INFLUENCE OF HYDROGEN ORDERING ON THE PROTON SPIN-LATTICE RELAXATION TIME IN SUPERSTOICHIOMETRIC LANTHANUM DIHYDRIDES LaH_{2+c}

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Introduction

The system under consideration. We consider the β-phase of lanthanum hydrides LaH_{2+c}, where N metal atoms form a fcc lattice, 2N tetrahedral interstices are occupied by 2N hydrogen atoms (denoted as H_T-atoms), and on the set of N octahedral interstices are distributed the additional *c*N hydrogen atoms (denoted as H_O-atoms). The subsystem of H_O-atoms undergoes disorder-order and order-order transitions [1]. Correspondingly the high-temperature disordered state at temperature T_{tr1} is replaced by the "ordered state I" and at temperature T_{tr2} by the "ordered state II". Phase diagram of the ordering subsystem is presented in Fig.1 [2].

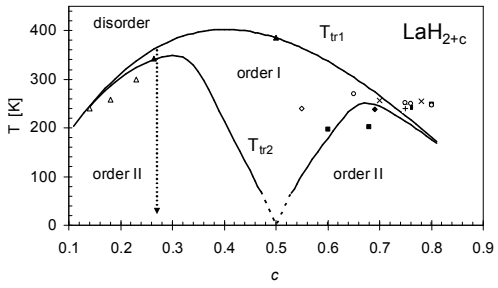

Fig.1

The problem under consideration. In articles [3] we had analytically considered the possible modifications of the temperature dependence of proton spin-lattice relaxation time T_1 in metal hydrides caused by the hydrogen ordering processes. In [4] were given the results of precise NMR measurements of lanthanum hydrides. The aim of the present report can be formulated as an attempt of the numerical calculations of $T_1(T)$ dependence in lanthanum hydride on comparing with the experimental results [4].

Proton spin-lattice relaxation time in hydrides

It is well known that

$$T_1^{-1} = T_{1d}^{-1} + T_{1e}^{-1} + T_{1p}^{-1} \quad , \qquad (1)$$

where T_1 is the total spin-lattice relaxation time, T_{1d} is the spin-lattice relaxation caused by dipole-dipole interactions, T_{1e} is that caused by conduction electrons, and T_{1p} – caused by paramagnetic impurities. As we wish to compare our results with the measurements [4] performed on "pure" $LaH_{2.27}$, we shall assume that $T_{1p}^{-1} = 0$.

For electronic contribution will be used the Korringa relation

$$T_{1e} = K / T, \qquad (2)$$

and for the dipole-dipole contribution - the well known expression, written as

$$T_{1d}^{-1} = \tau \, [J^H(T)\Sigma_j^H + J^M(T)\,\Sigma_j^M] \, , \qquad (3)$$

where $J^H(T)$ and $J^M(T)$ are temperature-dependent factors, τ^{-1} is the hydrogen jump frequency,

$$\tau = \tau_0 \exp (E_a / k_B T). \qquad (4)$$

E_a is the hydrogen jump activation energy.

$\Sigma_j^M = \Sigma_j^M (r_j^{-6})$ denotes summation over all metal atoms, and r_j denote the distances between the given interstitial H-atom and all metal lattice sites.

$$\Sigma_j^H = [\Sigma_{jT}^H (r_j^{-6}) + \Sigma_{jO}^H \, n_j(T)(r_j^{-6})] \qquad (5)$$

denotes the sum over all tetrahedral and octahedral interstitial positions. Here r_j denote the distances between the position, actually occupied by the "resonant" hydrogen atom, and other interstitial positions. It is assumed that all tetrahedral interstices are occupied by H_T-atoms with a constant probability $n_H = 1$. Octahedral positions are occupied by H_O-atoms with the probability $n_j(T) \le 1$. In the high-temperature disordered state $n_j(T) = c$ = const., while in the low-temperature ordered configurations $n_j(T) = n_1(T), n_2(T), n_3(T)$; and, generally, $n_1 \neq n_2 \neq n_3$.

Hydrogen ordering deforms slightly the metal lattice that implies small displacements of metal atoms and H_T-atoms, but we neglect this effect and assume that hydrogen ordering changes only the sum $\Sigma_{jO}^H \, n_j(T)(r_j^{-6})$.

Results of numerical calculations.

In Fig.2 is shown redistribution of H_O-atoms in both ordered states.

