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Nuclear magnetic resonance line shape of ^{139}La in non-stoichiometric lanthanum hydrides at low temperatures

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Abstract

The ^{139}La nuclear magnetic resonance of lanthanum hydrides in LaH_{2+x} (x = 0.32, 0.38, 0.40, 0.74) was measured over the temperature range 2.3 to 303 K. A single, temperature-dependent line width was found in $LaH_{2.74}$ above 250 K, whereas a complex spectrum was observed at lower temperatures. The low temperature line shape can be described as the superposition of two resonances with the same intensity but different electric field gradients and Knight shift tensors. They were correlated with two lanthanum sites in the $LaH_{2.75}$ superlattice proposed on the basis of neutron diffraction and specific heat measurements. For the $LaH_{2.32}$–$LaH_{2.40}$ samples, the spectrum can also be decomposed into two resonances. However, in this case, one line can be attributed to the $LaH_{2.5}$ superlattice and the origin of the second line is briefly discussed.

1. Introduction

The absorption of hydrogen by lanthanum leads to the formation of hydrides whose compositions may vary between $LaH_{1.95}$ and LaH_3. The structure of the $LaH_{1.95}$ is of the CaF_2 type, where the hydrogen atoms occupy the tetrahedral sites in the f.c.c. lattice of lanthanum. When more hydrogen is introduced, the hydrogen atoms enter the octahedral sites of the fluorite lattice. When all the sites are filled, this gives a BiF_3-type structure. A solid solution of hydrogen within the octahedral sublattice can be assumed for intermediate H/La ratios. This picture commonly used in the past needs some modification in the view of recent neutron as well as X-ray structural studies.

Titcomb *et al.* [1], in their neutron investigations of some early lanthanide (Ln) hydrides have revealed the existence of a superstructure over some range of the H/Ln concentrations. The formula $LnH_{2.5}$ has been attributed to this superstructure. In this structure, only some specific octahedral sites are occupied. Later, Fedotov *et al.* [2], also using the neutron technique, indicated the possibility of the existence of another superlattice. Its composition corresponds to an ideal stoichiometry of $LnH_{2.25}$. A characteristic feature of all the superstructures mentioned is their tetragonality. Evidence for this is provided also by X-ray data reported by Boroch *et al.* [3]. Furthermore, according to these authors, there is no continuous solid solution in the LaH_2–LaH_3 system in the temperature range 110–400 K. Also, the existence of the simple cubic BiF_3-type structure for LaH_3 is questioned.

The structural problems associated with hydrogen ordering in an La–H system can also be monitored by ^{139}La nuclear magnetic resonance (NMR). This is because the ^{139}La nucleus, having a non-zero quadrupole moment, is very sensitive to its neighbourhood. Actually, the transition from the cubic to the tetragonal phase at the H/La ratio near 2.75 already has been checked by ^{139}La NMR [4, 5]. De Groot *et al.* [5] found two ^{139}La resonances at low temperatures (below about 243 K) and one of their interpretations assumes that one signal comes from an $LaH_{2.5}$ superstructure and the other from $LaH_{2.5+x}$ phase. In contrast, the existence of the $LaH_{2.5}$ superlattice is probably limited to the H/La ratios 2.37–2.48 [2]. Therefore, its appearance at the compositions close to $LaH_{2.75}$ seems improbable.

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The present studies were undertaken to clarify this interpretation as well as to extend the NMR technique to the other hydrogen concentrations. The higher magnetic fields and lower temperatures than those used in previous experiments should provide a more solid base for the interpretation of the results obtained.

2. Experimental details

The lanthanum hydride samples were obtained using elemental lanthanum metal (99.9% pure from Rare Earth Products Ltd.) and following a procedure which has been described in detail for samarium hydrides [6].

The ^{139}La NMR experiments were carried out with a Bruker MSL 300 spectrometer at frequencies of 15.28, 34.96 and 42.4 MHz. The spectra were obtained by the Fourier transform of the free induction decay (FID) following a single pulse. To record the central $(-1/2 \leftrightarrow 1/2)$ transition, we have used r.f. excitation pulses much shorter than those corresponding to the 90° pulse in liquid $LaCl_3$, *i.e.* our reference sample. Owing to random quadrupole interactions, non-central transitions may occur quite near the central line. As the r.f.-induced transition rates for satellites are smaller than those for the central transition, we used very short pulses for which the pulse–angle dependence is linear. To diminish the linear phase errors, the sampling was started in the middle of an r.f. pulse, the first data points were zeroed and then the baseline of the spectrum corrected. Temperatures in the range 2.3–303 K were achieved by the methods and associated instrumentation described elsewhere [8].

