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Ionic Conductivity in Three Crystalline Phases of LiBH_4 under Pressure

Bertil Sundqvist^{a*}, Mingguang Yao^b and Ove Andersson^a

^a*Department of Physics, Umeå University, SE-90187 Umeå, Sweden;*

^b*State Key Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China*

Abstract.:

The AC electrical conductivity of LiBH_4 was investigated below 2 GPa between 1 Hz and 1.6 MHz. The high temperature phase has an ionic conductivity of up to 0.01 S cm^{-1} while the low temperature phases have conductivities two orders of magnitude lower. All phases show an Arrhenius behaviour with activation energies E_a between 0.5 and 0.7 eV, in good agreement with earlier data except for phase III, which is found to have the highest activation energy of the phases studied. The high temperature phase has a minimum in E_a near 1 GPa, close to the triple point, correlated with a sudden change in activation volume. These features may indicate an isostructural phase transition. The conductivities of the ambient temperature phases increase temporarily by an order of magnitude after transitions between these phases, probably due to new diffusion channels via structural defects. The phase diagram agrees well with earlier results.

Keywords: ionic conductivity; phase transition; phase diagram; dielectric measurements; complex hydride

Title Page Footnote:

*Corresponding author. Email: bertil.sundqvist@physics.umu.se

Introduction

Because of their very high gravimetric hydrogen contents, complex hydrides are considered good candidates for hydrogen storage in mobile applications [1]. This has also led to a strong interest in their high pressure structures and properties, primarily to investigate the possibilities to create structures with an increased volumetric hydrogen density. The high pressure and high temperature phase diagrams of these materials have thus been a hot research topic over the last few years [2-4]. As an example, LiBH_4 contains 18.4 weight percent hydrogen and its structural phase diagram has recently been investigated in detail [2-8], revealing, for example, an interesting structural metastability [6,8].

Interest in these materials has recently increased even further following the recent discovery of very high conductivities by both Li^+ [9,10] and Na^+ [11,12] ions in several complex hydrides, including LiBH_4 . Hydrides usually have a wide band gap which rules out electronic conduction, and the very high observed conductivities of order $10^{-2} \text{ S cm}^{-1}$ are thus entirely due to ionic transport. The conductivity and other properties of LiBH_4 have already been extensively investigated by many methods [10], and the conductivity was also recently investigated under high pressures between 2 and 6 GPa by Takamura *et al.* [13] in three of the four solid phases existing below 6 GPa and 500 K [2-4,7].

In this work we present new data, complementary to those presented in earlier studies [9,13]. We have carried out measurements in the pressure range 0.1 to 2 GPa on all three phases existing in this pressure range, closing the gap between existing zero-pressure and high-pressure data in the high temperature phase I, adding data in the range 0.7 – 2 GPa for the high pressure phase III and providing the first data for the ambient phase I under pressure. The data also give phase transition coordinates in excellent agreement with earlier studies and verify interesting and potentially useful hysteresis phenomena. Also, compression-induced disorder is shown to give a temporary order-of-magnitude improvement in the ionic conductivity at room temperature, hinting at possibilities to further improve the conductivities of these versatile materials.

Experimental details

The material studied was taken from the same batch of 99.9% Sigma-Aldrich LiBH_4 as used in earlier studies [5,6,8]. The material had been stored in a closed container in a dry, Argon-filled glove-box between the studies. A weighted amount of the material in powder form was placed between two cylindrical stainless steel electrodes in a cylindrical hole centered on the axis of our standard 45 mm TeflonTM pressure cell. Kanthal heaters were provided above and below the assembly and the temperature T was measured by a type K thermocouple close to the sample position. The electrodes were 10.7 mm in diameter and 5 mm high, and the measured sample thickness after compression was $1.35 \pm 0.05 \text{ mm}$. The relatively massive electrodes and the small thickness of the cylindrical sample plate ensured a good temperature homogeneity in the sample during the experiments. Pressure was generated by a hydraulic press in a piston-and-cylinder device, 45 mm in internal diameter, and the actual pressure was calculated from the load using a calibration function based on an earlier Manganin gauge calibration.

