TOPICAL REVIEW

Surface science studies of metal hexaborides

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Abstract

Over 30 years of surface science research on metal hexaborides are reviewed. Of this class of compounds, lanthanum hexaboride has been the subject of the majority of the studies because of its outstanding properties as a thermionic emitter. The use of LaB$_6$ cathodes as an electron source stems from the unusually low work function of $\sim$2.5 eV for the (100) surface combined with a low evaporation rate at high temperatures. Of particular interest has been the determination of the surface geometric and electronic structure responsible for the low work function and how the work function is affected by various adsorbates. The low-index faces of single crystals of LaB$_6$ and other hexaborides have been studied with a variety of ultrahigh vacuum surface science methods to gain a better understanding of the structure and properties of the clean surfaces as well as their interactions with gases such as O$_2$, H$_2$O and CO.

Keywords: lanthanum hexaboride, thermionic emission, work function measurements, surface science studies

1. Introduction

Like many of the lighter elements, such as carbon, nitrogen, and oxygen, boron forms compounds with most metals and in some of their properties, borides are similar to carbides, nitrides, and oxides. However, in comparing the structures of borides with those of other solids it is readily apparent that borides constitute a unique class of materials that cannot be understood by analogy to other binary compounds with metals. This is particularly true for borides with stoichiometries of MB$_n$ with $n \geq 2$. Such borides are members of a broader class of materials known as the boron-rich solids [1], which includes compounds of boron with metals as well as with non-metals such as carbon. The different forms of elemental boron itself are also members of this class. The boron-rich solids are all characterized by two- or three-dimensional networks of covalently bonded boron atoms. These boron networks are generally electron deficient by themselves but can be stabilized by electron donation from metal atoms. The unique structures found in borides and in boron compounds are associated with the prevalence of electron-deficient bonding that arises from the simple fact that a boron atom has three electrons in four valence orbitals. This gives rise to the well-known three-center two-electron bonding found throughout boron chemistry. Lipscomb has noted, for example, the common bonding motifs found among boron hydrides and in the boron-rich solids [2]. Fehlner [3] further expounded on the common bonding themes in metaloboranes and transition metal borides. The structures and general properties of boron and borides have been known for many decades [4] and recent work has been reviewed by Albert and Hillebrecht [5]. The proceedings of the International Symposium on Boron, borides, and related compounds provides updates every three years to general research in this field [6]. While the bulk properties of the boron-rich solids have been widely studied [4], far less is known about their surface structure and chemistry. Nevertheless, surface studies of boron and borides have been a persistent, if minor, component of this field for several decades. The purpose of this review is to summarize...
this research with a particular emphasis on the surfaces of hexaborides.

The work considered here is restricted to surface studies that meet certain demanding experimental criteria. These include the use of large single-crystal samples; specialized techniques that are sensitive to the topmost few atomic layers; and ultrahigh vacuum conditions. Without the use of single crystals, it is difficult if not impossible to draw meaningful conclusions about the atomic structure of the surface, which can often differ substantially from the corresponding bulk-terminated plane. For a variety of practical reasons, the single crystals used in surface science studies need to have areas of a few mm² to around 1 cm². Since large single crystals of many interesting materials cannot be prepared, the number of boron-rich solids that have been studied by surface science techniques is necessarily limited. Because the atoms at the surface constitute a small fraction of the total number of atoms in a macroscopic sample, most measurement techniques provide information on bulk properties only. Establishing the intrinsic properties of the topmost atomic layer of a given material requires that once an atomically clean surface is prepared, the surface must remain free of contamination from the atmosphere, at least long enough for the measurement to be made. In general, this condition requires vacuum with pressures of less than $1 \times 10^{-9}$ torr. Vacuum conditions are also necessary for the operation of surface probes that rely on the impingement or emission of charged particles. Even with these restrictions, there have been a considerable number of surface science studies of various hexaborides over the past few decades, and yet this appears to be the first comprehensive review of this subject.

Many studies of hexaboride surfaces have been motivated by the widespread use of crystals of LaB$_6$, and to a lesser extent of CeB$_6$, as cathodes in electron-emitting devices. This application stems from the low work function and high stability of these hexaborides at high temperatures. Whereas surface science studies involving the use of single-crystal samples and ultrahigh vacuum conditions are often performed to gain a better understanding of such technologically important subjects as corrosion, catalysis, sensing, etc., the studies are generally performed under idealized conditions that are remote from the application. This is not the case for hexaboride surface studies as LaB$_6$ cathodes are used in single-crystal form—to expose the lowest work function plane—and are operated in high to ultrahigh vacuum conditions. Rarely are the conditions of a surface science study so closely aligned with the conditions used in the application.

