Lithium nickel borides: evolution of [NiB] layers driven by Li pressure

Volodymyr Gvozdetskyi  
*Iowa State University*, volodya@iastate.edu

Yang Sun  
*Ames Laboratory*

Xin Zhao  
*Ames Laboratory*

Gourab Bhaskar  
*Iowa State University*, gbhaskar@iastate.edu

Scott L. Carnahan  
*Iowa State University and Ames Laboratory*, scottc@iastate.edu

See next page for additional authors

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Abstract
Here we show the effect of Li chemical pressure on the structure of layered polymorphs with LiNiB composition: RT-LiNiB (room temperature polymorph) and HT-LiNiB (high temperature polymorph), resulting in stabilization of the novel RT-Li1+xNiB (x ∼ 0.17) and HT-Li1+yNiB (y ∼ 0.06) phases. Depending on the synthesis temperature and initial Li content, precisely controlled via hydride route synthesis, [NiB] layers undergo structural deformations, allowing for extra Li atoms to be accommodated between the layers. In situ variable temperature synchrotron and time-dependent laboratory powder X-ray diffraction studies suggest Li step-wise deintercalation processes: RT-Li1+xNiB → RT-LiNiB (high temp.) → LiNi3B1.8 → binary Ni borides and HT-Li1+yNiB → HT-LiNiB (high temp.) → LiNi3B1.8 → binary Ni borides. Quantum chemistry calculations and solid state 7Li and 11B NMR spectroscopy shed light on the complexity of real superstructures of these compounds determined from high resolution synchrotron powder diffraction data.

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Authors
Volodymyr Gvozdetskyi, Yang Sun, Xin Zhao, Gourab Bhaskar, Scott L. Carnahan, Colin P. Harmer, Feng Zhang, Raquel A. Ribeiro, Paul C. Canfield, Aaron J. Rossini, Cai Zhuang Wang, Kai-Ming Ho, and Julia V. Zaikina
Lithium nickel borides: evolution of [NiB] layers driven by Li pressure†

Volodymyr Gvozdetskyi,a Yang Sun, b Xin Zhao, b Gourab Bhaskar, a, b Scott L. Carnahan,a,b Colin P. Harmer,a,b Raquel A. Ribeiro, c Paul C. Canfield, b,c Aaron J. Rossini, a,b Cai-Zhuang Wang, d,b,c Kai-Ming Ho c and Julia V. Zakhina d,a

Here we show the effect of Li chemical pressure on the structure of layered polymorphs with LiNiB composition: RT-LiNiB (room temperature polymorph) and HT-LiNiB (high temperature polymorph), resulting in stabilization of the novel RT-Li1.8NiB (x ~ 0.17) and HT-Li1.9yNiB (y ~ 0.06) phases. Depending on the synthesis temperature and initial Li content, precisely controlled via hydride route synthesis, [NiB] layers undergo structural deformations, allowing for extra Li atoms to be accommodated between the layers. In situ variable temperature synchrotron and time-dependent laboratory powder X-ray diffraction studies suggest Li step-wise deintercalation processes: RT-Li1.8–xNiB → HT-Li1.8–xNiB (high temp.) → HT-NiB, binary Ni and HT-Li1.9yNiB → HT-Li1.9yNiB (high temp.) → binary Ni borides. Quantum chemistry calculations and solid state 7Li and 11B NMR spectroscopy shed light on the complexity of real superstructures of these compounds determined from high resolution synchrotron powder diffraction data.

Introduction

The story of lithium nickel borides began in 1976 when four ternary phases were identified in the Li–Ni–B system.1–3 Crystal structures were reported for three of these compounds, LiNi3B1.8 (MgNi3B2 structure type, P63/22 space group), Li2Ni3B6 (Cr27,27,27 space group), and Li2.8Ni16B8 (Li3Ni16B8, Pm3m). Only a tentative composition of 1:1:1 was assigned for the fourth compound, a phase with the richest Li content. To the best of our knowledge, no other ternary compounds in all A–T–B systems (A = alkali metal, T = Ti–Zn) have been reported. The lack of the ternary A–T–B compounds can be due to the drastically different reactivity of refractory boron (melting point 2348 K) and alkali metals (boiling point 944–1615 K) making traditional synthesis methods (e.g. arc melting) non-applicable.

The hydride synthesis route, where salt-like alkali metal hydrides are used as a source of alkali metals, has been successfully utilized for the preparation of alkali/alkali-earth antimonides, arsenides, germanides, and silicides.4–10 Application of this method for the Li–Ni–B system significantly shortened the synthesis time of ternary phases. For instance, LiNi3B1.8 can be synthesized in a span of ~24 hours compared with the previously reported 3-month annealing for the reaction of elements.9 The hydride route also permitted the compositional control and comprehensive screening of unknown compounds. This way, two lithium nickel boride polymorphs RT-LiNiB (room temperature polymorph) and HT-LiNiB (high temperature polymorph), with unique layered crystal structures, were discovered.11 In these polymorphic compounds, Li layers, featuring hexagonal-like or squared motif, alternate with nearly planar [NiB] layers, whose structure differs depending on the polymorph (Fig. 1). A structural relationship between the RT-LiNiB and HT-LiNiB polymorphs, Li-depleted phase LiNi3B1.8, Ni3B, and Li has been found,11 indicating on the [NiB] framework evolves with the changing of Li content and/or temperature variation (Fig. S1†).

