were scalar relativistic, including mass-velocity and Darwin terms. Spin-orbit interaction was neglected.

In these self-consistent *ab initio* calculations the crystal is subdivided into overlapping spheres, centered around each atom, in which the potential is spherically symmetric. The total volume of the spheres must equal the unit-cell volume. Just as in our calculations of the stable binary Y-Fe compounds,[15,16] we performed calculations for YFe_{12} with the radius ratio $r_Y:r_{Fe}$ of Y and Fe spheres equal to 1.35. For all inequivalent Fe atoms the same sphere radius was used.

The effect of substitutions was investigated by calculations of the hypothetical compounds YFe_8M_4 (M = Ti, V, Cr, Mn, Mo, and W), in which the M atoms occupy the 8(i) sites competely. With this procedure, the symmetry of the $ThMn_{12}$ structure is not broken. We chose $r_M:r_{Fe}=1.11$, 1.06, 1.0, 1.0, 1.12, and 1.12 for M = Ti, V, Cr, Mn, Mo, and W, respectively, and in all cases $r_Y:r_{Fe}=1.35$ was used. The positions of the (i) and (j) sites, which have one coordinate that is not fixed by the space-group symmetry, were assumed to be equal to those obtained by neutron diffraction for $YFe_{10}V_2$ (see Table I). For all calculations a constant c/a ratio was used ($c/a=0.5617$).

IV. RESULTS

Figure 4 shows the calculated volume dependence of the total magnetic moment per formula unit of the hypothetical compounds YFe_{12} and YFe_8M_4 (M = Ti, V, Cr, Mo, and W). The experimental volumes and the total and local magnetic moments are given in Table II. In Fig. 4 the experimental volumes (estimated by extrapolation from the data in Fig. 3) are indicated by an arrow. It should be noted that for Ti, Mo, and W the uncertainty in this estimate is at least ±2 Å^3/formula-unit, and that in these cases the effect of distortions of the crystal structure (change of x_1, x_2, and c/a lattice parameters) on the calculated magnetization could be quite significant. The crosses in Fig. 4 indicate the magnetic moments at the equilibrium volumes that were obtained from a fit of the calculated total energy to a parabolic function.

A similar type of calculation as presented above was performed for YFe_8Mn_4. This compound exists (see Fig. 1), but its magnetic structure is not ferromagnetic or ferrimagnetic, but antiferromagnetic.[22] It has the same complex noncollinear structure as YMn_{12}. Just as in the case of Ti, V, Cr, Mo, and W, Mn atoms also show a strong preference for the 8(i) sites. A calculation for YFe_8Mn_4, which was started with a ferromagnetic spin configuration, resulted—after a large number of iterations—in a stable ferrimagnetic solution with the following magnetic moments on the Y, Fe(f), Mn(i), and Fe(j) sites: $-0.25\mu_B$, $1.52\mu_B$, $-1.78\mu_B$, and $1.84\mu_B$, respectively. The calculation was performed at the experimental unit-cell volume of YFe_8Mn_4 (171 Å^3/formula-unit). It should be noted that the calculations do not allow for noncollinear solutions. The results show that even if the spin structure had been ferrimagnetic instead of antiferromagnetic, Mn additions would have led to a very strong reduction of the total moment, because of the large antiparallel Mn moments.

Two important conclusions can be drawn from Fig. 4. First, the moment reduction by transition-metal substitutions is quite strong, but the dependence of the reduction

TABLE II. Total and local magnetic moments of YFe_{12} and YFe_8M_4 compounds, calculated at the experimental volume (V_{expt}, estimated by extrapolation from the data in Fig. 3). (f.u. denotes formula unit.)