### 2. Growth of single crystals

There are three properties of LaB$_6$ that make it the best thermionic emitter: 1 A low work function; 2 A low rate of evaporation relative to electron emission at high temperature; and 3 A constant surface composition as material evaporates. The first report of the superior properties of LaB$_6$ as a cathode material was by Lafferty [7], who measured a work function of 2.66 eV from Richardson plots of the measured thermionic emission current versus temperature. He used polycrystalline material prepared from sintered boride powders. Lafferty’s identification of LaB$_6$ as a potentially useful cathode material did not lead to immediate application as issues of mounting and poisoning had to be resolved [8–12]. Because work functions vary with crystallographic orientation, cathodes made from single crystals of LaB$_6$, oriented to expose the surface with the lowest work function, are preferred. This led to the development of methods of growing large single crystals of LaB$_6$ and other hexaborides. A simple way to obtain single crystals is to grow them in an aluminum flux [13, 14], but such crystals tend to be too impure for use as cathodes. They are also rather small, making them difficult to use in surface science studies. Larger single crystals of refractory borides can be grown by crucible-free float-zone methods but the first attempts [15, 16] did not produce crystals of high purity. By using three passes of the molten float zone, Tanaka et al [17] succeeded in growing LaB$_6$ crystals with no detectable impurities. They obtained a crystalline rod 7 mm in diameter and 60 mm in length. Methods of growing hexaboride single crystals were reviewed by Davis et al [18].

A key issue in studies of single-crystal samples is whether the surface retains the structure of the bulk plane that is exposed when the surface forms. Figure 1 shows bulk-terminated (100) and (111) planes of hexaborides of the cubic CsCl structure with B$_6$ octahedron at the cube corners and a metal atom in the center of the cell. The B$_6$ octahedra are linked together into a three-dimensional network structure. An explanation for the basic electronic structure of the metal hexaborides was provided by a simple molecular orbital calculation by Longuet–Higgins and Roberts in 1954 [19] who showed that the lattice of interconnected B$_6$ octahedra requires 20 electrons per B$_6$ unit to fill its bonding orbitals, whereas only 18 valence electrons are available from the boron atoms alone. Thus the boron lattice requires transfer of two electrons from each metal atom. For trivalent metals, the third valence electron enters into a metallic band imparting metal-like properties, whereas for hexaborides of the divalent metals there is a band-gap between the highest occupied states and the lowest.

![Figure 1. Side and top views of the structure of the (100) and (111) surfaces of LaB$_6$.](image-url)
unoccupied states. Despite the approximations used in this simple model, the basic description and conclusions reached in [19] are retained in more recent calculations [20–22]. As shown in figure 1, if the bulk-terminated (100) surface is metal terminated, it would consist of metal atoms arranged in a square lattice with $B_6$ octahedra located below the center of the square. In the bulk structure, there would be an interoctahedral bond directed perpendicular to the plane shown that would serve to link the $B_6$ units below the plane to the $B_6$ layer above the plane; therefore, there is necessarily a boron dangling bond at the surface. In principle, the topmost atomic layer of a bulk-terminated (100) plane could consist either of metal or boron atoms. However, the experimental results described below indicate that the (100) surface is metal terminated, as drawn in figure 1. In contrast, the (111) surface is boron terminated, and if the $B_6$ units retain their basic shape, then triangular faces of the octahedra would be parallel to the surface. Both the (100) and (111) surfaces are unreconstructed, meaning that the size and shape of the two-dimensional unit cell for the surface and the bulk-terminated plane are the same. Although the (100) and (111) surfaces are the most commonly studied, the other surfaces that have been studied will be described below on a case-by-case basis.

The work of Tanaka and co-workers at what was then the National Institute for Research in Inorganic Materials (NIRIM) on the growth of rare earth hexaboride crystals led to some of the first surface science studies of hexaborides at the same institute [23–25]. Similar early studies at other institutions used Auger electron spectroscopy (AES) to examine hexaboride surfaces of either polycrystalline samples [26], crystals grown in an aluminum flux [27, 28] or crystals grown by a variant of the floating zone method [29]. A field ion microscopy study also used aluminum-flux-grown crystals [30].

3. Hexaboride surface structure

Low energy electron diffraction (LEED) [31] is the most commonly used method for studying surface structure. The diffraction pattern readily reveals whether the size and shape of the surface unit cell are the same as those of the bulk-terminated plane, or whether the surface has undergone reconstruction to yield a two-dimensional lattice that differs from that of the bulk. The first LEED patterns of lanthanum hexaboride were reported in 1977 for the (100), (111), and (110) surfaces by Oshima et al [25]. They found that whereas the (100) and (111) surfaces yield (1 × 1) patterns, indicating that no reconstruction occurs, the (110) surface shows additional spots due to reconstruction. Subsequent studies have also shown LEED patterns of (100) [32–36] and (111) [36] surfaces of LaB$_6$ confirming the results of Oshima et al [25]. For the LaB$_6$(110) surface, the reconstruction was confirmed by Bas et al [37] and Nishitani et al [36] who observed a $c(2 \times 2)$ pattern at room temperature, which changed into a $(1 \times 1)$ pattern at 860°C. Figure 2 shows the $c(2 \times 2)$ structure of LaB$_6$(110) proposed by Nishitani et al [36, 38], in which the La atoms are displaced towards each other to form pairs while the boron lattice retains its basic structure. Other aspects of surface structure, such as the identity of the atoms comprising the topmost atomic layer (the surface termination), and quantitative determination of atomic positions within the unit cell can, in principle, be determined from a comparison of measured and computed LEED spot intensities versus electron beam energy [31, 39]. However, this approach has yet to be applied to any of the boron-rich solids. Instead, more detailed information on the surface structures than can be provided from LEED patterns alone have come from studies using other techniques.