Layered lithium nickel borides are of interest from the functional materials perspective. Firstly, ~33 at% of Li is stored between [NiB] layers in RT- and HT-LiNiB (9.1 wt% of Li as compared to 8.8 wt% of Li in LiC6 anode material) gives these compounds potential for applications in Li-ion batteries. Secondly, due to the unique arrangement of Li and [NiB] layers in their structures, exfoliation of these materials can open a
pathway to novel two-dimensional (2D) nickel borides.\textsuperscript{11,12} The search for 2D borides or MBene has been accelerated after successful preparation of the 2D transition metal carbides or MXenes.\textsuperscript{13,14} MXenes are extensively studied due to their attractive thermal, magnetic, mechanical and electric properties.\textsuperscript{15–20} MBenes were predicted to have two fascinating properties\textsuperscript{21–24} but have not yet been obtained experimentally, despite several prominent attempts.\textsuperscript{24–28}

Recent theoretical investigation of the Li–Ni–B system\textsuperscript{29} revealed a new Li-rich compound Li\textsubscript{2}NiB, whose structure is derived from \textit{RT}-LiNiB. According to the calculations, only a little extra energy is needed to accommodate an additional Li layer in the structure of the LiNiB parent phase. Here, we have experimentally explored the Li-rich compositions of the Li–Ni–B phase diagram and discovered two compounds that are Li-enriched versions of \textit{RT}-LiNiB and \textit{HT}-LiNiB polymorphs. Both \textit{RT}-Li\textsubscript{1+}NiB (\textit{x} ∼ 0.17) and \textit{HT}-Li\textsubscript{1+}NiB (\textit{y} ∼ 0.06) phases feature layered crystal structures with the original topology of the \{NiB\} layers modified due to the incorporation of extra Li between the layers. We use \textit{in situ} synchrotron and laboratory powder X-ray diffraction, solid state NMR spectroscopy, and quantum chemical calculations to study structural relationships, reactivity, and phase transformations upon heating or exposure to air of these lithium-rich layered nickel borides.

Table 1  Family of layered lithium nickel borides

| Phase (space group) | \(a, \AA\) | \(b, \AA\) | \(c, \AA\) | \(\alpha,^\circ\) | \(\beta,^\circ\) | \(\gamma,^\circ\) | \(V, \AA^3\) | \(V/Z,\AA^3\) | Ref. |
|---------------------|-----------|-----------|-----------|--------------|--------------|--------------|----------|----------|-----|
| \textit{RT}(m)-Li\textsubscript{1+}NiB \{P2\textsubscript{1}/c\}\textsuperscript{a} | 4.6114 | 4.8333 | 6.156 | 90 | 109.607 | 90 | 129.26 | 32.32 | 11 |
| \textit{RT}(m)-Li\textsubscript{1+}NiB \{P2\textsubscript{1}/c\}\textsuperscript{b} | 18.451 | 4.8336 | 6.1573 | 90 | 109.636 | 90 | 517.21 | 32.33 | 11 |
| \textit{RT}(m)-Li\textsubscript{1+}NiB \{Cmc\}\textsuperscript{c} | 4.8341 | 6.1573 | 8.6888 | 90 | 90 | 90 | 258.62 | 32.33 | 11 |
| \textit{RT}(m)-Li\textsubscript{1+}NiB \{P2\textsubscript{1}/c\}\textsuperscript{d} | 18.277(1) | 4.86606(5) | 6.1818(2) | 90 | 107.623(1) | 90 | 524.00(2) | 32.75 | This work |
| \textit{RT}(t)-Li\textsubscript{1+}NiB \{P1\} | 18.2763(4) | 4.86589(3) | 18.5447(5) | 89.9810(7) | 107.6202(9) | 90.056(2) | 1571.82(3) | 32.75 | This work |
| \textit{HT}-Li\textsubscript{1+}NiB \{P2\textsubscript{1}/m\} | 3.9095 | 8.8087 | 7.5234 | 90 | 90.070 | 90 | 259.08 | 32.39 | 11 |
| \textit{HT}(m)-Li\textsubscript{1+}NiB \{P2\textsubscript{1}/c\}\textsuperscript{d} | 3.92591(7) | 7.5593(1) | 8.8181(2) | 90 | 92.6245(7) | 90 | 261.42(1) | 32.68 | This work |
| \textit{HT}(t)-Li\textsubscript{1+}NiB \{P1\} | 7.85184(9) | 15.1183(2) | 8.8179(1) | 89.9079(7) | 92.6271(5) | 90.0008(5) | 1043.63(3) | 32.68 | This work |

\textsuperscript{a} Different polytypes of \textit{RT}-LiNiB compound. \textsuperscript{b} Superstructure of two polytypes of \textit{RT}-LiNiB. \textsuperscript{c} Idealized structure of \textit{RT}-Li\textsubscript{1+}NiB compound. \textsuperscript{d} Idealized structure of \textit{HT}-Li\textsubscript{1+}NiB compound. \textsuperscript{e} Volume normalized per formula units.

**Results and discussion**

**Synthesis and composition**

In our recent study,\textsuperscript{11} the Li–Ni–B ternary system was evaluated using an adaptive genetic algorithm (AGA) search for potentially stable ternary phases. As a result, a \textit{RT}-LiNiB compound with a unique layered structure was computationally predicted and further synthesized experimentally using the hydride route. The structure of \textit{RT}-LiNiB can be represented as almost planar [NiB] layers alternating with Li layers (Fig. 1).

