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Metallic and non-metallic lanthanum hydrides studied by means of proton nuclear magnetic resonance

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Abstract. The proton nuclear magnetic resonance (T_1 , T_2 , linewidth) is measured for lanthanum hydrides LaH_x ($2.0 \leq x \leq 3.0$) at temperatures between 4 K and 300 K and Larmor frequencies of 300 MHz and 50 MHz. In addition to the resonance line narrowing and the increase of the spin-lattice relaxation rate for temperatures above 200 K, originating from the well established type of thermally activated proton hopping motion in lanthanum hydrides, a low-temperature motion-induced relaxation anomaly is derived for temperatures below 40 K. Thus the Korringa relaxation contribution in metallic $\text{LaH}_{2.0}$ is most reliably separated in the 40–200 K temperature range.

1. Introduction

It has been known for more than forty years now that rare-earth dihydrides like LaH_2 are metals with one lanthanum 5d-like conduction electron per formula unit, and that trihydrides are semiconductors, which is suggestive of an ionic description as $\text{La}^{3+}(\text{H}^-)_3$ [1]. Recent interest in this field dates from the observation that rare-earth hydride mirrors can be switched reversibly and comparatively quickly from reflectivity to transparency for visible light via the hydrogen content [2, 3]. Whereas it is well known that band filling and atomic order play a significant role in the metal–semiconductor transition [4], important aspects are currently not yet understood. Thus the influence of Coulomb correlation of the conduction electrons is a matter of current controversy [5].

Whereas simple self-consistent electronic band-structure calculations led to a description of trihydrides like YH_3 as semi-metals with considerable band overlap (1.5 eV), already small Peierls-like shifts of the H atoms relative to their symmetric positions resulted in considerable lowering of the total energy and a highly reduced density of states of the electron and hole band at the Fermi energy. Structural instabilities and special types of hydrogen ordering are familiar for rare-earth hydrides, anyway [6]. New density functional calculations (LDA), with symmetry reduced to $P3$, indicated a direct gap of 0.8 eV, which—taking the assumed inaccuracy of the method into account—might very well agree with the optical transparency [7].

On the other hand, in the description considering correlated electrons [8], starting at LaH_2 with all tetrahedral interstitial sites of the face-centred-cubic (fcc) lanthanum lattice occupied with hydrogen, hydrogen atoms additionally introduced at octahedral interstitial sites would present magnetic impurities with spin $-1/2$ forming strongly coupled singlets with the lanthanum 5d-like conduction electrons as in a Kondo-insulator model. At the LaH_3 end, the removal of hydrogen from the octahedral sites of insulating LaH_3 would lead to strongly localized electrons, that give an impurity band only for high enough doping (of the order of

20%). In this respect it was emphasized that the spatial extent of a 1s orbital of a negatively charged H^- ion would be three times larger than that of a standard H atom [9].

Nuclear magnetic resonance (NMR) and relaxation have given a great deal of relevant information concerning hydrogen motion in rare-earth hydrides at high temperatures in the past [10, 11]. It is evident that the NMR technique applied to the low-temperature range could be of considerable help in unravelling details of the electronic structure. One main obstacle results from the substantial proton NMR linewidth caused by magnetic dipole interaction of the highly concentrated proton nuclear magnetic moments in the temperature range where motional narrowing is lacking. Another difficulty follows from structural instabilities—raising doubts as regards the simple face-centred-cubic crystal structure in the LaH_2 – LaH_3 ‘isostructural’ series. This gives rise to several H-concentration-dependent, and frequently also temperature-dependent, structural distortions [12–14]. Thus a careful separation of the electronic and structural phenomena reflected by NMR relaxation is required.

For LaH_x compounds the metal–non-metal transition was suggested to occur in the $x \approx 2.84$ – 2.89 range [4, 15]. In the following, we show that it is indeed the case that the Korringa-like relaxation contribution, clearly separable for $LaH_{2.0}$, cannot be distinguished for $LaH_{2.89}$ any longer. The accuracy of the separation of the conduction electron contribution to the proton spin–lattice relaxation is limited by the influence of a low-temperature motion-related relaxation contribution. The appearance of a second Bloembergen–Purcell–Pound-like (BPP-like [16]) relaxation maximum has already been reported for other hydrides [17]. It might originate from proton hopping between the inequivalent tetrahedral and octahedral sites or to distorted interstitial sites.