The first clear indications of La termination for the LaB$_6$(100) surface came from the low surface B/La ratio of 2.3–2.6 obtained by Swanson and Dickinson [40] from measured Auger electron spectra using tabulated sensitivity factors for boron and lanthanum. This conclusion was further supported by the angle-resolved x-ray photoelectron spectra (XPS) of Aono et al [41] in which the B 1s and La4d$_{3/2}$,5/2 peak intensities were measured as a function of angle from the surface normal. A plot of the metal-to-boron peak-height ratio was well fit with a calculated ratio based on a La-terminated surface model. A similar approach was applied to the SmB$_6$(100) surface, where the XPS data implied that the surface was only partly metal terminated [33]. Support for this interpretation of the XPS data for SmB$_6$(100) was provided by ion scattering spectroscopy (ISS) data. Unlike the other rare-earth hexaborides, the Sm atoms in SmB$_6$ are present in both the +3 and +2 oxidation states, a conclusion that was also reached in an earlier XPS study of SmB$_6$ [42]. The finding that the LaB$_6$(100) surface is fully La terminated, whereas the SmB$_6$(100) surface is only partially Sm terminated, was used to account for the higher work function of 4.2 eV for the latter surface compared to the value of 2.4 eV for the former [23]. Similar to the angle-resolved XPS results, Chambers and Swanson [43] used angle-resolved AES to conclude that the LaB$_6$(100) surface is La terminated. Swanson and McNeeley [35] also considered the relationship between surface termination and work function for the (100) surfaces of the hexaborides of La, Ce, Sm and Ba. The boron-to-metal ratio at the surface was characterized with AES. The work functions, measured by both a retarding-field method and through Richardson plots

![Figure 2. Proposed $c(2 \times 2)$ structure for LaB$_6$(110). (Reproduced with permission from [38] ©1982 Elsevier.)](image-url)
of the thermionic emission, were found to increase for the different hexaborides in the order CeB$_6$(100) \( < \) LaB$_6$(100) \( < \) SmB$_6$(100) \( < \) BaB$_6$(100). Although a correlation between surface atomic ratio and work function was found, the authors concluded that the main determinant of the work function variation is the shift of the conduction band edge relative to the Fermi level. Related to the question of surface termination is the issue of preferential enrichment of one metal over the other in mixed hexaborides of the form La$_{1-x}$,$M_x$B$_6$, which was investigated with AES by Nakazawa et al [27] for $M$ = Ce and Pr. They found that the surface was enriched in La at high temperature and they attributed this to the lower heats of vaporization of Ce and Pr relative to La. Futamoto and Kawabe [30] used field ion microscopy to conclude that the (100) surfaces of LaB$_6$, SmB$_6$, and La$_{0.55}$Sm$_{0.42}$B$_6$ were metal terminated.

The correlation of work function and surface structure has also been investigated for the (110) and (111) surfaces of LaB$_6$. The (110) surface reconstructs as indicated by observation of a \( c(\times 2 \times 2) \) LEED pattern [36–38] whereas like the (100) surface, LaB$_6$(111) retains a \((1 \times 1)\) structure at all temperatures. Angle-resolved XPS and ISS were used to show that on the (111) surface, a boron layer lies above the La layer, whereas for the (110) surface the topmost layer consists of lanthanum atoms, but they are not as high above the topmost boron layer as for the (100) surface. Table 1 compares the work function values obtained by Nishitani et al [36] for the (100), (110) and (111) surfaces of LaB$_6$ with the values obtained earlier by Oshima et al [25] and by Swanson and Dickinson [44]. Swanson et al [45] have also summarized various work function measurements for several LaB$_6$ surfaces, including the rarely studied (321) and (346) surfaces. Gesley and Swanson [46] measured work functions for the (310), (210) and (211) surfaces by thermionic emission and field-emission retarding-potential measurements. Uijtewaal et al [47] used \textit{ab initio} calculations to obtain theoretical values for the work functions of various surfaces of LaB$_6$, and concluded that the (100) surface has the lowest value at 2.07 eV.

Although there are variations with crystallographic orientation, the work function values of various LaB$_6$ surfaces are all considerably lower than those of transition metal surfaces. Thus, as noted by Nishitani et al [36], although the surface dipole layer formed by the positively charged La atoms being located above the negatively charged B$_6$ layer of LaB$_6$(100) may lower the work function of this surface relative to other LaB$_6$ surfaces, it would not explain the unusually low work function values of all LaB$_6$ surfaces. Instead, they noted that a correlation of work function with the density of conduction electrons established by Lang and Kohn [48] would also predict a low work function of LaB$_6$. This would then imply that although surface structure can lead to some variations in work function, the overall low work function is a bulk property of LaB$_6$.

The surface termination of LaB$_6$(100) has also been directly addressed with atomically resolved images obtained with scanning tunneling microscopy (STM) [49, 50]. Consistent with a La-terminated surface, the images showed a simple square lattice of bright spots with a lattice constant of 4.1 Å. Also apparent in the images were dark patches amounting to about 10% of the topmost atomic layer. They were consistent with either La vacancies or with contamination, with the most likely contaminant being oxygen. If the dark patches consist of La atom vacancies and if these vacancies are not accompanied by B atom vacancies in the next layer, then the STM results imply a significant deviation at the surface from the ideal LaB$_6$ stoichiometry. From careful measurements of the gas in equilibrium with hot polycrystalline LaB$_6$ samples, Storms and Mueller [51] concluded that the surface has a congruently vaporizing composition (CVC) of LaB$_6$0.04–LaB$_6$0.07, depending on bulk composition. Congruent vaporization has been confirmed by others [52, 53]. An interesting unresolved issue is the microscopic mechanism by which the La and B atoms leave the LaB$_6$ lattice and enter the gas phase while preserving a CVC. Mass spectrometric studies have shown that only La and B atoms evaporate from the clean surface [44, 54].