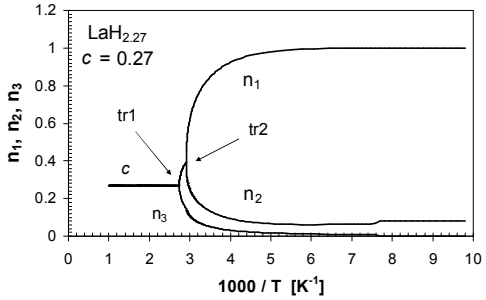

Fig. 2

Temperature variations of equilibrium occupation numbers n_1, n_2 , n_3 shown in Fig.2 are calculated following the scheme [1].

All numerical calculations we have performed for one compound – $LaH_{2.27}$ (i.e. for c = 0.27), indicated in Fig. 1 by a arrow. Results of experimental determination of $T_1(T)$ dependence in this compound [4] is presented in Fig.3.

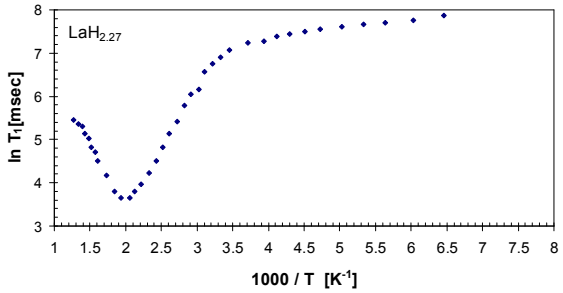

Fig. 3

In Fig.4a we give the theoretical $T_1(T)$ dependence calculated following expressions (1) – (5), on neglecting the ordering effects and using the values of fitting parameters K, τ_0 and E_a proposed in [4], while in Fig. 4b is given the difference in $T_1(T)$ dependences calculated with and without taking into account the ordering effects (illustrated by Fig.2).

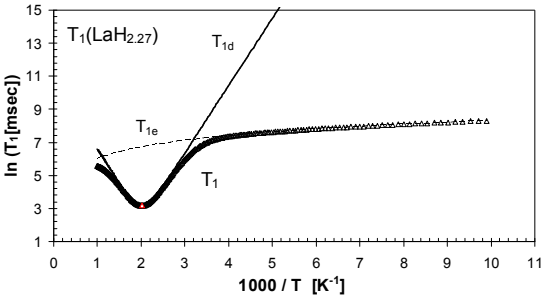

Fig. 4a

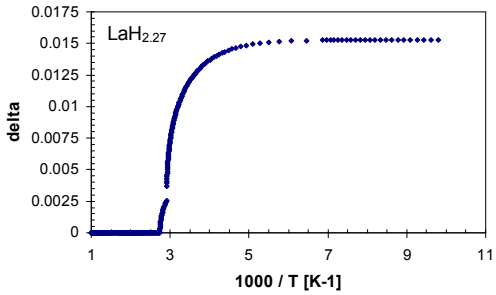

Fig. 4b

In Fig.4b "delta" indicate the difference between the values of $T_1(T)$ dependences calculated on taking into account the ordering effects, and assuming the disordered distribution of H_O-atoms at all temperatures. As it can be seen the difference seems to be very small to be registered in the measurements.

Fig.5 illustrates the description of experimental points (Fig.3) by the theoretical curve (Fig.4).

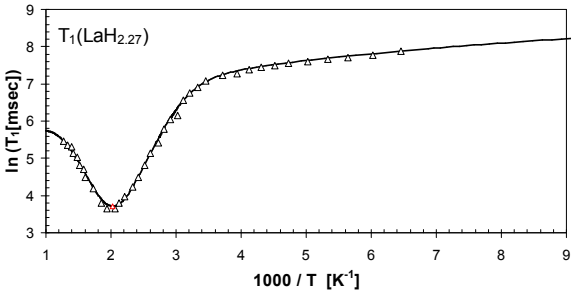

Fig. 5

Conclusions

1. In the hydrides LaH_{2+c} besides the ordering subsystem of H_O-atoms there exist the unchanged subsystems of H_T-atoms and metal atoms. For this reason the direct effects of hydrogen ordering reflected in changes of the sums in (5) are masked. In transition metal hydrides (Nb-H, V – H) the situation is better as all hydrogen atoms undergo the ordering process.
2. Nevertheless the ordering processes can influence on the $T_1(T)$ dependences on modifying the hydrogen mobility by variations of the jump activation energy E_a. This effect was pointed out in [5]. We hope that subsequent investigations will illuminate this problem.

References

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