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Nuclear magnetic resonance study of the Sm_2Fe_{17} carbides

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Abstract

The ^{147}Sm and ^{149}Sm NMR spin echo spectra and the spin echo decays of $Sm_2Fe_{17}C_x$ for $x = 0$, 0.5, 1 and about 3 at 4.2 K are reported. The quadrupole septets in the spectra are assigned to the samarium 6c site with different numbers of carbon atoms occupying the neighbouring 9e interstitial sites. A significant influence of carbon neighbours on the Sm quadrupole splitting and hyperfine field is observed and is attributed to a strong change of the Sm valence electron distribution and polarisation caused by carbon neighbours. From the quadrupole splittings the values of the lattice electric field gradient and the corresponding crystal electric field coefficient A_2^0 are derived. For the Sm sites with 0 (3) carbon nearest neighbours the A_2^0 value of -66 Ka_0^{-2} (-350 Ka_0^{-2}) is obtained.

Keywords: Sm_2Fe_{17} carbides; NMR spectra

1. Introduction

The compound Sm_2Fe_{17} belongs to the family of high performance permanent magnet materials deriving from Sm_2Co_{17}. However, the fairly low Curie temperature and the planar magnetocrystalline anisotropy of Sm_2Fe_{17} prevented its application to permanent magnets until recently, when it was found that its properties could be significantly improved by the introduction of light atoms such as carbon or nitrogen on the interstitial sites in the structure [1,2]. The effect of N or C on the crystal electric field at the rare earth (RE) site causes the easy magnetisation direction (EMD) to switch from the *c*-plane to the *c*-axis, leading to a huge rise of the magnetocrystalline anisotropy. The Curie temperature of the compound increases considerably from below 400 K for Sm_2Fe_{17} to above 700 K for its nitride and carbide. The amount of carbon that can be introduced into the lattice by co-melting is limited to about 1–1.5 C atoms per formula unit. A much larger amount of carbon, close to 3 C atoms per formula unit, can be introduced into the lattice by heating the host Sm_2Fe_{17} in an atmosphere of hydrocarbons [3].

In the rhombohedral Th_2Zn_{17}-type crystal structure of RE_2Fe_{17}, Fig. 1, the Sm atoms occupy a single site 6c, whereas the Fe atoms occupy four inequivalent sites 6c, 9d, 18f and 18h. Carbon atoms enter the octahedral 9e sites [4]. There are three 9e nearest neighbour (NN) sites to an RE atom, located around it in the plane perpendicular to the *c*-axis.

Nuclear magnetic resonance is a useful tool for studying individual site properties. The present study was undertaken in order to determine the local influence of carbon on the samarium site and to compare it with that of nitrogen and hydrogen reported elsewhere [5,6]

2. Experimental

The Sm_2Fe_{17} sample and the carbides $Sm_2Fe_{17}C_x$ with $x = 0.5$ and 1 were prepared by arc melting of appropriate amounts of constituents. About 10% excess of Sm was used to compensate for evaporation losses during arc melting. The samples were vacuum annealed for 2 weeks at 1050°C. The carbide with x close to three was prepared by heating a fine Sm_2Fe_{17} powder for 3 h at 500°C in 1 bar of acetylene.

The NMR measurements were carried out at 4.2 K

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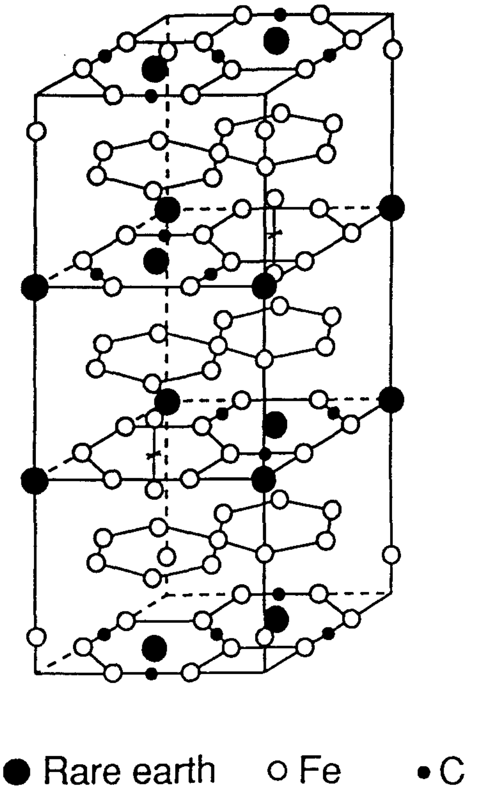

