



## Hydrogen-induced reduction of electric field gradient in $\text{La}_2\text{Fe}_{14}\text{BH}_x$ studied by NMR on $^{139}\text{La}$

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Received 10 July 2003; received in revised form 30 September 2003; accepted 17 October 2003 by C. Tejedor

### Abstract

The  $^{139}\text{La}$  NMR spin-echo spectra of  $\text{La}_2\text{Fe}_{14}\text{BH}_x$  are reported. Since lanthanum has no 4f electrons, the observed quadrupole splittings are directly proportional to the lattice part of the electric field gradient,  $V_{zz}^{\text{lat}}$ . This quantity decreases as the content of interstitial hydrogen  $x$  grows. To describe the fall-off of  $V_{zz}^{\text{lat}}$ , a dimensionless function  $f_2(x)$  is introduced, normalised so that  $f_2(0) = 1$ . Analysis of the new and earlier published data obtained by several experimental techniques demonstrates that the reduction of both the second-order crystal field parameter  $A_{20}$  and the lattice electric field gradient  $V_{zz}^{\text{lat}}$  is described by the same function  $f_2(x)$  in all  $\text{R}_2\text{Fe}_{14}\text{BH}_x$ . The only distinction that needs to be made is between R being a light and a heavy rare earth. © 2003 Elsevier Ltd. All rights reserved.

PACS: 75.30.Gw; 75.50.Ww; 76.60.Lz

Keywords: A. Permanent magnets; D. Magnetic anisotropy; A. Hydrogenated intermetallic compounds; D. Electric field gradient

Hydrogenation is known to reduce the crystal field (CF) acting on the rare earth (RE) in the  $\text{R}_2\text{Fe}_{14}\text{B}$  hard magnetic materials. This effect was deduced in Refs. [1,2] from observation of spontaneous spin-reorientation transitions (SRT) in a number of hydrides  $\text{R}_2\text{Fe}_{14}\text{BH}_x$ , the transition point  $T_{\text{SR}}$  being a function of hydrogen content  $x$ . The more reliable data were obtained on the second-order CF parameter  $A_{20}$ , whose reduction is described by a dimensionless function  $f_2(x) \equiv A_{20}(x)/A_{20}(0)$ . When  $T_{\text{SR}}$  is in the room temperature range (as is the case for  $\text{R}_2\text{Fe}_{14}\text{BH}_x$  with  $\text{R} = \text{Er}, \text{Tm}$ )  $A_{20}$  can be determined in a rather direct way from  $T_{\text{SR}}$ , see Eq. (5) of Ref. [1]. The characteristics of the

iron sublattice which appear in that formula are usually taken from the isostructural  $\text{Y}_2\text{Fe}_{14}\text{BH}_x$ .

The function  $f_2(x)$  was also deduced from the electric field gradient  $V_{zz}$  on the nucleus  $^{161}\text{Dy}$  in the  $\text{Dy}_2\text{Fe}_{14}\text{BH}_x$  series [3]. The thus defined  $f_2(x)$  was found to agree well with the one determined from the room temperature SRT. This demonstrates that a proportionality relation,  $A_{20} = -1/4DeV_{zz}^{\text{lat}}$ , holds between  $A_{20}$  and the 'lattice' part of  $V_{zz}$  (the remaining part of  $V_{zz}$  comes from the anisotropic 4f shell; at saturation it is a known constant). This proportionality should be regarded merely as an experimental fact established for the  $\text{R}_2\text{Fe}_{14}\text{BH}_x$  series and valid within these limits. Ab initio electronic structure calculations [4] demonstrated that there is no physical reason for the dimensionless parameter  $D$  to be a universal constant, even less so to equal unity as predicted by the point-charge model.

One should note that the experiments which led to the

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determination of  $f_2(x)$  in previous works were mainly conducted on  $R_2Fe_{14}BH_x$  with heavy RE,  $R = Dy, Er, Tm$  [1–3]. It is known, however, that the sequence of filling the crystallographically inequivalent interstitial sites in  $R_2Fe_{14}BH_x$  by hydrogen depends on whether  $R$  is a light or a heavy RE [5], therefore one might expect to find a different function  $f_2(x)$  for the  $R_2Fe_{14}BH_x$  with light RE. The latter are far more important for applications than their heavy-RE counterparts. However, suitable data on the light-RE hydrides are limited to  $Pr_2Fe_{14}BH_x$  and even in that case the less accurate technique of fitting room temperature magnetisation curves had to be used to deduce  $f_2(x)$ , since no spontaneous SRT was discovered in the room temperature range [2]. In addition, the last determined point of the dependence  $f_2(x)$ , corresponding to  $x = 5.5$ , was not reliable, because  $Pr_2Fe_{14}BH_{5.5}$  was found not to be an easy-axis magnet at room temperature and thus making properly textured powder samples with that composition was impossible.

