ELSEVIER

Journal of Alloys and Compounds 330–332 (2002) 361–364

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

A nuclear magnetic resonance study of $SmMn_2H_2$

H. Figiel[a,*], Cz. Kapusta[a,b], A. Budziak[a], P.C. Riedi[b]

[a]Department of Solid State Physics, Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, 30-059 Cracow, Poland
[b]Department of Physics and Astronomy, University of St. Andrews, St. Andrews, Fife, KY16 9SS Scotland, UK

Abstract

A ^{147}Sm and ^{149}Sm nuclear magnetic resonance study of the hydride $SmMn_2H_2$ at 4.2 K is reported. Well resolved quadrupole septets are observed in the spectra of both isotopes. The value of the hyperfine field, 342.7 T, corresponds with the fully polarised magnetic state, $J_z = J = 5/2$, of samarium in the compound. The magnitude of the electric field gradient derived from the line separation in the spectra and the quadrupole oscillations of the spin echo decay curves reveals a considerable lattice contribution to the electric field gradient. The results are discussed in terms of the influence of hydrogen on the contribution of Sm to the magnetocrystalline anisotropy of the compound and a conclusion about the magnetic structure of the compound is given.

Keywords: Nuclear magnetic resonance; Hydrides; Intermetallic compounds; Ferrimagnets; Magnetocrystalline anisotropy

1. Introduction

The compounds of manganese with rare earth (RE) metals exhibit very interesting magnetic and structural properties. They include numerous phase transitions and a variety of magnetic structures depending on the temperature and the chemical composition. Especially interesting among them are the compounds $REMn_2$ which crystallise in the cubic C15 and hexagonal C14 structures, depending on the rare earth element. The compounds easily absorb hydrogen, which enters the interstitial sites in the crystallographic structure [1]. This often leads to a considerable modification of the crystallographic structure and to dramatic changes of the magnetic properties. The effect of hydrogenation on the structural and magnetic properties has been thoroughly studied on the C15 Laves phase $REMn_2$ compounds [2–4], but few reports on the hexagonal C14 type compounds can be found in the literature. The compound $SmMn_2$ at room temperature exhibits the C14 structure (space group $P6_3/mmc$) which undergoes an orthorhombic distortion at the temperature of the onset of antiferromagnetic order, 86 K. Hydrogen uptake considerably increases the magnetic ordering temperature, which for $SmMn_2H_2$ is almost three times as high as that of the parent $SmMn_2$ compound and amounts to 248 K [5]. The compound $SmMn_2H_2$ exhibits a ferrimagnetic order with a small net magnetic moment [5]. Upon magnetic ordering it undergoes a peculiar segregation into two phases of slightly different hydrogen content, $x=1.9$ and $x=2.1$ per $SmMn_2H_x$ formula unit, respectively [5]. In order to obtain information on the magnetic properties of the compound at the atomic level, a study of the Sm sublattice by means of the nuclear magnetic resonance of the ^{147}Sm and ^{149}Sm nuclei has been undertaken.

2. Experimental and results

Nuclear magnetic resonance (NMR) measurements were carried out on the powder sample of $SmMn_2H_2$, the same as that used in the previous structural study [5]. The NMR measurements have been carried out at 4.2 K using an automated, frequency swept spin–echo spectrometer [6]. The ^{147}Sm and ^{149}Sm spin echo spectra (echo intensity vs. frequency) and spin echo decays (echo intensity vs. pulse separation) have been measured. The spectra of ^{147}Sm and ^{149}Sm are shown in Figs. 1 and 2, respectively. An example of the spin echo decay curve for ^{149}Sm is presented in Fig. 3.

3. Discussion

The spectra of both isotopes consist of well resolved septets of equidistant lines. They correspond to a much larger magnetic interaction than the quadrupole interaction

---

*Corresponding author. Tel.: +48-12-617-2554; fax: +48-12-631-3457.
E-mail address: figiel@uci.agh.edu.pl (H. Figiel).

0925-8388/02/$ – see front matter
PII: S0925-8388(01)01432-3

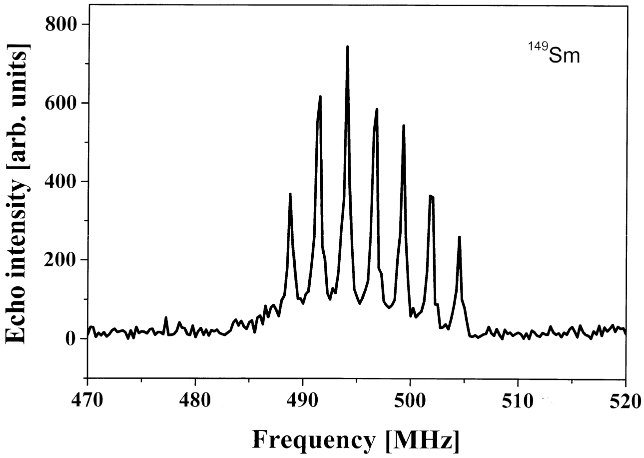

Fig. 1. The ^{149}Sm NMR spin echo spectrum of $SmMn_2H_2$ at 4.2 K.