Fig. 1. The unit cell of rhombohedral $RE_2Fe_{17}C_x$ (after Ref. [4]): large empty circles, RE; small empty circles, Fe; small filled circles, C 9e sites.

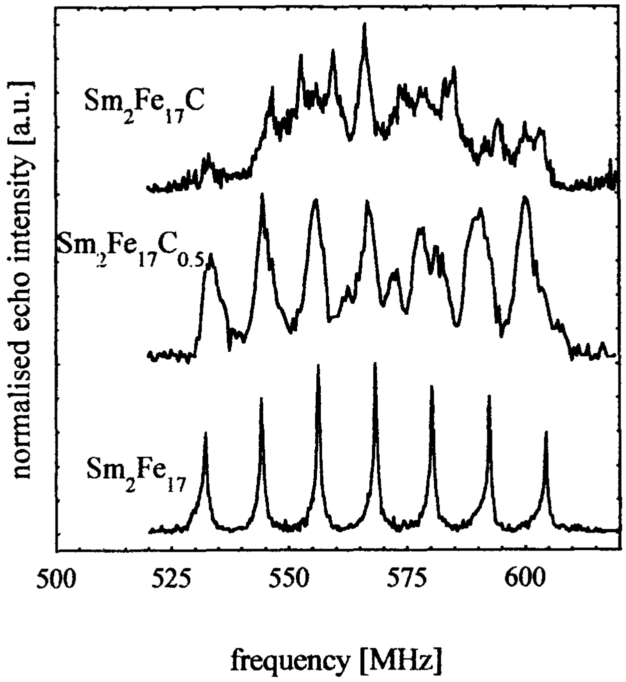

Fig. 2. The ^{147}Sm NMR spectra of $Sm_2Fe_{17}C_x$ at 4.2 K.

using an automated computer controlled spin-echo spectrometer [7]. The ^{147}Sm and ^{149}Sm spin echo spectra were obtained using a pulse sequence 1/10/2 μs at a constant amplitude. The spectra are presented in Figs. 2 and 3. The spin echo decays shown in Fig. 4 were obtained by varying the spacing τ between the r.f. pulses in the sequence $1/\tau/2$ μs, changed in steps of 0.05 μs.

3. Results

3.1. Spin echo spectra

The ^{147}Sm and ^{149}Sm spectra of Sm_2Fe_{17}, Figs. 2 and 3, are basically the same as obtained in Ref. [8] except for differences in line intensities caused by the frequency response of the NMR apparatus. The quadrupole splitting for ^{147}Sm and the magnetic induction B_e of the hyperfine field (HFF) obtained from the spectra in the same way as in Ref. [6] amount to 12.0 MHz and 323.3 T (central frequency 568.3 MHz). Central frequencies, the corresponding HFF and quadrupole splittings are collected in Table 1.

In the ^{147}Sm spectrum of $Sm_2Fe_{17}C_{0.5}$ the linewidths are much larger than in the host Sm_2Fe_{17} and, in addition to the main septet, a weaker one appears. The quadrupole splitting of the main septet amounts to 10.6 MHz and the HFF is 322.3 T (central frequency 566.5 MHz). The weaker septet has a quadrupole splitting of 9 MHz and an HFF of 331.0 T (central frequency 581.8 MHz). This septet can be assigned to Sm sites with one carbon atom as the nearest neigh-