However, as evident from high-resolution synchrotron data, the real structure is more complex and includes intergrowth of two polytypes (Table 1). Above 1173 K \textit{RT}-LiNiB transforms to its high-temperature polymorph \textit{HT}-LiNiB featuring different topology of [NiB] and Li layers (Fig. 1).

Previously we showed\textsuperscript{10,11} the hydride route is feasible for preparation of ternary lithium nickel borides providing fast reactions and accurate compositional control. The experimentally determined, LiH : Ni : B = 1.3 : 1 : 1.5, molar ratio results in phase-pure samples of LiNiB phases with minimal excess of LiH and B needed.\textsuperscript{11} A further increase of the LiH ratio to values of 1.4 to 1.9 leads to stabilization of two new phases \textit{RT}-Li\textsubscript{1+}NiB and \textit{HT}-Li\textsubscript{1+}NiB (Table 1, Fig. 2). A slight excess of lithium hydride (LiH : Ni : B = 1.4 : 1 : 1.15) is necessary for the synthesis of the \textit{HT}-Li\textsubscript{1+}NiB compound. For stabilization of the \textit{RT}-Li\textsubscript{1+}NiB phase, a considerable excess of LiH...

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**Fig. 1** Crystal structure of \textit{RT}-LiNiB and \textit{HT}-LiNiB polymorphs.

**Fig. 2** Temperature-composition diagram for the synthesis of layered lithium nickel borides.
must be used (LiH : Ni : B = 1.9 : 1 : 1.15). Moreover, we found that synthesis of RT-Li$_{1+x}$NiB compound requires that the sample be ground and annealed following the initial heating of precursors. After the first annealing, samples always comprise the RT-LiNiB phase. RT-LiNiB was the major phase and only a small amount of RT-Li$_{1+x}$NiB compound was detected experimentally in the sample synthesized with loading composition LiH : Ni : B = 1.6 : 1 : 1.15. With a further increase in Li content, the fraction of RT-Li$_{1+x}$NiB increases accordingly (Fig. S2†), while loading composition LiH : Ni : B = 1.9 : 1 : 1.15 gives phase pure RT-Li$_{1+x}$NiB samples.

As evident from the high-resolution synchrotron powder X-ray diffraction (PXRD) data (Fig. 3), experimental PXRD patterns of RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB compounds are similar. Both feature an intensive peak corresponding to the interlayer distance of $d \sim 4.34$–4.41 Å between the [NiB] layers (yellow-shaded, Fig. 3). In contrast, the structure of [NiB] layers in two phases is different, resulting in the difference in PXRD patterns (blue-shaded, Fig. 3).

Crystal structures

Determination of RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB crystal structures is challenging for several reasons: (1) extreme air-sensitivity (vide infra), (2) hydride synthesis did not yield large enough crystals suitable for laboratory single crystal X-ray diffraction; (3) the presence of light elements, Li and B, which makes X-ray data less informative, since heavier Ni atoms dominate X-ray scattering. Therefore, we used a synergistic combination of PXRD data refinement and theoretical calculations to elucidate crystal structures of RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB. Solving structures from PXRD data yields the positions of Ni atoms, thus the [NiB] layers (Tables S1–S6†). The structure of Li layers, including the atomic coordinates of extra-Li atoms in RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB, was determined using theoretical calculations.

Variations of [NiB] layers. Comparison of RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB crystal structures with their respective parent phases RT*$m$-LiNiB and HT-LiNiB are shown in Fig. 4 and 5. Additional Li atoms neither change the topology of [NiB] layers in the case of RT-Li$_{1+x}$NiB nor the stacking sequence of [NiB] layers (Tables S1–S3†). Thus, RT-Li$_{1+x}$NiB exhibits the same space group and Wyckoff sequence of the atomic sites as RT*$m$-LiNiB (Tables 1, S1–S3†), while variation in the monoclinic $\beta$-angle is responsible for variations in the PXRD pattern (Fig. 3 and 4). The stacking sequence of [NiB] layers for both RT-Li$_{1+x}$NiB and RT-LiNiB is ABCB (Fig. 4).

Fig. 3  Experimental synchrotron powder X-ray diffraction patterns of RT-LiNiB [11], HT-LiNiB [11], RT-Li$_{1+x}$NiB and HT-Li$_{1+y}$NiB. The most intense characteristic peak $d \sim 4.34$–4.41 Å corresponds to the distance between [NiB] layers and is common for all phases. However, compounds have different atomic arrangement within the [NiB] layers, as indicated by the different sequence of the diffraction peaks in the blue-shadowed region, an enlarged view is shown on the right.
Li layers in RT-Li_{1+x}NiB phase. A constrained GA search for the structure of the Li layers was performed while fixing the positions of Ni and B atoms to those in the experimentally determined structure (P2_1/c space group, Table 1). Since the complex “Li_{1+x}” packing can only be modeled by a superlattice, we performed the search on the supercell of the current lattice. The structure searching is very challenging for RT-Li_{1+x}NiB structure, because it already contains 48 atoms for x = 0 (i.e. Li_{16}Ni_{16}B_{16}). On the other hand, as indicated in Fig. 4, the layered structure of RT-Li_{1+x}NiB contains only AB- and BC-types of [NiB] stacking. Therefore, we searched for the Li layers between the AB and BC stacking types of [NiB] layers separately to reduce the computational cost. We built a smaller Li_{8}Ni_{8}B_{8} lattice with only AB- or BC-type NiB layers. Two different searches with the lattices extended along b and c direction by 1 × 2 × 2 (i.e. Li_{12+m}Ni_{12}B_{32} with m = 1, 2, 3, 4) and 1 × 3 × 3 (i.e. Li_{18+m}Ni_{18}B_{36} with n = 2, 4, 6, 8, ..., 18) were performed. With 1 × 2 × 2 supercell, no energetically favored structures were found. Interestingly, as shown in Fig. 6a, the search with 1 × 3 × 3 supercell revealed an energetically stable Li packing with 16.7% excess of Li compared to the RT-LiNiB parent phase.

