NMR study of $Sm_2Co_{17}H_x$ hydrides

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Abstract

An NMR study of $Sm_2Co_{17}H_x$ ($x = 0$, 1.5, 4.6) hydrides is reported. The [147]Sm and [149]Sm spin echo spectra were measured on powder samples at 4.2 K with no applied magnetic field. The quadrupole septets (nuclear spin I of both Sm isotopes is 7/2) observed in the spectra are attributed to Sm sites with different numbers of hydrogen nearest neighbours located at the 9(e) and 18(g) sites in the crystal structure. Hydrogen neighbours at 9(e) sites cause a decrease of Sm hyperfine field, whereas hydrogen at 18(g) sites causes its increase, which is attributed to the changes of an anisotropic contribution of spin dipolar origin. The 9(e) neighbours cause a decrease of the quadrupole splitting, which corresponds to an increase of the lattice contribution to the electric field gradient. Hydrogen at 18(g) sites causes a slight decrease of the lattice electric field gradient. The results are analysed in terms of electron transfer between hydrogen and samarium sites and the difference between the effect of hydrogen at the 9(e) and 18(g) sites on the magnetocrystalline anisotropy is discussed.
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1. Introduction

During the last decades, the search for new permanent magnets has turned towards rare earth (RE) and transition metal (TM) element based compounds. The TM sublattice principally provides a large magnetization and RE provides most of the magnetocrystalline anisotropy which originates from the aspherical 4f charge distribution of the RE ion interacting with the crystal electric field. It has been observed that the introduction of light, non-metallic elements (e.g. hydrogen, carbon or nitrogen) onto interstitial sites can give rise to the enhancement of the T_C of the RE_2Fe_{17} compounds by more than 100% due to magneto-volume effect on the Fe magnetisation [1,2]. It can also cause a considerable increase of the magnetocrystalline anisotropy due to the enhancement of the crystal electric field. The effect of carbon and nitrogen on both quantities is much larger than that of hydrogen. In nuclear magnetic resonance the electronic and magnetic properties of the individual element sites are probed by the magnetic hyperfine fields (HFF) and electric field gradients (EFG) at nuclei. In the previous NMR study the properties of the $Sm_2Fe_{17}H_x$ hydrides were reported [3]. In order to determine the influence of hydrogen on the Sm sites in the $Sm_2Co_{17}H_x$ hydrides the present study was undertaken.

The compound Sm_2Co_{17} crystallizes in the rhombohedral structure (Th_2Zn_{17}), the same as Sm_2Fe_{17}. Sm occupies a single site 6(c) and Co occupies four inequivalent sites: 18(h), 18(f), 9(d), 6(c). The introduction of hydrogen preserves the structure of the parent material. Neutron diffraction experiments on the isostructural $Nd_2Fe_{17}H_x$ showed that for x up to three hydrogen occupies the octahedral 9(e) sites and for larger x it occupies up to one-third of tetrahedral sites 18(g), which leads to the maximum content $x = 5$ [4]. There are three 9(e) and six 18(g) nearest neighbour sites to an Sm site (Fig. 1).

2. Experimental

Fine Sm_2Co_{17} powders were used to prepare the hydride samples. Hydriding was carried out in H_2 gas atmosphere at 100 °C in a constant volume reactor.

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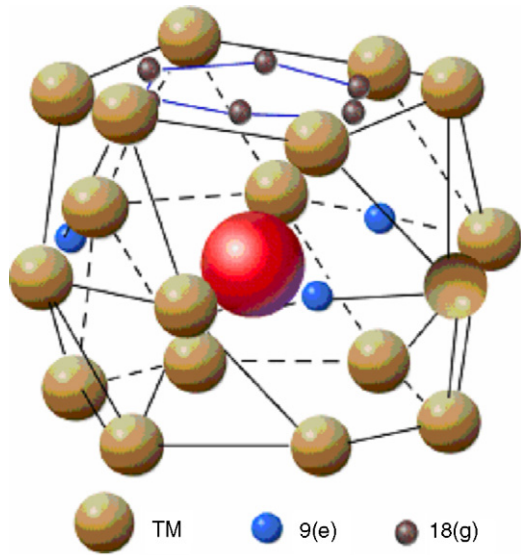*E-mail address:* yass@agh.edu.pl (M. Borowiec).

Fig. 1. The local environment of the samarium site in the structure.

Fig. 2. Spin echo NMR spectra of [147]Sm at 4.2 K. The outermost lines of the septets corresponding to 0–3 hydrogen 9(e) neighbours are marked.