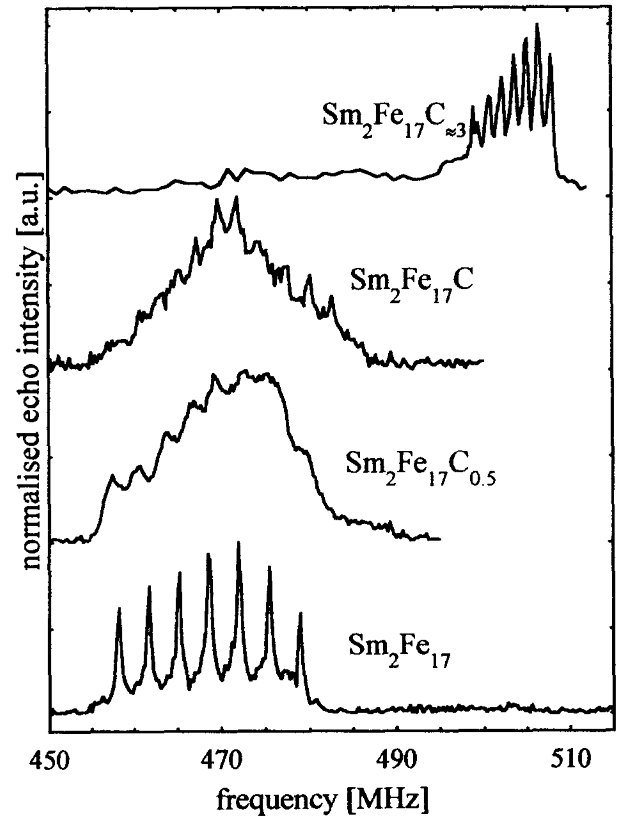

Fig. 3. The ^{149}Sm NMR spectra of $Sm_2Fe_{17}C_x$ at 4.2 K.

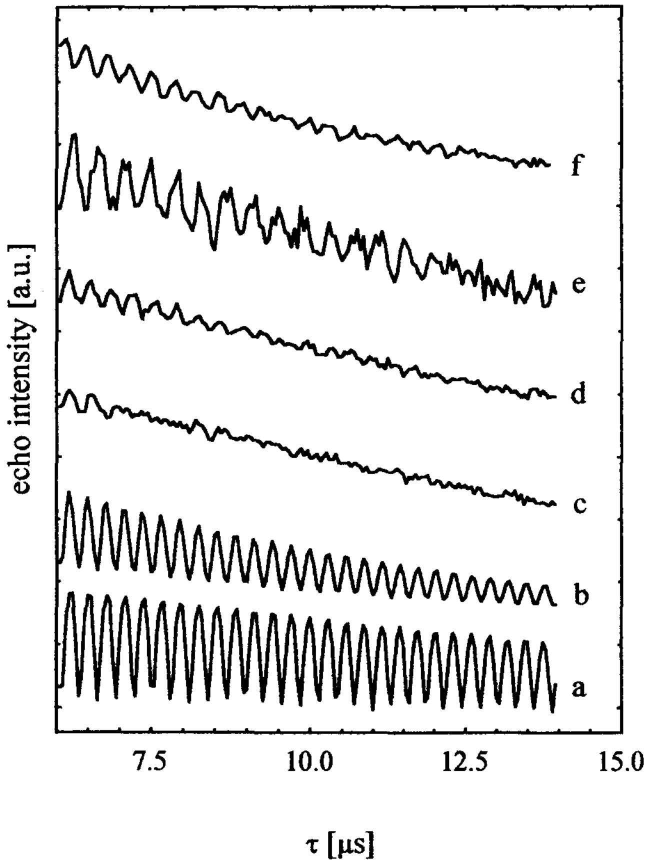

Fig. 4. The ^{149}Sm spin echo decays (echo amplitude vs. pulse separation τ) for $Sm_2Fe_{17}C_x$ at 4.2 K: (a) Sm_2Fe_{17}, 479 MHz; (b) Sm_2Fe_{17}, 461 MHz; (c) $Sm_2Fe_{17}C_{0.5}$, 479 MHz; (d) $Sm_2Fe_{17}C_{0.5}$, 461 MHz; (e) $Sm_2Fe_{17}C$, 479 MHz; (f) $Sm_2Fe_{17}C$, 461 MHz.

bour, which is the second most populated configuration after no carbon neighbours if one assumes a random distribution of carbon over the 9e sites, as for the Y_2Fe_{17} carbides [5].