The Li layer configuration with x = 0.167 is stable in both AB-type and BC stacking types since they have the same formation energy as RT-LiNiB. Incorporation of extra Li atoms into the Li layer is accomplished by shortening of Li–Li distances to 2.6–2.8 Å, resulting in the denser hexagonal lattice (Fig. 6c) compared to RT-LiNiB (Li–Li distances ~2.8–3.1 Å). The configurations with intermediate Li excess 0 < x < 0.167 form combinations of loose (x = 0) and dense (x = 0.167) hexagonal lattices, resulting in a locally disordered packing motif and have an excess in the formation energy in a range of 3 meV (Fig. 6a).

Li layers in HT-Li_{1+y}NiB phase. We performed a similar GA search of the Li layers by implementing constraints to fix the
positions of Ni and B atoms as those in the experimentally determined structure of HT-Li$_{1+y}$NiB (space group P2$_1$/c). Only Li positions were optimized during the structure searches. The $2 \times 2 \times 1$ supercell was used in the search with 32 Li atoms for $x = 0$. The number of excessive Li atoms ranges from 2 to 10, i.e., Li$_{32+}$Ni$_{32}$B$_{32}$ with $k = 0, 2, 4, ..., 10$. In the constraint searches, EAM (embedded atom method$^{13}$) classical potential selected from the AGA searches was used to screen the structures, and the final structures were then relaxed by DFT. For $y = 0$, Li atoms form a square lattice as plotted in the lower panel of the Fig. 7. The Li layer is similar to that experimentally found for HT-LiNiB.$^{11}$ With the increase of Li content, Li atoms tend to have coordination numbers larger than 4, e.g., 5 or 6 (Fig. 7a). Eventually, after adding enough Li atoms, such as in Li$_{16}$Ni$_{32}$B$_{32}$, Li atoms form a modulated hexagonal lattice. The addition of a small amounts of Li atoms lowers the formation energy of HT-Li$_{1+y}$NiB at first (Fig. 7a), while for $y > 0.125$, the structure becomes less stable, even though with positive formation energies. The internal pressure induced by incorporating more Li atoms inside the structure as the function of $y$ is plotted in Fig. 7b. If the unit cell is not allowed to expand (solid points), adding more Li atoms significantly increases this pressure for $y > 0.1$, again indicating the possible structural instability of HT-Li$_{1+y}$NiB with large $y$. Therefore, we estimate the upper limit for $y$ in HT-Li$_{1+y}$NiB to be 0.125.

**Overall structure.** Careful analysis of synchrotron powder XRD patterns of the RT-Li$_{1+y}$NiB or HT-Li$_{1+y}$NiB compounds reveals the plethora of the low-intensity Bragg peaks (Fig. S3†). Part of these diffraction peaks can be accounted by superstructures, obtained by multiplying of the unit cell parameters by a factor of 2 or 3 and simultaneous lowering of the symmetry to triclinic: $a_{superstr} = a$, $b_{superstr} = b$, $c_{superstr} = 3 \times c$, $Z_{superstr} = 3 \times Z$ for RT-Li$_{1+y}$NiB; $a_{superstr} = 2 \times a$, $b_{superstr} = 2 \times b$, $c_{superstr} = c$, $Z_{superstr} = 4 \times Z$ for HT-Li$_{1+y}$NiB (Tables 1 and S1–S6, cif files are provided in ESI†). We utilized these unit cells and created the structural models with [NiB] layers obtained from the PXRD data and Li layers found computationally, as described above. Rietveld refinement of these models resulted in a satisfactory fit (Tables S1, S4, Fig. S4–S11†), allowing for fitting of low intensity diffraction peaks while accounting for additional Li atoms between [NiB] layers. The obtained structural models are consistent with denser packing of Li atoms within the layer. As it is highlighted in Fig. 8, the denser packing of Li atoms results in 2 or 3 Li atoms per each Ni$_6$B$_2$ hexagonal unit, while solely 2 Li atoms per Ni$_6$B$_2$ are present in RT-LiNiB and HT-LiNiB parent structures (Fig. 8). This is accompanied by shortening of the interatomic distances between Li atoms. We also note that not all low intensity diffraction peaks can be accounted by the triclinic supercell (Fig. S3†), and the real structure of RT-Li$_{1+y}$NiB or HT-Li$_{1+y}$NiB might be even more complex (modulated or even larger cell), however the present model agrees fairly well with PXRD data, has reasonable bond distances and accounts for extra Li atoms in the structures. Most Li–B bonds in the structures of RT-Li$_{1+y}$NiB and HT-Li$_{1+y}$NiB compounds have the same length as in the parent compounds ($d_{Li-B} \sim 2.3–2.4$ Å) (Fig. S12†). However, due to the distortion of Li-layers in the Li-enriched RT-Li$_{1+y}$NiB and HT-Li$_{1+y}$NiB compounds (Fig. 6 and 7), some of the Li atoms have longer distances to the nearest B atoms (2.4–2.6 Å).