STM reveals that like most metal surfaces with low Miller indices, the LaB$_6$(100) surface on a larger scale consists of flat (100) terraces separated by steps. Whereas monatomic step heights are invariably observed on the low-index surfaces of the metallic elements, the steps on LaB$_6$(100) are 4.1 Å, i.e. one unit cell, in height. Furthermore, the steps are unusually straight, and form kinks at right angles to the step directions. The step structure thus reveals that the surface consists of La-terminated terraces and La-terminated steps and thus there are no boron-terminated areas. A similar step structure was even observed by STM in air on freshly cleaved LaB$_6$(100) crystals [55], although images could not be obtained after prolonged air exposure. These previous experiments on LaB$_6$(100) were performed in the early days of scanning tunneling microscopy research. While they demonstrated the feasibility of using the method to study borides, the much better instrumentation available today would no doubt yield a great deal more information on the atomic structure of such surfaces.

Surface vibrational spectroscopy can provide information on structure through comparison with calculated results based on suitable models. Nagao et al used high resolution electron energy loss spectroscopy (HREELS) to measure surface phonon dispersion curves for the LaB$_6$(100) surface [56, 57]. The higher frequency modes correspond to vibrations of the $B_6$ octahedra, and by fitting the results with an initial set of force constants obtained for bulk LaB$_6$, the authors concluded that the $B_6$ octahedra at the surface expand in a direction parallel to the surface by 0.04 Å. A similar approach was used to investigate the relaxation of the

**Table 1.** Work function values (in eV) for the (100), (110) and (111) surfaces of LaB$_6$ from UPS and thermionic emission (TE) measurements.

| Surface | Nishitani \textit{et al} [36] (UPS) | Swanson \textit{et al} [44] (TE) | Oshima \textit{et al} [25] (TE) |
|---------|---------------------------------|-------------------------------|---------------------------|
| (100)   | 2.3                             | 2.52–2.7                      | 2.85                      |
| (110)   | 2.5                             | 2.60                          | 2.68                      |
| (111)   | 3.3                             | 2.90                          | 3.40                      |
boron-terminated LaB$_6$(111) surface [58, 59], and a stiffening of the bonding within the boron network at the surface was found. Specifically, the force constant for the interoctahedral B–B bonds of the surface B$_6$ octahedra increases by 50% relative to the corresponding bulk force constant [59].

Related to the geometric structure of hexaboride surfaces are their surface electronic structures, which can be investigated with photoelectron spectroscopy and other techniques. Angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) was used by Aono et al. [24, 60] to study LaB$_6$(100) and by Nishitani et al. [61] to study the (100), (111) and (110) surfaces of LaB$_6$. In each case surface electronic states were identified and their two-dimensional dispersion curves were measured. The surface states were distinguished from the peaks due to bulk states by the fact that they disappeared with oxygen exposure, occurred in a region where there are no bulk states, and persisted with high intensity even to grazing emission angles. Two surface states were indentified on each of the three surfaces studied. For LaB$_6$(100), the two states occur at almost the same energy of about 2.3 eV below the Fermi level for normal emission, but are well separated at points further from the center (the $\Gamma$ point) of the Brillouin zone. For the (111) surface, a single surface state is observed at the $\Gamma$ point at 1.7 eV below the Fermi level and shows a maximum dispersion to 2.6 eV below the Fermi level at the M point. The other surface state is seen only off the surface normal at about 1.5 eV and shows only a slight dispersion of 0.3 eV. On the (110) surface, the two surface states are at about 1.8 and 3.0 eV and show small dispersions of only about 0.2 eV. In each case, the surface states were associated with boron dangling bonds, of which there are one, two, and three per unit cell for the (100), (110) and (111) surfaces, respectively. Further confirmation of the identity of the surface states of LaB$_6$(100) was provided by electron emission spectroscopy following impingement by He$^+$ ions [62], heavier noble gas ions [63] or by metastable He atoms [64]. As greater surface sensitivity is achieved by using impinging atoms or ions, Souda et al. [62] were able to clearly distinguish a B 2s, 2p surface state from a bulk B 2s, 2p state, as only the former is observed from impingement with He$^+$ ions, whereas both states are seen with UPS. Nishitani et al. [61] found that exposure to oxygen eliminated both the c(2 $\times$ 2) LEED pattern and the surface states of LaB$_6$(110), and thereby concluded that the surface states are associated with the c(2 $\times$ 2) structure. However, in a more recent study the same surface state features as for LaB$_6$(110) were found for NdB$_6$(110), which has only a (1 $\times$ 1) rather than a c(2 $\times$ 2) LEED pattern [65]. Consistent with the idea that the surface state seen on LaB$_6$(100) is associated with the boron dangling bonds, a surface state at the same energy was also seen by photoemission on the (100) surfaces of CeB$_6$, PrB$_6$, and NdB$_6$ [66]. Unlike La, these metals have occupied 4f levels but it was found that the surface states were not affected by the presence of the 4f electrons. The same conclusion was also reached in the photoemission study of NdB$_6$(110) [65]. Whereas photoemission spectra provide information on the occupied states, inverse photoemission has been used to characterize the unoccupied states a few eV above the Fermi level for a LaB$_6$(100) surface [67]. Unoccupied surface states associated with the La 5d and La 4f levels were found at the Fermi level and 6.8 eV above it, respectively. The measured dispersion of the unoccupied La 5d surface states differed from the dispersion calculated with density functional theory for a La-terminated slab comprising 13 planes of La atoms [68]. However, these calculations were quite successful in reproducing the dispersions of the occupied levels. Whereas all of the electronic properties of hexaborides described above were based on measurements of samples at room temperature, Medicirlera et al. [69] obtained UPS and XPS data for a LaB$_6$ single crystal of unspecified orientation at temperatures as low as 15 K. They found that a pseudogap develops at the Fermi level at temperatures below 100 K. The asymmetry in the peak for the B 1s core level of the hexaborides of La, Ce, Pr, and Nd was attributed to slightly different binding energies of bulk and surface boron [70]. It was also noted that there is a small decrease in the B 1s binding energy with increasing 4f binding energy among these rare earth hexaborides.

