Magnetization and ^{57}Fe hyperfine fields in $Y_2Fe_{17}Z_{3-\delta}$ (Z = H, C, or N) interstitial compounds

Qi-nian Qi, Hong Sun, R. Skomski, and J. M. D. Coey
Department of Pure and Applied Physics, Trinity College, Dublin 2, Ireland
(Received 26 December 1991)

Measured magnetization and ^{57}Fe hyperfine fields at $T \sim 0$ K for Y_2Fe_{17} and $Y_2Fe_{17}Z_{3-\delta}$, with Z=H, C, or N and $\delta \sim 0.5$, are analyzed to determine the influence of the interstitial atoms on the 3*d* magnetism. All are weak ferromagnets with a nearly-full 3*d* subband, although when Z=N, the magnetic moment of $38.1\mu_B$ is very close to the fully saturated value of $39.4\mu_B$. On a local scale, the order of hyperfine fields $B_{hf}^{4f}(=35\ T) > B_{hf}^{6g}(=33\ T) > B_{hf}^{12j}(=30\ T) > B_{hf}^{12k}(=28\ T)$ is different from that of the local magnetic moments given by several recent band calculations for Y_2Fe_{17}, $\mu^{4f}(=2.5\mu_B) > \mu^{12j}(=2.2\mu_B) > \mu^{12k}(=2.0\mu_B) > \mu^{6g}(=1.9\ \mu_B)$, reflecting a large 4*s*-transferred hyperfine field at 6g sites which have very short Fe-Fe distances. The volume of samples with Z=C and N are identical, and so the chemical effects of the interstitials can be distinguished; both the local magnetic moment and hyperfine fields are systematically smaller in the carbide than the nitride by 5% and 12%, respectively.

I. INTRODUCTION

The ability of rare-earth (R) –3*d*-transition-metal (T) intermetallics to absorb large quantities of certain main-group atoms (Z) in a gas-phase reaction at temperatures ~500 °C, thereby forming expanded R-T-Z interstitial compounds, offers the prospect of tuning the magnetic properties by *gas-phase interstitial modification.*[1] The changes in magnetic properties are greatest for the iron compounds, where the Curie temperature T_C increases, for example, from 325 K in Y_2Fe_{17} to 694 K in $Y_2Fe_{17}N_{2.6}$.[2] Similar increases are found for other 2:17 rare-earth iron nitrides[3,4] and carbides[5–7] prepared by the gas-phase interstitial modification process. The process is also effective for other R-T structure types such as 1:12,[8–10] 6:23,[11] and 1:7.[12]

A large body of literature exists on R-T hydrides.[13] The increases of Curie temperature are smaller for the R_2Fe_{17} hydrides (150 K)[14,15] than for the nitrides and carbides, but there are analogies and differences in the absorption and/or disproportionation behavior[16] as well as the changes in magnetic properties which make for an interesting comparison.

Here we focus on the Y_2Fe_{17} interstitial compounds where yttrium acts as a "nonmagnetic" rare earth, in order to study the influence of the interstitials on the 3*d* magnetism. Y_2Fe_{17} is a ferromagnet with *c*-plane anisotropy having the hexagonal Th_2Ni_{17} structure, illustrated in Fig. 1. Like the closely related rhombohedral Th_2Zn_{17} structure, the hexagonal Th_2Ni_{17} structure is derived from $CaCu_5$ by ordered substitution of Fe_2 dumbbell-shaped structures on one third of the Ca sites, but the stacking sequence differs in the two 2:17 polytypes which are close in energy. Furthermore there may be some deviation from the ideal one third of Fe_2 (4f) dumbbell-shaped molecules,[17] so the formula would then be $Y_{2-x}Fe_{17+2x}$, with $|x| \leq 0.1$. The defect structure of any given sample will reflect its thermal history, and this may introduce small differences in the intrinsic magnetic properties.

Numerous structural studies have been conducted to locate the interstitial nitrogen in $R_2Fe_{17}N_{3-\delta}$, including EXAFS for R = Sm,[18,19] and neutron diffraction for R = Y,[20–22] Pr,[23] and Nd.[20–22,24] Nitrogen has a neutron scattering length $b_N = 0.93 \times 10^{-12}$ cm which makes it easy to locate accurately. All the studies indicate that nitrogen is predominantly on the 6h octahedral sites in the hexagonal structure (9e sites in the rhombohedral structure). The best fit of high resolution powder data has been obtained with exclusive occupancy of these sites in the Pr compound.[23] In the case of Y, Ibberson *et al.* placed 12% of the N on the 12i site,[20] whereas, Yang *et al.*[21] and Jaswal *et al.*[22] reported exclusive 6h site occupation.

No structural studies of fully loaded carbides have

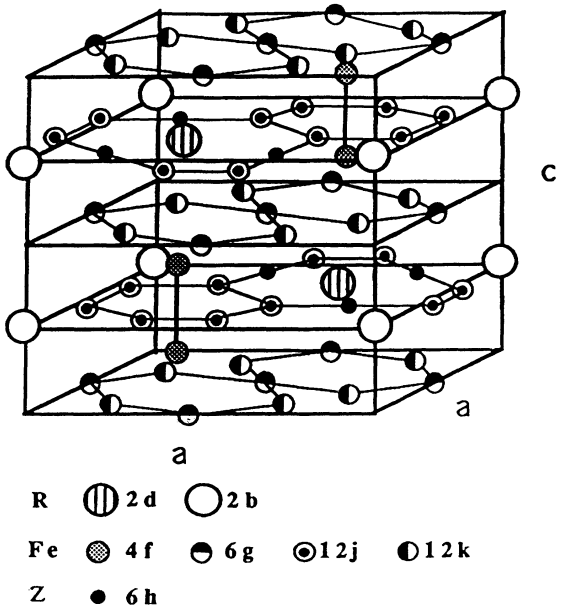

FIG. 1. Hexagonal structure of Y_2Fe_{17} showing the 6h interstitial site.

TABLE I. Structural and magnetic properties for Y_2Fe_{17} and $Y_2Fe_{17}Z_{3-\delta}$ (Z=H, C, or N) compounds.