The amount of hydrogen in the compound was determined from the difference of pressure before and after the reaction. It amounts to $x = 1.5$ and 4.6 for the two hydride samples prepared. The X-ray diffraction measurements showed that the hydrides obtained are single phase. The parent compound as well as the hydrides have the easy magnetisation direction along the crystallographic c-axis.

Measurements of the [147]Sm and [149]Sm spin echo spectra have been carried out at 4.2 K and zero applied magnetic field using an automated spin echo NMR spectrometer [5]. The [147]Sm spectra are presented in Fig. 2. The [149]Sm spectra (not shown) are consistent with the [147]Sm spectra but much less resolved due to a smaller nuclear quadrupole moment of the [149]Sm isotope. The spectrum of the parent intermetallic compound Sm_2Co_{17} consists of a single, quadrupole split septet. In the spectrum of the $x = 1.5$ hydride four septets can be identified. As at this value of x hydrogen occupies the 9(e) sites, the septets can be attributed to the Sm sites with 0–3 hydrogen atoms at these nearest neighbour sites. For $Sm_2H_{17}H_{4.6}$ two quadrupole septets are observed. At this concentration the 9(e) sites are fully occupied and the remaining hydrogen is distributed over one-third of the 18(g) sites. Using the binomial distribution function allowed us to attribute the septet with higher intensity to Sm with three 9(e) and two 18(g) hydrogen neighbours, whereas the septet with lower intensity could be attributed to Sm with three 9(e) and one 18(g) hydrogen neighbours. From the central frequencies ν_0 of each septet the values of the hyperfine field B were obtained using the equation: $\nu_0 = Cg_nB$ with $C = -7.6231$ MHz/T and $g_n = -0.2306$ for [147]Sm [6]. The values of the hyperfine field are collected in Table 1, together with the quadrupole splittings derived from the line separation within the septets. The theoretical probabilities $P(n, x/3)$ of the respective configurations of hydrogen
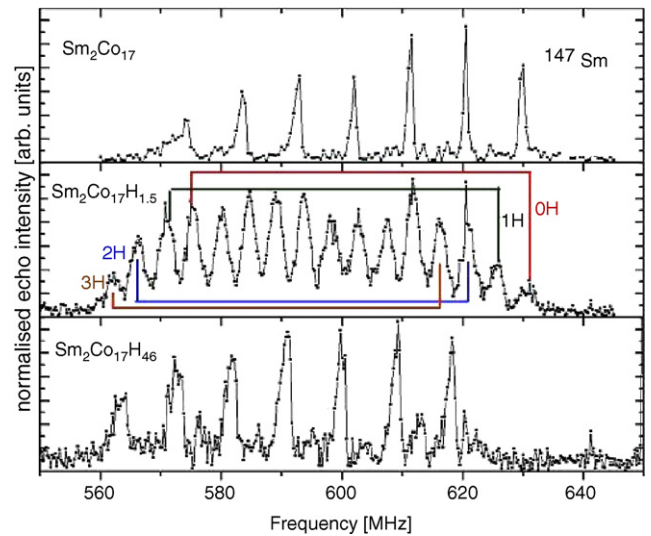
neighbours derived for both hydrogen contents from the binomial distribution function and the experimental values derived from the relative intensities of the septets, $S(n, x/3)$, are also included.

3. Discussion

An inspection of the results collected in Table 1 shows that hydrogen neighbours at the 9(e) sites cause a decrease of Sm HFF compared to the unhydrided Sm_2Co_{17}. One hydrogen neighbour causes a decrease of the HFF by 2.53 T. For the two and three hydrogen 9(e) neighbours the decrease amounts to 5.53 and 7.88 T, respectively. Relatively small hydrogen atoms are expected to influence the samarium valence electrons with the most extensive wave functions, i.e. mostly the 6sp ones. Thus the effect can be assigned to an increase of the 6sp electron contribution. The increased 6sp contribution partly cancels the dominant 4f electron contribution, which is mostly of orbital origin and is of opposite sign to that of the 6sp one. The result is consistent with our previous [145]Nd NMR results on $Nd_2Co_{17}H_x$, where a decrease of the neodymium hyperfine field due to hydrogen neighbours was observed [7]. Hydrogen neighbours at 18(g) sites cause an increase of the Sm hyperfine field, that can be

Table 1
The values of central line frequencies in the septets ν_0, quadrupole splitting ν_q, electric field gradient V_{ii}, theoretical occupation probability of n hydrogen atoms at the 9(e) and 18(g) sites, $P(n, x/3)$, the corresponding experimental values derived from the relative intensities of the septets, $S(n, x/3)$ and the concentration x of hydrogen in $Sm_2Co_{17}H_x$