In addition to the rare earth elements, the alkaline earth metals Ca, Sr, and Ba also form hexaborides of the same structure. However, their surface properties have received little attention. This is at least partly due to the difficulty of growing large single crystals because of the relatively high volatility of the metals. Nevertheless, a few studies have been performed. Swanson and McNeely [35] reported work function measurements and AES analysis of the composition for the (100) surface of a BaB$_6$ crystal obtained by precipitation from molten aluminum. They measured a work function of 3.4 eV, which although higher than the values they obtained in the same study for the (100) surfaces of LaB$_6$ and CeB$_6$, was lower than the value of 3.92 eV obtained for SmB$_6$(100). Based on AES peak-height ratios, they suggest that the BaB$_6$(100) surface may be terminated by B$_6$ octahedra. This interesting observation has never been reinvestigated by other workers. Meegoda et al. [71] used AES to characterize the surface of a CaB$_6$ crystal that had been prepared from an aluminum flux as described by Otani and Mori [72, 73]. They were particularly interested in detecting any contamination of the surface by iron. This was motivated by a report [74] that La-doped CaB$_6$ is a ferromagnet with a Curie temperature of 600 K, a surprising finding given that none of the constituent elements are magnetic. Mori and Otani suggested that the magnetic properties could be explained by iron contamination of the CaB$_6$ surface during preparation. Using AES and depth profiling, Meegoda et al. [71] detected Fe and found that it was concentrated in the surface region of the CaB$_6$ crystal. They also found that after the surface contamination was removed, the surface B/Ca ratio was 5.8, a value generally higher than found in metal-terminated rare earth hexaborides, implying, as found for BaB$_6$ [35], that the surface has both metal and boron terminated regions. Theoretical work [47] suggests that substitution of Ba for La at a LaB$_6$(100) surface reduces the work function to 1.43 eV, a prediction that has yet to be investigated experimentally.
4. Chemisorption on hexaboride surfaces

In addition to studies of the structure and properties of the clean surfaces of the hexaborides, there have been many reports on the adsorption and reaction of atoms and molecules on these surfaces. In particular, oxidation of the surfaces after exposure to O₂ has been repeatedly examined. This has been partly motivated by a desire to understand the effect of poisoning on the performance of LaB₆ cathodes. As CO and H₂O are common background gases in even the best ultrahigh vacuum environments, the interactions of these gases with hexaboride surfaces should be of interest. Studies have also been performed to see if adsorbed Cs, which has a low work function itself, can lower the work function of hexaboride surfaces and hence increase their thermionic emission. Although H₂ is a common background gas, the interaction of hydrogen with hexaboride surfaces has received little attention. One study [75] indicates that LaB₆ powders can catalyze hydrogen–deuterium exchange, but there are no reports on the interaction of H₂ with hexaboride single crystal surfaces. Chemisorption of individual species on hexaboride surfaces is reviewed below.

4.1. Oxygen

In the first study of its type, Oshima and Kawai [76] used AES to characterize an initially clean LaB₆(211) surface after a short exposure to air. Not surprisingly, while air exposure led to oxygen adsorption it also resulted in carbon contamination. The air exposure greatly diminished the B peak, but heating to about 1200 °C and above restored it to maximum intensity. The oxygen contamination decreased steadily with heating temperature but was not fully eliminated until heating to 1600 °C. The intensity of the carbon peak decreased with heating to 1500 °C, but above this temperature increased again, which the authors attributed to diffusion of the carbon from the bulk. Berrada et al [26] used AES and XPS to study sintered and melted polycrystalline LaB₆ and CeB₆ samples that were exposed to air. As expected, contamination by both carbon and oxygen was observed. Klauser and Bas [77] used AES to monitor La, B and O concentrations on the (100), (111) and (110) surfaces of LaB₆ versus O₂ pressure with the crystals held at constant temperatures of 1500–1600 K. The results showed a stronger decrease in B than La as the surface O concentration increased. A similar study by Bas et al [37] showed that the c(2 × 2) reconstruction of clean LaB₆(110) was converted to a (1 × 1) surface with oxygen exposure.

