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Structural study of LiB to 70 GPa

A. Lazicki,[1] Russell J. Hemley,[2] W. E. Pickett,[3] and Choong-Shik Yoo[4]
[1]*Département de Physique Théorique et Appliquée, CEA/DAM/DIF, 91680 Bruyères-le-Châtel, France*
[2]*Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA*
[3]*Department of Physics, University of California–Davis, Davis, California 95616, USA*
[4]*Institute for Shock Physics, Washington State University, Pullman, Washington 99164, USA*

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The interest in low-*Z* superconducting analogs to MgB_2 has motivated a search for new high-pressure phases in metal boride systems. Phases of LiB have electronic features intermediate between those of MgB_2 and intercalated graphites, and are expected to exhibit superconductivity. A previously unknown series of layered metal-sandwich structures that are suggested to form under pressure has been identified by *ab initio* data-mining techniques. We report on an experimental effort to search for structural changes in LiB related to the predicted novel behavior. We find that LiB, while becoming increasingly disordered, maintains its ambient pressure structure up to at least 70 GPa. At 5 GPa, however, we observe an abrupt change in the evolution of c/a as a function of pressure, which is likely related to pressure-induced filling of Li-B bonding states.

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Interest in simple compounds of boron and other low-*Z* elements increased significantly after the surprising discovery of superconductivity in MgB_2.[1] In this compound, E_{2g} phonon modes couple strongly to $p\sigma$ states in boron. The strong electron-phonon coupling of carriers in the boron $p\pi$ bands to high-frequency phonons arising from the strong bonding results in a superconducting critical temperature of 40 K, the highest among all *s*-*p* metals. The search for structural and electronic analogs with similar properties has so far been unsuccessful, and the possibility that new phases may be stabilized by pressure has been proposed, theoretically. The case of lithium monoboride has been addressed in several studies.[2–5] Superficially at least, $LiB \equiv (Li^+)_2B_2$ is isovalent with $Mg^{2+}B_2$, and in both cases the cations are largely but not completely ionized. LiB has also been suggested to have technological application as an anode material for thermal batteries because of its light weight and electrochemical properties.

Ambient pressure LiB crystallizes in a structure (α-LiB) with hexagonal close-packed Li atoms and an interpenetrating sublattice of hexagonally arrayed one-dimensional (1D) chains of boron atoms. The boron atoms along the chains are disordered, with an average interatomic spacing that is incommensurate with the lithium lattice spacing, leading to a slightly lithium-rich compound with a stoichiometry of ≈ 0.9.[6] Indeed, it has been shown experimentally and theoretically that LiB has a wide field of stability for formation ($LiB_x; 0.82 < x < 1.0$) with almost no energy barrier between the different compositions, even at zero temperature.[3] Earlier studies had mistakenly identified some of the different boron deficient variations (Li_5B_4, Li_7B_8) as rhombohedral.[7,8] Detailed neutron-diffraction studies by Wörle and Nesper[6] accurately identify the α phase, including the average interatomic spacing of the disordered boron atoms, from a steplike feature in the diffraction pattern. They describe the structure as a sixfold column of Li atoms completely encasing one-dimensional chains of boron atoms (Fig. 1, inset).

The theoretical calculations have verified that α-LiB indeed has strong B-B covalent bonds and metallic conductivity similar to MgB_2 but, as a result of unfavorable bands at the Fermi level, there is much weaker electron-phonon coupling and the superconducting T_c is predicted to be extremely low, if the material superconducts at all.[2] However, other potential crystal structures suggested by various theoretical methods are found to be comparable in energy to α-LiB and favored under moderate compression. Rosner and Pickett[2] proposed an unusual siliconlike cubic *c*-LiB structure that may be stabilized near 1 GPa but is not predicted to be a superconductor. A later study by Kolmogorov and Curtarolo[3] identified a class of new structures in binary alloys using *ab initio* techniques combined with efficient data mining. The structures which they term metal-sandwich phases, consist of variously alternating hexagonal and triangular layers of the elemental components. They are demonstrated to be