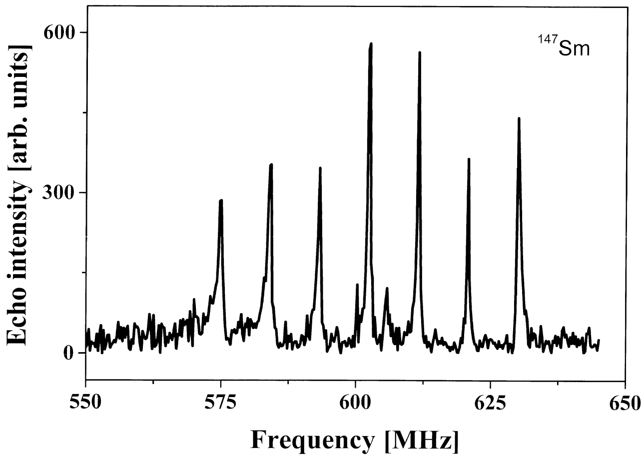

Fig. 2. The ^{147}Sm NMR spin echo spectrum of $SmMn_2H_2$ at 4.2 K.

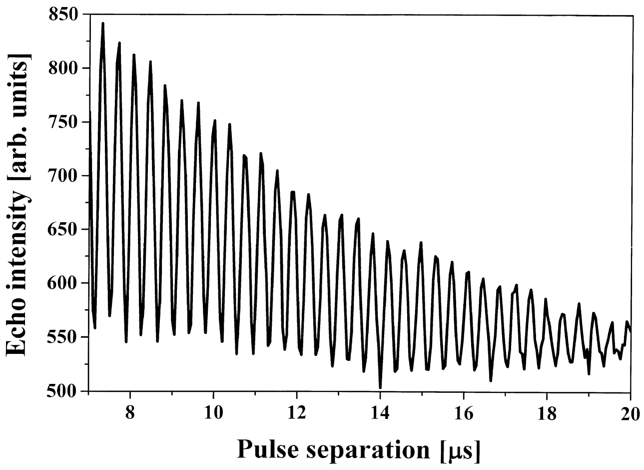

Fig. 3. The spin–echo decay curve of ^{149}Sm in $SmMn_2H_2$ at 4.2 K and 494 MHz. The pulse separation τ is the spacing between the pulses in the two pulse sequence, so the spacing between the first pulse and the echo is 2τ.

(nuclear spin of both isotopes $I=7/2$). The frequencies corresponding to the central lines of the septets, ν_0 amount to 602.5 MHz and 496.7 MHz for ^{147}Sm and ^{149}Sm, respectively. This corresponds to the effective magnetic field at the Sm nucleus which is mostly of the hyperfine origin:

$$B_{\mathrm{hf}} = 2\pi\nu_0/\gamma_{\mathrm{n}} \tag{1}$$

where γ_{n} is the nuclear gyromagnetic ratio of the isotope. Accounting for the effect of 'hyperfine anomaly' related to different radii of the isotopes [7,8], one obtains the same value of the hyperfine field equal to 342.7 T for both isotopes. This is similar to that of Sm in its ferromagnetic intermetallics with 3d elements [9], and is close to the free ion value of 338 T [7]. This indicates that Sm is magnetically ordered at 4.2 K and is in the fully polarised state with $J_z=J=5/2$.

The quadrupole splitting of the spectra, Figs. 1 and 2, is a result of the interaction of the nuclear quadrupole moment with the electric field gradient. The values of the line spacing derived from the spectra amount to ν_{q} (^{147}Sm)$=$9.19 MHz, ν_{q}(^{149}Sm)$=$2.61 MHz. The oscillations observed in the spin echo decay curves, Fig. 3, which are of quadrupolar origin [10], can also provide the value of the quadrupole splitting. This value, ν'_{q}(^{149}Sm)$=$2.62 MHz, is the same within the error margin as the line spacing of the spectra.