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**Fig. 7** (a) Energetics of HT-Li$_{1+y}$NiB structure as a function of $y$. Formation energies are calculated as $E_f = (\varepsilon$(Li$_{1+y}$NiB) – $y \times \varepsilon$(Li) – $\varepsilon$(LiNiB))/(3 + $y$), where the P2$_1$/m structure is used for $y = 0$. Top views of the Li layers in the optimized structures are plotted in the lower panel of (a). (b) Pressure of the HT-Li$_{1+y}$NiB structure calculated as the function of $y$. (c) Volume per formula unit of the HT-Li$_{1+y}$NiB generated structure calculated as the function of $y$. Note that here a $2 \times 2 \times 1$ supercell was used. Structure relaxations were carried out for two scenarios: unit cell fixed to the $2 \times 2 \times 1$ supercell during relaxation (solid circles) and full relaxation (hollow squares).

**Fig. 8** Comparison of RT-Li$_{1+y}$NiB and HT-Li$_{1+y}$NiB with the RT-LiNiB and HT-LiNiB parents. Light green and blue highlighted areas emphasize denser packing of Li atoms in the case of RT-Li$_{1+y}$NiB and HT-Li$_{1+y}$NiB, leading to 3 Li atoms per each Ni$_6$B$_2$ distorted hexagon.
Temperature stability, reactivity and phase transformations

High-temperature synchrotron powder X-ray diffraction (HT-PXRD) was used to study the thermal stability of \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \). Samples were vacuum-sealed into silica capillaries for high temperature PXRD experiments. Upon heating Li is gradually “leached” from the structure, presumably reacting with silica. This leads to \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \) transformation into \( \text{RT-LiNiB} \) and \( \text{HT-LiNiB} \) at 461 and 473 K, respectively (Fig. 9a and b). This again confirms the presence of extra Li atoms in \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \) compared to their parent compounds. With a further increase in temperature above 684 K, \( \text{RT-LiNiB} \) transforms to Li-depleted \( \text{LiNi}_{1.8}\text{B}_1 \) phase and binary \( \text{NiB} \). Between 684 K and 885 K, all three phases, \( \text{RT-LiNiB}, \text{LiNi}_{1.8}\text{B}_1 \) and binary \( \text{NiB} \), are present. Above ~885 K, binary nickel borides \( \text{NiB}, \text{Ni}_2\text{B}, \text{Ni}_3\text{B} \) are the major products.

Interestingly, HT-PXRD data of the \( \text{HT-LiNiB} \) polymorph (Fig. S13b) shows considerable structural distortion, which was refined in the same structure type (same space group \( \text{P}2_1/m \) and Wyckoff sequence) (Table S7†). The distorted structure features substantially deformed \( \text{Ni}_6\text{B}_2 \) units within \([\text{NiB}] \) layers and the relative shift of \([\text{NiB}] \) layers (Fig. S13c and d†). This distorted structure was only observed in \textit{in situ} PXRD experiments, while attempts to quench it from ~620 K were not successful. With further increase in temperature, the \( \text{HT-LiNiB} \) phase decomposes into Li-depleted \( \text{LiNi}_{1.8}\text{B}_1 \), and finally, binary Ni borides similarly to \( \text{RT-LiNiB} \) polymorph (Fig. S13†).

Air stability of \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \). In addition to the temperature, the transition between \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \) compounds and their respective parents \( \text{RT-LiNiB} \) and \( \text{HT-LiNiB} \) can be driven by oxidation with oxygen in air. \( \text{HT-Li}_{1+x}\text{NiB} \), if exposed to air, rapidly transforms to the \( \text{HT-LiNiB} \) phase (Fig. S14†). However, decomposition of the \( \text{RT-Li}_{1+x}\text{NiB} \) phase in air is considerably slower (Fig. 10). The higher reactivity of \( \text{HT-Li}_{1+x}\text{NiB} \) might originate from the considerably distorted Li-layer in the structure as well longer Li-B bonds, compared to the \( \text{RT-Li}_{1+x}\text{NiB} \) (Fig. 6, 7 and Fig. S12†).

Powder X-ray diffraction patterns of \( \text{RT-Li}_{1+x}\text{NiB} \) show its evolution in air is completed within 160 min (Fig. 10). The process is relatively fast during the first ~1 hour (patterns in blue) and slows down afterwards. The last acquired powder pattern (at 160 min) contains mostly the \( \text{RT-LiNiB} \) compound with traces of the initial \( \text{RT-Li}_{1+x}\text{NiB} \). Also, the fraction of \( \text{LiOH}+\text{H}_2\text{O} \) increases with the exposure time, suggesting that the overall process can be described as follows: \( \text{Li}_{1+x}\text{NiB} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{LiNiB} + x\text{LiOH}+\text{H}_2\text{O} \), which again confirms the presence of extra-Li in \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \) compounds.