	ν_0 (MHz)	ν_q (MHz)	B (T)	V_{ii} ($\times 10^{20}$ V/m^2)	x	n	$P(n, x/3)$	$S(n, x/3)$
Sm_2Co_{17}	602.00	9.30	339.23	−203	0	0	1	1.00
$Sm_2Co_{17}H_{1.5}$								
1 septet	589.00	9.00	331.74	−197	1.5	3	0.125	0.12
2 septet	593.00	9.00	333.99	−197	1.5	2	0.375	0.30
3 septet	599.50	9.17	337.09	−200	1.5	1	0.375	0.29
4 septet	603.00	9.33	339.62	−207	1.5	0	0.125	0.29
$Sm_2Co_{17}H_{4.6}$								
1 septet	590.60	9.09	332.60	−199	4.6	$3_{9(e)}, 2_{18(g)}$	0.65	0.85
2 septet	594.75	9.00	334.98	−197	4.6	$3_{9(e)}, 1_{18(g)}$	0.286	0.14

attributed to a decrease of the 6sp contribution. A possible explanation of the effect is that the changes of the contribution to the hyperfine field concern the spin dipolar contribution from the 6p and, possibly, 5d orbitals. In such a case the increased spin polarisation of these orbitals lying in the basal plane of the hexagonal structure due to hydrogen 9(e) neighbours could explain a decrease of the Sm hyperfine field. In the case of hydrogen 18(g) neighbours an increase of the polarisation of the 6p and 5d orbitals out of the hexagonal plane is expected, that would cause an increase of the total hyperfine field.

The values of the electric field gradient at the samarium nuclei in different compounds and for different configurations of hydrogen neighbours, Table 1, were obtained from the line separations within the septets using the formula: $V_{ii} = 2I(2I − I)h\nu_q/3e|Q_n|$, where V_{ii} is the EFG component along the hyperfine field direction and Q_n is the nuclear quadrupole moment, for ^{147}Sm $Q_{147} = −2.08 \times 10^{−24}$ cm^2. The NMR signal in these compounds corresponds mainly to the domain wall edges, i.e. to the directions of Sm magnetic moments which are close to the easy magnetisation direction, which is the c-axis. Thus, the values of the EFG determined from the quadrupole split spectra correspond to the c-axis component of the EFG. It can be expressed as a sum: $V_{ii} = V_{ii}(4f) + V_{ii}(latt)$, where $V_{ii}(4f)$ is the contribution from the 4f electrons and $V_{ii}(latt)$ is the "lattice" contribution from the uneven occupation of the 5d and 6p orbitals of the parent atom due to the presence of neighbours in the lattice, as well as from the charge distribution at the adjacent sites [8]. Assuming the unchanged value of $V_{ii}(4f)$ with hydriding, a decrease of the EFG caused by hydrogen 9(e) neighbours can be attributed to an increase of the lattice EFG, since their c-axis components are of the opposite sign. For the 18(g) hydrogen neighbours a slight decrease of the lattice EFG is observed. The effect can be attributed to an electron density transfer from samarium towards hydrogen. In the case of hydrogen 9(e) it corresponds to the appearance of an effective negative charge in the hexagonal plane around samarium. For hydrogen 18(g) this corresponds to the appearance of a negative charge out of the plane, which has the opposite impact on the EFG at the samarium site.

Using the relation between the second order crystalline electric field (CEF) coefficient and the lattice EFG: $A_2^0 = −D/4eV_{cc}(latt)$, where $D = 1/320$ [9], an increase of the magnitude of the CEF coefficient due to the hydrogen 9(e) neighbours is obtained. It corresponds to a strengthening of the uniaxial anisotropy of the compound. For hydrogen 18(g) a slight weakening of the uniaxial anisotropy is derived.

4. Conclusions

The samarium spin echo NMR study provided resolved quadrupole split spectra corresponding to individual Sm sites with different number of hydrogen neighbours at the 9(e) and 18(g) sites. The different values of hyperfine field and electric field gradient obtained for the different Sm sites show that hydrogen affects the electronic structure at the Sm sites in a local and anisotropic way. The opposite tendencies of the changes of the hyperfine field due to the hydrogen 9(e) and 18(g) neighbours is attributed to their influence on the anisotropic spin dipolar contribution to the hyperfine field.

An increase of the lattice contribution to the electric field gradient due to the hydrogen 9(e) neighbours and its slight decrease due to the 18(g) neighbours is observed. This corresponds to an electron transfer from the samarium site towards hydrogen and results in a strengthening of the uniaxial anisotropy due to the 9(e) neighbours and its slight weakening due to the 18(g) hydrogen neighbours.

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