The impedance of the sample assembly was measured between 1 Hz and 1.58 MHz using a Solartron SI 1260 Impedance/Gain-phase analyzer in four-probe mode, modelling the sample as a parallel R-C combination. The complex impedance of the sample was expressed as $Z = Z' - jZ''$, and from a Cole-Cole plot of Z'' versus Z' the DC conductivity could be found by extrapolation to zero frequency at each pressure-temperature coordinate visited. Three such plots are shown in Figure 1. For the two less conductive low-temperature phases (see phase diagram in Figure 2) the impedance plots showed the expected near-elliptical trajectory with frequency and the sample resistance was found from the extrapolated high-impedance intercept with the Z' axis (Figure 1a). In the highly conductive high temperature phase we had to take into account the fact that the stainless steel electrodes do not allow Li transport. The electrodes were modelled in the usual way

[9-14] as a second parallel R–C combination connected in series with the sample, giving a second arc at higher impedances. In this case, the sample resistance was found by an extrapolation of the low-impedance behaviour of this curve (Figure 1c). In the intermediate state, observed during phase transitions, the impedance curve traced out parts of both R–C ellipses and the sample resistance could be found from the position of the interelliptic minimum (Figure 1b).

Experimental results and discussion

General overview of the experimental data

In the low-pressure range, LiBH_4 has three different structural phases and in Figure 2 we show the relevant part of the phase diagram, adapted from Refs. [7] and [8]. At ambient conditions (phase II) the structure is orthorhombic with $Pnma$ symmetry, while heating gives a transition into the hexagonal ($P6_3mc$) phase I. The high pressure phase III is formed on compression beyond about 0.7 GPa, has a pseudo-tetragonal structure with $Ama2$ symmetry and is metastable down to zero pressure below 200 K. The phase boundaries at and above room temperature were first identified by Pistorius [15] by differential thermal analysis (DTA), while the complicated II-III boundary (dashed curves) at low temperature [5,6,8] and the crystal structures [7] have been mapped more recently. On crossing the I-III boundary Pistorius always found double anomalies in the temperature and inferred the existence of a fourth phase (IV) in a narrow intermediate temperature range. However, later diffraction experiments [7] failed to identify any such structure, showing only mixtures of phases I and III in this area, and we show only a single phase boundary in Figure 2.

A first series of measurements were carried out by measuring the temperature dependence of the sample impedance at several selected pressures in the range 0.1 to 2.0 GPa, changing the temperature in steps of about 10 K. Typical data obtained at individual measurement points are shown in Figure 1, and in Figure 3 we show the resistance R , measured at 0.3 and 1.5 GPa, as a function of inverse temperature. These pressures were chosen in order to demonstrate data in all three structural phases. At 0.3 GPa (squares) measurements begin and end at room temperature in phase II, and a reversible phase transition into phase I occurs near $T^{-1} = 0.0027 \text{ K}^{-1}$. At 1.5 GPa, the temperature cycle starts in phase III and a transition to/from phase I occurs near 0.0026 K^{-1} . Very similar curves were found at other pressures, and it is obvious that the conductivities of phases II and III are very similar. Also, data measured with increasing and decreasing T were usually in very good agreement, and the figure shows that $\log R$ is a linear function of T^{-1} . The straight lines shown have been fitted to the data for increasing temperature in each phase. During the pressure increase the pressure dependence of R was also measured at room temperature in the range 0.5 – 1.2 GPa in order to observe the II-III phase transition.

When decreasing pressure, continuous measurements were again made at room temperature from 1.7 to 0.18 GPa to find the pressure dependence of the resistance and the III-II transition, and verification runs were carried out as functions of temperature at 1.0 and 0.4 GPa to check that the data obtained agreed with those obtained with increasing pressure. In a final run the transitions into phase I were then studied in detail by very slow heating at 1.1 and 0.37 GPa.