In the ^{147}Sm spectrum of $Sm_2Fe_{17}C$ the pattern of a strong septet and a weaker one also appear, Fig. 2. The weaker septet, however, is stronger than that of $Sm_2Fe_{17}C_{0.5}$. The quadrupole splitting of the main septet amounts to 10.7 MHz and the HFF is 322.3 T (central frequency 566.5 MHz). The weaker septet has a quadrupole splitting of 8.5 MHz and an HFF of 330.0 T (central frequency 580.0 MHz). As with $Sm_2Fe_{17}C_{0.5}$, this septet is also attributed to Sm sites with one carbon atom as the nearest neighbour. Its intensity compared with that of the 0 C sites is larger than in $Sm_2Fe_{17}C_{0.5}$, which agrees with the larger calculated probability of finding 1 C sites in this compound than in $Sm_2Fe_{17}C_{0.5}$, assuming a random distribution of carbon over 9e sites.

For the carbide $Sm_2Fe_{17}C_x$ with $x \approx 3$ only a very weak signal was detected. This was attributed to a very strong uniaxial anisotropy of the compound which dramatically reduces the NMR enhancement, as with the fully nitrided compound [6]. For ^{147}Sm it would require several weeks of signal averaging in order to obtain a reasonably resolved spectrum. As the ^{149}Sm spectrum is less than half as wide as that of ^{147}Sm it could be measured in a reasonable time, Fig. 3. It contains a well-resolved septet centred at 503.5 MHz with a low frequency tail. The septet is attributed to Sm with 3 C NN, the configuration with the maximum probability for $Sm_2Fe_{17}C_x$ with $x \approx 3$. The low frequency shoulder has been attributed by us to the Sm environments with less than 3 C NN. The quadrupole splitting of the septet fitted with seven equidistant lines amounts to 1.50 MHz and the HFF is 347.2 T, which is 23.9 T larger than that of the host Sm_2Fe_{17}.

3.2. Spin echo decays

The ^{149}Sm spin echo decays measured at various frequencies show characteristic oscillations caused by quadrupole interactions [9]. An oscillation period τ_q is related to the quadrupole splitting $\Delta\nu_q$ by the equation $\Delta\nu_q\tau_q = 1$. In order to determine accurately the quadrupole splittings in the unresolved ^{149}Sm spectra of $Sm_2Fe_{17}C_{0.5}$ and $Sm_2Fe_{17}C$, the spin echo decays were taken at the low frequency side (461 MHz), where we have a predominant contribution to the signal from 0 C Sm sites, and at the high frequency side (479 MHz), where the sites with C neighbours contribute to the NMR signal.

For $Sm_2Fe_{17}C_{0.5}$ a pattern with well-developed quadrupole oscillations at low frequencies is obtained, Fig. 4(d). The frequency corresponds to a quadrupole splitting of 2.90 MHz. At the high frequency side, Fig. 4(c), very weak, strongly damped oscillations, with indications of at least two frequencies, are observed and their values cannot be reliably determined. For $Sm_2Fe_{17}C$ well-resolved oscillations are obtained at both sides of the ^{149}Sm spectrum. The quadrupole splittings of 2.86 MHz at low frequencies and 2.47 MHz at high frequencies are derived respectively.

4. Discussion

4.1. HFFs

The values of the HFF (B_e) were derived from the central frequencies of the septets shown in Figs. 2 and 3 using the formula: $\nu_0 = Cg_nB_e$ with $C = -7.6231$ MHz T^{-1} and $g_n = -0.2306$ for ^{147}Sm [10,11]. The HFF on Sm nuclei in these materials is dominated by a huge contribution from the orbital moment of the 4f electrons. As the coupling between the Sm and Fe spins is antiparallel, and the Sm spin and orbital moments are also antiparallel coupled, the contribution is positive with respect to the local magnetisation