	V_{expt} (Å^3/f.u.)	m_{calc} (μ_B/f.u.)	Local magnetic moments (μ_B/atom) Y(i)	Fe(f)	M(i)	Fe(j)
YFe_{12}	170.3	24.2	−0.39	1.86	2.32	2.26
YFe_8Ti_4	180.8	7.9	−0.34	1.42	−0.55	1.44
YFe_8V_4	174.0	8.4	−0.23	1.41	−0.57	1.48
YFe_8Cr_4	169.0	8.8	−0.22	1.41	−0.66	1.67
YFe_8Mo_4	179.0	8.9	−0.18	1.23	−0.23	1.40
YFe_8W_4	179.0	8.8	−0.17	1.23	−0.21	1.34

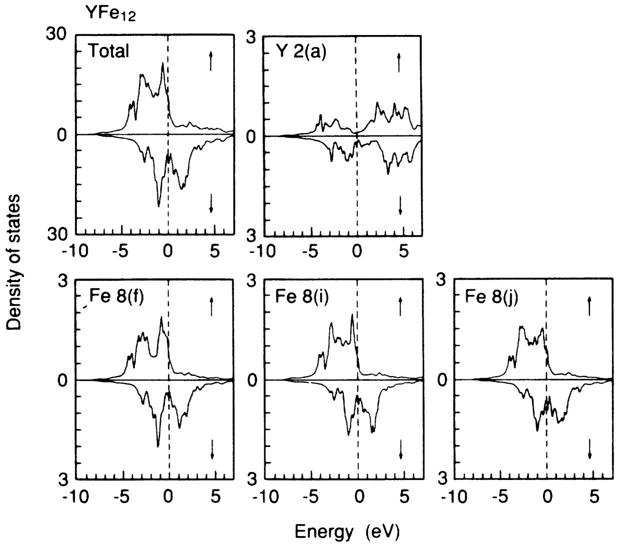

FIG. 5. Total density of states of YFe_{12}, and partial density of states at Y, Fe(f), Fe(i), and Fe(j) sites, calculated at the estimated experimental volume. The energy is taken with respect to the Fermi level (dashed line). Units: states/(eV formula-unit spin) for the total DOS and states/(eV atom spin) for the partial DOS.

on the type of M is weak. In the series M=Cr,V,Ti the calculated average moment at the experimental volumes decreases slightly. Second, the difference between the volume calculated by minimizing the total energy, and the experimental volume, is in some cases quite large. It varies from 3.4% for YFe_8W_4 to 9.3% for YFe_8Cr_4. Therefore, predictions of differences in the moment reduction would be quite different if they were based on the calculated volumes instead of on the experimental volumes. In the next section we compare the calculated moments with the experimental data and with local moments in some structurally related compounds.

In Fig. 5 the total and partial densities of states of YFe_{12} are shown. The compound can be classified as a weak ferromagnet, because the majority-spin band is not occupied completely. However, the moments at the (i) site are at the edge of strong ferromagnetism. Table II shows that the highest local moment ($2.32\mu_B$) was found at this site.

V. DISCUSSION

A. Average Fe moments in YFe_{12}

By an extrapolation of the experimental moments of $YFe_{12-x}V_x$ compounds, Verhoef *et al.* have estimated that the average moment m_{expt} per Fe atom of YFe_{12} is $2.08\mu_B$.[8] The calculated value at the experimental volume $m_{\text{calc}}(V_{\text{expt}})$ is $2.02\mu_B$, which is in good agreement with m_{expt}, particularly if one takes into account that the experimental total moment also contains a small orbital contribution m_{orb}. For YFe_{12} this contribution is not known, but from the order of magnitude of the experimental orbital moment in bcc-Fe ($0.09\mu_B$) and $LuFe_2$ ($0.07\mu_B$, Ref. 23), and the calculated orbital moments in Y_2Fe_{17} and $Nd_2Fe_{14}B$ [$(0.0-0.11)\mu_B$ Ref. 24] and $CeFe_2$ ($0.08\mu_B$, Ref. 25), it seems fair to estimate that the average orbital moment is $(0.05-0.10)\mu_B$ per Fe site in YFe_{12}.