Below 1 GPa, measurements were usually carried out up to about 425 K in order to have sufficiently wide temperature ranges in both phases to obtain accurate values for the conduction parameters by fitting a theoretical expression. Above 1 GPa it was necessary to use increasing higher maximum temperatures because of the slope of the I-III phase line, and at 2 GPa the measurements were extended to 468 K. All data in the figures are shown in terms of the measured resistance, but if desired this can be converted to electrical conductivity σ as $\sigma = 0.149/R \text{ S cm}^{-1}$ (with R in Ω). As shown in Figure 3, the resistance changes by about

seven orders of magnitude in our experiments and although the results were usually quite stable and repeatable, in some extreme cases the limitations of the equipment led to a reduced accuracy. When the resistance approached or exceeded $10^8 \Omega$ (corresponding to a resistivity of about $10^9 \Omega\text{cm}$) near room temperature at the highest pressures, the scatter became very large and the extrapolated elliptical arc used to find the sample resistance was not very well defined. Similarly, the accuracy of the bridge was limited at the highest temperatures at low pressure when the resistance was below 20Ω ($\sigma > 7.5 \cdot 10^{-3} \text{ S cm}^{-1}$), and the highest electrical conductivity recorded here was thus about 0.01 S cm^{-1} . Higher conductivities should be expected at higher temperatures.

Conduction properties of LiBH₄

The resistivity ρ of an ionic conductor is usually described by an Arrhenius behaviour,

$$\rho = AT^m \exp(E_a/k_B T), \quad (1)$$

where k_B is Boltzmann's constant, E_a is an activation energy for ionic motion, usually described as jumps between discrete sites, and m may equal 0, $1/2$, or 1 in different models depending on the mechanism assumed for the "attempt frequency" for ionic motion [16]. The basic equation with $m = 1$ was derived long ago from thermodynamic considerations of diffusive motion with a temperature independent attempt frequency [17], but it has been noted experimentally [16] that the best fits to real data are given by different values of m for different materials.

Visually, the present data show an excellent linearity when the logarithm of R is plotted as a function of inverse temperature T^{-1} (see Figure 3), and there is no *a priori* reason to choose any particular value of m . We have, therefore, fitted Eq. (1) to our data using both $m = 0$ and $m = 1$, with very similar deviations and qualities of fit, although $m = 0$ usually gives marginally "better" results. (This is not surprising, considering the limited ranges of temperature studied and the dominance of the exponential term in Eq. (1).) Even though LiBH₄ is a quite compressible material [18] the geometrical factors relating R to ρ change little with T and p compared to the exponential factor in Eq. (1). We have thus simply fitted Eq. (1) to our data for the resistance to find the activation energy and its dependence on pressure for the three phases studied. Because earlier work on LiBH₄ [9,10,13] has been presented and fitted in terms of conductivity times temperature (σT) versus T^{-1} , corresponding to $m = 1$ in Eq. (1), all fitted data for E_a presented below have been calculated in this model to enable a direct comparison. It should be noted that different values of m give quite small differences in the final values for E_a , and that these differences vary little with pressure. In phase I all fitted values for E_a are 7-8 percent larger when fitted with $m = 1$ than when fitted with $m = 0$, while in phases II and III the average difference is only 4 - 5 percent but the individual variations between runs larger.

We show in Figure 4 fitted values for the activation energies in the three structural phases investigated. The data shown were all collected during the first pressure increase from 0.1 to 2.0 GPa. We have not included the data from the very first heating run in phase II at 0.1 GPa in our analysis, because the results from this run gave an unusually large apparent activation energy. We believe that this was due to an incomplete compression deformation of the sample before this first measurement, and that a final compaction occurred during heating such that the full density was not obtained until after the transition into phase I near 375 K. Also, we do not show the data obtained on cooling at 0.9 GPa, where we have reason to believe that a complex transformation event occurred (see section on the phase diagram). Data obtained for decreasing pressure and during the second pressure cycle showed an increased scatter, probably because the sample became increasingly more deformed and contained an increasing number of defects. This was not obvious from the raw resistance data, except in some special cases discussed below, but resulted mainly in an increased scatter in the fitted parameters. However, most fitted values were still in very good agreement with data from the first cycle.