Solid-state NMR spectroscopy

To further shed light on the evolution of Li and B coordination environment upon incorporation of extra-Li in the structures of \( \text{RT-Li}_{1+x}\text{NiB} \) and \( \text{HT-Li}_{1+x}\text{NiB} \) compounds, \( ^7\text{Li} \) and \( ^{11}\text{B} \) solid-state magic angle spinning (MAS) NMR spectra were collected (Fig. 11a). The \( ^7\text{Li} \) MAS NMR spectra of \( \text{RT-Li}_{1+x}\text{NiB} \) compound
The NMR spectroscopy data also confirms the high reactivity of \(HT-Li_{1+y}NiB\) compound, which rapidly transforms in the air to \(HT-LiNiB\) compound (Fig. S14†). Fig. 11b shows the evolution of NMR spectra of a \(HT-Li_{1+y}NiB\) sample with time while the sample is undergoing magic angle spinning in a 2.5 mm rotor. The nitrogen gas used for spinning is approximately 99.9% pure and the 2.5 mm rotors are not gas-tight. Hence the reaction is likely driven by the slow diffusion of residual oxygen and water in the MAS gas into the sample. There are clear variations in intensities of five observed \(^7\text{Li}\) peaks, likely because of the changes in Li local environment between the layers. Li is also partly deintercalated and forms LiO, explaining the increased intensity of the 5th peak. During the course of MAS experiments, the \(^{11}\text{B}\) solid-state NMR spectra of \(HT-Li_{1+y}NiB\) become more similar in appearance to \(HT-LiNiB\).

The \(^{11}\text{B}\) solid-state NMR spectrum for \(RT-Li_{1+y}NiB\) and \(HT-Li_{1+y}NiB\) is consistent with their metallic behavior. The 150–220 ppm range of \(^{11}\text{B}\) chemical shifts is similar to the chemical shift observed for \(RT-LiNiB\) and \(HT-LiNiB\) compounds\(^9_{,11}\) and other metallic borides and borocarbides.\(^9_{,12}_6\) Boron atoms in all \(RT-Li_{1+y}NiB\), \(RT-LiNiB\), \(HT-LiNiB\), \(HT-Li_{1+y}NiB\) layered phases form B-B pairs, which are further surrounded by 6 Ni atoms (Fig. 1, 4 and 5). However, the different topology of the layers, as well as differences in boron coordination by Li, likely explains the observed differences in the \(^{11}\text{B}\) solid-state NMR spectra.

**Magnetic properties**

Temperature dependence of the molar magnetic susceptibility in the range 5–300 K of \(RT-Li_{1+y}NiB\) and \(HT-Li_{1+y}NiB\) (Fig. S15†) is consistent with both phases being temperature-independent Pauli paramagnets. No magnetic ordering was observed down to 5 K. The field dependence of the magnetization in the same temperature range (Fig. S15†) at high magnetic field (10 000 Oe–50 000 Oe) is linear with no tendency for saturation, which is again consistent with temperature-independent paramagnetism. Small deviation from linearity of the field dependence of the magnetization at low magnetic field (0–10 000 Oe, see Fig. S15†) could be attributed to some magnetic moment bearing impurity, concentration of which is under the detection limit of X-ray analysis (below 1%). The magnetic susceptibility values were estimated to be in the range of 0.7–1.2 × 10\(^{-4}\) emu mol\(^{-1}\) (Fig. S15†). The parent compounds \(RT-LiNiB\) and \(HT-LiNiB\) also exhibit temperature-independent paramagnetism.\(^11\) Thus, incorporation of additional

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**Fig. 11** (a) \(^7\text{Li}\) and \(^{11}\text{B}\) MAS solid-state NMR spectra of \(RT-Li_{1+y}NiB\) in comparison to \(RT-LiNiB\) phase. (b) \(^7\text{Li}\) and \(^{11}\text{B}\) MAS solid-state NMR spectra of \(HT-Li_{1+y}NiB\) in comparison to \(HT-LiNiB\) phase. The time in minutes after starting the magic angle spinning is indicated. (c) Variation in intensities of characteristic peaks (1, 2, 3, 4, 5) with time.

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have two major peaks at ~265 and ~80 ppm and a minor one at ~0 ppm. The peak at 0 ppm originates from diamagnetic impurity phases, such as LiO (2.8 ppm), LiOH-H\(_2\)O (0.4 ppm), or LiOH (1.3 ppm), and is also present in \(^7\text{Li}\) MAS NMR spectrum of \(RT-LiNiB\) phase.\(^11\) The peak at 265 ppm is most likely due to a Li metal impurity,\(^33\) as a result of the significant excess of LiH required for synthesis and its further decomposition upon heating. The peak at ~80 ppm is attributed to the \(RT-Li_{1+y}NiB\) phase and is consistent with a single type of Li site expected in the structure. It is slightly positively shifted compared to the peak at ~75 ppm for \(RT-LiNiB\) phase but within the range of \(^7\text{Li}\) chemical shifts in other Li-containing intermetallics.\(^9,11\) The slight increase in the \(^7\text{Li}\) chemical shift for \(RT-Li_{1+y}NiB\) as compared to \(RT-LiNiB\) can likely be attributed to the subtle differences in the Li coordination environment in the two compounds. The increased width of the \(^7\text{Li}\) peak may be a result of the increased complexity of \(RT-Li_{1+y}NiB\) structure, where extra Li atoms are incorporated between the [NiB] layers, leading to a variety of local \(^7\text{Li}\) environments and distribution of shifts. The peak at ~80 ppm is shifted to higher frequencies compared to the diamagnetic signal, indicative of Knight shift from conduction electrons, and thus metallic behavior is expected for \(RT-Li_{1+y}NiB\) phase. The \(^7\text{Li}\) MAS NMR spectra of \(HT-Li_{1+y}NiB\) is akin to \(HT-LiNiB\) and is distinct from that of \(RT-Li_{1+y}NiB\) and \(RT-LiNiB\). There are two intense peaks at ~55–65 ppm and two peaks with lower intensity at ~95 and 110 ppm, in addition to the peak at ~0 ppm (diamagnetic impurity, e.g. Li\(_2\)O). Multiple peaks with positive chemical shifts are expected for \(HT-Li_{1+y}NiB\), since it would be consistent with its metallic nature and a structure model with three Li sites (2a, 2c, 4e, \(P_2_1/c\)).