To fill this gap, we have chosen to carry out a study of  $f_2(x)$  on  $R_2Fe_{14}BH_x$  with  $R = La$ , ‘the lightest RE’, which we expect to differ most from the heavy-RE case. Lanthanum has an added advantage—its 4f shell is empty and therefore  $V_{zz}^{lat}$  is the sole contribution to  $V_{zz}$ . Thus, in this Letter we present the results on  $f_2(x)$  as deduced from  $^{139}La$  NMR data on  $La_2Fe_{14}BH_x$ .

The  $La_2Fe_{14}B$  ingot was prepared by induction melting of the 99.9%-pure elements mixed in the proportion 2:13:1, using the so-called cold crucible method under argon atmosphere. The subsequent heat treatment consisted of 1 h at 800 °C and 3.5 h at 840 °C. Traces of  $\alpha$ -Fe were detected in the resulting material by means of X-ray diffraction and thermomagnetic analysis. Hydride samples with the highest content of hydrogen were obtained by exposing pieces of the original ingot, previously degased under vacuum, to several bars of hydrogen gas at 150 °C. The maximum hydrogen uptake was determined gravimetrically. Samples with intermediate hydrogen contents were subsequently produced by heating calculated amounts of the fully-hydrogenated and hydrogen-free compounds to 350–400 °C in small silica ampoules. The lattice parameters were found using a Guinier–Hägg camera with  $Cr K\alpha$  radiation. The Curie points were determined by means of a home-made Faraday-type thermomagnetic balance. The saturation magnetisation was measured on an Oxford Instruments vibrating-sample magnetometer at room temperature in an applied magnetic field of 8 T. The NMR spin-echo experiments were performed on polycrystalline samples of  $La_2Fe_{14}BH_x$ , with  $x = 0, 1, 2, 3$  and 4, at  $T = 4.2$  K using an automated spectrometer [6]. The 0.2/1000/0.4  $\mu s$  pulse sequence was used.

Hydrogenation of  $La_2Fe_{14}B$  leads to a significant lattice expansion, as can be seen in Fig. 1(a), where the lattice parameters of  $La_2Fe_{14}BH_x$  are plotted against hydrogen content  $x$ . The magnitude of this expansion is similar to that observed in other  $R_2Fe_{14}BH_x$  [7]. The hydrogen-induced

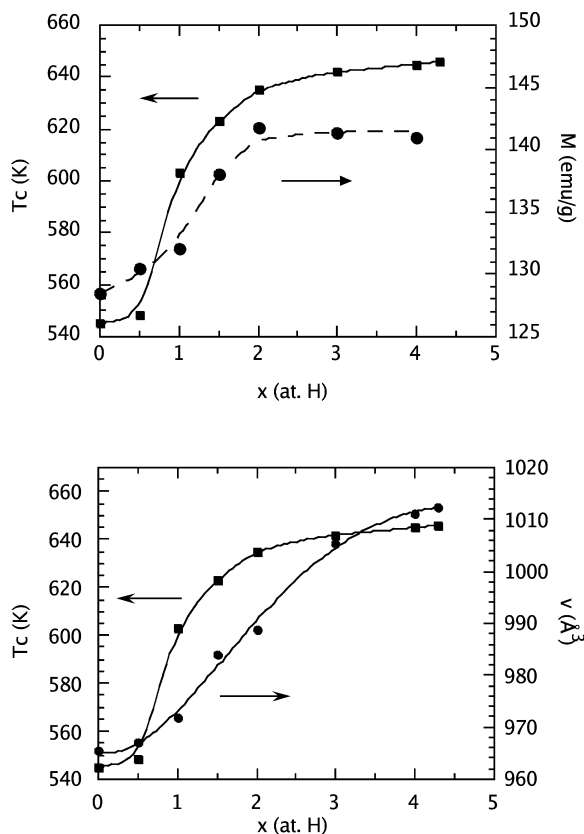


Fig. 1. Unit cell volume, saturation magnetisation at room temperature and the Curie point of  $La_2Fe_{14}BH_x$  vs. hydrogen content  $x$ .

lattice expansion is accompanied by an enhancement of both the saturation magnetisation and the Curie temperature, Fig. 1(b). Thus, the Curie point rises by about 100 K, in agreement with earlier data [7]. Note that the maximum at  $x = 2$  in the  $M(x)$  dependence of Fig. 1(b) is caused by a higher content of  $\alpha$ -iron in the  $La_2Fe_{14}BH_2$  sample.