If m_{orb} is approximately $(0.05-0.1)\mu_B$ in YFe_{12} the calculated average moment at the calculated volume, which is $1.71\mu_B$, is significantly too low. This is due to the underestimation of the volume. For Fe and most Y-Fe compounds, we found a difference between V_{calc} and V_{expt} of 6–7 %,[16] but for YFe_{12} the volume was underestimated by almost 9% (see Fig. 4). A first contribution to the underestimation of the volume is the incorrect treatment of exchange and correlation effects in strongly correlated electron systems (Fe sublattice) within the LSD approximation. A second contribution is related to the Y sublattice. In ASW as well as in full potential linearized augmented-plane-wave calculations[26] the volume of elemental hcp Y is underestimated by approximately 7%. As far as we know, this error is not understood at present. Other contributions to the volume error might be related to the use of the atomic-sphere approximation and to the use of values for the crystal-structure parameters c/a, x_1, and x_2 which were derived from $YFe_{10}V_2$. However, we found that the effects of small changes of these parameters within physically reasonable limits were much too small to explain the difference between V_{calc} and V_{expt}.

B. Moment reduction in $YFe_{12-x}M_x$ compounds

Table III gives the calculated and experimental moment reduction ($-\Delta\bar{m}/\Delta x$) in $YFe_{12-x}M_x$ compounds, due to replacement of Fe atoms by M atoms. The theoretical values were derived from calculations at the estimated experimental volume for hypothetic YFe_{12} and YFe_8M_4 (see Table II). The most accurate experimental values have been obtained for M=V, because $YFe_{12-x}V_x$ compounds exist in a large part of the interval $0 \le x \le 4$, and within this interval a linear relationship between m and x holds within the experimental accuracy.[8] For compounds containing Ti and W, which exist only in a small part of the interval $0 \le x \le 4$ close to $x=1$ (see Fig. 1), it is difficult to judge the validity of a comparison between the experimental values of $-\Delta\bar{m}/\Delta x$ and the theoretical values that were based on calculations for $x=0$ and 4. In these cases the largest differences between theory and experiment were found. The calculated increase in the moment reduction in the series Cr–V–Ti is qualitatively in agreement with the experimental trend.

It is of interest to compare the moment reduction in $YFe_{12-x}M_x$ compounds with the moment reduction in $Fe_{1-x}M_x$ bcc disordered solid solutions. In the latter systems also, the moment reduction increases in the series Cr–V–Ti. The average moment m varies approximately linearly with the average valence Z. Williams *et al.*[27] have emphasized that this is due to the average valence Z. Williams *et al.*[27] have emphasized that this is due to the pinning of the minority-spin Fermi level to the deep and broad central valley in the d band. The results of

TABLE III. (i) Moment reduction ($-\Delta\bar{m}/\Delta x$) in $YFe_{12-x}M_x$ compounds. (ii) Moment reduction in a model in which the number of minority-spin electrons is independent of x ($\Delta n\downarrow = 0$). (iii) Moment reduction in dilute bcc $Fe_{1-x}M_x$ disordered solid solutions.

$-\Delta\bar{m}/\Delta x$	(i) $YFe_{12-x}M_x$ (calc.)	$YFe_{12-x}M_x$ (expt.)	(ii) $\Delta n\downarrow = 0$	(iii) $Fe_{1-x}M_x$ (expt.)
M=Ti	4.2	4.9[a],6.0[b]	4	3.4(1)[c]
=V	4.0	4.4	3	3.2(3)[d]
=Cr	3.9	4.2[a]	2	2.3(2)[c]
=Mo	3.9			
=W	3.9	3.5[a]		

[a] Reference 8.

[b] Value obtained from the saturation magnetization M_s of $YFe_{11}Ti$, given by Bo-Ping Hu *et al.* (Ref. 29), using the extrapolated value of M_s of YFe_{12}, given by Verhoef *et al.* (Ref. 8).

[c] *Magnetic Properties of Metals*, Vol. 19a of *Landolt-Börnstein, Functional Relationships in Science and Technology*, edited by H. P. J Wijn (Springer, Berlin, 1986).