Compound	a (nm)	c (nm)	V (nm^3)	T_C (K)	M (μ_B/f.u.)
Y_2Fe_{17}	0.848	0.826	0.514	325	32.8
$Y_2Fe_{17}H_{2.7}$	0.854	0.829	0.524	475	31.8
$Y_2Fe_{17}C_{2.2}$	0.866	0.840	0.546	660	36.1
$Y_2Fe_{17}N_{2.5}$	0.865	0.844	0.547	694	38.1

been published. Early x-ray diffraction studies on $R_2Mn_{17}C_{3-\delta}$ with $\delta\sim2$ showed octahedral site occupancy for carbon.[25,26] A neutron study by Helmholdt and Bushcow[27] on a sample with R=Nd and $\delta\sim2.5$ prepared from the melt also indicates exclusive octahedral site occupancy for the interstitial carbon atoms. The interstitial site occupancy in the hydrides is rather different. Neutron studies by Isnard *et al.* on deuterated material for R=Ce, Nd, Ho,[28] and Pr[29] showed that hydrogen occupies both octahedral 6h (9e) and tetrahedral 12i (18g) sites in almost equal proportions.

Here we examine the total and local magnetization and Curie temperature of Y_2Fe_{17}, and study the influence of interstitials on these properties. Most results are given for carbide and nitride samples with a high degree of 6h site occupancy ($\sim$80%), and a hydride with a similar number of interstitial atoms.

II. EXPERIMENTAL METHODS

The Y_2Fe_{17} alloy was first made by arc melting 3N pure metals, and annealing in vacuum at 1000 °C for 50 h. The nitride was prepared by exposing small quantities ($\sim$50 mg) of finely ground powder in 1 bar of nitrogen at 550 °C for about 3 h, as described previously.[2,3] The carbide was prepared by heating the powder for 2 h at 550 °C in 1 bar of butane in the thermopiezic analyzer,[30] and then pumping to remove any hydrogen or unreacted butane before cooling. A similar procedure was carried out for Y_2Fe_{17} with hydrogen in the thermopiezic analyzer to prepare the hydride, except that heating was for half an hour at 250 °C in 1 bar of hydrogen. The nitrogen content of the nitride was deduced from the pressure drop observed in the thermopiezic analyzer on cycling back to room temperature to be $x=2.5\pm0.2$. The hydrogen content of the hydride was determined by the same method to be $x=2.7\pm0.2$. The carbon content of the carbide was determined by pressure change or weighing to be $x=2.2\pm0.2$.

The hydride was essentially an expanded pure phase, whereas the carbide and nitride contained in addition traces ($<5\%$) of poorly crystallized α-Fe, which is a product of the disproportionation reaction that follows carbon and nitrogen absorption.[31] By x-ray diffraction the crystal structures of the nitride, carbide, and hydride were similar to the Th_2Ni_{17}-type hexagonal structure of their parent compound.

Magnetization measurements were made using a vibrating-sample magnetometer (VSM), calibrated with a 50-mg Ni sphere; an axial magnetic field of up to 5 T was produced by a superconducting magnet or a transverse

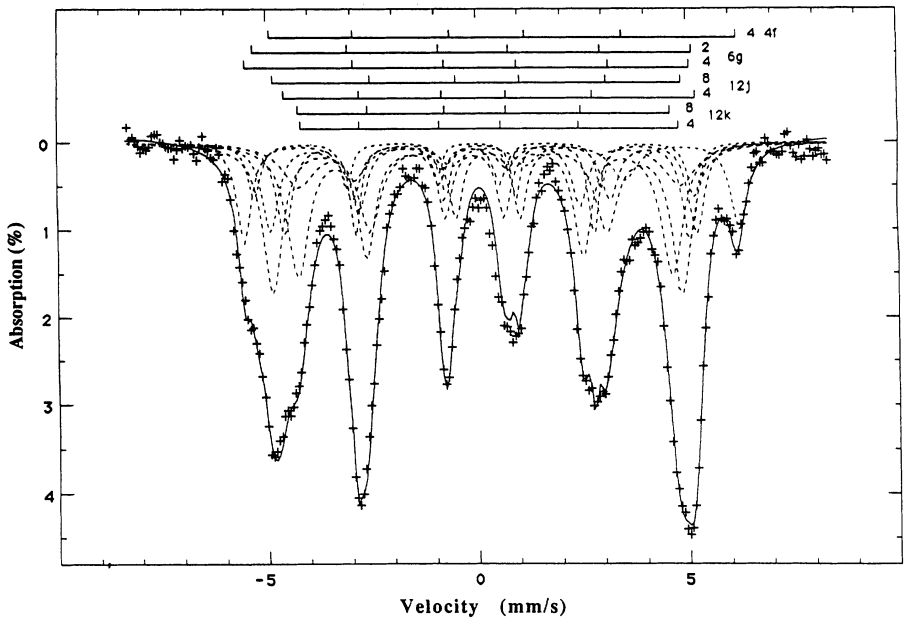

FIG. 2. The ^{57}Fe Mössbauer spectrum of Y_2Fe_{17} at 15 K with the fit shown as a full curve. The broken lines refer to subspectra proposed for the four inequivalent Fe sites.

TABLE II. Hyperfine fields for each crystallographic site of Y_2Fe_{17} and $Y_2Fe_{17}Z_{3-\delta}$ (Z = H, C, or N) deduced from ^{57}Fe Mössbauer spectra.

Compound	Temp. (K)	4f	6g	12j	12k	$\langle B_{hf} \rangle$ (T)
Y_2Fe_{17}	15	34.6	32.9	29.7	28.2	30.3
	293	18.5	14.8	10.8	3.0	9.7
$Y_2Fe_{17}H_{2.7}$	15	34.6	29.6	29.3	26.8	29.1
	293	28.1	24.5	23.4	21.9	23.6
$Y_2Fe_{17}C_{2.2}$	15	36.3	34.1	30.8	26.5	30.5
	293	33.4	30.6	25.7	23.2	26.6
$Y_2Fe_{17}N_{2.5}$	15	40.1	36.7	35.0	31.9	34.8
	293	37.1	33.9	31.2	29.1	31.6

magnetic field of 1.5 T was produced by an electromagnet. Curie temperatures were deduced from thermomagnetic scans in a fixed field of 4 mT. The Mössbauer spectra were obtained using a constant acceleration spectrometer with a 20-mCi source of ^{57}Co in rhodium. The samples consisted of about 20 mg/cm^2 of $Y_2Fe_{17}Z_{3-\delta}$ powder mixed with icing sugar to form homogeneous and isotropic absorbers. The velocity scale was calibrated using an α-Fe absorber at room temperature. Sample temperature was either room temperature (293 K) or 15 K ($T \sim 0$ K), obtained with a closed-cycle two-stage helium refrigerator (Air Products HC-2).