The NMR spectra of  $La_2Fe_{14}H_x$ ,  $x = 0, 2, 3$  and 4, are shown in Fig. 2.

The spectrum of the host compound  $La_2Fe_{14}B$  shows two resolved quadrupolar septets ( $^{139}La$  has a nuclear spin of 7/2). The central lines of the septets are situated at 217 and 266 MHz and correspond to the values of hyperfine field of 35.8 and 43.9 T, respectively. Ab initio electronic structure calculations [8] predict a larger hyperfine field for the 4f site. Therefore, the high-frequency septet can be attributed to the 4f and the low-frequency one to the 4g site [9]. Line splittings within the septets carry the information on the intensity of the electric field gradient on the corresponding sites. Thus, the gaps between the components of the high-frequency septet are 2.0 MHz wide, whereas the lines of the low-frequency septet are separated by some 4.2 MHz. Assuming a negative sign for  $V_{zz}^{lat}$ , as in  $Nd_2Fe_{14}B$ , these splittings correspond to  $V_{zz}^{lat} = -11.6 \times 10^{21}$  and

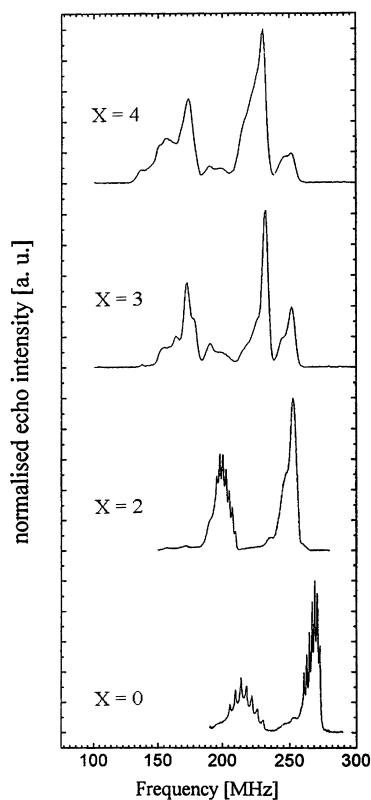


Fig. 2.  $^{139}\text{La}$  NMR spectra of  $\text{La}_2\text{Fe}_{14}\text{BH}_x$ .  $x = 0, 2, 3, 4$ .

$-5.5 \times 10^{21} \text{ V/m}^2$ , respectively, on the 4f and 4g sites (The quadrupole moment of  $^{139}\text{La}$  is taken equal to 0.21 barn [10]).

Taking up one or two atoms of hydrogen per formula unit leads to a shift of the lines towards lower frequencies. The line splittings determined from the spectra for  $x = 1$  and  $x = 2$  (only the latter one is shown in Fig. 2), as well as from quadrupole oscillations of the spin-echo decays [11], equal 2.4 MHz (4g) and 0.9 MHz (4f).

For the hydrogen content  $x = 3$  extra lines appear at lower frequencies. These lines become dominant at  $x = 4$ . The quadrupole splittings of these lines, determined from the oscillations of the spin-echo decays, amount to 1.0 MHz (4g) and 0.7 MHz (4f).

The observed quadrupole splittings were normalised to unity at  $x = 0$ , separately for the 4f and 4g sites. For each  $x$ , the average of the resulting two reduced values of quadrupole interaction was computed and plotted against  $x$ , see the open triangles in Fig. 3. Such presentation has the advantage that it does not require precise knowledge of the nuclear quadrupole moment  $Q$ . Also shown in Fig. 3 are the earlier published data on  $f_2(x)$  for  $\text{R}_2\text{Fe}_{14}\text{BH}_x$  with  $\text{R} = \text{Pr}$  (open circles) and with heavy RE (dark symbols). The latter include the  $^{161}\text{Dy}$  Mössbauer data of Ferreira et al. [3] (dark triangles) averaged over the two inequivalent sites.