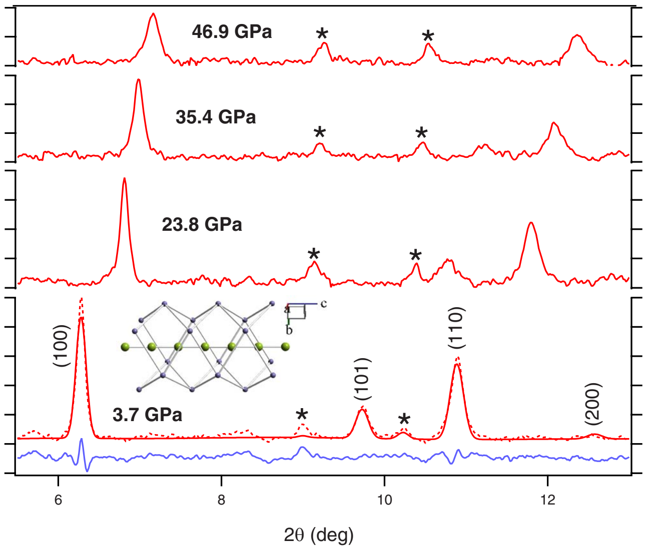

FIG. 1. (Color online) X-ray diffraction patterns of LiB with ascending pressure. Asterisks indicate diffraction from the Re gasket. Inset: α-LiB showing the encapsulated boron chains. Boron atoms are green (larger), lithium are purple (smaller).

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energetically and dynamically stabilized with respect to α-LiB at very moderate compression. These new phases are marked by a high density of boron bonding σ states at the Fermi level and phonon mode frequencies almost identical to those of MgB_2, suggesting at first that the superconducting T_c would be similar to or higher than that of MgB_2. Further theoretical studies eventually predicted a T_c that is somewhat lower: 10–15 K, as a result of a low density of B $p\pi$ states at the Fermi level, and the mechanism for superconductivity was shown to be something midway between that of MgB_2 and the graphite intercalates.[5] It was suggested that alloying the metal-sandwich phases with metal diborides has the effect of increasing the stability of these phases and offers further opportunities for tuning the electronic structure toward the MgB_2-type superconductor.[3] We have fabricated LiB and pressurize the samples, using x-ray diffraction techniques to examine structural changes and possible new high-pressure phases, particularly those in the proposed metal-sandwich structure.

I. EXPERIMENTAL METHODS

LiB samples were prepared by heating stoichiometric quantities of lithium and boron under argon in sealed niobium capsules at 400 C for 6 h, and then 700 C for 12 h. No effort was made to extract excess lithium by heating above 800 C (Ref. 9) or by reaction with tetrahydrofuran naphlathene solution.[10] The predominant phase formed under these conditions is the known α-LiB phase. Samples were loaded into diamond-anvil cells with flat ($300 \rightarrow 500$ μm) culet sizes, using rhenium gasket material and a variety of pressure transmitting media (neon, argon, and helium). LiB is hygroscopic and all loadings were performed in an inert argon or helium atmosphere. X-ray diffraction of the pressurized samples was measured at sector 16 IDB of the Advanced Photon Source and at the ID27 beamline of the European Synchrotron Radiation Facility. Diffraction patters were analyzed with the FIT2D and GSAS programs.[11]

II. RESULTS

Sample diffraction patterns for LiB are shown in Fig. 1. The weakness of the scattering from lightweight LiB superimposed on the strong background of diamond Compton scattering makes a detailed structural analysis under pressure very difficult. Above 5 GPa we are only able to discern three diffraction peaks: (100), (101), and (110). The (100) and (110) peaks reflect scattering from both the lithium and boron hexagonal sublattices, which overlap perfectly due to their commensurate spacing in the x-y plane, and alignment of their c axes. It is impossible, however, to detect the diffuse scattering observed by Wörle and Nesper indicating the average (incommensurate) interatomic spacing of the disordered B chains in the z direction. Thus, we are unable to verify the exact stoichiometry of our compound. We can track changes in symmetry in the x-y plane but spacing along z can only be measured for the (ordered) Li sublattice. We observe that the hexagonal base is maintained up to 70 GPa. The spacing between the hexagonal planes along the c axis is more difficult to follow. Even in an optimally hydrostatic helium pressure medium, all diffraction peaks get broader and weaker as pressure is increased, and this is particularly true for the (101) reflection, which becomes indistinguishable from the background by 50 GPa. This behavior is more pronounced under less hydrostatic conditions; in fact, in the absence of a pressure medium all crystalline diffraction peaks are lost by ~30 GPa.