We are not aware of any previous data in the pressure range investigated here, but we can compare our data with the zero-pressure data of Matsuo *et al.* [9] and the data obtained at 2 GPa and higher by Takamura *et al.* [13]. For phase I, the agreement is excellent. Matsuo *et al.* find $E_a = 0.53$ eV at atmospheric pressure, while extrapolating our data to $p = 0$ GPa gives 0.535 eV. At the high pressure end we find $E_a = 0.54$ at 2.0 GPa, while Takamura *et al.* find a 10% higher value of 0.59 eV. However, we find a stronger pressure dependence and the difference becomes smaller if data are extrapolated to higher pressures. For the low pressure, low temperature phase II, Matsuo *et al.* find $E_a = 0.69$ eV, in excellent agreement with the value 0.70 eV found by us in the first heating run at 0.1 GPa. As discussed above we consider this value much too high, probably because our material was not completely compacted. All later data for this phase are much lower, and an extrapolation to zero pressure gives a value of 0.57 eV. No earlier data exist with which to compare our high pressure data for this phase. For phase III, finally, the scatter in our data is higher than for the other phases, but we consistently find values for E_a which are higher than those obtained for phases I and II and which reach 0.69 eV at 2.0 GPa. Here our data differ from those of Takamura *et al.*, who find that this phase has the *lowest* values of E_a of all the three phases (I, III and V) investigated by them, with a value of only 0.49 eV at 2 GPa. In general, however, the agreement between the different sets of data is very good and the present results underline the earlier observation that the activation energies in the different structural phases differ surprisingly little. Almost all of the differences between the observed conductivities are due to differences in the prefactor in Eq. (1).

We find that E_a increases with increasing pressure by very similar rates in the two low-temperature phases, 0.059 eV GPa⁻¹ in phase II and 0.054 eV GPa⁻¹ in phase III, although the latter value is rather uncertain due to the large scatter in the data. The most interesting feature of the data shown in Figure 4 is the observed change in sign of the slope dE_a/dp for phase I near 0.9 GPa. The data for phase I show a particularly small scatter compared to the other phases, and the change in slope is probably not a random feature. We have fitted straight lines to the data above and below 0.8 GPa, with slopes -0.050 and $+0.040$ eV GPa⁻¹, respectively.

Another important quantity is the activation volume ΔV , which can be found from the isothermal pressure coefficient of ρ as

$$\Delta V = R_G T (\partial \ln \rho / \partial p)_T, \quad (2)$$

where R_G is the ideal gas constant. We have interpolated our measured isobaric data using Eq. (1) to obtain sets of isothermal data at several temperatures. For phases II and III the scatter in the data was too large for a reliable determination of ΔV , probably due to the presence of a large and random number of defects (see below), but data for R at 390 K and 420 K in phase I are shown in Figure 5. Applying Eq. (2) to these data without correction for the volume compression we find zero-pressure values $\Delta V = 4.35$ and 5.5 cm³mol⁻¹ at 390 and 420 K, respectively, decreasing rapidly with increasing pressure to about 2.2 and 2.6 cm³mol⁻¹, respectively near 0.7 GPa. The very sharp change in slope of the resistance curves at this pressure is reflected by a sudden jump in ΔV to about 5.7 and 6.3 cm³mol⁻¹, followed by a gradual decrease which at 420 K seems to saturate near 3 cm³mol⁻¹ near 2 GPa, in excellent agreement with data from Takamura *et al.* [13].

Because the activation parameters should depend on the microscopic structure and dynamics of the lattice, both the minimum in E_a and the sharp increase in ΔV point to the existence of an instability in the structure of phase I. This is particularly interesting because they occur close to the pressure at which the structural triple point is observed at lower temperatures. The anomalies observed might be caused by either an isostructural transition of the lattice or a change in the vibrational, librational or rotational dynamics of the molecules (for example a freezing of the molecular rotation [19]), or both. We note that there has been a large theoretical controversy [20-24] regarding the actual structure and stability of phase I, for which most theoretical calculations show that the experimentally observed structure should be unstable and cannot exist. Further theoretical investigations seem to be necessary in order to explain the relationships between structure, stability and transport in this phase.

