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#### INTERNAL ROTATION AND PHASE TRANSITIONS IN LANTHANUM TETRAHYDROBORATES

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Using the  $^1\text{H}$ ,  $^{11}\text{B}$ ,  $^{139}\text{La}$  NMR and relaxation NMR methods, we have investigated the molecular dynamics in  $\text{La}(\text{BH}_4)_3$  and its adduct with tetrahydrofuran  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$ . We have observed phase transitions connected with the change in the nature of the internal rotation (reorientation) of the  $\text{BH}_4^-$  anions. We have determined the barrier to reorientation of the  $\text{BH}_4^-$  anions and the THF molecules in the investigated compounds, and we have shown that the change in the mobility of the THF molecule does not lead to a phase transition.

Internal rotation of the  $\text{BH}_4^-$  anions and disordering of the atoms in high-symmetry tetrahydroborates of alkali metals is closely connected with phase transition in these compounds [1]. In the transition to the low-symmetry compounds of the type  $\text{M}^{n+}(\text{BH}_4)_n$ , the hydrogen atoms cannot be located in structurally and chemically equivalent positions. In compounds of the type  $\text{Ln}(\text{BH}_4)_3 \cdot \text{THF}$ , according to x-ray diffraction data [2-4] the coordination interaction of the lanthanide ions  $\text{Ln}^{3+}$  with the  $\text{BH}_4^-$  ions is accomplished using hydrogen bridges. Reorientation of the  $\text{BH}_4^-$  anions should lead to intramolecular exchange of bridge and terminal hydrogen atoms. It has remained unclear to what degree the role of dynamic effects and disordering of the hydrogen atoms is important for the structure of the given compounds.

In this work, using steady-state and pulsed NMR methods at the  $^1\text{H}$ ,  $^{11}\text{B}$ , and  $^{139}\text{La}$  nuclei, we have investigated the dynamic effects in lanthanum tetrahydroborate and its adduct with tetrahydrofuran.

#### EXPERIMENTAL

The samples of  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$  were synthesized by an exchange reaction of lanthanum chloride with sodium tetrahydroborate in tetrahydrofuran (THF) using the technique described in [5]:



For the synthesis we used  $\text{NaBH}_4$  purified by recrystallization from an aqueous solution of alkali with subsequent extraction by diethyleneglycol dimethyl ether (diglyme) and drying at  $200^\circ\text{C}$  under vacuum. The  $\text{NaBH}_4$  content in the product obtained was not less than 99 mass %. The lanthanum chloride for carrying out the synthesis according to Eq. (1) was obtained by ether-acid drying of the crystal hydrate  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$  and was finally dried at  $190^\circ\text{C}$  under vacuum. The  $\text{LaCl}_3$  content in the product obtained was not less than 99 mass %. The tetrahydrofuran was dried and distilled above lithium aluminum hydride. All the operations were carried out under an atmosphere of dry inert gas.

In the starting materials and products, the lanthanum was determined complexometrically with Trilon B using xylenol orange; the boron was determined potentiometrically by

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TABLE 1. Calculated and Experimental Values of  $T_1(B)$  and  $T_1(H)$  at Relaxation Minima

$T_1$ , ms	Isotropic reorientation	$C_3$	$C_2$	$La(BH_4)_3$	$La(BH_4)_3 \cdot 3 THF$
$T_1(^{11}B)$	14,08	21,1	21,1	76±15	110±10
$T_1(^1H)$	4,16	6,075	6,62	17,1±0,9	56,0±6
$T_1(^{11}B)$	3,38	3,47	3,19	4,4±1,0	2,0±0,4
$T_1(^1H)$					

titration of mannitoboric acid with base; the chlorine was determined by the Volhard method; the sodium was determined by flame photometry; the hydride hydrogen was determined volumetrically.

The product obtained from reaction (1) was crystallized twice from THF and dried at room temperature under vacuum.

	La	B	H <sub>hydr</sub>
Found, mass %	34.81	8.14	3.04
Calculated for $La(BH_4)_3 \cdot 3THF$ , mass %	34.75	8.11	3.02

The  $La(BH_4)_3$  samples were obtained by desolvation of  $La(BH_4)_3 \cdot 3THF$  using the technique in [6].

	La	B	H <sub>hydr</sub>
Found, mass %	74.96	17.51	6.49
Calculated for $La(BH_4)_3$ , mass %	75.73	17.68	6.59

The IR spectra of lanthanum tetrahydroborate and its tetrahydrofuranate, taken on the SPECORD 75-IR spectrophotometer in petrolatum oil, are identical to the IR spectra of these complexes given in [7].

The nuclear magnetic resonance (NMR) spectra of the  $^1H$ ,  $^{11}B$ , and  $^{139}La$  nuclei were obtained using a wide-line NMR spectrometer [8] based on the Jeol JNM-4H-100. The spin-lattice relaxation times for the  $^{11}B$  and  $^1H$  nuclei were measured on the modified IS-3 pulse spectrometer [9]. The sample temperature was varied by blowing nitrogen gas through the cryostats of the spectrometers.