The value V_{ii} of the component of the electric field gradient (EFG) along the direction of the magnetic hyperfine field can be obtained from the value of the line spacing by using the formula:

$$|V_{\mathrm{ii}}| = \frac{2I(2I-1)h\,\Delta\nu_{\mathrm{q}}}{3e|Q|} \tag{2}$$

where I, Q and h are the nuclear spin, nuclear quadrupole moment and Planck constant, respectively. The quadrupole moment for ^{147}Sm was taken with the value $Q(147)=-0.265b$ [11]. The EFG at the Sm nucleus is a sum of the dominant contribution from the 4f electron shell and the 'lattice' contribution. The latter arises from the asphericity of the outer 5d and 6p electrons of the parent ion resulting from bonding with neighbouring ions as well as from the charges of these neighbours [12]. As the Sm ion is in its fully polarised magnetic state with $J_z=J=5/2$, we can take the value of the 4f electron contribution $V_{\mathrm{ii}}(4\mathrm{f})=-249\times10^{20}$ Vm^{-2}, as determined for other ferromagnetic Sm intermetallics [13]. Since the 4f contribution is dominant, the absolute value of the electric field gradient of 201×10^{20} V/m^2 obtained from the quadrupole splitting corresponds to the negative sign of V_{ii}. Accounting for the 'quadrupole anomaly' in analogy to the hyperfine anomaly [7], the same values of the EFG V_{ii} is obtained for both isotopes. The lattice contribution can be derived from the formula:

$$V_{\mathrm{ii}}(\mathrm{latt}) = V_{\mathrm{ii}} - V_{\mathrm{ii}}(4\mathrm{f}). \tag{3}$$

It has a positive value of 48×10^{20} V/m^2. Considering the fact that the lattice contribution is positive whereas the 4f contribution is negative we arrive at the conclusion that the Sm moment lies along its ‘easy’ direction or one of its easy directions [13]. A single value of the electric field gradient means that the spectra we observe correspond to a single Sm site. As the neighbouring hydrogen atoms are expected to have a large influence on the hyperfine field and electric field gradient on the Sm site [14], it can be deduced that the Sm site has a unique hydrogen environment. This would mean that hydrogen occupies the crystallographic sites in an ordered way, similarly to that reported for $YMn_2D_{1.15}$ [15]. At the temperature of the NMR measurements, 4.2 K, the sample consists of comparable amounts of two phases containing slightly different amounts of hydrogen ($x=1.9$ and 2.1, respectively) [5]. Considering this fact one would expect the presence of Sm sites with different number of hydrogen neighbours and, thus, different hyperfine fields and quadrupole splittings. Indeed, some traces of additional lines are visible, especially in the ^{147}Sm spectrum (Fig. 2), which is better resolved. However, in order to get a decisive answer on the hydrogen ordering in the structure of both phases a neutron study on deuterided samples, isotopically enriched with ^{154}Sm, because of a huge neutron incoherent cross-section of natural abundance hydrogen and samarium, is needed.

The electric field gradient tensor at the samarium site in $SmMn_2$ is axially symmetric and we assume that this holds also for $SmMn_2H_2$. The c-axis of the hexagonal system corresponds to the EFG component of the largest magnitude. This component, V_{cc}(latt) can be related to the crystalline electric field (CEF) coefficient, A_2^0 [12,14]:

$$A_2^0 = -(D/4)\, e\, V_{cc}(\text{latt}). \quad (4)$$

The phenomenological parameter D has the value 1/320 as obtained from a comparison of a Mössbauer spectroscopy study with bulk magnetic data for Gd_2Fe_{17} and other 3d intermetallics [16].

Very sharp lines in the quadrupole spectra denote that the signal corresponds to a unique value of the angle between the samarium moment direction and the c-axis. If we assume that the samarium anisotropy preference dominates that of manganese, the possible directions of the Sm moments are along the c-axis or perpendicular to it. In the first case would be negative and in the second case A_2^0 would be of the opposite sign and two times larger in magnitude. Because of positive V_{cc} value we get the negative value of the CEF coefficient equal $A_2^0=-125.3$ Ka_o^{-2}, which means, that the ‘easy’ direction is along the c-axis. The magnitude of A_2^0 is comparable to that in the highly anisotropic permanent magnet materials Sm_2Co_{17} and $Nd_2Fe_{14}B$.

The contribution of samarium to the magnetocrystalline anisotropy in the lowest order approximation is proportional to A_2^0. It is quantitatively described by the anisotropy constant K_1 [17]:

$$K_1(\text{Sm}) = -\tfrac{3}{2}\alpha_J\langle r^2\rangle A_2^0\langle O_2^0\rangle. \quad (5)$$

As for samarium $\alpha_J>0$, the negative A_2^0 corresponding to the alignment of the Sm moments along the c-axis is related to $K_1>0$.