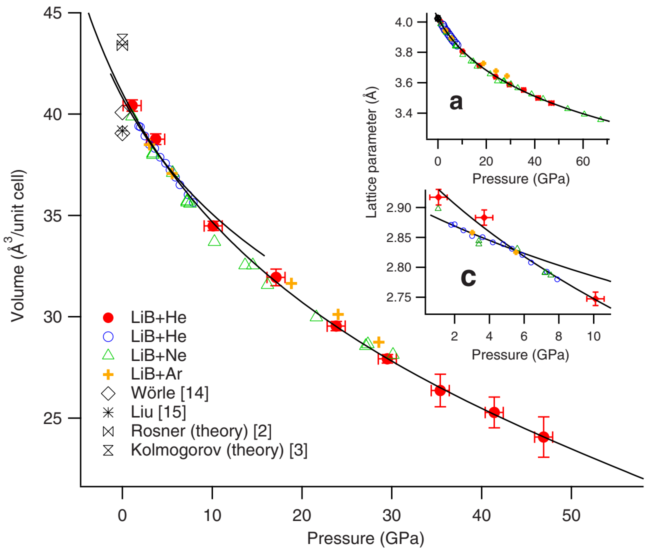

FIG. 2. (Color online) Equation of state of LiB compared with previous results. Inset: a and c lattice parameters as a function of pressure. The c lattice parameter can be measured up to 47 GPa but is here magnified around 5 GPa to show the change in slope. The data were fit with a Birch-Murnaghan equation of state (parameters summarized in Table I). For simplicity, error bars are shown for the first data set only. Error is similar or larger for other data sets.

One of the distinctive features is that near 5 GPa, the pressure dependence of the c lattice parameter undergoes a change in slope. The equation of state and changes in the unit-cell parameters as a function of pressure are shown in Fig. 2 (summarized in Table I) and compared with previous experimental and theoretical studies performed at ambient conditions. Scatter in the data collected in Ne is due to difficulty in precisely identifying the LiB(101) peak position because of overlap with Ne diffraction peaks. In the less hydrostatic Ar,[13] the sample is shown to stiffen at lower pressure. At 5 GPa, the stiffness of the lattice along the c direction drops by half while remaining essentially unchanged along the a-b planes and the pressure derivative drops appreciably.

III. DISCUSSION

While the lattice spacing within the a-b hexagonal planes that we measure agrees very well with past studies, the c lattice parameter is about 1.5% larger than previously determined for 1:1 LiB (Ref. 6) (stoichiometry assumed, based on ratios of starting materials). They have shown that the c-lattice constant is very sensitive to the precise stoichiometry of the sample. Excess lithium results in a contraction of

TABLE I. Birch-Murnaghan equation of state fitting parameters for volume as a function of pressure and parameters for lattice constant as a function of pressure fit with the "linearized" Birch-Murnaghan equation of state (Ref. 12), for diffraction collected from LiB loaded in He. Below 5 GPa, the data are sufficiently sparse and scattered that the pressure derivative of the bulk modulus (B') must be fixed.

	a_0 (Å)	c_0 (Å)	V_0 (Å^3)	B_0 (GPa)	B'_0	B_{0a} (GPa)	B_{0c} (GPa)
$P<5$ GPa	4.034(3)	2.896(4)	40.8(1)	48(3)	4(fixed)	42(2)	67(7)
$P>5$ GPa	4.03(1)	2.96(1)	41.0(2)	47(2)	2.87(6)	45(4)	33(2)

the c lattice constant, because the additional electrons that they donate to the system fill Li-B bonding states, reducing the coulomb repulsion between boron atoms in the chains which are aligned with the c axis. Wörle *et al.* predict that a 3% increase in c lattice constant corresponds to changing composition from $y=0.82$ to $y=1.0$ in LiB$_y$. Theoretical calculations of Kolmogorov *et al.*[3] indicate that the difference in composition resulting from this change in lattice parameter must be much smaller ($\Delta y=0.03$); the LiB compound assumed to have a 1:1 stoichiometry was actually lithium rich. This effect would account for discrepancy between experiment and theory for the commensurate (1:1) LiB phase. Assuming that the stoichiometry of $y\sim 0.88$ found from the relative Li and B interatomic spacing by Wörle *et al.*[14] is correct at a lattice spacing of $c=2.792$ Å, the starting composition of our sample would have been $\sim$0.92, based on the predicted trend.[3] Differences between studies may arise from different sample synthesis methods. In past attempts a lithium-rich mixture was heated at relatively lower temperature. It is possible that our long heating at higher temperature resulted in removal of some excess lithium, an effect suggested previously [9]