3. Results and discussion

The temperature and the magnetic field dependence of the spectra were studied in the $LaH_{2.74}$, $LaH_{2.32}$, $LaH_{2.38}$ and $LaH_{2.40}$ samples. They belong to two different composition ranges [3]. The first range, *i.e.* $LaH_{2.74}$, characterizes itself by a cubic-to-tetragonal phase transition as well as by a sharp increase in resistivity at a temperature of about 250 K [3, 8]. The possibility of a superstructure of $LaH_{2.75}$ at lower temperatures should be considered.

The second range of compositions, *i.e.* $LaH_{2.32}$–$LaH_{2.40}$, may show already at room temperature a tetragonal distortion of the metal matrix. The superstructure network is expected to have an ideal stoichiometry of $LaH_{2.25}$ or $LaH_{2.50}$. Thus we will discuss separately the results obtained for $LaH_{2.74}$ and those obtained for the other compositions.

3.1. $LaH_{2.74}$

At temperatures of 303–250 K, the ^{139}La NMR spectrum consists of a single resonance line, the width of which increases with decreasing temperature. This behavior is shown in Fig. 1. Therefore, it is characteristic that the line width does not depend on the resonance frequency. This result agrees with the findings reported earlier [5].

In general, the random distribution of the hydrogen atoms among different interstitial sites should produce a non-zero electric field gradient interacting with the ^{139}La quadrupole moment. However, owing to the fast motion of the hydrogen atoms, the quadrupole effects are averaged out to a large extent. When the hydrogen mobility slows down at lower temperatures, this effect becomes less effective and line broadening follows. Since this broadening does not depend on the frequency used, it can be considered as a first-order quadrupolar effect [9]. Remarkable changes in the spectrum were seen below about 230–225 K, where some features characteristic of the second-order quadrupole and Knight shift anisotropy appeared. They became much more pronounced at still lower temperatures. A typical example of such a spectrum, taken at $T = 4.3$ K, is shown in Fig. 2(a).

To analyse this shape, one has to consider the most general form of the nuclear hamiltonian, *i.e.* including nuclear Zeeman, nuclear dipolar, nuclear electric quadrupolar and anisotropic magnetic shift interactions. The presence of these effects leads to a complex structure of the line shape, especially for a powder specimen. The degree of complexity increases further if there is more than one non-equivalent nucleus in a crystal unit cell. To make this problem manageable, we have devised a special computer program which makes it possible to simulate various situations.

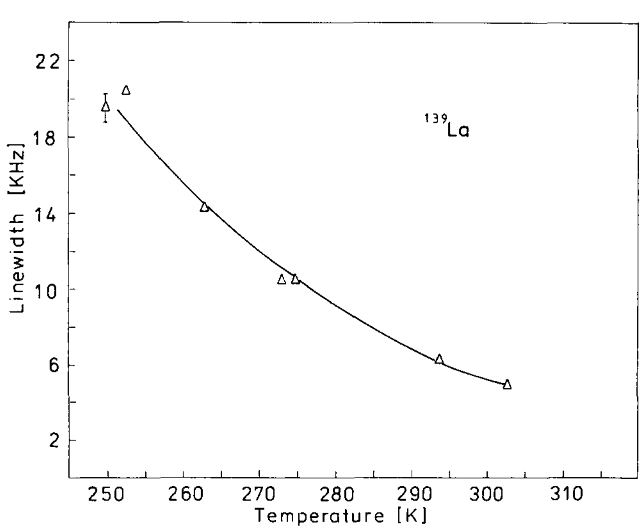

Fig. 1. Temperature dependence of the ^{139}La resonance line width in $LaH_{2.74}$. The line width is the FWHM.