## RESULTS

The most important result of the NMR study is the fact that in the temperature dependences of the spin-lattice relaxation times of the  $^1H$  and  $^{11}B$  nuclei in  $La(BH_4)_3$ , at 210 K we observe a jumpwise change (Fig. 1) indicating the existence of a structural phase transition.

In the 95-110 K temperature region, the dependence of the logarithm of  $T_1$  on the reciprocal temperature is linear. This means that the frequency of the reorientational jumps  $\nu_c$  of the  $BH_4^-$  anions per unit time is described by an Arrhenius law [10]:

$$\nu_c = \nu_0 \exp(-E_a/kT),$$

where  $\nu_c$  is the correlation frequency of the motion;  $E_a = 1.2 \pm 0.2$  kcal/mole is the activation barrier;  $\nu_0$  is a constant. The minimum values of  $T_1(^1H)$  and  $T_1(^{11}B)$  differ substantially from those calculated for the  $BH_4^-$  ions with the intramolecular distance  $R(B-H) = 1.26$  Å [11] (see Table 1). From the large width of the relaxation minima ( $\sim 90$  K) and taking into account the disagreement between the experimental and calculated values of  $T_1$ , we may conclude that in  $La(BH_4)_3$  there are positions of the  $BH_4^-$  anions which are slightly different structurally and have different correlation frequencies  $\nu_c$ .

In order to refine the relaxation mechanism for the  $^{11}B$  nuclei, we calculated the ratios of the minimum values of  $T_1(^{11}B)/T_1(^1H)$ . As is evident from the table, the experimental ratio  $T_1(^{11}B)/T_1(^1H)$  is consistent with a purely dipole-dipole mechanism for the interaction of the nuclei within experimental accuracy limits, and the quadrupole coupling constant of the  $^{11}B$  nuclei in the low-temperature phase is less than  $\sim 1$  kHz.

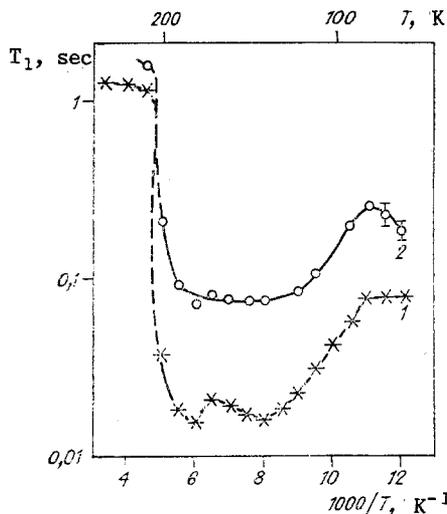


Fig. 1

Fig. 1. Temperature dependences of the spin-lattice relaxation times  $T_1$  in  $\text{La}(\text{BH}_4)_3$ : 1)  $^1\text{H}$  (26 MHz); 2)  $^{11}\text{B}$  (13 MHz).

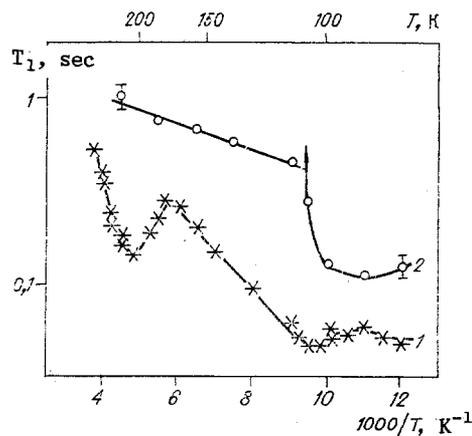


Fig. 2

Fig. 2. Temperature dependences of the spin-lattice relaxation times  $T_1$  in  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$ : 1)  $^1\text{H}$  (26 MHz); 2)  $^{11}\text{B}$  (13 MHz).

The experimental value of the second moment of the  $^1\text{H}$  NMR spectrum at room temperature, equal to  $5.2 \pm 0.3 \text{ G}^2$ , is due to intermolecular interaction. This result is found in excellent agreement with the fact that the width of the  $^{11}\text{B}$  NMR spectra in  $\text{La}(\text{BH}_4)_3$  ( $\sim 3 \text{ G}$ ), practically does not change during the phase transition. From this it follows that the bridge and terminal hydrogen atoms in the compounds are chemically (charge) equivalent. We may also suggest that the observed second moment of the  $^{11}\text{B}$  NMR line ( $2.9 \pm 0.1 \text{ G}^2$ ) is also due to dipolar intermolecular interactions. When the temperature is lowered to 190 K, the width of the  $^{11}\text{B}$  NMR signal does not change, which indicates retention of isotropic reorientation of the  $\text{BH}_4^-$  anions even in the low-temperature phase of  $\text{La}(\text{BH}_4)_3$ . As has already been noted, this is evidence for high symmetry of the environment of the boron nuclei, which practically does not change during the phase transition and is close to cubic.