Several studies have shown that adsorbed oxygen causes a large increase in the work function of LaB₆ surfaces [34, 38, 78, 79]. The results of Nishitani et al [38] for the work function versus oxygen exposure for the (100), (110) and (111) surfaces of LaB₆ are presented in figure 3. In each case, the work function increases steadily before reaching a plateau after exposures of 1–3 L (note that throughout this article L stand for Langmuir = 1 × 10⁻⁶ toorr s). For the (100) surface an inflection point in the curve after about 1 L was noted earlier by the same authors [78]; its presence correlates with the dependence of oxygen coverage on exposure, which in turn implies a highly coverage dependent sticking probability that starts near zero, reaches a maximum of 1 for a 1.4 L exposure, and then falls back to zero as the coverage reaches saturation. Similar magnitudes of the work function changes were reported by Chambers et al [79] and by Goldstein and Stozak [34], although in the latter case the change with O coverage was linear, but in the former a non-linear dependence similar to that of Nishitani et al [38] was observed.

Techniques such as AES or XPS that have been used to investigate the interaction of oxygen with hexaboride surfaces do not provide direct information on the initial oxygen adsorption site. This issue is better investigated using surface vibrational spectroscopy. Figure 4 shows a recent comparison of spectra obtained with the techniques of HREELS and reflection absorption infrared spectroscopy (RAIRS) [80]. The HREEL spectrum is slightly better resolved than the one obtained in an earlier study of O on the (100) surfaces of LaB₆ and PrB₆ [81], but the interpretation is essentially the same. Thus, the intense peak at 282 cm⁻¹ with an unresolved shoulder at 226 cm⁻¹ in the HREELS spectra, which are well below the region accessible with RAIRS, are associated with La–O stretching vibrations of oxygen atoms bridge bonded between two La atoms. The peaks at higher wavenumber are mainly associated with vibrations of the B₆ octahedra. In the absence of oxygen, the vibrations of the boron lattice are screened by the conduction electrons. The surface vibrations are observable with HREELS even in the absence of adsorbates, but they are greatly diminished in intensity, particularly for electrons scattered in the specular direction [56, 57]. The relatively narrow peak at 734 cm⁻¹

Figure 3. Work function dependence on oxygen exposure for the (100), (110) and (111) surfaces of LaB₆. (Reproduced with permission from [38] ©1982 Elsevier.)
in the HREEL spectrum has the same full width at half maximum (FWHM) of 55 cm\(^{-1}\) as the elastic peak, meaning that its actual width is below the instrumental resolution. This peak is resolved into two components at 717 and 740 cm\(^{-1}\) in the RAIR spectrum. The separation of these two components and their relative intensities are associated with the natural abundance ratio of the \(^{11}\text{B}\) and \(^{10}\text{B}\) isotopes. The weak peak at 920 cm\(^{-1}\) in the HREEL spectrum is observed at 922 cm\(^{-1}\) with RAIRS. The very broad loss feature with maximum intensity at 1202 cm\(^{-1}\) in the HREEL spectrum is partly replicated in the RAIR spectrum. Most notably, the higher resolution available with RAIRS does not lead to the resolution of separate peaks in this region. The overall shape of the feature is also somewhat different in the RAIR and HREEL spectra, but this may reflect different O coverages in the two cases as the shape changes with coverage.

For oxygen adsorption on the LaB\(_6\)(111) surface, the HREELS [82] and RAIRS [80] results have some similarities but also some notable differences. For the clean (111) surface, the surface vibrations are much more intense than on the clean (100) surface in the HREEL spectra. This difference is attributed to less screening by the metal 5d electrons as the La layer is below the topmost B layer on the (111) surface. Upon oxygen adsorption, the intensity of the surface vibrations increases, but the prominent peak at 282 cm\(^{-1}\), seen on the (100) surface due to O atoms bridge bonded between two La atoms, is absent, consistent with the lack of La bridge sites on the (111) surface. The peaks observed at higher wavenumbers for O on the (111) surface were attributed to a combination of boron lattice and boron oxide vibrations.

The interpretation of the experimental surface vibrational spectra was greatly aided by lattice dynamical calculations based on initial force constants obtained from studies of the bulk hexaborides. Based on these calculations it was concluded that the relatively sharp and intense peak seen with HREELS in figure 4 at 734 cm\(^{-1}\) was due to a surface phonon, mainly attributable to motion of the topmost B atom of the surface B\(_6\) units. It was further argued that this phonon had the correct symmetry to be surface dipole allowed. This conclusion was confirmed by a more recent calculation from first principles [68]. Figure 5 shows the calculated LaB\(_6\)(100) surface phonon spectral density at the \(\Gamma\) point, with the different colors corresponding to projections onto surface La (red), surface B (dark blue) and subsurface B (light blue) atoms. The green bars above the peaks correspond to the experimental HREELS results of Nagao et al [56]. Among other details, the theoretical results confirm that the strong and sharp peak observed with HREELS in figure 4 at 734 cm\(^{-1}\) is due to a phonon localized on the surface boron atoms.