Table 1
Central frequencies v_0, *HFFs* B_e, quadrupole splittings $\Delta\nu_q$, the corresponding electric field gradients V_{ii} and the lattice EFG V_{cc}(latt) obtained for $Sm_2Fe_{17}C_x$

Sample (septet, isotope)	ν_0 (MHz)	B_e (T)	$\Delta\nu_q$ (MHz)	V_{ii} (10^{20} V m^{-2})	V_{cc}(latt) (10^{20} V m^{-2})
Sm_2Fe_{17}					
^{147}Sm	568.3	323.3	12.0	−262	26
			3.47	−262	
			3.45[a]	−261[a]	
$Sm_2Fe_{17}C_{0.5}$					
main, ^{147}Sm	566.5	322.3	10.6	−232	
main, ^{149}Sm			2.90[a]	−217[a]	
				−225[b]	
weak, ^{147}Sm	581.8	331.0	9.0	−197	
$Sm_2Fe_{17}C$					
main, ^{147}Sm	566.5	322.3	10.7	−234	
main, ^{149}Sm			2.86[a]	−214[a]	
				−224[b]	25
weak, ^{147}Sm	580.0	330.0	8.5	−186	
weak, ^{149}Sm			2.47[a]	−185[a]	
				−186[b]	64
$Sm_2Fe_{17}C_{x\approx3}$					
main, ^{149}Sm	503.5	347.2	1.50	−112	137

[a] Denotes the values obtained from quadrupole oscillations of the spin echo decays.
[b] Marks the V_{ii} values averaged over both isotopes.

direction of the compound. The much smaller contribution to HFF arising from polarisation of Sm valence electrons by the Fe magnetic moments, called the transferred HFF, is of opposite direction. In our recent NMR study of $Y_2Fe_{17}A_x$ (A = N, C) it was found, that carbon and nitrogen nearest neighbours reduce dramatically the transferred HFF at the yttrium site [5]. Thus, the larger HFF for Sm 3 C environments than for 0 C ones is attributed to a decrease of the transferred HFF caused by carbon. For the Sm_2Fe_{17} nitride a similar effect of nitrogen was observed. Its magnitude for 3 N neighbours, however, amounts to 9.0 T only, which is much smaller than 23.9 T for 3 C neighbours, but is consistent with the effects observed for the Y_2Fe_{17} nitride and carbide, where carbon has a larger effect on the HFF also.

The difference in HFF between 1 C and 0 C sites amounts to 7.7 T. For the 3 C sites the change in HFF expressed per one carbon neighbour amounts to 8 T which is slightly larger than for 1 C sites. The result is consistent with that for the Y_2Fe_{17} carbides [5] where the carbon influence on the yttrium HFF, per one C neighbour, was also found to increase with increasing number of nearest neighbour C atoms.

4.2. Quadrupole splittings

From the quadrupole splittings $\Delta\nu_q$ derived from the line separations of the spectra and from the quadrupole oscillations, the corresponding values of the EFG components along the HFF V_{ii} were derived using the formula

$$|V_{ii}| = 2I(2I-1)h\Delta\nu_q/3e|Q_n| \qquad (1)$$

where I is the nuclear spin (7/2 for ^{147}Sm and ^{149}Sm), h is Planck's constant, e is the elementary charge and Q_n is the nuclear quadrupole moment. The value $Q_n(147) = -0.265(25)b$ [10] was used and the ratio of quadrupole splittings between the two isotopes $\Delta\nu_q(147)/\Delta\nu_q(149)$ was taken to be 3.4602, allowing for the difference of nuclear radii of the isotopes (hyperfine anomaly) [11]. The values of V_{ii} are collected in Table 1.

The EFG at the Sm nucleus originates mainly from a nonspherical distribution of the 4f electron density of the parent ion, as well as from the asphericity of the 6p and 5d electron density of the parent ion due to the presence of neighbouring atoms in the lattice [12]. Thus, the EFG component along the HFF direction may be written as

$$V_{ii} = V_{ii}(4f) + V_{ii}(\text{latt}) \qquad (2)$$

As the Fe–Sm exchange is much stronger than the crystalline electric field interaction, samarium preserves its fully polarised ground state with $J_z = J = 5/2$, irrespective of the direction of magnetisation. Thus, $V_{ii}(4f)$ is independent of the magnetic moment direction and has its maximum value denoted as $V_{zz}(4f)$.