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Li atoms does not affect the magnetic properties. This is in stark contrast to the partial deintercalation of Li from para-magnetic LiNiB, inducing magnetic ordering in Li$_{1-x}$NiB.12

Experimental

Synthesis

Starting materials for the synthesis were powders of lithium hydride (AlfaAesar, 99.4%), nickel (AlfaAesar, 99.996%), and boron (AlfaAesar, amorphous & crystalline, 98%). All manipulations of the starting materials and samples were performed in an argon-filled glovebox with $p(O_2) < 1$ ppm. Powders of the starting materials (total mass = 0.3 g) were weighted in LiH: Ni : B = 1.9 : 1 : 1.15 ($RT$-Li$_{1+}$NiB) and 1.4 : 1.15 ($HT$-Li$_{1+}$NiB) molar ratios and loaded into polystyrene grinding vial with slip-on cap. These loading compositions were determined empirically to get the highest yield of the target phases. The vials were then sealed into double-sided polypropylene bag under argon atmosphere and brought out for the powder mixing/milling using ball-mill (8000M MIXER/MILL) for 18 min (vials were enclosed in poly-bags during the process to ensure O$_2$-free environment). Afterward, freshly prepared fine powders were loaded in Ta tubes inside argon-filled glovebox. The metal containers were sealed by arc-melting and placed into silica reactors equipped with Swagelok safety check valves to prevent over-pressurization of the reactors due to the release of hydrogen gas during the heat treatment. The silica reactors were evacuated down to $4 \times 10^{-5}$ Bar and slowly (1.25 K min$^{-1}$) heated from room temperature to 1173 K, held at that temperature for 12 hours and quenched into cold water for the preparation of $HT$-Li$_{1+}$NiB phase or cooled to room temperature by switching off furnace in the case of $RT$-Li$_{1+}$NiB phase. The second annealing of the manually ground sample loaded to the Ta tube using the same temperature profile was necessary to obtain $RT$-Li$_{1+}$NiB, otherwise $RT$-LiNiB compound forms. The synthesized compounds are air and moisture sensitive.

Powder X-ray diffraction

The purity of polycrystalline samples was checked using Rigaku MiniFlex600 powder diffractometer with Cu Ka radiation ($\lambda = 1.54051$ Å) and Ni-K$_{\beta}$ filter. Data were collected in zero-background plate holder for air-sensitive samples at room temperature. Phase analysis was performed using the PDF-2 database incorporated into PDFL2 program software.36 Powder diffractograms during controlled samples oxidation in the air were collected using open zero-background plate holder with ~10 min time intervals.

Crystal structure determination from synchrotron powder X-ray diffraction data

High-resolution synchrotron powder diffraction data were collected at beamline 11-BM-B Advanced Photon Source (APS), Argonne National Laboratory at 295 K and 100 K and $\lambda = 0.412815$ Å for a sample of $HT$-Li$_{1+}$NiB and $\lambda = 0.412818$ Å for a sample of $HT$-Li$_{1+}$NiB. Data were collected at ambient pressure.

The unit cell symmetry, metrics, and atomic arrangement in the structures of $RT$-Li$_{1+}$NiB and $HT$-Li$_{1+}$NiB were obtained using program FOX for the $ab$ initio structure determination from powder diffraction.37 After indexing, positions of heavy Ni atoms were determined and further refined in the triclinic space group $P1$. After the atomic coordinates of heavy Ni atoms were found, the structure was analyzed with the program Platon,38 and the correct space group was determined. The residual electron density peaks were assigned to tentative B and Li atomic positions based on the analysis of interatomic distances.

$RT$-Li$_{1+}$NiB. Indexing of the high-resolution synchrotron powder X-ray diffraction data using program FOX resulted in the $P$-monoclinic unit cell (space group $P2_1/c$, $a = 18.277$, $b = 4.8660$, $c = 6.1818$ Å, $\beta = 107.623^\circ$, $V = 524.00$ Å$^3$ at 295 K, $Z = 16$). Ni atoms occupy four 4e sites. Further refinements showed residual electron density peaks, which were assigned to be B in four 4e sites and Li in four 4e sites based on the analysis of interatomic distances.

$HT$-Li$_{1+}$NiB. Indexing of the high-resolution synchrotron powder X-ray diffraction data using program FOX resulted in the $P$-monoclinic unit cell (space group $P2_1/c$, $Z = 8$, $a = 3.92591$, $b = 7.5593$, $c = 8.8181$ Å, $\beta = 92.6245$, $V = 261.42$ Å$^3$). Ni atoms occupy two 4e sites. Further refinements showed residual electron density peaks assigned to be B in 4e, 4e, and Li occupying 2a, 2c, 4e sites based on the analysis of interatomic distances.