Mössbauer spectra were fitted to seven or eight independent Lorentzian magnetic sextets corresponding to the four inequivalent Fe sites; 6g, 12j, and 12k sites are fitted with two subspectra with intensity ratio 2:1 corresponding to groups of magnetically inequivalent sites when the direction of magnetization lies perpendicular to the c axis.[32,33] The same 1:2:4:2:4:2:2 intensity constraint for the $I^{6g_1}:I^{6g_2}:I^{12j_1}:I^{12j_2}:I^{12k_1}:I^{12k_2}:I^{4f}$ site intensities was previously used to fit Mössbauer spectra of R_2Fe_{17}[33] and $R_2Fe_{17}Z_{3-\delta}$ (Z = N, ^{33}C[34]). Linewidths of outer, middle, and inner pair of lines were allowed to vary independently to take account of a small distribution in hyperfine fields due to defects in the structure. These linewidths were all in the range 0.15–0.36 mm/s full width at half maximum, in the order of $\Gamma_{3,4} < \Gamma_{2,5} < \Gamma_{1,6}$.

III. RESULTS

Results on the unit cell parameters, Curie temperature, and magnetization are brought together in Table I, where it can be seen that the lattice expansion of the nitride and carbide are very similar (6% volume expansion). The nitride has a slightly larger Curie temperature and magnetization at $T = 4.2$ K, expressed in Bohr magnetons/(formula unit). In either case, the magnetization increases by 10–15 %, whereas the Curie temperature increase is more than 100%. The effects of hydrogen are different. The volume expansion is only 2%, the Curie temperature increases by 46%, and the magnetization actually falls.

Figure 2 shows the Mössbauer spectrum of Y_2Fe_{17} at 15 K, together with details of the fit to seven Lorentzian sextets for the four crysallographic sites. In the fit, the intensities of the components are constrained as described above. Each pair of sextets for the 6g, 12j, or 12k sites has the same isomer shift, but a different quadrupole splitting and hyperfine field due to the magnetization lying along one of three equivalent symmetry directions in the plane. Table II lists the average hyperfine field at each site, and the overall average. The order is $B_{hf}^{4f} > B_{hf}^{6g} > B_{hf}^{12j} > B_{hf}^{12k}$. In view of the calculated moments following the order $\mu^{4f} > \mu^{12j} > \mu^{12k} > \mu^{6g}$ (see Discussion in the next section) we also sought an acceptable fit to the data with the hyperfine fields in this order, but it could not be achieved. The goodness of fit parameter χ^2 was 1.02 per degree of freedom for the fit of Fig. 2, and significantly larger ($\chi^2 > 1.54$) for any fit that respected the order of the moments.

Figure 3 shows Mössbauer spectra for the interstitial compounds at 15 K and room temperature. The same fitting procedure and constraints were applied as for Y_2Fe_{17}, including variable linewidths allowed to reflect variations in local environment resulting from incompletion of site occupancy by C or N. Trends for the isomer shifts and hyperfine fields at the four sites across the series are shown in Fig. 4.

TABLE III. Magnetic moments and hyperfine field in Y_2Fe_{17} and $Y_2Fe_{17}Z_{3-\delta}$ (Z = H, C, or N).

Compound	m (μ_B/f.u.)	m_{Fe} (μ_B/Fe)	B_{hf} (T)	B_{cp} (T)	B_{4s} (T)	B_{orb} (T)	B_{hf}/m_{Fe} (T/μ_B)
Y_2Fe_{17}	32.8	1.98	−30.3	−22.4	−9.4	1.5	−15.3
$Y_2Fe_{17}H_{3-\delta}$	31.8	1.92	−29.1	−21.7	−8.9	1.5	−15.2
$Y_2Fe_{17}C_{3-\delta}$	36.1	2.17	−30.5	−24.5	−6.8	0.8	−14.1
$Y_2Fe_{17}N_{3-\delta}$	38.1	2.29	−34.8	−25.9	−9.7	0.8	−15.2

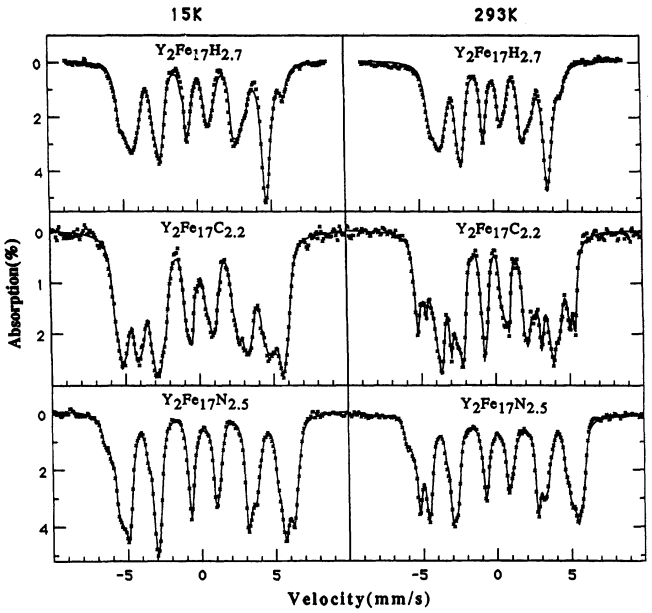

FIG. 3. The ^{57}Fe Mössbauer spectra of $Y_2Fe_{17}Z_{3-\delta}$ (Z=H, C, or N) at 15 and 293 K with fits shown as full curves.

It is difficult to assert that fits to any such complicated Mössbauer spectra are definitive, but those we present have the virtue of obeying the crystallographic constraints and providing consistent trends across the series which are capable of physical interpretation.