2. Experimental details

Lanthanum hydrides of six different stoichiometries between $LaH_{2.84}$ and $LaH_{3.0}$ and the metallic compound $LaH_{2.0}$ were prepared from highest-purity lanthanum at the Material Preparation Center of Ames Laboratory (United States Department of Energy), Iowa. The stoichiometry was analysed twice and given to an error bar of ± 0.015 . The powder samples were sealed in quartz crucibles of 5 mm diameter for the NMR measurements. A Bruker MSL 300 spectrometer, an Oxford Instruments variable-temperature gas-flow cryostat, home-built probe heads and magnetic fields of a 7 T superconductor or an electromagnet were used for the proton NMR at 300 MHz or 50 MHz. An inversion–recovery spin-echo sequence with phase cycling was adopted for the measurement of the spin–lattice relaxation time T_1 . The pulse lengths amounted to 3.2 μs and 1.6 μs , respectively. The linewidth was derived via Fourier transformation of the second half of the echo.

3. Discussion of the results

Figure 1 shows the temperature dependence of the proton spin–lattice relaxation rate for two ‘non-metallic’ LaH_x samples at a measuring frequency of 300 MHz. No pronounced difference in $1/T_1$ rate for $x = 2.89$ and 3.0 is visible. In addition to the familiar increase of $1/T_1$ at temperatures above 200 K, caused by the high-temperature hopping motion of the protons (used also for hydrogen charging) [10, 11], an additional maximum at about $T = 25$ K is recognized. Its increase and shift to lower temperature (of about 15 K) for the lower frequency (50 MHz) points to a thermally activated BPP-like relaxation mechanism (figure 2). The temperature dependence of the linewidth is dominated by the motional narrowing influence of proton motion at temperatures of 200 K and above (figure 3). As can be seen from the solid

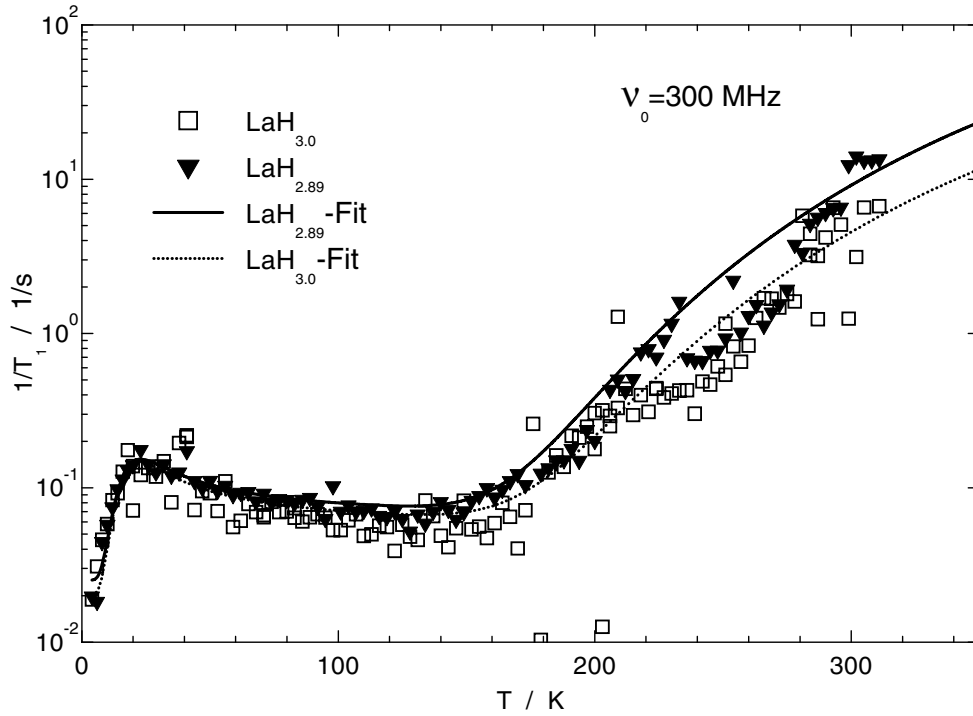


Figure 1. Proton spin–lattice relaxation rate versus temperature for $\text{LaH}_{2.89}$ and $\text{LaH}_{3.0}$. The solid and dotted lines show the fit with a constant and two BPP-like contributions as explained in the text.

lines in figures 1 to 3, these relaxation phenomena for the high hydrogen concentrations and thus non-metallic samples can be reasonably described by standard models.