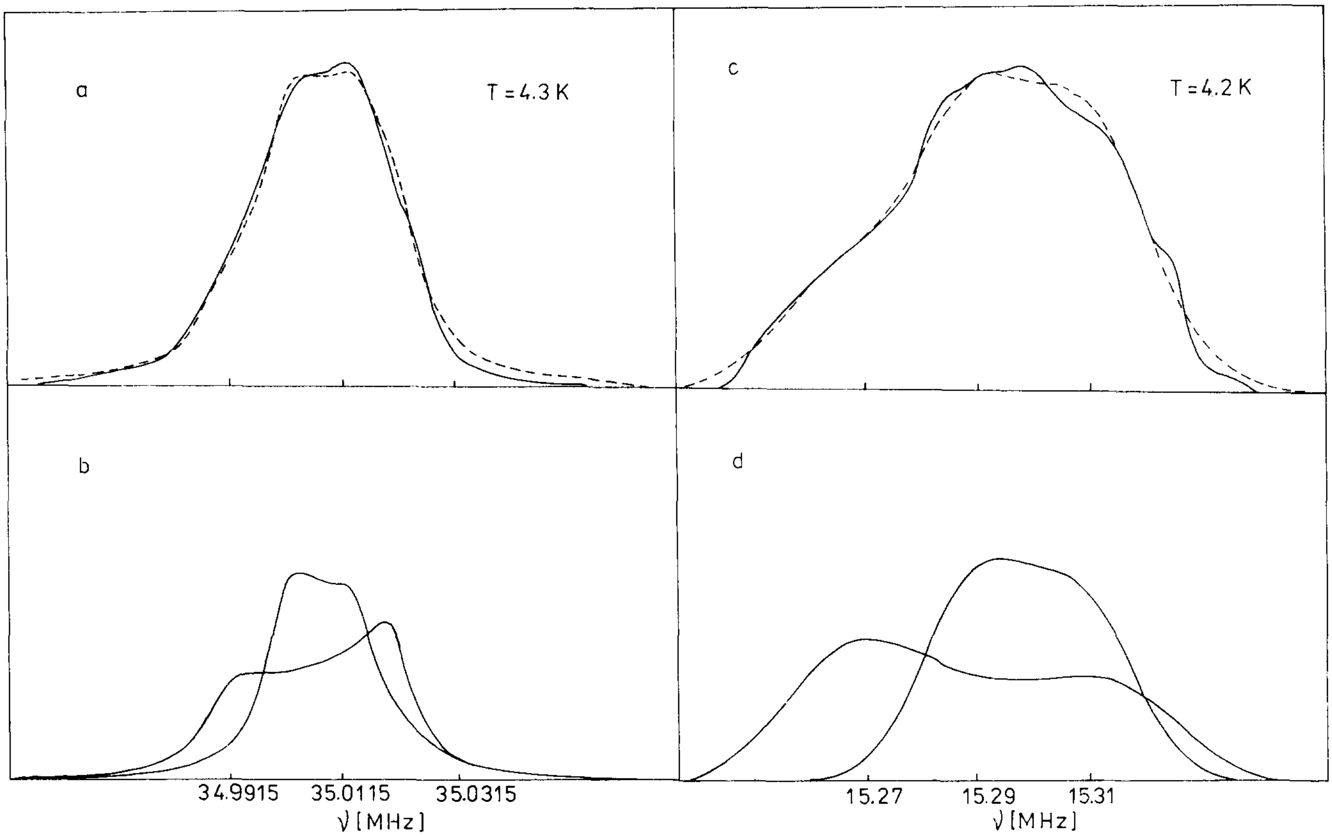

Fig. 2. Examples of ^{139}La spectra at liquid helium temperature in $LaH_{2.74}$: (a) experimental (solid line) and computer-generated (dashed line) spectra at nominal frequency $\nu_L = 34.96$ MHz (lorentzian symmetric broadening); (b) two different components (lines) corresponding to their superposition showed in (a) by dashed line spectrum; (c) the same as (a) but taken at $\nu_L = 15.28$ MHz (gaussian symmetric broadening); (d) the same as (b) but at $\nu_L = 15.28$ MHz.