The signal from the  $^{139}\text{La}$  nuclei is very weak in intensity and was registered with a modulation amplitude of 20 G, close to the width of the signal (from our estimates, about 12 G). Obviously, the low signal intensity is connected with the low symmetry of the environment of the lanthanum nuclei. In studying the adduct of lanthanum tetrahydroborate with tetrahydrofuran  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$ , it has been observed that the differences in the temperature dependences  $T_1$  in this compound from the analogous dependences in  $\text{La}(\text{BH}_4)_3$  involve especially the lowering of the phase transition temperature down to 110 K (Fig. 2). In the 210 K region, from the  $T_1(^1\text{H})$  data we observe a relaxation minimum at  $T_1 = 140 \text{ msec}$ , the magnitude of which corresponds to the averaged part of the dipole-dipole interaction with  $M_2 = 0.25 \pm 0.02 \text{ G}^2$ . This value of  $M_2$  gives a basis for proposing that the observed mobility process is connected with activational motion of the tetrahydrofuran molecules with  $E_a = 3.6 \pm 0.5 \text{ kcal/mole}$ .

From the table it is evident that the experimental ratio  $T_1(^{11}\text{B})/T_1(^1\text{H})$  in  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$  is somewhat less than those calculated for reorientation of the anions in the purely dipole-dipole interaction. We may suggest that there is an additional contribution to the relaxation of the boron nuclei, such as due to quadrupole interactions which are different from zero.

It is interesting that in the 110-250 K temperature region the slope of the  $\ln T_1(^{11}\text{B})$  curve is less than the slope of the  $\ln T_1(^1\text{H})$  curve. This also indicates the presence of a relaxation mechanism connected with spin-phonon coupling of the  $^{11}\text{B}$  nuclei in the lattice of the adduct. The results obtained are confirmed by the results of a study of the NMR spectra at room temperature. The  $^1\text{H}$  NMR signal consists of a narrow signal from the protons in the  $\text{BH}_4^-$  anion and a broad signal from the protons in the tetrahydrofuran molecule,  $-\text{OC}_4\text{H}_8$ . The  $^{11}\text{B}$  NMR spectrum is a singlet line with parameters close to the parameters of

the  $^{11}\text{B}$  NMR spectrum in  $\text{La}(\text{BH}_4)_3$ . The doublet shape of the resonance line of the  $^{139}\text{La}$  NMR signal is described by second-order quadrupole effects [12]. From the magnitude of the splitting, we estimated the magnitude of the quadrupole coupling constant  $e^2Qq_{zz}/h = 2.8$  MHz.

#### CONCLUSION

The investigation carried out shows that in the low-symmetry compounds  $\text{La}(\text{BH}_4)_3$  and  $\text{La}(\text{BH}_4)_3 \cdot 3\text{THF}$ , as in the high-symmetry  $\text{MBH}_4$ , phase transitions occur. An unexpected result is the fact that the symmetry of the environment of the boron ions for these phase transitions practically does not change and remains close to cubic. The activation energy for reorientation of the  $\text{BH}_4^-$  ion (1.2 kcal/mole) is somewhat overestimated, if we start from the difference in the electronegativity of the boron and hydrogen ions (2.0 and 2.15). This may mean that the nature of the barrier to reorientation of the  $\text{BH}_4^-$  anion in lanthanum tetrahydroborates is connected with the van der Waals interaction of the tetrahedral  $\text{BH}_4^-$  groups with the environment. From the  $^{139}\text{La}$  NMR data it follows that the coordination sphere of the triply-charged lanthanum is characterized by low-symmetry of the arrangement of the  $\text{BH}_4^-$  and THF ( $\text{OC}_4\text{H}_8$ ) ligands, and the  $\text{La}^{3+}-\text{BH}_4^-$  bond has predominantly ionic character. Consequently, the potential energy of the  $\text{BH}_4^-$  anions in the lattice is the sum of the strong isotropic ionic component and the substantially weaker anisotropic van der Waals component. In the low-temperature phases, for both compounds we observe structurally nonequivalent positions for the  $\text{BH}_4^-$  anions, retained in the high-temperature phase. The phase transitions in the studied compounds are connected with a change in the nature of the hydrogen atom distribution. Due to the low height of the barriers, the reorientational mobility sets in even at low temperatures, and in the phase transition region the value of  $\nu_c$  reaches  $10^{10}$ - $10^{11}$  Hz. For such a high reorientational frequency, there may be substantial effects from correlation rotation of the anions, leading to a change in the hydrogen atom distribution in the structure and an order-disorder type phase transition.

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