IV. DISCUSSION

A. Bulk magnetization

A useful starting point in the discussion of the magnetization of 3d intermetallics is the idea of strong ferromagnetism, which provides an upper limit to the magnetic moment that can be expected, given the number of electrons in the compound. A strong ferromagnet has the $3d\uparrow$ states fully occupied. When they are only partially occupied, the compound is a weak ferromagnet. The moment corresponding to strong ferromagnetism can be obtained from the *magnetic valence model,*[35] assuming the constituents contribute to a common *spd* band structure. The magnetic valence is defined as $Z_m = 2N_d^{\uparrow} - Z_c$, where $N_d^{\uparrow}=0$ for Y, 5 for Fe and Z_c is the chemical valence; $Z_c=3$ for Y and 8 for Fe. The average moment per atom is then $\langle m \rangle = \langle Z_m \rangle + 2N_{sp}^{\uparrow}$, where $\langle Z_m \rangle$ is the average magnetic valence per atom and $N_{sp}^{\uparrow}$ is the occupancy of the unpolarized *sp* band, supposed to be ~ 0.3. For Y_2Fe_{17}, this yields a moment corresponding to strong ferromagnetism of $39.4\mu_B$, which is somewhat greater than the observed value of $32.8\mu_B$ obtained by extrapolating the data obtained on free powder to $1/B_0^2=0$, or the single-crystal value of $34.2\mu_B$.[17] This indicates, and detailed band calculations[36–40] confirm, that the $3d\uparrow$ states are not completely full in Y_2Fe_{17}, which is therefore a weak ferromagnet.

Applying the magnetic valence model to the interstitial compounds leads to a problem. Taking $Z_c=1$, 4, and 5 for H, C, and N yields moments of $38.2\mu_B$, $29.2\mu_B$, and $26.2\mu_B$ for the $Y_2Fe_{17}Z_3$ compounds, whereas the observed values (Table I) are actually greater. The assumption of a common band structure with a small Z_{sp} occupancy is blamed. It is more reasonable to consider the nitrogen or carbon electrons in a separate atomic level far below the Fermi level.[39] All the interstitial compounds then appear as weak ferromagnets, although the moment of the nitride, $38.1\mu_B$, is very close to that expected for fully saturated, strong ferromagnetism ($39.4\mu_B$), as the $3d\uparrow$ band is very nearly full. No further volume expan-

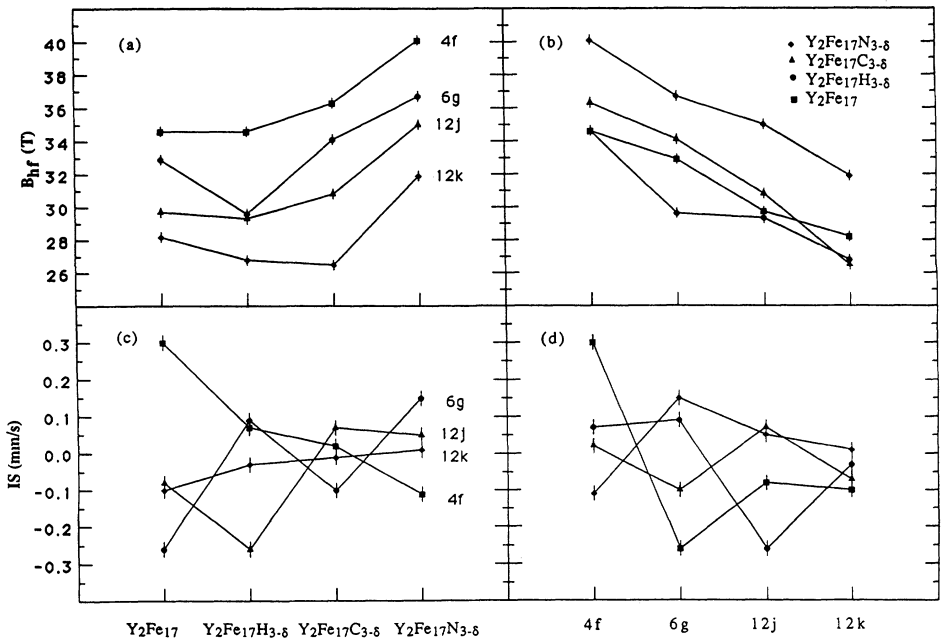

FIG. 4. Average hyperfine fields [(a) and (b)] and isomer shifts (relative to metallic iron) [(c) and (d)] at four inequivalent Fe sites for Y_2Fe_{17} and $Y_2Fe_{17}Z_{3-\delta}$ (Z=H, C, or N), measured at 15 K.

TABLE IV. Calculated atomic moments in Y_2Fe_{17} (in units of μ_B/atom).

Method	4f Fe	6g Fe	12j Fe	12k Fe	2b,2d Y	Average Fe moment	Ref.
TB Recursion	2.31	1.55	1.86	1.79		1.83	36
TB Recursion	2.45	2.15	2.09	2.10	−0.43	2.15	37
SC ASW	2.29	1.91	2.25	1.97	−0.29	2.10	38
NSC LCAO	2.96	1.78	2.23	2.14	−0.24	2.20	39
SC LMTO	2.41	1.91	2.35	2.12	−0.41	2.20	40
SC LMTO	2.53	1.92	2.25	2.00	−0.46	2.14	22

sion or band narrowing can increase the magnetic moment per formula unit beyond this value. Indeed further volume expansion will cause the technically important magnetization per unit volume, M, to decrease.

The volume expansion of the carbide and nitride compounds are virtually identical, yet there are differences in the magnetic moment and average hyperfine field (Tables I and II) which must be of chemical origin. The increases in both quantities are less in the carbide than in the nitride. A simple explanation of the moment difference would be the greater electronegativity of N than C, leading to greater electronic charge transfer to N than C. However, the difference in magnetization of $2\mu_B$/(formula unit) would require an extra charge transfer of $\frac{2}{3}$ of an electron per nitrogen or more, because the ferromagnetism is not strong. There is no evidence of such large charge transfers in XANES measurements[19] or atomic calculations,[39] which support an atomic picture for the nitrogen.