For the high-temperature narrowing of the linewidth, the relation [18]

$$\left(\frac{1}{T_2}\right)^2 = \frac{4 \ln 2}{\pi} M_2 \arctan\left(\frac{\pi \tau_H}{(4 \ln 2) T_2}\right) \quad (1)$$

is fitted to figure 3, assuming activated variation of the correlation time:

$$\tau_H = \tau_{H,0} \exp(Q_H/k_B T). \quad (2)$$

Values of $\sqrt{M_2} = 52$ kHz, $\tau_{H,0} = 5.3 \times 10^{-9}$ s and $Q_H/k_B = 1970$ K are obtained for $\text{LaH}_{2.89}$. In order to describe low- and high-temperature spin–lattice relaxation (figures 1 and 2), the simplified relation [19, 20]

$$\frac{1}{T_1} = R_L \frac{\tau_L(T)}{1 + (\omega \tau_L(T))^2} + R_H \frac{\tau_H(T)}{1 + (\omega \tau_H(T))^2} + R_0 \quad (3)$$

with $\tau_L(T)$ analogous to equation (2) was used and allowed a reasonable fit to the data. In order to reduce the number of adjustable parameters, the proton–proton and proton– ^{139}La dipole–dipole contribution as well as proton–conduction electron hyperfine contributions, all modulated by self-diffusion motion of the protons, were thus subsumed in one effective contribution. It was shown by comparison of the proton relaxation behaviour in TmH_x and LaH_2 at low temperature that relaxation via paramagnetic impurities can be parametrized by a temperature-independent rate R_0 [21]. For $\text{LaH}_{2.89}$ ($\text{LaH}_{3.0}$) $R_L = 4.8 \times 10^8$ s $^{-2}$ (6.7×10^8 s $^{-2}$), $\tau_{L,0} = 7.6 \times 10^{-11}$ s (5.1×10^{-11} s) and activation energies of $Q_L/k_B =$

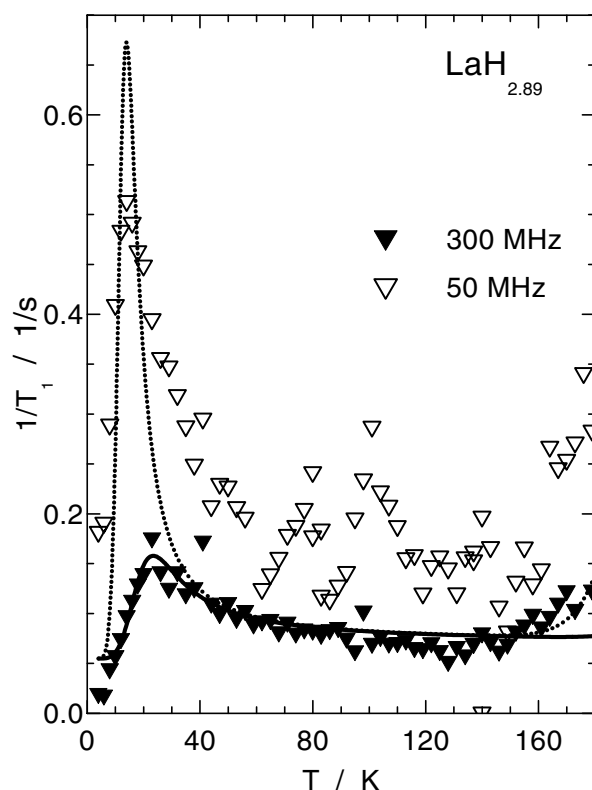


Figure 2. The influence of the Larmor frequency on the low-temperature proton spin–lattice relaxation anomaly in $\text{LaH}_{2.89}$. The solid and dotted lines show the comparison with a BPP-like relaxation mechanism.

44.4 K (45.0 K) were derived, with an expectedly small temperature-independent impurity contribution $R_0 = 2.5 \times 10^{-2} \text{ s}^{-1}$ ($2.0 \times 10^{-2} \text{ s}^{-1}$). The width of the low-temperature BPP maximum is underestimated at low frequency (figure 2) by this description. This may point to a more complicated mechanism than simple thermally activated hopping motion as the origin of the low-temperature relaxation anomaly. R_H was fitted, but $\tau_{H0} = 5.3 \times 10^{-9} \text{ s}$ ($1.2 \times 10^{-9} \text{ s}$) and $Q_H = 1970 \text{ K}$ (1870 K) were taken from the linewidth analysis. The latter parameters compare reasonably with those reported in [10, 11] for the ‘real’ high-temperature range. The low-temperature relaxation anomalies are undeniable, but much weaker than the high-temperature contributions, as can be visualized from figure 1 as well as figure 3 (i.e. increase below 50 K).