[d] M. V. Nevitt and A. T. Aldred, J. Appl. Phys. **34**, 463 (1963).

electronic-structure calculations of 3*d*-transition-metal impurities in Fe by Dederichs *et al.*[28] essentially support this view. A decrease of the impurity valence by one electron then leads to a decrease of the number of majority-spin electrons by one, whereas the number of minority-spin electrons remains constant ($\Delta n\downarrow = 0$). The values of $-\Delta\bar{m}/\Delta x$ which follow from this model have been given in the fourth column of Table III. The experimental values of $-\Delta\bar{m}/\Delta x$ for dilute bcc $Fe_{1-x}M_x$ solid solutions, which are given in the fifth column, agree fairly well with the predictions of the simple model, particularly for M=V and Cr, for which a large range of solutions exists.

For $YFe_{12-x}M_x$ compounds, the experimental differences in $-\Delta\bar{m}/\Delta x$ for M=Ti, V, and Cr, are much smaller than for the $Fe_{1-x}M_x$ alloys, and the absolute values of $-\Delta\bar{m}/\Delta x$ are all much larger. In the calculations we found an even smaller spread of values of $-\Delta\bar{m}/\Delta x$ around a value of 4.0. Figure 6 shows that in bcc Fe the valley between minority-spin bonding and antibonding 3*d* bonds is broader and deeper than in YFe_{12}. Therefore a strong-pinning model ($\Delta n\downarrow = 0$) does not yield such a good description of the variation of m with x for $YFe_{12-x}M_x$ compounds, as it does for $Fe_{1-x}M_x$ alloys.

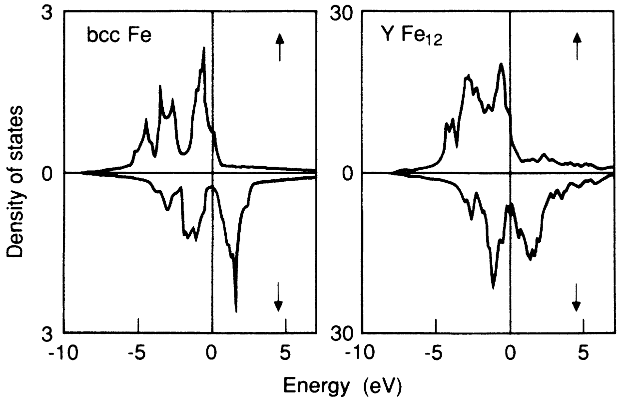

FIG. 6. Comparison of total density of states of bcc-Fe and YFe_{12} calculated at the experimental volume and at the estimated experimental volume, respectively.

The relatively large moment reduction in $YFe_{12-x}M_x$ compounds is partly due to the fact that the M atoms preferentially occupy the 8(i) sites, at which in YFe_{12} the highest-spin local moments are found. They are even higher than the spin moments in bcc Fe ($2.32\mu_B$ versus $2.12\mu_B$). In order to investigate this effect of preferential site occupation, we have performed two additional calculations for YFe_8V_4, with V atoms at the (f) and (j) sites, respectively. All crystal-structure parameters and Wigner-Seitz radii were kept the same. In Table IV a comparison of the calculated local moments and of the calculated moment reductions is given. As expected, the moment reduction is smaller for the hypothetical cases of preferential site occupation at the (f) or (j) sites. For $YFe_{10}V_2$ the magnetization with V atoms only at (i) sites is expected to be approximately 7% lower than in the case of V atoms only at (f) sites.

De Mooij and Buschow[1] have explained the preferential site occupation from a consideration of the free enthalpy. They showed that Y-M pair interactions are

TABLE IV. Results of band-structure calculations for hypothetical YFe_8V_4 compounds, with V at 8(f), 8(i), and 8(j) sites. Local moments m and the total moment per formula unit, m_{tot}, are given in μ_B. The method for calculating the moment reduction $-\Delta\bar{m}/\Delta x$ has been discussed in the text.