Given that the HREELS results implied oxygen adsorption on La sites, the issue of the initial adsorption site of O on LaB\(_6\)(100) was reinvestigated by Perkins et al [83] with XPS. After a 10 LO\(_2\) exposure at room temperature, the La 3d peaks developed distinct higher binding energy shoulders whereas the B 1s peak was unaffected (figure 6). However, for a 1000 LO\(_2\) exposure at an elevated temperature of 1000 K, a chemically shifted B 1s peak at 193.3 eV, characteristic
of boron oxide, developed alongside the main B 1s peak at 188.4 eV. Under the same conditions the components of the La 3d peaks associated with oxidized La became even more pronounced. The results confirmed that oxygen initially adsorbs at La sites and that only for the more heavily oxidized surface is oxygen bound to both La and B sites. This contrasts with conclusions reached in earlier studies that the initial adsorption sites are either boron [34] or involve both boron and lanthanum [43, 78, 79]. Berrada et al [26] also used XPS to study the oxidation of hexaboride surfaces, but only considered heavily oxidized cases where oxygen bonding to both La and B sites occurs.

Related to the issue of oxygen adsorption site is the identity of the oxygen-containing molecules that desorb from the surface at high temperature as observed with mass spectrometry by the technique of temperature programmed desorption (TPD). Davis and Chambers [84] found that the desorption mainly occurs as BO, LaO, and B₂O₂, with the latter species being the dominant boron oxide desorbed. Desorption of the principal oxide of boron, B₂O₃, is only observed for high O₂ exposures at 1000 K. Bas et al [37] reported desorption of BO and LaO following O₂ exposure to a LaB₆(110) surface but did not mention whether they looked for B₂O₂ or B₂O₃. A later study examined in great detail oxide desorption from a LaB₆(100) surface for oxygen exposures that ranged from 0.01 to 10 L with the surface held at either 300 or 1000 K [54]. Figure 7(a) shows the temperature programmed desorption results for BO, B₂O₂, and LaO after a 1 LO₂ exposure to the surface at room temperature, whereas figure 7(b) shows the corresponding results after a 50 LO₂ exposure with the surface at 1000 K. Each species displays a distinct desorption profile. In this figure, LaO desorbs as a single peak at 1425 K in figure 7(a) but shifts to 1480 K for the more heavily oxidized sample in figure 7(b). Over the full range of O₂ exposures at 300 K, the LaO desorption shows some multicomponent structure, but the desorption peaks occur over a narrow range of temperatures from 1420 to 1450 K. The BO desorption also occurs as a single peak at about the same temperature as the LaO peak in figure 7. Other results in [54] that are not shown here reveal that over the full range of oxygen exposures at 300 K, the BO peak occurs at about 1480 K for the lowest O₂ exposures, but develops a second component at about 1420 K. The B₂O₂ desorption is rather complex, as is apparent even for the limited results shown in figure 7. For room-temperature adsorption, it is shown in ref [54] that B₂O₂ desorption changes markedly with O₂ exposure, starting with a single peak at around 1425 K for the lowest exposure, then evolving to a profile with a dominant peak at 1150 K, and a second component at about 1250 K, with continuous desorption up to about 1480 K, where the desorption abruptly falls to zero. The B₂O₂ species appear to play a central role in the oxidation of boron and boron-rich solids. A study of B₂O₃ deposited directly onto a boron surface showed that B₂O₂ was the dominant desorption product [85, 86]. The reaction of boron and B₂O₃ to produce B₂O₄ can also be used to deposit a thin film of solid B₂O₂ onto surfaces for characterization of this boron suboxide with techniques such as XPS [87, 88].

![Figure 7. Thermal desorption profiles for LaO, B₂O₂, and BO following exposures of LaB₆(100) to O₂.](image-url)

### 4.2. Cesium

Chambers et al [79] used AES and work function changes to characterize the (100) and (111) surfaces of LaB₆ following adsorption of Cs alone and coadsorbed with oxygen. For both surfaces, Cs lowered the work function to minimum values of 1.97 and 1.88 eV when deposited onto initially clean (100) and (111) surfaces, respectively. When coadsorbed with oxygen, the work function for both surfaces decreased even further to only 1.35 and 1.47 eV. The work function dependence on cesium coverage is complex, with a distinct minimum reached at a coverage less than the saturation value, before it rises again. On the oxygen precovered surfaces, the work function decreases monotonically with Cs coverage. The coverage dependence of the work function was better described by an image-dipole model of adsorption compared to a mutual depolarization model. The results are compared to analogous studies of work function changes for oxygen and cesium adsorption on tungsten surfaces.

In a companion paper, Chambers et al [89] used temperature programmed desorption to investigate Cs adsorption on the LaB₆(100) surface. At the lowest coverages, the Cs desorbs as a single broad peak centered at about 680 K, whereas at the highest coverages it desorbs over a temperature range from 350 to 900 K with at least three unresolved components recognizable in the overall broad desorption envelope. Desorption of Cs from a surface precovered with...
one monolayer of oxygen is shifted to higher temperatures, with a single peak at around 980 K for the lowest Cs coverages. The thermal desorption of Cs\(^+\) ions was also measured, and occurs as a narrower peak at 1000 K that grows in at constant temperature for increasing Cs coverage. The fact that Cs desorbs at such high temperatures is indicative of the strong bonding to the surface, as would be expected for an ionic species. Although the first ionization potential of Cs is 3.9 eV and the work function of the LaB\(_6\)(100) surface in this case was 2.7 eV, the additional 1.2 eV of energy needed to form the surface ion is supplied by the higher binding energy of Cs\(^+\) to the surface compared to Cs neutral.