At low pressure there is a general trend of increasing c/a ratio up to $\sim$5 GPa, beyond which it abruptly begins to decrease (Fig. 3). Although there is some scatter in the data, this trend was observed in all our studies. The initial relatively slower decrease in the lattice spacing along the boron chains vs within the hexagonal planes is not surprising considering the strong covalent boron-boron sigma bonds and the fact that the lithium interatomic spacing is much smaller along the c axis and Coulomb repulsion accordingly higher than within the hexagonal planes. The decrease in c/a above 5 GPa may then be related to the c-lattice compression observed in earlier studies[6] that occurs as a result of the increased filling of bonding states as the Li content is increased. We were not able to detect any diffraction from free elemental lithium in our sample so we are not able to comment on the likelihood that some unreacted excess lithium might have been available, which only begins to be incorporated above 5 GPa. However, the electronic changes induced purely by pressure may change the bonding character in this system, having a similar effect. It is apparent from the efforts to relax the structure theoretically that the boron-boron interatomic interactions along the 1D chains dominate the compression behavior along z. Rosner and Pickett[2] have demonstrated that compressing these chains has the effect of lowering the energy of the B $p\sigma$ bonds and increasing the dispersion of the p_{xy} states. Bonding between Li and the now more available B p_{xy} states would then have the same effect as adding more electrons to the system; repulsion between layers would be reduced and compressibility along z increased. An increased correlation between the Li and B sublattices may also explain the increasing disorder along z, evidenced by the broadening and loss of intensity in the (101) peak: the Li sublattice is becoming disordered along z as well.

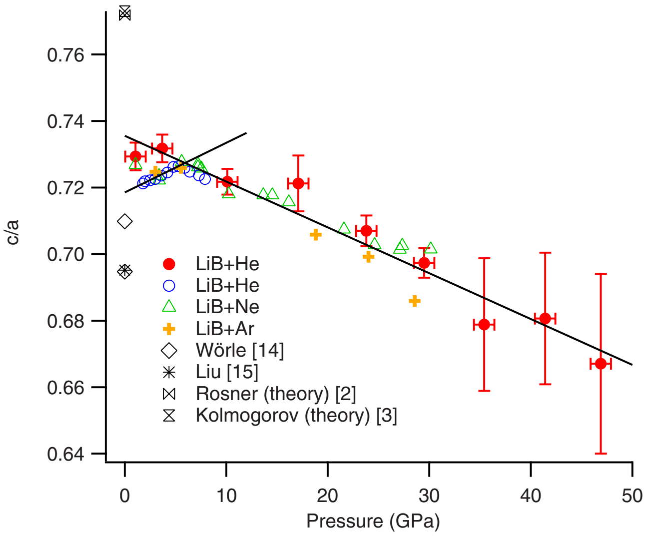

FIG. 3. (Color online) Evolution of c/a as a function of pressure. Lines are guides to the eye. Error bars are shown for LiB+He data sets only. For the other data sets the error is larger.

Above 5 GPa, the trend is close to linear and gives no indication of further transitions up to 50 GPa. Although it is not possible to measure the c-lattice parameter above 50 GPa, the structure within the hexagonal planes has been observed up to 70 GPa without measurable discontinuities, indicating that no high-pressure phase transition takes place over this range of conditions. No evidence for a transition was found by preliminary laser heating of sample at 50 GPa to induce a potential kinetically hindered transformation. Our results do not rule out the possibility that under different synthesis conditions metal-sandwich phases of LiB may be formed. This study demonstrates that, at very least, the kinetic barriers to formation from the pressurized α phase are high.

IV. CONCLUSION

We have demonstrated that the theoretically proposed "metal-sandwich" phases of LiB, which under pressure are calculated to be energetically more stable than the ambient α-LiB phase, are not formed by compressing α-LiB up to at least 70 GPa. The ambient pressure phase is maintained. However, near 5 GPa the structure undergoes an abrupt change in the evolution of the c/a ratio with pressure, possibly indicating electronic changes leading to increased bonding between the Li and B sublattices. Upon continued pressure increase the structure becomes increasingly disordered. Heating of the disordered LiB has not been observed to induce a transition to a more stable ordered phase.

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