	V-atom position 8(f)	8(i)	8(j)
m(a)	−0.19	−0.23	−0.12
m(f)	−0.66	1.41	1.41
m(i)	1.85	−0.57	1.93
m(j)	1.62	1.48	−0.72
m_{tot}	10.48	8.36	10.00
$-\Delta\bar{m}/\Delta x$	3.4	4.0	3.6

expected to contribute positively to the free enthalpy, whereas Fe—M bonds stabilize YFe$_{12-x}M_x$ compounds. Using Table I, it can be easily seen that a preferential occupation of M atoms at (i) sites minimizes the number of direct Y—M bonds, and maximizes the number of Fe—M bonds. As a consequence of the large number of direct Y—Fe bonds if M atoms occupy only (i) sites, the induced magnetization of the Y atoms is more negative than for the other types of preferential site occupation (see Table IV), in spite of the fact that in this case the total magnetization is relatively low. In the case of rare-earth atoms at the Y sites, the strongest R-Fe coupling is therefore found for M atoms at the (i) site. This is expected to lead to a relatively large contribution of the R atoms to the total magnetization and the magnetocrystalline anisotropy at room temperature. Since we cannot discuss this issue more quantitatively at present, it is difficult to judge whether this advantage of an (i)-site preference for M atoms is of more importance than the disadvantage related to the relatively large moment reduction.

C. Local magnetic moments

It is interesting to compare the local moments calculated for YFe$_{12}$ with those calculated for YFe$_5$ and Y$_2$Fe$_{17}$ (see Ref. 15). Y$_2$Fe$_{17}$ and YFe$_{12}$ can be formed by replacing one-third or one-half, respectively, of the Y atoms in YFe$_5$ by a so-called dumbbell pair of Fe atoms. Figure 7 shows that the size order of the moments (with respect to their magnitude) can be understood well from the structural relations with (hypothetical) YFe$_5$. In YFe$_{12}$, for example, the 8(i) sites are derived partly from the dumbbell sites and partly from 2(c) sites in YFe$_5$. In Y$_2$Fe$_{17}$, as well as in YFe$_{12}$, sites of this type have the largest moments. The order of the calculated magnetic moments in Y$_2$Fe$_{17}$ is in good agreement with the results of spin-polarized neutron diffraction on a Lu$_2$Fe$_{17}$ single crystal.[30]

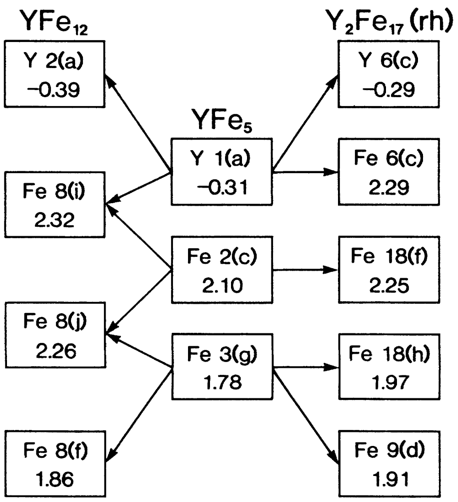

FIG. 7. Schematic diagram of structural relations between YFe$_5$, Y$_2$Fe$_{17}$, and YFe$_{12}$ in the CaCu$_5$, Th$_2$Zn$_{12}$, and ThMn$_{12}$ structures, respectively, and local magnetic moments in μ_B, calculated at the experimental volumes.