The program uses the approach of Baugher *et al.* [10] to solve the problem. It includes the quadrupole effects to the second-order and the completely anisotropic magnetic shift tensor. The following parameters were used in their description. The assymetry parameter η is defined as

$$\eta = (V_{xx} - V_{yy})/V_{zz} \tag{1}$$

where V_{xx}, V_{yy} and V_{zz} are the three principal values of the electric field gradient. The principal axes of the gradient are chosen so that $|V_{zz}| \geqslant |V_{yy}| \geqslant |V_{xx}|$ which makes $0 \leqslant \eta \leqslant 1$. The largest principal value of the electric field gradient tensor $V_{zz} = eq$ gives

$$\nu_Q = 3e^2qQ/2I(2I-1)h \tag{2}$$

which is the lowest pure quadrupole frequency when $\eta = 0$. In eqn. (2), eQ is the nuclear electric quadrupole moment, I is the nuclear spin and h is Planck's constant.

A second set of parameters is connected with the magnetic shift tensor. Here, we have used slightly different notation from that of Baugher *et al.* [10], because the Knight shift rather than the chemical shift occurs in the lanthanum hydrides. This was accomplished by substituting $(-K_x, -K_y, -K_z)$ for $(\sigma_1, \sigma_2, \sigma_3)$ in their expressions. The components of the Knight shift tensor define the following set of parameters:

$$K_{\text{iso}} = \tfrac{1}{3}(K_x + K_y + K_z)$$
$$K_{\text{ax}} = \tfrac{1}{6}(2K_z - K_x - K_y) \tag{3}$$
$$K_{\text{aniso}} = \tfrac{1}{2}(K_y - K_x)$$

The parameters mentioned above give the resonance frequency for the central transition $(-1/2 \leftrightarrow 1/2)$ of a single crystal [10]. In a powder sample there are "crystallites" with random orientations relative to a constant external magnetic field. The resonance condition then must be averaged over all the possible orientations to obtain the correct spectrum. Moreover, the discontinuities which appear in such a spectrum are smoothed out by inhomogeneities in dipolar fields and electric field gradients. This is taken into account by folding the spectrum with a gaussian or lorentzian function.

Even when using computer-assisted theoretical simulations of the experimental spectra, further assumptions on the $LaH_{2.74}$ structure are required to extract the parameters given in eqns. (1)–(3). As was mentioned in the introduction, a superstructure network is expected at lower temperatures for the lanthanum hydrides. Actually, such suggestions came from the low temperature specific heat analysis of $LaH_{2.69}$, $CeH_{2.70}$ and $NdH_{2.70}$ [11]. Drulis and Staliński [11] interpreted their data using the theoretical model of Khachaturyan [12]. This model is almost anti-isomorphic to the $CeH_{2.25}$ superstructure [2]. In that structure, the composition $LaH_{2.75}$ is obtained by substituting vacancies by the hydrogen atoms and vice vèrsa. Neglecting a small tetragonal deformation, the unit cell is doubled along the c axis and contains eight formula units. Its space group is denoted by Schoenflies symbol D_{4h}^{17} and by the standard symbol *I*4/*mmm*. The metal atoms are located in 4e and 4c positions, whereas the hydrogens are in 16mm tetrahedral sites and 4d and 2b octahedral sites. Thus, there are two different lanthanum sites (4e and 4c), each of them having eight hydrogen nearest neighbours, and five and four next-nearest hydrogens respectively. The second-nearest hydrogen neighbours form a pyramid and square respectively (see Fig. 3). The first neighbours (16mm) of the lanthanum atom represent a cubic environment, while the second-nearest neighbours contribute to an electric field gradient which may have a non-zero value at the metal site. The calculation of its components q and η based upon a point-ion lattice model gave the values shown in the Table 1. Except for K_{aniso} (4e) = 0, all the other components of the Knight shift tensors may have any value, as is expected from the symmetry considerations. Since the numbers of 4c and 4e atoms are equal, the intensity (area) ratio of the spectral components should be 1:1. Finally, we may expect that the gaussian and/or lorentzian broadening for each lanthanum position can be different.