Finally, high pressure studies under quasi-hydrostatic conditions always imply some deformation of the sample material. In this experiment the sample is pressed between two cylindrical electrodes and a certain uniaxial pressure component can be expected. Due to the low shear strength of the material the sample will suffer plastic flow and large lattice distortions are expected. As already mentioned above, it is obvious from some of the data that such effects have been present, especially in the room temperature phases where annealing effects are expected to be slow. This is probably the main reason why the data for E_a show a smaller scatter in the high temperature phase I than in the phases II and III, and in principle the data for the low temperature phases should be more accurate for the structure freshly formed during cooling at elevated temperature than it is during heating after a pressure change. The most clear indications of such lattice distortions were obtained at the transitions between phases II and III at room temperature. Two examples are shown in Figure 6. The transition from phase II into phase III observed near 0.77 GPa with increasing pressure is relatively sharp and well defined, while the reverse transition near 0.47 GPa on decreasing pressure is slower and more smeared. The very strong hysteresis is also in good agreement with our earlier observations [5,6,8]. What is particularly interesting, however, is that all such transitions observed were associated with a drop in resistance by about one order of magnitude, *irrespective of the direction of the pressure change*. After each transition there was a slow increase with time and a faster increase with increasing/decreasing pressure towards the “normal” value, and after the next heating/cooling cycle into phase I and the formation of fresh low temperature phase the resistance value is back at a value close to the initial one. We conclude that the $II \leftrightarrow III$ transformations are associated with the formation of a large number of lattice defects (grain boundaries, vacancies, interstitials, dislocations, etc.), and that these defects significantly improve the conduction properties after each transformation by providing new diffusion pathways or channels for the Li^+ ions. With time and with increasing temperature these defects heal, causing an increase in the resistivity back to the “normal” equilibrium value.

Phase diagram of $LiBH_4$

As shown in Figure 3, the transitions between the low-temperature phases II and III and the high-temperature phase I are easily observed, and in the phase diagram in Figure 2 we have plotted the approximate transition temperatures observed. Open circles denote increasing temperature and dots decreasing temperature. In most runs no attempt was made to select experimental coordinates to obtain an accurate transition temperature and the error bars indicate simply the last (first) temperature at which the initial (final) phase was observed, but in some cases an experimental point was accidentally observed during the transition process (see data at 1.5 GPa in Figure 3) which allowed a more accurate estimate. In these cases we defined the transition point as the point where $\log R$ was halfway between the resistances of the two phases; using the 50% point of the change in R would have given higher values for the transition temperatures.

In the verification run at 1.0 GPa, carried out during the pressure decrease, the temperature was decreased very slowly in order to get a particularly accurate value for the transition pressure. However, in that case the sample structure evidently supercooled, and instead of the usual slow transition evolving with temperature we observed a very fast exothermal transformation (< 1 min) at 356 K.

At 0.9 GPa, very close to the triple point pressure, the transformation from the stable phase III to phase I occurred at the expected temperature (solid triangle). On cooling, a very unusual temperature dependence was observed (Figure 7). Plotting the resistance data together with data for phases II and III at higher and lower pressures, it was found that the jumps in the curve were compatible with a double transformation, first from phase I into the low-pressure phase II near 360 K, then into phase III below about 320 K. Such a behaviour is also compatible with the known phase diagram (Figure 3), especially if we assume that rapid cooling gives a small drop in the true pressure because of the gasket friction in the cylinder.

As already discussed above, transitions between the room-temperature phases II and III were also observed (Figure 6) and the observed coordinates for these transformations are plotted in Figure 2 for both increasing (solid dots) and decreasing (open circles) pressure. We have already commented on the very large pressure hysteresis observed for this transition; it was observed earlier [6] that the high pressure phase III is actually metastable to atmospheric pressure below 200 K.

In the final two temperature runs at 1.1 GPa and 0.37 GPa the transformations from the low temperature phases II and III into the high temperature phase I were observed in detail by very slow heating. The results from these runs are plotted in Figure 8 and the observed mid-point temperatures are plotted as solid triangles in Figure 2. The two transitions occur at very similar temperatures, but the actual temperature dependences of resistance are obviously different. For the II – I transition we find a smooth transition behaviour, and the transition occurs over a relatively narrow range of temperatures. The III – I transition, on the other hand, occurs over a noticeably larger range in temperatures and has a rather wide foot, or step, feature. As mentioned above, Pistorius [15] found double transformations at this phase line, and an earlier study of the thermal conductivity and specific heat also found indications of a two-step process at this boundary [7]. However, since careful diffraction studies [7] gave no indications of an intermediate phase with a different structure in this region, only mixtures of the two phases on either side of the phase line, we conclude that the step-like feature probably originates in a complicated two-step phase transformation between these structurally very different phases. Also, in spite of the rather low temperature resolution in the present studies it is clear from Figure 2 that the I $\leftrightarrow$ III transition is associated with stronger and more consistent hysteresis (and supercooling) effects than the I $\leftrightarrow$ II transformation.