Rietveld refinement with the GSAS II software package was further performed using the derived structural models. The profile parameters, background parameters, zero shift, and cell parameters were refined first. The background was fitted using a shifted 24-points linear interpolation function, a pseudo-Voigt function was applied to generate the profile shape. Atomic coordinates of Ni atoms were refined, while atomic coordinates of light B and Li atoms were fixed to the values obtained computationally. Experimental details and crystallographic data are compiled in Tables S1–S3, Fig. S4–S7† ($RT$-Li$_{1+}$NiB), and Tables S4–S6, Fig. S8–S11† ($HT$-Li$_{1+}$NiB). The final refinements of the structures were performed with isotropic displacement parameters for all atoms. Crystal structures were visualized using the program VESTA.$^{39,40}$

In situ high-temperature synchrotron powder X-ray diffraction (HT-PXRD). Transformation of the $RT$-LiNiB, $HT$-LiNiB, $RT$-Li$_{1+}$NiB, and $HT$-Li$_{1+}$NiB compounds at elevated temperatures was evaluated from in situ high-temperature synchrotron X-ray powder diffraction data collected at beamline 17-BM-B APS ($\lambda = 0.24158$ Å). Powdered samples were filled into 0.7 mm outer diameter thick-walled (0.1 mm) silica capillaries and sealed under vacuum. Capillaries were mounted on a standard base equipped with two coiled resistance heaters. The further details of experimental setup can be found elsewhere.41 High energy synchrotron X-ray diffraction spectra were collected in the temperature range 295–1000 K.

Solid-state NMR spectroscopy. $^7$Li and $^{11}$B solid state NMR spectra were measured on a Bruker widebore 9.4 T ($v_{11} = \ldots$)
400 MHz) NMR magnet equipped with a Bruker Avance III HD spectrometer. All spectra were acquired using a 2.5 mm triple resonance MAS probe. Samples were diluted to approximately 50 weight% in powdered polyfluoroethylene to minimize conductivity effects and packed into MAS rotors while still under inert atmosphere. The MAS rate was 25 kHz in all cases.

**Magnetic properties.** Magnetic measurements were performed on polycrystalline samples (m = 50 mg), which were loaded under an inert atmosphere in EPR quartz tubes and sealed under vacuum. The data were collected using a Quantum Design MPMS XL and MPMS3 SQUID Magnetometer DC. Magnetic susceptibility was measured in an applied field of 1000 Oe, in the 5–300 K range. Field-dependent measurements were carried out at 2 K, 5 K and 300 K.

**Computational methods.** The crystal structure searches were performed using the adaptive genetic algorithm (AGA),\(^{10,31}\) AGA integrates auxiliary interatomic potentials and first-principles calculations in an adaptive manner to ensure high efficiency and accuracy. Interatomic potentials based on the embedded-atom method (EAM)\(^{12}\) were chosen as the auxiliary classical potentials to describe the Li–Ni–B system (see ref. 11 for more details). The packing of Li atoms in \(RT\)-Li\(_{1+}\)NiB and \(HT\)-Li\(_{1+}\)NiB were determined using constraint genetic algorithm (GA) searches by fixing the atomic positions on the NiB layers. During the searches, no symmetry constraint was applied. The EAM potential obtained from the AGA search was also used to screen the high-energy structures, the final structures from constraint GA were relaxed and evaluated by first-principles calculations.

First-principles calculations were carried out using the density functional theory (DFT) within a generalized gradient approximation (GGA) of the exchange–correlation functional as implemented in the VASP code.\(^{42,43}\) The projector augmented-wave method\(^{44}\) was used to describe the valence configuration: 1s\(^2\)2s\(^1\) for Li, 3d\(^8\)4s\(^2\) for Ni, and 2s\(^2\)2p\(^1\) for B. The GGA exchange–correlation energy functional parametrized by Perdew, Burke, and Ernzerhof was used.\(^{45}\) A plane-wave basis was used with a kinetic energy cutoff of 650 eV. The Monkhorst–Pack’s scheme\(^{46}\) was adopted for Brillouin zone sampling using a k-point grid with a spacing of 2\(\pi \times 0.033\) Å\(^{-1}\), and the ionic relaxations stopped when the forces on every atom became smaller than 0.01 eV Å\(^{-1}\).

**Conclusions**

Li chemical pressure is a driving force for the formation of \(RT\)-Li\(_{1+}\)NiB and \(HT\)-Li\(_{1+}\)NiB, which accommodate up to 16.7% and 12.5% excess Li into their structure compared to their parent compounds \(RT\)-LiNiB and \(HT\)-LiNiB. The crystal structures of \(RT\)-Li\(_{1+}\)NiB and \(HT\)-Li\(_{1+}\)NiB compounds are similar to that of \(RT\)-LiNiB and \(HT\)-LiNiB, built up from alternating Li layers with hexagonal or squared motif respectively, and [NiB] layers. The complex Li environments in layers of these two new compounds were determined using DFT methods, while subtle variations in the [NiB] layers were elucidated from synchrotron powder X-ray diffraction. Deintercalation of Li from the [NiB] layers was observed at elevated temperatures resulting in the gradual “leaching” of Li from the layers of these Li-enriched compounds and their subsequent transformation into their parent phases: \(RT\)-Li\(_{1+}\)NiB → \(RT\)-LiNiB at 461 K and \(HT\)-Li\(_{1+}\)NiB → \(HT\)-LiNiB at 473 K. Upon further heating decomposition into LiNi\(_3\)B\(_{1.8}\) and finally, into binary nickel borides (∼900 K) takes place. Upon oxidation in air at room temperature, both \(RT\)-Li\(_{1+}\)NiB and \(HT\)-Li\(_{1+}\)NiB phases slowly release Li and transform to \(RT\)-LiNiB and \(HT\)-LiNiB compounds, respectively. Controlled oxidation and deintercalation as a route of further modification of layered LiNiB structures is a subject of future investigation.

**Conflicts of interest**

There are no conflicts to declare.

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