### 4.3. Carbon monoxide

In addition to its relevance to the performance of LaB\(_6\) cathodes, the interaction of CO with hexaboride surfaces can be used to probe the extent to which the chemical properties of the metallic hexaborides compare with those of the transition metals that are used in heterogeneous catalysis. A general rule for the effectiveness of a metal for catalyzing a particular reaction is that the reactants need to adsorb strongly or even dissociatively, but the products should be weakly adsorbed so that they can be removed intact at moderate temperatures. Vibrational spectroscopy of chemisorbed CO is particularly useful as a probe of the chemical properties of metal surfaces, as the intense C–O stretch frequency correlates with the adsorption site and with the strength of the bonding between the molecule and the surface. Yorisaki et al [90] used RAIRS and XPS to obtain experimental data on the interaction of carbon monoxide with the LaB\(_6\)(100) and LaB\(_6\)(111) surfaces and employed density functional theory to help interpret the results. Figures 8 and 9 show RAIR spectra as a function of CO exposure to the (100) and (111) surfaces, respectively. Both surfaces adsorb CO molecularly at low temperatures, but in markedly different forms. On the LaB\(_6\)(111) surface, CO initially adsorbs at 90 K in a form that yields an unusually low frequency C–O stretching mode at 1502–1512 cm\(^{-1}\). With gentle annealing to 120 K, the CO switches to a bonding environment characterized by multiple C–O stretch values from 1980 to 2080 cm\(^{-1}\), assigned to one, two, or three CO molecules terminally bonded to the B atoms of a triangular B\(_3\) unit at the (111) surface. In contrast, on the LaB\(_6\)(100) surface only a single CO stretch is observed at 2094 cm\(^{-1}\), which is assigned to a CO molecule bonded on top of a La atom. The maximum intensity of the CO stretch vibration on the (100) surface is higher than on the (111) surface by a factor of 5. This difference is related to the different orientations of the CO molecules on the two surfaces and to reduced screening of the CO dynamic dipole moment on the (100) surface, where the bonding occurs further from the surface plane. On LaB\(_6\)(100), XPS measurements indicate that CO dissociates on the surface at temperatures above 400 K. Swanson et al [91] used AES to show that CO exposure to LaB\(_6\)(100) at room temperature led to the development of surface carbon and oxygen. This was likely due to dissociative adsorption, although it is difficult to tell from AES results if the signals were due to atomic carbon and oxygen or to chemisorbed CO molecules.

![Figure 8.](image_url)
temperatures from 90 K to room temperature, and spectra were acquired after heating to temperatures as high as 1200 K. Figure 10 shows HREEL and RAIR spectra for H₂O exposures at room temperature. The results indicate that water dissociates upon adsorption to produce surface hydroxyl species as revealed by the OH stretch peak at 3646 – 3671 cm⁻¹. For D₂O exposures, the corresponding OD stretch is observed at 2701 cm⁻¹. The HREEL spectra following room temperature adsorption also reveal low frequency loss features near 300 cm⁻¹ that are quite similar to results obtained following O₂ exposure and are attributed to the La–O stretch of O atoms or OH groups bridge-bonded between two La atoms. The finding that H₂O exposure can produce an oxidized surface similar to what is obtained after O₂ exposure was confirmed by TPD [97]. For exposures at 90 K, water adsorbs molecularly in the form of monomers at low coverages whereas at higher coverages at 90 K it forms amorphous solid water. Compared to other surfaces, a temperature of 90 K is quite high for the observation of monomeric water. However, the RAIR spectra for multilayer water on LaB₆(100) are similar to spectra of films of amorphous solid water seen on other surfaces. Yorisaki et al [92] speculated that the ability of the LaB₆(100) surface to adsorb water as a monomer is probably due to a combination of a high binding energy to the La sites, which compensates for the energy that would be gained by formation of hydrogen-bonded clusters, and the relatively large La–La distance that precludes hydrogen bonding for water molecules adsorbed on adjacent sites.

5. Conclusions

The surface properties of metal hexaborides have been extensively studied for more than thirty years. Many of these studies have been motivated by the widespread use of LaB₆ as a cathode in electron emitting devices. The superior thermionic emission characteristics of LaB₆ stem from an intrinsic property of its surfaces: unusually low work functions. While the determination of the fundamental properties of hexaboride surfaces is best done using well characterized single crystals studied under ultrahigh vacuum conditions, the surface properties thus established are highly relevant to a variety of applications. Hexaboride thin films have been considered for applications as decorative and/or hard coatings [98]. Aside from applications of single crystals as electron emitting cathodes, properties of field emitter arrays of LaB₆ have been described [99]. Hexaboride surfaces also...
show promise as supports for transition metal catalysts [100]. There has been a great deal of recent interest in the synthesis, properties, and applications of hexaboride nanostructures. As nanoscale materials have very high surface-to-volume ratios, their surface properties are of utmost importance, yet are often difficult to study directly. Recent research on hexaboride nanostructures was reviewed by Ji et al [101], and it was found that the extensive prior work on the surface properties of these materials was highly beneficial to this new area of nanoscience research. While the earliest studies were focused on the structure and properties of the clean surfaces and their interactions with oxygen, several recent reports have revealed that species like CO and H$_2$O can molecularly adsorb under some conditions, and dissociate under other conditions, which indicates that the hexaborides might be useful as catalysts. This is yet another area that would be promising for future research on the surface properties of metal hexaborides.

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