It is more reasonable to attribute the 5% smaller carbide moment to a greater hybridization with iron 3d orbitals. This is reflected in the greater Miedema parameter n_{WS} of carbon (values for N, Fe, and C are 4.10, 5.36, and 6.86, respectively[42]), which means that the electrons in C-Fe bonds will tend to occupy bonding states with a build-up of charge in the interatomic region near the boundary of the Wigner-Seitz cell with consequent covalent reduction of the iron moment, whereas electrons in N-Fe bonds tend to avoid the interatomic region, and occupy more localized, antibonding states.

Interpretation of the chemical effect on the average hyperfine fields is trickier since there are three main contributions that may be distinguished in a metal

$$B_{hf}=B_{cp}+B_{4s}+B_{orb}\ .$$

The first of these, B_{cp} is due to the core polarization of 1s, 2s, and 3s shells by the 3d moment. This has recently been calculated by Coehoorn *et al.* for a range of Y-Fe intermetallics,[43] who find that B_{cp} is accurately proportional to the 3d moment, with a constant of proportionality of $-11.3\ \mathrm{T}/\mu_B$. B_{4s}, however, is due both to polarization of the 4s valence electrons of the same atom which gives a positive contribution, and to the transferred hyperfine field from interaction with neighboring atoms. The third term is related to the orbital moment of iron, which is typically of order $0.1\mu_B$ in iron-rich intermetallics.[44] The proportionality factor here is $42\ \mathrm{T}/\mu_B$.[45] The orbital contribution is anisotropic, and it can be deduced experimentally by noting that the average hyperfine field in Tm_2Fe_{17}, where the magnetization lies along the c axis, is 1.5 T higher than for Er_2Fe_{17}, where the moment lies in the c plane.[33] Furthermore, this term is not significantly different in the carbide or nitride, since there is a similar decrease of 0.8 T at the spin reorientation transitions observed as a function of temperature for $R_2Fe_{17}Z_{3-\delta}$ where R = Er or Tm and Z = N[46] or C.[47] We conclude that the lower magnitude of the hyperfine field in the carbide must be attributed to a positive 4s transferred hyperfine field (Table III).

Finally, it is worth noting that the relation between the average iron moment, obtained after correcting m for the small moments residing on Y, C, or N (see below) and average hyperfine field is $\sim -15.3\ \mathrm{T}/\mu_B$ in Y_2Fe_{17}, the hydride and nitride, but $-14.1\ \mathrm{T}/\mu_B$ in the carbide.

B. Local magnetization and hyperfine field

1. Y_2Fe_{17}

There have been six independent spin-polarized calculations of local moments in this compound[37–42] which are summarized in Table IV. Despite the different calculation methods, some self-consistent some not, there is an encouraging measure of agreement among these results. Apart from the calculation of Szpunar which gives a large 6g site moment, and the calculation of Inoue and Shimizu which systematically underestimates the magnitudes, the results indicate

$$\mu^{4f}\ (=2.5\mu_B)>\mu^{12j}\ (=2.2\mu_B)>\mu^{12k}\ (=2.0\mu_B)>\mu^{6g}\ (=1.9\mu_B)$$

with an average iron moment of $2.1\mu_B$. There is also a small negative moment of $-0.4\mu_B$ residing on the yttrium.[48] In view of the sign, this should be mainly of 4d character.[49]

The iron moments are sensitive to local coordination and nearest-neighbor distances. Yttrium neighbors reduce the iron moment, and in amorphous $Y_{1-x}Fe_x$ alloys, where it is possible to vary the composition continu-

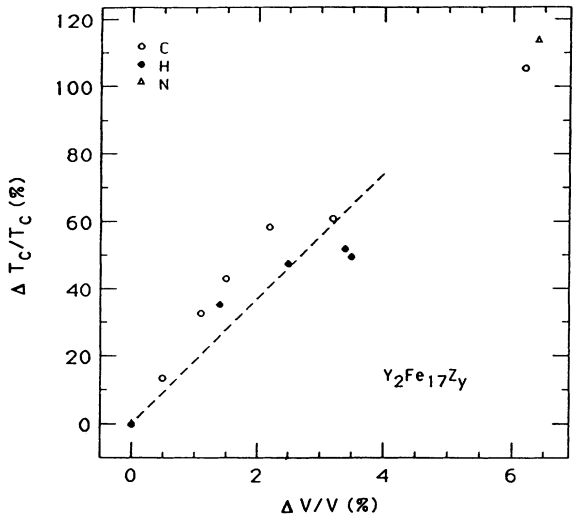

FIG. 5. Curie temperature as a function of volume increase of Y-Fe compounds.

ously, it has been found that the iron moment is destroyed completely when $x < 0.4$.[50] Large numbers of iron neighbors tend to increase the iron moment.

The nearest-neighbor coordination of the four iron sites in Y_2Fe_{17} is summarized in Table V.[41] From these considerations we would expect the largest iron moment to be on the 4f dumbbell site, which has one rare-earth neighbor, and the smallest to be on the 12k site, with three rare-earth neighbors, and only nine iron neighbors, i.e.,

$$\mu^{4f} > \mu^{6g} \sim \mu^{12j} > \mu^{12k}$$

6g and 12j have the same coordination numbers, but the crucial feature seems to be the very short Fe-Fe distance, which is 0.1-Å shorter for 6g than 12j. The calculation by Coehoorn[38] also indicates that the 6g moment is the one that increases most rapidly as the lattice expands.

The ^{57}Fe hyperfine fields follow the order suggested by coordination rather than local moment

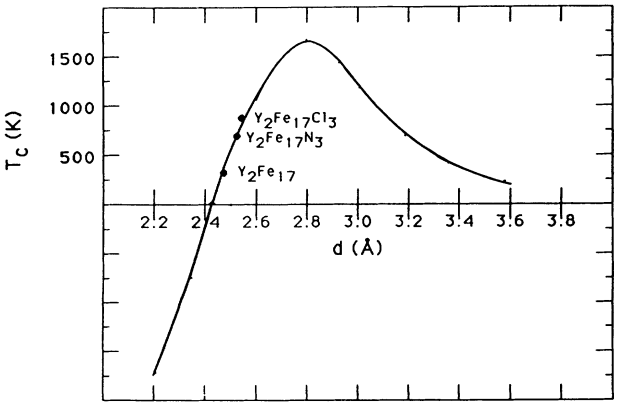

FIG. 6. Modified Slater-Néel curve for Y_2Fe_{17} interstitial compounds.