The fully polarised state of the samarium 4f electron shell indicates that there is a strong exchange interaction with the manganese spins and, therefore, a significant magnetic moment on the Mn sites. Considering the very small value of the magnetisation per formula unit it can be deduced that the samarium moments are aligned along the c-axis or perpendicular to it, whereas the manganese moments are possibly antiferromagnetically aligned. The large magnetocrystalline anisotropy (large K_1) is consistent with the observation, that the hydride has the C14 hexagonal structure [5]. Large magnetocrystalline anisotropies are often observed in hexagonal RE-3d metal compounds [9]. The antiferromagnetic ordering of Mn moments deduced here is consistent with the general behaviour of manganese in the other RE compounds and hydrides, where Mn sublattices show an antiferromagnetic collinear or non collinear order.

4. Conclusions

The large value of the hyperfine field at the Sm nuclei in $SmMn_2H_2$ at 4.2 K, close to that of the Sm^{3+} ion denotes that the magnetic moments of samarium are magnetically ordered and the Sm 4f electron shell is in the fully polarised magnetic state, $J_z=J=5/2$. This indicates that the exchange interaction acting on the samarium 4f shell from the manganese 3d electron spins is large.

A significant lattice electric field gradient is found at the samarium site, which corresponds to a large value of the magnetocrystalline anisotropy energy.

The Sm spectra suggest that hydrogen atoms are possibly ordered in the crystal lattice of the compound in a way which preserves a unique hydrogen environment of the Sm site.

The magnetic moments of samarium exhibit a ferromagnetic alignment, whereas the magnetic ordering within the manganese sublattices is possibly antiferromagnetic.

Acknowledgements

Work supported by the State Committee for Scientific Research, Poland, grant No. 2P03B 144-15 and the Engineering and Physical Sciences Research Council, UK.

References

[1] G. Wiesinger, G. Hilscher, Magnetism of hydrides, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, Vol. 6, Elsevier, Amsterdam, 1991.

[2] H. Figiel, J. Przewoznik, V. Paul-Boncour, A. Lindbaum, E. Gratz, M. Latroche, M. Escorne, A. Percheron-Guegan, P. Mietniowski, J. Alloys Comp. 274 (1998) 29.
[3] J. Zukrowski, J. Przewoznik, K. Krop, M. Strecker, G. Wortmann, J. Alloys Comp. 261 (1997) 47.
[4] J. Przewoznik, J. Zukrowski, K. Freindl, E. Japa, K. Krop, J. Alloys Comp. 284 (1999) 31.
[5] H. Figiel, A. Budziak, J. Zukrowski, Solid State Commun. 111 (1999) 519.
[6] J.S. Lord, P.C. Riedi, Meas. Sci. Technol. 6 (1995) 149.
[7] B. Bleaney, in: J.R. Elliot (Ed.), Magnetic Properties of Rare Earth Metals, Plenum, New York, 1972, Chapter 8.
[8] H. Figiel, Cz. Kapusta, N. Spiridis, G. Stoch, P.C. Riedi, M. Rosenberg, J. Magn. Magn. Mater. 104–107 (1992) 1198.
[9] Cz. Kapusta (1), P.C. Riedi, G.J. Tomka, in: K.H.J. Buschow (Ed.), Handbook of Magnetic Materials, Vol. 11, Elsevier, Amsterdam, 1998, p. 407.
[10] H. Abe, H. Yasuoka, A. Hirai, J. Phys. Soc. Jpn. 21 (1966) 77.
[11] J.G. England, I.S. Grant, J.A.R. Griffith, D.E. Evans, D.A. Eastham, G.W.A. Newton, P.M. Walker, J. Phys. G 16 (1990) 105.
[12] R. Coehoorn, K.H.J. Buschow, J. Appl. Phys. 69 (1991) 5590.
[13] Cz. Kapusta, M. Rosenberg, P.C. Riedi, M. Katter, L. Schultz, J. Magn. Magn. Mater. 134 (1994) 106.
[14] Cz. Kapusta, P.C. Riedi, Interstitial intermetallic alloys, in: F. Grandjean, G.J. Long, K.H.J. Buschow (Eds.), NATO ASI Series, Kluwer, Dordrecht, 1995, p. 497.
[15] M. Latroche, V. Paul-Boncour, A. Percheron-Guegan, F. Bourée-Vigneron, G. André, Physica B 276–278 (2000) 666.
[16] P.C.M. Gubbens, A.M. van der Kraan, K.H.J. Buschow, Hyp. Int. 53 (1989) 37.
[17] B-P. Hu, H-S. Li, J. Gavigan, J.M.D. Coey, J. Phys.: Cond. Matter 1 (1989) 755.