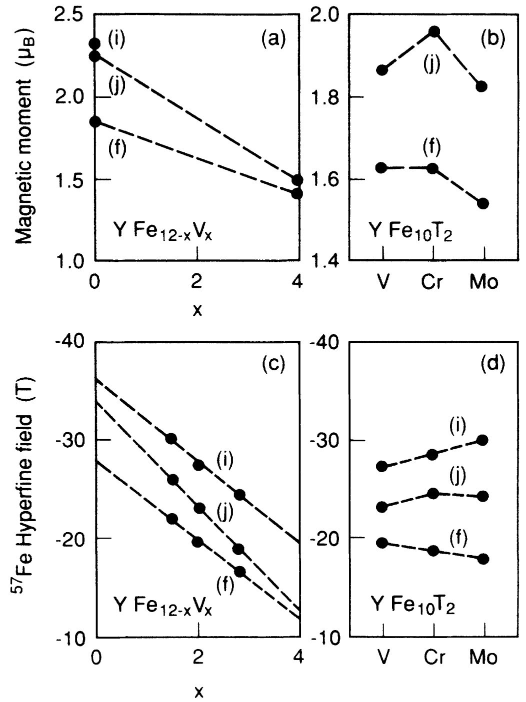

FIG. 8. (a) Calculated Fe moments in YFe$_{12}$ and YFe$_8$V$_4$; (b) Fe moments in YFe$_{10}$T$_2$ compounds, obtained by interpolation between calculated moments in YFe$_{12}$ and YFe$_8T_4$; (c) experimental average hyperfine fields in YFe$_{12-x}$V$_x$ compounds (Ref. 33); (d) experimental average hyperfine fields in YFe$_{10}T_2$ compounds (Ref. 33).

Neutron-powder-diffraction experiments for YFe$_{12-x}M_x$ compounds have not yet led to a conclusion about the precise size of the average moments at the (f), (i), and (j) sites. The range of values that was obtained for these moments in RFe$_{10}$V$_2$ compounds (R=Y,Nd,Tb,Dy,Ho,Er) (Refs. 17, 31, and 32) is $(1.6–2.0)\mu_B$, $(1.15–2.0)\mu_B$, and $(1.5–2.0)\mu_B$, respectively. Due to the low concentration of R atoms, only a small variation of the local Fe moments due to R-Fe coupling is expected. This is supported by the results of Mössbauer spectroscopy on RFe$_{10}$V$_2$ compounds.[33] From a linear interpolation between the band-structure calculations of YFe$_{12}$ and YFe$_8$V$_4$, the average local spin moments in the (f) and (j) sites in YFe$_{10}$V$_2$ are expected to be approximately $1.6\mu_B$ and $1.9\mu_B$, respectively. It is not yet possible to judge the validity of this prediction from the neutron-diffraction results. The calculations show that the V moments at (i) sites have a large negative spin polarization. This might explain the small values of the effective (i) magnetic moment found by neutron diffraction for some of the RFe$_{10}$V$_2$ compounds.

^{57}Fe Mössbauer spectroscopy of YFe$_{12-x}$V$_x$ compounds was performed by Denissen *et al.*[33] In Figs. 8(c) and 8(d) the average hyperfine fields at 4.2 K in

$YFe_{12-x}V_x$ compounds and $YFe_{10}T_2$ compounds (T=V,Cr,Mo), respectively, are shown. Whereas the highest hyperfine field could be assigned with certainty to the (i) site, an assignment of the two lower hyperfine fields to the (f) and (j) site cannot be based on the results from Mössbauer spectroscopy alone, because the total intensity of the subspectra and the statistical distribution of V neighbors is equal for both sites (see Table I). In Fig. 8(a) the calculated Fe moments for YFe_{12} and YFe_8V_4 are given. A linear decrease of the (f) and (j) moments is suggested by the dashed line. If it is assumed that the hyperfine fields increase with increasing local moment, a comparison between Figs. 8(a) and 8(c) shows that a good qualitative agreement between theory and experiment is obtained by assigning the lowest hyperfine fields to the 8(f) site. Also, the variation of the hyperfine fields at (f) and (j) sites in $YFe_{10}T_2$ (T=V, Cr, Mo) is described well by the calculations of this assignment is made. The local moments given in Fig. 8(b) were obtained by a linear interpolation between the calculated values for YFe_{12} and YFe_8T_4 compounds.