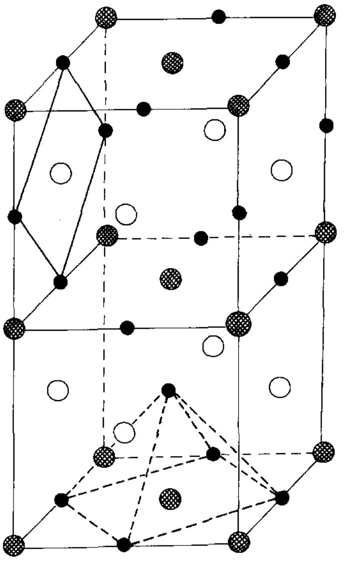

Fig. 3. Unit cell of $LaH_{2.75}$ superstructure. ◍ La (4e), ○ La (4c), ● H (octahedral site). For clarity, the hydrogen atoms in tetrahedral positions are not shown.

TABLE 1. The calculated values of q and η for the $LaH_{2.75}$ superstructure model

Atom number	Position	q	η	$\nu_Q(1)/\nu_Q(2)$
1	4c	−29.49	0.02	1.96
2	4e	−15.04	0	

The results have been obtained by a straightforward summation over 100 276 octahedral hydrogen sites. The q values are in units of Z/a_0^3, where eZ is the charge of the hydrogen atom and a_0 is the lattice parameter.

To summarize, if we adopt the above structural model for the interpretation of the ^{139}La NMR, then certain conditions have to be fulfilled. We have used them in our computer-synthesized spectra. Figure 2(a) shows the spectrum calculated in this way (the dashed line superposed on the experimental results) for $\nu_L = 34.96$ MHz. Figure 2(b) shows the two components belonging to the La (1) and La (2) nuclei resonance lines. A similar fit has been carried out at $\nu_L = 15.28$ MHz and is shown in Fig. 2(c). The decomposition of the simulated spectrum into two parts, corresponding to different lanthanum positions, is presented in Fig. 2(d). The sets of parameters which yield the calculated spectra for both the observation frequencies are listed in Table 2.

3.2. $LaH_{2.32}$, $LaH_{2.38}$ and $LaH_{2.40}$

A typical example of a spectrum for these concentrations is shown in Fig. 4(a). Its characteristic features differ significantly from those observed for $LaH_{2.74}$ in Fig. 2(a). In particular, the central part of the spectrum does not display the structure for the resonance with $\eta = 0$ [9]. The shape is rather close to the calculated shape for $\eta = 1$. Actually, an electric field gradient tensor with a high η value is anticipated for the $LaH_{2.5}$ superstructure [5]. In contrast, the existence of this superstructure for the compositions studied here is expected [2]. Thus we have calculated spectrum assuming $\eta = 1$ and allowing a superposition of two resonances. (No satisfactory fit is obtained when one considers only one resonance with $\eta = 1$.) The result of such a simulation, which gives the best possible reproduction of experimental curve, is shown in Fig. 4(a) (dashed line). The decomposition of that spectrum into two separate lines is shown in Fig. 4(b). The values of the parameters involved are listed in Table 3. The relative intensity of the two lines (I_2/I_1) is 0.322. For still lower temperatures ($T = 2.3$ K), Fig. 2(c) shows the experimental spectrum together with that calculated, based on the parameters in Table 3. It can be seen that they differ only slightly from the spectra taken at $T = 133$ K. The low temperature spectra for the remaining samples $LaH_{2.32}$ and $LaH_{2.40}$ are very similar

TABLE 2. NMR fit parameters for the ^{139}La spectrum in $LaH_{2.74}$

	Line 1		Line 2	
	$\nu_L = 34.96$ MHz	$\nu_L = 15.28$ MHz	$\nu_L = 34.96$ MHz	$\nu_L = 15.28$ MHz
ν_Q (MHz)	0.595	0.595	0.3	0.3
η	0.02	0.02	0	0
K_{ax} (%)	0.022	0.037	−0.03	−0.04
K_{aniso} (%)	−0.0006	−0.004	0	0
K_{iso} (%)	0.14	0.137	0.13	0.15
$\Delta\nu_{1/2}$ (kHz)	8.6		8.4	
$m_2^{1/2}$ (kHz)		10.4		8.5

All the measurements were made at 4.2 K. The quantities $\Delta\nu_{1/2}$ and m_2 are the lorentzian FWHM and the gaussian second moment respectively.