From the 1.50 MHz quadrupole splitting of ^{149}Sm

for 3 C environments the value $V_{ii} = -112 \times 10^{20}$ V m^{-2} is derived. As the 4f electron contribution to the EFG is dominant and negative, we attribute a negative sign to V_{ii}. The NMR signal in these highly anisotropic materials originates mainly from domain wall edges (DWEs); thus for the uniaxial carbide with x close to three it corresponds to local magnetic moment directions close to the c-axis. Neglecting a possible small change of V_{zz}(4f) with carbon content we take for it the value of -249×10^{20} V m^{-2} as determined for Sm_2Fe_{17} in Ref. [6]. Applying Eq. (2) we obtain for V_{cc}(latt) a value of 137×10^{20} V m^{-2}. Using a similar procedure for 1 C environments in $Sm_2Fe_{17}C$, which is also uniaxial, we obtain the V_{cc}(latt) value of 64×10^{20} V m^{-2}. The lattice EFG value for 3 C neighbours is larger than that of 122×10^{20} V m^{-2} obtained for 3 N neighbours in the Sm_2Fe_{17} nitrides, which means that carbon influence on it is larger than that of nitrogen.

The electric field gradient V_{ii} for 0 C environments in $Sm_2Fe_{17}C_{0.5}$ is slightly larger (4%) than that in $Sm_2Fe_{17}C$. There are two possible reasons for this: a conical magnetic structure of $Sm_2Fe_{17}C_{0.5}$ with the EMD tilted at an angle ϑ from the c-axis, or a change of V_{zz}(4f) between the samples. It was found that V_{zz}(4f) in Sm_2Fe_{17} is larger by 20% than that for the free Sm^{3+} ion; the effect was attributed to a contraction of the 4f shell in the presence of neighbouring atoms in the crystal lattice [6]. As the interatomic distances increase with increasing carbon content, a slight change of V_{zz}(4f) towards an absolute value lower than that of Sm_2Fe_{17} has to be considered. This would result in a decrease of magnitude of the total EFG. In contrast, a lack of resolved quadrupole oscillations at the high frequency side of the ^{149}Sm spectrum of $Sm_2Fe_{17}C_{0.5}$ indicates that the sample possibly has a conical structure. In such a structure the sites with 1 C (and 2 C) neighbours having a two-fold axis as the highest symmetry axis, would no longer be equivalent. It would result in a spread of quadrupole splittings and, consequently, in a lack of a resolved quadrupole oscillation pattern. Thus, we can conclude, that $Sm_2Fe_{17}C_{0.5}$ at 4.2 K has a conical structure with its EMD slightly tilted from the c-axis, whereas $Sm_2Fe_{17}C$ is uniaxial with the EMD direction along the c-axis.

For Sm_2Fe_{17} the value of $\Delta\nu_q$ derived from the spin echo decay oscillations is in good agreement with the observed line splitting. However, a discrepancy occurs for $Sm_2Fe_{17}C_{0.5}$ and $Sm_2Fe_{17}C$. The values obtained from the line spacings are larger by 10%. Since the NMR signal originates from DWE regions, it corresponds to a range of quadrupole splittings reflecting a spread of local magnetic moments directions around the c-axis. As the individual quadrupole splittings increase with an increase of the tilting angle, the overall quadrupole splitting is larger than that corresponding to the c-axis direction. The quadrupole splitting derived from the strongly damped spin echo decay oscillations therefore possibly underestimates the splitting. In the planar Sm_2Fe_{17}, where we have a much narrower distribution of quadrupole splittings, the oscillations are weakly damped and the values of quadrupole splittings obtained from line spacings and the spin echo decay oscillations agree very well. Thus, it is justified to take for the value of V_{ii} its average from both methods.