Often the experimental hyperfine fields are converted to local moments by means of a constant conversion factor, which is equal to the ratio of the average hyperfine field to the average magnetic moment per Fe atom.[34,35] Within such a procedure the induced moments at the Y site are neglected. In spite of the good agreement of the trend (with respect to x) and the order of the calculated local moments and the hyperfine fields at the different symmetry sites, we should emphasize that in reality only the main contribution to the hyperfine field, the contribution from the spin density at the nucleus due to 1*s*, 2*s*, and 3*s* core shells, is proportional to the local 3*d*-spin magnetic moment. Other important contributions are (i) the contribution of the orbital moment, and (ii) the contribution from the spin density at the nucleus due to 4*s* valence electrons, which is partly determined by the interaction with the nearest-neighbor atoms. We are currently calculating the size of the latter contributions for a large number of binary compounds which contain Fe. I plan to discuss the results in a separate paper.[36]

VI. CONCLUDING REMARKS

One of the aims of the work presented in this paper was to investigate how much it is possible to predict from *ab initio* calculations the magnetic properties of the hypothetical compounds YFe_{12} and the decrease of the magnetization due to substitutions which stabilize this compound in the $ThMn_{12}$ structure. Reliable predictions would be of great help as a guideline or experimental work. The results in the present paper show that in this respect the calculations are unsuccessful. The main reason for this is that YFe_{12} and the $YFe_{12-x}M_x$ compounds are weak ferromagnets, in the sense that the majority-spin 3*d* band is not completely occupied. Therefore, magnetization is quite sensitive to relatively small changes of the lattice parameters and the unit-cell volume. Due to the underestimation of the unit-cell volume, for which some possible explanations were given in Sec. V, the calculated magnetization of YFe_{12} at the calculated equilibrated volume is significantly lower than the estimated experimental value. Furthermore, for the YFe_8M_4 compounds calculations at the calculated equilibrium volumes predict an increase of the magnetization in the series Cr–V–Ti, whereas experimentally a decrease is observed.

For YFe_{12} as well as for the YFe_8M_4 compounds the agreement between the calculated and the experimental total magnetization is good if the volumes obtained by extrapolation of experimental data for the $YFe_{12-x}M_x$ compounds are used. In YFe_{12} large moments are found at the 8(i) and 8(j) sites ($2.32\mu_B$ and $2.26\mu_B$), and smaller moments at the 8(f) sites ($1.86\mu_B$). The order of the calculated local moments is consistent with the calculated moments we obtained previously for the structurally related compounds Y_2Fe_{17} and hypothetical YFe_5. Neutron-powder-diffraction experiments on $RFe_{10}V_2$ compounds reported in the literature have not yet led to a precise determination of the local moments. The analysis is complicated by the large number of structural and magnetic degrees of freedom. It would be of interest to perform spin-polarized neutron diffraction at low temperature on a series of $YFe_{12-x}V_x$ single crystals, in order to verify the predictions concerning the local moments which were given in this paper.

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[1] D. B. de Mooij and K. H. J. Buschow, J. Less-Common Met. **136**, 207 (1988). K. H. J. Buschow and D. B. de Mooij, in *Concerted European Action on Magnets*, edited by I. V. Mitchell, J. M. D. Coey, D. Givord, I. R. Harris, and R. Hanitsch (Elsevier Applied Science, London, 1989), p. 63.

[2] K. Ohashi, T. Yokoyama, R. Osugi, and Y. Tawara, IEEE Trans. Magn. **MAG-23**, 3101 (1987).

[3] K. Ohashi, Y. Tawara, R. Osugi, J. Sakurai, and Y. Komura, J. Less-Common Met. **139**, L1 (1988).

[4] A. Müller, J. Appl. Phys. **64**, 249 (1988).

[5] Y. C. Yang, B. Kebe, W. J. James, J. Déportes, and W. Yelon, J. Appl. Phys. **52**, 2077 (1981).

[6] I. Felner, J. Less-Common Met. **72**, 241 (1980); I. Felner, I. Nowik, and M. Seh, J. Magn. Magn. Mater. **38**, 172 (1983); I. Felner, M. Seh, M. Rahavy, and I. Nowik, J. Phys. Chem. Solids **42**, 369 (1981).