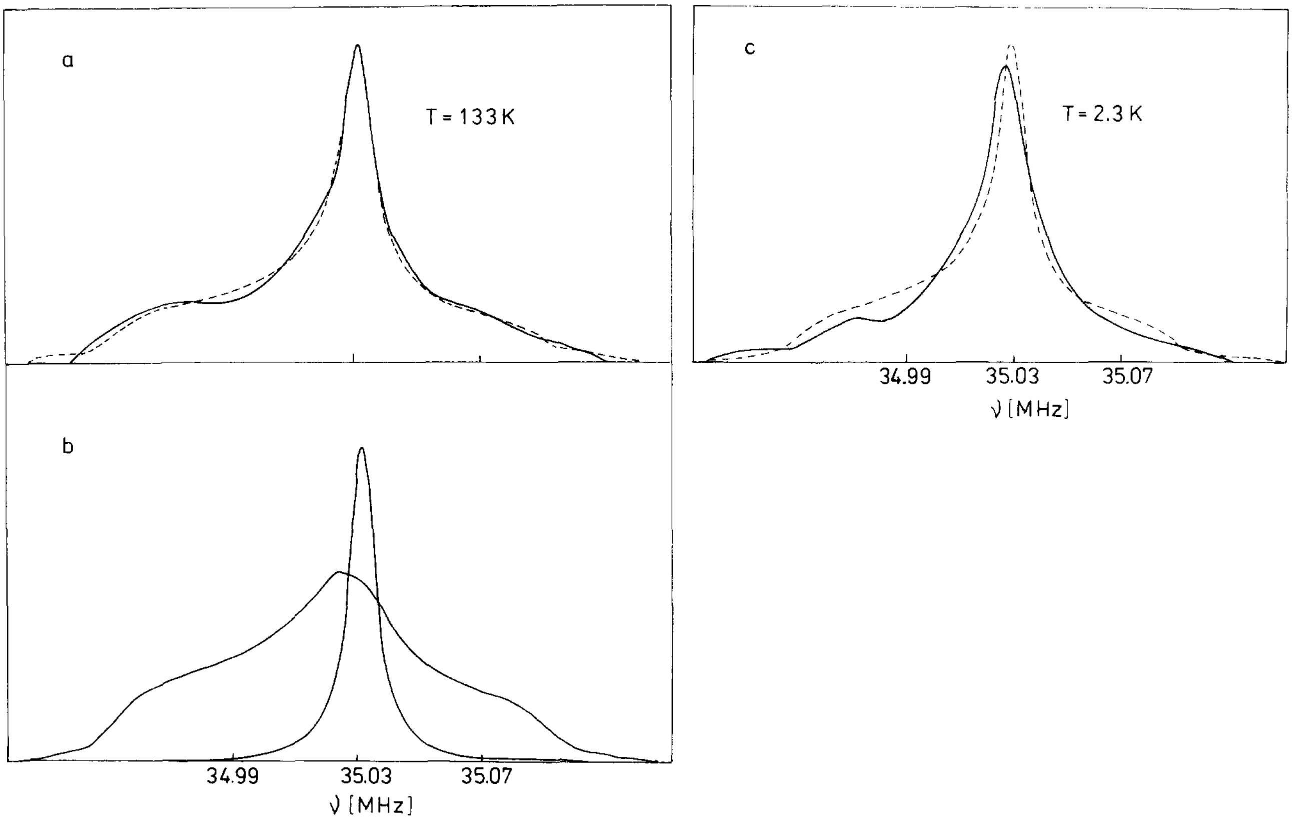

Fig. 4. Example of ^{139}La spectra in $LaH_{2.38}$ at $\nu_L = 34.96$ MHz; (a) experimental (solid line) and computer-simulated (dashed line) at $T = 133$ K; (b) two components (resonance lines) corresponding to their superposition shown in (a) (dashed line); (c) the same as (a) but at $T = 2.3$ K. The NMR fit parameters are the same as in (a).

to that in Fig. 4. However, the intensity of the "narrow" component ($\Delta\nu_{1/2} = 10.5$ kHz) is remarkably higher in $LaH_{2.40}$ than in $LaH_{2.32}$. At the lower frequency $\nu_L = 15.28$ MHz, the recorded spectra show essentially the "narrow" line, while the other line vanishes in noise.