TABLE V. Site environment and interatomic distance between Fe atoms for Y_2Fe_{17} (in Å).

Site	Fe 4f		Fe 6g		Fe 12j		Fe 12k		Y 2b,2d		Average nearest-neighbor		
	d_{Fe-Fe}	n	d_{Fe-Fe}	n	d_{Fe-Fe}	n	d_{Fe-Fe}	n	d_{Fe-Y}	n	d_{Fe-Fe}	n	d_{Fe-Y}	n
12k	2.66	1	2.44	2	2.57	4	2.44	2	3.30	1	2.52	9	3.23	3
									3.30	1				
									3.10	1				
12j	2.73	2	2.43	2	2.46	2	2.57	4	2.99	2	2.55	10	2.99	2
6g	2.58	2			2.43	4	2.44	4	3.20	2	2.46	10	3.20	2
4f	2.39	1	2.58	3	2.73	6	2.66	3	2.94	1	2.65	13	2.94	1

$$B_{\rm hf}^{4f}\ (=35\ {\rm T}) > B_{\rm hf}^{6g}\ (=33\ {\rm T}) > B_{\rm hf}^{12j}\ (=30\ {\rm T}) > B_{\rm hf}^{12k}\ (=28\ {\rm T})\ .$$

There is no constant factor relating hyperfine field and local moment, the proportionality varying from -13.5 to $-17.3\ {\rm T}/\mu_B$ according to the site. The average hyperfine field is nevertheless proportional to the average iron moment for a series of Y-Fe intermetallics, with a factor of $-14.8\ {\rm T}/\mu_B$,[51] suggesting that in a compound with several sites, the effect of the transferred hyperfine field somehow averages out.

A rough breakdown of the hyperfine field at the four sites into core polarization, 4*s* and orbital contributions is given in Table VI. The magnitude of the 4*s* term is especially large at 6g sites. This term appears to depend at least exponentially on distance, besides reflecting the coordination of the site.

2. $Y_2Fe_{17}Z_3$

Three calculations have been carried out which examine the effect of volume expansion alone on the local moments,[38,40] and there are others that include in addition the effect of nitrogen[22,39] or carbon.[52] There are no calculations with hydrogen. Results are summarized in Table VII. Unfortunately, there is much less accord than for the pure compound. The non-self-consistent LCAO calculations of Li *et al.*[39,52] yield a wider spread of atomic moment values due to local redistribution of the charge than the self-consistent LMTO calculation.[22] The self-consistent calculations do not agree in the order of the moments, nor does the influence of nitrogen coordination emerge clearly. The 12j and 12k sites each have one nitrogen nearest neighbor, whereas the 4f and 6g sites each have none.

The order of hyperfine fields is the same as for the pure Y_2Fe_{17}:

$$\text{nitride}, B_{\rm hf}^{4f}\ (=40\ {\rm T}) > B_{\rm hf}^{6g}\ (=37\ {\rm T}) > B_{\rm hf}^{12j}\ (=35\ {\rm T}) > B_{\rm hf}^{12k}\ (=32\ {\rm T})\ ,$$

$$\text{carbide}, B_{\rm hf}^{4f}\ (=36\ {\rm T}) > B_{\rm hf}^{6g}\ (=34\ {\rm T}) > B_{\rm hf}^{12j}\ (=31\ {\rm T}) > B_{\rm hf}^{12k}\ (=27\ {\rm T})\ ,$$

but it is difficult to comment on the relative importance of core polarization and 4*s* contributions in the absence of any consensus concerning the values of the local moments. We therefore confine our remarks to the 4f moment which is the largest in all calculations except that of Beuerle,[40] and whose hyperfine field of 40 T in the nitride is quite exceptional for a metal. On the one hand, the 40 T may reflect core polarization due to an exceptionally large iron moment produced by charge transfer out of the $3d\downarrow$ states at that site.[39] On the other hand, if the iron moment is only $2.6\mu_B$, the 4*s* contribution must be as large as -15.3 T (Table VI). Some further evidence is provided by the isomer shift data of Fig. 4(c), where δ decreases very substantially from 0.30 mm/s at 4f sites in Y_2Fe_{17} to -0.11 mm/s in $Y_2Fe_{17}N_{3-\delta}$. The effect of volume expansion alone would be to increase δ by approximately 0.06 mm/s. A reduction of the isomer shift by 0.47 mm/s is therefore attributable to a change in the $3d/4s$ occupation at the 4f site, and is consistent with a loss of ~ 0.5 3*d* electrons at that site.[39] However accurate measurements of the local moments by neutron diffraction are now needed.

It is interesting that carbon reduces the hyperfine field by about 10% with respect to nitrogen at all sites, with only a small extra effect at 12j and 12k which are directly coordinated by an interstitial.

C. Exchange

The most striking effect of the interstitials is the enormous increase in Curie temperature. It is now established from both experiments[3] and calculations[39,40,52] that this effect is primarily due to the volume expansion. The chemical nature of the interstitial is secondary. Figure 5 is a compilation of data for different concentrations of H, C, and N in Y_2Fe_{17}.

The discussions of the magnetization in Sec. IV A led to the conclusion that the 3*d* band is almost fully spin polarized in these compounds and that further band narrowing will not increase the magnetic moment beyond $39.4\mu_B$. The expansion-induced increase of the Curie temperature therefore reflects the volume dependence of the exchange interactions, rather than any significant change in the iron moments themselves.

What then is the highest Curie temperature that could be achieved in a 2:17 compound? At some point, the rise of T_C with volume expansion must saturate, and T_C will begin to fall again at large interatomic spacing since the exchange interactions ultimately depend on the overlap of the wave functions of adjacent atoms. This idea was expressed in the classic Slater-Néel curve,[53] which can be rescaled for 2:17 compounds as follows. The volume when $T_C=0$ K (486.2 Å^3) was inferred from the pressure

TABLE VI. Site moments and hyperfine fields in Y_2Fe_{17}.