The data points in Fig. 3 fall clearly into two distinct

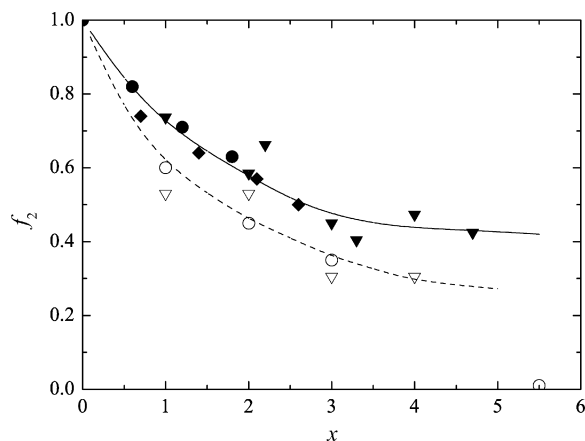


Fig. 3. Reduced second-order CF and electric field gradients on the RE in  $\text{R}_2\text{Fe}_{14}\text{BH}_x$ , normalised to unity at  $x = 0$  and plotted vs.  $x$ :  $\circ$   $\text{R} = \text{Pr}$ , deduced from anisotropy fields at room temperature [2];  $\nabla$   $\text{R} = \text{La}$ , NMR data averaged over two inequivalent sites, this work;  $\bullet$   $\text{R} = \text{Er}$  and  $\blacklozenge$   $\text{R} = \text{Tm}$ , deduced from spontaneous SRT data [1];  $\blacktriangledown$   $\text{R} = \text{Dy}$ , Mössbauer data averaged over the two sites [3]. The smooth curves are guides for the eye.

groups, according to  $\text{R}$  being either a light or a heavy RE (open and filled symbols, respectively). This division is regardless of the fact that within each group there are both bulk magnetic and averaged nuclear spectroscopic data. Nor does it matter that the quadrupole splittings measured on  $^{161}\text{Dy}$  had to be corrected by deducting a large contribution of the 4f shell of Dy [3], in order to isolate the term  $\propto V_{zz}^{\text{lat}}$ , whereas in our own  $^{139}\text{La}$  NMR experiments it was measured directly. When experimental errors are taken into account, it becomes clear that within each group the data obtained with different techniques are essentially in agreement with each other.

The open symbols in Fig. 3 lie well below the dark ones, however both mark falling dependences  $f_2(x)$ . This means unfortunately, that interstitial hydrogen destroys the main source of RE magnetic anisotropy—the second-order CF—in  $\text{R}_2\text{Fe}_{14}\text{B}$  and that it does so more efficiently in the light RE-based members of the family. Such behaviour is in stark contrast with the  $\text{R}_2\text{Fe}_{17}$  compounds, where hardly any difference was found between the values of quadrupole splitting in  $\text{Sm}_2\text{Fe}_{17}$  and in its hydride  $\text{Sm}_2\text{Fe}_{17}\text{H}_{2.9}$  [12]. The rapid decay of the RE anisotropy, accompanied by a significant decline of the iron sublattice anisotropy [1,13], outweighs the moderate improvements to the saturation magnetisation and the Curie point, brought about by the hydrogenation.

To summarise, hydrogenation results in a significant reduction of both the second-order CF and the electric field gradient on the RE nuclei in  $\text{R}_2\text{Fe}_{14}\text{BH}_x$ . Depending on whether  $\text{R}$  is a light or a heavy RE, this reduction is described by one of the two possible unique functions of hydrogen content  $f_2(x)$ . Within each half of the RE series, one and the same function  $f_2(x)$  applies, as demonstrated by

the analysis of data obtained by several experimental techniques.

### Acknowledgements

This work was supported by the Ministry of Science and Technology of Spain, Project MAT02/166, and by the Domingo Martínez Foundation (Spain), Project No. 4.7. M.D.K. acknowledges the financial support of the Spanish Ministry of Education, Culture and Sports (SAB2000-0084) during his stay on sabbatical leave in Zaragoza. Cz.K. and P.C.R. acknowledge a support from the Engineering and Physical Sciences Research Council, UK, and from the Faculty of Physics and Nuclear Techniques, AGH University of Science and Technology, Poland.

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