The line width exhibits a weak temperature dependence which can be attributed to the paramagnetic impurities present in our samples. The difference between the nearly constant value of the line width at higher temperatures and that for $T = 4.2$ K is of the order of 1.65 kHz. The excessive line width depends on temperature as CT^{-n}, where C and n are constants. This type of relationship has been found in the spin–lattice relaxation induced by paramagnetic ions [13].

The two-component character of the spectrum (Fig. 4) can be explained in two ways: first, as a result of two lanthanum sites with different point symmetries or, secondly, as a coexistence of two different phases. The first possibility arises if we assume that, in addition to the hydrogen occupation of 4a ($x = y = z = 0$) positions

TABLE 3. NMR fit parameters for the ^{139}La spectrum in $LaH_{2.38}$ taken at $T=133$ K and $\nu_L=34.96$ MHz

	Line 1	Line 2
ν_Q (MHz)	0.86	0
η	1	0
K_{ax} (%)	−0.024	0
K_{aniso} (%)	−0.039	0
K_{iso} (%)	0.19	0.19
$\Delta\nu_{1/2}$ (kHz)	13	10.5
$I_2/I_1=0.322$		

specific to the "ideal" $LaH_{2.5}$ superstructure [2], the second kind of 4a ($x=y=0$ and $z=0.5$) sites are partly occupied. These lanthanum nuclei, having in their nearest surroundings both sites occupied by hydrogen atoms, would experience nearly cubic symmetry. As a result, the electric field gradient at those sites will be very small and a symmetric line shape is expected. The intensity ratio of the nearly "cubic" line to the quadrupole split line for $LaH_{2.38}$ is $I_c/0.19I_q \cong 0.3$ and this would need about 6% of the 4a ($x=y=0$ and $z=0.5$) positions to be occupied. (The factor of 0.19 in the denominator takes into account that we observe only the $1/2 \leftrightarrow -1/2$ central transition of the quadrupole influenced line.) This amount of deuterium atoms occupying the second 4a positions was reported for $CeD_{2.43}$ at $T=300$ K [2]. However, similar estimations for $LaH_{2.40}$, would imply an occupation number almost three times larger. The question is whether or not such a high degree of disorder is compatible with the $LaH_{2.5}$ superlattice.

The second possibility implies the coexistence of the superstructure phase with the cubic phase. The cubic phase may be a remnant of a cubic high temperature phase [3]. However, the X-ray studies of the LaH_2–LaH_3 system indicate an extremely small (or absent) tetragonal deformation for the $LaH_{2.35}$–$LaH_{2.40}$ region and the authors [3] do not exclude the existence of a "different structure" which is not adequately determined. In addition, a low temperature cubic phase in this system appears for the compositions above $LaH_{2.5}$ and exists as a single phase between $LaH_{2.58}$ and $LaH_{2.63}$ [3]. The structural properties of that phase are not completely known yet. Possibly, our observations are a precursor of that phase.

Finally, let us mention earlier deuterium NMR investigations in the lanthanum deuterides [14]. The complex nature of the ^2H spectra was observed. Nevertheless, among the other components a "narrow" line was found. This has been attributed to the deuterium sites retaining a nearly cubic symmetry. This corresponds well with our ^{139}La "narrow" line observed for $LaH_{2.32}$–$LaH_{2.40}$ compositions.

4. Conclusions

The phase transition in lanthanum hydride for an H/La ratio close to 2.75 at about 250 K has been confirmed. The spectrum below $T=250$ K can be decomposed into two resonance lines. However, in contrast to previous studies [5], the results are interpreted as the effect of two non-equivalent lanthanum sites in the $LaH_{2.75}$ superstructure.

Also, the superposition of the two lines describes the observed spectra for the $LaH_{2.32}$–$LaH_{2.40}$ hydrides. A strong quadrupole interaction with $\eta=1$ is characteristic of one component, whereas the second resonance is represented by another single symmetric line. The former can be attributed to the $LaH_{2.5}$-type superstructure and the latter comes from the lanthanum nuclei having surroundings with a cubic symmetry. However, the origin of this phenomenon is not definitively determined yet.

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