Site	Moment (μ_B)	$B_{\rm hf}$ (T)	$B_{\rm CP}$ (T)	B_{4s} (T)	$B_{\rm orb}$ (T)	$B_{\rm hf}$/moment (T/μ_B)
4f	2.5	−34.6	−28.3	−10.9	4.6	−13.8
6g	1.9	−32.9	−21.5	−11.6	0.2	−17.3
12j	2.2	−29.7	−24.9	−5.8	1.0	−13.5
12k	2.0	−28.2	−22.6	−7.1	1.5	−14.1

TABLE VII. Calculated atomic moments in expanded Y_2Fe_{17} and $Y_2Fe_{17}Z_3$ (Z=N and C) (in unity of μ_B/atom).

Compound	Method	4f Fe	6g Fe	12j Fe	12k Fe	2b,2d Y	6h Z	Average Fe moment	Ref.
Y_2Fe_{17}	SC LMTO	2.50	2.25	2.55	2.50	−0.38		2.47	40
Y_2Fe_{17}	NSC LACO	2.96	2.00	2.58	2.44	−0.35		2.47	52
Y_2Fe_{17}	SC ASW	2.45	2.21	2.41	2.26	−0.51		2.33	38
$Y_2Fe_{17}N_3$	NSC LACO	3.45	3.11	2.22	1.69	−0.07	−0.12	2.33	39
$Y_2Fe_{17}N_3$	SC LMTO	2.65	2.53	2.01	2.57	−0.33	−0.04	2.37	22
$Y_2Fe_{17}C_3$	NSC LACO	2.94	2.54	2.08	1.74	−0.29	−0.08	2.14	52

dependence of T_C, and the bulk modulus. Further points at $V=514.3$ Å^3 and $V=547.3$ Å^3 are taken from Y_2Fe_{17} and $Y_2Fe_{17}N_3$. The tail of the curve varies as $e^{-(d-2.80\text{ Å})/a_0}$, where a_0 is Bohr radius (0.53 Å) and d average Fe-Fe distance estimated from the hexagonal cell volume by $34d^3=V$.

The conclusion from Fig. 6 is that the maximum Curie temperature would be about 1700 K, at a volume expansion of about 45%. The structural stability of the phase will be compromised long before this, but it is worthwhile trying to insert interstitial atoms with larger atomic volumes such as boron, silicon, phosphorus, or chlorine into the octahedral sites. The hypothetical compound $Y_2Fe_{17}Cl_3$, for example, could have $T_C\sim900$ K, and $\Delta V/V\sim9\%$.

V. CONCLUSIONS

The magnetization of Y_2Fe_{17}, and $Y_2Fe_{17}N_3$ in particular, reflects an almost completely spin-polarized 3d band. The variations in the local moments at the iron sites from 1.9 to 2.5μ_B in Y_2Fe_{17} are due to local charge redistribution of a fraction of an electron per site.

The hyperfine fields at the different sites are not proportional to the spin moments, mainly on account of the 4s transferred hyperfine field which is most important at 6g sites because of the short Fe-Fe distances, and at 4f sites where the iron coordination number is large.

The primary effect of the interstitial atoms on the magnetic properties is related to volume expansion. They serve as atomic impurities which dilate the lattice. Chemical effects are secondary, but nitrogen has less influence than carbon in reducing the magnetization by forming covalent bonds with iron.

Further increases in Curie temperature beyond 700 K can be envisioned provided bulkier interstitial impurities can be found which will diffuse into Y_2Fe_{17} without destroying the hexagonal crystal structure.

ACKNOWLEDGMENTS

This work forms part of the Concerted European Action on magnets. It was supported as part of the BRITE/EURAM program of the European Commission. We are grateful to Professor Y. P. Li for helpful discussion of the band calculations and Justin Lawler for making the magnetization measurements.

[1]J. M. D. Coey, Phys. Scr. **39**, 21 (1991).
[2]J. M. D. Coey and Hong Sun, J. Magn. Magn. Mater. **87**, L251 (1990).
[3]Hong Sun, J. M. D. Coey, Y. Otani, and D. P. F. Hurley, J. Phys. Condens. Matter **2**, 6465 (1990).
[4]K. H. J. Buschow, R. Coehoorn, D. B. de Mooij, K. de Waard, and T. H. Jacobs, J. Magn. Magn. Mater. **92**, L35 (1990).
[5]J. M. D. Coey, Hong Sun, Y. Otani, and D. P. F. Hurley, J Magn. Magn. Mater. **98**, 76 (1991).
[6]Hong Sun, Y. Otani, and J. M. D. Coey, J. Magn. Magn. Mater., **104–107**, 1439 (1992).
[7]B. P. Hu and G. C. Liu, Solid State Commun. **79**, 785 (1991).
[8]Y. C. Yang, X. D. Zhang, L. S. Kong, Q. Pan, and S. L. Ge, Appl. Phys. Lett. **58**, 2042 (1991).
[9]J. M. D. Coey, Y. Otani, Hong Sun, and D. P. F. Hurley, J. Mag. Soc. Jpn. **15**, 769 (1991) (in Japanese).
[10]D. P. F. Hurley and J. M. D. Coey, J. Phys. Condens. Matter (to be published).
[11]D. Fruchart (private communication).
[12]M. Katter, J. Wecker, and L. Schultz, J. Appl. Phys. **70**, 3188 (1991).
[13]D. Fruchart and S. Miraglia, J. Appl. Phys. **69**, 5578 (1991).
[14]X. Z. Wang, K. Donnelly, J. M. D. Coey, B. Chevalier, J. Etourneau, and T. Berlureau, J. Mater. Sci. **23**, 329 (1988).
[15]B. Rupp, A. Resnik, D. Shaltiel, and P. Rogl, J. Mater. Sci. **23**, 2133 (1988).
[16]J. M. D. Coey, Hong Sun, and Y. Otani, in *Proceedings of the Sixth International Symposium on Magnetic Anisotropy and Coercivity in Rare Earth Transition Metal Alloys* (Carnegie Mellon University, Pittsburgh, Pennsylvania, 1990), p. 36.
[17]M. T. Averbuch-Pouchot, R. Chevalier, J. Deportes, B. Kebe, and R. Lemaire, J. Magn. Magn. Mater. **68**, 190 (1987).
[18]J. M. D. Coey, J. F. Lawler, Hong Sun, and J. E. M. Allan, J. Appl. Phys. **69**, 3007 (1991).
[19]T. W. Capehart, R. K. Mishra, and F. E. Pinkerton, Appl. Phys. Lett. **58**, 1395 (1991).
[20]R. M. Ibberson, O. Moze, T. H. Jacobs, and K. H. J. Buschow, J. Phys. Condens. Matter **3**, 1219 (1991).
[21]Y. C. Yang and J. L. Yang, in *Proceedings of the 2nd International Conference on Rare Earth Development and Application, Beijing, 1991* (Chinese Academy of Sciences, Peking, 1991). Vol. 2, p. 567.
[22]S. S. Jaswal, W. B. Yelon, G. C. Hadjipanayis, Y. Z. Wang, and D. J. Sellmyer, Phys. Rev. Lett. **67**, 644 (1991).
[23]O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart, and J. Pannetier, Phys. Rev. B **45**, 2920 (1992).