It is important to note that all attempts to improve the quality of the fit by adding a linearly temperature-dependent term representative for a Korringa-like conduction electron contribution failed in the concentration range $2.84 \leq x \leq 3.0$ as expected for an insulator, giving an upper limit of a linear slope of $5 \times 10^{-5} \text{ K}^{-1} \text{ s}^{-1}$ (about 2% of the Korringa rate for $\text{LaH}_{2.0}$).

In figure 4, the proton spin–lattice relaxation rate of metallic $\text{LaH}_{2.0}$ is compared with that of $\text{LaH}_{2.89}$ using a linear scale. The inset shows clearly the non-linearity of the low-temperature variation. If the low-temperature motion-induced relaxation contribution were to be neglected, Korringa slopes varying between 3.1×10^{-3} and $1.8 \times 10^{-3} \text{ K}^{-1} \text{ s}^{-1}$ would be derived for

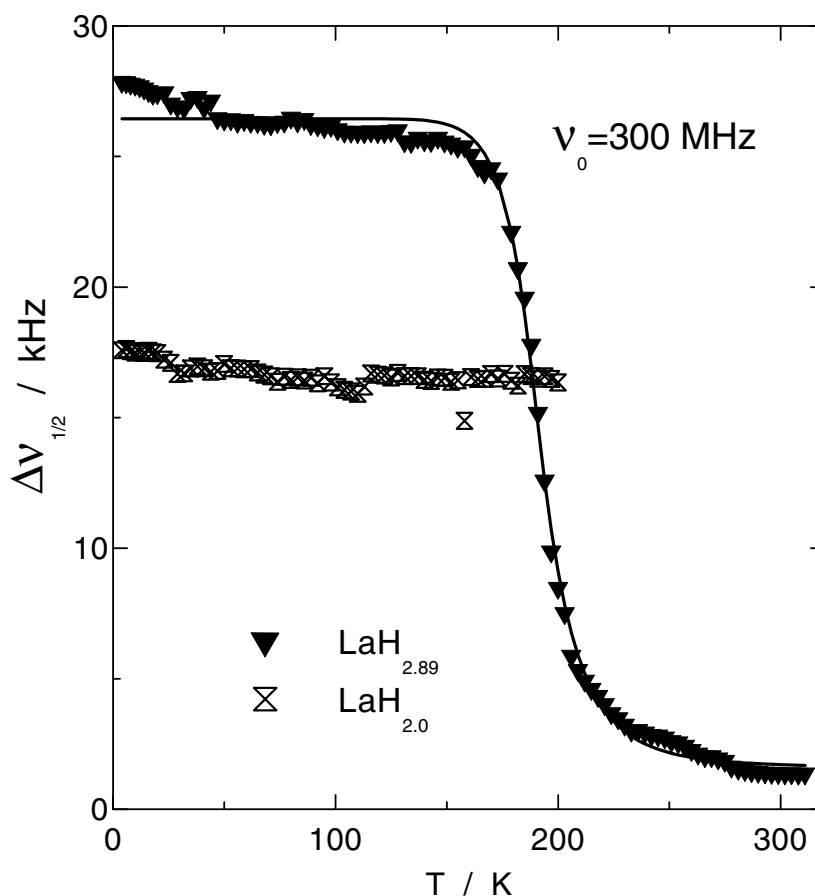


Figure 3. The temperature dependence of the proton NMR linewidth, derived from the Fourier transform of the second half of the echo in inversion–recovery T_1 -measurements. For the solid-line fit, see the text.

$\text{LaH}_{2.0}$ depending on the T -range used for the analysis, correlated with zero-temperature intercepts of 0.07 to 0.28 s^{-1} . However, as can be seen from the actual fit to the data, the expression used, equation (3) with addition of a linear term, gives a much better description of the data. Evidently, the type of proton motion responsible for the low-temperature anomaly is not restricted to hydrogen stoichiometries close to $x = 3$, but is realized already for $x \approx 2.0$. The Korringa slope amounts thus to $3.13 \times 10^{-3} \text{ K}^{-1} \text{ s}^{-1}$ (and shows the weakest sensitivity to the parameters of equation (3) in the 40 – 200 K range). Using the density of states of $12.4 \text{ states Ryd}^{-1}/\text{unit cell}$ determined from specific heat measurements [22], a hyperfine coupling parameter of $A_{\text{H}}(\text{LaH}_2) = 145 \text{ MHz}$ is derived, about one order of magnitude smaller than the coupling constant $A_{\text{H}} = 1420 \text{ MHz}$ for the 1s electron in the hydrogen atom [23]. This may be qualitatively interpreted as an indication that the conduction electron at the Fermi surface of $\text{LaH}_{2.0}$, supposed to be mostly of La 5d -like character, ‘spends’ at least about 10% of its probability at each hydrogen site.