[7] Wang Xiang-Zhong, B. Chevalier, T. Burlureau, J. Etourneau, J. M. D. Coey, and J. M. Cadogan, J. Less-Common Met.

138, 235 (1988).

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

[9] M. W. Dirken, R. C. Thiel, and K. H. J. Buschow, J. Less-Common Met. **146**, L15 (1989).

[10] Hong-Shuo Li, Bo-Ping Hu, J. P. Gavigan, J. M. D. Coey, L. Pareti, and O. Moze, J. Phys. (Paris) Colloq. **49**, C8-541 (1988).

[11] For $SmFe_{10}V_2$, $H_A \simeq 8$ T was found [D. B. de Mooij (private communication)].

[12] M. Solzi, L. Pareti, O. Moze, and W. I. F. David, J. Appl. Phys. (to be published).

[13] J. Ding and M. Rosenberg, J. Magn. Magn. Mater. **80**, 105 (1989).

[14] L. Schultz and J. Wecker, J. Magn. Magn. Mater. **80**, 115 (1989).

[15] R. Coehoorn, Phys. Rev. B **39**, 13 072 (1989).

[16] R. Coehoorn, J. Phys. (Paris) Colloq. **49**, C8-301 (1988).

[17] R. B. Helmhodt, J. J. Vleggaar, and K. H. J. Buschow, J. Less-Common Met. **138**, L11 (1988).

[18] O. Moze, and L. Pareti, M. Solzi, and W. I. F. David, Solid State Commun. **66**, 465 (1988).

[19] A. R. Williams, J. Kübler, and C. D. Gellat, Jr., Phys. Rev. B **19**, 6094 (1979).

[20] U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[21] J. F. Janak, Solid State Commun. **25**, 53 (1978).

[22] Y. C. Yang, B. Kebe, W. J. James, J. Déportes, and W. Yelon, J. Appl. Phys. **52**, 2077 (1981).

[23] D. Givord, A. Gregory, and J. Schweizer, J. Magn. Magn. Mater. **15-18**, 293 (1980).

[24] B. Szpunar, J. Less-Common Met. **127**, 55 (1987).

[25] O. Eriksson, L. Nordström, M. S. S. Brooks, and B. Johansson, Phys. Rev. Lett. **60**, 2523 (1988).

[26] G. H. O. Daalderop and H. J. F. Janssen (private communication).

[27] A. R. Williams, V. L. Moruzzi, A. P. Malozemoff, and K. Terakura, IEEE Trans. Magn. **MAG-19**, 1983 (1983).

[28] P. H. Dederichs, H. Akai, S. Blügel, N. Stefanou, and R. Zeller, in *Alloy Phase Stability*, edited by G. M. Stocks and A. Gonis (Kluwer, Dordrecht, The Netherlands, 1989), p. 377.

[29] Bo Ping Hu, Hong-Shuo Li, J. P. Gavigan, and J. M. D. Coey, J. Phys. Condens. Matter (to be published).

[30] D. Givord, Ph.D. thesis, Université de Grenoble, 1973.

[31] R. B. Helmholdt, J. J. M. Vleggaar, and K. H. J. Buschow, J. Less-Common Met. **144**, 209 (1988).

[32] W. G. Haije, R. B. Helmholdt, A. Spijkerman, F. R. de Boer, and K. H. J. Buschow, J. Less-Common Met. (to be published).

[33] C. J. M. Denissen, R. Coehoorn, and K. H. J. Buschow, J. Magn. Magn. Mater (to be published).

[34] P. C. M. Gubbens, J. H. J. van Apeldoorn, A. M. van der Kraan, and K. H. J. Buschow, J. Phys. F **4**, 921 (1974).

[35] R. Fruchart, P. L'Heritier, P. Dalmas de Réotier, D. Fruchart, P. Wolfers, J. M. D. Coey, L. P. Ferreira, R. Guillen, P. Vulliet, and A. Yaouanc, J. Phys. F **17**, 483 (1987).

[36] R. Coehoorn (unpublished).