[24]S. Miraglia, J. L. Soubeyroux, C. Kolbeck, O. Isnard, D. Fruchart, and M. Guillot, J. Less-Common Met. **171**, 51 (1991).
[25]G. Block and W. Jeitschko, Inorg. Chem. **25**, 279 (1968).
[26]G. Block and W. Jeitschko, J. Solid State Chem. **70**, 271 (1987).
[27]R. B. Helmholdt and K. H. J. Buschow, J. Less-Common Met. **155**, 15 (1985).
[28]O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart, and A. Stergiou, J. Less-Common Met. **162**, 273 (1990).
[29]O. Isnard, S. Miraglia, J. L. Soubeyroux, D. Fruchart, and A. Stergiou (unpublished).
[30]D. H. Ryan and J. M. D. Coey, J. Phys. E **19**, 693 (1986).
[31]J. M. D. Coey and D. P. F. Hurley, J. Magn. Magn. Mater., **104–107**, 1098 (1992).
[32]W. Steiner and R. Haferl, Phys. Status Solidi A **42**, 739 (1977).
[33]Bo-ping Hu, Hong-shuo Li, Hong Sun, and J. M. D. Coey, J. Phys. Condens. Matter **3**, 3983 (1991).
[34]Qi-nian Qi, Hong Sun, and J. M. D. Coey, Hyperfine Interact. (to be published).
[35]A. R. Williams, V. L. Moruzzi, A. P. Malozemoff, and K. Tekura, IEEE Trans. Magn. **MAG-19**, 1983 (1983).
[36]J. Inoue and M. Shimizu, J. Phys. F **15**, 1511 (1985).
[37]B. Szpunar and J. A. Szpunar, J. Appl. Phys. **57**, 4130 (1985).
[38]R. Coehoorn, Phys. Rev. B **39**, 13 072 (1989).
[39]Y. P. Li, Hong-shuo Li, and J. M. D. Coey, Phys. Status Solidi B **166**, K107 (1991).
[40]T. Beuerle, P. Braun, and M. Fähnle, J. Magn. Magn. Mater. **94**, L11 (1991).
[41]D. Givord and R. Lemaire, IEEE Trans. Magn. **MAG-10**, 109 (1974).
[42]A. R. Miedema, P. F. de Chatel, and F. R. de Boer, Physica **100B**, 1 (1980).
[43]R. Coehoorn, C. J. M. Denissen, and R. Eppenga, J. Appl. Phys. **69**, 6222 (1991).
[44]O. Eriksson, B. Johansson, R. C. Albers, A. M. Boring, and M. S. S. Brooks, Phys. Rev. B **42**, 2707 (1990).
[45]H. Ebert, P. Strange, and B. L. Gyorffy, J. Phys. F **18**, L135 (1988).
[46]Bo-ping Hu, Hong-shuo Li, Hong Sun, and J. M. D. Coey, Solid State Commun. **76**, 587 (1990).
[47]Qi-nian Qi, M. Kuz'min, Hong Sun, and J. M. D. Coey, J. Alloys Compounds (to be published).
[48]J. G. M. Armitage, T. Dumelow, P. C. Riedi, and J. S. Abell, J. Phys. Condens. Matter **1**, 3987 (1989).
[49]I. A. Campbell, J. Phys. F **2**, L47 (1972).
[50]K. Moorjani and J. M. D. Coey, *Magnetic Glasses* (Elsevier, New York, 1984), p. 269.
[51]P. C. M. Gubbens, J. H. F. van Apeldoorn, A. M. van der Kraan, and K. H. J. Buschow, J. Phys. F **4**, 921 (1974).
[52]Y. P. Li and J. M. D. Coey (unpublished).
[53]L. Néel, Ann. Phys. (Paris) **5**, 269 (1936).

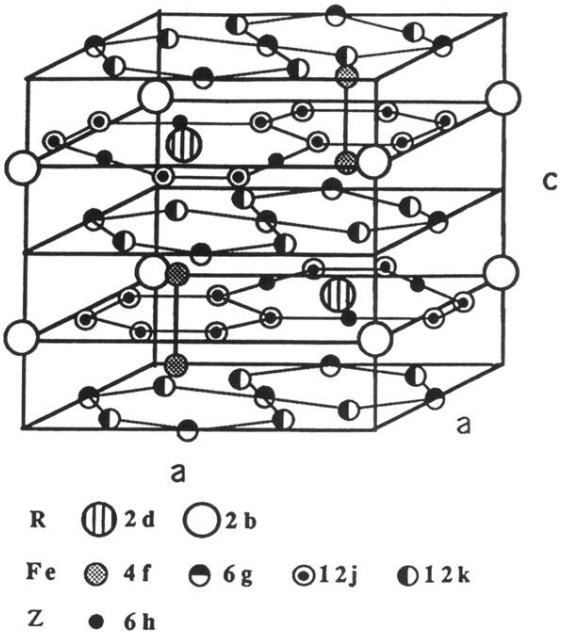

FIG. 1. Hexagonal structure of Y_2Fe_{17} showing the 6h interstitial site.