Due to the lower proton density of LaH_2 compared to $\text{LaH}_{2.89}$, its proton NMR linewidth in the low-temperature range is considerably reduced (figure 3). The calculated ratio $M_2(\text{LaH}_{2.89}):M_2(\text{LaH}_{2.0}) = 2.8 \times 10^8 \text{ s}^{-2}:1.4 \times 10^8 \text{ s}^{-2}$ compares favourably with the ratio

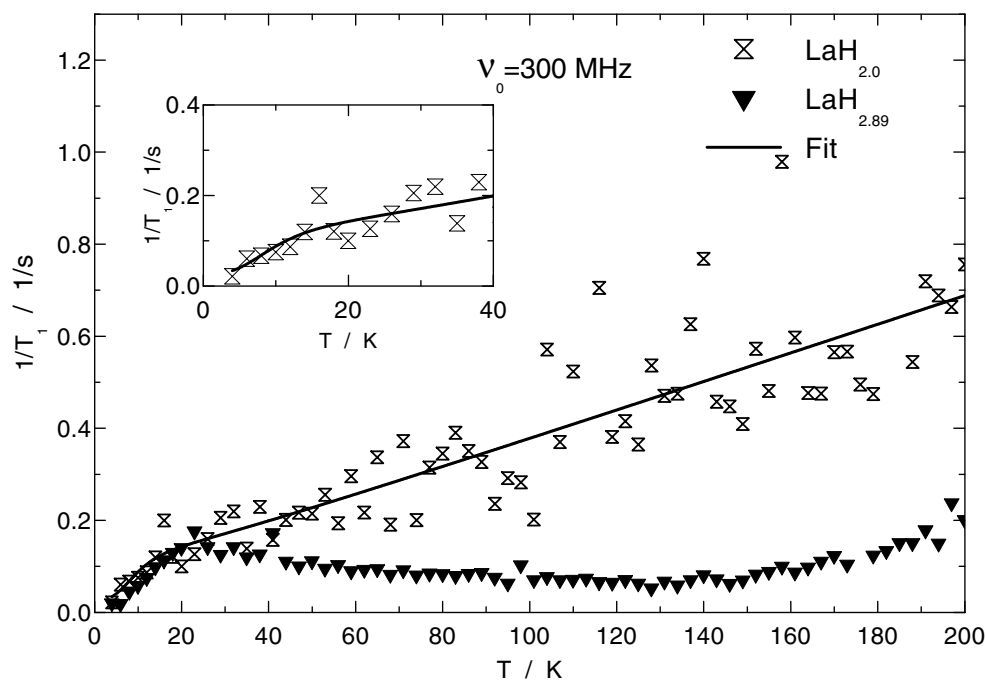


Figure 4. The proton spin–lattice relaxation rate of metallic $\text{LaH}_{2.0}$ in comparison with that of $\text{LaH}_{2.89}$. The solid-line fit, considering the Korringa-like contribution, is explained in the text. The inset shows the low-temperature non-linearity in more detail.

of $3.8 \times 10^8 \text{ s}^{-2}$ – $2.0 \times 10^8 \text{ s}^{-2}$ obtained from the observed linewidths of about 25 kHz and 16 kHz [24]. For the calculation, the tetrahedral and the occupied octahedral proton sites as well as the lanthanum sites were taken into consideration ($a = 5.613 \text{ \AA}$ [12, 13]).

4. Concluding remarks

We have demonstrated that the temperature range must be carefully selected, if the Korringa-like contribution of conduction electrons to the proton spin–lattice relaxation is to be separated from other contributions with reasonable accuracy for lanthanum hydrides. We have shown that, in addition to the high-temperature proton motion, which has been studied carefully in the past [10, 11] and is used for hydrogen charging of the lanthanum hydrides, an additional type of low-temperature motion is reflected by a relaxation maximum in the 15–25 K range for frequencies of 50 and 300 MHz. The corresponding structural implications as regards the electronic structure of lanthanum hydrides have to be considered in any attempt to understand the metal–non-metal transition of these fascinating compounds.

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