Conclusions

The results presented in this report are in very good general agreement with earlier studies of the electrical conductivity at atmospheric pressure. The conductivities observed are similar to those observed earlier for LiBH₄ and other Li⁺ ion conductors [9,10] and somewhat higher than those found for similar Na⁺ ion conductors [11,12]. Our results also agree well with earlier results at pressures of 2 GPa and above [13], except that we find phase III to have the highest activation energy of the phases studied instead of the lowest, as found by Takamura et al. [13]. The good agreement extends also to the observed pressure dependence of the activation energies. Furthermore, the transformation coordinates observed are in excellent agreement with our earlier data for the phase diagram.

The strong hysteresis and supercooling behaviour observed at both the I $\leftrightarrow$ III and II $\leftrightarrow$ III transitions suggest that both dense high pressure phases and conducting high temperature phases might be stabilized at lower temperatures or pressures to make them available for technological development. In fact, it has already been shown that the very high ionic conductivity of phase I can be retained even at room temperature by replacing 25% of the LiBH₄ by LiI [10].

Several interesting features were observed regarding phase I, the high temperature phase with superionic conduction properties. There is a minimum in the observed activation energy E_a near 1 GPa; the activation volume ΔV shows a step increase by about a factor of two at approximately the same pressure; the phase boundary for the I $\leftrightarrow$ II transition has an unusual negative slope; and the transformation between phases I and III is connected with a quite large hysteresis and seems to occur by a two-step mechanism. These features all seem to be related to structural effects, and are possibly all caused by the same underlying mechanism. Calculations usually find that the experimentally observed structure for phase I should be unstable and thus should not exist, and it might thus be just marginally stable. On cooling below 0.9 GPa it transforms in the orthorhombic phase I and above this into the pseudo-tetragonal phase III, and it is not unreasonable to assume that the features observed in the activation parameters near 0.9 GPa are connected with an increased density

of defects in the pressure range close to the triple point, where three different structures have very similar energies. In fact, the large step change in the activation volume suggests the existence of an isostructural phase transition or a major change in the lattice dynamics of phase I in this pressure range. Clearly, further theoretical and experimental investigations need to be carried out in order to understand the complex properties of this scientifically and technologically interesting phase.

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Figure captions

Figure 1. Complex impedance curves in three different temperature ranges. See text for details.

Figure 2. Phase diagram for LiBH_4 , showing phase lines obtained in earlier work [7,8]. Full lines denote equilibrium phase boundaries, dashed lines observed hysteresis effects [8]. Symbols denote transformation points observed in this work; different symbols denote experiments crossing different phase boundaries. Closed (open) symbols denote increasing (decreasing) temperature or pressure. See text for further details.

Figure 3. Measured resistance R as a function of inverse temperature T^{-1} at 0.3 GPa (squares) and 1.5 GPa (circles). Filled symbols denote heating, open symbols cooling. The straight lines have been fit to the results for increasing temperature.

Figure 4. Experimentally found activation energies E_a for ionic conduction in the three phases of LiBH_4 . Circles denote phase I, squares phase II and triangles phase III, open symbols denote measurements with decreasing temperature, closed symbols increasing temperature.

Figure 5. Isothermal pressure dependence of the sample resistance R in phase I at 390 K (upper curve) and 420 K (lower curve). The straight lines have been fitted to the points above and below 0.8 GPa.

Figure 6. Pressure dependence of the sample resistance at room temperature. Filled symbols denote increasing pressure, open symbols decreasing pressure.

Figure 7. Resistance observed during cooling at 0.9 GPa, showing double transition behaviour. Lines are guides for the eye only.

Figure 8. Transformations into phase I studied by very slow heating, from phase II at 0.37 GPa (squares) and from phase III at 1.1 GPa (triangles).

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8