4.3. Relation to the magnetocrystalline anisotropy

The lowest order term of the CEF interaction corresponds to the interaction of the quadrupole moment of the 4f electron shell with the EFG produced mainly by the asphericity of the 5d and 6p shells of the parent atom resulting from the presence of neighbours in the lattice [13]. The CEF coefficient A_2^0 used in the CEF formalism is proportional to this EFG. The lack of a strict relation between EFG at the nucleus and the EFG experienced by the 4f shell means that only an approximate relation can be used:

$$A_2^0 = -(D/4)eV_{cc}(\text{latt}) \tag{3}$$

Taking for the coefficient D an empirical value of 1/320, as obtained from a comparison of a Mössbauer spectroscopy study with bulk magnetic data for Gd_2Fe_{17} and other RE–3d intermetallics [14], the CEF coefficients A_2^0 for the Sm sites with different numbers of carbon neighbours in the compound can be determined. The value of A_2^0 obtained for Sm_2Fe_{17} amounts to -66 Ka_0^{-2} as was determined in Ref. [6] (a_0 is the Bohr radius). For the sites with 1 C neighbour in the carbides we get -162 Ka_0^{-2} and for the sites with 3 C NN we obtain the value of -350 Ka_0^{-2}. We assume that, as with the Sm_2Fe_{17} nitrides, the individual site values of A_2^0 do not vary significantly with carbon content, so they are representative for the whole $Sm_2Fe_{17}C_x$ series.

The change of A_2^0 caused by 1 C neighbour amounts to -96 Ka_0^{-2}, whereas 3 C neighbours change A_2^0 by -284 Ka_0^{-2}, which corresponds to -95 Ka_0^{-2} per one C neighbour. Since the values are very close to each other, the contributions to A_2^0 from the individual carbon neighbours are deduced to be additive. For the Sm_2Fe_{17} nitrides the contribution to A_2^0 expressed per one N neighbour was found to increase with increasing number of N neighbours.

The value of A_2^0 for 3 N sites in the Sm_2Fe_{17} nitrides derived from the corresponding value $V_{cc}(\text{latt}) = 122 \times 10^{20}$ V m^{-2} amounts to -309 Ka_0^{-2}, (not -358 Ka_0^{-2} as was erroneously derived in Ref. [6]), which is smaller than for the 3 C sites in the carbides. This implies that the hypothetical $Sm_2Fe_{17}C_3$ has a larger magnetocrystalline anisotropy than $Sm_2Fe_{17}N_3$.

5. Conclusions

Well-resolved quadrupole spectra of ^{147}Sm and quadrupole oscillations of spin echo decays of ^{149}Sm in the Sm_2Fe_{17} carbides allowed the determination of the HFF and EFG values for the Sm sites with 0, 1 and 3 C neighbours. A strong influence of C neighbours on both the HFF and the EFG was found and attributed to a strong influence of carbon neighbours on the Sm valence electron distribution and polarisation.

The decrease of the transferred HFF at the Sm sites with increasing C NN number is attributed to a strong reduction of polarisation of Sm valence electrons by magnetic moments of neighbouring Fe atoms. A similar decrease of the transferred HFF was observed also for the nitride, but the reduction of the transferred HFF, as expressed per one C neighbour, increases with increasing number of C neighbours, in contrast to the nitrides, where the opposite tendency was found.

Carbon neighbours cause a huge increase of the lattice EFG at the Sm sites. The effect of subsequent C neighbours appears to be additive, in contrast to that of nitrogen, where the effect expressed per one N neighbour increases with increasing number of N neighbours. Different tendencies of HFF and EFG changes in the carbides from those in the nitrides indicate differences between the Sm–C and the Sm–N bondings.

The CEF coefficient A_2^0 derived for the Sm sites with 3 C neighbours amounts to $-350\ Ka_0^{-2}$, about 10% larger than that for the 3 N sites in the nitrides. Thus, for the fully carbided material $Sm_2Fe_{17}C_3$ a larger magnetocrystalline anisotropy than that of the corresponding nitride $Sm_2Fe_{17}N_3$ can be predicted.

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